Doctoral Thesis

Methodological advances in theoretical spectroscopy for bio and inorganic molecules

Author(s):
Luber, Sandra E.

Publication Date:
2009

Permanent Link:
https://doi.org/10.3929/ethz-a-005967550

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
Methodological Advances
in
Theoretical Spectroscopy
for Bio and Inorganic Molecules

A dissertation submitted to

ETH ZURICH

for the degree of

Doctor of Sciences

presented by
Sandra Erika Luber
MSc ETH Chemistry, ETH Zurich
born 16.02.1981
citizen of Germany

accepted on the recommendation of
Prof. Dr. Markus Reiher, examiner
Prof. Dr. Gunnar Jeschke, co-examiner

2009
## Contents

I Zusammenfassung v

II Abstract vii

1 Introduction 1
   1.1 Methods of theoretical chemistry 3
   1.2 Born–Oppenheimer approximation 6
   1.3 Harmonic approximation 8
   1.4 Kohn–Sham density functional theory 10
   1.5 Outline of this work 11

2 General Theory of Molecular Properties 13
   2.1 Coupling of a Dirac electron to external potentials 16
   2.2 Four-component framework 18
   2.3 Transition to two-component Hamiltonians 23
      2.3.1 Vector-potential-dependent Foldy–Wouthuysen transformation 23
      2.3.2 Vector-potential-independent Foldy–Wouthuysen transformation 24
         2.3.2.1 Removal of $A$-dependent odd terms 26
         2.3.2.2 Simultaneous elimination of $V$- and $A$-dependent odd terms 29
      2.3.3 Iterative infinite-order decoupling in $V$ and $A$ 33
   2.4 Molecular magnetic properties 35
      2.4.1 Rayleigh–Schrödinger perturbation theory for the Dirac equation 37
      2.4.2 Perturbation theory with perturbation-independent unitary transformations 38
      2.4.3 Perturbation theory with perturbation-dependent unitary transformations 40

3 Theory of Raman Optical Activity Spectroscopy 45
   3.1 Derivation of the molecular property tensors 47
      3.1.1 Hamiltonian describing the interaction with electromagnetic fields 47
### CONTENTS

#### 3.1.2 Determination of the wave function perturbed by the electromagnetic field ........................................... 51
3.1.3 The induced electric-dipole moments .......................................... 54
3.1.4 The Raman and Raman optical activity polarizability tensors 56

#### 3.2 The general Raman and Raman optical activity intensities ............................................. 59
3.2.1 Dynamic electromagnetic multipole fields ........................................ 59
3.2.2 Evaluation of the intensity expressions ........................................ 62

#### 3.3 Far-from-resonance approximation ................................................. 66
3.3.1 Origin dependence .................................................................. 71

#### 3.4 Resonance Raman optical activity ................................................... 76
3.4.1 Sum-over-states formulation and the Condon approximation 77
3.4.2 Time-dependent formulation and resonance with a single excited electronic state ............................................ 80
3.4.3 Resonance with two excited electronic states .................................. 84

#### 3.5 Relevance of individual contributions to Raman optical activity spectra ..................................................... 86
3.5.1 The bond polarizability model ......................................................... 86
3.5.2 Atomic contributions to intensities ................................................ 89
3.5.3 Localization of normal modes ........................................................ 90

#### 3.6 Intensity-carrying modes ............................................................. 94
3.6.1 Hypothetical distortions with maximum infrared intensities 95
3.6.2 Raman intensity-carrying modes ...................................................... 97
3.6.3 Intensity-carrying modes in Raman optical activity spectroscopy ................................................................. 99
3.6.4 Examples of intensity-carrying modes ........................................... 100

4 Algorithmic Developments ................................................................. 107
4.1 Efficient calculation of Raman optical activity property tensors . 107
4.2 Intensity-Tracking ............................................................. 112
4.2.1 Theoretical background ................................................................. 112
4.2.1.1 The mode-tracking algorithm ......................................................... 112
4.2.1.2 Intensity-tracking ................................................................. 113
4.2.2 Infrared intensity-tracking .............................................................. 117
4.2.2.1 Organic molecules ................................................................. 118
4.2.2.2 Δ(δδδ)-Tris(ethylenediaminato)cobalt(III) .............................. 121
4.2.2.3 Purpose-driven optimization of high-intensity normal modes ................................................................. 124
4.2.4 Intensity-tracking in practice: Schrock's dinitrogen molybdenum complex ................................................................. 129
4.2.3 Raman and Raman optical activity intensity-tracking ........... 133

5 Raman Optical Activity Spectra of Metal Complexes ................................................................. 137
5.1 Basis-set and density-functional dependence ....................... 137
5.2 Discussion of the spectra ........................................................... 142
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>Influence of chiral ligands on the spectra</td>
<td>146</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Degree of ligand substitution</td>
<td>147</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Ligand chirality</td>
<td>150</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Geometrical isomers</td>
<td>151</td>
</tr>
<tr>
<td>5.3.4</td>
<td>Δ versus Λ configuration</td>
<td>159</td>
</tr>
<tr>
<td>6</td>
<td>Raman Optical Activity Investigation of Biomolecules</td>
<td>161</td>
</tr>
<tr>
<td>6.1</td>
<td>Resonance Raman optical activity study of naproxen</td>
<td>161</td>
</tr>
<tr>
<td>6.1.1</td>
<td>Comparison to experimental spectra</td>
<td>162</td>
</tr>
<tr>
<td>6.1.2</td>
<td>Effect of the second excited electronic state</td>
<td>165</td>
</tr>
<tr>
<td>6.2</td>
<td>Raman optical activity spectra of 1,6-anhydro-β-D-glucopyranose</td>
<td>171</td>
</tr>
<tr>
<td>6.2.1</td>
<td>Influence of conformation and solvent</td>
<td>173</td>
</tr>
<tr>
<td>6.2.1.1</td>
<td>Chair versus boat conformation</td>
<td>173</td>
</tr>
<tr>
<td>6.2.1.2</td>
<td>Influence of the orientation of the hydrogen atoms in hydroxyl groups</td>
<td>174</td>
</tr>
<tr>
<td>6.2.1.3</td>
<td>Solvent effects</td>
<td>175</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Comparison of calculated and experimental spectra</td>
<td>177</td>
</tr>
<tr>
<td>6.2.2.1</td>
<td>Populations of the conformers</td>
<td>177</td>
</tr>
<tr>
<td>6.2.2.2</td>
<td>Construction of spectra and comparison to experiment</td>
<td>180</td>
</tr>
<tr>
<td>6.3</td>
<td>Raman optical activity signatures of tryptophan side chains</td>
<td>185</td>
</tr>
<tr>
<td>6.4</td>
<td>Investigation of secondary structure elements of α- and 310-helices</td>
<td>191</td>
</tr>
<tr>
<td>6.4.1</td>
<td>Analysis of the Raman optical activity spectra</td>
<td>193</td>
</tr>
<tr>
<td>6.4.1.1</td>
<td>Comparison to experimental spectra</td>
<td>197</td>
</tr>
<tr>
<td>6.4.1.2</td>
<td>Identifying signatures of α- and 310-helices</td>
<td>199</td>
</tr>
<tr>
<td>6.4.2</td>
<td>Effect of explicit solvation on the spectrum of the α-helix</td>
<td>200</td>
</tr>
<tr>
<td>6.5</td>
<td>Metallothioneins: proteins with irregular structure</td>
<td>203</td>
</tr>
<tr>
<td>6.5.1</td>
<td>Comparison of the crystal and the model structure</td>
<td>204</td>
</tr>
<tr>
<td>6.5.2</td>
<td>Analysis of the calculated spectrum</td>
<td>206</td>
</tr>
<tr>
<td>6.5.3</td>
<td>Comparison to experimental data</td>
<td>211</td>
</tr>
<tr>
<td>7</td>
<td>Summary and Outlook</td>
<td>215</td>
</tr>
<tr>
<td>A</td>
<td>Implementations</td>
<td>221</td>
</tr>
<tr>
<td>A.1</td>
<td>The program package SNF</td>
<td>221</td>
</tr>
<tr>
<td>A.2</td>
<td>The program package AKIRA</td>
<td>222</td>
</tr>
<tr>
<td>A.3</td>
<td>The program package DNR</td>
<td>223</td>
</tr>
<tr>
<td>B</td>
<td>Computational Methodology</td>
<td>225</td>
</tr>
<tr>
<td>C</td>
<td>Notation</td>
<td>229</td>
</tr>
<tr>
<td>D</td>
<td>List of Abbreviations</td>
<td>233</td>
</tr>
<tr>
<td>E</td>
<td>Publications and Talks</td>
<td>235</td>
</tr>
</tbody>
</table>
F  Acknowledgements  237
I. Zusammenfassung

Spektroskopie ist in der alltäglichen Arbeit von Chemikern ein unentbehrliches Mittel für die Identifikation und Charakterisierung von Molekülen. In dieser Hinsicht stellen die heutzutage untersuchten Moleküle z.B. aufgrund ihrer Größe oder ihrer komplizierten räumlichen Struktur oft eine Herausforderung dar, was die Extraktion der gewünschten Information einzig anhand von spektroskopischen Messungen schwierig oder sogar unmöglich macht. Theoretische Methoden sind eine wertvolle Ergänzung zum Experiment, da sie Spektren berechnen und vorhersagen können. Dadurch lassen sich nicht nur experimentelle Ergebnisse leichter interpretieren, sondern es können auch zusätzliche Informationen gewonnen werden, bezüglich derer ein Experiment blind sein kann. Diese Doktorarbeit befasst sich mit theoretischer Spektroskopie von den theoretischen Grundlagen und der Implementierung effizienter Algorithmen bis zu deren Anwendung auf anspruchsvolle Probleme der Molekülphysik und Chemie.

Der erste Teil dieser Arbeit umfasst die theoretische Behandlung von molekularen Eigenschaften im relativistischen Fall ausgehend von der Dirac-Gleichung für ein Elektron im elektromagnetischen Feld, was der allgemeinste Ansatzpunkt für die Ableitung der Theorie molekularer Eigenschaften ist. Eine Vielzahl relativistischer quantenchemischer Verfahren ist in der Vergangenheit entwickelt worden, von sehr genau, aber rechenzeitintensiven vierkomponentigen Methoden bis zu weniger aufwendigen quasi-relativistischen zweikomponentigen Techniken wie der Douglas–Kroll–Hess-(DKH)-Transformationstheorie, auf die der Schwerpunkt in dieser Arbeit gelegt ist. Es wird ferner gezeigt, unter welchen Umständen paramagnetische und diamagnetische Beiträge in der relativistischen Theorie auftreten und wie magnetfeldabhängige Eigenschaften effizient in das DKH-Verfahren eingebunden werden können.

Der restliche Teil dieser Arbeit befasst sich mit Infrarot-(IR)- und Raman-Schwingungsspektroskopie, aber vor allem mit der chiralen Variante der Raman-Optischen-Aktivität-(ROA)-Spektroskopie, mit der die Stereochemie von Molekülen erforscht werden kann. Die theoretischen Grundlagen für die Bestimmung von molekularen Auslenkungen mit höchster Intensität werden hergeleitet. Diese Auslenkungen stellen hypothetische Schwingungen dar und entsprechen nicht den Normalmoden des betreffenden Moleküls. Trotzdem veranschaulichen sie auf eine einfache Art und Weise, welche Bewegungen im Moleküll für hohe Intensitäten in den Spektren verantwortlich sind, was meistens, und besonders für große Moleküle und im Fall der Raman- und ROA-Spektroskopie, nicht immer so offensichtlich ist. In diesem Zusammenhang wird
ein effizienter Algorithmus (‘Intensity-Tracking’) für die selektive Berechnung von Normalmoden mit hoher IR-, Raman- oder ROA-Intensität vorgestellt. Es werden folglich ausschließlich die intensiven Normalmoden, die in einem Spektrum von Interesse sind, berechnet, was eine Reduktion der Rechenzeit zur Folge hat, wenn geeignete Auswahl- und Konvergenzkriterien gewählt werden. Dieses Verfahren ermöglicht einen schnellen Zugang zu den wichtigsten Charakteristika von IR-, Raman- und ROA-Spektren molekularer Systeme, deren Spektren ansonsten nur von einer sehr rechenzeitintensiven vollständigen Schwingungsrechnung erhalten werden können.

II. Abstract

Spectroscopy is an essential tool for the identification and characterization of molecules in the daily work of chemists. In this regard, the molecular systems studied nowadays are often quite challenging due to, e.g., their large size or their complicated spatial structure, which makes it difficult or even impossible to deduce the desired information solely from spectroscopic measurements. Theoretical methods are a valuable complement to experiment since spectroscopic spectra can be calculated and predicted. In this way, not only the interpretation of the experimental results is facilitated but also additional information, which is not available from experimental data, can be obtained. The topic of this work is therefore theoretical spectroscopy including the development of theoretical foundations, the implementation of efficient algorithms, and their application to different types of molecules.

The first part is concerned with the theoretical treatment of molecular properties in a relativistic framework starting from Dirac’s equation for a single electron in an electromagnetic field, which is the most general starting point for quantum chemical calculations. A variety of relativistic quantum chemical approaches has been developed in the past, including very accurate, but computationally demanding four-component methods and computationally cheaper quasi-relativistic two-component methods like the Douglas–Kroll–Hess (DKH) transformation theory, which is focused on in this thesis. It is shown how paramagnetic and diamagnetic contributions emerge in relativistic theory and how magnetic-field-dependent properties can be efficiently treated within the DKH procedure.

The remaining part deals with vibrational infrared (IR), Raman, and, in particular, Raman optical activity (ROA) spectroscopy, which is the chiral variant of Raman spectroscopy and probes the stereochemistry of molecules. The theoretical foundations for the determination of molecular distortions carrying maximum intensity are devised. These are hypothetical modes, which do not resemble normal modes of the molecule. Nevertheless, they visualize in a simple way the motions of the molecule leading to high intensity, which is mostly not that obvious, especially for large molecules and in the case of Raman and ROA spectroscopy. In this context, an efficient algorithm (‘intensity-tracking’) for the selective calculation of normal modes with high IR, Raman, or ROA intensity is developed. Solely the intense normal modes of interest are targeted, which results in a reduction of the computational effort if appropriate selection and convergence criteria are applied. This approach enables a fast access to the most important features in IR, Raman, and ROA spectra of molecular systems,
whose spectra could otherwise only be obtained by a full vibrational calculation with prohibitively high computational cost. The second important algorithmic achievement presented in this thesis is the efficient calculation of ROA spectra, which is based on the employment of density-fitting techniques for the ROA property tensor evaluation, carried out by the program package TURBOMOLE in combination with the massively parallel and restart-friendly implementation of the Snf program package. This set-up makes the calculation of ROA spectra for molecules with a high number of atoms and with large basis sets possible. As a consequence, the first ROA spectra of chiral metal complexes can be presented. In addition, ROA spectra of different organic molecules are investigated, ranging from a small sugar molecule, whose ROA spectra are examined with an emphasis on solvent effects, over the amino acid tryptophan, which gives rise to characteristic side chain bands in ROA spectra, to α- and 310-helices. The final example is rat metallothionein, which contains turns as the only secondary structure elements. This protein is the by far largest molecule, for which a full quantum chemical calculation of a ROA spectrum has been performed up to date. The basic assumption for the above-mentioned ROA calculations is that resonances with excited electronic states do not occur. In order to handle such resonance situations, the theory of vibrational Resonance Raman optical activity (RROA) has to be applied. In this thesis, an extension of the RROA theory, which has originally been formulated for a single excited electronic state in the sum-over-states ansatz, to two electronically excited states is given as well as a corresponding time-dependent formulation. In addition, the first RROA calculations which include vibronic details of the electronic states in resonance are presented for the analgesic naproxen since this is the only molecule for which RROA spectra have been measured.
1. Introduction

The design of molecules which perform a particular, pre-defined function is one of the central goals of modern chemistry involving the fields of materials science to nanotechnology and from biochemistry to synthetic biology. An important example is the design of proteins or metal complexes that catalyze a given chemical reaction [1–3]. A prerequisite for such a design is, of course, the understanding of the interplay of structure and catalytic function. To study such interactions, one needs experimental techniques that unambiguously identify structural elements of proteins or metal complexes during their catalytic activity in their natural environment. Even though X-ray crystallography can be employed to obtain accurate structures with atomic resolution, often a heavy atom has to be present in the structure [4]. Furthermore, it only provides static snapshots of the structure and cannot be applied in solution. Employing nuclear magnetic resonance (NMR) spectroscopy is another possibility to obtain protein structures in solution, but its time resolution is limited due to the application of radio-frequency pulses [5]. For this reason, NMR spectroscopy is not suited for studying fast structural changes or for investigating very flexible or disordered protein conformations. Therefore, complementary spectroscopic techniques are needed. One alternative method is provided by vibrational spectroscopy, which can be directly applied to molecules in solution and which potentially allows for femtosecond time resolution [6, 7].

The methods applied routinely in chemistry are mainly infrared (IR) and Raman spectroscopy [8–12], which are, however, not sensitive to the chirality of molecules. In today’s syntheses, chiral molecules play an important role. The identification of enantiomers is a crucial point since each of them possesses different chemical properties and hence reacts in diverse ways. Popular examples for chiral molecules are the naturally occurring molecule limonene, whose enantiomers smell like oranges and turpentine, respectively, [13] and the drug thalidomide, which was taken by pregnant women against morning sickness and lead to birth defects of the children because one enantiomer caused fetal-tissue damages [14].

The determination of the absolute configuration is not straightforward and often accomplished by application of empirical rules of thumb or time-consuming synthetic routes. Historically, optical rotation [15, 16] and electronic circular dichroism [17, 18] have been the foremost spectroscopic methods for the study of chiral molecules [19]. However, more powerful methods have been devised
by chiroptical spectroscopies in the IR region, namely the vibrational circular
dichroism (VCD) [18, 20] and vibrational Raman optical activity (ROA) [21–23]
techniques. Due to the high number of vibrations in large molecules, a wealth
of data is usually obtained compared to methods probing merely the \textit{electronic}
structure of a molecule and provides more information on the system under
study.

In contrast to VCD, which is nowadays a well-established experimental and
theoretical method, ROA spectroscopy is still in its infancy. This may be due to
the fact that ROA spectrometer have become commercially available only since
2001 [24] although the first ROA spectra have already been measured in 1973 [25]
and 1975 [26]. Nevertheless, the great potential of ROA spectroscopy has been
revealed by measurements of molecules ranging from small organic molecules
like the deuterated \((R)-[^2H_1,^2H_2,^2H_3]\)-neopentane [4, 27] to large biomolecules
including proteins and viruses [28–36].

Even though a considerable number of ROA spectra has been recorded in the
past decades, the understanding of the underlying mechanisms remains rather
incomplete. Therefore, the interpretation of measured ROA spectra and the
assignment of spectral signatures to specific structure elements of, for instance,
biomolecules have mainly been based on the ROA spectra of certain proteins
or model polypeptides for which the structure has been determined by X-ray
crystallography (see, e.g., Ref. [37]) or on a careful comparison of different
measured spectra, also using statistical techniques such as multivariate analysis
methods [38, 39].

\textit{Ab initio} calculations of ROA spectra allow for the prediction of the ROA
spectrum for a given molecular structure from the first principles of quantum
mechanics. By comparing the calculated spectra of several potential structures
to the one observed in experiment it is possible to determine which of
the considered structures is measured in experiment. In contrast to the
large molecules measured, however, calculations have solely been possible for
small organic molecules due to the high computational effort (see, for example,
Refs. [19, 27, 40–54]). For the interpretation of ROA spectra of proteins and for
the identification of secondary structure signatures, one has to construct models
for secondary structure elements. Since realistic models require rather large
polypeptides, accurate \textit{ab initio} calculations of ROA spectra for such systems
are hampered by the huge computational demand.

Hence, one goal of this work is to improve on ROA calculations making the
treatment of large molecules like helices and metal complexes feasible. Moreover,
the exploration of the novel field of vibrational Resonance ROA (RROA) is
undertaken. This enforces the study of, for instance, the sensitivity of ROA
spectroscopy to the secondary structure of helices and the chirality of metal
complexes. Since the spectra become crowded if large molecules are involved,
new strategies for the analysis of such spectra are applied.

Beside this, methodological improvements like the powerful calculation of IR,
Raman, and ROA spectra by the selective calculation of only the intense parts
of the spectrum, examination of the origin of intensity via intensity-carrying modes (ICMs), and an efficient theoretical treatment of molecular properties in a relativistic framework are presented.

1.1 Methods of theoretical chemistry

The most accurate description of all interactions of particles with electromagnetic fields provides Quantum Electrodynamics (QED) \cite{55, 56}. However, the features described by QED like self-energy, vacuum polarization, particle creation and annihilation processes \cite{57–62} can be safely disregarded for the problems examined in theoretical chemistry. Due to these peculiarities, QED is far too complicated for chemical and spectroscopic purposes. As a consequence, the starting point for quantum chemistry is the quantum mechanical equation of motion,

$$
\hat{H} = \frac{i\hbar}{\partial t} |\Psi(r_e, R_{\text{nuc}}, t)\rangle = H |\Psi(r_e, R_{\text{nuc}}, t)\rangle,
$$

(1.1)

where $\hbar$ is Planck’s constant divided by $2\pi$. The elementary particles treated in quantum chemistry are the nuclei and electrons. $H$ is the many-particle Hamiltonian containing the nuclear and electronic kinetic-energy operators and the nucleus–nucleus, nucleus–electron, and electron–electron interaction operators. The wave function $|\Psi(r_e, R_{\text{nuc}}, t)\rangle$ depends on the nuclear and electronic coordinates collected in $R_{\text{nuc}}$ and $r_e$, respectively, and on the time $t$. In the following, several ansätze employed in quantum chemistry for the Hamiltonian $H$ and for the wave function $|\Psi(r_e, R_{\text{nuc}}, t)\rangle$ will be shortly summarized.

A remedy to the shortcoming of QED offers Dirac’s relativistic theory of the electron. Nevertheless, so-called fully relativistic calculations based on the Dirac Hamiltonian are computationally very demanding and only applicable to rather small molecules. Thus, a plethora of relativistic approximations to Dirac’s theory of the electron has been developed. In this context, mainly two methodological branches have emerged, namely elimination and transformation techniques (see Fig. 1.1), which reduce the originally four-dimensional structure of the Dirac Hamiltonian to a two-component form.

The most prominent among elimination techniques are the Normalized Elimination of the Small Component (NESC) \cite{63–65} and Regular Approximations \cite{66–69} [e.g., Zeroth Order Regular Approximation (ZORA) \cite{70}]. Whereas, the Douglas–Kroll–Hess (DKH) method relies on a unitary transformation of the Dirac equation \cite{71–73} and provides well-defined, analytical operator expressions. The latter approach will be of paramount importance for the theoretical treatment of electromagnetic properties described in detail in chapter 2.
Figure 1.1: Schematic presentation of some methods of theoretical chemistry and approximations chosen in this work for the calculation of the vibrational spectra.

Simplified one-component forms both of elimination and of transformation techniques have been devised by neglect of all spin-dependent terms in the resulting equations. Such so-called scalar-relativistic one-component approaches are in
wide use because they can be implemented into standard nonrelativistic quantum chemical packages without much effort. As the spectroscopic phenomena relevant for this thesis depend mostly on the electron distribution of the valence region, further simplifications can be introduced through so-called valence-only Hamiltonians where the potential generated by core electrons has been approximated via a suitably parameterized effective core potential [74]. Moreover, most relativistic effects (spin–orbit coupling and contraction of inner shells of atoms) stem from the core region of the molecular system under study so that relativistic corrections can easily be incorporated into such effective potentials. The electrons in the valence region can therefore formally be treated in a nonrelativistic one-component scheme based on the Schrödinger equation. All these Hamiltonians, which are derived by approximations to the Dirac Hamiltonian, are one-electron Hamiltonians, which can straightforwardly employed for the one-electron terms in the many-particle Hamiltonian, i.e., for the electronic kinetic energy and the nucleus–electron interaction operators. The electron–electron interaction is usually included via the standard instantaneous Coulomb interaction, which can simply be added to the one-electron terms. Relativistic corrections to the electron–electron interaction may be considered via the Breit interaction operator [75, 76]. The nuclei are treated within nonrelativistic Schrödinger quantum mechanics since their motion is very slow compared to the speed of light so that relativistic effects are negligibly small [77].

After the brief presentation of approximate Hamiltonians needed in Eq. (1.1), we will now focus on the choice of a suitable wave function $|\Psi(r_e, R_{\text{nuc}}, t)\rangle$. After separating the electronic and nuclear degrees of freedom in Eq. (1.1) via the Born–Oppenheimer (BO) approximation (see section 1.2), the wave function accounting for the electronic part depends parametrically on the nuclear coordinates. The most simple form of a many-electron wave function, which fulfills the Pauli principle, can be chosen in form of an antisymmetrized product of one-electron functions (so-called orbitals), which is known as Slater determinant and represents the basis for the Hartree–Fock (HF) theory [78]. Solution of the HF equations yields the optimized set of orbitals giving rise to the lowest electronic energy. However, an exact solution for the many-electron wave function requires a more sophisticated ansatz. In principle, HF theory yields an infinitely large set of orbitals and only those are selected for the construction of the HF wave function which lead to the Slater determinant with the lowest electronic energy. However, in order to obtain the correct many-electron wave function, a complete set of such Slater determinants is needed. Since all remaining orbitals can also be used to form Slater determinants, a linear combination of all such many-electron functions can be applied to obtain an ansatz for the correct many-electron wave function. Every single Slater determinant represents an electronic configuration and the linear expansion of an exact many-electron wave function in terms of Slater determinants is thus called Configuration Interaction (CI) [79]. The expansion coefficients are determined within a variational scheme. In addition, alternative methods to calculate these
expansion coefficients have been developed, such as Møller–Plesset perturbation theory (MP) [80] and Coupled-Cluster (CC) [81, 82] approaches. If all Slater determinants that can be generated from the corresponding HF orbitals are taken into account in such a linear expansion, then full CI is obtained. The difference in the electronic energy from a HF and a full CI calculation is called correlation energy.

Beyond wave-function-based methods, also approaches relying on the total electron density exist, known as density functional theory (DFT) [83–86]. The formal basis for expressing the exact ground-state energy of a system as an explicit functional of the electronic energy is provided by the Hohenberg–Kohn theorems [87]. Although DFT is approximate in the sense that the exact exchange–correlation functional is not known, the existing density functionals, which are obtained by fitting to experimental data, give very good results, also for kinds of molecules which were not included into the test set employed for the fitting procedure. In addition, the number of parameters comprised in the density functionals is quite small, which is in contrast to the heavily parametrized semi-empirical methods.

Wave-function-based methods become the more time-demanding the higher the quality of the wave-function ansatz is. The investigation of the molecules shown in this work by these approaches would have hardly been possible due to the large size of the systems studied. Therefore, DFT has been an excellent compromise between efficiency and reliability of the results, also due to efficient density-fitting techniques, which additionally result in a considerable speed-up of the calculations (see section 4.1). The method of choice is Kohn–Sham DFT (KS-DFT) which is described in more detail in section 1.4.

1.2 Born–Oppenheimer approximation

One method for the calculation of vibrational spectra is Molecular Dynamics (MD), where the motion, and hence the vibrational frequencies, of an assembly of molecules and the corresponding intensities can be obtained from appropriate correlation functions [88–91]. Nevertheless, MD simulations based on quantum mechanics are computationally very demanding. This is even true for Car–Parrinello MD [92,93]. Therefore, the route chosen in this work for the calculation of vibrational frequencies is based on the time-independent Schrödinger equation employing the BO approximation (moreover, the harmonic approximation (see section 1.3) is employed, which is well justified for the type of vibrations relevant to ROA spectra).

For the derivation of the latter, we start with the time-dependent Schrödinger equation, which is written for an eigenstate of a particular system $|\psi_n(r_e, R_{\text{nuc}}, t)\rangle$ as (the superscript ‘nr’ indicates the nonrelativistic framework)

$$i\hbar \frac{\partial}{\partial t} |\psi_n(r_e, R_{\text{nuc}}, t)\rangle = H |\psi_n(r_e, R_{\text{nuc}}, t)\rangle$$

(1.2)
with the time-independent Hamiltonian \( H = T_{\text{nuc}} + T_e + V_{\text{nuc,nuc}} + V_{\text{e,nuc}} + V_{\text{e,e}} \). \( T_{\text{nuc}} \) and \( T_e \) denote the nuclear and electronic kinetic-energy operators, respectively, which include the momentum operator \( p_k = -i\hbar \nabla_k \):

\[
T_{\text{nuc}} = \sum_{k=1}^{M} \frac{p_k^2}{2m_k} = \sum_{k=1}^{M} \left( -\frac{\hbar^2}{2m_k} \nabla_k^2 \right),
\]

\[
T_e = \sum_{k=1}^{N_e} \left( -\frac{\hbar^2}{2m_e} \nabla_k^2 \right).
\]

\( N_e \) is the number of electrons (with electron mass \( m_e \)) and \( M \) the total number of the nuclei with nucleus \( k \) having mass \( m_k \). The electronic coordinates for electron \( l \) are contained in the vector \( \mathbf{r}_l \) and the ones for nucleus \( k \) in \( \mathbf{R}_k \). \( V_{\text{nuc,nuc}} \), \( V_{\text{e,nuc}} \), and \( V_{\text{e,e}} \) are the operators describing the Coulomb interaction between the nuclei, between electrons and nuclei, and between the electrons, respectively (in SI units):

\[
V_{\text{nuc,nuc}} = \sum_{k=1}^{M} \sum_{l>k}^{M} \frac{Z_k Z_l}{4\pi \varepsilon_0 |\mathbf{R}_k - \mathbf{R}_l|},
\]

\[
V_{\text{e,nuc}} = \sum_{k=1}^{M} \sum_{l=1}^{N_e} \frac{q_e Z_k}{4\pi \varepsilon_0 |\mathbf{r}_l - \mathbf{R}_k|},
\]

\[
V_{\text{e,e}} = \sum_{k=1}^{N_e} \sum_{l>k}^{N_e} \frac{q_e^2}{4\pi \varepsilon_0 |\mathbf{r}_k - \mathbf{r}_l|},
\]

where \( Z_k \) denotes the charge of nucleus \( k \), \( q_e = -e \) is the charge of an electron with \( e \) being the elementary charge, and \( \varepsilon_0 \) is the permittivity of free space. The elementary particles, i.e., the electrons and nuclei, are treated as nonpolarizable point-like particles and, as a consequence, only electrostatic monopole interactions are considered because no electrostatic many-body effects on the pair interaction occur [56]. \( V_{\text{e,nuc}} \) depends on both the electronic and nuclear coordinates so that their movement is coupled. As the Hamiltonian does not change in time, the wave function can be separated into a time- and spatial-dependent part:

\[
|\psi_n(r_e, \mathbf{R}_{\text{nuc}}, t)\rangle = \exp \left( -\frac{i}{\hbar} E_n t \right) |\psi_n(r_e, \mathbf{R}_{\text{nuc}})\rangle.
\]

The time-independent nonrelativistic Schrödinger equation is thus given as

\[
H |\psi_n(r_e, \mathbf{R}_{\text{nuc}})\rangle = E_n |\psi_n(r_e, \mathbf{R}_{\text{nuc}})\rangle.
\]

The BO approximation [94] is applied throughout this work. It enables the separation of the nuclear and electronic motion due to a product ansatz for the wave function,

\[
|\psi_n(r_e, \mathbf{R}_{\text{nuc}})\rangle = |\varphi_n(r_e, \mathbf{R}_{\text{nuc}})\rangle |\chi_n(\mathbf{R}_{\text{nuc}})\rangle.
\]
\[ |n_e (r_e, \tilde{R}_{nuc}) \rangle \] are the nuclear and electronic wave functions, respectively. The electronic wave function is now parametrically dependent on the nuclear coordinates, i.e., a change in the nuclear coordinates leads to a change in the electronic wave function. Furthermore, the action of \( T_{nuc} \) onto \( |n_e (r_e, \tilde{R}_{nuc}) \rangle \) is neglected so that the electronic Schrödinger equation is given by

\[
[T_e + V_{nuc,nuc} + V_{e,nuc} + V_{e,e}] |n_e (r_e, \tilde{R}_{nuc}) \rangle = E_{el,n} |n_e (r_e, \tilde{R}_{nuc}) \rangle. \tag{1.11}
\]

The electrons follow the nuclear motion adiabatically and it is assumed that they make no transitions to another state. A potential energy surface (PES) defined by \( E_{el,n} (R_{nuc}) \) can now be calculated by solving Eq. (1.11) for different nuclear positions.

The electronic energy \( E_{el,n} (R_{nuc}) \) is necessary for the solution of the nuclear Schrödinger equation

\[
[T_{nuc} + E_{el,n} (R_{nuc})] |n_r \chi_n (R_{nuc}) \rangle = E_n |n_r \chi_n (R_{nuc}) \rangle, \tag{1.12}
\]

which describes the motion of the nuclei on the PES.

### 1.3 Harmonic approximation

Another approximation usually adopted in the calculation of vibrational frequencies is the so-called harmonic approximation for a local minimum region of the PES [95, 96]. Due to the parametric dependence of the electronic wave function on the nuclear coordinates, \( E_{el,n} (R_{nuc}) \) is only be determined pointwise. For smaller molecules (containing not more than about four atoms) it is feasible to calculate the PES explicitly. Around ten points per internal degree of freedom are needed in order to interpolate the PES, which results for a triatomic molecule in 10\(^3\) structure calculations. For larger molecules, \( E_{el,n} (R_{nuc}) \) is usually not known analytically. Therefore, \( E_{el,n} (R_{nuc}) \) is expanded in a Taylor series around an equilibrium structure with the position \( O_{equil} \), which is indicated by the subscript ‘0’, and truncated after the second-order term:

\[
E_{el,n} (R_{mw}) = E_{el,n} (O_{equil}) + \sum_{k=1}^{M} \left( \frac{\partial E_{el,n}}{\partial R_{kw}} \right)_{0} R_{kw}^m + \frac{1}{2} \sum_{k,j=1}^{M} \left( \frac{\partial^2 E_{el,n}}{\partial R_{kw} \partial R_{jw}} \right)_{0} R_{kw}^m R_{jw}^m + \cdots. \tag{1.13}
\]

For the sake of simplicity, the coordinate origin is set to the minimum of the potential energy. The nuclear coordinates contained in \( R_{nuc} \) are formulated in terms of mass-weighted coordinates, \( R_{mw}^{kw} \), which are evaluated for each atom \( k \) with mass \( m_k \) according to \( R_{kw}^m = \sqrt{m_k} R_{kw} \). The first derivative in Eq. (1.13) is zero since the expansion is around the equilibrium structure. The matrix in
the second-order term containing the derivatives of $E_{el,n}$ with respect to the mass-weighted nuclear coordinates is called Hessian matrix $M^{mw}$. Inserting Eq. (1.13) into the nuclear Schrödinger equation, Eq. (1.12), we arrive at

$$T_{nuc} + \frac{1}{2} \sum_{k,j=1}^{M} R^{mw}_{ka} \left( \frac{\partial^2 E_{el,n}}{\partial R^{mw}_{ka} \partial R^{mw}_{ja}} \right) R^{mw}_{ja} \right] \left| \hat{T}_n \chi_n(R_{nuc}) \right>= E_n \left| \hat{T}_n \chi_n(R_{nuc}) \right>.$$ (1.14)

Bringing $E_{el,n}(O_{equil})$ to the right-hand side of Eq. (1.14) and introducing the nuclear kinetic energy $E_v^n = E_n - E_{el,n}(O_{equil})$, we obtain

$$T_{nuc} + \frac{1}{2} (R^{mw})^T \cdot M^{nw} \cdot R^{mw} \right] \left| \hat{T}_n \chi_n(R_{nuc}) \right>= E_v^n \left| \hat{T}_n \chi_n(R_{nuc}) \right>.$$ (1.15)

In order to split Eq. (1.15) into decoupled equations, we search for linear combinations of the mass-weighted nuclear coordinates which diagonalize the Hessian matrix. This is achieved with the help of so-called normal coordinates $Q_k$.

$$Q_k = \sum_{j=1}^{M} L_{kj} R^{mw}_{ja} = L_k \cdot R^{mw}.$$ (1.16)

$L_k$ is the normal mode belonging to normal coordinate $Q_k$ and describes the collective motion of the nuclei along $Q_k$. Transformation of Eq. (1.15) into the basis of the $3M$ normal coordinates $Q_k$ collected in the vector $Q$ leads to

$$T^{(Q)}_{nuc} + \frac{1}{2} (Q)^T \cdot M^{(Q)} \cdot Q \right] \left| \hat{T}_n \chi_n(Q) \right>= E_v^n \left| \hat{T}_n \chi_n(Q) \right>.$$ (1.17)

with

$$M^{(Q)} = L^T \cdot M^{nw} \cdot L,$$ (1.18)

$$M^{(Q)}_{kj} = \frac{\partial^2 E_{el,n}}{\partial Q_k \partial Q_j} = 0, \quad \forall \ k \neq j.$$ (1.19)

The columns of the matrix $L$ are the normal modes in terms of mass-weighted Cartesian displacements. Thus, we have $3M$ decoupled differential equations,

$$\left[ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q^2_k} + \frac{1}{2} M^{(Q)}_{kk} Q^2_k \right] \left| v_{n,k} \right> = \epsilon_{n,k} \left| v_{n,k} \right>.$$ (1.20)

which have the form of harmonic oscillator equations with analytically known eigenfunctions $|v_{n,k}\rangle$ and the quantum numbers $v_{n,k}$. The nuclear wave function is a product of the harmonic oscillator wave functions, $|\hat{T}_n \chi_n(Q)\rangle = \Pi_{k=1}^{3M} |v_{n,k}\rangle$, and $E_v^n$ is the sum of the corresponding eigenvalues, $E_v^n = \sum_{k=1}^{3M} \epsilon_{n,k}$. 

The angular frequency $\omega_k$, belonging to normal coordinate $Q_k$, is obtained via $\omega_k = \sqrt{M_{kk}}$. The corresponding vibrational frequency is given by $\nu_k$ via $\omega_k = 2\pi\nu_k$ and the wavenumber $\tilde{\nu}_k$ by $\tilde{\nu}_k = \nu/c$, where $c$ is the speed of light. Anharmonicity effects are obtained by higher-order terms in the Taylor expansion of Eq. (1.13). The only study about anharmonic corrections to ROA spectra has been carried out by Danček et al. [97] for the alanine and proline zwitterions by applying the Vibrational Configuration Interaction [98–100] and Vibrational Self-Consistent Field [98,99,101,102] methods as well as perturbation theory [103–106]. The improvement of the spectra by inclusion of anharmonicities has been found to be small, especially in the region from 200 to 1800 cm$^{-1}$. This is in accordance with the results found for Raman spectra, for which a very good agreement of the harmonic frequencies obtained from DFT with experimental fundamental ones has been observed [107–113]. Therefore, we do not consider anharmonic corrections in this work, which would, in addition, also make the calculations computationally more expensive [114–116].

1.4 Kohn–Sham density functional theory

In order to solve the nuclear Schrödinger equation given in Eq. (1.12), which is required for the determination of the normal modes (see section 1.3), we need a fast and reliable method for the calculation of the electronic energy. KS-DFT [83,84,86,117–121] is currently the method of choice rendering also the calculation of larger molecular systems possible. The basis for KS-DFT is the assertion that for every interacting system with ground-state density $\rho_{KS}(r_1)$ a non-interacting system exists with the same ground-state density. Non-interacting means that there are no interaction terms explicitly containing coordinates of two electrons. In general, $r_1$ and $r_2$ indicate the coordinates of electron 1 and 2, respectively. As a consequence, the density of the interacting system can be written as the density constructed from a single Slater determinant containing only one-electron functions (KS orbitals) $\{|k_{i\sigma}\}$ (in general, $\sigma$ and $\tau$ denote the spin eigenfunctions of the $z$-component of the spin operator $S$) of non-interacting fermions. The KS one-particle equations with functions $|k_{i\sigma}\rangle$ and the corresponding energies $\epsilon_{i\sigma}$ are for a fixed set of nuclei given by

$$H_{KS}^{KS}|k_{i\sigma}(r_1)\rangle = [T_e + v_{eff}(r_1)]|k_{i\sigma}(r_1)\rangle = \epsilon_{i\sigma}|k_{i\sigma}(r_1)\rangle.$$  \hspace{1cm} (1.21)

The Hamiltonian $H_{KS}^{KS}$ comprises the kinetic energy $T_e = [-\hbar^2/(2m_e)]\nabla^2$ and the effective potential $v_{eff}(r_1)$ (again in SI units),

$$v_{eff}(r_1) = v_{e,nuc}(r_1) + v_{coul}(r_1) + v_{xc}(r_1)$$

$$= \sum_{k=1}^{M} \frac{q_e Z_k}{4\pi \epsilon_0 |r_1 - R_k|} + \frac{q_e^2}{4\pi \epsilon_0} \int \frac{\rho_{KS}(r_2)}{|r_1 - r_2|} dr_2 + \frac{\partial E_{xc}[\rho_{KS}]}{\partial \rho_{KS}(r_1)}.$$  \hspace{1cm} (1.22)
which consists of the external potential $v_{\text{e,nuc}}(r)$, the Coulomb potential $v_{\text{coul}}(r_1)$, and the exchange–correlation potential $v_{\text{xc}}(r_1)$. Since the exact exchange–correlation functional $E_{\text{xc}}[\rho^{\text{KS}}]$ is not known, many different approximate density functionals have been devised. The ones employed in this work are the BP86 [122, 123], BLYP [122, 124], and B3LYP [124–126] density functionals. BP86 and BLYP are pure density functionals whereas B3LYP is a hybrid density functional, which employs Becke’s three-parameter hybrid-exchange functional [125] and the Lee, Yang, and Parr (LYP) correlation functional [124] and contains 20% exact HF-type exchange admixture. A modified version of B3LYP with 15% exact exchange admixture is the so-called B3LYP$^*$ density functional, which has shown to yield better spin-state energy splittings for transition metal complexes [127–132]. Molecular orbitals are expressed as linear combinations of the one-electron basis functions, which is known as linear combination of atomic orbitals.

1.5 Outline of this work

At the beginning of this thesis, the treatment of molecular properties via external electromagnetic perturbation in the most fundamental quantum mechanical framework is described, which yields the most universal approach for the calculation of electromagnetic properties. After the presentation of Dirac’s one-electron equation in electromagnetic fields and underlying theoretical foundations given in sections 2.1 and 2.2, several approaches for the incorporation of the magnetic vector potential into quasi-relativistic theories within the DKH approach are investigated in section 2.3. In addition to that, Rayleigh–Schrödinger perturbation theory for the calculation of magnetic properties in the infinite-order DKH approach is presented in section 2.4.

The calculations carried out in this work deal mainly with the quite young, but very promising technique of ROA spectroscopy. For ROA spectroscopy, only some terms of the multipole-expanded external electromagnetic field created by incident light are needed. In order to provide the theoretical basis, a derivation of the ROA theory is given in section 3.1. The evaluation of ROA intensities is presented first for the general case in section 3.2 and then for the far-from-resonance approximation in section 3.3 (with an emphasis on the origin dependence of the ROA tensors due to the implementational part of this work) and for resonance with excited electronic states in section 3.4. Different procedures for the analysis of ROA spectra, which include the assessment of the bond polarizability model as well as localization of ROA intensities and normal modes, are presented in section 3.5. As it is difficult to predict which distortions in molecules lead to high IR, Raman, or ROA intensity, the concept of the ICMs, which are virtual modes with maximum intensity, is developed in section 3.6.

The algorithmic developments presented in this thesis concern, on the one hand, the efficient evaluation of ROA tensors within time-dependent KS-DFT
(TDKS-DFT) employing response theory which is briefly described in section 4.1. On the other hand, a smart approach for the selective calculation of high-intensity normal modes in IR, Raman, and ROA spectroscopy is developed in section 4.2. Tests for a set of molecules applying different convergence and selection criteria can be found in the very same section. A short overview of the main implementations is given in appendix A.

The remaining part of this thesis is dedicated to the analysis of calculated vibrational spectra. In chapter 5, ROA spectra of chiral metal complexes are presented in combination with the assessment of the dependence on the density functionals and the basis set size employed (sections 5.1 and 5.2). The sensitivity of ROA spectroscopy to cobalt complexes differing only in the number or configuration of the chiral ligands is investigated in section 5.3.

The last chapter of this thesis deals with spectra of different kinds of organic molecules. First, Raman and ROA spectra of the analgesic naproxen, which is the only molecule for which a RROA spectrum has been measured so far [133], is studied both in the far-from-resonance and resonance approximation (section 6.1). Next, the off-resonance ROA and Raman spectra of the sugar molecule 1,6-anhydro-\(\beta\)-\(D\)-glucopyranose are explored in section 6.2 with a focus on the influence of conformation and solvent effects. Most bands of peptide ROA spectra are dominated by the peptide backbone. However, specific bands are related to the conformation of amino acid side chains. An example is the amino acid tryptophan, which gives rise to a well visible band in experimental ROA spectra. Since there have been some uncertainties regarding the dependence of the sign of this band on the molecular structure, ROA calculations are presented in section 6.3. Beyond that, ROA spectra of different helical structures are analyzed in section 6.4, and, finally, the ROA spectrum of rat metallothionein is shown in section 6.5, which is the by far largest molecule for which a full first-principles ROA calculation has been accomplished up to date.
2. General Theory of Molecular Properties

The methods for the calculation of spectroscopic properties are often based on the nonrelativistic framework of Schrödinger quantum mechanics. However, the coupling of the radiation field to the quantized matter field can only be rigorously done in terms of a relativistic theory [56]. Especially, the theoretical prediction of magnetic resonance parameters, for example, requires a relativistic framework, in particular, if heavy elements are involved [134,135] (for additional literature, we refer to Refs. [136–145] for g-tensors, Refs. [142,146–152] for hyperfine coupling tensors, Refs. [153–171] for nuclear magnetic shielding constants, and Refs. [157,172–175] for spin–spin coupling constants). Therefore, we start our theoretical treatment with Dirac’s equation for one electron in an electromagnetic field, which is the most general approach for the calculation of spectroscopic properties [176]. Of course, QED is the fundamental theory from the physical point of view but it is far too complicated for the systems studied in chemistry [56].

The Dirac operator for an electron in an electromagnetic field is given by [the units employed in this section are Gaussian units (compare appendix C)] [56]

\[
D = \begin{pmatrix} \beta \gamma_0 c^2 + c \alpha \cdot p + V - q_e \alpha \cdot A \\ V + m_e c^2 \\ c \sigma \cdot (p - q_e c A) \\ V - m_e c^2 \end{pmatrix} = D_0 \equiv D_1,
\]

(2.1)

The Pauli vector \( \mathbf{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \) with the spin matrices \( \sigma_x, \sigma_y, \) and \( \sigma_z \) and the Dirac matrices \( \beta \) and \( \alpha = (\alpha_x, \alpha_y, \alpha_z) \) have the following definitions [177]:

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},
\]

(2.2)

\[
\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}, \quad \text{and} \quad \beta = \begin{pmatrix} 1_2 & 0 \\ 0 & -1_2 \end{pmatrix}.
\]

(2.3)

The scalar potential \( V \) describes for atomic and molecular systems the interactions between the electron and the nuclei (in the following just referred to as the external potential) aside of additional external scalar potentials. \( A \) denotes the magnetic vector potential. Since the Dirac operator is a \( (4 \times 4) \) matrix, the wave functions consist of four-component spinors where the upper two components are the so-called large component \( |\Psi^L\rangle \) and the lower two the small component \( |\Psi^S\rangle \).
The Dirac operator for one electron is the basis for effective one-electron equations in many-electron theory. As can be seen in Eq. (2.1), $D$ comprises only a term linear in the magnetic vector potential, $D_1$, which gives rise to so-called paramagnetic contributions. Employing Rayleigh–Schrödinger perturbation theory, the corresponding second-order energy $E^p_2$ is given as (compare, e.g., Ref. [178]),

$$E^p_2 = \text{Re}\langle \psi_0 | D_1 | \psi_1 \rangle$$  \hspace{1cm} (2.4)

with $|\psi_0\rangle$ and $|\psi_1\rangle$ being the zeroth- and first-order wave functions and employing the condition $\langle \psi_0 | \psi_1 \rangle = 0$. The NMR shielding tensor expression, for instance, depends linearly on the vector potentials generated by the external magnetic fields and the nuclear magnetic moment.

The nonrelativistic Pauli equation can be derived from Eq. (2.1) by starting with the Dirac equation employing the mechanical (or kinematical or linear) momentum operator $\pi = \mathbf{p} - \frac{q}{c} \mathbf{A}$ (minimal coupling). We shift the energy scale by $-m_e c^2$ in order to have a better comparison with the nonrelativistic energy of a free electron given by Schrödinger’s equation where the lowest possible energy value is zero. The Dirac equation is obtained as

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\Psi^L \rangle \\ |\Psi^S \rangle \end{pmatrix} = c \begin{pmatrix} (\sigma \cdot \pi) |\Psi^S \rangle \\ (\sigma \cdot \pi) |\Psi^L \rangle \end{pmatrix} - 2m_e c^2 \begin{pmatrix} 0 \\ |\Psi^S \rangle \end{pmatrix} + V \begin{pmatrix} |\Psi^L \rangle \\ |\Psi^S \rangle \end{pmatrix}$$  \hspace{1cm} (2.5)

and its lower part as

$$\left( i\hbar \frac{\partial}{\partial t} + 2m_e c^2 - V \right) |\Psi^S \rangle = c (\sigma \cdot \pi) |\Psi^L \rangle.$$  \hspace{1cm} (2.6)

The energy $E \rightarrow i\hbar \partial / \partial t$ and the potential $V$ are small compared to the rest energy $m_e c^2$ for nonrelativistic energies. Therefore, the so-called kinetic-balance condition [56] is invoked,

$$|\Psi^S \rangle \approx \frac{\sigma \cdot \pi}{2m_e c} |\Psi^L \rangle,$$  \hspace{1cm} (2.7)

which leads by insertion into the upper part of Eq. (2.5) to

$$i\hbar \frac{\partial}{\partial t} |\Psi^L \rangle = \frac{(\sigma \cdot \pi)(\sigma \cdot \pi)}{2m_e} |\Psi^L \rangle + V |\Psi^L \rangle.$$  \hspace{1cm} (2.8)

Employing $(\sigma \cdot \pi)(\sigma \cdot \pi) = \pi^2 - \frac{\hbar}{c}(\sigma \cdot \text{curl}\mathbf{A}) = \pi^2 - \frac{\hbar}{c}(\sigma \cdot \mathbf{B})$ with curl$\mathbf{A} = \nabla \times \mathbf{A}$, the Pauli equation is derived as

$$i\hbar \frac{\partial}{\partial t} |\Psi^L \rangle = \left( \frac{\pi^2}{2m_e} - \frac{q_e \hbar}{2m_e c} (\sigma \cdot \mathbf{B}) + V \right) |\Psi^L \rangle.$$  \hspace{1cm} (2.9)

$\mathbf{B}$ is the magnetic field.
The Pauli Hamiltonian with a term bilinear in \( A \) representing the so-called diamagnetic contributions is given by

\[
H_{\text{Pauli}} = \frac{p^2}{2m_e} + V - \frac{q_e}{2m_e c} \mathbf{p} \cdot \mathbf{A} - \frac{q_e \hbar}{2m_e c} \mathbf{A} \cdot \mathbf{p} - \frac{q_e^2}{2m_e c^2} \mathbf{\sigma} \cdot \mathbf{B} + \frac{q_e^2 c^2}{2m_e c^2} \mathbf{A}^2
\]

(2.10) and in the Coulomb gauge \(-i\hbar \text{div} \mathbf{A} = -i\hbar \nabla \cdot \mathbf{A} = 0\) as

\[
H_{\text{Pauli}} = \frac{p^2}{2m_e} + V - \frac{q_e}{m_e c} \mathbf{A} \cdot \mathbf{p} - \frac{q_e \hbar}{m_e c} \mathbf{\sigma} \cdot \mathbf{B} + \frac{q_e^2 c^2}{2m_e c^2} \mathbf{A}^2.
\]

(2.11)

We consider this a proper nonrelativistic operator, although the strict \( c \to \infty \) limit would, of course, make the magnetic terms vanish [179]. The second-order energy is now a sum of para- and diamagnetic contributions, \( \text{nr} E_p^2 \) and \( \text{nr} E_d^2 \):

\[
\text{nr} E_2 = \text{nr} E_p^2 + \text{nr} E_d^2 = \text{Re} \langle \psi_0 | H_1 | \psi_1 \rangle + \langle \psi_0 | H_2 | \psi_0 \rangle.
\]

(2.12)

As a consequence, the NMR shielding tensor, for example, depends not only linearly, but also bilinearly on the vector potential. Since no such bilinear term is included in the Dirac equation, the question has raised how a diamagnetic contribution comparable to the one in the nonrelativistic case may be obtained in relativistic theory.

In this context, a Gordon decomposition of the current density was successfully employed to produce diamagnetic terms [180–182]. Diamagnetic terms also arise from an orbital decomposition and the restricted magnetic-balance approach [170]. Another approach involves the negative-energy states, the so-called positronic states. Sternheim showed in 1962 by applying several approximations [183] that a diamagnetic operator can be obtained from the second-order energy. The summation over the positronic states for deriving diamagnetic contributions was studied by various authors [184–186]. However, it should be possible to represent a property like the NMR shielding tensor on the basis of electronic states only. According to an interesting idea by Kutzelnigg [178] this is possible via transformation techniques. Kutzelnigg proposed a unitary transformation which depends on the vector potential and generates magnetic operators which closely resemble the para- and diamagnetic operators of the nonrelativistic Pauli Hamiltonian in Eq. (2.11) if higher order terms in \( A \) are neglected (as is the case in perturbation approaches to molecular properties, i.e., in response theory). Employing these operators, the coupling of the positive and negative energy states through the \( A \)-dependent terms can be diminished. It should be noted that Kutzelnigg’s transformation is, of course, only exact if the corresponding series expansion is not truncated but comprises all infinitely many terms.

Already in 2005, Visscher [187] compared various computational approaches for the calculation of NMR shielding tensors: the linear response four-component method, different approximations which lead to the Sternheim approach up to
the formulae derived with Kutzelnigg’s transformation. In this first comparison, these diverse approaches gave quite different results. Especially surprising are the deviations between the results obtained from the full response approach and employing Kutzelnigg’s transformation since both methods are in principle identical as we will reconsider later. Several reasons are possible for the differing results: (i) The differences have been attributed to the application of the point dipole model, which describes the nuclear magnetic field, because it yields divergent results if several terms are not included [169,188] as was first shown by Kutzelnigg [189,190]. In order to avoid the singularities due to the vector potential of a magnetic point dipole moment Xiao et al. [169] proposed an analogous unitary transformation at the matrix level. However, Visscher employed a Gaussian-shaped nuclear charge distribution (and, hence, a finite nucleus) and also Gaussian basis functions with not too large exponents so that effects due to divergences are rather unlikely [191]. (ii) The factor 1/2 in the second term of the operator which in Kutzelnigg’s formalism resembles \( H_2 \) could have been omitted since this factor is missing in the original paper by Kutzelnigg [178] and in the one by Visscher [187]. However, the implementation considered the correct operator [191]. Visscher suspects that missing positive-energy–negative-energy orbital rotations or the standard restricted kinetic-balance for negative-energy states might produce the differences [191]. In contrast to Visscher’s pilot study, similar results were found by Zaccari et al. [192] for the linear response within the elimination of the small component framework and Kutzelnigg’s approach. It is worth noting that the problem of the diamagnetic term arises because of the fact that we are familiar with the nonrelativistic theory. If the relativistic theory of electrons would have been the theory first proposed within quantum theory, the question of the diamagnetic term would not have been as imminent as it appears to us now. However, the nonrelativistic limit would have led us to this issue then later on. Considering the fact that quasi-relativistic theories like the DKH approach [71–73,193] bridge the gap between the four-component picture and the nonrelativistic formulation, these quasi-relativistic theories should be investigated with respect to the question of what happens to the electromagnetic potentials [176] since a theory like DKH which expands the Dirac Hamiltonian in terms of the potentials would be necessarily involved in order to explain to which powers the vector potential terms arise in the various approximate relativistic or even nonrelativistic operators. Since we aim at an analytical understanding, we search for explicit, well-defined operator expressions. For computational purposes, however, numerical “infinite-order” methods [63,194–201] may also be of interest (see section 2.3.2.3).

2.1 Coupling of a Dirac electron to external potentials

Since we discuss in the following part of this chapter how to incorporate vector-potential-dependent operators in (quasi-)relativistic electron theories, the basics of how this is done in the case of the one-electron Dirac equation is briefly
2.1. Coupling of a Dirac electron to external potentials

We start with the unperturbed one-electron Dirac equation in Lorentz covariant form [202],

\[ [\gamma_\mu p_\mu - ie c] |\psi\rangle = 0, \] (2.13)

where \( \gamma_\mu = (\gamma, \gamma_4) \) contains the matrices \( \gamma = -i\beta\alpha \) and \( \gamma_4 = \beta \). \( p_\mu = -i\hbar \partial/\partial x_\mu \) contains the four coordinates \( x_\mu = (x, y, z, \text{ict}) \). Though it is not necessary to introduce the imaginary unit in the time-like coordinate [177], we follow the notation of Ref. [202]. The interaction of an electron with an electromagnetic field can be described via the four-potential

\[ A_\mu = (A, iA_0) \] (2.14)

with the scalar potential \( A_0 = \Phi \). The inclusion of electromagnetic potentials in the Dirac equation in such a way that Lorentz covariance is preserved is known as the principle of minimal coupling:

\[ p_\mu \rightarrow p_\mu - qe/pc A_\mu. \] (2.15)

The gauge invariance is also preserved by the principle of minimal coupling. Since the magnetic vector potential is uniquely defined only up to a certain gauge, we request that the field-dependent Dirac equation continues to be gauge invariant, i.e., that the modification of the four-potential with respect to the gauge choice will at most result in a phase shift of the wave function. The gauge transformation of the potential \( A_\mu \) can be written as

\[ A_\mu \rightarrow A_\mu + \frac{\partial}{\partial x_\mu} \chi(x_\mu), \] (2.16)

where \( \chi \) is an arbitrary well-behaving function fulfilling \( \sum_\mu \partial^2 \chi(x_\mu)/\partial x_\mu^2 = 0 \) [202]. In order to leave the form of the Dirac equation unchanged, the phase of the wave function should change in the following way:

\[ |\psi\rangle \rightarrow \exp \left( iqe/\hbar c \chi(x_\mu) \right)|\psi\rangle. \] (2.17)

If the gauge transformation is applied to the Dirac equation,

\[ \left[ \gamma_\mu p_\mu - qe/pc \gamma_\mu A_\mu - qe/pc \gamma_\mu \frac{\partial}{\partial x_\mu} \chi(x_\mu) - imec \right] \exp \left( iqe/\hbar c \chi(x_\mu) \right) |\psi\rangle = 0, \] (2.18)

and moving \( \exp \left( iqe/\hbar c \chi(x_\mu) \right) \) to the left, we obtain

\[ \exp \left( iqe/\hbar c \chi(x_\mu) \right) \left\{ \gamma_\mu p_\mu + (-i\hbar)\gamma_\mu \left[ iqe/\hbar c \frac{\partial}{\partial x_\mu} \chi(x_\mu) \right] - qe/pc \gamma_\mu A_\mu - qe/pc \gamma_\mu \frac{\partial}{\partial x_\mu} \chi(x_\mu) - imec \right\} |\psi\rangle = 0. \] (2.19)
Multiplication from the left by \( \exp \left( -i \frac{qe}{\hbar c} \chi(x_\mu) \right) \) finally yields

\[
\left[ \gamma_\mu p_\mu - \frac{qe}{c} \gamma_\mu A_\mu - im_e c \right] |\psi\rangle = 0,
\]

which matches Eq. (2.13) and, thus, is still Lorentz covariant. Furthermore, it can be seen in the previous equations that the additional terms produced by \( A_\mu \) and \( p_\mu \) cancel because of the gauge independence and so Eq. (2.20) is indeed gauge invariant.

### 2.2 Vector-potential-dependent unitary transformations in the four-component framework

In this section we derive a general formulation of Kutzelnigg’s transformation [178] and compare it to the transformation proposed by Foldy and Wouthuysen [203]. For a better understanding of the discussion, it is necessary to write the Dirac operator in the following manner:

\[
D = \beta m_e c^2 + c\alpha \cdot p + V + \lambda(-qe \alpha \cdot A) = \mathcal{E}_{0,0} + \mathcal{O}_{0,0} + \mathcal{E}_{1,0} + \lambda \mathcal{O}_{0,1}.
\]

\( \mathcal{E} \) represents block-diagonal, so-called even terms, i.e., \([\mathcal{E}, \beta] = 0\), and \( \mathcal{O} \) off-diagonal, so-called odd ones which anticommute with \( \beta \). In general, “[\( ,\)]” and “\{,\}” indicate commutators and anticommutators, respectively. The subscripts of the even and odd terms denote the order in \( V \) and \( A \), respectively, whereas the subscript of the \( D \) terms, in analogy to the \( H \) terms in the nonrelativistic case, only indicates the order in \( A \). The dimensionless parameter \( \lambda \) is introduced in order to define an expansion parameter for the perturbation theory. Thus, \( \lambda \) can be understood as a parameter which measures the strength of the perturbation caused by the magnetic field [178].

As already mentioned in the introduction of this chapter, there is no obvious counterpart in relativistic theory which resembles the diamagnetic contribution obtained in the nonrelativistic Pauli-Hamiltonian for an electron in a magnetic field [compare Eq. (2.11)]. Kutzelnigg [178] suggested a unitary transformation of the Dirac Hamiltonian, which minimizes the coupling of the small and large components through the magnetic field \( A \) by removing the off-diagonal operator \(-qe \alpha \cdot A\), but not \( c\alpha \cdot p \). This transformation is given by

\[
\tilde{D} = \exp (\lambda W) D \exp (-\lambda W)
\]

and can be expanded employing the Baker–Campbell–Hausdorff formula [178]. However, we apply the most general form of a unitary transformation [73],

\[
U = a_0 1 + \sum_{k=1}^{\infty} a_k \lambda^k W^k,
\]
with the odd and antihermitian expansion parameter $W$ — consequently, the special choice as an exponential is not necessary then — yielding the expanded transformed Dirac Hamiltonian [178]
\[
\tilde{D} = \tilde{D}_0 + \lambda \tilde{D}_1 + \lambda^2 \tilde{D}_2 + O(\lambda^3) \quad \text{with} \quad \tilde{D}_0 = D_0.
\] (2.24)

Following Kutzelnigg, we now ask the question of how to define $W$ so that we get para- and diamagnetic expressions. Therefore, we also look for a unitary transformation that removes the off-diagonal operator $-q_e \alpha \cdot A$ to the leading order of $\lambda$ [178].

In order to achieve this, $W$ has to be first order in $A$, which is indicated by $W_{0,1}$. With the transformation in Eq. (2.23), we explicitly write the unitary transformation of the Dirac equation given in Eq. (2.21) (for the sake of brevity, we set $\lambda = 1$ in the following),
\[
\tilde{D} = UDU^\dagger
\]
\[
= \left( a_0 \mathbf{1} + \sum_{k=1}^{\infty} a_k W_{0,1}^k \right) \left( \mathcal{E}_{0,0} + \mathcal{O}_{0,0} + \mathcal{E}_{1,0} + \mathcal{O}_{0,1} \right)
\times \left( a_0 \mathbf{1} + \sum_{k=1}^{\infty} (-1)^k a_k W_{0,1}^k \right)
= \mathcal{E}_{0,0} + \mathcal{E}_{1,0} + \mathcal{O}_{0,0} + \mathcal{O}_{0,1} + \mathcal{E}_{0,1}
+ \mathcal{O}_{1,1} + \mathcal{E}_{0,2} + \mathcal{E}_{1,2} + \mathcal{O}_{0,2} + \cdots.
\] (2.25)

The coefficient $a_1$ is fixed as $a_1 = 1$ because it solely defines a scaling of $W$ [73]. For the sake of simplicity, we set $a_0 = 1$ in the following. The $A$-containing first- and second-order terms are
\[
\mathcal{O}_{0,1} = [W_{0,1}, \mathcal{E}_{0,0}] + \mathcal{O}_{0,1},
\] (2.26)
\[
\mathcal{O}_{1,1} = [W_{0,1}, \mathcal{E}_{1,0}],
\] (2.27)
\[
\mathcal{E}_{0,1} = [W_{0,1}, \mathcal{O}_{0,0}],
\] (2.28)
\[
\mathcal{E}_{0,2} = [W_{0,1}, \mathcal{O}_{0,1}] + \frac{1}{2} [W_{0,1}, [W_{0,1}, \mathcal{E}_{0,0}]],
\] (2.29)
\[
\mathcal{E}_{1,2} = \frac{1}{2} [W_{0,1}, [W_{0,1}, \mathcal{E}_{1,0}]],
\] (2.30)
\[
\mathcal{O}_{0,2} = \frac{1}{2} [W_{0,1}, [W_{0,1}, \mathcal{O}_{0,0}]].
\] (2.31)

In order to remove the odd terms $\mathcal{O}_{0,1}$ and $\mathcal{O}_{1,1}$ containing the vector potential to first order, the condition
\[
-q_e \alpha \cdot A = W_{0,1} \beta m_e c^2 - \beta m_e c^2 W_{0,1} + W_{0,1} V - VW_{0,1}
\] (2.33)
with
\[
[W_{0,1}, V] = 0
\] (2.34)
has to be fulfilled. The expression for \( W_{0,1} \) is obtained as

\[
W_{0,1} = -\frac{\beta q_e \alpha \cdot \mathbf{A}}{2m_e c^2}, \tag{2.35}
\]

which is exactly the same as the one obtained by Kutzelnigg [178] except that we have applied the most general unitary transformation instead of the exponential parameterization for the derivation.

\( \tilde{D}_1 \) is given by

\[
\tilde{D}_1 = \mathcal{O}'_{0,1} + \mathcal{O}_{1,1} + \mathcal{E}_{0,1} = 0 + 0 + [W_{0,1}, \mathcal{O}_{0,0}] = \left[ -\frac{\beta q_e \alpha \cdot \mathbf{A}}{2m_e c^2}, \alpha \cdot \mathbf{p} \right]
\]

At first sight, the unitary transformation proposed by Kutzelnigg leads to seemingly different expressions for the first- and second-order energies, \( \mathcal{D}_1 \) in perturbation theory compared to the ones derived from the Dirac equation. Thus, \( \tilde{D}_1 \) resembles the nonrelativistic \( H_1 \) operator except for the factor \( \beta \) which indicates that \( \tilde{D}_1 \) is four-dimensional. The \( \mathbf{A}^2 \)-involving operator is obtained via

\[
\tilde{D}_2 = \mathcal{E}_{0,2} + \mathcal{E}_{1,2} + \mathcal{O}_{0,2}
\]

\[
= [W_{0,1}, \mathcal{O}_{0,1}] + \frac{1}{2}[W_{0,1}, [W_{0,1}, \mathcal{E}_{1,0}]] + \frac{1}{2}[W_{0,1}, [W_{0,1}, \mathcal{E}_{0,0}]]
\]

\[
+ \frac{1}{2}[W_{0,1}, [W_{0,1}, \mathcal{O}_{0,0}]]. \tag{2.37}
\]

Since \([W_{0,1}, \mathcal{E}_{1,0}] = 0\) and \( \frac{1}{2}[W_{0,1}, [W_{0,1}, \mathcal{E}_{0,0}]] = -\frac{1}{2}[W_{0,1}, \mathcal{O}_{0,1}] \), we write

\[
\tilde{D}_2 = \frac{1}{2} \left[ -\frac{\beta q_e \alpha \cdot \mathbf{A}}{2m_e c^2}, q_e \alpha \cdot \mathbf{A} \right] + \frac{1}{2} \left[ -\frac{\beta q_e \alpha \cdot \mathbf{A}}{2m_e c^2}, \frac{\beta q_e \alpha \cdot \mathbf{A}}{2m_e c^2}, \alpha \cdot \mathbf{p} \right]
\]

\[
= \beta H_2 + \frac{q_e}{4m_e c^2} \{ H_1, \alpha \cdot \mathbf{A} \}. \tag{2.38}
\]

The nonrelativistic \( H_2 \) operator is exactly recovered except for the factor \( \beta \) in \( \tilde{D}_2 \) and an odd second order specific relativistic correction term [see Eq. (2.38)]. At first sight, the unitary transformation proposed by Kutzelnigg leads to seemingly different expressions for the first- and second-order energies, \( ^K E_1 \) and \( ^K E_2 \), in perturbation theory compared to the ones derived from the Dirac equation (compare Ref. [178]). However, the energy expressions must be equivalent in order to prove consistency of Kutzelnigg’s idea. Kutzelnigg already showed in his paper that the first-order energy \( \langle \psi_0 | \tilde{D}_1 | \psi_0 \rangle \) employing the transformed
Hamiltonian is the same as the one from the Dirac equation, \( \langle \psi_0 | D_1 | \psi_0 \rangle \). Hence, \( K E_1 = D E_1 \).

Now the question arises if this is also true for the second-order energy. We employ \( \langle \psi_0 | \psi_1 \rangle = 0 \) and the special form of the first-order perturbed transformed wave function,

\[
\mathbf{\tilde{\psi}}_1 = |\psi_1 + W_{0,1} \psi_0 \rangle,
\]

in an analogous way to Ref. [178]. Since \( D_0 = \mathcal{E}_{0,0} + \mathcal{O}_{0,0,0} + \mathcal{E}_{1,0} \) and \( D_1 = \mathcal{O}_{0,1} \), we can write \( \mathbf{\tilde{D}}_1 = D_1 + [W_{0,1}, D_0] \) and \( \mathbf{\tilde{D}}_2 = [W_{0,1}, D_1] + 1/2 [W_{0,1}, [W_{0,1}, D_0]] \). The paramagnetic and diamagnetic energies obtained from the transformed Hamiltonian [compare Eqs. (2.36) and (2.38)] are calculated as

\[
K E_2^p = \text{Re} \langle \psi_0 | \mathbf{\tilde{D}}_1 | \mathbf{\tilde{\psi}}_1 \rangle = \text{Re} \langle \psi_0 | D_1 - D_0 W_{0,1} + W_{0,1} D_0 | \psi_1 + W_{0,1} \psi_0 \rangle \\
= \text{Re} \langle \psi_0 | D_1 | \psi_1 \rangle - \text{Re} \langle \psi_0 | D_0 W_{0,1} | \psi_1 \rangle + \text{Re} \langle \psi_0 | W_{0,1} D_0 | \psi_1 \rangle \\
+ \text{Re} \langle \psi_0 | D_1 W_{0,1} | \psi_0 \rangle - \text{Re} \langle \psi_0 | D_0 W_{0,1}^2 | \psi_0 \rangle \\
+ \text{Re} \langle \psi_0 | W_{0,1} D_0 W_{0,1} | \psi_0 \rangle 
\]

and

\[
K E_2^d = \langle \psi_0 | \mathbf{\tilde{D}}_2 | \psi_0 \rangle = \langle \psi_0 | [W_{0,1}, D_1] + 1/2 [W_{0,1}, [W_{0,1}, D_0]] | \psi_0 \rangle \\
= \langle \psi_0 | W_{0,1} D_1 | \psi_0 \rangle - 1/2 \langle \psi_0 | D_1 W_{0,1} | \psi_0 \rangle \\
+ 1/2 \langle \psi_0 | D_0 W_{0,1}^2 | \psi_0 \rangle - 2 W_{0,1} D_0 W_{0,1} + W_{0,1}^2 D_0 | \psi_0 \rangle. 
\]

Applying the general relationship \( \langle \psi_0 | D_0 \mathbf{\tilde{A}} | \psi_0 \rangle = E_0 \langle \psi_0 | \mathbf{\tilde{A}} | \psi_0 \rangle \), where \( \mathbf{\tilde{A}} \) is an arbitrary operator, we arrive at

\[
K E_2^p = \text{Re} \langle \psi_0 | D_1 | \psi_1 \rangle - \text{Re} E_0 \langle \psi_0 | W_{0,1} | \psi_1 \rangle + \text{Re} \langle \psi_0 | W_{0,1} D_0 | \psi_1 \rangle \\
+ \text{Re} \langle \psi_0 | D_1 W_{0,1} | \psi_0 \rangle - \text{Re} E_0 \langle \psi_0 | W_{0,1}^2 | \psi_0 \rangle \\
+ \text{Re} \langle \psi_0 | W_{0,1} D_0 W_{0,1} | \psi_0 \rangle 
\]

and

\[
K E_2^d = \langle \psi_0 | W_{0,1} D_1 | \psi_0 \rangle - \langle \psi_0 | D_1 W_{0,1} | \psi_0 \rangle + E_0 \langle \psi_0 | W_{0,1}^2 | \psi_0 \rangle \\
- \langle \psi_0 | W_{0,1} D_0 W_{0,1} | \psi_0 \rangle.
\]

Since the contributions from \( K E_2^d \) are real, we can simplify \( K E_2^p + K E_2^d \) to

\[
K E_2^p + K E_2^d = \text{Re} \langle \psi_0 | D_1 | \psi_1 \rangle - \text{Re} E_0 \langle \psi_0 | W_{0,1} | \psi_1 \rangle + \text{Re} \langle \psi_0 | W_{0,1} D_0 | \psi_1 \rangle \\
+ \text{Re} \langle \psi_0 | D_1 W_{0,1} | \psi_0 \rangle - \text{Re} \langle \psi_0 | D_1 W_{0,1} | \psi_0 \rangle \\
+ \text{Re} E_0 \langle \psi_0 | W_{0,1}^2 | \psi_0 \rangle - \text{Re} \langle \psi_0 | W_{0,1}^2 | \psi_0 \rangle \\
+ \text{Re} \langle \psi_0 | W_{0,1} D_0 W_{0,1} | \psi_0 \rangle - \text{Re} \langle \psi_0 | W_{0,1} D_0 W_{0,1} | \psi_0 \rangle \\
+ \text{Re} \langle \psi_0 | W_{0,1} D_1 | \psi_0 \rangle 
\]

\[
= \text{Re} \langle \psi_0 | D_1 | \psi_1 \rangle - \text{Re} E_0 \langle \psi_0 | W_{0,1} | \psi_1 \rangle + \text{Re} \langle \psi_0 | W_{0,1} D_0 | \psi_1 \rangle \\
+ \text{Re} \langle \psi_0 | W_{0,1} D_1 | \psi_0 \rangle.
\]
Employing \((D_0 - E_0)|\psi_1\rangle = -(D_1 - E_1)|\psi_0\rangle\) and \(\text{Re} \langle \psi_0 | W_{0,1} | \psi_0 \rangle = 0\) because of the antihermiticity of \(W_{0,1}\), the last term in Eq. (2.44) is rewritten as

\[
\text{Re} \langle \psi_0 | W_{0,1} D_1 | \psi_0 \rangle = \text{Re} \langle \psi_0 | W_{0,1} (D_1 - E_1) | \psi_0 \rangle + \text{Re} \langle \psi_0 | W_{0,1} E_1 | \psi_0 \rangle
- \text{Re} \langle \psi_0 | W_{0,1} (D_0 - E_0) | \psi_1 \rangle + E_1 \text{Re} \langle \psi_0 | W_{0,1} | \psi_0 \rangle
= -\text{Re} \langle \psi_0 | W_{0,1} (D_0 - E_0) | \psi_1 \rangle.
\] (2.45)

Thus, \(kE_p^p + kE_d^d\) can be written as

\[
kE_p^p + kE_d^d = \text{Re} \langle \psi_0 | D_1 | \psi_1 \rangle + \text{Re} \langle \psi_0 | W_{0,1} (D_0 - E_0) | \psi_1 \rangle
- \text{Re} \langle \psi_0 | W_{0,1} (D_0 - E_0) | \psi_1 \rangle
= \text{Re} \langle \psi_0 | D_1 | \psi_1 \rangle = E_p^p,
\] (2.46)

which is nothing else but the usual paramagnetic term derived from the Dirac equation (for another derivation, see Ref. [188]).

Compared to Kutzelnigg’s approach, the transformation proposed by Foldy and Wouthuysen (FW) [203] additionally includes the removal of the other odd term \(\mathcal{O}_{0,0} = c\mathbf{\alpha} \cdot \mathbf{p}\), i.e., an expansion parameter which consists of a sum \(W_{0,1} + W_{0,0}\) is invoked, where \(W_{0,0}\) is \(\mathbf{p}\)-dependent:

\[
-O_{0,1} - O_{0,0} = [W_{0,1} + W_{0,0}, \mathcal{E}_{0,0}].
\] (2.47)

Employing Eq. (2.21) we obtain

\[
q(c\mathbf{\alpha} \cdot \mathbf{A} - c\mathbf{\alpha} \cdot \mathbf{p}) = (W_{0,1} + W_{0,0})\beta m_e c^2 - \beta m_e c^2(W_{0,1} + W_{0,0}),
\] (2.48)

which leads to

\[
W_{0,1} + W_{0,0} = -\frac{\beta(q(c\mathbf{\alpha} \cdot \mathbf{A} - c\mathbf{\alpha} \cdot \mathbf{p}))}{2m_e c^2}.
\] (2.49)

If we now employ \(W_{0,1} + W_{0,0}\) instead of \(W_{0,1}\) in Eqs. (2.26) to (2.31), we arrive — besides other terms containing the odd term \(c\mathbf{\alpha} \cdot \mathbf{p}\) and \(V\) — at a Hamiltonian providing the same magnetic terms \(\tilde{D}_1\) and \(\tilde{D}_2\) as the one employed by Kutzelnigg. \(\tilde{D}_0\), however, now contains the even term \(\beta p^2/2m_e\) instead of the odd term \(c\mathbf{\alpha} \cdot \mathbf{p}\). As a consequence, this Hamiltonian contains, apart from relativistic corrections, terms which resemble the corresponding nonrelativistic Hamiltonian (except for the factor \(\beta\) because it is still a four-component theory) and leads to an obvious separation of para- and diamagnetic contributions. The part of the Hamiltonian resembling the nonrelativistic terms is bounded from below and no mathematical problems arise [204–206].

It should be noted that the classification in Eqs. (2.26) to (2.31) does not explicitly treat the operators which would arise due to the cross terms between \(W_{0,1}\) and \(W_{0,0}\).

Since the FW transformation — contrary to Kutzelnigg’s one — removes also the odd term containing the momentum in addition to the \(\mathbf{A}\)-dependent one, it may be of interest for two-component methods leading to easily recognizable para- and diamagnetic contributions even in quasi-relativistic frameworks. However, one has to deal carefully with relativistic correction terms obtained by the first- or higher-order FW transformations [204, 205, 207].
2.3 Transition to two-component Hamiltonians

An alternative to four-component methods are two-component approaches, which avoid the calculation of the small component of the four-component spinor by removing all odd terms in the Hamiltonian. Often, they yield computationally advantageous approaches. In general, there are two boundary conditions for two-component Hamiltonians: At infinite order of decoupling, they should lead to the same result as the one obtained with four-component theory, and they should lead to expressions of the nonrelativistic theory. However, the perturbation theory approach to molecular properties imposes less strict conditions as only the low-order energy expressions must be reproduced exactly. In the following, we will focus on DKH theory, which provides the well-defined decoupling scheme [207] and show several approaches how one can incorporate the vector-potential-dependent Dirac Hamiltonian. The starting point is always the free-particle FW (fpFW) transformation, which may contain the vector potential as will be discussed in section 2.3.1. We will also refer to this vector-potential-containing FW transformation as a fpFW transformation since it is of the same form like the ‘standard’ fpFW transformation given later in Eq. (2.60). The \( A \)-independent fpFW transformation will be employed in section 2.3.2. The DKH Hamiltonian is then given as the upper left part of the transformed Hamiltonian, i.e., it can be derived from the four-component Hamiltonian by replacing \( \beta \) by \( \frac{1}{2} \), the \( 2 \times 2 \) unit matrix, and \( \alpha \) by \( \sigma \) in the even terms.

2.3.1 Vector-potential-dependent Foldy–Wouthuysen transformation

The first step of the DKH procedure must be the fpFW [207], which leads to a well-defined order in \( V \) of the odd terms for the successive decoupling to specific higher orders in \( V \). In order to introduce the vector potential \( A \), the transformation can be made dependent on the magnetic field via replacement of the momentum operator \( p \) by the mechanical momentum operator \( \pi = p - \frac{2}{c} A \) in the Dirac operator,

\[
D^{(\pi)} = \beta mc^2 + c\alpha \cdot \pi + V,
\]

and transform it with the fpFW unitary transformation, where also \( p \) was replaced by \( \pi \),

\[
U^{(\pi)}_0 = A_\pi (1 + \beta R_\pi).
\]

The kinematic factors are given as

\[
A_\pi = \sqrt{\frac{E_\pi + mc^2}{2E_\pi}},
\]

\[
R_\pi = \frac{c\alpha \cdot \pi}{E_\pi + mc^2} = \mathcal{R}_\pi \alpha \cdot \pi
\]
employing
\[ E_\pi = \sqrt{(\alpha \cdot \pi)^2 c^2 + m_e^2 c^4}. \] (2.54)
This produces a transformed Hamiltonian \( \hat{D}(\pi) = \mathcal{E}(\pi) + \mathcal{O}(\pi) \) with the even and odd terms
\[ \mathcal{E}(\pi) = \beta E_\pi + A_\pi V A_\pi + A_\pi \mathcal{R}_\pi \alpha \cdot \pi V \alpha \cdot \pi \mathcal{R}_\pi A_\pi, \]
\[ \mathcal{O}(\pi) = \beta A_\pi [\mathcal{R}_\pi \alpha \cdot \pi, V] A_\pi. \] (2.55) (2.56)
For the calculation of magnetic properties for which derivatives with respect to the magnetic field \( B \) are necessary, \( E_\pi \) has to be expanded in powers of \( A \).

Alternatively, the FW transformation can be performed in a successive way instead of the closed form above, which leads, at least for the terms resembling the nonrelativistic Hamiltonian, to well-behaving expressions (compare section 2.2). Eq. (2.49) for the expansion parameter has been employed by Foldy and Wouthuysen for the first transformation, followed by a second transformation which also removes the odd term containing \( V \).

We can try to remove the odd term containing \( V \) already in the first transformation, employing \( W(0) \) since the condition for removal of the odd terms now changes to
\[ -\mathcal{O}_{0,1} - \mathcal{O}_{0,0} = [W_{x,1}^{(0)}, \mathcal{E}_{0,0} + \mathcal{E}_{1,0}], \]
\[ q_e \alpha \cdot A - c \alpha \cdot p = W_{x,1}^{(0)} \beta m_e c^2 - \beta m_e c^2 W_{x,1}^{(0)} + W_{x,1}^{(0)} V - V W_{x,1}^{(0)}. \] (2.57) (2.58)

Since \( W_{x,1}^{(0)} \) does not commute with \( V \) because of its \( p \)-dependence, we may use the matrix representation in the position-space basis (\( k \) and \( q \) denote the functions of the position-space basis set) in order to derive an expression for \( W_{x,1}^{(0)} \). This results in
\[ \langle k | W_{x,1}^{(0)} | q \rangle = (2\beta m_e c^2 - \langle q | V | q \rangle + \langle k | V | k \rangle)^{-1} \langle k | c \alpha \cdot p - q_e \alpha \cdot A | q \rangle. \] (2.59)

### 2.3.2 Vector-potential-independent Foldy–Wouthuysen transformation

As can be seen in the previous section, the magnetic-field-dependent fpFW leads to quite complicated expressions. In order to avoid the associated difficulties one can start from the Dirac operator in Eq. (2.21) and perform a magnetic-field-independent fpFW transformation [203],
\[ U_0 = A_p (1 + \beta R_p), \] (2.60)
with the kinematic factors

\[ A_p = \sqrt{E_p + m_e c^2} / 2E_p, \quad (2.61) \]
\[ R_p = \frac{c\alpha \cdot p}{E_p + m_e c^2} = R_p \alpha \cdot p, \quad (2.62) \]

which contain the energy–momentum relation

\[ E_p = \sqrt{p^2 c^2 + m_e^2 c^4}. \quad (2.63) \]

This leads to the Hamiltonian

\[ D_{\text{DKH}1} = U_0 D U_0^\dagger = \mathcal{E}_{0,0} + \mathcal{E}_{1,0} + \mathcal{O}_{1,0} + \mathcal{O}_{0,1}, \quad (2.64) \]

which includes besides the zeroth-order term \( \mathcal{E}_{0,0} = \beta E_p \) even and odd terms being exactly first order in \( V \) and \( A \) [163, 209, 210]:

\[ \mathcal{E}_{1,0} = A_p V A_p + A_p R_p \alpha \cdot p V \alpha \cdot p R_p A_p, \quad (2.65) \]
\[ \mathcal{E}_{0,1} = \beta A_p \{ R_p \alpha \cdot p, (-q_e \alpha \cdot A) \} A_p, \quad (2.66) \]
\[ \mathcal{O}_{1,0} = \beta A_p [R_p \alpha \cdot p, V] A_p, \quad (2.67) \]
\[ \mathcal{O}_{0,1} = A_p (-q_e \alpha \cdot A) A_p - A_p R_p \alpha \cdot p (-q_e \alpha \cdot A) \alpha \cdot p R_p A_p. \quad (2.68) \]

Classification of, e.g., \( \mathcal{E}_{1,0} \) to the order in \( 1/c \) is not possible since the factors in Eqs. (2.61) – (2.63) would have to be expanded in powers of \( c \). For the latter, a convergent series can only be obtained for non-ultrarelativistic values of the momentum [193, 207], which may be difficult to fulfill in a complete momentum-space basis.

A second transformation is performed as the next step in the DKH procedure,

\[ D_{\text{DKH}2} = U_1 D_{\text{DKH}1} U_1^\dagger \]
\[ = \left( a_0^{(1)} 1 + \sum_{k=1}^{\infty} a_k^{(1)} W_{x,y}^{(1)} k \right) \left( \mathcal{E}_{0,0} + \mathcal{E}_{1,0} + \mathcal{E}_{0,1} + \mathcal{O}_{1,0} + \mathcal{O}_{0,1} \right) \]
\[ \times \left( a_0^{(1)} 1 + \sum_{k=1}^{\infty} (-1)^k a_k^{(1)} W_{x,y}^{(1)} k \right) \]
\[ = \mathcal{E}_{0,0} + \mathcal{E}_{1,0} + \mathcal{E}_{0,1} + \mathcal{O}_{1,0}^{(2)} + \mathcal{O}_{0,1}^{(2)} + \mathcal{O}_{x,y}^{(2)} + \mathcal{O}_{x+1,y}^{(2)} \]
\[ + \mathcal{O}_{x+1,y}^{(2)} + \mathcal{O}_{x+2,y+1}^{(2)} + \mathcal{O}_{x+2,y+1}^{(2)} + \mathcal{E}_{x+2,y+1}^{(2)} \]
\[ + \mathcal{O}_{2x+1,2y}^{(2)} + \mathcal{O}_{2x+2,2y+1}^{(2)} + \cdots, \quad (2.69) \]

where \( x = 1 \lor y = 1 \) and \( x, y \in \mathbb{Z} \) in general. The superscript ‘(2)’ indicates that the corresponding terms may be changed in a following transformation. The values of \( x \) and \( y \) can be chosen differently depending on the aim of the decoupling procedure.
2.3.2.1 Removal of $A$-dependent odd terms

For removal of the odd terms which are first order in $A$, the second transformation is performed with $A$-dependent expansion parameter $W_{x,1}^{(1)}$. The $x$ value is determined by the choice of which $A$-containing odd terms should be removed (only the odd terms which are independent of $V$ or also the ones containing $V$ in addition to $A$):

$$D_{DKH2} = U_1 D_{DKH1} U_1^\dagger = \left( a_0^{(1)} 1 + \sum_{k=1}^{\infty} a_k^{(1)} (W_{x,1}^{(1)})^k \right) \left( \epsilon_{0,0} + \epsilon_{1,0} + \mathcal{O}_{0,1} + \mathcal{O}_{1,0} + \mathcal{O}_{0,1} \right) \times \left( a_0^{(1)} 1 + \sum_{k=1}^{\infty} (-1)^k a_k^{(1)} (W_{x,1}^{(1)})^k \right)$$

$$= \epsilon_{0,0} + \epsilon_{1,0} + \epsilon_{0,1} + \mathcal{O}_{1,0} + \mathcal{O}_{0,1} + \mathcal{O}_{1,1} + \mathcal{O}_{x,1} + \mathcal{O}_{x+1,1} + \mathcal{O}_{x,2} + \mathcal{E}_{x+1,1}$$

$$+ \epsilon_{x,2} + \epsilon_{x,2} + \epsilon_{x+1,2} + \mathcal{O}_{2x+1,2} + \mathcal{O}_{2x,3} + \cdots. \quad (2.70)$$

Employing $a_0^{(1)} = 1$ and $a_1^{(1)} = 1$ as before, the even and odd terms of first- and second order in $A$ besides $\epsilon_{0,1}$ and $\mathcal{O}_{0,1}$ are obtained as:

$$\epsilon_{x+1,1} = [W_{x,1}^{(1)}, \mathcal{O}_{1,0}], \quad (2.71)$$

$$\mathcal{O}_{x,1}^{(2)} = [W_{x,1}^{(1)}, \epsilon_{0,0}], \quad (2.72)$$

$$\mathcal{O}_{x+1,1}^{(2)} = [W_{x,1}^{(1)}, \epsilon_{1,0}], \quad (2.73)$$

$$\epsilon_{x,2} = [W_{x,1}^{(1)}, \mathcal{O}_{0,1}], \quad (2.74)$$

$$\epsilon_{2x,2} = \frac{1}{2} [W_{x,1}^{(1)}, [W_{x,1}^{(1)}, \epsilon_{0,0}]], \quad (2.75)$$

$$\epsilon_{2x+1,2} = \frac{1}{2} [W_{x,1}^{(1)}, [W_{x,1}^{(1)}, \epsilon_{1,0}]], \quad (2.76)$$

$$\mathcal{O}_{x,2}^{(2)} = [W_{x,1}^{(1)}, \epsilon_{0,1}], \quad (2.77)$$

$$\mathcal{O}_{2x+1,2}^{(2)} = \frac{1}{2} [W_{x,1}^{(1)}, [W_{x,1}^{(1)}, \mathcal{O}_{0,0}]]. \quad (2.78)$$

In order to eliminate all odd terms linear in $A$,

$$\mathcal{O}_{0,1}^{(2)} + \mathcal{O}_{x,1}^{(2)} + \mathcal{O}_{x+1,1}^{(2)} = 0, \quad (2.79)$$

$W_{x,1}^{(1)}$ must fulfill the following condition:

$$-\mathcal{O}_{0,1} = [W_{x,1}^{(1)}, (\epsilon_{0,0} + \epsilon_{1,0})]. \quad (2.80)$$

As can be seen in this equation, $W_{x,1}^{(1)}$ will feature an $x$ value not equal to zero, i.e., a non-vanishing dependence on $V$. In order to arrive at the kernel representation for $W_{x,1}^{(1)}$, we write this equation in terms of matrix elements.
in the momentum representation, where $k$ and $q$ denote eigenfunctions of the momentum operator, as (compare Ref. [211])

$$-\langle k|\mathcal{O}_{0,1}|q \rangle = \langle k|W_{x,1}^{(1)}\mathcal{E}_{0,0}|q \rangle - \langle k|\mathcal{E}_{0,0}W_{x,1}^{(1)}|q \rangle + \langle k|W_{x,1}^{(1)}\mathcal{E}_{1,0}|q \rangle \tag{2.81}$$

In order to simplify the equation, we employ the oddness of $W_{x,1}^{(1)}$ and apply $\{W_{x,1}^{(1)},\beta\} = 0$,

$$-\langle k|\mathcal{O}_{0,1}|q \rangle = -\beta\langle k|W_{x,1}^{(1)}E_p|q \rangle - \beta\langle k|E_pW_{x,1}^{(1)}|q \rangle + \langle k|W_{x,1}^{(1)}\mathcal{E}_{1,0}|q \rangle \tag{2.82}$$

where we separated the operator products via a resolution of the identity in the last step, i.e., we employed $\int_{-\infty}^{\infty} dl \langle l|l \rangle = 1$ (and analogously for $|l'|$ and $|l''|$). The fact that $E_p$, $A_p$, and $\mathcal{R}_p\alpha \cdot p$ are diagonal in the momentum representation leads to the following equation:

$$-\langle k|\mathcal{O}_{0,1}|q \rangle = -\int_{-\infty}^{\infty} \beta\langle k|W_{x,1}^{(1)}l \rangle \delta(l - q)\langle q|E_p|q \rangle dl$$

$$-\int_{-\infty}^{\infty} \beta\langle k|E_p|k \rangle \delta(k - l)\langle l|W_{x,1}^{(1)}|q \rangle dl$$

$$+ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle k|W_{x,1}^{(1)}l \rangle \delta(l - l')\langle l'|A_p|l'' \rangle \langle l''|W_{x,1}^{(1)}|q \rangle dl dl' dl''$$

$$\delta(l'' - q)\langle q|A_p|q \rangle dl dl' dl''$$

$$+ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle k|W_{x,1}^{(1)}l \rangle \delta(l - l')\langle l'|A_p\mathcal{R}_p\alpha \cdot p|l'' \rangle \langle l''|V|l'' \rangle \delta(l'' - q)\langle q|\alpha \cdot p\mathcal{R}_pA_p|q \rangle dl dl' dl''$$
\[
- \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle k|A_p|k \rangle \delta(k-l) \langle l|V|l' \rangle \delta(l' - l'') \\
\langle l'|A_p|l'' \rangle \langle l''|W_{x,1}^{(1)}|q \rangle dl dl' dl'' \\
- \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle k|A_p R_p \alpha \cdot p|k \rangle \delta(k-l) \langle l|V|l' \rangle \\
\delta(l' - l'') \langle l''|\alpha \cdot p R_p A_p|l'' \rangle \langle l''|W_{x,1}^{(1)}|q \rangle dl dl' dl'' \\
= - \beta \langle k|W_{x,1}^{(1)}|q \rangle \langle q|E_p|q \rangle - \beta \langle k|E_p|k \rangle \langle k|W_{x,1}^{(1)}|q \rangle \\
+ \int_{-\infty}^{\infty} \langle k|W_{x,1}^{(1)}|l' \rangle \langle l'|A_p|l'' \rangle \langle l''|V|q \rangle \langle q|A_p|q \rangle dl' \\
+ \int_{-\infty}^{\infty} \langle k|W_{x,1}^{(1)}|l' \rangle \langle l'|A_p R_p \alpha \cdot p|l'' \rangle \langle l''|V|q \rangle \langle q|\alpha \cdot p R_p A_p|q \rangle dl' \\
- \int_{-\infty}^{\infty} \langle k|A_p|k \rangle \langle k|V|l'' \rangle \langle l''|A_p|l'' \rangle \langle l''|W_{x,1}^{(1)}|q \rangle dl'' \\
- \int_{-\infty}^{\infty} \langle k|A_p R_p \alpha \cdot p|k \rangle \langle k|V|l'' \rangle \\
\langle l''|\alpha \cdot p R_p A_p|l'' \rangle \langle l''|W_{x,1}^{(1)}|q \rangle dl''. \tag{2.83}
\]

In order to arrive at a kernel representation of \( W_{x,1}^{(1)} \), we want matrix elements \( \langle k|W_{x,1}^{(1)}|q \rangle \). This is achieved if the conditions
\[
\langle l'|V|q \rangle = \langle q|V|q \rangle \delta(l' - q), \tag{2.84}
\]
\[
\langle k|V|l'' \rangle = \langle k|V|k \rangle \delta(l'' - k) \tag{2.85}
\]
can be fulfilled which leads to the contribution of only diagonal matrix elements containing the external potential \( V \) though \( V \) is not diagonal in momentum space. Eq. (2.83) is then given by
\[
- \langle k|O_{0,1}|q \rangle = - \beta \langle k|W_{x,1}^{(1)}|q \rangle \langle q|E_p|q \rangle - \beta \langle k|E_p|k \rangle \langle k|W_{x,1}^{(1)}|q \rangle \\
+ \langle k|W_{x,1}^{(1)}|q \rangle \left[ \langle q|A_p|q \rangle \langle q|V|q \rangle \langle q|A_p|q \rangle \\
+ \langle q|A_p R_p \alpha \cdot p|q \rangle \langle q|V|q \rangle \langle q|\alpha \cdot p R_p A_p|q \rangle \right] \\
- \left[ \langle k|A_p|k \rangle \langle k|V|k \rangle \langle k|A_p|k \rangle + \langle k|A_p R_p \alpha \cdot p|k \rangle \langle k|V|k \rangle \right. \\
\left. \langle k|\alpha \cdot p R_p A_p|k \rangle \right] \langle k|W_{x,1}^{(1)}|q \rangle \tag{2.86}
\]
so that the matrix element is obtained as
\[
\langle k|W_{x,1}^{(1)}|q \rangle = \left[ \beta \left( \langle q|E_p|q \rangle + \langle k|E_p|k \rangle \right) - \langle q|E_{1,0}|q \rangle + \langle k|E_{1,0}|k \rangle \right]^{-1} \left( \langle k|O_{0,1}|q \rangle \right). \]

\( \langle k|W_{x,1}^{(1)}|q \rangle \) cannot uniquely be classified with respect to \( V \). This problem does not arise if only the \( A \)-dependent odd terms, which do not contain any power of the external potential, are eliminated, leading to \( x = 0 \). \( W_{0,1}^{(1)} \) must fulfill the following condition,
\[
- O_{0,1} = [W_{0,1}^{(1)}, \mathcal{E}_{0,0}] \tag{2.87}
\]
in order to assure that \( \mathcal{O}_{0,1} + \mathcal{O}_{x,1}^{(2)} = 0 \). The matrix element of \( W_{0,1}^{(1)} \) is given by
\[
\langle k | W_{0,1}^{(1)} | q \rangle = (\beta |q | E_p |q \rangle + \beta \langle k | E_p |k \rangle)^{-1} \langle k | \mathcal{O}_{0,1} | q \rangle.
\] (2.88)

For the sake of brevity, we introduce the short-hand notation \( E_{qq} = \langle q | E_p |q \rangle = \langle q | E_{pq} |q \rangle \), \( A_{qq} = \langle q | A_p |q \rangle = \langle q | A_{pq} |q \rangle \), \( \mathcal{R}_{qq} = \langle q | \mathcal{R}_p |q \rangle = \langle q | \mathcal{R}_{pq} |q \rangle \), \( \langle \alpha \cdot p \rangle_{qq} = \langle q | (\alpha \cdot p)_{pq} |q \rangle \), \( V_{kk} = \langle k | V |q \rangle = \langle k | V_{pq} |pq \rangle \), \( \mathcal{A}_{kk} = \langle k | \mathcal{A} |q \rangle = \langle k | A_{pq} |q \rangle \), \( \mathcal{O}_{kk} = \langle k | \mathcal{O} |q \rangle = \langle k | \mathcal{O}(k, q) |q \rangle \), and \( \mathcal{E}_{kk} = \langle k | \mathcal{E} |q \rangle = \langle k | \mathcal{E}(k, q) |q \rangle \).

It should be noted that, starting from Eq. (2.21), the elimination of terms linear in \( V \) can be performed in an analogous way by choosing \( W_{1,v}^{(1)} \) (compare, e.g., Ref. [209] for explicit expressions of the decoupling of the magnetic-field-dependent Dirac Hamiltonian with respect to \( V \)).

### 2.3.2.2 Simultaneous elimination of \( V \)- and \( A \)-dependent odd terms

In order to get rid of the \( V \)- and \( A \)-dependent odd terms simultaneously, a second transformation with a \( V \)- and \( A \)-dependent expansion parameter, \( W_{1,1}^{(1)} \), is carried out resulting in the following even and odd terms (up to the second power in \( V \) and \( A \)) besides \( \mathcal{E}_{0,0} \), \( \mathcal{E}_{0,1} \), \( \mathcal{E}_{1,0} \), \( \mathcal{O}_{1,0} \) and \( \mathcal{O}_{0,1} \):
\[
\begin{align*}
\mathcal{E}_{2,1}^{(2)} &= [W_{1,1}^{(1)}, \mathcal{O}_{1,0}], \\
\mathcal{O}_{1,1}^{(2)} &= [W_{1,1}^{(1)}, \mathcal{E}_{0,0}], \\
\mathcal{O}_{2,1}^{(2)} &= [W_{1,1}^{(1)}, \mathcal{E}_{1,0}], \\
\mathcal{E}_{1,2}^{(2)} &= [W_{1,1}^{(1)}, \mathcal{O}_{0,1}], \\
\mathcal{E}_{2,2}^{(2)} &= \frac{1}{2} [W_{1,1}^{(1)}, [W_{1,1}^{(1)}, \mathcal{E}_{0,0}]], \\
\mathcal{O}_{1,2}^{(2)} &= [W_{1,1}^{(1)}, \mathcal{E}_{0,1}].
\end{align*}
\] (2.89) (2.90) (2.91) (2.92) (2.93) (2.94)

In order to remove the external and magnetic potential to first order,
\[
\mathcal{O}_{1,0} + \mathcal{O}_{0,1} + \mathcal{O}_{1,1}^{(2)} = 0,
\] (2.95)
the following condition has to be fulfilled:
\[
-\mathcal{O}_{1,0} - \mathcal{O}_{0,1} = [W_{1,1}^{(1)}, \mathcal{E}_{0,0}].
\] (2.96)

The kernel of \( W_{1,1}^{(1)} \) is then given as (employing an analogous notation as in section 2.3.2.1)
\[
W_{1,1}^{(1)}(k, q) = W_{1,1}^{(1)}(k, q) + W_{0,1}^{(1)}(k, q) = \beta \frac{\mathcal{O}_{1,0}(k, q)}{E_{pq} + E_{pq}} + \beta \frac{\mathcal{O}_{0,1}(k, q)}{E_{pq} + E_{pq}}
\] (2.97)
with the energy-damped external potential

\[ \tilde{V}_{pq} = \frac{V_{pq}}{E_p + E_q} \]  

(2.98)

and the energy-damped magnetic potential

\[ \tilde{A}_{pq} = \frac{A_{pq}}{E_p + E_q} \]  

(2.99)

This result has already been derived in the literature [163, 209, 210, 212, 213]. The paramagnetic contribution being linear in \( A \) can be obtained from \( E_{0,1} \) whose upper diagonal block is given as

\[ E_{0,1}^{(p)} = A_p \{ R_p \sigma \cdot p, (-q_e \sigma \cdot A) \} A_p. \]  

(2.100)

Employing that \( A_p \to 1 \) and \( R_p \to (2m_e c)^{-1} \) in the nonrelativistic limit [210], we arrive at \( H_1 \) of the Pauli Hamiltonian [see Eq. (2.11)]. The diamagnetic contribution corresponding to \( A^2 \) terms can be derived from the even terms \( E_{1,2}^{(d)} \) and \( E_{2,2}^{(d)} \) (we neglect the odd term \( O_{1,2}^{(2)} \) and also the cross terms containing the external potential \( V \)),

\[ E_{0,2}^{(d)} = \frac{1}{2} [W_{0,1}, O_{0,1}], \]  

(2.101)

In order to derive an expression which resembles \( H_2 \) in the nonrelativistic Hamiltonian, we keep the upper diagonal block with only the terms

\[ E_{0,2}^{(d)} \approx \frac{1}{2} [A_p (-q_e \sigma \cdot \tilde{A}) A_p, A_p (-q_e \sigma \cdot A) A_p], \]  

(2.102)

which lead in the nonrelativistic limit — considering that \( E_p \) is second order in \( c \) — to an expression of second order in \( 1/c \) corresponding to \( H_2 \) in Eq. (2.11). The other terms included in Eq. (2.101) are of higher than second order in \( 1/c \). This result is, of course, also found if only a decoupling of \( A \) is performed like shown in section 2.3.2.1.

As can be seen in Eq. (2.97) — or could already be recognized by a closer look at the starting equation —, \( W_{1,1}^{(1)} \) consists of a sum of odd terms, one corresponding to \( V \), i.e., \( W_{1,0}^{(1)} \), and one belonging to \( A \), i.e., \( W_{0,1}^{(1)} \). Writing explicitly \( W_{1,0}^{(1)} + W_{0,1}^{(1)} \) instead of \( W_{1,1}^{(1)} \), additional even and odd terms arise; for example, additional even terms containing \( V \) and \( A \) contributing to \( E_{1,1}^{(2)} \) result from \( \frac{1}{2} \{ W_{1,0}^{(1)} W_{0,1}^{(1)} + W_{0,1}^{(1)} W_{1,0}^{(1)} , E_{0,0} \} \) since the squaring of \( W_{1,0}^{(1)} + W_{0,1}^{(1)} \) in the transformation [compare Eq. (2.69)] leads to \( (W_{1,0}^{(1)} + W_{0,1}^{(1)})^2 = (W_{1,0}^{(1)})^2 + W_{1,0}^{(1)} W_{0,1}^{(1)} + W_{0,1}^{(1)} W_{1,0}^{(1)} + (W_{0,1}^{(1)})^2 \) with bilinear cross terms in \( V \) and \( A \). This leads to peculiarities in the definition of the orders in DKH theory. In the literature, the products bilinear in \( V \) and \( A \) have not been treated explicitly yet and so these cross terms are treated as second-order terms.
As a consequence, \( W_{1,0}^{(1)} = W_{1,0}^{(1)} + W_{0,1}^{(1)} \) [see Eq. (2.97)] in Eqs. (2.89) – (2.94), the following even and odd terms up to second order in the potentials besides \( \mathcal{E}_{0,1} \) and \( \mathcal{E}_{1,0} \) are obtained:

\[
\mathcal{E}_{1,1} = [W_{1,0}^{(1)}, \mathcal{O}_{0,1}] + [W_{0,1}^{(1)}, \mathcal{O}_{1,0}] + \frac{1}{2} (W_{1,0}^{(1)} W_{0,1}^{(1)} + W_{0,1}^{(1)} W_{1,0}^{(1)}, \mathcal{E}_{0,0})
\]

\[
\mathcal{E}_{0,0} = [W_{1,0}^{(1)}, \mathcal{O}_{0,1}] + \frac{1}{2} [W_{1,0}^{(1)}, [W_{1,0}^{(1)}, \mathcal{E}_{0,0}]],
\]

\[
\mathcal{E}_{2,0} = [W_{0,1}^{(1)}, \mathcal{O}_{1,0}] + \frac{1}{2} [W_{1,0}^{(1)}, [W_{0,1}^{(1)}, \mathcal{E}_{0,0}]],
\]

\[
\mathcal{O}_{1,1}^{(2)} = \mathcal{O}_{1,0} + [W_{1,0}^{(1)}, \mathcal{E}_{0,0}],
\]

\[
\mathcal{O}_{0,1}^{(2)} = \mathcal{O}_{0,1} + [W_{0,1}^{(1)}, \mathcal{E}_{0,0}],
\]

\[
\mathcal{O}_{1,1}^{(2)} = [W_{1,0}^{(1)}, \mathcal{E}_{0,1}] + [W_{0,1}^{(1)}, \mathcal{E}_{1,0}],
\]

\[
\mathcal{O}_{2,0}^{(2)} = [W_{1,0}^{(1)}, \mathcal{E}_{1,0}],
\]

\[
\mathcal{O}_{0,2}^{(2)} = [W_{0,1}^{(1)}, \mathcal{E}_{0,1}].
\]

However, if the orders in a DKH expansion should not be classified according to the sum of the powers of the potentials in each term but according to the power of each potential, i.e., of \( V \) and \( A \), then the coupling terms bilinear in \( V \) and \( A \) should also be removed in the second transformation \( U_1 \):

\[
\mathcal{O}_{1,0}^{(2)} + \mathcal{O}_{0,1}^{(2)} + \mathcal{O}_{1,1}^{(2)} = 0.
\]

As a consequence,

\[
-\mathcal{O}_{1,0} - \mathcal{O}_{0,1} = [W_{1,0}^{(1)} + W_{0,1}^{(1)}, \mathcal{E}_{0,0}] + [W_{1,0}^{(1)}, \mathcal{E}_{0,1}] + [W_{0,1}^{(1)}, \mathcal{E}_{1,0}]
\]

has to be fulfilled by the parameters \( W_{0,1}^{(1)} \) and \( W_{1,0}^{(1)} \). Assuming that this equation can be split into two equations in the following way, the expressions for the kernels of \( W_{1,0}^{(1)} \) and \( W_{0,1}^{(1)} \) are derived via

\[
-\mathcal{O}_{1,0} = [W_{1,0}^{(1)}, \mathcal{E}_{0,0}] + [W_{1,0}^{(1)}, \mathcal{E}_{0,1}]
\]

and

\[
-\mathcal{O}_{0,1} = [W_{0,1}^{(1)}, \mathcal{E}_{0,0}] + [W_{0,1}^{(1)}, \mathcal{E}_{1,0}]
\]

as \( W_{1,0}^{(1)}(k, q) = [\beta (E_{p_y} + E_{p_x}) - \mathcal{E}_{0,1}(q, q) + \mathcal{E}_{0,1}(k, k)]^{-1} \mathcal{O}_{1,0}(k, q) \) and

\( W_{0,1}^{(1)}(k, q) = [\beta (E_{p_y} + E_{p_x}) - \mathcal{E}_{0,1}(q, q) + \mathcal{E}_{0,1}(k, k)]^{-1} \mathcal{O}_{0,1}(k, q) \).

The kernel of \( W_{1,0}^{(1)} + W_{0,1}^{(1)} \) is rather complicated if the odd term bilinear in \( V \) and \( A \) is removed in the second transformation \( U_1 \). Therefore, it is easier and also more intuitive to treat this bilinear term as a second-order term and
to remove it in the third transformation (with expansion parameter $W^{(2)} = W_{1,1}^{(2)} + W_{2,0}^{(2)} + W_{0,2}^{(2)}$) which removes all second-order odd terms.

For the rest of this work, we define the order of the DKH procedure as the sum of the powers of the potentials $V$ and $A$ in each term. Therefore, we will partly skip the subscripts of the expansion parameters $W^{(k)}$ since they consist of a sum of different contributions (like $W_{1,1}^{(2)}$, $W_{2,0}^{(2)}$, and $W_{0,2}^{(2)}$ for $W^{(2)}$) for the simultaneous decoupling of $V$ and $A$. The total order of $W$ in the potentials is anyhow indicated by the superscript (except for the numerical procedure presented in section 2.3.2.3).

In order to eliminate the second-order odd terms in the third transformation,

$$O_{1,1}^{(3)} + O_{2,0}^{(3)} + O_{0,2}^{(3)} = 0,$$

the condition

$$-(O_{1,1}^{(2)} + O_{2,0}^{(2)} + O_{0,2}^{(2)}) = [W_{2,0}^{(2)} + W_{0,2}^{(2)} + W_{1,1}^{(2)}, \varepsilon_{0,0}]$$

has to be fulfilled. Separating this equation into three equations

$$-O_{1,1}^{(2)} = [W_{1,1}^{(2)}, \varepsilon_{0,0}],$$

$$-O_{2,0}^{(2)} = [W_{2,0}^{(2)}, \varepsilon_{0,0}],$$

$$-O_{0,2}^{(2)} = [W_{0,2}^{(2)}, \varepsilon_{0,0}],$$

which is again reasonable because we may choose three parameters as we wish, the kernels of the expansion parameters, which are second-order integral operators in momentum space, are derived as

$$W_{1,1}^{(2)}(i, j, k) = \frac{\beta W_{1,0}^{(1)}(i, j) \varepsilon_{0,1}(j, k) - \varepsilon_{0,1}(i, j) W_{1,0}^{(1)}(j, k)}{E_p + E_p}$$

$$+ \frac{\beta W_{0,1}^{(1)}(i, j) \varepsilon_{1,0}(j, k) - \varepsilon_{1,0}(i, j) W_{0,1}^{(1)}(j, k)}{E_p + E_p},$$

$$W_{2,0}^{(2)}(i, j, k) = \frac{\beta W_{1,0}^{(1)}(i, j) \varepsilon_{1,0}(j, k) - \varepsilon_{1,0}(i, j) W_{1,0}^{(1)}(j, k)}{E_p + E_p},$$

$$W_{0,2}^{(2)}(i, j, k) = \frac{\beta W_{0,1}^{(1)}(i, j) \varepsilon_{0,1}(j, k) - \varepsilon_{0,1}(i, j) W_{0,1}^{(1)}(j, k)}{E_p + E_p},$$

where the kernel of $W_{1,0}^{(1)}$ and $W_{1,0}^{(1)}$ is given in Eq. (2.97). In DKH theory, only the upper left part of the even operators is needed. So, the even terms in the previous equations are given as

$$\varepsilon_{1,0}(j, k) = A_{p_i} V_{p_j, p_k} A_{p_k} + A_{p_i} R_{p_j, p_k} (\sigma \cdot p)_{p_j} V_{p_j, p_k} (\sigma \cdot p)_{p_k} R_{p_k} A_{p_k},$$

$$\varepsilon_{0,1}(j, k) = A_{p_j} \{ R_{p_j, p_k} (\sigma \cdot p)_{p_j} (-q_e \sigma \cdot A)_{p_j, p_k}$$

$$+ (-q_e \sigma \cdot A)_{p_j, p_k} (\sigma \cdot p)_{p_k} R_{p_k} \} A_{p_k}. $$
2.3.2.3 Iterative infinite-order decoupling in $V$ and $A$

An automated analytical evaluation of molecular properties within the DKH framework up to arbitrary order is feasible [213]. The expansion parameter in the $(k+1)$-th unitary transformation is derived from

$$[W^{(k)}, \mathcal{E}_{0,0}] = -\mathcal{O}^{(k)}. \quad (2.125)$$

However, the explicit form of this decoupling procedure focused on $V$-containing odd terms, whereas other odd magnetic-field-dependent terms were neglected in that implementation. For the combined elimination of the odd $V$- and $A$-terms, this scheme can be extended. It has just to be considered that the odd term $\mathcal{O}^{(k)}$ is now given as

$$\mathcal{O}^{(k)} = \sum_{a=0}^{k} \mathcal{O}_{a,k-a}^{(k)} \quad (2.126)$$

and the expansion parameter $W^{(k)}$ as

$$W^{(k)} = \sum_{a=0}^{k} W_{a,k-a}^{(k)} \quad (2.127)$$

A numerical iterative decoupling scheme up to “infinite order” in $V$ was presented by Matveev et al. [214], which is closely related to the “infinite-order” two-component method developed by Barysz and coworkers [215–217] and the iterative solution of the $X$ operator, which relates the large and small components of the untransformed Dirac spinor, in the matrix representation [197, 199]. The infinite-order denomination is put in quotation marks in order to emphasize that in these approaches no expansion is actually performed.

In the following, a modification is presented which treats general electromagnetic properties. As a first step, the fpFW transformation is applied. Afterwards, a modified version of the generalized unitary transformation given in Eq. (2.69) is performed [66, 214]:

$$D_{\infty} = U_{\infty}^\dagger D_{\infty}^{\text{DKH}} U_{\infty} \quad (2.128)$$

with $U_{\infty} = 1 + W^{(\infty)} / \sqrt{1 - (W^{(\infty)})^2}$. Since we are interested in the removal of the $V$- and $A$-dependent odd terms, we employ $V$- and $A$-dependent $W = W^{(x)}$ with $x \to \infty$ for decoupling to “infinite order”. The superscript ‘$(x)$’ indicates that the parameter $W^{(x)}$ is derived iteratively and denotes the iteration. The odd terms, which should be eliminated, are obtained as

$$0 = \mathcal{O}_{1,0} + \mathcal{O}_{0,1} + [\mathcal{E}_{0,0} + \mathcal{E}_{1,0} + \mathcal{E}_{0,1}, W^{(\infty)}] - W^{(\infty)} (\mathcal{O}_{1,0} + \mathcal{O}_{0,1}) W^{(\infty)} \quad (2.129)$$
and the Hamiltonian containing the even terms as

$$D_\infty = (1 - (W^{(\infty)})^2)^{-\frac{1}{2}} (\mathcal{E}_{0,0} + \mathcal{E}_{1,0} + \mathcal{E}_{0,1} + [\mathcal{O}_{1,0} + \mathcal{O}_{0,1}, W^{(\infty)}])$$

$$- W^{(\infty)} (\mathcal{E}_{0,0} + \mathcal{E}_{1,0} + \mathcal{E}_{0,1}) W^{(\infty)} (1 - (W^{(\infty)})^2)^{-\frac{1}{2}}. \tag{2.130}$$

The \(x\)-th approximation to \(W^{(\infty)}\) can, under the assumption that the last term in Eq. (2.129) is small, be determined via iterative solution of the following equations:

$$[\mathcal{E}_{0,0}, W^{(1)}] = -\mathcal{O}_{1,0} - \mathcal{O}_{0,1}, \tag{2.131}$$

$$[\mathcal{E}_{0,0}, W^{(2)}] = -\mathcal{O}_{1,0} - \mathcal{O}_{0,1} - [\mathcal{E}_{1,0} + \mathcal{E}_{0,1}, W^{(1)}], \tag{2.132}$$

$$[\mathcal{E}_{0,0}, W^{(k)}] = -\mathcal{O}_{1,0} - \mathcal{O}_{0,1} - [\mathcal{E}_{1,0} + \mathcal{E}_{0,1}, W^{(k-1)}]$$

$$+ W^{(k-1)} (\mathcal{O}_{1,0} + \mathcal{O}_{0,1}) W^{(k-1)}, \quad k = 3, \ldots, x \tag{2.133}$$

The convergence criterion can be defined in an analogous way to the one in Ref. [214] as

$$\delta = \frac{||X^{(k)} - X^{(k-1)}||}{r} \tag{2.134}$$

with

$$r = ||X^{(1)}|| = \max \left| \frac{\langle k | \mathcal{O}_{1,0}^{SL} + \mathcal{O}_{0,1}^{SL} | q \rangle}{\langle k | E_p | k \rangle + \langle q | E_p | q \rangle} \right| \tag{2.135}$$

and

$$\langle k | X | q \rangle = \left[ \langle k | E_p | k \rangle + \langle q | E_p | q \rangle \right]^{-1} \left[ \langle k | \mathcal{O}_{1,0}^{SL} + \mathcal{O}_{0,1}^{SL} \right.$$

$$- W^{SL} \{\mathcal{E}_{LL}^{1,0} + \mathcal{E}_{LL}^{0,1}\} + \{\mathcal{E}_{SS}^{1,0} + \mathcal{E}_{SS}^{0,1}\} W^{SL}$$

$$- W^{SL} \{\mathcal{O}_{1,0}^{LS} + \mathcal{O}_{0,1}^{LS}\} W^{SL} | q \rangle \right],$$

where the superscripts ‘LL’ and ‘SS’ denote the upper left and lower right and LS and SL the upper right and lower left blocks of the Hamiltonian, respectively, containing the \(V\)- and \(A\)-dependent terms. Only the lower left block of \(W\) is required (see appendix of Ref. [214]).

After convergence to the desired \(x\)-th approximation of \(W^{(\infty)}\) has been achieved, the renormalization factors \((1 - W^{(\infty)})^{-\frac{1}{2}}\) can be evaluated. These factors can be approximated by \((1 - W^{(\infty)})^{-\frac{1}{2}} \approx 1 + \frac{1}{2} (W^{(\infty)})^2 \) [214], which results for the first order in the same expressions as the decoupling procedure shown in the previous section [compare Eqs. (2.89) – (2.99)] or derivations in Refs. [163, 209, 210, 213]. Obviously, differences between the modified procedures based on the one by Wolf and Reiher [213] and on the one by Matveev et al. [214] exist for higher
orders. Applying the first one, odd terms of a well-defined order in \( V \) and \( A \) are eliminated in the \((k+1)\)-th transformation with \( W^{(k)} \) [compare Eq. (2.125)]. The determination of the odd terms, however, becomes complicated for higher orders due to the increasing number of cross terms between \( V \) and \( A \). In contrast to that, terms of different orders are removed by each approximation of \( W \) in the modified numerical decoupling shown above. As can be seen in Eq. (2.133), \( W^{(k)} \) contains odd terms whose highest power in \( V \) and \( A \) is \( 2k^3 \cdot 6 - 1 \). For example, \( W^{(5)} \) contains odd terms up to the 23rd-power in \( V \) and \( A \).

### 2.4 Molecular magnetic properties

In this section, we briefly reconsider Rayleigh–Schrödinger perturbation theory, which can be straightforwardly applied in the Dirac picture, and reformulate it then for the infinite-order DKH approach considering both perturbation-dependent and perturbation-independent unitary transformations. Although our reasoning in the following is universally applicable to any magnetic-field-like perturbation, we focus on mixed properties like the NMR shielding tensor. Therefore, we consider the strength of a homogeneous external magnetic field \( B \) and the magnetic moment \( m_{\text{mag}}^k \) of the \( k \)th nucleus as the perturbation parameters \( \lambda \) and \( \kappa \):

\[
\begin{align*}
\lambda &= |B|, \\
\kappa &= |m_{\text{mag}}^k|.
\end{align*}
\]

The corresponding magnetic vector potentials at position \( r \) are related to \( B \) and \( m_{\text{mag}}^k \) as follows [218, 219]:

\[
\begin{align*}
A_O &= \frac{1}{2} B \times (r - O) = \frac{1}{2} \mathbf{u} \times (r - O), \\
A_k &= m_{\text{mag}}^k \times \frac{(r - R_k)}{|r - R_k|^3} = \frac{\mathbf{v} \times (r - R_k)}{|r - R_k|^3},
\end{align*}
\]

where \( O \) is an arbitrary fixed gauge origin, \( R_k \) is the position of the \( k \)th nucleus while \( \mathbf{u} \) and \( \mathbf{v} \) are unit vectors pointing in the direction of \( B \) and \( m_{\text{mag}}^k \), respectively. Inserting \( A = A_O + A_k \) into the Dirac equation obeying the minimal-coupling recipe [as in Eq. (2.1)], the perturbation-dependent Hamiltonian can be written as

\[
D(\lambda, \kappa) = D_{00} + \lambda D_{10} + \kappa D_{01}
\]

\[
= \beta m_e c^2 + c\alpha \cdot p - \lambda q_e \alpha \cdot \left[ \frac{1}{2} \mathbf{u} \times (r - O) \right] \\
- \kappa q_e \alpha \cdot \left[ \frac{\mathbf{v} \times (r - R_k)}{|r - R_k|^3} \right]
\]
and the perturbation-dependent Dirac equation is given by

\[ D(\lambda, \kappa)\psi(\lambda, \kappa) = E(\lambda, \kappa)\psi(\lambda, \kappa), \quad (2.141) \]

where \( E(\lambda, \kappa) \) is the eigen-energy and \( |\psi(\lambda, \kappa)\rangle \) the wave function. In contrast to the previous notation, we have introduced two subscripts for the different parts of the Dirac operator in order to distinguish the \( B \)- and \( m^\text{mag} \)-dependent parts.

A first-order property is defined as the first derivative of \( E(\lambda, \kappa) \) with respect to a perturbation parameter such as \( \lambda \) or \( \kappa \). For example (under the assumption that the electron spin is aligned along the axis defined by \( v \) ) \( E_{01} \) corresponds to the isotropic hyperfine coupling constant:

\[ E_{01} = \left( \frac{dE(\lambda, \kappa)}{d\kappa} \right)_{\lambda = 0, \kappa = 0} = \left. \frac{d\langle \psi(\lambda, \kappa)|D_{00} + \kappa D_{01}|\psi(\lambda, \kappa)\rangle}{d\kappa} \right|_{\lambda = 0, \kappa = 0}. \quad (2.142) \]

A second-order property is, for example, the mixed second derivative of \( E(\lambda, \kappa) \) with respect to both perturbational parameters. In the example considered here the components of the NMR shielding tensor are defined as

\[ \sigma^k_{uv} = E_{11} = \left( \frac{d^2E(\lambda, \kappa)}{d\lambda d\kappa} \right)_{\lambda = 0, \kappa = 0} = \left. \frac{d^2\langle \psi(\lambda, \kappa)|D(\lambda, \kappa)|\psi(\lambda, \kappa)\rangle}{d\lambda d\kappa} \right|_{\lambda = 0, \kappa = 0}. \quad (2.143) \]

For the calculation of the expectation value \( \langle \psi(\lambda, \kappa)|D(\lambda, \kappa)|\psi(\lambda, \kappa)\rangle \) in the DKH framework, it is necessary to apply the vector-potential-dependent unitary transformation \( U(\lambda, \kappa) \), which can be constructed as described in section 2.3 as \( U(\lambda, \kappa) = \cdots U_2(\lambda, \kappa)U_1(\lambda, \kappa)U_0 \) with \( U_0 \) being the magnetic-field-independent fpFW transformation (alternatively, the \( A \)-dependent fpFW transformation \( U_0^{(A)} \) could also be employed), to the Dirac Hamiltonian:

\[
\tilde{D}^\infty(\lambda, \kappa) = U(\lambda, \kappa)D(\lambda, \kappa)U(\lambda, \kappa)^\dagger \\
= \begin{pmatrix}
\tilde{D}^\infty(\lambda, \kappa)^{LL} & 0 \\
0 & \tilde{D}^\infty(\lambda, \kappa)^{SS}
\end{pmatrix}.
\quad (2.144)
\]

The corresponding wave function for the positive-energy solutions is given by

\[
|\tilde{\phi}(\lambda, \kappa)\rangle = U(\lambda, \kappa)|\psi(\lambda, \kappa)\rangle = \begin{pmatrix}
|\tilde{\phi}^L(\lambda, \kappa)\rangle \\
0
\end{pmatrix}.
\quad (2.145)
\]

As a consequence, the energy expectation value in the DKH framework reads

\[
\langle \tilde{\phi}^L(\lambda, \kappa)\left|\tilde{D}^\infty(\lambda, \kappa)\right|^{LL}\tilde{\phi}^L(\lambda, \kappa)\rangle.
\quad (2.146)
\]
In principle, this expectation value contains unitary matrices that must be differentiated if \( U = U(\lambda, \kappa) \) according to Eqs. (2.142) and (2.143) [220]. Eqs. (2.142) and (2.143) are a recipe for evaluating properties variationally. However, in practical implementations this is usually associated with numerical derivatives leading to not very accurate results and a high computational effort. Assuming that perturbations \( \lambda \) and \( \kappa \) are sufficiently small one can evaluate first- and second-order properties by means of perturbation theory.

### 2.4.1 Rayleigh–Schrödinger perturbation theory for the Dirac equation

First, we expand \( D(\lambda, \kappa), E(\lambda, \kappa), \) and \( |\psi(\lambda, \kappa)\rangle \) in powers of \( \lambda \) and \( \kappa \) [218],

\[
D(\lambda, \kappa) = D_{00} + \lambda D_{10} + \kappa D_{01}, \\
|\psi(\lambda, \kappa)\rangle = |\psi_{00}\rangle + \lambda|\psi_{10}\rangle + \kappa|\psi_{01}\rangle + \lambda\kappa|\psi_{11}\rangle + \cdots, \\
E(\lambda, \kappa) = E_0 + \lambda E_{10} + \kappa E_{01} + \lambda\kappa E_{11} + \cdots.
\]

After substituting Eqs. (2.147) to (2.149) into Eq. (2.141) we collect terms as coefficients to different powers of \( \lambda \) and \( \kappa \):

\[
\begin{align*}
\lambda^0\kappa^0 & : \quad D_{00}|\psi_{00}\rangle = E_{00}|\psi_{00}\rangle, \\
\lambda^1\kappa^0 & : \quad D_{10}|\psi_{00}\rangle + D_{00}|\psi_{10}\rangle = E_{10}|\psi_{00}\rangle + E_{00}|\psi_{10}\rangle, \\
\lambda^0\kappa^1 & : \quad D_{01}|\psi_{00}\rangle + D_{00}|\psi_{01}\rangle = E_{01}|\psi_{00}\rangle + E_{00}|\psi_{01}\rangle, \\
\lambda^1\kappa^1 & : \quad D_{10}|\psi_{01}\rangle + D_{01}|\psi_{10}\rangle + D_{00}|\psi_{11}\rangle = E_{11}|\psi_{00}\rangle + E_{10}|\psi_{01}\rangle + E_{01}|\psi_{10}\rangle + E_{00}|\psi_{11}\rangle.
\end{align*}
\]

For simplicity, we adopt the following orthogonality condition:

\[
\langle \psi(\lambda, \kappa)|\psi_{00}\rangle = \langle \psi_{00}|\psi(\lambda, \kappa)\rangle = 1.
\]

In view of first-order properties, we consider as an example the \( \lambda^0\kappa^1 \) term from Eq. (2.152). Multiplication from the left by \( \langle \psi_{00}| \) and integration yields

\[
\langle \psi_{00}|D_{01}|\psi_{00}\rangle + \langle \psi_{00}|D_{00}|\psi_{01}\rangle = \langle \psi_{00}|E_{01}|\psi_{00}\rangle + \langle \psi_{00}|E_{00}|\psi_{01}\rangle.
\]

Keeping in mind that

\[
\langle \psi_{00}|D_{00}|\psi_{01}\rangle = \langle D_{00}\psi_{00}|\psi_{01}\rangle = \langle E_{00}\psi_{00}|\psi_{01}\rangle = \langle \psi_{00}|E_{00}\psi_{01}\rangle,
\]

we obtain

\[
\langle \psi_{00}|D_{01}|\psi_{00}\rangle = E_{01}\langle \psi_{00}|\psi_{00}\rangle.
\]

Thus, the first-order energy correction \( E_{01} \) is given by

\[
E_{01} = \langle \psi_{00}|D_{01}|\psi_{00}\rangle.
\]
For the mixed second-order properties, we similarly obtain the energy correction $E_{11}$, which contains in the case of the Dirac equation in an electromagnetic field [see Eq. (2.1)] only a paramagnetic contribution:

$$E_{11} = E_{11}^p = \text{Re} \langle \psi_{00} | D_{10} | \psi_{01} \rangle + \text{Re} \langle \psi_{00} | D_{01} | \psi_{10} \rangle.$$  
(2.159)

With the help of Dalgarno’s exchange theorem [218, 221], $E_{11}^p$ can be rewritten as

$$E_{11}^p = 2 \text{Re} \langle \psi_{00} | D_{10} | \psi_{01} \rangle.$$  
(2.160)

The first-order response wave function $| \psi_{10} \rangle$ can be expressed from the $\lambda^1 \kappa^0$ condition in Eq. (2.151):

$$(D_{10} - E_{10}) | \psi_{00} \rangle = -(D_{00} - E_{00}) | \psi_{10} \rangle.$$  
(2.161)

### 2.4.2 Perturbation theory with perturbation-independent unitary transformations

In this subsection we consider the effect of insertions of unperturbed unitary transformations on the perturbation theory as described in the previous section. Our goal is to exploit the two-component character of the DKH approach for property calculations. As a first step, the unitary transformation $U = \cdots U_2 U_1 U_0$, which completely decouples the unperturbed Dirac Hamiltonian $D_{00}$,

$$D_{00}^\infty = U D_{00} U^\dagger = \begin{pmatrix} [D_{00}^\infty]_{LL} & 0 \\ 0 & [D_{00}^\infty]_{SS} \end{pmatrix}$$  
(2.162)

with the corresponding wave function

$$| \phi_{00} \rangle = U | \psi_{00} \rangle = \begin{pmatrix} | \phi_{L0}^0 \rangle \\ 0 \end{pmatrix},$$  
(2.163)

is applied to the magnetic-vector-potential-dependent Dirac equation

$$UD(\lambda, \kappa) U^\dagger | \psi(\lambda, \kappa) \rangle = E(\lambda, \kappa) U | \psi(\lambda, \kappa) \rangle.$$  
(2.164)

The transformed perturbation-dependent parts of the Dirac Hamiltonian, $D_{10}^\infty = UD_{10} U^\dagger$ and $D_{01}^\infty = UD_{01} U^\dagger$, are not block-diagonal since they also contain odd terms. Contrary to $| \phi_{00} \rangle$, the perturbed wave functions (e.g., $| \phi_{10} \rangle = U | \psi_{10} \rangle$, $| \phi_{01} \rangle = U | \psi_{01} \rangle$, $| \phi_{11} \rangle = U | \psi_{11} \rangle$) show no zero small component.

Because of the perturbation-independence of $U$, expansions like in Eqs. (2.147) – (2.149) are sufficient:

$$D^\infty(\lambda, \kappa) = D_{00}^\infty + \lambda D_{10}^\infty + \kappa D_{01}^\infty, \quad (2.165)$$

$$| \phi(\lambda, \kappa) \rangle = | \phi_{00} \rangle + \lambda | \phi_{10} \rangle + \kappa | \phi_{01} \rangle + \lambda \kappa | \phi_{11} \rangle + \cdots, \quad (2.166)$$

$$E(\lambda, \kappa) = E_0 + \lambda E_{10} + \kappa E_{01} + \lambda \kappa E_{11} + \cdots. \quad (2.167)$$
As expected, the resulting expressions for the energy corrections remain unchanged. However, now they are obtained through multiplication by \( \langle \phi_{00} \rangle \) instead of \( \langle \psi_{00} \rangle \) from the left and subsequent integration.

For first-order properties, the advantages of this formulation are obvious — insertions of \( U \) allow us to reduce the exact evaluation of \( E_{01} \) and \( E_{10} \) through \( | \phi_{00} \rangle \) to a two-component formulation. Since the lower two-components of \( | \phi_{00} \rangle \) are zero, \( E_{01} \) and \( E_{10} \) are determined by the \( LL \) block of \( D_{01}^\infty \) and \( D_{10}^\infty \):

\[
E_{01} = \langle \phi_{00} | D_{01}^{LL} | \phi_{00} \rangle, \tag{2.168}
\]

\[
E_{10} = \langle \phi_{00} | D_{10}^{LL} | \phi_{00} \rangle. \tag{2.169}
\]

Explicit expressions for the DKH Hamiltonian which are derived from the magnetic-vector-potential-containing Dirac Hamiltonian through the decoupling of \( V \) (and not of \( A \)) are given in the literature, see, e.g., Ref. [209].

As an example, we write out \( D_{01}^{DKH} = U_0 D_{01} U_0^\dagger \), which is obtained from the Dirac operator after the magnetic-field-independent fpFW transformation,

\[
D_{01}^{DKH} = \begin{pmatrix}
A_p R_p \sigma \cdot p X A_p + A_p X A_p \cdot p R_p A_p & A_p X A_p - A_p R_p \sigma \cdot p X \sigma \cdot p R_p A_p \\
A_p X A_p - A_p R_p \sigma \cdot p X \sigma \cdot p R_p A_p & -A_p R_p \sigma \cdot p X A_p - A_p X \sigma \cdot p R_p A_p
\end{pmatrix}
\]

with

\[
X = -q_0 \sigma \cdot \left( \frac{v \times (r - R_k)}{|r - R_k|^3} \right). \tag{2.171}
\]

As can be seen from the previous equation, the number of \( p \) operators entering the \( LL \)-component of \( D_{01}^{DKH} \) is no longer even (unlike for electrical properties such as electrical field gradients).

The evaluation of mixed second-order properties is not so straightforward since we now need both the unperturbed and perturbed wave functions \( | \phi_{00} \rangle \) and \( | \phi_{10} \rangle \). The main computational challenge is the determination of the latter:

\[
(D_{00}^\infty - E_{00}) | \phi_{10} \rangle = -(D_{10}^\infty - E_{10}) | \phi_{00} \rangle. \tag{2.172}
\]

It is important to realize that it is impossible to find a unitary transformation, which transforms \( | \phi_{00} \rangle \) and \( | \phi_{10} \rangle \) to a picture in which their small components will be zero at the same time. So, Eq. (2.172) is a general four-component one-electron equation. Fortunately, one can reduce it to two-component equations,

\[
(D_{00}^\infty - E_{00})^{LL} | \phi_{01}^L \rangle = -(D_{01}^\infty - E_{01})^{LL} | \phi_{00}^L \rangle, \tag{2.173}
\]

\[
(D_{00}^\infty - E_{00})^{SS} | \phi_{01}^S \rangle = -(D_{01}^\infty)^{SL} | \phi_{00}^L \rangle, \tag{2.174}
\]

where both the \( LL \) and \( SL \) blocks of the transformed operator \( D_{01}^\infty \) are needed. Having obtained the first-order perturbed wave function, the second-order energy correction \( E_{11}^p \) can be evaluated like shown in Eqs. (2.159) and (2.160) as

\[
E_{11} = E_{11}^p = 2Re \langle \phi_{00} | D_{10}^\infty | \phi_{01} \rangle. \tag{2.175}
\]
2.4.3 Perturbation theory with perturbation-dependent unitary transformations

Now we explore another way to modify the perturbation approach employing a perturbation-dependent unitary transformation

\[ U(\lambda, \kappa) = U_{00} + \lambda U_{10} + \kappa U_{01} + \lambda \kappa U_{11} + \cdots, \]

which achieves the total decoupling of the perturbed Dirac Hamiltonian \( D(\lambda, \kappa) \) [compare Eqs. (2.144) and (2.145)]. As was shown in section 2.4.2 for perturbation-independent transformations, the first-order wave functions [compare Eqs. (2.144) and (2.145)] achieve the total decoupling of the perturbed Dirac Hamiltonian \( D_{01}^\infty \) and \( D_{00}^\infty \) are not block-diagonal since the perturbation-independent transformation \( U \) results only in a vanishing small component for the unperturbed wave function \( |\phi_{00}\rangle \) and a block-diagonal form of \( D_{00}^\infty \). In contrast to this, the perturbation-dependent transformation \( U(\lambda, \kappa) \) leads to a Hamiltonian

\[
\tilde{D}^\infty(\lambda, \kappa) = U(\lambda, \kappa) D_{00} U(\lambda, \kappa)^\dagger + U(\lambda, \kappa) \lambda D_{10} U(\lambda, \kappa)^\dagger + U(\lambda, \kappa) \kappa D_{01} U(\lambda, \kappa)^\dagger + \cdots
\]

\[
= U_{00} D_{00} U_{00}^\dagger + \lambda(U_{10} D_{00} U_{00}^\dagger + U_{00} D_{10} U_{00}^\dagger + U_{00} D_{01} U_{00}^\dagger) + \kappa(U_{01} D_{00} U_{00}^\dagger + U_{00} D_{01} U_{00}^\dagger + U_{00} D_{00} U_{00}^\dagger) + \cdots
\]

\[
\equiv \tilde{D}_{00}^\infty
\]

with each term being block-diagonal. The corresponding positive-energy wave function is given as

\[
|\tilde{\phi}(\lambda, \kappa)\rangle = U(\lambda, \kappa) |\psi_{00}\rangle + U(\lambda, \kappa) \lambda |\psi_{10}\rangle + U(\lambda, \kappa) \kappa |\psi_{01}\rangle + \cdots
\]

\[
= U_{00} |\psi_{00}\rangle + \lambda(U_{10} |\psi_{00}\rangle + U_{00} |\psi_{10}\rangle) + \kappa(U_{01} |\psi_{00}\rangle + U_{00} |\psi_{01}\rangle) + \cdots
\]

\[
\equiv |\tilde{\phi}_{00}\rangle
\]

\[
|\tilde{\phi}_{00}\rangle = |\phi_{00}\rangle \quad \text{and} \quad \tilde{D}_{00}^\infty = D_{00}^\infty. \]

Since the total operator \( \tilde{D}^\infty(\lambda, \kappa) \) is block-diagonal, the determination of the first-order perturbed wave function \( |\tilde{\phi}_{10}\rangle \) (or, analogously, \( |\tilde{\phi}_{01}\rangle \)), which is needed in order to derive the energy correction \( E_{11}^p \) [compare Eq. (2.159)], is now possible in a purely two-component framework:

\[
(\tilde{D}_{00}^\infty - E_{00})^{LL} |\tilde{\phi}_{10}^L\rangle = -(\tilde{D}_{01}^\infty - E_{01})^{LL} |\tilde{\phi}_{00}^L\rangle, \quad (2.179)
\]

\[
(\tilde{D}_{00}^\infty - E_{00})^{SS} |\tilde{\phi}_{01}^S\rangle = -(\tilde{D}_{01}^\infty - E_{01})^{SS} |\tilde{\phi}_{00}^S\rangle. \quad (2.180)
\]

In contrast to Eqs. (2.173) and (2.174), the two-component equations are not coupled anymore because the \( \tilde{D}_{00}^\infty \) operator contains only even components.
In order to demonstrate that the first-order energy correction is the same no matter if $U$ or $U(\lambda, \kappa)$ is employed, we collect the terms of different powers in $\lambda$ and $\kappa$:

\[ \lambda^0 \kappa^0 : \quad \hat{D}_{00}^{\infty}(\tilde{\phi}_{00}) + \hat{D}_{00}^{\infty}(\tilde{\phi}_{10}) = E_{10} |\tilde{\phi}_{00}\rangle + E_{00} |\tilde{\phi}_{10}\rangle, \quad (2.181) \]

\[ \lambda^0 \kappa^1 : \quad \hat{D}_{01}^{\infty}(\tilde{\phi}_{00}) + \hat{D}_{00}^{\infty}(\tilde{\phi}_{01}) = E_{01} |\tilde{\phi}_{00}\rangle + E_{00} |\tilde{\phi}_{01}\rangle, \quad (2.182) \]

\[ \lambda^1 \kappa^1 : \quad \hat{D}_{11}^{\infty}(\tilde{\phi}_{00}) + \hat{D}_{10}^{\infty}(\tilde{\phi}_{01}) + \hat{D}_{01}^{\infty}(\tilde{\phi}_{10}) + \hat{D}_{00}^{\infty}(\tilde{\phi}_{11}) = E_{11} \tilde{\phi}_{00} + E_{10} |\tilde{\phi}_{01}\rangle + E_{01} |\tilde{\phi}_{10}\rangle + E_{00} |\tilde{\phi}_{11}\rangle. \quad (2.183) \]

$E_{01}$ is obtained by multiplication of the $\lambda^0 \kappa^1$ equation with $\langle \tilde{\phi}_{00} |$ from the left and integration,

\[ E_{01} = \langle \tilde{\phi}_{00} | \hat{D}_{01}^{\infty} | \tilde{\phi}_{01} \rangle + \frac{\langle \tilde{\phi}_{00} | \hat{D}_{00}^{\infty} | \tilde{\phi}_{01} \rangle - \langle \tilde{\phi}_{00} | E_{00} | \tilde{\phi}_{01} \rangle}{E_{01}} = 0. \quad (2.184) \]

Here, we have taken advantage of the fact that

\[ \langle \tilde{\phi}_{00} | \hat{D}_{00}^{\infty} | \tilde{\phi}_{01} \rangle = \langle \hat{D}_{00}^{\infty} | \tilde{\phi}_{01} \rangle = \langle E_{00} \tilde{\phi}_{00} | \tilde{\phi}_{01} \rangle = \langle \tilde{\phi}_{00} | E_{00} | \tilde{\phi}_{01} \rangle. \quad (2.185) \]

At first glance, $E_{01}$ seems to differ from Eq. (2.168) because Eq. (2.184) can be written as

\[ E_{01} = \langle \tilde{\phi}_{00} | U_{00} D_{01} U_{00}^\dagger | \tilde{\phi}_{00} \rangle + \langle \tilde{\phi}_{00} | U_{01} D_{00} U_{01}^\dagger | \tilde{\phi}_{00} \rangle + \langle \tilde{\phi}_{00} | U_{00} D_{00} U_{01}^\dagger | \tilde{\phi}_{00} \rangle. \quad (2.186) \]

Indications from studies of electrical field gradients [222] show a small difference at least for the finite-order DKH approach. However, the additional terms vanish at infinite order [209]:

\[ \langle \tilde{\phi}_{00} | U_{01} D_{00} U_{01}^\dagger | \tilde{\phi}_{00} \rangle + \langle \tilde{\phi}_{00} | U_{01} D_{00} U_{01}^\dagger | \tilde{\phi}_{00} \rangle = E_{00} \left[ \langle \psi_{00} | U_{00}^\dagger U_{01} | \psi_{00} \rangle + \langle \psi_{00} | U_{01}^\dagger U_{00} | \psi_{00} \rangle \right] \\
= E_{00} \left[ \langle \psi_{00} | U_{00}^\dagger U_{01} + U_{01}^\dagger U_{00} | \psi_{00} \rangle \right] \\
= E_{00} \left[ \langle \psi_{00} | \left( \frac{d[U^\dagger(\lambda, \kappa) U(\lambda, \kappa)]}{d\kappa} \right)_{\lambda = 0, \kappa = 0} | \psi_{00} \rangle \right] = 0. \quad (2.187) \]

Convergence of the series for both cases $U$ and $U(\lambda, \kappa)$ with respect to the DKH order remains to be studied.

Next, we consider the mixed second-order energy $E_{11}$. If $U(\lambda, \kappa)$ is applied, $E_{11}$ contains a diamagnetic contribution $E_{11}^d$,

\[ E_{11}^d = \langle \tilde{\phi}_{00} | \hat{D}_{11}^{\infty} | \tilde{\phi}_{00} \rangle \quad (2.188) \]

with

\[ \hat{D}_{11}^{\infty} = U_{10} D_{00} U_{10}^\dagger + U_{01} D_{00} U_{01}^\dagger + U_{10} D_{01} U_{10}^\dagger + U_{01} D_{10} U_{01}^\dagger + U_{10} D_{10} U_{01}^\dagger + U_{11} D_{00} U_{11}^\dagger + U_{00} D_{00} U_{11}^\dagger + U_{00} D_{00} U_{11}^\dagger. \quad (2.189) \]
Compared to $E_{11}^p$ obtained with perturbation-independent unitary transformations [see Eq. (2.175)], the paramagnetic contribution $E_{11}^p$ contains now additional terms and is written as

\[
E_{11}^p = \text{Re} \left[ \langle \tilde{\phi}_{00} | D_{10}^\infty | \tilde{\phi}_{10} \rangle + \langle \tilde{\phi}_{00} | D_{01}^\infty | \tilde{\phi}_{01} \rangle \right]
\]

\[
= \text{Re} \left[ \langle \tilde{\phi}_{00} | U_{00} D_{01} U_{00}^\dagger | \tilde{\phi}_{10} \rangle + \langle \tilde{\phi}_{00} | U_{00} D_{10} U_{00}^\dagger | \tilde{\phi}_{01} \rangle \right.

+ \langle \tilde{\phi}_{00} | U_{00} D_{00} U_{01}^\dagger | \tilde{\phi}_{10} \rangle + \langle \tilde{\phi}_{00} | U_{00} D_{00} U_{10}^\dagger | \tilde{\phi}_{01} \rangle

\]

\[
+ \langle \tilde{\phi}_{00} | U_{01} D_{00} U_{10}^\dagger | \tilde{\phi}_{10} \rangle + \langle \tilde{\phi}_{00} | U_{10} D_{00} U_{00}^\dagger | \tilde{\phi}_{01} \rangle

\]

\[
- \langle \tilde{\phi}_{00} | E_{01} | \tilde{\phi}_{10} \rangle - \langle \tilde{\phi}_{00} | E_{10} | \tilde{\phi}_{01} \rangle \right].
\]  

(2.190)

In the following, we will show that the diamagnetic terms vanish in combination with the new paramagnetic contributions in the infinite-order approach so that $E_{11}$ remains unchanged regardless whether we use $U$ or $U(\lambda, \kappa)$. Considering that $|\tilde{\phi}_{10}\rangle = U_{00} |\psi_{00}\rangle + U_{10} |\psi_{00}\rangle$ and $|\tilde{\phi}_{01}\rangle = U_{00} |\psi_{01}\rangle + U_{01} |\psi_{00}\rangle$, some terms in Eqs. (2.188) and (2.190) containing $D_{00}$ can be eliminated with a small modification of the trick employed for $E_{01}$:

\[
\langle U_{00} | \psi_{00}\rangle |U_{11} D_{00} U_{00}^\dagger |U_{00} |\psi_{00}\rangle + \langle U_{00} | \psi_{00}\rangle |U_{00} D_{00} U_{11}^\dagger |U_{00} |\psi_{00}\rangle

+ \langle U_{00} | \psi_{00}\rangle |U_{00} D_{00} U_{01}^\dagger U_{10} |\psi_{00}\rangle + \langle U_{00} | \psi_{00}\rangle |U_{00} D_{00} U_{10}^\dagger U_{01} |\psi_{00}\rangle

= \langle \psi_{00}\rangle |U_{00} |U_{11} E_{00} |\psi_{00}\rangle + \langle E_{00} | \psi_{00}\rangle |U_{01}^\dagger U_{10} |\psi_{00}\rangle + \langle E_{00} | \psi_{00}\rangle |U_{01} |U_{10}^\dagger |\psi_{00}\rangle

+ \langle E_{00} | \psi_{00}\rangle |U_{10}^\dagger U_{01} |\psi_{00}\rangle

= E_{00} \left( \psi_{00} \left| \frac{d[U(\lambda, \kappa)U(\lambda, \kappa)]}{d\lambda} \right|_{\lambda = 0} \right)_{\kappa = 0} \psi_{00} = 0. 
\]

(2.191)

Other terms of Eqs. (2.188) and (2.190) containing $D_{00}$ can be eliminated via

\[
\langle \tilde{\phi}_{00} | U_{01} D_{00} U_{10}^\dagger |U_{00} |\psi_{00}\rangle + \langle \tilde{\phi}_{00} | U_{01} D_{00} U_{00}^\dagger |U_{10} |\psi_{00}\rangle

= \langle \tilde{\phi}_{00} | U_{01} D_{00} \left( U_{10} U_{00} + U_{00} U_{10} \right) |\psi_{00}\rangle

= \left( \tilde{\phi}_{00} \left| U_{01} D_{00} \left( \frac{d[U(\lambda, \kappa)U(\lambda, \kappa)]}{d\lambda} \right)_{\lambda = 0} \right| \psi_{00} \right) = 0,
\]

(2.192)

\[
\langle \tilde{\phi}_{00} | U_{10} D_{00} U_{01}^\dagger |U_{00} |\psi_{00}\rangle + \langle \tilde{\phi}_{00} | U_{10} D_{00} U_{00}^\dagger |U_{01} |\psi_{00}\rangle = 0. 
\]

(2.193)

Sums of terms containing $D_{01}$ and $D_{10}$ in Eqs. (2.188) and (2.190) yield zero in the same fashion:

\[
\langle \tilde{\phi}_{00} | U_{00} D_{01} U_{10}^\dagger |U_{00} |\psi_{00}\rangle + \langle \tilde{\phi}_{00} | U_{00} D_{01} U_{00}^\dagger |U_{10} |\psi_{00}\rangle = 0,
\]

(2.194)

\[
\langle \tilde{\phi}_{00} | U_{00} D_{10} U_{01}^\dagger |U_{00} |\psi_{00}\rangle + \langle \tilde{\phi}_{00} | U_{00} D_{10} U_{00}^\dagger |U_{01} |\psi_{00}\rangle = 0. 
\]

(2.195)

The remaining additional terms containing $D_{10}$, $E_{10}$ and $|\psi_{10}\rangle$ in Eqs. (2.188) and (2.190) vanish also:

\[
\langle \psi_{00} | U_{10}^\dagger U_{01} D_{10} |\psi_{00}\rangle - \langle \psi_{00} | U_{00}^\dagger E_{10} U_{01} |\psi_{00}\rangle

+ \langle \psi_{00} | D_{00} U_{01}^\dagger U_{00} |\psi_{10}\rangle + \langle \psi_{00} | U_{10}^\dagger U_{00} D_{00} |\psi_{10}\rangle = 0.
\]

(2.196)
This can be shown as follows: Adding the terms \(-\langle \psi_0 | U_{00}^\dagger U_{01} E_{10} | \psi_0 \rangle\) + \langle \psi_0 | U_{00}^\dagger U_{01} E_{10} | \psi_0 \rangle\) we get
\[
\langle \psi_0 | U_{00}^\dagger U_{01} D_{00} | \psi_1 \rangle - \langle \psi_0 | U_{00}^\dagger U_{01} E_{10} | \psi_1 \rangle + \langle \psi_0 | D_{00} U_{01}^\dagger | \psi_1 \rangle = 0.
\] (2.197)

Employing \((D_{00} - E_{10})|\psi_0\rangle = -(D_{00} - E_{00})|\psi_10\rangle\), the first and last terms in this equation cancel and we arrive at
\[
\langle \psi_0 | U_{00}^\dagger U_{01} D_{00} | \psi_1 \rangle - \langle \psi_0 | U_{00}^\dagger U_{01} E_{10} | \psi_1 \rangle + \langle \psi_0 | D_{00} U_{01}^\dagger | \psi_1 \rangle = 0.
\] (2.198)

In a similar way, it can be shown that
\[
\langle \psi_0 | U_{00}^\dagger U_{10} D_{01} | \psi_0 \rangle - \langle \psi_0 | U_{00}^\dagger E_{01} U_{10} | \psi_0 \rangle + \langle \psi_0 | D_{00} U_{10}^\dagger U_{00} | \psi_0 \rangle + \langle \psi_0 | U_{00}^\dagger U_{10} D_{00} | \psi_0 \rangle = 0
\] (2.199)
is fulfilled.
Hence, we arrive at the important result that the energy correction is the same no matter whether \(U\) or \(U(\lambda, \kappa)\) is applied. Employing the perturbation-dependent transformation, we just obtain additional contributions to the paramagnetic and diamagnetic terms by adding and subtracting the diamagnetic contributions from \(E_{11}\). For each particular choice of \(U(\lambda, \kappa)\) this splitting will be defined differently.
3. Theory of Raman Optical Activity Spectroscopy

After the treatment of molecular properties in a (quasi)-relativistic framework, we now focus on the theory of Raman optical activity, which is based on the development reported in Refs. [23,223–226]. Following the developments in the preceding chapter, we employ a semi-classical treatment, i.e., the molecule is treated quantum mechanically and the electromagnetic field classically. Within response theory as needed in this chapter, we do not need to explicitly differentiate between nonrelativistic and relativistic unperturbed states and hence drop such indices like ‘nr’. Moreover, the four non-redundant components of the four-potential, \( \Phi(r,t) \) and \( A(r,t) \), are conveniently replaced by the redundant three-component electric and three-component magnetic fields, \( E(r,t) \) and \( B(r,t) \), respectively.

Classical electric and magnetic fields are completely described by Maxwell’s equations [23,227] [SI units are employed for the remaining part of this thesis (compare appendix C)]:

\[
\begin{align*}
\nabla \cdot D(r,t) &= \rho(r,t), \\
\nabla \cdot B(r,t) &= 0, \\
\text{curl} E(r,t) + \frac{\partial B(r,t)}{\partial t} &= 0, \\
\text{curl} H(r,t) - \frac{\partial D(r,t)}{\partial t} &= J(r,t).
\end{align*}
\]

\( D(r,t) \) and \( H(r,t) \) are the electric displacement and magnetic field strengths, respectively. The charge and current densities are indicated by \( \rho(r,t) \) and \( J(r,t) \), respectively. Together with the Lorentz force law, Maxwell’s equations totally describe the interaction of electric and magnetic fields with charged particles and currents.

The electric and magnetic fields are determined by the scalar potential \( \Phi(r,t) \) and the vector potential \( A(r,t) \), respectively, which satisfy the following equations:

\[
\begin{align*}
E(r,t) &= -\nabla \Phi(r,t) - \frac{\partial A(r,t)}{\partial t}, \\
B(r,t) &= \text{curl} A(r,t).
\end{align*}
\]

\( \Phi(r,t) \) and \( A(r,t) \) are not uniquely defined by Eqs. (3.5) and (3.6) and change under gauge transformations (see section 2.1). In the preceding chapter, we chose \( V = q_e \Phi \).
Besides the Coulomb gauge $\nabla \cdot \mathbf{A}(\mathbf{r}, t) = 0$, there are other frequently chosen gauges. One important example is the Lorentz gauge,
\[
\nabla \mathbf{A}(\mathbf{r}, t) + \frac{1}{v^2} \frac{\partial \Phi(\mathbf{r}, t)}{\partial t} = 0,
\]
which allows a decoupling of the magnetic and scalar potentials:
\[
\nabla^2 \mathbf{A}(\mathbf{r}, t) - \frac{1}{v^2} \frac{\partial^2 \mathbf{A}(\mathbf{r}, t)}{\partial t^2} = -\mu \mu_0 J(\mathbf{r}, t),
\]
\[
\nabla^2 \Phi(\mathbf{r}, t) - \frac{1}{v^2} \frac{\partial^2 \Phi(\mathbf{r}, t)}{\partial t^2} = -\frac{\rho(\mathbf{r}, t)}{\epsilon \epsilon_0}.
\]
$\epsilon$ is the dielectric constant and $\mu$ the magnetic permeability of a specific material and $\epsilon_0$ and $\mu_0$ are the vacuum permittivity and permeability, respectively. $v = (\mu_0 \epsilon_0)^{-1/2}$ is the speed of the electromagnetic wave, which reduces to $c = (\mu_0 \epsilon_0)^{-1/2}$ in vacuo. Solutions of Eqs. (3.8) and (3.9) for the magnetic and scalar potentials at $\mathbf{R}$ give rise to the so-called retarded potentials
\[
\mathbf{A}(\mathbf{R}, t) = \frac{\mu \mu_0}{4\pi} \int \frac{J(\mathbf{r}, t - |\mathbf{R} - \mathbf{r}|/c) d^3 r}{|\mathbf{R} - \mathbf{r}|},
\]
\[
\Phi(\mathbf{R}, t) = \frac{1}{4\pi \epsilon_0} \int \frac{\rho(\mathbf{r}, t - |\mathbf{R} - \mathbf{r}|/c) d^3 r}{|\mathbf{R} - \mathbf{r}|},
\]
where $\mathbf{r}$ is the position of the volume element belonging to the charge and current densities. The perturbations by $\mathbf{J}(\mathbf{r})$ and $\Phi(\mathbf{r})$ at $\mathbf{r}$ need a time $|\mathbf{R} - \mathbf{r}|/c$ to travel the distance $|\mathbf{R} - \mathbf{r}|$.

In case of a plane (i.e., depending only on one spatial coordinate) harmonic electromagnetic wave possessing a single frequency (so-called monochromatic wave), the electric and magnetic fields in the absence of charges and currents are given by
\[
\mathbf{E}(\mathbf{r}, t) = \text{Re} \left[ \tilde{\mathbf{E}}^{(0)} \exp \left( i [\kappa \cdot \mathbf{r} - \omega t] \right) \right] \mathbf{e}_1,
\]
\[
\mathbf{B}(\mathbf{r}, t) = \text{Re} \left[ \tilde{\mathbf{B}}^{(0)} \exp \left( i [\kappa \cdot \mathbf{r} - \omega t] \right) \right] \mathbf{e}_2
\]
with the wave vector $\kappa = \frac{\omega}{c} \mathbf{n}$ constructed from the propagation vector $\mathbf{n}$ with the magnitude equal to the refractive index $n = |\mathbf{n}| = (\mu \epsilon)^{1/2}$ and the angular frequency of the wave, $\omega$, which can be calculated from the velocity and the wavelength $\lambda$ via $\omega = 2\pi v/\lambda$. The sign of the exponent has been chosen according to Ref. [23]. $\tilde{\mathbf{E}}^{(0)}$ and $\tilde{\mathbf{B}}^{(0)}$ are the constant complex amplitudes of the electric and magnetic fields, respectively, and $\mathbf{e}_1$ and $\mathbf{e}_2$ constant unit vectors. Thus, the electric-field vector always points into the direction of $\mathbf{e}_1$ giving rise to a linearly polarized electromagnetic wave. In circularly polarized electromagnetic waves, the electric field vector describes a helix in the direction of wave propagation, forming a circle when looking at a fixed point in space. Such waves can be constructed by superposition of linearly polarized waves.

The components of the magnetic field in Eq. (3.13) can be determined via [23]
\[
\mathbf{B} = \mathbf{n} \times \mathbf{E}.
\]
3.1 Derivation of the molecular property tensors

The interaction of molecules with electric and magnetic fields leads to a change in particular properties of the molecule, which is then measured in experiment. Since we assume that the perturbation caused by the electromagnetic radiation is small we employ perturbation theory for the calculation of the response of the molecule to the external fields.

3.1.1 Hamiltonian describing the interaction with electromagnetic fields

In order to derive the perturbation-containing Hamiltonian \( H = H^{(0)} + H^{\text{int}} \), where \( H^{(0)} \) is the Hamiltonian of the free particle and \( H^{\text{int}} \) the perturbation-dependent part considering the irradiation by classical magnetic and electric fields, we first present the classical Hamiltonian for a charged particle in a electromagnetic field, which was employed in Ref. [23] for the derivation of the Hamiltonian, following Ref. [56].

The starting point is the classical Lagrangian with the kinetic energy \( T \) and the potential energy \( V \),

\[
L(r, \dot{r}, t) = T(r, \dot{r}, t) - V(r, \dot{r}, t) = \frac{1}{2}m\dot{r}^2 - q\Phi(r, t) + q\dot{r} \cdot A(r, t),
\]  

(3.15)

where \( m \) is the mass and \( q \) the charge of the particle. \( r \) contains the \( f \) generalized coordinates \( r_i \), which completely specify the system, and \( \dot{r} \) their derivatives \( \dot{r}_i \) with respect to time, e.g., the generalized velocities.

Employing the Euler–Lagrange equations

\[
\frac{d}{dt} \frac{\partial L}{\partial \dot{r}_i} - \frac{\partial L}{\partial r_i} = 0, \quad \forall \quad i = 1, \ldots, f
\]  

(3.16)

together with Eqs. (3.5) and (3.6), the equation of motion involving the Lorentz force \( F_L \) is obtained,

\[
m\ddot{r} = F_L = q \left[ E(r, t) + \dot{r} \times B(r, t) \right].
\]  

(3.17)

The canonical momentum \( p^c_i \) conjugated to the coordinate \( q_i \) is written as

\[
p^c_i = \frac{\partial L}{\partial \dot{r}_i}
\]  

(3.18)

so that

\[
p^c = m\ddot{r} + qA(r, t),
\]  

(3.19)

which differs from the mechanical momentum \( \pi \),

\[
\pi = m\ddot{r} = p^c - qA(r, t),
\]  

(3.20)
in the presence of a magnetic field.

Finally, the Hamiltonian is derived via a Legendre transformation replacing the velocities \( \dot{r} \) by \( p_c \):

\[
H(r, p_c, t) = \sum_{i=1}^{f} p_i \dot{r}_i(r, p_c, t) - L(r, \dot{r}, t) = \frac{1}{2m} [p_c - qA(r, t)]^2 + q\Phi(r, t). \tag{3.21}
\]

Since we aim at a description of a quantum system incorporating the interaction of electric and magnetic fields, we employ the correspondence principle, where the canonical momentum \( p_c \) is replaced by the operator \( \hat{p} = -i\hbar \nabla \) and the position \( r \) by the position operator \( \hat{r} \). For the sake of brevity, we omit the operator hats in the following as has already been done in the previous sections. The nonrelativistic semi-classical Hamiltonian describing \( G \) particles (with particle \( i \) having position \( r_i \), momentum \( p_i \), charge \( q_i \), and mass \( m_i \)) is then calculated as

\[
H = \sum_{i=1}^{G} \left[ -\frac{\hbar^2}{2m_i} \nabla_i^2 + V(r_i) + \frac{iq_i}{2m_i} A(r_i, t) \cdot \nabla_i + \frac{q_i^2}{2m_i} A^2(r_i, t) + q_i \Phi(r_i, t) \right]
= \sum_{i=1}^{G} \left[ \frac{1}{2m_i} p_i^2 + V(r_i) - \frac{q_i}{2m_i} p_i \cdot A(r_i, t) - \frac{q_i}{2m_i} A(r_i, t) \cdot p_i + \frac{q_i^2}{2m_i} A^2(r_i, t) + q_i \Phi(r_i, t) \right]. \tag{3.22}
\]

and employing the Coulomb gauge as

\[
H = \sum_{i=1}^{G} \left[ \frac{1}{2m_i} p_i^2 + V(r_i) - \frac{q_i}{m_i} A(r_i, t) \cdot p_i + \frac{q_i^2}{2m_i} A^2(r_i, t) + q_i \Phi(r_i, t) \right]. \tag{3.23}
\]

Solely the electric and magnetic potentials due to the external irradiation are considered. \( V(r) \) contains the electrostatic interactions generated by internal fields. In addition, magnetic and retardation effects due to inter-particle interactions exist. These can be included via the Breit interaction operator [228–242], which can be subdivided in a magnetic (Gaunt) [75] and a retardation term [76].
The latter emerges since electromagnetic interactions are transmitted at the speed of light and is also found in classical theory [56], for which the corresponding interaction energy was derived by Darwin [243].

The perturbation-dependent nonrelativistic Hamiltonian $H^\text{int}$, based on the interaction part of the classical Hamiltonian in Eq. (3.21), can also be derived from the Pauli Hamiltonian [see Eq. (2.10)], which is a two-component equation for the electron containing the electron spin operator $s = \frac{\hbar}{2}\sigma$. The Pauli equation is the one, which should be employed in nonrelativistic theory dealing with magnetic interactions [56]. By neglecting the spin interaction and extension to the many-particle case, we also arrive at one-component equations with the Hamiltonian in Eq. (3.22).

Our aim is to provide an interaction Hamiltonian $H^\text{int}$ expressed in terms of electric and magnetic multipoles. In order to achieve this, several methods have been derived like, for example, unitary transformations of Eq. (3.22). We refer to Refs. [244–247] for a detailed description of different approaches. A quite simple suggestion has been presented by Barron and Gray [23, 248] which exploits a special type of gauge expanding the scalar and vector potentials in the following way:

$$\Phi(r, t) = \Phi(0, t) - r_\alpha E_\alpha(0, t) - \frac{1}{2} r_\alpha r_\beta [\nabla_\alpha E_\beta(r, t)]_0 + \cdots, \quad (3.24)$$

$$A_\alpha(r, t) = \frac{1}{2} \epsilon_{\alpha\beta\gamma} B_\beta(0, t) r_\gamma + \frac{1}{3} \epsilon_{\alpha\gamma\delta} r_\beta [\nabla_\beta B_\gamma(r, t)]_0 r_\delta + \cdots, \quad (3.25)$$

where the subscript ‘0’ indicates that $\Phi(r, t)$ and $A(r, t)$ are expanded around the point $r = 0$. $\epsilon_{\alpha\beta\gamma}$ is the $\alpha\beta\gamma$ component of the antisymmetric third-rank (Levi-Civita) unit tensor. $r_\alpha r_\beta$ is the outer product of $r_\alpha$ and $r_\beta$ and $(B \times r)_\alpha = \epsilon_{\alpha\beta\gamma} B_\beta r_\gamma$. The first term in Eq. (3.25) is the familiar expression $A_\alpha = \frac{1}{2} \epsilon_{\alpha\beta\gamma} B_\beta r_\gamma$, which is only valid for homogeneous static magnetic fields. Considering Eqs. (3.5) and (3.6), it is shown that the expansions of $\Phi(r, t)$ and $A(r, t)$ are valid if the components of the electric and magnetic fields can be expanded as [23, 249]

$$E_\alpha(r, t) = E_\alpha(0, t) + r_\beta [\nabla_\beta E_\alpha(r, t)]_0 + \cdots, \quad (3.26)$$

$$B_\alpha(r, t) = B_\alpha(0, t) + r_\beta [\nabla_\beta B_\alpha(r, t)]_0 + \cdots. \quad (3.27)$$

Inserting Eqs. (3.24) and (3.25) into Eq. (3.22), we obtain a modified expression for the interaction Hamiltonian

$$H^\text{int} = \sum_{i=1}^{G} \left\{ -q_i r_{i\alpha} E_\alpha(0, t) - q_i \frac{1}{2} r_{i\alpha} r_{i\beta} [\nabla_{i\alpha} E_\beta(r_i, t)]_0 - \frac{q_i}{2m_i} (B(0, t) \times r_i)_\alpha p_{i\alpha} + \cdots \right\}$$

$$= -\mu_\alpha E_\alpha(0, t) - \theta^c_{\alpha\beta} [\nabla_\alpha E_\beta(r, t)]_0 - m_\alpha B_\alpha(0, t) + \cdots, \quad (3.28)$$
where \( \mathbf{r} \) contains all \( \mathbf{r}_i \). In the second line of Eq. (3.28), we introduced the components of the electric-dipole moment operator \( \mathbf{\mu} \), the electric-quadrupole moment operator \( \mathbf{\theta}^c \) and the magnetic-dipole moment operator \( \mathbf{m} \), respectively, which are given by

\[
\mu_\alpha = \sum_{i=1}^{G} q_i r_{i\alpha},
\]

(3.29)

\[
\theta_{\alpha\beta}^c = \sum_{i=1}^{G} q_i r_{i\alpha} r_{i\beta},
\]

(3.30)

\[
m_\alpha = \sum_{i=1}^{G} \frac{q_i}{2m_i} \epsilon_{\alpha\beta\gamma} r_{i\beta} p_{i\gamma},
\]

(3.31)

where the spin-dependent part of \( m_\alpha \) does not occur since we have already neglected this interaction in our Hamiltonian. The electric-quadrupole moment in the interaction term \( \theta_{\alpha\beta}^c (\nabla_\alpha \nabla_\beta (\mathbf{r}, t))_0 \) contains six different elements \( \theta_{\alpha\beta} \) but only five are independent [250]. This can be verified by expanding the energy \( E \) of an electric point charge \( q \) with coordinates \( \mathbf{r}_\alpha \) around a point \( \mathbf{0} \) in a potential \( \Phi \) generated by external charges [251],

\[
E = E_0 + q \Phi_0 + q (\nabla_\alpha \Phi)_0 r_\alpha + \frac{1}{2} (\nabla_\alpha \nabla_\beta \Phi)_0 r_\alpha r_\beta + \cdots
\]

\[
= E_0 + q \Phi_0 + \mu_\alpha (\nabla_\alpha \Phi)_0 + \frac{1}{2} \theta_{\alpha\beta}^c (\nabla_\alpha \nabla_\beta \Phi)_0 + \cdots. \tag{3.32}
\]

Due to Laplace’s theorem,

\[
\nabla^2 \Phi_0 = 0,
\]

(3.33)

we can write the electric-quadrupole moment in the traceless form

\[
\theta_{\alpha\beta} = \frac{1}{2} q (3r_\alpha r_\beta - r^2 \delta_{\alpha\beta}),
\]

(3.34)

with \( r^2 = r_x^2 + r_y^2 + r_z^2 \) and \( \delta_{\alpha\beta} \) is the \( \alpha\beta \) element of the Kronecker delta. The power series in Eq. (3.24) is then obtained as

\[
E = E_0 + q \Phi_0 + \mu_\alpha (\nabla_\alpha \Phi)_0 + \frac{1}{3} \theta_{\alpha\beta} (\nabla_\alpha \nabla_\beta \Phi)_0 + \cdots. \tag{3.35}
\]

It can be seen that the electric-quadrupole contributions in Eqs. (3.32) and (3.35) are equal to each other [252],

\[
\frac{1}{2} \theta_{\alpha\beta}^c (\nabla_\alpha \nabla_\beta \Phi)_0 = \frac{1}{2} q r_\alpha r_\beta (\nabla_\alpha \nabla_\beta \Phi)_0 = \frac{1}{3} q (3r_\alpha r_\beta - r^2 \delta_{\alpha\beta} + r^2 \delta_{\alpha\beta}) (\nabla_\alpha \nabla_\beta \Phi)_0
\]

\[
= \frac{1}{3} \theta_{\alpha\beta} (\nabla_\alpha \nabla_\beta \Phi)_0 + \frac{1}{6} q r^2 \delta_{\alpha\beta} (\nabla_\alpha \nabla_\beta \Phi)_0
\]

\[
= 0. \tag{3.36}
\]
because the last term vanishes due to the Laplace equation given in Eq. (3.33). The irradiation with electromagnetic fields induces electric and magnetic multipole moments in a molecule, which are connected to the incident electromagnetic field by molecular property tensors. In the following, we derive these property tensors by taking expectation values of the multipole moment operators and the molecular wave functions perturbed by the external electric and magnetic fields. We focus on the magnetic-dipole, electric-dipole, and electric-quadrupole moments since these are important for Raman optical activity spectroscopy. For the sake of brevity, the time and space dependence of the wave functions and of the electric and magnetic fields will not be explicitly indicated anymore.

### 3.1.2 Determination of the wave function perturbed by the electromagnetic field

We start with the time-dependent Schrödinger equation,

\[
\left( -\frac{i\hbar}{\partial t} - H^{(0)} \right) |\tilde{\psi}\rangle = H^{\text{int}} |\tilde{\psi}\rangle, \tag{3.37}
\]

with

\[
H^{(0)} = \sum_{i=1}^{G} \left\{ \frac{1}{2m_i} \mathbf{p}_i^2 + V(\mathbf{r}_i) \right\}, \tag{3.38}
\]

\[
H^{\text{int}} = \left\{ -\mu_\alpha [E_\alpha]_0 - \frac{1}{3} \theta_{\alpha\beta} [\nabla_\alpha E_\beta]_0 - m_\alpha [B_\alpha]_0 + \cdots \right\}. \tag{3.39}
\]

The subscript ‘0’ denotes the origin of the molecular system under study. With \( H^{\text{int}} = 0 \), the remaining Hamiltonian \( H^{(0)} \) is time-independent and the solution of Eq. (3.37) reads (compare section 1.2)

\[
|\tilde{\psi}\rangle = \sum_n c_n |\psi_n\rangle \exp(-i\omega_n t) \tag{3.40}
\]

where \( \omega_n \) denotes the angular frequency and \( \hbar \omega_n \) the eigenvalue of eigenstate \( |\psi_n\rangle \). \( c_n \) are the time-independent expansion coefficients and the sum runs over all eigenstates of the molecule.

We can write the perturbing radiation for which we assume a harmonic monochromatic plane-wave field with angular frequency \( \omega_L \) for the general case with complex amplitudes as

\[
(\tilde{E}_\beta)_0 = \left[ \tilde{E}^{(0)} \exp(i\mathbf{k} \cdot \mathbf{r}) \right]_\beta \exp(-i\omega_L t) = \tilde{E}^{(0)}_\beta \exp(-i\omega_L t), \tag{3.41}
\]

\[
(\tilde{E}^*_\beta)_0 = \tilde{E}^{(0)*}_\beta \exp(i\omega_L t), \tag{3.42}
\]

\[
(\tilde{B}_\beta)_0 = \tilde{B}^{(0)}_\beta \exp(-i\omega_L t), \tag{3.43}
\]

\[
(\tilde{B}^*_\beta)_0 = \tilde{B}^{(0)*}_\beta \exp(i\omega_L t). \tag{3.44}
\]
\( \tilde{E}_\beta^{(0)} \) and \( \tilde{B}_\beta^{(0)} \) are the \( \beta \) components of the complex electric- and magnetic-field amplitudes, respectively. The superscript ‘0’ indicates the molecule’s origin. The following relationships of the real and imaginary radiation field components of the electric field [and in an analogous way for the magnetic field and the electric-field gradient] are employed:

\[
(\tilde{E}_\beta)_0 = \frac{1}{2}[(\tilde{E}_\beta) + (\tilde{E}_\beta^*)] = \frac{1}{2}[\tilde{E}_\beta^{(0)} \exp(-i\omega_Lt) + \tilde{E}_\beta^{(0)*} \exp(i\omega_Lt)], \tag{3.45}
\]

\[
(\tilde{E}_\beta)_0 = -\frac{i\omega_L}{2}[(\tilde{E}_\beta)_0 - (\tilde{E}_\beta^*)_0] = -\frac{i\omega_L}{2}[\tilde{E}_\beta^{(0)} \exp(-i\omega_Lt) - \tilde{E}_\beta^{(0)*} \exp(i\omega_Lt)]. \tag{3.46}
\]

The molecular wave functions are modified due to the external fields by adding expansion terms depending on the electric and magnetic fields [202, 253–255]:

\[
|\psi_n^\gamma\rangle = \left[|\psi_n\rangle + |\psi_n^{a\beta}\rangle(\tilde{E}_\beta)_0 + |\psi_n^{b\beta}\rangle(\tilde{E}_\beta^*)_0 + |\psi_n^{c\beta}\rangle(\tilde{B}_\beta)_0 + |\psi_n^{d\beta}\rangle(\tilde{B}_\beta^*)_0 + |\psi_n^{e\beta\gamma}\rangle(\nabla_\beta\tilde{E}_\gamma)_0 + \cdots \right] \exp(-i\omega_n t) \tag{3.47}
\]

with

\[
|\psi_n^{x\beta}\rangle = \sum_{j \neq n} x_j^{\beta} |\psi_j\rangle, \quad x = a, b, c, d, \tag{3.48}
\]

\[
|\psi_n^{x\beta\gamma}\rangle = \sum_{j \neq n} x_j^{\beta\gamma} |\psi_j\rangle, \quad x = e, f, \tag{3.49}
\]

where \( |\psi_j\rangle \) are the excited-state wave functions, \( x_j^{\beta\gamma} \) and \( x_j^{\beta\gamma} \) expansion coefficients, and the normalization condition

\[
\langle \psi_n | \psi'_n \rangle = 1 = \langle \psi_n | \psi_n \rangle + \langle \psi_n | \psi_n^{a\beta} \rangle(\tilde{E}_\beta)_0 + \langle \psi_n | \psi_n^{b\beta} \rangle(\tilde{E}_\beta^*)_0 + \langle \psi_n | \psi_n^{c\beta\gamma} \rangle(\tilde{B}_\beta)_0 + \langle \psi_n | \psi_n^{d\beta\gamma} \rangle(\tilde{B}_\beta^*)_0 + \cdots \tag{3.50}
\]

is employed. The time derivative of the wave function, introduced in Eq. (3.37), is given by

\[
\frac{\partial |\psi_n'\rangle}{\partial t} = -i\omega_n |\psi_n'\rangle - i\omega_L \exp(-i\omega_n t)[|\psi_n^{a\beta}\rangle(\tilde{E}_\beta)_0 + |\psi_n^{b\beta}\rangle(\tilde{E}_\beta^*)_0 + |\psi_n^{c\beta\gamma}\rangle(\tilde{B}_\beta)_0 + |\psi_n^{d\beta\gamma}\rangle(\tilde{B}_\beta^*)_0 + \cdots]. \tag{3.51}
\]

The interaction Hamiltonian can be reformulated by means of Eqs. (3.43) and (3.45) as

\[
H^{\text{int}} = -\mu_\beta \frac{1}{2}[(\tilde{E}_\beta)_0 + (\tilde{E}_\beta^*)_0] - \frac{1}{3}\beta_\gamma \frac{1}{2}[(\nabla_\beta\tilde{E}_\gamma)_0 + (\nabla_\beta\tilde{E}_\gamma^*)_0] - m_\beta \frac{1}{2}[(\tilde{B}_\beta)_0 + (\tilde{B}_\beta^*)_0] + \cdots. \tag{3.52}
\]
Inserting Eqs. (3.47), (3.51), and (3.52) into Eq. (3.37) results in

\[
\begin{align*}
\{ &\hbar \omega_n |\psi_n\rangle + |\psi_n^\alpha\rangle (\tilde{E}_\beta) + |\psi_n^\beta\rangle (\tilde{B}_\beta) + |\psi_n^\gamma\rangle (\tilde{B}_\gamma) + |\psi_n^\delta\rangle (\tilde{H}_\delta) \\
+ &|\psi_n^\varepsilon\rangle (\nabla_\beta \tilde{E}_\gamma) + |\psi_n^f\rangle (\nabla_\beta \tilde{E}_\gamma) + \cdots \} \\
+ &\hbar \omega_L [|\psi_n^\alpha\rangle (\tilde{E}_\beta) - |\psi_n^\beta\rangle (\tilde{B}_\beta) + |\psi_n^\gamma\rangle (\tilde{B}_\gamma) + |\psi_n^\delta\rangle (\tilde{H}_\delta) \\
+ &|\psi_n^\varepsilon\rangle (\nabla_\beta \tilde{E}_\gamma) + |\psi_n^f\rangle (\nabla_\beta \tilde{E}_\gamma) + \cdots ] \exp (-i \omega_L t)
\end{align*}
\]

Collecting the terms with the \((\tilde{E}_\beta)\) contributions, we obtain

\[
\hbar \omega_n |\psi_n^\alpha\rangle + \hbar \omega_L |\psi_n^\alpha\rangle - H^{(0)} |\psi_n^\alpha\rangle = -\frac{\mu^\beta}{2} |\psi_n\rangle ,
\]

which gives by multiplying from the left with \(\langle \psi_j |\)

\[
\hbar [\omega_n + \omega_L - \omega_j] \langle \psi_j |\psi_n^\alpha\rangle = -\frac{1}{2} \langle \psi_j |\mu^\beta |\psi_n\rangle .
\]

In the following, we employ the short-hand notation \(|\psi_x\rangle = |x\rangle\) and \(|\psi'_x\rangle = |x'\rangle\) with \(x\) denoting the eigenstates \(n, j\) etc., \(\omega_n - \omega_j = \omega_{nj} = -\omega_j\) as well as the fact that \(\langle \psi_j |\psi_n^\alpha\rangle = a_j^\beta\). We get

\[
a_j^\beta = \frac{\langle j |\mu^\beta |n\rangle}{2\hbar (\omega_{jn} - \omega_L)} , \tag{3.56}
\]

\[
|\psi_n^\alpha\rangle = \sum_{j \neq n} \frac{\langle j |\mu^\beta |n\rangle}{2\hbar (\omega_{jn} - \omega_L)} |j\rangle . \tag{3.57}
\]

In a similar way, the terms containing \((\tilde{E}_\gamma)\), \((\tilde{B}_\gamma)\), \((\tilde{H}_\delta)\), \((\nabla_\beta \tilde{E}_\gamma)\), and
we are now able to calculate the electric-dipole moment of the molecule in the previous section, we have determined the perturbed wave function as an expectation value of the electric-dipole moment operator:

\[
(\mu_\alpha)_{nn} = \langle n'|\mu_\alpha|n'\rangle.
\] (3.63)

Inserting the expression for the perturbed wave function [see Eq. (3.47)], we obtain

\[
(\mu_\alpha)_{nn} - \langle n|\mu_\alpha|n\rangle = \langle n|\mu_\alpha|\psi_n^{b\beta}\rangle_0 + \langle n|\mu_\alpha|\psi_n^{b\beta}\rangle_0 (\tilde{E}_\beta)_0 + (\tilde{E}_\beta)_0\langle \psi_n^{b\beta}|\mu_\alpha|n\rangle + (\tilde{E}_\beta)_0\langle \psi_n^{b\beta}|\mu_\alpha|n\rangle + \cdots
\] (3.64)

Combining Eqs. (3.57) and (3.58) with Eqs. (3.45) and (3.46), the terms containing \((\tilde{E}_\beta)_0\) and \((\tilde{E}_\beta)_0^*\) read

\[
\langle n|\mu_\alpha|\psi_n^{a\beta}\rangle_0 + \langle n|\mu_\alpha|\psi_n^{b\beta}\rangle_0 (\tilde{E}_\beta)_0 + \sum_{j\neq n} \langle n|\mu_\alpha|j\rangle \langle j|\mu_\beta|n\rangle_0 \langle \tilde{E}_\beta\rangle_0 + \sum_{j\neq n} \langle n|\mu_\alpha|j\rangle \langle j|\mu_\beta|n\rangle_0 \langle \tilde{E}_\beta\rangle_0^*
\]

\[
= \sum_{j\neq n} \langle n|\mu_\alpha|j\rangle \langle j|\mu_\beta|n\rangle \frac{\omega_{jn}[(\tilde{E}_\beta)_0 + (\tilde{E}_\beta)_0] + \omega_L[(\tilde{E}_\beta)_0 - (\tilde{E}_\beta)_0]}{\omega_{jn}^2 - \omega_L^2}
\]

\[
= \sum_{j\neq n} \langle n|\mu_\alpha|j\rangle \langle j|\mu_\beta|n\rangle \frac{2\omega_{jn}(\tilde{E}_\beta)_0}{\omega_{jn}^2 - \omega_L^2} - \frac{2i(\tilde{E}_\beta)_0}{\omega_{jn}^2 - \omega_L^2}
\] (3.65)
and

\[
\langle \tilde{E}_\beta \rangle_0 \langle \psi_{n \alpha}^\alpha | \mu_\alpha | n \rangle + \langle \tilde{E}_\beta^* \rangle_0 \langle \psi_{n \beta}^\beta | \mu_\alpha | n \rangle = \sum_{j \neq n} \frac{\langle n | \mu_\beta | j \rangle \langle j | \mu_\alpha | n \rangle}{2 \hbar} \left[ \frac{2 \omega_{jn}(E_\beta)_0}{(\omega_{jn}^2 - \omega_L^2)} + \frac{2i \omega_{jn}(E_\beta^*_0)}{(\omega_{jn}^2 - \omega_L^2)} \right]
\]

so that their sum is given by [255]

\[
\left[ \sum_{j \neq n} \frac{\omega_{jn} \langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle}{\hbar (\omega_{jn}^2 - \omega_L^2)} \right] (E_\beta)_0 = \sum_{j \neq n} \frac{i \langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle}{\hbar (\omega_{jn}^2 - \omega_L^2)} + \sum_{j \neq n} \frac{i \langle n | \mu_\beta | j \rangle \langle j | \mu_\alpha | n \rangle}{\hbar (\omega_{jn}^2 - \omega_L^2)} (E_\beta)_0
\]

\[
= (\alpha_{\alpha \beta})_{nn}(E_\beta)_0 + \frac{1}{\omega_L}(\alpha_{\alpha \beta})_{nn}(E_\beta)_0
\]

(3.66)

The expectation value of the electric-dipole moment operator can be calculated in a similar way employing the terms with the magnetic field and electric-field gradients [256, 257],

\[
(\mu)_{nn} = (\alpha_{\alpha \beta})_{nn}(E_\beta)_0 + \frac{1}{\omega_L}(\alpha_{\alpha \beta})_{nn}(E_\beta)_0 + \frac{1}{3}(A_{\alpha \beta \gamma})_{nn}(\nabla_\beta E_\gamma)_0 + \frac{1}{3\omega_L}(A'_{\alpha \beta \gamma})_{nn}(\nabla_\beta \tilde{E}_\gamma)_0 + (G_{\alpha \beta})_{nn}(B_\beta)_0 + \frac{1}{\omega_L}(G'_{\alpha \beta})_{nn}(\tilde{B}_\beta)_0 + \ldots
\]

(3.67)

with the real dynamic molecular property tensor components

\[
(\alpha_{\alpha \beta})_{nn} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Re}(\langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle),
\]

(3.69)

\[
(\alpha'_{\alpha \beta})_{nn} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Im}(\langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle),
\]

(3.70)

\[
(A_{\alpha \beta \gamma})_{nn} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Re}(\langle n | \mu_\alpha | j \rangle \langle j | \theta_\gamma | n \rangle),
\]

(3.71)

\[
(A'_{\alpha \beta \gamma})_{nn} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Im}(\langle n | \mu_\alpha | j \rangle \langle j | \theta_\gamma | n \rangle),
\]

(3.72)

\[
(G_{\alpha \beta})_{nn} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Re}(\langle n | \mu_\alpha | j \rangle \langle j | m_\beta | n \rangle),
\]

(3.73)

\[
(G'_{\alpha \beta})_{nn} = \frac{2}{\hbar} \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Im}(\langle n | \mu_\alpha | j \rangle \langle j | m_\beta | n \rangle),
\]

(3.74)
For the expectation values of the components of the magnetic-dipole and electric-quadrupole moments, the following expressions are obtained [23, 256, 257]:

\[
(\theta_{\alpha\beta})_{nn} = (A_{\gamma\alpha\beta})_{nn}(E_{\gamma})_0 - \frac{1}{\omega_L}(A'_{\gamma\alpha\beta})_{nn}(\dot{E}_{\gamma})_0 + \cdots, \tag{3.75}
\]

\[
(m_{\alpha})_{nn} = (G_{\beta\alpha})_{nn}(E_{\beta})_0 - \frac{1}{\omega_L}(G'_{\beta\alpha})_{nn}(\dot{E}_{\beta})_0 + \cdots. \tag{3.76}
\]

### 3.1.4 The Raman and Raman optical activity polarizability tensors

The dynamic molecular property tensors in Eqs. (3.69) to (3.74) are derived on the basis of the perturbed wave functions of the \(n\)-th eigenstate describing an elastic scattering process (Rayleigh scattering) where the initial and final wave functions are equal. However, we are interested in Raman scattering, which is an inelastic scattering process and corresponds to initial and final wave functions, \(|i\rangle\) and \(|f\rangle\), respectively, differing in a vibrational quantum of energy. The corresponding real part of the transition electric-dipole moment can be written as [253, 254]

\[
(\mu_{\alpha})_{fi} = (f'\|\mu_{\alpha}\|i') + ((f'\|\mu_{\alpha}\|i')^*), \tag{3.77}
\]

where the factor 1/2 is omitted due to the definition usually employed in the literature [11]. Inserting the expressions for the perturbed wave functions \(|f'\rangle\) and \(|i'\rangle\) according to Eq. (3.47) results in

\[
(\mu_{\alpha})_{fi} = \langle f | \mu_{\alpha} | i \rangle \exp(i\omega_{fi}t) + \langle i | \mu_{\alpha} | f \rangle \exp(-i\omega_{fi}t)
\]

\[
+ \sum_{j \neq i} \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{2\hbar(\omega_{ji} - \omega_L)}(\tilde{E}_{ji}^{(0)}) \exp(-i[\omega_L - \omega_{fi}]t)
\]

\[
+ \sum_{j \neq i} \frac{\langle i | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | f \rangle}{2\hbar(\omega_{ji} - \omega_L)}(\tilde{E}_{ji}^{(0)*}) \exp(i[\omega_L - \omega_{fi}]t)
\]

\[
+ \sum_{j \neq i} \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \mu_{\beta} | i \rangle}{2\hbar(\omega_{ji} + \omega_L)}(\tilde{E}_{ji}^{(0)}) \exp(-i[\omega_L + \omega_{fi}]t)
\]

\[
+ \sum_{j \neq i} \frac{\langle i | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | f \rangle}{2\hbar(\omega_{ji} + \omega_L)}(\tilde{E}_{ji}^{(0)*}) \exp(i[\omega_L + \omega_{fi}]t)
\]

\[
+ \sum_{j \neq f} \frac{\langle f | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{2\hbar(\omega_{jf} - \omega_L)}(\tilde{E}_{jf}^{(0)}) \exp(-i[\omega_L - \omega_{fi}]t)
\]

\[
+ \sum_{j \neq f} \frac{\langle i | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | f \rangle}{2\hbar(\omega_{jf} + \omega_L)}(\tilde{E}_{jf}^{(0)*}) \exp(i[\omega_L - \omega_{fi}]t)
\]

\[
+ \sum_{j \neq f} \frac{\langle i | \mu_{\beta} | j \rangle \langle j | \mu_{\beta} | f \rangle}{2\hbar(\omega_{jf} - \omega_L)}(\tilde{E}_{jf}^{(0)}) \exp(-i[\omega_L + \omega_{fi}]t)
\]

\[
+ \sum_{j \neq f} \frac{\langle i | \mu_{\beta} | j \rangle \langle j | \mu_{\beta} | f \rangle}{2\hbar(\omega_{jf} + \omega_L)}(\tilde{E}_{jf}^{(0)*}) \exp(i[\omega_L + \omega_{fi}]t) + \cdots. \tag{3.78}
\]
The first two terms on the right-hand side of Eq. (3.78) correspond to spontaneous emission of radiation with an angular frequency $\omega_{fi}$. The terms containing $\omega_L - \omega_{fi}$ describe Raman and Rayleigh scattering. The case with $\omega_{fi}$ being negative or positive corresponds to anti-Stoke and Stokes scattering, respectively, whereas Rayleigh scattering is present for $\omega_{fi} = 0$.

As a consequence, the Raman transition polarizability tensor is obtained as

$$
\langle \mu_\alpha \rangle_{fi} = \frac{1}{2\hbar} \sum_{j \neq f,i} \left[ \frac{\langle f|\mu_\alpha|j\rangle\langle j|\mu_\beta|i\rangle}{\omega_{ji} - \omega_L} + \frac{\langle f|\mu_\beta|j\rangle\langle j|\mu_\alpha|i\rangle}{\omega_{jj} + \omega_L} \right]$

$$
\times \left( \tilde{E}_\beta(0) \right) \exp (-i[\omega_L - \omega_{fi}]t) + \frac{1}{2\hbar} \sum_{j \neq f,i} \left[ \frac{\langle i|\mu_\beta|j\rangle\langle j|\mu_\alpha|i\rangle}{\omega_{ji} - \omega_L} + \frac{\langle i|\mu_\alpha|j\rangle\langle j|\mu_\beta|i\rangle}{\omega_{jj} + \omega_L} \right]$

$$
\times \left( \tilde{E}_\beta(0)^* \right) \exp (i[\omega_L - \omega_{fi}]t)
$$

(3.79)

with the general polarizability tensor [23,258,259]

$$
\langle \alpha_{\alpha\beta} \rangle_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \left[ \frac{\langle f|\mu_\alpha|j\rangle\langle j|\mu_\beta|i\rangle}{\omega_{ji} - \omega_L} + \frac{\langle f|\mu_\beta|j\rangle\langle j|\mu_\alpha|i\rangle}{\omega_{jj} + \omega_L} \right].
$$

(3.80)

The final states are now excluded from the summation over the states $|j\rangle$ in addition to the initial states. This is satisfied since their contribution is mostly zero. In the few cases with non-zero contributions, these contributions are found to be negligibly small [260].

For the case of real wave functions and field amplitudes, we arrive at

$$
\langle \mu_\alpha \rangle_{fi} = \frac{1}{2} \langle \alpha_{\alpha\beta} \rangle_{fi} E_\beta^{(0)} \left[ \exp (-i[\omega_L - \omega_{fi}]t) + \exp (i[\omega_L - \omega_{fi}]t) \right].
$$

(3.81)
similar way as

\[
(G_{\alpha\beta})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | m_{\beta} | i \rangle}{\omega_{ji} - \omega_L} + \frac{\langle f | m_{\beta} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{\omega_{jf} + \omega_L},
\]

(3.82)

\[
(G_{\alpha\beta})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | m_{\alpha} | j \rangle \langle j | \mu_{\beta} | i \rangle}{\omega_{ji} - \omega_L} + \frac{\langle f | \mu_{\beta} | j \rangle \langle j | m_{\alpha} | i \rangle}{\omega_{jf} + \omega_L},
\]

(3.83)

\[
(A_{\alpha,\beta\gamma})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \theta_{\beta\gamma} | i \rangle}{\omega_{ji} - \omega_L} + \frac{\langle f | \theta_{\beta\gamma} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{\omega_{jf} + \omega_L},
\]

(3.84)

\[
(A_{\alpha,\beta\gamma})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | \theta_{\beta\gamma} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{\omega_{ji} - \omega_L} + \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \theta_{\beta\gamma} | i \rangle}{\omega_{jf} + \omega_L}.
\]

(3.85)

\(G\) is the electric-dipole–magnetic-dipole, \(G\) the magnetic-dipole–electric-dipole, \(A\) the electric-dipole–electric-quadrupole, and \(A\) the electric-quadrupole–electric-dipole polarizability tensor. Up to this point, we have assumed that the electronic energy levels are discrete, i.e., they have an infinite lifetime due to the uncertainty principle. However, this is often not the case, especially for such resonance situations, where the frequency of the incident radiation is equal to an electronic transition frequency of the molecule. Usually, this finite lifetime is accounted for by the introduction of an imaginary damping term \(i\Gamma\), which is for electronic transitions proportional to the width of the corresponding electronic state and inverse proportional to its lifetime. The initial and final states are taken to have a discrete energy value and, therefore, their damping constants are set to zero.

Including the damping constants into the expressions for the tensors in Eqs. (3.80) to (3.85), the general polarizability tensors are derived as

\[
(\alpha_{\alpha\beta})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \mu_{\beta} | i \rangle}{\omega_{ji} - \omega_L - i\Gamma_j} + \frac{\langle f | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{\omega_{jf} + \omega_L + i\Gamma_j},
\]

(3.86)

\[
(G_{\alpha\beta})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | m_{\beta} | i \rangle}{\omega_{ji} - \omega_L - i\Gamma_j} + \frac{\langle f | m_{\beta} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{\omega_{jf} + \omega_L + i\Gamma_j},
\]

(3.87)

\[
(G_{\alpha\beta})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | m_{\alpha} | j \rangle \langle j | \mu_{\beta} | i \rangle}{\omega_{ji} - \omega_L - i\Gamma_j} + \frac{\langle f | \mu_{\beta} | j \rangle \langle j | m_{\alpha} | i \rangle}{\omega_{jf} + \omega_L + i\Gamma_j},
\]

(3.88)

\[
(A_{\alpha,\beta\gamma})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \theta_{\beta\gamma} | i \rangle}{\omega_{ji} - \omega_L - i\Gamma_j} + \frac{\langle f | \theta_{\beta\gamma} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{\omega_{jf} + \omega_L + i\Gamma_j},
\]

(3.89)

\[
(A_{\alpha,\beta\gamma})_{fi} = \frac{1}{\hbar} \sum_{j \neq f,i} \frac{\langle f | \theta_{\beta\gamma} | j \rangle \langle j | \mu_{\alpha} | i \rangle}{\omega_{ji} - \omega_L - i\Gamma_j} + \frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \theta_{\beta\gamma} | i \rangle}{\omega_{jf} + \omega_L + i\Gamma_j}.
\]

(3.90)

We have adopted the opposite-sign convention for the imaginary damping terms according to Refs. [11,261–263].
The induced oscillating electric-dipole, magnetic-dipole and electric-quadrupole moments are expressed with the electric- and magnetic-field amplitudes employing Eqs. (3.86) to (3.90) as

\[(\rho^{(0)}_{\alpha})_{fi} = (\alpha_{\alpha\beta})_{fi}\tilde{E}^{(0)}_{\beta} + \frac{1}{3}(A_{\alpha\beta\gamma})_{fi}\nabla_{\beta}\tilde{E}^{(0)}_{\gamma} + (G_{\alpha\beta})_{fi}\tilde{B}^{(0)} + \cdots, \quad (3.91)\]
\[(m^{(0)}_{\alpha})_{fi} = (G_{\alpha\beta})_{fi}\tilde{E}^{(0)}_{\beta} + \cdots, \quad (3.92)\]
\[(\theta^{(0)}_{\alpha\beta})_{fi} = (A_{\gamma\alpha\beta})_{fi}\tilde{E}^{(0)}_{\gamma} + \cdots. \quad (3.93)\]

### 3.2 The general Raman and Raman optical activity intensities

For the calculation of ROA intensities, a connection between the incident and scattered electromagnetic fields is required. The change of the molecule due to the irradiation has been considered in the previous section by molecular property tensors. Now, we have to determine the scattered electromagnetic fields, which are then expressed in terms of the property tensors.

#### 3.2.1 Dynamic electromagnetic multipole fields

The fields generated by the time-varying electric and magnetic multipoles of the molecule under study induced by the incident radiation need to be predicted in order to know which effects are measured in experiment. For this, we assume that the charge and current densities \(\rho(r, t)\) and \(J(r, t)\), respectively, giving rise to the scattered radiation oscillate harmonically with angular frequency \(\omega\) in time due to the incident monochromatic light:

\[\rho(r, t) = \rho^{(0)}(r) \exp(-i\omega t), \quad (3.94)\]
\[J(r, t) = J^{(0)}(r) \exp(-i\omega t). \quad (3.95)\]

The retarded potentials [see Eqs. (3.10) and (3.11)] are then given by

\[\Phi(R, t) = \frac{1}{4\pi\varepsilon\varepsilon_0} \int \frac{\rho^{(0)}(r) \exp\left[i\kappa|\mathbf{R} - \mathbf{r}| - \omega t\right]}{|\mathbf{R} - \mathbf{r}|} d\mathbf{r}, \quad (3.96)\]
\[A(R, t) = \frac{\mu\mu_0}{4\pi} \int \frac{J^{(0)}(r) \exp\left[i\kappa|\mathbf{R} - \mathbf{r}| - \omega t\right]}{|\mathbf{R} - \mathbf{r}|} d\mathbf{r}. \quad (3.97)\]

Considering a distant field point, i.e., \(R = |\mathbf{R}| >> r = |\mathbf{r}|\), and evaluating the
terms $1/|\mathbf{R} - \mathbf{r}|$ and $|\mathbf{R} - \mathbf{r}|$ \cite{23,249,255} employing the binomial expansion

$$
\frac{1}{|\mathbf{R} - \mathbf{r}|} = (R^2 - 2R_r + r^2)^{-1/2}
$$

$$
= \frac{1}{R} \left( 1 + \frac{1}{R^2}[r^2 - 2R_r] \right)^{-1/2}
$$

$$
|\mathbf{R} - \mathbf{r}| = R \left[ 1 + \frac{1}{R^2} \left( \frac{3R_r R_\sigma r_\sigma}{R^4} - \delta_{\alpha\beta} \frac{r^2}{R^2} \right) + \cdots \right]. \quad (3.98)
$$

the exponential-containing term of Eq. (3.96) is expanded as

$$
e^{i\kappa |\mathbf{R} - \mathbf{r}|} / |\mathbf{R} - \mathbf{r}| = \frac{e^{i\kappa R}}{R} \left[ 1 + \frac{1}{R^2} \left( \frac{3R_r R_\sigma r_\sigma}{R^4} - \delta_{\alpha\beta} \frac{r^2}{R^2} \right) - \frac{i\kappa R_r}{R} \right]
$$

$$
- \frac{i\kappa}{2} \left( \frac{3R_r R_\sigma r_\sigma}{R^3} - \delta_{\alpha\beta} \frac{r^2}{R} \right) - \frac{\kappa^2 R_r R_\sigma r_\sigma}{2R^2} + \cdots \right]. \quad (3.100)
$$

Assuming that the continuous charge density $\rho^{(0)}(\mathbf{r})$ consists of discrete point charges $q_i$ at positions $\mathbf{r}_i^{(0)}$ and thus writing $\rho^{(0)}(\mathbf{r}) = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i^{(0)})$, it is found that

$$
\Phi(\mathbf{R}, t) = \frac{\epsilon^{i(\kappa R - \omega t)}}{4\pi \epsilon_0 R} \left( \frac{R_\alpha \mu_\alpha^{(0)}}{R^2} + \frac{R_\alpha R_\beta \theta_{\alpha\beta}^{(0)}}{R^4} - \frac{i\kappa R_r}{R} \right)
$$

$$
- \frac{\kappa^2 R_r R_\beta \theta_{\alpha\beta}^{(0)}}{2R^2} - \frac{\sum_i q_i r_i^{(0)} r_i^{(0)}}{2R^2} + \cdots \right). \quad (3.101)
$$

The dynamic vector potential should also be expressed by the multipole moments. In order to achieve this, we start with the continuity equation,

$$
\nabla \cdot \mathbf{J}(\mathbf{r}, t) + \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = 0, \quad (3.102)
$$

which changes by using Eq. (3.94) to

$$
\nabla \cdot \mathbf{J}^{(0)} = i\omega \rho^{(0)}, \quad (3.103)
$$

where $\mathbf{J}^{(0)} = \mathbf{J}^{(0)}(\mathbf{r})$ and $\rho^{(0)} = \rho^{(0)}(\mathbf{r})$.

Multiplying by a tensor function $f$ and integrating over the volume element $dV$, which is bounded by the surface $S$, we get

$$
\int_V f(\nabla_\alpha J_\alpha^{(0)}) dV = \int_V \nabla_\alpha (f J_\alpha^{(0)}) dV - \int_V J_\alpha^{(0)} (\nabla_\alpha f) dV
$$

$$
= i\omega \int_V \rho^{(0)} f dV. \quad (3.104)
$$
3.2. The general Raman and Raman optical activity intensities

Employing Gauss’ theorem,

\[ \int_S J^{(0)} \cdot dS = \int_V \nabla \cdot J^{(0)} dV, \] (3.105)

where \( S \) denotes the closed surface of the volume \( V \) and \( S \) is the outer normal vector perpendicular to the plane \( S \) [56], we can write

\[ \int_V \nabla \alpha (f J^{(0)}_\alpha) dV = \int_S f J^{(0)}_\alpha dS \alpha = 0, \] (3.106)

since the integration over \( S \) is performed beyond the boundary of the current and charge distribution.

As a consequence, it is found for Eq. (3.104) that

\[ \int_V J^{(0)}_\alpha (\nabla f J^{(0)}_\alpha) dV = -i \omega \int_V \rho^{(0)} f dV. \] (3.107)

For \( f = 1 \), \( \int_V \rho^{(0)} dV = 0 \), i.e., the molecule has to be assumed as being electrically neutral for the subsequent derivations. Employing \( f = r_\alpha \), \( f = r_\beta r_\alpha \), and the facts that

\[ \epsilon_{\alpha\beta\gamma}\epsilon_{\mu\nu} = \delta_{\alpha\mu}\delta_{\beta\nu} - \delta_{\alpha\nu}\delta_{\beta\mu}, \] (3.108)

\[ J^{(0)}_\beta r_\alpha - J^{(0)}_\alpha r_\beta = \epsilon_{\alpha\beta\gamma}(r \times J^{(0)})_\gamma, \] (3.109)

\[ \nabla_\gamma(r_\alpha r_\beta J^{(0)}_\gamma) = 2J^{(0)}_\alpha r_\beta + \epsilon_{\alpha\beta\gamma}(r \times J^{(0)})_\gamma + i \omega r_\alpha r_\beta \rho^{(0)}, \] (3.110)

the following expressions are obtained [23, 249]:

\[ \int_V J^{(0)}_\alpha dV = -i \omega \mu^{(0)}_\alpha, \] (3.111)

\[ \int_V J^{(0)}_\alpha r_\beta dV = \frac{1}{2} \epsilon_{\alpha\beta\gamma} \int_V (r \times J^{(0)})_\gamma dV - i \omega \sum_i q_i r^{(0)}_i r^{(0)}_i = -\epsilon_{\alpha\beta\gamma} m^{(0)}_\gamma - i \frac{\omega}{2} \sum_i q_i r^{(0)}_i r^{(0)}_i. \] (3.112)

Employing \( \omega = c \kappa/n \) in combination with Eq. (3.100), the magnetic potential is described by

\[ A_\alpha(R, t) = -\frac{\mu_0}{4\pi R} e^{i(\kappa R - \omega t)} \left( \frac{\epsilon_{\alpha\beta\gamma} R_\beta m^{(0)}_\gamma}{R^2} + \frac{i c \kappa \mu^{(0)}_\alpha}{n} - \frac{i \epsilon_{\alpha\beta\gamma} R_\beta m^{(0)}_\gamma}{R} \right) \]

\[ + \frac{i c \kappa R_\beta \sum_i q_i r^{(0)}_i r^{(0)}_i}{2n R^2} + \frac{c \kappa^2 R_\beta \sum_i q_i r^{(0)}_i r^{(0)}_i}{2n R} + \ldots \] (3.113)

The electric field can now be determined with the help of Eq. (3.5). For the case of distances \( R \) which are much larger than the wavelength of the incident
light only terms containing $1/R$ are important. The components of the radiated complex electric field $\tilde{E}(R, t)$ are then evaluated as

$$\tilde{E}_\alpha(R, t) = \frac{\omega^2 \mu_0}{4\pi R} e^{i(\kappa R - \omega t)} \left[ \mu_\alpha^{(0)} - \frac{n_\alpha n_\beta}{n^2} \mu_\beta^{(0)} - \frac{1}{c} \epsilon_{\alpha\beta\gamma} n_\beta m_\gamma^{(0)} - \frac{i\omega}{3c} \left( n_\beta \theta^{(0)}_{\alpha\beta} - \frac{n_\alpha n_\beta n_\gamma \theta^{(0)}_{\beta\gamma}}{n^2} \right) + \cdots \right]. \quad (3.114)$$

### 3.2.2 Evaluation of the intensity expressions

The scattered light measured in experiment is the one produced by the oscillating electric and magnetic multipoles, which occur due to the irradiation by electromagnetic fields with angular frequency $\omega_L$ and propagation vector $n^i$. The $\alpha$ component of the scattered electric field at a distance $R$ from the molecular origin with the propagation vector $n_d$ and the angular frequency $\omega_d$ is given employing Eq. (3.114) as the real part of

$$\tilde{E}^d_\alpha = \frac{\omega^2 \mu_0}{4\pi R} e^{i(\kappa_d R - \omega_d t)} \left[ \mu_\alpha^{(0)} - \frac{n_\alpha n_\beta}{n^2} \mu_\beta^{(0)} - \frac{1}{c} \epsilon_{\alpha\beta\gamma} n_\beta m_\gamma^{(0)} - \frac{i\omega_d}{3c} \left( n_\beta \theta^{(0)}_{\alpha\beta} - \frac{n_\alpha n_\beta n_\gamma \theta^{(0)}_{\beta\gamma}}{n^2} \right) + \cdots \right]. \quad (3.115)$$

We assume vacuum, i.e., $\mu = \epsilon = 1$ and $n^2 = \epsilon \mu = 1$, and $\kappa_d = \omega_d n_d/c$. The multipole moments are given in terms of the polarizability tensors according to Eqs. (3.91) to (3.93). Eq. (3.91) can be completely written in terms of $\tilde{E}_\beta^{(0)}$ employing Eq. (3.14) and the fact that

$$\nabla_\gamma \tilde{E}_\beta^{(0)} = \nabla_\gamma \left[ \tilde{E}_\beta^{(0)} \exp (i\kappa \cdot r) \right] = i\kappa_\gamma \tilde{E}_\beta^{(0)} = \frac{i\omega_L n_\gamma}{c} \tilde{E}_\beta^{(0)} \quad (3.116)$$

as

$$\mu_\alpha^{(0)} = \left[ \alpha_{\alpha\beta} + \frac{i\omega_L n_\gamma}{3c} A_{\alpha,\beta\gamma} + \frac{1}{c} \epsilon_{\gamma\delta\beta} n^i G_{\alpha\gamma} + \cdots \right] \tilde{E}_\beta^{(0)} \quad (3.117)$$

Thus, Eq. (3.115) is written as

$$\tilde{E}^d_\alpha = \frac{\omega^2 d \mu_0}{4\pi R} e^{i(\kappa_d R - \omega_d t)} a_{\alpha\beta} \tilde{E}_\beta^{(0)} \quad (3.118)$$

with the general scattering tensor

$$a_{\alpha\beta} = \alpha_{\alpha\beta} + \frac{1}{3c} (\omega_L n^i A_{\alpha,\beta\gamma} - \omega_d n^i_d A_{\beta,\gamma\alpha}) + \frac{1}{c} (\epsilon_{\gamma\delta\beta} n^i G_{\alpha\gamma} + \epsilon_{\gamma\delta\alpha} n^i_d G_{\beta\gamma}) + \cdots. \quad (3.119)$$

Eq. (3.118) relates the scattered electric field to the incident one.
The intensities measured in experiment depend on the polarization of the incident and scattered electric fields. Thus, the intensity $I$ of the scattered light is given in general by \[I(e^d, e^i) = 90K\langle |e^d_\alpha \alpha e^i_\beta|^2 \rangle\] (3.120)

with the components of the polarization vectors of the incident and scattered light, $e^i_\beta$ and $e^d_\alpha$, respectively, and the constant

$$K = \frac{1}{90} \left( \frac{\omega^2 \mu_0 E^{(0)}}{4\pi R} \right)^2.$$ (3.121)

The parentheses denote the average over all angles of orientation of the molecule with respect to the reference laboratory frame and $E^{(0)}$ is the real amplitude of the incident electric field. As can be seen from Eq. (3.120), the intensity is a combination of the property tensors. For ROA spectroscopy, we keep the terms $\alpha_\alpha \beta \alpha_\alpha \beta$, which are also needed for Raman spectroscopy, as well as the combination of $\alpha_\alpha \beta$ with $G_{\alpha \beta}$, $G_{\alpha \beta}$, $A_{\alpha, \beta \gamma}$, and $A_{\alpha, \beta \gamma}$, which are about a factor of $10^{-3}$ smaller than the products $\alpha_\alpha \beta \alpha_\alpha \beta$ [11, 224]. The terms containing no $\alpha_\alpha \beta$ elements are omitted since their contributions are about $10^{-6}$ smaller than the ones of the $\alpha_\alpha \beta \alpha_\alpha \beta$ combinations.

Many different experimental set-ups for ROA measurements have been developed. First, it can be chosen if linearly or circularly polarized (CP) light should be employed. We consider here only the latter case since this is the one favored in experiments (see Refs. [258, 264] for details about linearly polarized ROA). The ROA intensity is given as the intensity difference between right- and left-circularly polarized light, $I_R - I_L$. Usually, four different forms of CP ROA are distinguished:

- **ICP ROA**: the intensity difference of the Raman scattering for incident right- and left-circularly polarized light is measured [22, 25];

- **SCP ROA**: the intensity difference of the right- and left-circular polarization states in Raman scattering is determined [265];

- **DCPI ROA**: the incident beam is circularly polarized and the intensity difference of right- and left-circularly polarized light in the scattered beam is measured, whereby all polarization states are modulated in-phase [266–268];

- **DCPII ROA**: similar to DCPI ROA, except that the polarization states are modulated out-of-phase [266–268].

The standard scattering angles employed in experiments are 0° (forward scattering), 180° (backward scattering or backscattering), and 90° (right-angle scattering; see also Fig. 3.1). For the latter, additionally two different experimental
set-ups are distinguished for ICP and SCP ROA: one, where the scattered (for ICP ROA) and incident (for SCP ROA) beams are linearly polarized parallel to the scattering plane (depolarized scattering; indicated by $90^\circ$) and the other, where the linear polarization is perpendicular to the scattering plane (polarized scattering; abbreviated by $90^\circ$).

Combinations of the property tensors can be calculated which do not vary with the choice of the molecular coordinate frame (for details, we refer to Refs. [11, 23, 258, 269, 270]). These are the so-called invariants. For Raman spectroscopy, the following invariants are found [258] (the transition-defining subscripts ‘$fi$’ are omitted for the invariants and the tensor elements for the sake of brevity):

$$\alpha^2 = \frac{1}{9} \text{Im} [(\alpha_{\alpha\alpha}) (\alpha_{\beta\beta})^*],$$  

$$\beta_s(\alpha)^2 = \frac{1}{2} [3(\alpha_{\alpha\beta})^s(\alpha_{\alpha\beta})^{s*} - (\alpha_{\alpha\alpha})(\alpha_{\beta\beta})^*],$$  

$$\beta_a(\alpha)^2 = \frac{3}{2} [(\alpha_{\alpha\beta})^a(\alpha_{\alpha\beta})^{a*}].$$

Symmetric and antisymmetric parts of the tensors are in general evaluated according to

$$T_{\alpha\beta}^s = \frac{1}{2}(T_{\alpha\beta} + T_{\beta\alpha}),$$

$$T_{\alpha\beta}^a = \frac{1}{2}(T_{\alpha\beta} - T_{\beta\alpha}),$$

$$[\epsilon_{\alpha\gamma\delta} T_{\gamma,\delta\beta}]^s = \frac{1}{2}(\epsilon_{\alpha\gamma\delta} T_{\gamma,\delta\beta} + \epsilon_{\beta\gamma\delta} T_{\gamma,\delta\alpha}),$$

$$[\epsilon_{\alpha\gamma\delta} T_{\gamma,\delta\beta}]^a = \frac{1}{2}(\epsilon_{\alpha\gamma\delta} T_{\gamma,\delta\beta} - \epsilon_{\beta\gamma\delta} T_{\gamma,\delta\alpha}).$$

The ROA invariants are given by [258]

$$\alpha G = \frac{1}{9} \text{Im} [(\alpha_{\alpha\alpha})(G_{\beta\beta})^*],$$

$$\beta_s(G)^2 = \frac{1}{2} \text{Im} [3(\alpha_{\alpha\beta})^s(G_{\alpha\beta})^{s*} - (\alpha_{\alpha\alpha})(G_{\beta\beta})^*],$$

$$\beta_a(G)^2 = \frac{3}{2} \text{Im} [(\alpha_{\alpha\beta})^a(G_{\alpha\beta})^{a*}],$$

$$\beta_s(A)^2 = \frac{1}{2} \omega_L \text{Im} \{i(\alpha_{\alpha\beta})^s[(\epsilon_{\alpha\gamma\delta} A_{\gamma,\delta\beta})^{s*}],$$

$$\beta_a(A)^2 = \frac{1}{2} \omega_L \text{Im} \{i(\alpha_{\alpha\beta})^a[(\epsilon_{\alpha\gamma\delta} A_{\gamma,\delta\beta})^{a*} + (\epsilon_{\alpha\beta\gamma} A_{\delta,\gamma\delta})^{a*}]\}. $$
3.2. The general Raman and Raman optical activity intensities

Figure 3.1: A graphical representation of the geometry for ICP right-angle scattering.

The invariants including $G_{\alpha\beta}$ and $A_{\alpha,\beta\gamma}$ are calculated in an analogous way except that $\omega_L$ is replaced by $\omega_d$ in the electric-quadrupole invariants.

The ROA intensity is in principle obtained as a combination of the ROA invariants,

$$I_R - I_L \sim a\alpha G + b\beta_s(G)^2 + c\beta_a(G)^2 + d\beta_a(A)^2 + e\beta_a(A)^2 + f\alpha G$$

$$+ g\beta_s(G)^2 + h\beta_a(G)^2 + j\beta_s(A)^2 + k\beta_a(A)^2,$$

(3.134)

and the Raman intensity as

$$I_R + I_L \sim l\alpha^2 + m\beta_s(\alpha)^2 + n\beta_a(\alpha)^2,$$

(3.135)

where the coefficients $a, b, c, d, e, f, g, h, j, k, l, m,$ and $n$ are independent of each other. Often, the ROA effect is described by the dimensionless circular intensity difference

$$\Delta = \frac{I_R - I_L}{I_R + I_L}.$$

(3.136)

The ROA intensity for the backscattering DCPI set-up, for instance, is given by [we omit the constant $K$ in Eq. (3.121)] [258]

$$I_R - I_L(180^\circ) \sim \frac{8}{e}[6\beta_s(G)^2 + 2\beta_s(A)^2 - 6\beta_s(G)^2 + 2\beta_s(A)^2]$$

(3.137)

and the corresponding Raman intensity by

$$I_R + I_L(180^\circ) \sim 24\beta_s(\alpha)^2.$$

(3.138)
3.3 Far-from-resonance approximation

The property tensors in Eqs. (3.86)–(3.90) contain summations over all excited states \(|j\rangle\). However, the calculation of these expressions is only feasible for small molecules with a few relevant excited states. Otherwise, this sum-over-states ansatz is computationally too expensive. Several approximations have been derived in order to overcome this problem, which are known as the Placzek polarizability theory [253, 254]. First of all, the adiabatic approximation is applied for the separation of the molecular eigenstates \(|j\rangle\) into electronic \(|e_j\rangle\), rotational \(|c_j\rangle\), and vibrational parts \(|v_j\rangle\) (the translational part is eliminated by working in a set of molecule-fixed axes):

\[
|j\rangle = |e_j c_j v_j\rangle = |e_j\rangle |c_j\rangle |v_j\rangle,
\]

(3.139)

where a non-degenerate electronic state is assumed. The energy differences between the states \(|j\rangle\) and \(|i\rangle\) can then be expressed as

\[
\hbar \omega_{ji} = \hbar (\omega_{e_j c_i} + \omega_{v_j v_i}),
\]

(3.140)

where \(\hbar \omega_{v_j v_i}\) also contains the energy difference between the \(|e_j\rangle\) and \(|e_i\rangle\) electronic states. We skip the rotational contributions, which are accounted for by rotational averages in the intensity calculation, and take the wave functions to be real. In addition, it is assumed that the molecule is in its electronic ground state at the initial and final state, i.e., \(e_i = e_f = e_0\). The imaginary line widths \(\Gamma_j\) are omitted since we assume that the incident light is far away from any resonance with an electronic transition.

The electric-dipole–electric-dipole tensor in Eq. (3.86) is then written as

\[
(\alpha_{\alpha\beta})_{v_f e_0 v_i e_0} = \frac{1}{\hbar} \sum_{v_j \neq v_f, v_i} \frac{\langle v_f | \langle e_0 | \mu_\alpha | e_j \rangle \langle e_j | \mu_\beta | e_0 \rangle | v_j \rangle}{\omega_{v_j v_i} - \omega_L} \langle v_j | (e_j | \mu_\beta | e_0 \rangle | v_i \rangle \\
+ \frac{\langle v_f | (e_0 | \mu_\beta | e_j \rangle | v_j \rangle \langle e_j | \mu_\alpha | e_0 \rangle | v_i \rangle}{\omega_{v_j v_f} + \omega_L},
\]

(3.141)

As a next step, the vibronic details contained in \(\omega_{v_j e_i}\) are neglected since they are much smaller than \(\omega_{e_j e_0}\) if the far-from-resonance approximation is fulfilled. Then, there are no vibrational details in the denominator anymore and closure over the vibrational wave functions can be performed leading to

\[
(\alpha_{\alpha\beta})_{v_f e_0 v_i e_0} = \frac{1}{\hbar} \sum_{e_j \neq e_0} \frac{\langle v_f | \langle e_0 | \mu_\alpha | e_j \rangle \langle e_j | \mu_\beta | e_0 \rangle | v_i \rangle}{\omega_{e_j e_0} - \omega_L} \langle e_j | (e_0 | \mu_\beta | e_0 \rangle | e_i \rangle \\
+ \frac{\langle v_f | (e_0 | \mu_\beta | e_j \rangle | e_j | \mu_\alpha | e_0 \rangle | v_i \rangle}{\omega_{e_j e_0} + \omega_L}.
\]

(3.142)
Employing a common denominator and \( \{ e_0 | \mu_\alpha | e_j \} \{ e_j | \mu_\beta | e_0 \} = \{ e_0 | \mu_\beta | e_j \} \{ e_j | \mu_\alpha | e_0 \}, \)

we get [224]

\[
(\alpha_{\alpha\beta})_{v_f e_0 v_i e_0} = \langle v_f | \alpha_{\alpha\beta} | v_i \rangle = \left( \frac{2}{\hbar} \text{Re} \sum_{e_j \neq e_0} \frac{\omega_{e_j e_0} \{ e_0 | \mu_\alpha | e_j \} \{ e_j | \mu_\beta | e_0 \}}{\omega_{e_j e_0}^2 - \omega_L^2} \right) v_i \tag{3.143}
\]

We now introduce the adiabatic polarizability, \( \alpha_{\alpha\beta}(Q) \), which is a function of the normal coordinates \( Q_k \) collected in \( Q \). The nuclei are held in a fixed position whereas the electrons can move. \( \alpha_{\alpha\beta}(Q) \) is expanded in a Taylor series around \( Q = 0 \) and truncated after the second term, which is the so-called electrical harmonic approximation [11]:

\[
\alpha_{\alpha\beta}(Q) = (\alpha_{\alpha\beta})_0 + \sum_k \left( \frac{\partial \alpha_{\alpha\beta}}{\partial Q_k} \right)_0 Q_k. \tag{3.144}
\]

Considering the vibrational transitions, we arrive at

\[
[\alpha_{\alpha\beta}(Q)]_{v_f e_0 v_i e_0} = (\alpha_{\alpha\beta})_0 \langle v_f | v_i \rangle + \sum_k \left( \frac{\partial \alpha_{\alpha\beta}}{\partial Q_k} \right)_0 \langle v_f | Q_k | v_i \rangle. \tag{3.145}
\]

For \( M \) atoms, the vibrational wave functions can be written within the (mechanical) harmonic approximation as products of \( 3M - 6 \) (\( 3M - 5 \) for linear molecules) vibrational harmonic oscillator wave functions for all normal coordinates \( Q_k \) of the molecule (compare section 1.3) [95]:

\[
\langle v_f | v_i \rangle = \prod_{p=1}^{3M-6} \langle v_{f,p} | v_{i,p} \rangle = \prod_{p=1}^{3M-6} \delta_{v_{f,p}, v_{i,p}}, \tag{3.146}
\]

\[
\langle v_f | Q_k | v_i \rangle = \langle v_{f,k} | Q_k | v_{i,k} \rangle \prod_{p=1, p \neq k}^{3M-6} \langle v_{f,p} | v_{i,p} \rangle, \tag{3.147}
\]

\[
\langle v_{f,k} | Q_k | v_{i,k} \rangle = \begin{cases} 
\left( \frac{\hbar}{2\omega_k} v_{i,k} + 1 \right)^{1 \over 2}; & v_{f,k} = v_{i,k} + 1 \\
\left( \frac{\hbar}{2\omega_k} v_{i,k} \right)^{1 \over 2}; & v_{f,k} = v_{i,k} - 1 \land v_{i,k} \neq 0 \\
0; & \text{otherwise}
\end{cases} \tag{3.148}
\]

The simultaneous employment of the electrical and mechanical harmonic approximations is also termed double harmonic approximation. The first term on the right-hand side of Eq. (3.145) equals \( (\alpha_{\alpha\beta})_0 \) if \( v_{f,p} = v_{i,p} \) and vanishes if \( v_{f,p} \neq v_{i,p} \). This situation corresponds to Rayleigh scattering. The second term belongs to Raman scattering which is non-zero if \( (\partial \alpha_{\alpha\beta} / \partial Q_k)_0 \neq 0 \) and \( v_{f,p} = v_{i,p} \) except for \( v_{f,k} = v_{i,k} \). For \( v_{f,k} = v_{i,k} + 1 \), Stokes scattering occurs
and anti-Stokes scattering is present if \( v_{f,k} = v_{i,k} - 1 \). It is common practice to plot only the intensities and wavenumbers of the Stokes scattering in the spectrum [11].

Exploiting

\[
\langle e_0 | \mu_\alpha | e_j \rangle \langle e_j | m_\beta | e_0 \rangle = -\langle e_0 | m_\beta | e_j \rangle \langle e_j | \mu_\alpha | e_0 \rangle, \tag{3.149}
\]

\[
\langle e_0 | \mu_\alpha | e_j \rangle \langle e_j | \theta_{\beta\gamma} | e_0 \rangle = \langle e_0 | \theta_{\beta\gamma} | e_j \rangle \langle e_j | \mu_\alpha | e_0 \rangle, \tag{3.150}
\]

the expressions for the ROA tensors can be derived:

\[
(G'_{\alpha\beta})_{vf,ei,e0} = \langle v_f | G'_{\alpha\beta} | v_i \rangle = \left< v_f \left| -\frac{2}{\hbar} \text{Im} \sum_{e_j \neq e_0} \frac{\omega_L \langle e_0 | \mu_\alpha | e_j \rangle \langle e_j | m_\beta | e_0 \rangle}{\omega_{e_j e_0}^2 - \omega_L^2} \right| v_i \right>, \tag{3.151}
\]

\[
(G'_{\alpha\beta})_{vf,ei,e0} = \langle v_f | G'_{\alpha\beta} | v_i \rangle = \left< v_f \left| -\frac{2}{\hbar} \text{Im} \sum_{e_j \neq e_0} \frac{\omega_L \langle e_0 | m_\beta | e_j \rangle \langle e_j | \mu_\alpha | e_0 \rangle}{\omega_{e_j e_0}^2 - \omega_L^2} \right| v_i \right>, \tag{3.152}
\]

\[
(A_{\alpha,\beta\gamma})_{vf,ei,e0} = \langle v_f | A_{\alpha,\beta\gamma} | v_i \rangle = \left< v_f \left| \frac{2}{\hbar} \text{Re} \sum_{e_j \neq e_0} \frac{\omega_{e_j e_0} \langle e_0 | \mu_\alpha | e_j \rangle \langle e_j | \theta_{\beta\gamma} | e_0 \rangle}{\omega_{e_j e_0}^2 - \omega_L^2} \right| v_i \right>, \tag{3.153}
\]

\[
(A_{\alpha,\beta\gamma})_{vf,ei,e0} = \langle v_f | A_{\alpha,\beta\gamma} | v_i \rangle = \left< v_f \left| \frac{2}{\hbar} \text{Re} \sum_{e_j \neq e_0} \frac{\omega_{e_j e_0} \langle e_0 | \theta_{\beta\gamma} | e_j \rangle \langle e_j | \mu_\alpha | e_0 \rangle}{\omega_{e_j e_0}^2 - \omega_L^2} \right| v_i \right>, \tag{3.154}
\]

where we indicate the imaginary part of the \( G \) and \( G \) tensor components by a prime.

Making use of the BO approximation discussed in section 1.2, it can easily be seen that the nuclei do not contribute to the Raman and ROA tensors.

Since the electronic wave functions form an orthonormal set of functions, we find

\[
\langle e_f | \mu_\alpha | e_j \rangle = \left< e_f \left| \sum_{k=1}^M Z_k R_{k\alpha} \right| e_j \right> = \sum_{k=1}^M Z_k R_{k\alpha} \langle e_f | e_j \rangle = 0. \tag{3.155}
\]

In a similar way, we can demonstrate that the nuclear contributions to the electric-quadrupole transition moment vanish:

\[
\langle e_f | \theta_{\alpha\beta} | e_j \rangle = \left< e_f \left| \frac{1}{2} \sum_{k=1}^M (3R_{k\alpha} R_{k\beta} - R_{k\alpha}^2 \delta_{\alpha\beta}) \right| e_j \right> = \frac{1}{2} \sum_{k=1}^M (3R_{k\alpha} R_{k\beta} - R_{k\alpha}^2 \delta_{\alpha\beta}) \langle e_f | e_j \rangle = 0. \tag{3.156}
\]
3.3. Far-from-resonance approximation

For the magnetic-dipole operator, we additionally have to consider that the effect of the nuclear momentum operator, indicated by $P_k$ for nucleus $k$, acting on the electronic wave function is neglected, which is in accordance with the assumptions in section 1.2:

$$
\beta_s(\alpha)^2 = \beta_a(G)^2 = \beta_a(A)^2 = \beta_s(G)^2 = \beta_s(A)^2 = 0. \quad (3.158)
$$

In addition to that, the symmetric invariants reduce to [224]

$$
\begin{align*}
\alpha G &= -\alpha G = \alpha G' = \frac{1}{9}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})(G'_{xx} + G'_{yy} + G'_{zz}), \\
\beta_a(G)^2 &= -\beta_a(G)^2 = \beta(G')^2 \\
&= \frac{1}{2}(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta}) \\
&= \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})(G'_{xx} - G'_{yy}) + (\alpha_{xx} - \alpha_{zz})(G'_{xx} - G'_{zz}) \\
&+ (\alpha_{yy} - \alpha_{zz})(G'_{yy} - G'_{zz}) + 3(\alpha_{xy}(G'_{xy} + G'_{yx}) \\
&+ \alpha_{xz}(G'_{xz} + G'_{zx}) + \alpha_{yz}(G'_{yz} + G'_{zy}))], \\
\beta_s(A)^2 &= \beta_s(A)^2 = \beta(A)^2 \\
&= \frac{1}{2}\omega_L(\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta}) \\
&= \frac{1}{2}\omega_L[(\alpha_{yy} - \alpha_{xx})A_{z,xy} + (\alpha_{xx} - \alpha_{zz})A_{y,xx} + (\alpha_{zz} - \alpha_{yy})A_{x,yz} \\
&+ \alpha_{xy}(A_{y,yz} - A_{z,xy} + A_{z,xx} - A_{x,xz}) \\
&+ \alpha_{xz}(A_{y,zz} - A_{z,xy} + A_{x,yy} - A_{y,xx}) \\
&+ \alpha_{yz}(A_{x,zz} - A_{x,zy} + A_{y,yy} - A_{x,yx})]. \quad (3.161)
\end{align*}
$$

Thus, we rewrite the Raman invariants as

$$
\begin{align*}
\alpha^2 &= \alpha^2 = \frac{1}{9}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2, \\
\beta_s(\alpha)^2 &= \gamma^2 = \frac{1}{2}(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}) \\
&= \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 \\
&+ 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)]. \quad (3.163)
\end{align*}
$$
The transition defining labels $v_f e_0 v_i e_0$ were again omitted both for the invariants as well as for the individual tensor elements for the sake of brevity. Moreover, usually the contribution of the vibrational-quantum-number-containing integrals [compare Eq. (3.147)] are omitted in the calculations since they depend on the experimental set-up. For instance, not every molecule may be in its vibrational ground state at the temperatures where the measurements are performed [11, 107]. That is why we only employ the derivatives of the property tensors with respect to the normal coordinates for the calculation of the invariants.

In this far-from-resonance approximation, the difference between ICP and SCP ROA intensities vanishes and the ROA intensity for the DCPII set-up is found to be zero [224]. The SCP, ICP, and DCPI ROA intensities for the backward and forward set-ups, respectively, are now given [omitting the constant $K$ in Eq. (3.121)] by [258]

\begin{align}
I_R - I_L(180^\circ) & \sim \frac{8}{c} [12 \beta (G'')^2 + 4 \beta (A)^2], \\
I_R - I_L(0^\circ) & \sim \frac{8}{c} [90 \alpha G' + 2 \beta (G'')^2 - 2 \beta (A)^2].
\end{align}

The SCP and ICP ROA intensities for the polarized and depolarized set-ups, respectively, are evaluated as

\begin{align}
I_R - I_L(90_x^\circ) & \sim 4 \frac{c}{e} [45 \alpha G' + 7 \beta (G'')^2 + \beta (A)^2], \\
I_R - I_L(90_z^\circ) & \sim 8 \frac{c}{e} [3 \beta (G'')^2 - \beta (A)^2],
\end{align}

and the DCPI ROA intensity for right-angle scattering as

\begin{align}
I_R - I_L(90^\circ) & \sim 4 \frac{c}{e} [45 \alpha G' + 13 \beta (G'')^2 - \beta (A)^2].
\end{align}

The Raman intensities for the ICP and SCP set-ups are obtained as

\begin{align}
I_R + I_L(180^\circ) & \sim 4 [45 \alpha^2 + 7 \gamma^2], \\
I_R + I_L(0^\circ) & \sim 4 [45 \alpha^2 + 7 \gamma^2], \\
I_R + I_L(90_x^\circ) & \sim 2 [45 \alpha^2 + 7 \gamma^2], \\
I_R + I_L(90_z^\circ) & \sim 12 \gamma^2.
\end{align}

The term $45 \alpha^2 + 7 \gamma^2$ is called the Raman activity or scattering factor [11, 96]. For the DCPI set-up, the Raman intensities are evaluated according to [258]

\begin{align}
I_R + I_L(180^\circ) & \sim 24 \gamma^2, \\
I_R + I_L(0^\circ) & \sim 4 [45 \alpha^2 + \gamma^2], \\
I_R + I_L(90^\circ) & \sim 45 \alpha^2 + 13 \gamma^2.
\end{align}

The Raman intensity for the DCPII set-up does, in contrast to the DCPII ROA intensity, not vanish (see Ref. [258]).
3.3.1 Origin dependence

For the implementational part of this work it is necessary to consider the gauge-origin dependence of the $\alpha$, $G'$, and $A$ tensors \cite{225}. It is evident from Eqs. (3.164) to (3.167) that the ROA intensity differences are proportional to $a\alpha G' + b\beta(G')^2 + c\beta(A)^2$, where the coefficients $a$, $b$, and $c$ are not related to each other. These coefficients adopt different values depending on the experimental conditions. As a consequence, each invariant must be gauge independent individually.

Shifting the coordinate origin from $O$ to $O - a$ with $a$ having components $a_{ia}$, $a_{i\beta}$, and $a_{i\gamma}$ in the case of electron $i$ (whereby the $\alpha$, $\beta$, and $\gamma$ components have the same value for each electron), the electric-dipole and the magnetic-dipole transition moments transform for a neutral molecule in the length representation as \cite{23,271}

$$
\langle e_0|\mu_\alpha(O-a)|e_j \rangle = \langle e_0|q_e \sum_{i=1}^{N_e} [r_{ia} - a_{ia}]|e_j \rangle = \langle e_0|q_e \sum_{i=1}^{N_e} r_{ia}|e_j \rangle - q_e \sum_{i=1}^{N_e} a_{ia}\langle e_0|e_j \rangle = \langle e_0|\mu_\alpha(O)|e_j \rangle, \quad \forall \ e_0 \neq e_j,
$$

(3.176)

$$
\langle e_0|m_\alpha(O-a)|e_j \rangle = \langle e_0|q_e \sum_{i=1}^{N_e} \frac{1}{2} \epsilon_{\alpha\beta\gamma} (r_{i\beta} - a_{i\beta})p_{i\gamma}|e_j \rangle = \langle e_0|q_e \sum_{i=1}^{N_e} \frac{1}{2} (r_i \times p_i)_\alpha|e_j \rangle - \langle e_0|q_e \sum_{i=1}^{N_e} \frac{1}{2} (a_i \times p_i)_\alpha|e_j \rangle = \langle e_0|\mu_\alpha(O)|e_j \rangle - \langle e_0|q_e \sum_{i=1}^{N_e} \frac{1}{2} (a_i \times p_i)_\alpha|e_j \rangle, \quad \forall \ e_0 \neq e_j.
$$

(3.177)

$r_{ia}$ and $p_{ia}$ indicate the $\alpha$ component of the coordinate and momentum operator for electron $i$. Analogously, it can be shown that the transition moment containing the electric-quadrupole operator changes according to \cite{23,272} (no summation over repeated Greek indices is applied in this section)

$$
\langle e_0|\theta_{\alpha\beta}(O-a)|e_j \rangle = \langle e_0|\frac{1}{2} q_e \sum_{i=1}^{N_e} [3(r_{ia} - a_{ia})(r_{i\beta} - a_{i\beta}) - (r_i - a_i)^2 \delta_{\alpha\beta}]|e_j \rangle
$$

$$
= \langle e_0|\theta_{\alpha\beta}(O)|e_j \rangle - \frac{3}{2} a_\alpha \langle e_0|\mu_\beta(O)|e_j \rangle - \frac{3}{2} a_\beta \langle e_0|\mu_\alpha(O)|e_j \rangle + a_\gamma \langle e_0|\mu_\gamma(O)|e_j \rangle \delta_{\alpha\beta}, \quad \forall \ e_0 \neq e_j.
$$

(3.178)

The property tensors with the shifted origin $O - a$ then result in \cite{23}

$$
\alpha_{\alpha\beta}(O-a) = \alpha_{\alpha\beta}(O)
$$

(3.179)
and

\[
G'_{\alpha\beta}(O - a) = G'_{\alpha\beta}(O) - \frac{1}{\hbar} \sum_{\epsilon \neq \epsilon_0} \omega_L \frac{\omega_{\epsilon_0}^2}{\omega_{\epsilon_0}^2 - \omega_L^2} \\
\times \text{Im} \left( \langle \epsilon_0 | \mu_a(O) | \epsilon_j \rangle \langle \epsilon_j | \frac{q_e}{m_e} \sum_{i=1}^{N_e} (a_i \times p_i) | \epsilon_0 \rangle \right).
\]

Employing the many-electron Hamiltonian \( H(\{r_k\}) \) in relation

\[
\langle \epsilon_j | r_{i_\alpha} H(\{r_k\}) | \epsilon_0 \rangle = \hbar \omega_{\epsilon_0} \langle \epsilon_j | r_{i_\alpha} | \epsilon_0 \rangle,
\]

which holds for electronic eigenstates (see also Refs. [40, 273, 274]), and the operator identity [40, 82, 274]

\[
[r_{i_\alpha}, H(\{r_k\})] = \left[ r_{i_\alpha}, \frac{p^2_{i_\alpha}}{2m_e} \right] = \frac{1}{m_e} [r_{i_\alpha}, p_{i_\alpha}] p_{i_\alpha} = \frac{i\hbar}{m_e} p_{i_\alpha},
\]

which is valid if the potential-energy part of the Hamiltonian commutes with \( r_{i_\alpha} \), we obtain

\[
m_e^{-1} \langle \epsilon_j | p_{i_\alpha} | \epsilon_0 \rangle = (m_e i)^{-1} \langle \epsilon_j | [r_{i_\alpha}, p_{i_\alpha}] | \epsilon_0 \rangle = i^{-1} \langle \epsilon_j | r_{i_\alpha} H(\{r_k\}) | \epsilon_0 \rangle = i\hbar \omega_{\epsilon_0} \langle \epsilon_j | r_{i_\alpha} | \epsilon_0 \rangle.
\]

Then, the origin dependence of \( G'_{\alpha\beta} \) can be re-written as

\[
G'_{\alpha\beta}(O - a) = G'_{\alpha\beta}(O) + \frac{1}{\hbar} \sum_{\epsilon \neq \epsilon_0} \omega_L \omega_{\epsilon_0} \frac{i}{\omega_{\epsilon_0}^2 - \omega_L^2} \text{Re} \langle \epsilon_0 | \mu_a(O) | \epsilon_j \rangle \langle \epsilon_j | (a \times \mu) | \epsilon_0 \rangle \\
= G'_{\alpha\beta}(O) + \frac{1}{2} \omega_L \epsilon_{\beta\gamma} a_\alpha \alpha_{\alpha\beta}(O).
\]

The \( A \) tensor is also origin dependent,

\[
A_{\alpha,\beta\gamma}(O - a) = A_{\alpha,\beta\gamma}(O) - \frac{3}{2} a_\beta \alpha_{\alpha\gamma}(O) \\
- \frac{3}{2} a_\alpha \alpha_{\alpha\beta}(O) + a_\beta \alpha_{\alpha\delta}(O) \delta_{\beta\gamma}.
\]

If the invariants \( \beta(A)^2, \beta(G')^2, \) and \( \alpha G' \) are calculated, the origin dependence cancels provided that the tensors \( \alpha, G' \), and \( A \) transform as illustrated in Eqs. (3.179), (3.184), and (3.185), respectively. The tensors \( \alpha \) and \( A \) transform according to Eqs. (3.179) and (3.185) also in the case of a finite basis set, which leads to a gauge-origin independent \( \beta(A)^2 \) invariant [40] whether or not the basis set limit is achieved. However, Eq. (3.183) written for many-electron eigenstates becomes invalid for trial wave functions (like Slater determinants) since Eq. (3.181) does not hold exactly, but turns out to be always fulfilled for variational self-consistent field (SCF) and multi-configuration SCF wave functions.
functions [40]. The issue of incomplete one-electron basis sets plays also a role in Eq. (3.182) since it contains products of operators. For example,

\[ [r_{i\alpha}, p_{j\beta}] = i\hbar \delta_{\alpha\beta} \]  

(3.186)
does only hold if the one-electron basis set is complete since then we can write the matrix elements of the commutator in basis set representation with the basis functions \( |a\rangle, |b\rangle, \) and \( |c\rangle \) as [82]

\[
\sum_{abc} \left( \langle a| r_{i\alpha} |b\rangle \langle b| p_{j\beta} |c\rangle - \langle a| p_{i\alpha} |b\rangle \langle b| r_{j\beta} |c\rangle \right) = \sum_{ac} \left( \langle a| r_{i\alpha} p_{j\beta} |c\rangle - \langle a| p_{i\alpha} r_{j\beta} |c\rangle \right)
\]

(3.187)

with \( \sum_b |b\rangle \langle b| = 1.\)

The gauge error is a function of the distance between gauge and wave-function origin [275]. Early approaches like the Localized Orbital/local orRiGin [276] or Individual Gauge for Localized Orbitals [277] methods minimized the error due to the gauge-origin dependence by selecting gauges for localized wave functions. Nowadays, mostly London Atomic Orbitals (LAOs) [278] (also known as Gauge Including or Gauge Invariant Atomic Orbitals [279]) are employed for variational wave functions (see Refs. [280–283] for pioneering work on magnetic shielding, Ref. [284] on magnetic circular dichroism, Ref. [285] on g-tensors, Refs. [286–289] on nuclear shieldings, Refs. [290–292] on magnetizabilities, and Refs. [293, 294] on VCD). These give gauge-origin independent ROA intensity differences. The first ROA calculation employing LAOs was reported by Helgaker et al. [40] in 1994.

The form of a LAO \( |X_A(B, r, R_A)\rangle \) is given as follows [275]:

\[
|X_A(B, r, R_A)\rangle = e^{-\frac{i}{\hbar} \int e_{me}(\mathbf{A}_A - \mathbf{A}_B) \cdot \mathbf{r}} |b_A(r, R_A)\rangle.
\]

(3.188)

\( |b_A(r, R_A)\rangle \) is the basis function centered at position \( R_A \) and \( \mathbf{A}_A = 1/2 \mathbf{B} \times (R_A - \mathbf{O}) \) the vector potential at \( R_A \), which depends on the gauge origin \( \mathbf{O} \).

Employing the LAOs, the matrix elements of the overlap integrals and the ones containing the potential energy \( V \) (containing also the electrostatic interactions) and the mechanical momenta comprise only a difference in the vector potentials leading to an independence of the gauge origin (for the sake of brevity, we omit the explicit indication of the dependence on \( r, R_A, \) and \( R_B \) [275, 295]:

\[
\langle X_A | X_B \rangle = \left\langle b_A \left| e^{\frac{i}{\hbar} \int e_{me}(\mathbf{A}_A - \mathbf{A}_B) \cdot \mathbf{r}} \right| b_B \right\rangle,
\]

(3.189)

\[
\langle X_A | V | X_B \rangle = \left\langle b_A \left| e^{\frac{i}{\hbar} \int e_{me}(\mathbf{A}_A - \mathbf{A}_B) \cdot \mathbf{r}} \right| V \right| b_B \right\rangle,
\]

(3.190)

\[
\langle X_A \left| \frac{1}{2m_e} [\mathbf{p} - q_e \mathbf{A}]^2 \right| X_B \rangle
\]

\[
= \left\langle b_A \left| e^{\frac{i}{\hbar} \int e_{me}(\mathbf{A}_A - \mathbf{A}_B) \cdot \mathbf{r}} \right| \frac{1}{2m_e} [\mathbf{p} - q_e \mathbf{A}]^2 \right| b_B \right\rangle.
\]

(3.191)
Another option for obtaining gauge-origin independent results is the utilization of the electric-dipole operator in the velocity representation $\mathbf{\mu}^p$ instead of the length representation $\mathbf{\ell}$, in analogy to Eq. (3.183),

$$
\langle e_0 | \mu_{\alpha} | e_j \rangle = i \omega_{e_j e_0}^{-1} \left\langle e_0 \bigg| \sum_{i=1}^{N_e} \frac{q_i}{m_e} p_{i\alpha} \bigg| e_j \right\rangle = i \omega_{e_j e_0}^{-1} \langle e_0 | \mu_{\alpha}^p | e_j \rangle. \tag{3.192}
$$

The velocity representation of the electric-quadrupole operator $\theta^p$ is calculated via $\hbar \omega_{e_0 e_j} \langle r_{i\alpha} r_{i\beta} | e_0 \rangle = \langle e_j | [r_{i\alpha} r_{i\beta}, H(\{r_k\})] | e_0 \rangle = \frac{i \hbar}{m_e} \langle e_j | p_{i\alpha} r_{i\beta} + r_{i\alpha} p_{i\beta} - \hbar \delta_{\alpha\beta} | e_0 \rangle$. \[296-299\] as

$$
\langle e_j | \theta_{\alpha\beta}^p | e_0 \rangle = \langle i \omega_{e_j e_0}^{-1} \left\langle e_j \bigg| \frac{q_i}{m_e} \sum_{i=1}^{N_e} [p_{i\alpha} r_{i\beta} + r_{i\alpha} p_{i\beta}] \bigg| e_0 \right\rangle = \langle i \omega_{e_j e_0}^{-1} \langle e_j | \theta_{\alpha\beta}^p | e_0 \rangle. \tag{3.193}
$$

If the coordinate origin is altered from $O$ to $O - \mathbf{a}$, the electric-quadrupole operator in the velocity representation transforms like

$$
\langle e_0 | \theta_{\alpha\beta}^p (O - \mathbf{a}) | e_j \rangle = \langle e_0 | \theta_{\alpha\beta}^p (O) | e_j \rangle - a_{\alpha} \langle e_0 | \mu_{\beta}^p (O) | e_j \rangle - a_{\beta} \langle e_0 | \mu_{\alpha}^p (O) | e_j \rangle, \quad \forall \; e_0 \neq e_j. \tag{3.194}
$$

The property tensors in the velocity representation are then obtained as

$$
\alpha_{\alpha\beta}^p = \frac{2}{\hbar} \sum_{e_j \neq e_0} \frac{1}{\omega_{e_j e_0} (\omega_{e_j e_0}^2 - \omega_L^2)} \text{Re} \left( \langle e_0 | \mu_{\alpha}^p | e_j \rangle \langle e_j | \mu_{\beta}^p | e_0 \rangle \right), \tag{3.195}
$$

$$
G_{\alpha\beta}^p = \frac{2}{\hbar} \sum_{e_j \neq e_0} \frac{\omega_L}{\omega_{e_j e_0} (\omega_{e_j e_0}^2 - \omega_L^2)} \text{Re} \left( \langle e_0 | \mu_{\alpha}^p | e_j \rangle \langle e_j | m_{\beta} | e_0 \rangle \right), \tag{3.196}
$$

$$
A_{\alpha,\beta\gamma}^p = \frac{2}{\hbar} \sum_{e_j \neq e_0} \frac{1}{\omega_{e_j e_0} (\omega_{e_j e_0}^2 - \omega_L^2)} \text{Re} \left( \langle e_0 | \mu_{\alpha}^p | e_j \rangle \langle e_j | \theta_{\beta\gamma}^p | e_0 \rangle \right). \tag{3.197}
$$

The electric-dipole–electric-dipole tensor $\mathbf{\alpha}^p$ is obviously gauge-origin independent if the coordinate origin is moved from $O$ to $O - \mathbf{a}$ because the momenta $p_i$ do not change:

$$
\alpha_{\alpha\beta}^p (O - \mathbf{a}) = \alpha_{\alpha\beta}^p (O). \tag{3.198}
$$

In contrast to that, the $G^p$ and $A^p$ tensors are origin dependent:

$$
G_{\alpha\beta}^p (O - \mathbf{a}) = G_{\alpha\beta}^p (O) + \frac{1}{\hbar} \sum_{e_j \neq e_0} \frac{\omega_L}{\omega_{e_j e_0} (\omega_{e_j e_0}^2 - \omega_L^2)} \text{Re} \left( \langle e_0 | \mu_{\alpha}^p | e_j \rangle \langle e_j | \mu_{\beta}^p | e_0 \rangle \right) = G_{\alpha\beta}^p (O) + \frac{1}{2} \omega_L e_{\beta\gamma\delta} a_{\gamma} \alpha_{\alpha\delta}^p (O), \tag{3.199}
$$

$$
A_{\alpha,\beta\gamma}^p (O - \mathbf{a}) = A_{\alpha,\beta\gamma}^p (O) - a_{\beta} \alpha_{\alpha\gamma}^p (O) - a_{\gamma} \alpha_{\alpha\beta}^p (O). \tag{3.200}
$$
However, the gauge-origin dependence of the invariants $\alpha G'$, $\beta(G')^2$, and $\beta(A)^2$ turns out to vanish if the tensors $\alpha$, $G'$, and $A$ are given in the velocity representation and thus transform according to Eqs. (3.198)–(3.200). This is even true in the case of finite basis sets and we explicitly demonstrate the origin independence here for the $\beta(G')^2$ invariant.

Employing the intuitive notation $(a \times \alpha^p_a)_\beta \equiv \epsilon_{\beta\gamma\delta} \alpha_{\gamma\delta}^p$, inserting the origin shift of $G'$ given in Eq. (3.199) into the formula for $\beta(G')^2$ in Eq. (3.160), and considering that $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$, one obtains for $\beta(G')^2$ at the shifted origin $O - a$ in the velocity form (for the sake of clarity, the indication of the origin dependence of all tensor components is omitted in the following)

\[
\beta(G')^2(O - a) = \frac{1}{2} \left[ (\alpha^p_{xx} - \alpha^p_{yy})(G'^p_{xx} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_x - G'^p_{yy} - \frac{1}{2}\omega_L(a \times \alpha^p_y)_y) \\
\quad + (\alpha^p_{xx} - \alpha^p_{zz})(G'^p_{xx} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_x - G'^p_{zz} - \frac{1}{2}\omega_L(a \times \alpha^p_z)_z) \\
\quad + (\alpha^p_{yy} - \alpha^p_{zz})(G'^p_{yy} + \frac{1}{2}\omega_L(a \times \alpha^p_y)_y - G'^p_{zz} - \frac{1}{2}\omega_L(a \times \alpha^p_z)_z) \\
\quad + 3(\alpha^p_{xy}(G'^p_{xy} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_y + G'^p_{yx} + \frac{1}{2}\omega_L(a \times \alpha^p_y)_x) \\
\quad + \alpha^p_{xz}(G'^p_{xz} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_z + G'^p_{zx} + \frac{1}{2}\omega_L(a \times \alpha^p_z)_x)) \right] \\
= \beta(G')^2(O) + \frac{1}{2}\omega_L \left[ \alpha^p_{xx}(a_y \alpha^p_{xx} - a_z \alpha^p_{xy}) - \alpha^p_{xx}(a_z \alpha^p_{xx} - a_x \alpha^p_{yx}) \\
- \alpha^p_{yy}(a_y \alpha^p_{xx} - a_z \alpha^p_{xy}) + \alpha^p_{yy}(a_z \alpha^p_{xx} - a_x \alpha^p_{yx}) \\
+ \alpha^p_{xz}(a_y \alpha^p_{xx} - a_z \alpha^p_{xy}) - \alpha^p_{xz}(a_z \alpha^p_{xx} - a_x \alpha^p_{yx}) \\
- \alpha^p_{zz}(a_y \alpha^p_{xx} - a_z \alpha^p_{xy}) + \alpha^p_{zz}(a_z \alpha^p_{xx} - a_x \alpha^p_{yx}) \\
+ 3(\alpha^p_{xy}(a_z \alpha^p_{xx} - a_x \alpha^p_{xy}) + \alpha^p_{xy}(a_y \alpha^p_{xx} - a_x \alpha^p_{yx}) \\
+ \alpha^p_{zx}(a_x \alpha^p_{xx} - a_y \alpha^p_{zx}) + \alpha^p_{zx}(a_y \alpha^p_{xx} - a_x \alpha^p_{zy}) \\
+ \alpha^p_{yz}(a_x \alpha^p_{xx} - a_y \alpha^p_{yx}) + \alpha^p_{yz}(a_y \alpha^p_{xx} - a_x \alpha^p_{zy})) \right] \\
= \beta(G')^2(O). \tag{3.201}
\]

As one can see, the gauge dependence vanishes because the additional terms which arise due to the gauge dependence of $G'^p$ cancel each other.

It should be mentioned that the $\alpha G'$ invariant is also origin independent if it is obtained by the electric-dipole–electric-dipole tensor in the length representation, $\alpha$, and the electric-dipole–magnetic-dipole tensor in the velocity form, $G'^p$. For the calculation of $\alpha G'$, only the trace of $G'^p$ is needed which is always
origin independent because the terms which arise due to the origin shift are zero [14, 300]:

\[
\sum_{\alpha=x,y,z} G^{p}_{\alpha\alpha} (O - \alpha) = \sum_{\alpha=x,y,z} G^{p}_{\alpha\alpha} (O) + \sum_{\alpha=x,y,z, \epsilon_j \neq \epsilon_0} \sum_{i=1}^{N_e} \frac{\omega_L}{\omega_{\epsilon_j \epsilon_0} (\omega_{\epsilon_j \epsilon_0} - \omega_L^2)} \frac{q_e}{m_e} \sum_{i=1}^{N_e} (a_i \times p_i)_{\alpha} \langle \epsilon_0 | e_j \rangle \langle \epsilon_0 | e_j \rangle
\]

\[
= G^{p}_{\alpha\alpha} (O) + \sum_{\alpha=x,y,z, \epsilon_j \neq \epsilon_0} \sum_{i=1}^{N_e} \frac{\omega_L}{\omega_{\epsilon_j \epsilon_0} (\omega_{\epsilon_j \epsilon_0} - \omega_L^2)} \frac{q_e}{m_e} \sum_{i=1}^{N_e} (a_i \times p_i)_{\alpha} \langle \epsilon_0 | e_j \rangle \langle \epsilon_0 | e_j \rangle
\]

In summary, all ROA invariants are gauge-origin independent if the corresponding property tensors are calculated in the velocity representation [225, 301]. Alternatively, \( \alpha^p \) and \( G^p \) may be used to calculate \( \beta(G^p)^2 \) whereas \( \beta(A)^2 \) can also be obtained in the origin-invariant length representation [225]. \( \alpha G^p \) is origin independent if \( G^p \) is employed both in combination with \( \alpha \) and \( \alpha^p \).

### 3.4 Resonance Raman optical activity

The theory of RROA was developed in 1996 by Nafie [223]. Basically, a RROA spectrum gives rise to the same relative intensities that are observed in the parent resonance Raman (RR) spectrum if only one excited electronic state is in resonance. The sign of the signal as well as the ratio of the RROA and RR
intensities under these circumstances are determined by the electronic circular dichroism anisotropy ratio.

We present here a related theory of RROA including vibrational details on the excited-state PES that is closely following the corresponding RR theory. Both sum-over-states and time-dependent formulations will be given [226].

### 3.4.1 Sum-over-states formulation and the Condon approximation

The components of the general property tensors $T_{12}$ are given in analogy to section 3.1.4 (omitting the transition-defining subscripts ‘$f’$) as

$$T_{12}(\omega_L) = \frac{1}{\hbar} \sum_{j \neq f,i} \left\{ \frac{\langle f|o_1|j\rangle\langle j|o_2|i\rangle}{\omega_{ji} - \omega_L - i\Gamma_j} + \frac{\langle f|o_2|j\rangle\langle j|o_1|i\rangle}{\omega_{jf} + \omega_L + i\Gamma_j} \right\},$$

(3.203)

where $o_1$ and $o_2$ indicate components of the electric-dipole, magnetic-dipole, and electric-quadrupole moment operators.

The BO-approximation is applied, i.e., the contribution of the nuclear electric-dipole, magnetic-dipole, and electric-quadrupole moment operators vanish (see section 3.3), and, in addition, the rotational contributions are skipped. As we are dealing with different electronic states $|a\rangle$ and $|b\rangle$, we find for the electronic part of the electric-dipole matrix element ($r_k$ indicates the coordinates of electron $k$) that

$$\langle a|\mu|b\rangle = \left\langle v_a \left| \left( \sum_{k=1}^{N} q_k \mathbf{r}_k \right) e_b \right| v_b \right\rangle = \langle v_a | \mu_{el}^{ab}(\mathbf{R}) | v_b \rangle,$$

(3.204)

with the definition of the electronic part of the electric-dipole transition moment as a function of the nuclear coordinates. For the sake of simplicity, we write $\mu_{el}^{ab}(\mathbf{R})$ for the electronic part of the electric-dipole transition moment in this section.

Since $\mu_{el}^{ab}(\mathbf{R})$ is not known for all possible sets of nuclear coordinates (except maybe for small molecules with few degrees of freedom, where it can be calculated for a large number of molecular structures), it is usually expanded in a Taylor series. For vertical transitions as assumed here, the ground-state equilibrium structure $\mathbf{R}_{eq}$ is the reference point for this expansion. In the Condon approximation, we truncate this series already after the constant term obtained for the equilibrium structure so that only Franck–Condon terms are considered,

$$\langle a|\mu|b\rangle \approx \mu_{el}^{ab}(\mathbf{R}_{eq})\langle v_a | v_b \rangle.$$  

(3.205)

The next higher-order terms are the Herzberg–Teller terms, which depend on the change of $\mu_{el}^{ab}(\mathbf{R})$ with respect to the nuclear coordinates. These terms, however, will not be considered here. The same approximations can be invoked for the electric-quadrupole operator to arrive at

$$\langle a|\theta|b\rangle \approx \theta_{el}^{ab}(\mathbf{R}_{eq})\langle v_a | v_b \rangle,$$

(3.206)
where $\theta_{ab}^el(R_{eq})$ is the electronic matrix element of the electric-quadrupole operator evaluated at the equilibrium structure. Neglecting in addition the action of the nuclear momentum operator on the electronic wave function (see section 3.1.4), we obtain for the magnetic-dipole operator

$$\langle a|m|b \rangle \approx m_{ab}^{el}(R_{eq}) \langle v_a|v_b \rangle,$$

(3.207)

where $m_{ab}^{el}(R_{eq})$ is the electronic matrix element of the magnetic-dipole operator at the equilibrium structure. In the following (but not in the context of the time-dependent formulation), we will use the notation $m_{ab}^{el} = m_{ab}^{el}(R_{eq})$, and analogous abbreviations for $\theta_{ab}^{el}$ and $\mu_{ab}^{el}$. It should be noted that the BO approximation is applied in the following also to the case of two excited electronic states in resonance, i.e., we assume that these two states are close in resonance, but still so far away that the BO approximation holds.

From Eq. (3.203) it follows that all tensors occurring in the ROA intensity theory can, in this approximation, be written as (compare also section 3.3)

$$T_{12}(\omega_L) = \frac{1}{\hbar} \sum_{j \neq f,i} \sum_{v_f \neq v_j,v_i} \left\{ \frac{\theta_{1,0j}^{el} \theta_{2,j0}^{el} \langle v_f|v_j \rangle \langle v_j|v_i \rangle}{\omega_{v_jv_i} - \omega_L - i\Gamma v_j} + \frac{\theta_{2,0j}^{el} \theta_{1,j0}^{el} \langle v_f|v_j \rangle \langle v_j|v_i \rangle}{\omega_{v_jv_f} + \omega_L + i\Gamma v_j} \right\},$$

(3.208)

This expression is often further approximated under resonance conditions by neglecting the second term on the right-hand side. The first term involves an energy difference in the denominator that goes to zero for exact resonance conditions so that only the damping constant remains and it becomes much larger than the second term involving the energy sum in the denominator:

$$T_{12}(\omega_L) \approx \frac{1}{\hbar} \sum_{j \neq f,i} \sum_{v_f \neq v_j,v_i} \frac{\theta_{1,0j}^{el} \theta_{2,j0}^{el} \langle v_f|v_j \rangle \langle v_j|v_i \rangle}{\omega_{v_jv_i} - \omega_L - i\Gamma v_j} = \frac{1}{\hbar} \sum_{j \neq f,i} \sum_{v_f \neq v_j,v_i} \theta_{1,0j}^{el} \theta_{2,j0}^{el} W_{v_j}(\omega_L).$$

(3.209)

The terms in Dirac brackets in Eq. (3.209), i.e., the nuclear contributions, are identical for all property operators considered here within the approximations made. They necessarily involve an approximation for the shape of the PES in the ground and excited electronic states. For large molecules, one usually chooses the harmonic approximation for all states under consideration.

We can then further distinguish between the “vertical Franck–Condon” (VFC) and the “adiabatic Franck–Condon” (AFC) models [302,303]. In the first model, the harmonic approximation for the excited-state PES is implemented by a second-order Taylor-series expansion at the ground-state equilibrium position, whereas in the second case this expansion is carried out at the excited-state
minimum. For excitations that are dominated by short-time processes, the first model will in general be a good choice. Furthermore, it is computationally easier since it only requires a ground-state structure optimization as well as the calculation of the Hessian for each state under consideration at a single molecular structure, whereas the AFC model requires a separate structure optimization for each electronic state. Additional approximations can be introduced into the VFC model by considering only the linear term in the Taylor-series expansion for the structural dependence of the excited-state energy and by assuming that the second-order terms can be taken from the ground state. This is equivalent to assuming equal curvatures of the states and hence equivalent to equal vibrational frequencies and normal modes in the ground and excited states, but allowing for a displacement in the equilibrium position (gradient Franck–Condon model, GFC). The GFC model is also known by the name “independent mode, displaced harmonic oscillator” (IMDHO) model [304, 305]. The approximations can be improved on by also allowing for frequency changes in the excited states, but neglecting second-order terms for the excited-state PES that are off-diagonal in the basis of the ground-state normal modes (no Duschinsky rotations). The latter model is sometimes called “Hessian Franck–Condon” (HFC) model. For the GFC and HFC models, the expressions for the Franck–Condon integrals in Eq. (3.209), \( W_{ij}(\omega_L) \), are known analytically [306]. The relevant terms can either be calculated by a direct sum-over-states approach or by employing the time-dependent formalism of RR and optical spectroscopy [306]. The five tensors of Eqs. (3.86)–(3.90) are given in analogy to Eq. (3.209) as

\[
\alpha_{ij}(\omega_L) = \frac{1}{\hbar} \sum_{j \neq f, i} \sum_{v_f, v_i} \mu^{\text{el}}_{\alpha,0j} \mu^{\text{el}}_{\beta,j0} W_{ij}(\omega_L),
\]

(3.210)

\[
G_{ij}(\omega_L) = \frac{1}{\hbar} \sum_{j \neq f, i} \sum_{v_f, v_i} \mu^{\text{el}}_{\alpha,0j} m^{\text{el}}_{\beta,j0} W_{ij}(\omega_L),
\]

(3.211)

\[
G_{ij}(\omega_L) = \frac{1}{\hbar} \sum_{j \neq f, j} \sum_{v_f, v_i} m^{\text{el}}_{\alpha,0j} \mu^{\text{el}}_{\beta,j0} W_{ij}(\omega_L),
\]

(3.212)

\[
A_{ij}(\omega_L) = \frac{1}{\hbar} \sum_{j \neq f, i} \sum_{v_f, v_i} \mu^{\text{el}}_{\alpha,0j} \theta^{\text{el}}_{\beta,j0} W_{ij}(\omega_L),
\]

(3.213)

\[
A_{ij}(\omega_L) = \frac{1}{\hbar} \sum_{j \neq f, i} \sum_{v_f, v_i} \theta^{\text{el}}_{\beta,j0} \mu^{\text{el}}_{\alpha,j0} W_{ij}(\omega_L).
\]

(3.214)

Making use of the properties of the electronic transition moments, \( \mu^{\text{el}}_{\alpha,0j} \mu^{\text{el}}_{\beta,j0} = \mu^{\text{el}}_{\beta,0j} \mu^{\text{el}}_{\alpha,j0} = \mu^{\text{el}}_{\alpha,0j} m^{\text{el}}_{\beta,j0} = -\mu^{\text{el}}_{\beta,0j} m^{\text{el}}_{\alpha,j0} \), and \( \theta^{\text{el}}_{\beta,j0} \mu^{\text{el}}_{\alpha,j0} = \mu^{\text{el}}_{\alpha,0j} \theta^{\text{el}}_{\beta,j0} \), it is found that the antisymmetric components \((\alpha_{ij})^a\) vanish and that \((G_{ij})^a = -(G_{ij})^s = G_{ij}\) and \([\epsilon_{ij}(A_{ij})^a] = [\epsilon_{ij}(A_{ij})^s] = \epsilon_{ij} A_{ij}\) hold. Therefore, all antisymmetric invariants are zero and the total number of ROA invariants reduces to three: \(\alpha G, \beta_s(G)^2 = \beta(G)^2\), and \(\beta_s(A)^2 = \beta(A)^2\). These are the same invariants as obtained in the far-from-resonance approximation (see section 3.3). So, the
difference between the various types of CP ROA [except of the DCPII form (see Ref. [258])] vanishes and the ROA intensity for the backward scattering direction is obtained as (compare section 3.3)

\[ I_R - I_L(180^\circ) \sim \frac{8}{c}(12\beta(G)^2 + 4\beta(A)^2). \]  

(3.215)

The backscattering Raman intensity for the ICP and SCP variants is given, employing \( \beta_s(\alpha)^2 = \gamma^2 \) and \( \alpha^2 = a^2 \), by [258]

\[ I_R + I_L(180^\circ) \sim 45a^2 + 7\gamma^2 \]  

(3.216)

and the one for the DCPI experimental set-up by [258]

\[ I_R + I_L(180^\circ) \sim 6\gamma^2 \]  

(3.217)

since \( \beta_a(\alpha)^2 = 0 \).

3.4.2 Time-dependent formulation and resonance with a single excited electronic state

In RR theory, the so-called time-dependent theory is a way in order to reformulate steady-state spectra in terms of time-dependent quantities [11, 307–311]. We formulate it here for a general tensor component \( T_{\alpha \beta} \) so that it can also be applied to ROA property tensors [226].

Starting from Eq. (3.203), keeping only the resonant term and assuming resonance with a single excited electronic state (SES) labeled by \( j \), we obtain for the tensor component

\[
T_{12}(\omega_L) = \frac{1}{\hbar} \sum_{v_j \neq v_f, v_i} \frac{\langle v_f | \sigma_{1,j,0}^{\dagger} | v_j \rangle \langle v_j | \sigma_{2,j,0}^{\dagger} | v_i \rangle}{\omega_{v_j,v_i} - \omega_L - i\Gamma_{v_j}} \]

\[
= \frac{1}{\hbar} \sum_{v_j \neq v_f, v_i} \frac{\langle v_f | \sigma_{1,j,0}^{\dagger}(Q) | v_j \rangle \langle v_j | \sigma_{2,j,0}^{\dagger}(Q) | v_i \rangle}{\omega_{v_j,v_i} - \omega_L - i\Gamma_{v_j}},
\]

(3.218)

where the electronic transition moments are rewritten as functions of the nuclear-coordinate-dependent normal coordinates \( Q \). Applying the mathematical identity [11, 310]

\[
\frac{1}{\hbar} \int_0^\infty \exp \left\{-i(\omega_{v_j,v_i} - \omega_L - i\Gamma_{v_j})t\right\} dt = \frac{i}{\hbar} \int_0^\infty \exp \left\{-i(E_{v_j,v_i} - E - i\hbar\Gamma_{v_j})t\right\} dt,
\]

(3.219)
and assuming a common line width $\Gamma$ for all vibronic transitions, we arrive at

$$T_{12}(\omega_L) = \frac{i}{\hbar} \int_0^\infty \sum_{v_{j} \neq v_{i}} \exp \left\{ \frac{-i(E_{v_j} - E - i\hbar \Gamma)t}{\hbar} \right\} dt$$

$$\langle v_{j} | o_{1,0j}^{cl}(Q) | v_{i} \rangle \langle v_{j} | o_{2,j0}^{cl}(Q) | v_{i} \rangle$$

$$= \frac{i}{\hbar} \int_0^\infty \exp \left\{ \frac{i(E_{v_i} + E + i\hbar \Gamma)t}{\hbar} \right\} dt$$

$$\langle v_{j} | o_{1,0j}^{cl}(Q) \exp \{-iH_{ex}t/\hbar\} o_{2,j0}^{cl}(Q) | v_{i} \rangle.$$

(3.220)

Here, we employ $H_{ex}$, the Hamiltonian for vibrational motion in the excited state $[311]$, and performed closure over the vibrational states $|v_{j}\rangle$.

As a next step, we expand the operators in a Taylor series around the nuclear ground-state equilibrium geometry $Q_{0}$ employing all normal coordinates $Q_{k}$ of the molecule,

$$o_{1,0j}^{cl}(Q) = o_{1,0j}^{cl}(Q_{0}) \left\{ 1 + \sum_{k} \frac{1}{o_{1,0j}^{cl}(Q_{0})} \left( \frac{\partial o_{1,0j}^{cl}}{\partial Q_{k}} \right) Q_{k} + \cdots \right\},$$

(3.221)

and in an analogous way for $o_{2,j0}^{cl}(Q)$. Employing the notation

$$\langle \zeta_{f}^{o_{1,0j}} \rangle = \langle v_{j} \rangle \left\{ 1 + \sum_{k} \frac{1}{o_{1,0j}^{cl}(Q_{0})} \left( \frac{\partial o_{1,0j}^{cl}}{\partial Q_{k}} \right) Q_{k} + \cdots \right\},$$

(3.222)

$$| \zeta_{s}^{o_{2,j0}} \rangle = \left\{ 1 + \sum_{k} \frac{1}{o_{2,j0}^{cl}(Q_{0})} \left( \frac{\partial o_{2,j0}^{cl}}{\partial Q_{k}} \right) Q_{k} + \cdots \right\} | v_{i} \rangle,$$

(3.223)

$$| \zeta_{s}^{o_{2,j0}}(t) \rangle = \exp \{-iH_{ex}t/\hbar\} | \zeta_{s}^{o_{2,j0}} \rangle.$$

(3.224)

$T_{12}(\omega_L)$ is obtained as

$$T_{12}(\omega_L) = \frac{i}{\hbar} o_{1,0j}^{cl}(Q_{0}) o_{2,j0}^{cl}(Q_{0}) \int_0^\infty \exp \left\{ \frac{i(E_{v_i} + E + i\hbar \Gamma)t}{\hbar} \right\} dt$$

$$\langle \zeta_{f}^{o_{1,0j}} | \zeta_{s}^{o_{2,j0}}(t) \rangle.$$

(3.225)

$o_{1,0j}^{cl}(Q_{0})$ is nothing else than $o_{1,0j}^{cl}(R_{eq})$ in the previous section but now expressed in terms of normal coordinates.

The SES limit of Eq. (3.209),

$$T_{12}(\omega_L) = \frac{1}{\hbar} o_{1,0j}^{cl} o_{2,j0}^{cl} \sum_{v_{j} \neq v_{i}} \frac{\langle v_{j} | v_{j} \rangle \langle v_{j} | v_{i} \rangle}{\omega_{v_j v_i} - \omega_L - i\Gamma_{v_j}}$$

$$= \frac{1}{\hbar} o_{1,0j}^{cl} o_{2,j0}^{cl} \sum_{v_{j} \neq v_{i}} W_{v_j}(\omega_L),$$

(3.226)
yields in a similar way the time-dependent term, which is given by

$$T_{12}(\omega_L) = \frac{i}{\hbar} \sigma_{1j}^{\text{el}}(R_{\text{eq}}) \sigma_{2j0}^{\text{el}}(R_{\text{eq}}) \int_0^\infty \exp \left\{ \frac{i(E_{v_i} + E + i\hbar \Gamma)}{\hbar} \right\} dt \langle v_f | v_i(t) \rangle$$

(3.227)

with $|v_i(t)\rangle = \exp \{-iH_{\text{ext}}t/\hbar\} |v_i\rangle$, leading to the same ROA intensity expression as in Eq. (3.215).

In the case of a non-degenerate excited electronic state, the electronic transition moment shows a particular direction so that components of the property tensors may vanish. If we arbitrarily choose the $x$-direction in the molecule-fixed frame (analogously to Ref. [223]) for the direction of the electric-dipole moment (i.e., the $y$- and $z$-components of the electric-dipole moment are zero), then all components except for $\alpha_{xx}$ are zero, which can be written like in Eq. (3.209) or with the time-dependent expression for $\alpha_{xx}$ as (compare Refs. [312, 313])

$$\alpha_{xx} = \alpha^{\text{SES}}$$

(3.228)

with

$$\alpha^{\text{SES}} = \frac{1}{\hbar} |\mu_{0j}|^2 \sum_{v_j \neq v_i} W_{v_j}(\omega_L)$$

$$= \frac{i}{\hbar} |\mu_{0j}|^2 \int_0^\infty \exp \left\{ \frac{i(E_{v_i} + E + i\hbar \Gamma)}{\hbar} \right\} dt \langle v_f | v_i(t) \rangle.$$  

(3.229)

This has various consequences: because the only remaining component of $\alpha$ is the $\alpha_{xx}$ component, all antisymmetric invariants vanish. Furthermore, solely $G_{xx}$, $G_{xy}$, and $G_{xz}$ (and $\mathcal{G}_{xx}$, $\mathcal{G}_{xy}$, and $\mathcal{G}_{xz}$, of course) can contribute. Hence, the magnetic-dipole-containing invariants reduce to

$$\alpha G = \frac{1}{9} \text{Im}[(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})(G_{xx}^* + G_{yy}^* + G_{zz}^*)] = \frac{1}{9} \text{Im} [\alpha_{xx} G_{xx}^*]$$

$$= -\frac{1}{9} \text{Im} [\alpha_{xx} G_{xx}^*]$$

(3.230)

and

$$\beta_s(G)^2 = \text{Im} [\alpha_{xx} G_{xx}^*] = -\text{Im} [\alpha_{xx} G_{xx}^*],$$

(3.231)

whereas the electric-quadrupole-including invariants vanish since they contain no terms $\alpha_{xx} \epsilon_{xx\delta} A_{x,\delta x}^*$ or $\alpha_{xx} \epsilon_{xx\delta} A_{x,\delta x}^*$ which could lead to a non-vanishing contribution to the ROA intensity. The remaining Raman invariants then read

$$\alpha^2 = \frac{1}{9} |\alpha_{xx}|^2$$

(3.232)

and

$$\beta_s(\alpha)^2 = |\alpha_{xx}|^2.$$  

(3.233)
Writing the $G_{xx}$-tensor contribution also in the general way,

$$G_{xx} = G^{\text{SES}}$$  \hspace{1cm} (3.234)

with

$$G^{\text{SES}} = \frac{1}{\hbar} \mu_{0j}^\text{el} m_{j0}^\text{el} \sum_{v_j \neq v_f, v_i} W_{v_j}(\omega_L)$$

$$= \frac{i}{\hbar} \mu_{0j}^\text{el} m_{j0}^\text{el} \int_0^\infty \exp \left\{ \frac{i(E_{v_i} + E + i\hbar \Gamma)t}{\hbar} \right\} dt \langle v_f | v_i(t) \rangle,$$  \hspace{1cm} (3.235)

the remaining invariants are given by

$$\alpha G = \frac{1}{9} \Im \left[ (\alpha_{\alpha \alpha}) (G_{\beta \beta})^* \right] = \frac{1}{9} \Im \left[ \alpha^{\text{SES}} (G^{\text{SES}})^* \right]$$  \hspace{1cm} (3.236)

and

$$\beta(G)^2 = \frac{1}{2} \Im \left[ 3(\alpha_{\alpha \beta}) (G_{\alpha \beta})^{ss} - (\alpha_{\alpha \alpha}) (G_{\beta \beta})^* \right]$$

$$= \Im \left[ \alpha^{\text{SES}} (G^{\text{SES}})^* \right].$$  \hspace{1cm} (3.237)

Employing the sum-over-states formalism, the ROA intensity for the ICP backscattering set-up, for example, is now determined by the dipole and rotatory strengths, $F_{j0} = |\mu_{j0}^\text{el}|^2$ and $R_{j0} = \Im \{\mu_{0j}^\text{el} m_{j0}^\text{el}\}$, respectively, of the transition from the electronic ground state to the excited electronic state labeled by $j$:

$$I_R - I_L(180^\circ) \sim \frac{96}{c} \Im \left[ \alpha_{xx} G_{xx}^* \right]$$

$$= \frac{96}{c} \frac{1}{\hbar} \mu_{0j}^\text{el} \mu_{j0}^\text{el} \Im \{\mu_{0j}^\text{el} m_{j0}^\text{el}\}^* \sum_{v_j \neq v_f, v_i} W_{v_j}(\omega_L)^2$$

$$= \frac{96}{c} \frac{1}{\hbar} |\mu_{j0}^\text{el}|^2 \Im \{\mu_{0j}^\text{el} (m_{j0}^\text{el})^*\} \sum_{v_j \neq v_f, v_i} W_{v_j}(\omega_L)^2$$

$$= -\frac{96}{c} \frac{1}{\hbar} F_{j0} R_{j0} \sum_{v_j \neq v_f, v_i} W_{v_j}(\omega_L)^2.$$  \hspace{1cm} (3.238)

The Raman intensity is obtained as [223]

$$I_R + I_L(180^\circ) \sim 48 |F_{j0}|^2 \sum_{v_j \neq v_f, v_i} W_{v_j}(\omega_L)^2$$  \hspace{1cm} (3.239)

and the ROA intensity as [301]

$$I_R - I_L(180^\circ) = -\frac{2R_{j0}}{cF_{j0}} [I_R + I_L],$$  \hspace{1cm} (3.240)

i.e., the ROA spectrum is monosignate and its sign is determined by the rotatory strength.
3.4.3 Resonance with two excited electronic states

If more than one resonant electronic state contributes to the ROA intensity, the interference between these states has to be taken into account [226]. For the case of two electronic states labeled by $j_1$ and $j_2$, we can choose the molecule-fixed coordinate system as a spherical coordinate system [312] [described by the zenith angle $\lambda$ (running from 0 to $\pi$) and the azimuth angle $\phi$ (which can have values from 0 to $2\pi$)] so that the electric-dipole moment vector for the first resonant state $j_1$ is oriented along the positive $x$ axis and the second one for the resonant state $j_2$ lies in the $xy$ plane. The angle between these two vectors is $\phi''$. The expressions for the polarizability components are then obtained as (we assume $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$) [312]

$$\begin{align*}
\alpha_{xx} &= \alpha_{j_1} + \alpha_{j_2} \cos^2 \phi'', \\
\alpha_{xy} &= \alpha_{j_2} \cos \phi'' \sin \phi'', \\
\alpha_{yy} &= \alpha_{j_2} \sin^2 \phi'', \\
\alpha_{zz} &= \alpha_{yz} = \alpha_{xz} = 0, \\
\alpha_k &= \frac{1}{\hbar} |\mu_{0k}\|^2 \sum_{v_k \neq v_f, v_i} W_{v_k}(\omega_L) \\
&= \frac{i}{\hbar} |\mu_{0k}\|^2 \int_0^\infty \exp \left\{ \frac{i(E_{v_i} + E + i\hbar \Gamma)t}{\hbar} \right\} dt \langle v_f | v_i(t) \rangle, \\
\end{align*}$$

(3.241)
(3.242)
(3.243)
(3.244)
(3.245)

where $k$ is $j_1$ or $j_2$.

We can also write the magnetic-dipole moment vector with the help of the angles $\phi$ and $\lambda$. The first one is the angle between the positive $x$-axis, defined by $\mu_{0j_1}$, and the line from the origin of the coordinate system to the point determined by the considered vector projected on the $xy$ plane. The latter, $\lambda$, corresponds to the angle between the positive $z$ axis and the line from the origin to the point given by the considered vector in space. The positive $z$ axis is clearly defined since the positive $x$ and $y$ axes are determined by $\mu_{0j_1}$ and $\mu_{0j_2}$. Employing the notations $\phi'$ and $\lambda'$ for the two angles corresponding to the magnetic-dipole moment vector of the resonant state $j_1$ and analogously $\phi$ and $\lambda$ for the magnetic-dipole moment vector of the resonant electronic state $j_2$, the components of the $G$ tensor are calculated as

$$\begin{align*}
G_{xx} &= G_{j_1} \sin \lambda' \cos \phi' + G_{j_2} \sin \lambda \cos \phi \cos \phi'', \\
G_{xy} &= G_{j_1} \sin \lambda' \sin \phi' + G_{j_2} \sin \lambda \sin \phi \cos \phi'', \\
G_{xz} &= G_{j_1} \cos \lambda' + G_{j_2} \cos \lambda \cos \phi'', \\
G_{yx} &= G_{j_2} \sin \lambda \cos \phi \sin \phi'', \\
G_{yy} &= G_{j_2} \sin \lambda \sin \phi \sin \phi'', \\
\end{align*}$$

(3.246)
(3.247)
(3.248)
(3.249)
(3.250)
\[ G_{yz} = G_{j2} \cos \lambda \sin \phi'' , \quad (3.251) \]
\[ G_{zx} = G_{zy} = G_{zz} = 0 , \quad (3.252) \]
\[ G_k = \frac{1}{\hbar} \mu_{0k} \sum_{\nu_k \neq \nu_f} W_{\nu_k}(\omega_L) \]
\[ = \frac{i}{\hbar} \mu_{0k} \sum_{\nu_k \neq \nu_f} \int_0^\infty \exp \left\{ \frac{i(E_i + E + i\hbar \Gamma) t}{\hbar} \right\} dt \langle \nu_f | v_i(t) \rangle , \quad (3.253) \]

where \( k \) is again \( j1 \) or \( j2 \). Inserting the expressions for \( \alpha \) and \( G \) given above, we arrive at the following expressions for the magnetic-dipole-containing invariants:

\[ \alpha G = \frac{1}{9} \text{Im}[(\alpha_{xx} + \alpha_{yy})(G^*_{xx} + G^*_{yy})] \]
\[ = \frac{1}{9} \text{Im}[(\alpha_{j1} + \alpha_{j2} \cos^2 \phi'' + \alpha_{j2} \sin^2 \phi'')(G^*_{j1} \sin \lambda' \cos \phi' + G^*_{j2} \sin \lambda \cos \phi \cos \phi'') \]
\[ + G^*_{j2} \sin \lambda \sin \phi \sin \phi''] \]
\[ = \frac{1}{9} \text{Im}[(\alpha_{j1} + \alpha_{j2})(G^*_{j1} \sin \lambda' \cos \phi' + G^*_{j2} \sin \lambda \cos \phi \cos \phi'') \]
\[ + G^*_{j2} \sin \lambda \sin \phi \sin \phi''] \quad (3.254) \]

and

\[ \beta(G)^2 = \frac{1}{2} \text{Im}[2\alpha_{xx}G^*_{xx} - \alpha_{xx}G^*_{yy} - \alpha_{yy}G^*_{xx} + 2\alpha_{yy}G^*_{yy} + 3(\alpha_{xy}G^*_{xy} + \alpha_{xy}G^*_{yx})] \]
\[ = \frac{1}{2} \text{Im}[2(\alpha_{j1} + \alpha_{j2} \cos^2 \phi'')(G^*_{j1} \sin \lambda' \cos \phi' + G^*_{j2} \sin \lambda \cos \phi \cos \phi'') \]
\[ - (\alpha_{j1} + \alpha_{j2} \cos^2 \phi'')(G^*_{j2} \sin \lambda \sin \phi \sin \phi'') \]
\[ - \alpha_{j2} \sin^2 \phi''(G^*_{j1} \sin \lambda' \cos \phi' + G^*_{j2} \sin \lambda \cos \phi \cos \phi'') \]
\[ + 2\alpha_{j2} \sin^2 \phi''G^*_{j2} \sin \lambda \sin \phi \sin \phi'' \]
\[ + 3\alpha_{j2} \cos \phi'' \sin \phi''(G^*_{j1} \sin \lambda' \sin \phi' + G^*_{j2} \sin \lambda \sin \phi \sin \phi'') \]
\[ + 3\alpha_{j2} \cos \phi'' \sin \phi''G^*_{j2} \sin \lambda \cos \phi \sin \phi'' \quad (3.255) \]

(which may be further simplified).

The only \( A \) tensor components which are needed in this coordinate system for the \( \beta(A)^2 \) invariant are \( A_{x,xz}, A_{y,xz}, A_{y,zz} \), and \( A_{y,yz} \) so that this invariant is obtained as

\[ \beta(A)^2 = \frac{1}{2} \omega_L [\alpha_{xx} A_{y,yz} - \alpha_{yy} A_{x,yz} + \alpha_{xy}(A_{y,yz} - A_{x,zz})] . \quad (3.256) \]
3.5 Relevance of individual contributions to Raman optical activity spectra

3.5.1 The bond polarizability model

As is demonstrated for the far-from-resonance approximation in section 3.3, the ROA intensities are determined by different combinations of three ROA invariants. An on-going discussion about the magnitude of these invariants compared to each other and their contributions to the ROA intensities can be found in the literature, especially with respect to the importance of the electric-quadrupole contributions (for instance, see Refs. [258,314–324]). In order to get more detailed information, several simplifying models have been developed, e.g., the atom–dipole interaction [325–327] and the bond polarizability model [23,328–331]. In the latter, the property tensors in the Placzek approximation (see section 3.3) are written as sums of local group polarizability tensors including also the origin dependence of the tensors. Assuming that the bonds are completely electronically isolated [332,333] and that the molecules consist only of idealized axially symmetric achiral groups, it can be shown by symmetry considerations that the isotropic contributions vanish and that the anisotropic electric-dipole–magnetic-dipole and electric-dipole–electric-quadrupole invariants yield equivalent contributions, i.e., $\alpha G' = 0$ and $\beta (G')^2 = \beta (A)^2$. Employing this approximation, the formulae of the ROA intensities for the diverse scattering directions — compare Eqs. (3.164)–(3.167) — reduce considerably and the expression for the forward scattering experimental set-up even vanishes [317]. The assumptions in this model are certainly oversimplifications of the true electronic properties of a molecule. In order to assess the magnitude of the model-inherent drawbacks with respect to the $A$ tensor contribution, we analyze in the following spectra of molecules which were examined experimentally with respect to the applicability of the bond polarizability model.

Large contributions from the electric-dipole–electric-quadrupole invariant were supposed to exist, for instance, in experimental spectra of (−)-β-pinene [316], which, however, were found experimentally some years later to be large contributions from the $\alpha G'$ invariant [317]. In order to confirm this experimental conclusion, we calculated the spectra of (−)-β-pinene. The spectrum of the backward scattering direction is shown in the upper left part of Fig. 3.2. As can be seen by comparison to the experimental data (see Fig. 3.2), the peaks of the calculated spectrum reproduce the ones of the experimental spectrum very well. We found negligible deviations in the intensities in the wavenumber region below 2000 cm$^{-1}$ when the contributions of the electric-dipole–electric-quadrupole invariant were omitted.

Experimental measurements of (+)-trans-pinane suggested that the bond polarizability model is valid for the largest part of the vibrational modes [317,330]. If the model is valid for this molecule, the intensity for the forward scattering set-up should be zero. However, the calculated intensity in the spectrum of the
3.5. Relevance of individual contributions to Raman optical activity spectra

Figure 3.2: Calculated ROA spectra (property tensors: BLYP/rDPS:3-21G; force field: BP86/RI/TZVP) of (−)-β-pinene [upper left-hand side; back-scattering set-up; experimental spectrum (left-hand side) reproduced from Ref. [317]]; (−)-trans-pinane [upper right-hand side; backward scattering set-up; experimental spectrum (right-hand side) reproduced from Ref. [267]] and (2S,3S)-(−)(2,3)-dimethyloxirane (bottom; forward scattering direction). The upper part of each spectrum shows the plot without the $A$ tensor contribution, the lower panel provides the full reference spectrum.

Forward scattering set-up does not vanish and no significant deviations occur when omitting the $\beta(A)^2$ contribution, also not in the higher wavenumber region.
or in the spectra of the other scattering directions. As a consequence, it cannot be concluded for (+)-trans-pinane that the contribution of the $\beta(A)^2$ invariant is equivalent to the one of the $\beta(G')^2$ invariant and that the $\alpha G'$ invariant is zero, opposed to the predictions of the bond polarizability model. The calculated spectrum of the backward scattering direction is given on the top of the right-hand side of Fig. 3.2, together with an experimental one.

Ref. [334] suggested large electric-quadrupole contributions in case of (2S,3S)-(-)(2,3)-dimethyloxirane at 722 cm$^{-1}$ based on the assumption of vanishing isotropic contributions. The only significant deviations in our calculated spectra when omitting the electric-quadrupole contribution can be seen in the forward scattering spectrum at 720 cm$^{-1}$, which confirms the experimental finding, and around 3000 cm$^{-1}$ (see lower part of Fig. 3.2). The sign inversion at 720 cm$^{-1}$ (an in-plane deformational mode of the carbon atoms) occurs because the $\beta(A)^2$ invariant shows a large positive value of $203 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$ whereas $\beta(G')^2$ only amounts to $74 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$. The contribution of the isotropic invariant is negligibly small. The deviations above 2700 cm$^{-1}$ belong to C-H stretching modes and provide $\beta(A)^2$ values which are almost as large as the ones of $\beta(G')^2$.

Yu, Freedman, and Nafie performed an interesting comparison of several terpene molecules with respect to the contributions of the electric-dipole–electric-quadrupole invariant [319] for selected normal modes based on experimental spectra. They found that the $\beta(A)^2$ invariant has the same sign as the $\beta(G')^2$ invariant and is three times smaller on average. Even larger contributions of the $\beta(A)^2$ invariant were determined, e.g., for (-)-myrtenol for some of the chosen normal modes. It can be seen from our calculations that there are normal modes for which the values of the electric-quadrupole-containing invariant are larger than one third of the magnetic-dipole-containing invariant. However, the deviations in the spectra are small. The only noteworthy reductions in the intensity due to omission of the electric-dipole–electric-quadrupole contributions occur in the spectrum of the forward scattering direction (see the left part of Fig. 3.3) at the wavenumbers 1426 and 1439 cm$^{-1}$ (bending vibrational modes of the hydrogen atoms). For the first one, the corresponding contributions of the $\beta(A)^2$, $\beta(G')^2$, and $45\alpha G'$ invariants are $-537 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$, $-622 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$, and $674 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$, respectively. Comparing the corresponding contributions of each invariant at 1439 cm$^{-1}$, each invariant shows an opposite sign. Another interesting molecule is (-)-myrtenal because the experimental data for the normal modes chosen in Ref. [319] suggest that the $\beta(A)^2$ values often carry an opposite sign compared to the ones of $\beta(G')^2$. As an example, the one of the backscattering direction is given on the right-hand side of Fig. 3.3. For this experimental set-up, all peaks belonging to $\beta(A)^2$ values which have signs other than the corresponding $\beta(G')^2$ values show an increase in the intensity. However, no large deviations between the intensities calculated with and without the $\beta(A)^2$ contribution are observed.
3.5. Relevance of individual contributions to Raman optical activity spectra

Figure 3.3: Calculated ROA spectra (property tensors: BLYP/rDPS3-21G; force field: BP86/RI/TZVP) of (−)-myrtenol (left-hand side; forward scattering set-up) and (−)-myrtenal (right-hand side; backscattering set-up). The upper part of each spectrum shows the plot without the $\mathbf{A}$ tensor contribution, the lower panel provides the full reference spectrum.

These examples show that, for the largest parts of the spectra studied in this section, the bond polarizability model appears to be a too simple model in order to be applicable. Negligible $\mathbf{A}$ tensor contributions have also been obtained for chiral metal complexes (compare section 5.2).

3.5.2 Atomic contributions to intensities

As is shown in the preceding section, the electric-quadrupole-containing invariant is often negligibly small compared to the invariants with the magnetic-dipole contributions. However, it is not only possible to assess the origin of ROA intensities with respect to the contributions of the invariants but also the invariants themselves can be examined in view of local contributions. One ansatz starts from the normal modes, from which so-called “localized modes” can be obtained by a suitable transformation (see section 3.5.3). Another approach is the decomposition of the intensities into contributions of atoms or group of atoms. Such a scheme has been developed, e.g., for VCD spectroscopy by Nafie and coworkers [335–339]. In the far-from-resonance approximation of ROA spectroscopy, the intensity is determined by the invariants containing the property tensor elements differentiated with respect to the normal coordinates (compare section 3.3). Hug developed an approach for the evaluation of local contributions of atoms or group of atoms [340]. This approach has been applied to
several organic compounds \([48, 54, 324, 341, 342]\) and helical conformers of heptasilanes \([323]\). For example, contributions to the \(\beta(G')^2\) invariant for normal coordinate \(Q_k\) are obtained via

\[
[\beta(G')^2]_k \sim \frac{1}{2} \left[ 3 \left( \frac{\partial \alpha_{\alpha\beta}}{\partial Q_k} \right)_0 \left( \frac{\partial G_{\alpha\beta}'}{\partial Q_k} \right)_0 - \left( \frac{\partial \alpha_{\alpha\alpha}}{\partial Q_k} \right)_0 \left( \frac{\partial G_{\alpha\alpha}'}{\partial Q_k} \right)_0 \right]
= \frac{1}{2} \sum_{A,B} \sum_{i \in A, j \in B} \left[ 3 I_{k\alpha\beta}^A \left( \frac{\partial \alpha_{\alpha\alpha}}{\partial R_{\mu\nu}^m} \right)_0 \left( \frac{\partial G_{\alpha\alpha}'}{\partial R_{\mu\nu}^m} \right)_0 L_{kj\delta}^B - I_{k\alpha\beta}^A \left( \frac{\partial \alpha_{\alpha\alpha}}{\partial R_{\mu\nu}^m} \right)_0 \left( \frac{\partial G_{\alpha\alpha}'}{\partial R_{\mu\nu}^m} \right)_0 L_{kj\delta}^B \right].
\]

(3.257)

The indices \(A\) and \(B\) run over the atoms or group of atoms for which the analysis is performed. In analogy, the local decomposition of the other invariants can be derived. The contributions of the atoms are visualized by group coupling matrices (see, for example, sections 5.3, 6.3, and 6.4) as proposed by Hug \([340]\). The rows and columns correspond to the atoms or groups of atoms. The magnitude of their contribution is represented by the area of circles, which are filled if the sign of the contribution is positive and empty if negative. In addition, the off-diagonal elements are usually summed up leading to triangular matrices.

Employing the IR intensity

\[
I_k \sim \left( \frac{\partial \mu_\alpha^2}{\partial Q_k} \right)^2,
\]

(3.258)

the local decomposition scheme can straightforwardly extended to IR and Raman spectroscopy \([343]\) by re-writing the derivatives of the electric-dipole and electric-dipole–electric-dipole tensor elements, respectively, as

\[
I_k \sim \sum_l c_l \left( \frac{\partial P_l^{(1)}}{\partial Q_k} \right)_0 \left( \frac{\partial P_l^{(2)}}{\partial Q_k} \right)_0 = \sum_l c_l \sum_{A,B} \sum_{i \in A, j \in B} L_{k\alpha\beta}^A \left( \frac{\partial P_l^{(1)}}{\partial R_{\mu\nu}^m} \right)_0 \left( \frac{\partial P_l^{(2)}}{\partial R_{\mu\nu}^m} \right)_0 L_{kj\delta}^B.
\]

(3.259)

\(P_l^{(1)}\) and \(P_l^{(2)}\) are components of the appropriate property, i.e., of the electric-dipole moment vector in case of IR and of \(\alpha\) in case of Raman intensities. \(c_l\) indicate the weighting factors for the various derivatives.

### 3.5.3 Localization of normal modes

The vibrational spectra of large molecules are usually difficult to interpret because they comprise a huge number of close-lying normal modes, which can be delocalized over the whole molecule. Thus, individual normal modes are
3.5. Relevance of individual contributions to Raman optical activity spectra

often not resolved in experiment because many of them contribute to one band in the observed vibrational spectrum. This makes it difficult to analyze how structural changes influence the position and intensity of the bands. To overcome this problem, the methodology of analyzing the calculated spectra in terms of localized modes can be applied [343]. For these artificial modes, also the corresponding intensities can be determined leading to a better understanding of the origin of the bands in the spectrum.

In order to examine vibrational spectra in terms of localized modes, one considers a subset of a normal modes, which are usually those normal modes that contribute to one band in the vibrational spectrum. These normal modes are collected in the matrix $\tilde{Q}^{\text{sub}}$ and can be transformed to a set of localized modes by means of a unitary transformation $U$,

$$\tilde{Q}^{\text{sub}} = Q^{\text{sub}} U. \quad (3.260)$$

The unitary transformation is chosen such that it yields the “most localized” transformed modes. This is achieved by maximizing $\xi(\tilde{Q}^{\text{sub}}) = \xi(Q^{\text{sub}} U)$, where $\xi(\tilde{Q}^{\text{sub}})$ is a suitably defined criterion that measures how localized a set of transformed modes $\tilde{Q}^{\text{sub}}$ is [343]. Here and in the remaining part of this section, the tilde is used to denote the localized modes or other quantities that are defined with respect to these localized modes. The localizing unitary transformation $U$ can then be determined using the Jacobi-sweep method as discussed in Ref. [343]. For the localization criterion $\xi(\tilde{Q}^{\text{sub}})$, different definitions can be employed. We apply the atomic-contribution criterion [343],

$$\xi_{\text{at}}(\tilde{Q}^{\text{sub}}) = \sum_{p=1}^{a} \sum_{i=1}^{M} (\tilde{C}^{\text{sub}}_{ip})^2, \quad (3.261)$$

where $\tilde{C}^{\text{sub}}_{ip}$ is the contribution of nucleus $i$ to the normal mode $\tilde{L}^{\text{sub}}_p$, which can be measured by the fraction of the kinetic energy of this atom in the normal mode as [48, 95, 340]

$$\tilde{C}^{\text{sub}}_{pi} = (\tilde{\tilde{L}}^{\text{sub}}_{pi})^2. \quad (3.262)$$

This criterion measures the number of atomic centers which contribute to each of the modes. It leads to localized modes to which as few atomic centers as possible contribute.

The localized modes are not eigenvectors of the mass-weighted Hessian $M^{\text{mw}}$ and, therefore, have no direct physical significance. Nevertheless, they can be useful for the interpretation of calculated vibrational spectra. For polypeptides and proteins, where the normal modes can be delocalized combinations of vibrations on different amino acid residues, the localized modes are each dominated by a vibration of one single residue. Furthermore, the localized modes on different residues involve similar atomic displacements, i.e., the set of localized modes
obtained for one vibrational band consists of modes that are very similar, but are located on different residues.

In order to analyze the positions and shapes of the bands in the vibrational spectra, it is useful to define the (vibrational) coupling matrix $\tilde{\Omega}$ [343],

$$\tilde{\Omega} = U^T \Omega U,$$

(3.263)

where $\Omega$ is a diagonal matrix with the vibrational frequencies $\nu_p = \omega_p / 2\pi$ of the considered normal modes on the diagonal. The vibrational frequencies of the normal modes and the transformation matrix $U$ can be obtained from the coupling matrix $\tilde{\Omega}$ by diagonalization. The eigenvectors of $\tilde{\Omega}$ are the rows of the transformation matrix $U$ (columns of the inverse transformation $U^T$) and give the composition of the normal modes in the basis of localized modes.

As is discussed in Ref. [343], the diagonal elements $\tilde{\Omega}_{pp}$ of this coupling matrix can be interpreted as vibrational frequencies of the localized modes. For a set of localized modes that are similar but located on different residues, the frequencies of the localized modes are very similar, i.e., the localized modes are energetically (almost) degenerate. A shift in the position of a band in the vibrational spectrum can then be understood in terms of a shift of the frequencies of the localized modes. Since these localized modes are very similar, it is sufficient to consider only one representative localized mode for analyzing this shift.

The off-diagonal elements $\tilde{\Omega}_{pq}$ can be understood as coupling constants. In the case of two degenerate localized modes, the magnitude of the corresponding coupling constant corresponds to half the frequency splitting between two normal modes which arise as combination of these localized modes. For non-degenerate localized modes and for a larger number of localized modes, more complicated coupling patterns arise. However, the resulting vibrational frequencies of the normal modes can still be understood in regard to the frequencies of the localized modes $\tilde{\Omega}_{pp}$ and the coupling constants $\tilde{\Omega}_{pq}$ between them. The coupling constants $\tilde{\Omega}_{pq}$ are in general small for localized modes that are centered on groups which are not spatially close. Consequently, for each localized mode only couplings with a small number of other modes is significant. Furthermore, in the case of polypeptides and proteins, the coupling constants between localized modes on neighboring residues in similar secondary structure elements are very similar. Therefore, the coupling matrix $\tilde{\Omega}$ in general has a rather simple structure, which allows to understand how the more complicated delocalized normal modes arise.

**Analysis of vibrational intensities in terms of localized modes**

The vibrational frequencies of the localized modes and the coupling constants between the localized modes can be used to analyze the positions of the bands in the vibrational spectrum. In addition, the localized modes can also be employed for analyzing both the total intensities of these bands as well as their band shapes.
The total intensity of one band (i.e., the intensity integrated over the whole band), to which the \( a \) normal modes \( L_p^{\text{sub}} \) with corresponding normal coordinates \( Q_p^{\text{sub}} \) contribute, is given by

\[
I_{\text{band}} \propto \sum_{p=1}^{a} \sum_{l} c_l \left( \frac{\partial P_l^{(1)}}{\partial Q_p^{\text{sub}}} \right)_0 \left( \frac{\partial P_l^{(2)}}{\partial Q_p^{\text{sub}}} \right)_0
\]

\[
= \sum_{p=1}^{a} \sum_{l} c_l \sum_{i=1}^{M} L_{p_{\text{loc} i}} \left( \frac{\partial P_l^{(1)}}{\partial \left( R_{\text{mw}} \right)_{i\alpha}^{\text{sub}}} \right)_0 \left( \frac{\partial P_l^{(2)}}{\partial \left( R_{\text{mw}} \right)_{i\beta}^{\text{sub}}} \right)_0 L_{p_{\text{loc} i}}^{\text{sub}}, \tag{3.264}
\]

As is shown in Ref. [343], this total intensity is invariant under unitary transformations among the contributing modes, and, therefore, the total intensities of the considered band can also be expressed in terms of the localized modes with normal coordinates \( \tilde{Q}_{p}^{\text{sub}} \), i.e.,

\[
I_{\text{band}} \propto \sum_{p=1}^{a} \sum_{l} c_l \left( \frac{\partial P_l^{(1)}}{\partial \tilde{Q}_p^{\text{sub}}} \right)_0 \left( \frac{\partial P_l^{(2)}}{\partial \tilde{Q}_p^{\text{sub}}} \right)_0 \tilde{L}_{p_{\text{loc} i}}^{\text{sub}}, \tag{3.265}
\]

This makes it possible to analyze the total intensity of the band under study by means of the localized modes. Since the localized modes obtained for one band are in general rather similar, also the intensities with respect to the localized modes will be similar. Therefore, it will usually be sufficient to consider only one representative localized mode from this set in order to understand the effects that determine the total intensity of a certain band.

**Analysis of band shapes in terms of localized modes** While the total intensity of a band in the vibrational spectrum is invariant under a unitary transformation of the contributing normal modes, the intensities corresponding to the individual transformed modes differ from those of the normal modes. As a consequence, in order to understand the shapes of the bands in the vibrational spectrum, the localized modes and their corresponding intensities alone are not sufficient, but also the couplings between them as well as the cross-terms in the intensities arising due to these couplings have to be considered.

In a similar fashion as described in section 3.5.2 for the decomposition of IR, Raman, and ROA intensities into local contributions, intensities of the normal modes within a certain band can be analyzed in terms of contributions of the corresponding localized modes. The normal mode \( L_p^{\text{sub}} \) can be expressed via the localized modes as [343]

\[
L_p^{\text{sub}} = \sum_q U_{qp}^{T} L_{q}^{\text{sub}} = \sum_q U_{pq} L_{q}^{\text{sub}}, \tag{3.266}
\]
i.e., the coefficients are given by the \( p \)-th column of \( U^T \), which can be obtained as an eigenvector of the coupling matrix \( \tilde{\Omega} \). Therefore, the intensity \( I_p \) associated with this mode can be decomposed as

\[
I_p = \sum_{qr} [I_p]_{qr} = \sum_{qr} U_{pq} U_{pr} [I]_{qr}
\]

with the intensity coupling matrix

\[
[I]_{qr} = \sum_l c_l \left( \frac{\partial P_l^{(1)}}{\partial \tilde{Q}_q} \right)_0 \left( \frac{\partial P_l^{(2)}}{\partial \tilde{Q}_r} \right)_0.
\]

This intensity coupling matrix describes the intensity and the arising coupling terms by means of the localized modes. The same intensity coupling matrix can be applied to all normal modes in the considered subset. Its diagonal elements \( [I]_{qq} \) are then given by the intensity with respect to the localized mode \( \tilde{L}_q^{\text{sub}} \), while the off-diagonal elements arise due to the coupling between two localized modes. Since the localized modes associated with one band in the vibrational spectrum are usually similar for modes located on different parts of the considered system, these terms will — similar to the case of the coupling matrix \( \tilde{\Omega} \) — often show a simple structure that is relatively easy to understand.

### 3.6 Intensity-carrying modes

Techniques for the analysis of ROA intensities obtained from calculations were discussed in section 3.5 by comparison of values of invariants and decomposition into local contributions. These are valuable tools in order to simplify the interpretation of spectra, especially for the large amount of data provided by calculations. This information is not directly accessible in experiment, which is a great advantage of theoretical spectroscopy, and leads to a deeper understanding of the accomplishment of the final intensities observed in the spectrum. Nevertheless, these approaches help to analyze bands with high intensity obtained from calculations, but they do not predict which normal modes carry high intensity.

The prediction of normal modes leading to intense bands in the spectrum is a difficult task. This is not only the case for ROA spectroscopy, but already for IR spectroscopy, which measures the absorption of IR light (for reviews on IR laser chemistry we refer to Refs. [344–346]). A necessary condition for the generation of a visible band in the IR spectrum is that at least one derivative of an electric-dipole moment component with respect to a normal coordinate evaluated at the equilibrium position is non-zero [95] (see section 3.5.2). For small molecules, these derivatives can easily be deduced by investigating all possible vibrations. A standard example is carbon dioxide, \( \text{CO}_2 \), which shows a symmetric and an antisymmetric stretching vibration. Furthermore, two bending modes can be
found which form a degenerate pair and have the same frequency [11]. The symmetric stretching vibration is IR inactive since the electric-dipole moment change is zero. The situation is different for Raman spectroscopy, which requires a change of the polarizability during the vibration in order to be Raman active. The polarizability is a tensor relating the induced electric-dipole moment to the electric-field vector of the incident radiation (see section 3.1). In a qualitative picture, the polarizability can be understood as a measure for the deformability of the electron cloud around an atom or a molecule [347]. It is difficult to envisage how it changes during a vibration. Only in the case of high point-group symmetry a (non-)occurrence of bands can be predicted as highlighted by the so-called rule of mutual exclusion [11]. It states that Raman-active modes of molecules with a center of symmetry are not IR active and vice versa because the property operators in the intensity theory of both spectroscopic techniques strictly transform according to different irreducible representations of the point group of the molecule. In ROA spectroscopy [23, 25, 26], the situation is even more involved because not only electric-dipole, but also magnetic-dipole and electric-quadrupole interactions have to be considered.

An interesting aspect in this context is the concept of the ICMs [348,349], which are collective distortions of the molecular structure that carry all intensity and are in general not equal to normal modes. They allow one to understand which movements in the molecule bring about high intensity. This is especially attractive for molecules containing more than only a few atoms because the Raman and ROA property tensor as well as electric-dipole moment alterations are not straightforward to predict on the basis of conceptual arguments or by some rules of thumb. Torii et al. derived ICMs first for IR spectroscopy [348]. Three years later the concept was extended to (hyper)polarizabilities [349]. In this thesis, IR and Raman ICMs are derived in an alternative way and extended to ROA spectroscopy [350,351].

3.6.1 Hypothetical distortions with maximum infrared intensities

The derivative of the electric-dipole moment elements, needed for the IR intensity of normal coordinate $Q_k$ [compare Eq. (3.258)], can be written as

$$\left( \frac{\partial \mu_\alpha}{\partial Q_k} \right)_0 = \sum_{i=1}^{M} \left( \frac{\partial \mu_\alpha}{\partial R_{i\beta}^{\text{nw}}} \right)_0 \left( \frac{\partial R_{i\beta}^{\text{nw}}}{\partial Q_k} \right)_0$$

$$= \sum_{i=1}^{M} U_{\alpha,i\beta}^{\text{nw}} L_{ki\beta} = U_{\alpha}^{\text{nw}} \cdot L_k,$$

i.e., the Cartesian gradient $U_{\alpha}^{\text{nw}}$ of the electric-dipole moment component is projected onto the Hessian eigenvector $L_k$. Employing Eq. (3.269) the IR intensity can be expressed as

$$I_k \sim \left[ \left( U_{x}^{\text{nw}} \cdot L_k \right)^2 + \left( U_{y}^{\text{nw}} \cdot L_k \right)^2 + \left( U_{z}^{\text{nw}} \cdot L_k \right)^2 \right].$$
We search for a hypothetical mode $\tilde{L}_k$ which carries maximum IR intensity. Considering that $\sum_{i=1}^{M} (L_{ki\alpha})^2 = 1$, the condition for maximizing the intensity with respect to the vector components $L_{k(0)}^j$ of a guess vector $L_{k(0)}^j$ is given by

$$
\frac{\partial}{\partial L_{kj\beta}^{(0)}} \left[ \left( \sum_{i=1}^{M} U_{x,ia}^{mw} L_{ki\alpha}^{(0)} \right)^2 + \left( \sum_{i=1}^{M} U_{y,ia}^{mw} L_{ki\alpha}^{(0)} \right)^2 + \left( \sum_{i=1}^{M} U_{z,ia}^{mw} L_{ki\alpha}^{(0)} \right)^2 \right] - a_k \left( \sum_{i=1}^{M} (L_{ki\alpha}^{(0)})^2 - 1 \right) = 0,
$$

(3.271)

where the Lagrangian multiplier $a_k$ ensures normalization. Carrying out the differentiation yields

$$
2 \left[ \left( \sum_{i=1}^{M} U_{x,ia}^{mw} L_{ki\alpha}^{(0)} \right) U_{x,j\beta}^{mw} + \left( \sum_{i=1}^{M} U_{y,ia}^{mw} L_{ki\alpha}^{(0)} \right) U_{y,j\beta}^{mw} + \left( \sum_{i=1}^{M} U_{z,ia}^{mw} L_{ki\alpha}^{(0)} \right) U_{z,j\beta}^{mw} \right] - a_k L_{k(0)}^{(0)} = 0,
$$

(3.272)

which can be simplified, writing explicitly out the summation over repeated Greek indices, to

$$
\sum_{i=1}^{M} \sum_{\alpha=x,y,z} U_{a,ia\beta}^{mw} U_{a,j\gamma}^{mw} L^{(0)}_{k\beta\gamma} = a_k L^{(0)}_{k\beta},
$$

(3.273)

leading to the eigenvalue problem

$$
W \tilde{L}_k = a_k \tilde{L}_k.
$$

(3.274)

$\tilde{L}_k$ are the normalized solution vectors fulfilling Eq. (3.271). $W$ is a matrix of dimension $(3M,3M)$ with elements (summations are explicitly given)

$$
W_{j\beta\gamma} = \sum_{\alpha=x,y,z} U_{a,ia\beta}^{mw} U_{a,j\gamma}^{mw}
$$

(3.275)

and the eigenvalue $a_k$ is proportional to the IR intensity of $\tilde{Q}_k$,

$$
I_k \sim a_k = \left[ \left( \frac{\partial \mu_x}{\partial \tilde{Q}_k} \right)_0^2 + \left( \frac{\partial \mu_y}{\partial \tilde{Q}_k} \right)_0^2 + \left( \frac{\partial \mu_z}{\partial \tilde{Q}_k} \right)_0^2 \right],
$$

(3.276)

where $\tilde{Q}_k$ is the hypothetical normal coordinate corresponding to $\tilde{L}_k$.

In general, there are three intense modes corresponding to the $x$-, $y$-, and $z$-components of the electric-dipole moment. These are the ICMs \[348\], which were found by Torii et al. via an alternative derivation of Eq. (3.274) \[348\].
3.6.2 Raman intensity-carrying modes

In an analogous way, the ICMs for Raman spectroscopy can be derived. Starting from the double harmonic approximation (compare section 3.3), the Raman activity or scattering factor \([95, 96]\) for the normal coordinate \(Q_k\) is given as

\[
I_k = 45a^2 + 7\gamma^2 \\
= 12 \left[ \left( \frac{\partial \alpha_{xx}}{\partial Q_k} \right)_0 \left( \frac{\partial \alpha_{yy}}{\partial Q_k} \right)_0 + \left( \frac{\partial \alpha_{yy}}{\partial Q_k} \right)_0 \left( \frac{\partial \alpha_{zz}}{\partial Q_k} \right)_0 \right] \\
+ 3 \left[ \left( \frac{\partial \alpha_{xx}}{\partial Q_k} \right)_0 \left( \frac{\partial \alpha_{yy}}{\partial Q_k} \right)_0 + \left( \frac{\partial \alpha_{yy}}{\partial Q_k} \right)_0 \left( \frac{\partial \alpha_{zz}}{\partial Q_k} \right)_0 + \left( \frac{\partial \alpha_{xx}}{\partial Q_k} \right)_0 \left( \frac{\partial \alpha_{zz}}{\partial Q_k} \right)_0 \right] \\
+ 21 \left[ \left( \frac{\partial \alpha_{xy}}{\partial Q_k} \right)_0^2 + \left( \frac{\partial \alpha_{yz}}{\partial Q_k} \right)_0^2 + \left( \frac{\partial \alpha_{xz}}{\partial Q_k} \right)_0^2 \right].
\]

(3.277)

Introducing the vector of derivatives of the polarizability components with respect to mass-weighted Cartesian coordinates, \(U_{\alpha\beta}^\text{mw}\), the derivative of the polarizability with respect to \(Q_k\) can be written as

\[
\left( \frac{\partial \alpha_{\alpha\beta}}{\partial Q_k} \right)_0 = \sum_{i=1}^{M} \left( \frac{\partial \alpha_{\alpha\beta}}{\partial R_{i\gamma}^\text{mw}} \right)_0 \left( \frac{\partial R_{i\gamma}^\text{mw}}{\partial Q_k} \right)_0 = \sum_{i=1}^{M} U_{\alpha\beta,i}^\text{mw} L_{ki\gamma} = U_{\alpha\beta}^\text{mw} \cdot L_k.
\]

(3.278)

The Raman activity for normal coordinate \(Q_k\) is then evaluated as

\[
I_k = 12 \left\{ \left( U_{xx}^\text{mw} \cdot L_k \right)^2 + \left( U_{yy}^\text{mw} \cdot L_k \right)^2 + \left( U_{zz}^\text{mw} \cdot L_k \right)^2 \right\} \\
+ 3 \left\{ \left( U_{xx}^\text{mw} \cdot L_k \right) \left( U_{yy}^\text{mw} \cdot L_k \right) + \left( U_{xx}^\text{mw} \cdot L_k \right) \left( U_{zz}^\text{mw} \cdot L_k \right) \right\} \\
+ \left\{ \left( U_{xy}^\text{mw} \cdot L_k \right) \left( U_{yz}^\text{mw} \cdot L_k \right) \right\} + 21 \left\{ \left( U_{xy}^\text{mw} \cdot L_k \right)^2 \right\}.
\]

(3.279)

We now search for vectors \(\tilde{L}_k\) leading to the highest Raman activity. The condition of maximizing the scattering factor with respect to the elements of the guess vector \(L_k^{(0)}\) is given by (compare section 3.6.1)

\[
\frac{\partial}{\partial L_{kj\alpha}^{(0)}} \left[ I_k - a_k \left( \sum_{i=1}^{M} (\tilde{L}_{ki\alpha}^{(0)})^2 - 1 \right) \right] = 0.
\]

(3.280)

Employing \(b_k \equiv (2/3)a_k\) and writing explicitly out the summation over repeated
Greek indices yields

\[
8 \sum_{i=1}^{M} \sum_{\alpha=x,y,z}^{\beta=x,y,z} U_{\alpha\alpha,i}^{\text{mw}} U_{\alpha\beta,j}^{\text{mw}} \tilde{L}_{ki}^{(0)} + \sum_{i=1}^{M} \sum_{\alpha=x,y,z}^{\beta=x,y,z} U_{\alpha\beta,i}^{\text{mw}} U_{\beta\beta,j}^{\text{mw}} \tilde{L}_{ki}^{(0)}
\]

\[
+7 \sum_{i=1}^{M} \sum_{\alpha=x,y,z}^{\beta=x,y,z} U_{\alpha\beta,i}^{\text{mw}} U_{\alpha\beta,j}^{\text{mw}} \tilde{L}_{ki}^{(0)} = b_k \tilde{L}_{k}^{(0)},
\]

which leads similar as in section 3.6.1 to an eigenvalue problem

\[
W \tilde{L}_k = b_k \tilde{L}_k,
\]

where \( \tilde{L}_k \) are the normalized vectors fulfilling Eq. (3.280) and \( W \) is a matrix with elements (summations over repeated Greek indices are explicitly given)

\[
W_{\alpha\beta} = 8 \sum_{\alpha=x,y,z}^{\beta=x,y,z} \frac{\partial \alpha\alpha}{\partial \tilde{Q}_k} \left( \frac{\partial \alpha\alpha}{\partial \tilde{Q}_k} \right)^T + \sum_{\alpha=x,y,z}^{\beta=x,y,z} \frac{\partial \alpha\beta}{\partial \tilde{Q}_k} \left( \frac{\partial \alpha\beta}{\partial \tilde{Q}_k} \right)^T
\]

Introducing the hypothetical normal coordinates \( \tilde{Q}_k \) corresponding to the ICMs \( \tilde{L}_k \),

\[
\tilde{Q}_k = \sum_{i=1}^{M} \tilde{L}_{ki} r_{\text{mv}}^{\text{mw}},
\]

the eigenvalues \( b_k \) (with all summations written out) are given by

\[
b_k = 8 \left[ \sum_{\alpha=x,y,z}^{\beta=x,y,z} \left( \frac{\partial \alpha\alpha}{\partial \tilde{Q}_k} \right)^2 \right] + \sum_{\alpha=x,y,z}^{\beta=x,y,z} \left( \frac{\partial \alpha\alpha}{\partial \tilde{Q}_k} \right) \left( \frac{\partial \alpha\beta}{\partial \tilde{Q}_k} \right)
\]

\[
+7 \sum_{\alpha=x,y,z}^{\beta=x,y,z} \left( \frac{\partial \alpha\beta}{\partial \tilde{Q}_k} \right) \left( \frac{\partial \alpha\beta}{\partial \tilde{Q}_k} \right).
\]

These are not proportional to the Raman activity due to the fact that we have mixed terms \( \frac{\partial \alpha\alpha}{\partial \tilde{Q}_k} \frac{\partial \alpha\beta}{\partial \tilde{Q}_k} \) in addition to the terms of the type \( \frac{\partial \alpha\alpha}{\partial \tilde{Q}_k} \frac{\partial \alpha\alpha}{\partial \tilde{Q}_k} \) in \( I_k \) which do not lead to a factor of two in the differentiation. This is in contrast to the eigenvalue equation in the derivation of the IR ICMs in section 3.6.1 in which the eigenvalues are directly proportional to the IR intensity.
The diagonalization of $W$ in Eq. (3.282) yields only six nonzero eigenvalues corresponding to the six Raman ICMs, and thus most eigenvalues of $W$ vanish. The polarizability has six independent components, and therefore we get these six intense modes as has also been found by Torii [349]. However, Torii determined the Raman ICMs by employing an iterative procedure, projecting out an optimized ICM from the vector space and optimizing another ICM in the new vector space.

### 3.6.3 Intensity-carrying modes in Raman optical activity spectroscopy

For ROA spectroscopy, the intensity for the SCP, ICP, and DCPI backscattering set-ups in the far-from-resonance approximation (see section 3.3) is evaluated as

$$I_R - I_L(180^\circ) \sim \frac{8}{c} [12\beta(G')^2 + 4\beta(A)^2]. \quad (3.286)$$

For the intensity of normal coordinate $Q_k$, the derivatives of the tensor components with respect to $Q_k$ are needed, which are omitted here for the sake of brevity.

The condition for the determination of the most intense hypothetical [backscattering] mode leads to a similar eigenvalue equation as given in Eq. (3.282). Employing the notation $B^{mnw}$ for the mass-weighted Cartesian derivative of the $G'$ tensor elements and $C^{mnw}$ for the mass-weighted Cartesian $A$-tensor derivatives the matrix elements are evaluated as

$$W_{\alpha\beta,j} =$$

$$6 \sum_{\alpha = x, y, z} (U^{mnw}_{\alpha\alpha,i} B^{mnw}_{\alpha\beta,j} + B^{mnw}_{\alpha\alpha,i} U^{mnw}_{\alpha\beta,j}) - 3 \sum_{\alpha, \beta = x, y, z, \alpha \neq \beta} (U^{mnw}_{\alpha\beta,i} B^{mnw}_{\alpha\beta,j} + B^{mnw}_{\alpha\beta,i} U^{mnw}_{\alpha\beta,j})$$

$$+ 9 \sum_{\alpha, \beta = x, y, z, \alpha \neq \beta} (U^{mnw}_{\alpha\beta,i} B^{mnw}_{\alpha\beta,j} + B^{mnw}_{\alpha\beta,i} U^{mnw}_{\alpha\beta,j}) + \omega_L \left[ U^{mnw}_{yy,i} C^{mnw}_{xy,j} + C^{mnw}_{yy,i} U^{mnw}_{yy,j} \right], \quad (3.287)$$

where the summation over repeated Greek indices is explicitly given. The hypothetical mode with the highest ROA backscattering intensity is easily identified.
because the eigenvalues are proportional to the ROA intensity given in Eq. (3.286). In an similar way, ICMs can be derived for the forward (0°), polarized (90°), and depolarized (90°) scattering set-ups.

3.6.4 Examples of intensity-carrying modes

**L-tryptophan** As a first example, ICMs were calculated for the amino acid L-tryptophan [113, 351], whose vibrational spectra will be discussed in more detail in sections 4.2 and 6.3. Its most intense IR ICM is given in Fig. 3.4, for which a wavenumber of 927 cm⁻¹ was assigned in the first-iteration step of an intensity-tracking calculation (see section 4.2). This mode is dominated by the carbon atom of the carboxyl group which moves in a way combining stretching and out-of-plane deformational vibrations. The vibrations of the remaining part of the molecule are more or less deformational vibrations, both in- and out-of-plane. The most intense Raman and backscattering ROA ICMs are also shown in Fig. 3.4. In contrast to the IR ICM, the Raman ICM is mainly characterized by symmetric C–H stretching vibrations, whereas deformational vibrations do not dominate. This is also reflected in its wavenumber value of 2803 cm⁻¹. The ROA ICM of the backscattering experimental set-up corresponds to an assigned wavenumber of 2955 cm⁻¹, similar to the most intense Raman ICM. However, the mode also provides antisymmetric stretching vibrations.

Figure 3.4: The most intense IR (left-hand side), Raman (middle), and [backscattering] ROA (right-hand side) ICMs of L-tryptophan (BP86/RI/TZVP).

**Propane-1,3-dione** Although acetylacetone is a small molecule, the determination of the Raman activity of the vibrations is already not straightforward. Of course, the spectra are well known and understood [352–354], but it is difficult to predict what the ICMs look like and how they change from the neutral species to the anion. For the sake of simplicity and an easier understanding, we substitute the methyl groups of acetylacetone by hydrogen atoms resulting in propane-1,3-dione. The corresponding anion is also investigated since it serves as a ligand for the metal complex in the following paragraph.
The Raman ICMs of propane-1,3-dione are shown in Fig. 3.5 [351]. The most intense one consists of a symmetric stretching vibration, for which a wavenumber of 2837 cm$^{-1}$ was assigned in the first iteration step of an intensity-tracking calculation and which is in accordance with the calculated Raman spectrum containing these types of vibration, e.g., in the intense normal modes at 2938 and 2804 cm$^{-1}$. The vibration leads to an overall extension of the molecular shape, so it is intuitively expected that this kind of vibration conveys to a change in the polarizability. Nevertheless, the Raman activity formula in Eq. (3.277) includes differences of polarizability element derivatives, which can, of course, lead to cancellation of contributions of certain polarizability component derivatives so that a statement about the intensity cannot be made so easily.

Figure 3.5: The Raman ICMs of propane-1,3-dione (upper part) and propane-1,3-dionate (lower part) (BP86/RI/TZVPP).
The second most intense ICM provides stretching vibrations, in which especially one central hydrogen atom moves, accompanied by an antisymmetric stretching vibration of the carbonyl groups. A rocking vibration of the methylene group is observed in the third most intense ICM whereas the outer groups perform a mixture of stretching and deformational vibrations. The fourth ICM contains a symmetric weak stretching vibration of the outer groups, but, in contrast to the first ICM, a mixture of bond length stretching and bond angle changing vibration for the middle group. More or less only deformational vibrations are found in the fifth ICM, which are similar to the sixth most intense ICM, except that the groups move in the perpendicular plane.

The two Raman ICMs with the highest intensity of propane-1,3-dionate (see Fig. 3.5) are also mainly characterized by stretching vibrations. The most intense one (2541 cm$^{-1}$) is a totally symmetric vibration similar to the most intense ICM of propane-1,3-dione. Corresponding intense stretching vibrations in the calculated Raman spectrum are observed at 2572 cm$^{-1}$ for the outer two hydrogen atoms and at 3030 cm$^{-1}$ for the inner hydrogen atom. The second ICM (2373 cm$^{-1}$) shows a combination of antisymmetric stretching vibrations of the carbonyl groups. A similar vibration gives rise to the intense band at 2554 cm$^{-1}$ in the calculated Raman spectrum. The remaining ICMs are primarily characterized by deformational vibrations of the hydrogen atoms bound to the carbonyl groups: The third one contains an in-plane bending vibration, the fourth one an out-of-plane wagging and the fifth one an out-of-plane twist vibration. The sixth ICM is similar to the third ICM, featuring a bending vibration together with a stretching vibration of the middle hydrogen atom (though, the carbon atoms exhibit a more pronounced C–C bond stretching than in the third ICM).

**A-tris(propane-1,3-dionato)cobalt(III)** Acetylacetonate is often used as a ligand for metal complexes. In analogy to this, we investigate the chiral complex A-tris(propane-1,3-dionato)cobalt(III), which also exhibits ROA activity and which contains the simpler propane-1,3-dionate ligand. The Raman ICMs of A-tris(propane-1,3-dionato)cobalt(III) are shown in Fig. 3.6 [351]. They are basically characterized by stretching and in-plane deformational vibrations. The most intense Raman ICM provides a totally symmetric stretching combination of the C–H bonds, which resembles the most intense Raman ICM of the free anion except of the carbonyl stretching, which shows the reversed direction. The second Raman ICM combines symmetric and antisymmetric stretching vibrations. This is also found for the third Raman ICM except of one ligand, which resembles the in-plane deformational vibration and the antisymmetric stretching vibration of the second Raman ICM of propane-1,3-dionate. Similarities compared to the Raman ICMs of the free propane-1,3-dionate can be observed for the fourth Raman ICM, which provides bending vibrations like the third and six Raman ICMs of the free anion and some out-of-plane wagging like in the fourth Raman ICM of propane-1,3-dionate. The fifth and sixth Raman ICMs are similar in this regard and show another combination of these kinds of
vibrations. As a consequence, the Raman ICMs of the complex can in a large part be understood as composed of Raman ICMs of the free ligand.

Figure 3.6: The six Raman ICMs of Λ-tris(propane-1,3-dionato)cobalt(III) (BP86/RI/TZVPP).

In ROA spectroscopy, not only the electric-dipole–electric-dipole polarizability plays a role but also the magnetic-dipole and electric-quadrupole moment operators included in the $G'$ and $A$ tensors. It is difficult to imagine how this will affect the ROA ICM, but it is expected that the most intense ROA ICM of Λ-tris(propane-1,3-dionato)cobalt(III) is not equal to the most intense Raman ICM. As can be seen in Fig. 3.7, this is indeed the case. The Raman ICM features totally symmetric C–H stretching vibrations, the corresponding
ROA ICM for the backward scattering describes a mixture of deformational and stretching vibrations. This is especially the case for the outer hydrogen atoms of the ligands, which move differently for each of the three ligands. The ROA intensity expression of the polarized experimental set-up contains, like the one of the backward scattering, a sum of $\beta(G')^2$ and $\beta(A)^2$, in addition to the contribution from the $\alpha G'$ invariant [compare Eq. (3.166)], which, however, is found to be negligible for the most intense ICM.

Figure 3.7: The most intense ROA ICMs of \( \Lambda \)-tris(propane-1,3-dionato)cobalt(III) for the backward (top, left-hand side), polarized (top, right-hand side), forward (bottom, left-hand side), and depolarized (bottom, right-hand side) scattering experimental set-ups (BP86/RI/TZVPP).

As is shown in Fig. 3.7, the most intense ICM for the polarized scattering is very similar to the most intense ICM for the backward scattering. The most intense ICM of the forward scattering set-up is characterized by symmetric hydrogen stretching vibrations (see Fig. 3.7), which resembles the most intense Raman ICM. Nevertheless, the motion of the carbon and oxygen atoms is quite different. In contrast to the most intense ICM of the polarized experimental set-up, the absolute intensity of the most intense ICM for the forward scattering contains a large contribution from the $\alpha G'$ invariant. This is, however, not the case for less intense ICMs. The most intense ICM for the depolarized experimental set-up, also presented in Fig. 3.7, is very similar to the ones of the backward
3.6. Intensity-carrying modes

and polarized scattering set-ups.
All in all, this example shows how difficult it would be to predict the movements in molecules leading to high Raman intensities based on intuition, even in this simply structured metal complex, which is built up by only one kind of ligand. The situation is in fact more complicated for ROA intensities due to the involvement of magnetic-dipole and electric-quadrupole moment operators and the lengthy intensity formulae [compare Eqs. (3.164)–(3.167)] containing many differences between tensor-element derivatives, which are prohibitive for an intuitive understanding.
4. Algorithmic Developments for efficient Quantum Chemical Calculations of Infrared, Raman, and Raman Optical Activity Spectra

Two different, but complementary routes for the speed-up of ROA calculations have been explored in course of this thesis. On the one hand, the calculation of ROA tensors has been improved by evaluating them in the framework of KS-DFT employing density-fitting techniques. The corresponding theoretical foundations are given in the first section of this chapter. Due to the implementation of the (in the program package TURBOMOLE) missing electric-dipole–electric-quadrupole tensor (see appendix A), fast ROA calculations have become possible, which have been the prerequisite for the calculation of the ROA spectra presented in the following sections. On the other hand, the so-called intensity-tracking is described in section 4.2. It facilitates a fast access to theoretical IR, Raman, and ROA spectra of large molecules by selectively calculating normal modes with high intensity.

4.1 Efficient calculation of Raman optical activity property tensors

The first ROA calculation was performed by Bose et al. in 1989 [355]. They employed the static limit approximation for the property tensor calculations, where the dependence on the angular frequency of the incident light is neglected. Nowadays, linear response theory is employed [40, 43, 356–362], which gives the response of a system, initially in a stationary state, to a small perturbation, which is switched on slowly [363]. Since only KS-DFT is employed in this thesis, we derive the corresponding TDKS response framework for the evaluation of the ROA tensors in the far-from-resonance approximation in more detail.

The basis for DFT are the Hohenberg–Kohn theorems [87], of which the first one states that the ground-state electron density determines — within an additive constant — the external potential. An extension for time-dependent DFT (TD-DFT) [364] is provided by the Runge–Gross theorem [365] which proves that there is also a 1:1 correspondence between the time-dependent density $\rho^{KS}(r_1, t)$ and the external potential $v(r_1, t)$. Assuming an effective potential $v_{\text{eff}}(r_1, t)$ for a non-interacting electron system, whose orbitals $|k_{\alpha}(r_1, t)\rangle$ yield the same density as the interacting system, a TDKS one-particle equation is obtained [366,
with the time-dependent effective KS potential

\[ v_{\text{eff}}(\mathbf{r}_1, t) = v_{\text{ext}}(\mathbf{r}_1, t) + v_{\text{coul}}(\mathbf{r}_1, t) + v_{\text{xc}}(\mathbf{r}_1, t), \]

(4.2)

which is the time-dependent analogon of the effective potential in the static KS equation [see Eq. (1.22)].

In general, in the presence of an external electromagnetic field the momentum operator has to be replaced by the mechanical momentum

\[ \pi = p - q_e \mathbf{A}(\mathbf{r}_1, t) \]

and the external potential is given by

\[ v_{\text{ext}}(\mathbf{r}_1, t) = v_{\text{ext}}(\mathbf{r}_1, t) + v_{\text{appl}}(\mathbf{r}_1, t) \]

with

\[ v_{\text{appl}}(\mathbf{r}_1, t) = q_e \Phi(\mathbf{r}_1, t) \]

[compare, e.g., Eq. (3.22)]. The consideration of time-dependent external magnetic fields requires the employment of time-dependent current-density functional theory [363, 368–373]. However, this is not necessary for our purpose. The electric-dipole–magnetic-dipole tensor can be calculated employing TDKS-DFT since the current-density obtained from the TDKS equations equals the current-density of an interacting system [368].

The change in the KS density due to the perturbation can be written as [366]

\[ \delta \rho_\sigma^{\text{KS}}(\mathbf{r}_1, t) = \rho_\sigma^{\text{KS-per}}(\mathbf{r}_1, t) - \rho_\sigma^{\text{KS}}(\mathbf{r}_1, t), \]

(4.3)

where \( \rho_\sigma^{\text{KS-per}}(\mathbf{r}_1, t) \) is the density with and \( \rho_\sigma^{\text{KS}}(\mathbf{r}_1, t) \) the density without the perturbation at time \( t \). Since frequency-dependent property tensors are of interest for ROA spectra calculations, the frequency-dependent density response \( \delta \rho_\sigma^{\text{KS}}(\mathbf{r}_1, \omega) \) is obtained via a Fourier transform from the time-dependent density response and evaluated as [366]

\[ \delta \rho_\sigma^{\text{KS}}(\mathbf{r}_1, \omega) = \sum_{i,j} \delta P_{ij}^{\sigma}(\omega) \langle k_{i\sigma}(\mathbf{r}_1) | k_{j\sigma}(\mathbf{r}_1) \rangle \]

(4.4)

with the linear density-matrix response

\[ \delta P_{ij}^{\sigma}(\omega) = \chi_{ij\sigma}(\omega) \delta \varepsilon_{ij\sigma}^{\text{eff}}(\omega) \]

(4.5)

where

\[ \chi_{ij\sigma}(\omega) = \frac{n_{i\sigma} - n_{j\sigma}}{\hbar \omega - (\epsilon_{j\sigma} - \epsilon_{i\sigma})}. \]

(4.6)

\( |k_{i\sigma}(\mathbf{r}_1)\rangle \) and \( |k_{j\sigma}(\mathbf{r}_1)\rangle \) are ground-state (unperturbed) KS spin orbitals, obtained from the static KS equation [Eq. (1.21)] and \( \epsilon_{i\sigma} \) and \( \epsilon_{j\sigma} \) the corresponding orbital energies. \( n_{i\sigma} \) and \( n_{j\sigma} \) are the occupation numbers of KS orbitals \( |k_{i\sigma}(\mathbf{r}_1)\rangle \) and \( |k_{j\sigma}(\mathbf{r}_1)\rangle \), respectively. The perturbation \( \delta \varepsilon_{ij\sigma}^{\text{eff}}(\omega) \) introduced into the KS Hamiltonian due to the applied external field is, to linear order, given by [363]

\[ \delta \varepsilon_{ij\sigma}^{\text{eff}}(\omega) = \varepsilon_{ij\sigma}^{\text{appl}}(\omega) + \delta [\varepsilon_{ij\sigma}^{\text{coul}}(\omega) + \varepsilon_{ij\sigma}^{\text{xc}}(\omega)] \]

(4.7)
4.1. Efficient calculation of Raman optical activity property tensors

with

\[ v_{ij\sigma}^{\text{appl}}(\omega) = \langle k_{i\sigma}(r_1) | v_{\text{appl}}(r_1, \omega) | k_{j\sigma}(r_1) \rangle \]  \hspace{1cm} (4.8)

and

\[ \delta[v_{ij\sigma}^{\text{coul}}(\omega) + v_{ij\sigma}^{\text{xc}}(\omega)] = \sum_{kl\tau}[K_{ij\sigma,kl\tau}^{\text{coul}} + K_{ij\sigma,kl\tau}^{\text{xc}}(\omega)]\delta P_{kl\tau}^{\sigma}(\omega). \]  \hspace{1cm} (4.9)

A response from the Coulomb and exchange potentials exists because the density changes due to the external field so that the density response has to be solved iteratively.

The former part of the coupling matrix

\[ K_{ij\sigma,kl\tau}^{\text{coul}}(\omega) = \frac{q^2}{4\pi\varepsilon_0} \left\langle k_{i\sigma}(r_1) \left| \frac{1}{|r_1 - r_2|} k_{l\tau}(r_2) \right| k_{j\sigma}(r_1) \right\rangle \]  \hspace{1cm} (4.10)

and the latter as

\[ K_{ij\sigma,kl\tau}^{\text{xc}}(\omega) = \langle k_{i\sigma}(r_1) | f_{\sigma\tau}^{\text{xc}}(r_1, r_2, \omega) | k_{l\tau}(r_2) | k_{j\sigma}(r_1) \rangle, \]  \hspace{1cm} (4.11)

where usually the adiabatic approximation is applied for the exchange–correlation kernel

\[ f_{\sigma\tau}^{\text{xc}}(r_1, r_2, \omega) = \frac{\partial^2 E_{\text{xc}}[\rho^{\text{KS}}]}{\partial\rho^{\text{KS}}_\sigma(r_1) \partial\rho^{\text{KS}}_\tau(r_2)}. \]  \hspace{1cm} (4.12)

The subscripts ‘i’ and ‘j’ denote in the following occupied KS spin orbitals, whereas a and b indicate unoccupied ones. If the KS orbitals are real, the linear density matrix response can be determined via the coupled linear problem [363]

\[ \left[ \begin{array}{cc} A(\omega) & B(\omega) \\ B(\omega) & A(\omega) \end{array} \right] - \omega \left[ \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right] \left( \begin{array}{c} \delta P(\omega) \\ \delta P^*(\omega) \end{array} \right) = \left( \begin{array}{c} v_{\text{appl}}(\omega) \\ v_{\text{appl}}^*(\omega) \end{array} \right), \]  \hspace{1cm} (4.13)

which can be written with [368, 374]

\[ \Lambda(\omega) = \left( \begin{array}{cc} A(\omega) & B(\omega) \\ B(\omega) & A(\omega) \end{array} \right) \]  \hspace{1cm} (4.14)

and

\[ \Delta = \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right) \]  \hspace{1cm} (4.15)

as

\[ (\Lambda(\omega) - \omega\Delta) \left( \begin{array}{c} \delta P(\omega) \\ \delta P^*(\omega) \end{array} \right) = \left( \begin{array}{c} v_{\text{appl}}(\omega) \\ v_{\text{appl}}^*(\omega) \end{array} \right). \]  \hspace{1cm} (4.16)
$A$ and $B$ are the so-called orbital rotation Hessians with elements \[ A_{ia\sigma,jb\tau}(\omega) = \delta_{\sigma\tau} \delta_{ij} \delta_{ab} (\epsilon_{a\tau} - \epsilon_{ir}) + K_{ia\sigma,jb\tau}(\omega), \quad (4.17) \]
\[ B_{ia\sigma,jb\tau}(\omega) = K_{ia\sigma,jb\tau}(\omega). \quad (4.18) \]

$\delta P(\omega)$ contains the elements $\delta P_{ia\sigma}^\beta(\omega)$ of the density matrix response in the KS spin-orbital basis and $v_{\text{appl}}(\omega)$ the components $v_{ia\sigma}^\text{appl}(\omega)$.

In order to derive the ROA tensors, we employ in analogy to section 3 the multipole potential $v_{\text{appl}}(\omega) = -\mu_\alpha [E_\alpha(\omega)]_0 - \frac{1}{3} \theta_{\alpha\beta} [\nabla_\alpha E_\beta(\omega)]_0 - m_\alpha [B_\alpha(\omega)]_0 + \cdots$. The expectation value of the components of the real induced electric-dipole moment due to an electromagnetic perturbation can be written with the ROA tensors in the far-from-resonance approximation as [compare Eq. (3.68)] \[ \mu^\text{ind}_\alpha(\omega) = \alpha_{\alpha\beta}(\omega) [E_\beta(\omega)]_0 + G_{\alpha\beta}(\omega) [B_\beta(\omega)]_0 + \frac{1}{\omega} G'_{\alpha\beta}(\omega) [\dot{B}_\beta(\omega)]_0 + \cdots. \] (4.19)

As is obvious, $\alpha_\omega(\omega)$ is the response parameter of the induced electric-dipole moment to the applied electric field in first order so that its components can be calculated via

$$
\alpha_{\alpha\beta}(\omega) = \frac{\mu^\text{ind}_\alpha(\omega)}{[E_\beta(\omega)]_0}. \quad (4.20)
$$

Employing an external perturbation $v_{\text{appl},\beta}(\omega) = -\mu_\beta [E_\beta(\omega)]_0$, the induced electric-dipole moment component $\mu^\text{ind}_\alpha(\omega)$ is evaluated with the help of the density matrix response as

$$
\begin{align*}
\mu^\text{ind}_\alpha(\omega) &= (\mu_\alpha, \mu^*_\alpha) \left( \begin{array}{c} \delta P^\beta(\omega) \\ \delta P'^\beta(\omega) \end{array} \right) \\
&= (\mu_\alpha, \mu^*_\alpha) (\Lambda(\omega) - \omega \Delta)^{-1} \left( \begin{array}{c} v_{\text{appl},\beta}(\omega) \\ v'^{\text{appl},\beta}(\omega) \end{array} \right).
\end{align*}
$$

(4.21)

$\mu_\alpha$ is a vector containing components $\mu_{\alpha,ia}$, i.e., it consists of the $\alpha$ component of the electric-dipole moment operator in terms of the occupied and virtual KS spin orbitals. Inserting Eq. (4.21) into Eq. (4.20) yields

$$
\alpha_{\alpha\beta}(\omega) = -\text{Re}(\mu_\alpha, \mu^*_\alpha) (\Lambda(\omega) - \omega \Delta)^{-1} \left( \begin{array}{c} \mu_\beta \\ \mu^*_\beta \end{array} \right). \quad (4.22)
$$

In a similar fashion, the components of the $G'$ and $A$ tensors are evaluated [225, 376, 377]:

$$
\begin{align*}
G'_{\alpha\beta}(\omega) &= -\frac{1}{\omega} \text{Im}(\mu_\alpha, \mu^*_\alpha) (\Lambda(\omega) - \omega \Delta)^{-1} \left( \begin{array}{c} m_\beta \\ m^*_\beta \end{array} \right), \quad (4.23) \\
A_{\alpha,\beta\gamma}(\omega) &= -\text{Re}(\mu_\alpha, \mu^*_\alpha) (\Lambda(\omega) - \omega \Delta)^{-1} \left( \begin{array}{c} \theta_{\beta\gamma} \\ \theta^*_{\beta\gamma} \end{array} \right). \quad (4.24)
\end{align*}
$$
Resolution-of-the-identity density-fitting technique A popular method for the speed-up of KS-DFT calculations with pure density functionals, which do not involve computationally expensive Hartree–Fock exchange integrals (for the sake of clarity, we do not employ the bracket notation here)

\[ K_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \frac{q_e^2}{4\pi\varepsilon_0} \int \int k_{i\sigma}^*(\mathbf{r}_1)k_{j\sigma}^*(\mathbf{r}_2) \frac{1}{|r_1 - r_2|} k_{i\sigma}(\mathbf{r}_2)k_{j\sigma}(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2, \]

is the resolution-of-the-identity (RI) density-fitting method [363, 378–385]. The basic idea is the separation of the four-centre Coulomb integrals with the electron–electron repulsion integrals

\[ \frac{q_e^2}{4\pi\varepsilon_0} \int \int k_{i\sigma}^*(\mathbf{r}_1)k_{i\sigma}(\mathbf{r}_1) \frac{1}{|r_1 - r_2|} k_{j\sigma}^*(\mathbf{r}_2)k_{j\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \]

into three-center integrals employing an auxiliary basis for the density,

\[ \rho_{KS}(\mathbf{r}_2) \approx \rho_{KS,RI}(\mathbf{r}_2) = \sum_j a_j f_j(\mathbf{r}_2). \tag{4.25} \]

The coefficients \( a_i \) are usually chosen in such a way that

\[ \frac{q_e^2}{4\pi\varepsilon_0} \int \int [\rho_{KS}(\mathbf{r}_1) - \rho_{KS,RI}(\mathbf{r}_1)] \frac{1}{|r_1 - r_2|} [\rho_{KS}(\mathbf{r}_2) - \rho_{KS,RI}(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 = \min \tag{4.26} \]

holds. The approximate Coulomb integrals \( J_{ij}^{RI} \) are then obtained as

\[ J_{ij}^{RI} = \frac{q_e^2}{4\pi\varepsilon_0} \int \int k_{i\sigma}^*(\mathbf{r}_1)k_{i\sigma}(\mathbf{r}_1) \frac{1}{|r_1 - r_2|} \rho_{KS,RI}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \]

\[ = \frac{q_e^2}{4\pi\varepsilon_0} \sum_j a_j \int \int k_{i\sigma}^*(\mathbf{r}_1)k_{i\sigma}(\mathbf{r}_1) \frac{1}{|r_1 - r_2|} f_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \tag{4.27} \]

The Coulomb part of the coupling matrix in the TD-KS calculations, \( K_{ijkl}^{\text{coupl}} \), can be separated into three-centre integrals in an analogous way [363, 378]. Due to the RI approximation, the scaling of the calculation reduces from \( N_{bf}^4 \) to \( N_{aux} \cdot N_{bf}^3 \), where \( N_{bf} \) and \( N_{aux} \) are the number of basis and auxiliary basis functions, respectively [378].
4.2 Smart Approach to Infrared, Raman, and Raman optical activity spectra calculations: Intensity-Tracking

In standard vibrational spectra calculations, the harmonic approximation (see section 1.3) is employed and all normal modes and corresponding intensities are obtained. This leads not only to crowded spectra for large molecules, but also to a high computational effort, which usually increases with the number of atoms [112]. This effort, though, can be reduced by evaluation of solely a diminished number of normal modes applying the mode-tracking algorithm [386–388] for the selective calculation of normal modes. It employs a subspace iteration scheme without introducing any additional approximation except of the harmonic approximation. This procedure allows one to target only those collective motions that are of interest. However, a pre-defined guess for the relevant modes is needed, which is then converged to exact but selected normal modes of the system. The mode-tracking protocol has been successfully employed in a variety of different vibrational studies [46, 386–396].

In intensity calculations, predominantly the normal modes giving rise to high intensities are of interest because these are the ones easily recognized in the spectrum and of largest support in comparison with experimentally measured spectra. Yet, usually it is not known a priori which normal modes cause intense bands in the spectrum so that we do not have any good guess for the mode-tracking protocol and also, of course, not for the corresponding intensity.

A remedy is the intensity-tracking [113,350,351,397], which selectively tracks normal modes with high intensity without pre-defining guess modes for specific vibrations as in the mode-tracking approach. In contrast to RR spectra [397,398], the IR, Raman, and ROA spectra treated in this work often contain many intense normal modes. Consequently, a purely intensity-based selection could result in too many normal modes selected for optimization due to their high intensity, which would be less attractive especially in iterative solution procedures. Therefore, intensity-tracking is also combined with additional selection criteria like a predefined wavenumber range and the local contribution of certain atoms in order to demonstrate the benefits of the algorithm.

4.2.1 Theoretical background

Before the intensity-tracking ansatz is discussed, the most important steps of the underlying mode-tracking algorithm are briefly reviewed (for details, we refer to Ref. [386]).

4.2.1.1 The mode-tracking algorithm

Vibrational frequencies are usually determined by solving the eigenvalue equation

$$M^{\text{nmw}} L_k = \lambda_k L_k,$$

(4.28)
where $M^{\text{mw}}$ is the mass-weighted Hessian and $L_k$ and $\lambda_k$ are the normal mode and eigenvalue, respectively, to be determined (compare section 1.3). $\lambda_k$ is proportional to the square of the vibrational frequency of the normal mode $L_k$. In a mode-tracking calculation, the eigenvalues of the Hessian matrix are obtained via iterative solution of the equation

$$
(M^{\text{mw}} - \lambda_k^{(i)} L_k) = r_k^{(i)}
$$

with vector iteration methods similar to the one by Davidson [399]. The $i$-th iteration is denoted by superscript ‘$(i)$’ and $r_k^{(i)}$ is the residuum vector with the units hartree/[a.m.u. · bohr$^2$] (for brevity, we will skip the dimensions of the residuum vector in the following) corresponding to the approximate eigenvector $L_k^{(i)}$. The latter is expanded in a set of basis vectors $b_j$. For the first Cartesian mass-weighted basis vector $b_1 = L_k^{(0)}$, a guess is needed which is chosen to encode the scientific question with respect to a vibrational problem.

As a next step, the matrix–vector products

$$
\sigma_k = M^{\text{mw}} \cdot b_k
$$

are directly calculated without evaluation of the complete Hessian $M^{\text{mw}}$ as numerical directional derivatives of the analytical gradient of the electronic energy with respect to the basis vector $b_k$. From the reduced-dimensional Davidson matrix $\tilde{M}_{kl}^{\text{mw}} = b_k^T M^{\text{mw}} b_l$ in the $i$-th iteration the eigenvalues $\lambda_k^{(i)}$ and eigenvectors $c_k^{(i)}$ are obtained. An approximation to the exact eigenvector $L_k$ in Eq. (4.28) in the $i$-th iteration then reads

$$
L_k^{(i)} = \sum_{j=1}^{n(i)} c_k^{(i),j} b_j,
$$

where $n(i)$ is the total number of basis vectors employed in iteration $(i)$. As described in Ref. [386], also the residuum vectors $r_k^{(i)}$ can be constructed from the eigenpairs of the Davidson matrix. The next step is the selection of those approximate eigenvectors that should be further optimized. This can be accomplished in several ways. In a standard mode-tracking calculation, the eigenvectors are selected, for example, by overlap with the initial guess vector or with the selected eigenvectors of the previous iteration. The convergence of the selected eigenvectors is controlled by the magnitude of the residuum vectors. If all vectors are converged, the calculation is finished, otherwise the next iteration starts with additional basis vectors, which are generated via $b_{n(i)+l} = X^{(i)} r_k^{(i)}$ employing the preconditioner $X^{(i)}$. $l$ runs from 1 to the number of approximate eigenvectors, which are selected for further optimization.

### 4.2.1.2 Intensity-tracking

In contrast to the standard mode-tracking procedure, we are now interested in the normal modes with high intensity \textit{irrespective of their particular form of displacement}. 
We need a starting guess which contains information about the intensity and corresponds ideally to a mode with maximum intensity. The ICMs treated in section 3.6 are therefore the first choice for the guess vector employed in intensity-tracking calculations. For their evaluation, we need the matrices given in Eqs. (3.275), (3.283), and (3.287) in order to evaluate the eigenvector providing the most intense ICM. Since we usually do not have a full calculation available for the determination of the ICMs (otherwise no intensity-tracking calculation would be required), we need an alternative way for setting up these matrices.

**Calculation of the guess vector for IR intensity-tracking** For IR spectroscopy, we need the derivatives of the electric-dipole moment elements with respect to the Cartesian nuclear coordinates, which can be directly evaluated by the finite-field method [400, 401]:

\[
U_{\alpha,i\beta} = \left[ \frac{\partial \mu_{\alpha}}{\partial R_{i\beta}} \right]_0 = \left[ -\frac{\partial E_{el}}{\partial R_{i\beta}} \frac{\partial E_{el}}{\partial E_\alpha} \right]_0 = \left[ -\frac{\partial G_{i\beta}}{\partial E_\alpha} \right]_0. \tag{4.32}
\]

\(E_\alpha\) is the \(\alpha\) component of the applied external static electric field and \(G_{i\beta}\) the derivative of the electronic energy with respect to \(R_{i\beta}\). The derivatives of the electronic energy gradient \(G_{i\beta}\) with respect to the electric field are calculated via a three-point central difference formula [402],

\[
U_{\alpha,i\beta} \approx \left[ \frac{G_{i\beta}(E_\alpha + \Delta E_\alpha) - G_{i\beta}(E_\alpha - \Delta E_\alpha)}{2\Delta E_\alpha} \right]_0. \tag{4.33}
\]

They can thus be easily approximated from six single-point electronic energy gradient calculations in the presence of an electric field.

In addition, a very simple estimate for the elements of \(U_\alpha\) might be obtained by approximating the electric-dipole moment by (fixed) atomic partial charges, so that the electric-dipole moment derivatives can be obtained in a simple back-of-an-envelope calculation. Although this is computationally less demanding than the finite-field ansatz, in test calculations it turned out to be less successful [403].

As IR spectra are typically not dominated by one (or a few) intense bands, also other initial guess modes are tested that are even easier to set up. As can be seen in Eq. (3.270), the IR intensity is high if the overlap of \(U^\text{mw}_\alpha\) with \(L_k\) is large. That is why we also employ the relationship

\[
L_{k_{ja}}^{(0)} = |U^\text{mw}_{x_{ja}}| + |U^\text{mw}_{y_{ja}}| + |U^\text{mw}_{z_{ja}}| \tag{4.34}
\]

for the evaluation of the components of the initial guess. Furthermore, we use the modification

\[
L_{k_{ja}}^{(0)} = \sqrt{m_j} \left[ (U_{x_{ja}})^2 + (U_{y_{ja}})^2 + (U_{z_{ja}})^2 \right], \tag{4.35}
\]

where \(m_j\) denotes the mass of the corresponding atom, as well as an unspecified guess as a blind test (compare section 4.2.2.1). Preliminary calculations showed
that the difference in the convergence behaviour of the calculations is negligibly small if the guess vectors given in Eqs. (4.34) and (4.35) are employed and that the eigenvector determined via Eq. (3.274) even leads to worse results (see section 4.2.2.2). Therefore, only one of these approaches for the remaining IR intensity-tracking calculations is applied, namely the guess vector in Eq. (4.35). For comparison, some calculations are also performed with the unspecific guess.

**Initial guess for Raman and ROA intensity-tracking**  The most intense Raman ICM (see section 3.6.2) can be evaluated in a similar way to the determination of the IR starting distortion via the finite-field method [400]:

\[
U_{\alpha\beta,i} = \left[ \frac{\partial \alpha_{\alpha\beta}}{\partial R_{i\gamma}} \right]_0 = \left[ \frac{\partial \mu_{\alpha}}{\partial R_{i\gamma}} \right]_0 = \left[ \frac{\partial \mu_{\alpha}}{\partial \varepsilon_{\beta}} \right]_0 = \left[ \frac{\partial^2 G_{i\gamma}}{\partial \varepsilon_{\beta} \partial \varepsilon_{\alpha}} \right]_0.
\]

In principle, the guess vector for ROA intensity-tracking calculations would benefit from a similar procedure involving magnetic fields, but for the sake of simplicity, we rely also on the guess of Eq. (4.36) for the ROA intensity-tracking calculations.

It is obvious from the first equality sign in Eq. (4.36) that such a guess would benefit from analytic derivatives of the Raman and ROA polarizability tensors (and analogously of electric-dipole moments for IR spectroscopy) with respect to the nuclear coordinates \( R_{i\gamma} \) (see, e.g., Refs. [53, 404–406]). Hence, if such techniques are available, intensity-tracking can be even more efficient.

**Intensity-tracking procedure**  During the IR intensity-tracking calculation, we evaluate for each basis vector \( \mathbf{b}_j \) the electric-dipole moments of the structure distorted along this very same vector \( \mathbf{b}_j \) so that the derivatives of the electric-dipole moment components with respect to \( \mathbf{b}_j \) can be obtained employing the three-point central difference formula. The derivative of the electric-dipole moment components with respect to the approximate normal coordinate \( Q^{(i)}_k \) in the \( i \)-th approximation is calculated as

\[
\frac{\partial \mu_{\alpha}^{(i)}}{\partial Q^{(i)}_k} = \sum_{j=1}^{n^{(i)}} c_{k,j}^{(i)} \frac{\partial \mu_{\alpha,j}}{\partial \mathbf{b}_j}.
\]

The IR intensity is then given by

\[
I_k \sim \sum_{j=1}^{n^{(i)}} c_{k,j}^{(i)} \left[ \left( \frac{\partial \mu_{x,j}}{\partial \mathbf{b}_j} \right)^2 + \left( \frac{\partial \mu_{y,j}}{\partial \mathbf{b}_j} \right)^2 + \left( \frac{\partial \mu_{z,j}}{\partial \mathbf{b}_j} \right)^2 \right].
\]

The IR intensities of all approximate normal modes are calculated in each iteration, so that an approximate IR spectrum is available in each step. For
Raman/ROA intensity-tracking, the same procedure is performed but the corresponding property tensors and intensity expressions are evaluated instead of the electric-dipole moments and the IR intensity.

The second crucial point in an intensity-tracking calculation is the selection of those approximate normal modes that should be further optimized. In standard mode-tracking calculations, this root-homing step is carried out by comparing the overlap of the approximate normal modes in iteration \( i \) either with the initial guess vector or with those normal modes selected in iteration \( i-1 \). For intensity-tracking, however, we select the approximate normal modes with the highest IR/Raman/ROA intensity for further optimization and for the generation of the next basis vectors. Three different selection procedures are at hand:

(i) to select a fixed number of \( N \) normal modes which show the highest intensity,

(ii) to select so many high-intensity normal modes that the sum of their (relative) intensities is higher than a certain threshold,

(iii) to select all normal modes whose (relative) intensity exceeds a given threshold.

Procedure (i) leads to the generation of a maximum of \( N \) new basis vectors per iteration, whereas the number of new basis vectors per iteration is flexible when criteria (ii) and (iii) are applied. If all selected basis vectors are converged, the calculation is considered finished and an approximate spectrum is obtained.

However, all three criteria may lead to a large number of optimized normal modes if many vibrations feature high intensity, which is not unlikely in the case of large molecules. A remedy for reducing the number of calculated normal modes is the combination of intensity-tracking with further selection criteria in addition to the intensity-based ones. The additional criteria implemented for this work are the optimization of high-intensity normal modes in a specified frequency range as well as the optimization of intense normal modes that involve only selected atoms. The latter condition is tested by evaluating the norm

\[
|L_k^{\text{selected}}| = \sqrt{\sum_{i}^{\text{selected}} (L_{ki})^2},
\]

where the explicitly written sum runs over the set of chosen atoms. Only those normal modes are then considered for further optimization for which \( |L_k^{\text{selected}}| \) is larger than a certain threshold.

In addition, it is possible to solely track very local high-intensity normal modes. This is achieved by calculating the contribution of each atom to the norm of the approximate eigenvector and selecting the corresponding normal mode if this contribution exceeds a given value. If there is no approximate normal mode fulfilling a certain selection criterion, only the remaining criteria will be applied. If all approximate normal modes fail to meet the criteria (also the intensity-based ones), all available normal mode approximations are selected.
4.2.2 Infrared intensity-tracking

For extensive analyses of the IR intensity-tracking algorithm, a diverse test set of molecules was studied. The molecular structures selected are those of \((R)\)-epichlorhydrin, \((S)\)-methyloxirane, \((R)\)-alanine, \((M)\)-\(\sigma\)-[4]-helicene, \(\Delta(\delta\delta\delta)\)-tris(ethylenediaminato)cobalt(III), all-(S)-decaalanine, and of Schrock’s molybdenum complex, \([\text{HIPTNCH}_2\text{CH}_2\text{N}]\text{MoN}_2\) [HIPT (hexaisopropylterphenyl): 3,5-(2,4,6-\(i\)-Pr_3C_6H_2)_2C_6H_3] [407–410], depicted in Fig. 4.1.

Figure 4.1: Optimized structures (BP86/RI/TZVP) of \((R)\)-epichlorhydrin (1), \((S)\)-methyloxirane (2), \((R)\)-alanine (3), \((M)\)-\(\sigma\)-[4]-helicene (4), all-(S)-decaalanine (5), \(\Delta(\delta\delta\delta)\)-tris(ethylenediaminato)cobalt(III) (6), and Schrock’s dinitrogen molybdenum complex (7).
4.2.2.1 Organic molecules

In a first step, the intensity-tracking algorithm was applied to the small molecules (R)-epichlorhydrin (10 atoms), (S)-methyloxirane (10 atoms), and (R)-alanine (13 atoms). Several selection procedures were employed: (A) Selecting only the five approximate normal modes with the highest IR intensity (indicated in the following by \( N = 5 \), where \( N \) is the number of chosen approximate normal modes), (B) optimizing all high-intensity approximate normal modes whose intensity sum amounts to a certain relative intensity value \( I_{\text{sum}} \), and (C) choosing only normal modes with a relative IR intensity larger than a certain threshold \( I_{\text{min}} \). Besides the criterion in (A) with \( N = 5 \), also calculations employing the procedures in (B) and (C) with \( I_{\text{sum}} = 0.8 \), \( I_{\text{sum}} = 0.7 \), \( I_{\text{sum}} = 0.6 \) and \( I_{\text{min}} = 0.1 \), \( I_{\text{min}} = 0.2 \) and \( I_{\text{min}} = 0.3 \), respectively, were performed. For all these small molecules, the calculations required (almost) the full number of basis vectors if a convergence criterion of 0.0005 for the maximum element of the residuum vector \( (r_{\text{thres}}) \) was applied. No significant difference was found for \( r_{\text{thres}} = 0.001 \). As an example, the intensity-tracking IR spectrum of (R)-epichlorhydrin employing \( I_{\text{sum}} = 0.8 \) and \( r_{\text{thres}} = 0.0005 \) is shown in Fig. 4.2 together with the result from the full calculation. It can be seen that the intensity-tracking procedure indeed converges to the full spectrum of the conventional calculation since the latter and the spectrum from the intensity-tracking run are identical at the end of the calculations. The other selection procedures mentioned above also led to the full number of basis vectors and differed only slightly in the number of iterations.

The gain in computational effort in a mode-tracking calculation compared to a full semi-numerical frequency analysis [96] is given by the ratio of the number of basis vectors needed for convergence to the total number of degrees of freedom. The situation is changed if the diverse selection procedures in the intensity-tracking calculations are applied to \((M)\)-\(\sigma\)-[4]-helicene (21 atoms). The corresponding spectra are given in Fig. 4.2. It is obvious that all spectra feature converged bands for the C–H stretching vibrations at the higher wavenumber region about 3000 cm\(^{-1}\), which show by far the highest intensities in the spectrum. In spite of that, a different behaviour can be observed for the lower wavenumber range. The spectrum obtained with \( I_{\text{min}} = 0.1 \) totally resembles the one of the full calculation and required the total number (57) of basis vectors. \( I_{\text{min}} = 0.2 \) also yields a very good spectrum with 56 basis vectors comparable to the one obtained with \( I_{\text{sum}} = 0.8 \), for which 54 basis vectors were calculated. However, the significant bands at about 860 cm\(^{-1}\) were not converged if \( I_{\text{min}} = 0.3 \) (41 basis vectors), \( I_{\text{sum}} = 0.7 \) (40 basis vectors), and \( I_{\text{sum}} = 0.6 \) (32 basis vectors) were employed because the convergence of the high-intensity C–H stretching modes is already sufficient to satisfy these selection criteria. \( N = 5 \) (36 basis vectors) also resulted in converged normal modes for wavenumbers higher than 2900 cm\(^{-1}\) but all peaks with lower wavenumbers were not converged, including the intense peak at about 2470 cm\(^{-1}\). In general, a maximum value of 0.005 for \( r_{\text{thres}} \) was found in most cases to be appropriate in order to produce reliable
4.2. Intensity-Tracking

The choice of the selection procedures depends on the aim of the calculation. If solely a few bands with the highest intensity are searched, the procedure of optimizing only the $N$ most intense normal modes with, e.g., $N = 5$ is suitable. In the case of $(M)-\sigma-[4]$-helicene, also a small number of approximate normal modes was optimized if $I_{\text{sum}} = 0.6$, $I_{\text{sum}} = 0.7$ or $I_{\text{min}} = 0.3$ were applied since the spectrum shows a few high-intensity C–H stretching modes so that selecting the corresponding approximate normal modes is already sufficient to fulfill these selection criteria. In order to make sure that also vibrations in the wavenumber range below 2500 cm$^{-1}$, which is usually the interesting one in practical applications, are optimized, $I_{\text{sum}} = 0.8$, $I_{\text{min}} = 0.1$ or $I_{\text{min}} = 0.2$ should be applied. These statements, however, should not be seen as strict rules because the behaviour of the selection procedures of the intensity-tracking calculation depends, of course, on the spectral features of the investigated molecule.

As mentioned before, no reduction in computational effort was achieved for $(R)$-alanine with the intensity-tracking algorithm, but it can be expected that there will be a decrease for larger peptides like all-$(S)$-decaalanine (103 atoms).

As is obvious from Table 4.1, the computational effort for the calculation of (approximate) IR spectra is indeed considerably diminished for this molecule. In order to demonstrate that the calculation with the lowest number of basis vectors already yields a reliable approximate IR spectrum, the IR spectra of different iteration steps obtained with $I_{\text{min}} = 0.2$ (41 basis vectors) are shown in Fig. 4.3 together with the spectrum of the full calculation (303 normal modes). The most intense bands at around 3400 and 1600 cm$^{-1}$ are well reproduced in the intensity-tracking calculation. The intense peaks showing up at 3380, 1725, 1654, and 1517 cm$^{-1}$ in the full calculation were found in the intensity-tracking calculation at 3380, 1715, 1648, and 1593 cm$^{-1}$, respectively. The relative intensities do not exactly produce the ones of the full calculation because more bands overlap in the spectrum of the full calculation and the normal modes do not exactly resemble the ones of the full calculation due to the rather large threshold $r_{\text{thres}} = 0.005$. However, the most intense bands are easily recognizable in the spectrum obtained by the intensity-tracking calculation. 41 basis vectors were needed for this calculation, which gave rise to $41 \cdot 2 = 82$ displaced structures since the differentiation with respect to the basis vectors was done numerically via a three-point central difference formula [compare Eq. (4.33)] [402]. For each of these structures, the self-consistent field procedure lasted about one hour on one core of an AMD Opteron 270 machine and the analytic calculation of the electronic energy gradient and the determination of the electric-dipole moments about ten minutes. So, the total calculation in a non-parallel manner takes less than 96 hours (the time needed for additional steps in the intensity-tracking algorithm is negligible) compared to about 721 hours of a conventional semi-numerical calculation [96]. Any efficiency improvement in the energy and gradient calculations directly translates into a reduced effort in our semi-numerical calculation. Compared to entirely analytic implementations,
these calculations furthermore have the advantage, especially for the calculation of large molecules [96], that they can be performed in a massive-parallel manner so that the overall wall clock time for the intensity-tracking calculation (and, of course, also for the full calculation) can be reduced significantly.

Figure 4.2: Technical aspects of intensity-tracking calculations: (A) Demonstration of convergence to the exact IR spectrum in the limit of a complete basis: Intensity-tracking IR spectrum (BP86/RI/TZVP) of (R)-epichlorhydrin (1) employing $I_{\text{sum}} = 0.8$ and $r_{\text{thres}} = 0.0005$ compared to the conventional full calculation; (B) Analysis of root-homing options for a given convergence threshold per normal mode: Intensity-tracking IR spectra (BP86/RI/TZVP) of ($M$)-$\sigma$-[4]-helicene (4) obtained by applying different selection procedures and $r_{\text{thres}} = 0.0005$ together with the reference spectrum of the complete set of normal modes.

The procedure of selecting only the five highest-intensity normal modes ($N = 5$) also led to a well converged spectrum with a total number of 49 basis vectors. The same holds for the selection criteria $I_{\text{sum}} = 0.8$ (98 basis vectors), $I_{\text{sum}} = 0.7$ (64 basis vectors), and $I_{\text{min}} = 0.1$ (91 basis vectors). In contrast to that, a value of $I_{\text{sum}} = 0.6$ resulted in a spectrum which contains not all intense normal modes because not all important normal modes were chosen due to the low threshold. Therefore, at least a value of $I_{\text{sum}} = 0.7$ has to be set in order to get reliable approximate IR spectra for all-($S$)-decaalanine. All calculations in Table 4.1
4.2. Intensity-Tracking

were also carried out with \( r_{\text{thres}} = 0.001 \), but \( r_{\text{thres}} = 0.005 \) turned out to be sufficient.

Since IR spectra often contain a large number of intense normal modes (in contrast to, e.g., RR spectra), it may be possible that the initial guess is not decisive for the convergence of the algorithm. In order to test this assumption, we chose an unspecific guess, namely a breathing mode, where simply all coordinates are uniformly distorted. The results obtained with the breathing mode as initial guess are given in Table 4.1 and compared to those obtained with the finite-field guess according to Eq. (4.35). For the case of all-(S)-decaalanine, intensity-tracking calculations with the breathing mode chosen as a guess performed comparable to the guess gained by the finite-field ansatz [see Eq. (4.35)].

Table 4.1: Results of the intensity-tracking calculations [number of basis vectors (vectors), iterations, and converged normal modes (conv.)] for all-(S)-decaalanine (5) (total number of normal modes: 303) with the initial guess obtained by the finite-field method applying different selection procedures and values for the maximum component of the residuum vector; the values in parentheses present the results gained with a breathing mode as the initial guess.

<table>
<thead>
<tr>
<th>( r_{\text{thres}} )</th>
<th>0.005</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N = 5 )</td>
<td>vectors</td>
</tr>
<tr>
<td>( I_{\text{sum}} = 0.8 )</td>
<td>98 (114)</td>
</tr>
<tr>
<td>( I_{\text{sum}} = 0.7 )</td>
<td>64 (56)</td>
</tr>
<tr>
<td>( I_{\text{min}} = 0.1 )</td>
<td>91 (97)</td>
</tr>
<tr>
<td>( I_{\text{min}} = 0.2 )</td>
<td>41 (66)</td>
</tr>
</tbody>
</table>

4.2.2.2 \( \Delta(\delta\delta\delta)\)-Tris(ethylenediaminato)cobalt(III)

As an example for a transition-metal-containing molecule, we chose the metal complex \( \Delta(\delta\delta\delta)\)-tris(ethylenediaminato)cobalt(III), which contains 37 atoms. It has been subject of several theoretical investigations in the literature [225, 411–415] and a discussion of its ROA spectra can be find in section 5.

The results of the intensity-tracking calculations with \( r_{\text{thres}} = 0.005 \) and \( r_{\text{thres}} = 0.001 \) are shown in Table 4.2. The spectra for \( I_{\text{min}} = 0.1 \) and \( N = 5 \) as well as the result of the full calculation are given in Fig. 4.4. The most intense bands in the complete calculation can be found at 1594, 3345, and 3400 cm\(^{-1}\). These bands were converged in every intensity-tracking calculation listed in Table 4.2 that started from the usual finite-field guess [compare Eq. (4.35)] and they can also be observed in the spectra in Fig. 4.4 for the two plotted selection procedures. The next most intense peaks show up at about 1015, 1120, and 1420 cm\(^{-1}\), where the one at 1120 cm\(^{-1}\) carries the lowest intensity.
Figure 4.3: IR spectra (BP86/RI/TZVP) of all-(S)-decaalanine (5) for different iteration steps of the intensity-tracking calculation (bottom and middle) employing $I_{\text{min}} = 0.2$ and $r_{\text{thres}} = 0.005$. The reference spectrum at the top was obtained by a calculation of the complete set of normal modes. The arrow indicates the progress of the intensity-tracking iterations.

The two bands at about 1015 and 1420 cm$^{-1}$ were converged in all intensity-tracking calculations with this finite-field guess. In order to additionally achieve the optimization and convergence of the band at 1120 cm$^{-1}$, $r_{\text{thres}} = 0.001$ in combination with $I_{\text{min}} = 0.1$ or $I_{\text{sum}} = 0.8$ was necessary, which, however, led to the full set of normal modes. In some cases, especially the band at about 1015 cm$^{-1}$ shows a remarkably diminished relative intensity compared to the full calculation because only one intense peak was found instead of two intense ones in the full spectrum.

We tested also the eigenvector corresponding to the maximum IR intensity determined by Eq. (3.274) as initial guess for the intensity-tracking calculations. As can be seen in Fig. 4.4, the two most intense peaks at about 1594 and 3345 cm$^{-1}$ were converged in every calculation but other vibrations at lower wavenumbers were not well reproduced (except for the calculation with $I_{\text{min}} = 0.1$ and $r_{\text{thres}} = 0.001$). These two peaks with the highest intensity converged very fast and the calculations finished with such a small number of basis vectors.
that the other intense peaks were not found. The calculation with \( N = 5 \) in combination with \( r^{\text{thres}} = 0.005 \) and \( r^{\text{thres}} = 0.001 \) required 27 and 39 basis vectors, respectively, in contrast to 42 and 61 basis vectors in the case of the usual finite-field guess [Eq. (4.35)]. Similarly, \( I_{\min} = 0.1 \) and \( r^{\text{thres}} = 0.005 \) and the guess obtained from Eq. (3.274) lead to 12 calculated basis vectors instead of 89 employing the guess from Eq. (4.35) but the spectrum does not contain the intense bands at about 1015 and 1420 cm\(^{-1}\). The spectrum obtained with \( I_{\min} = 0.1, r^{\text{thres}} = 0.001, \) and the guess from Eq. (3.274) shows small differences, e.g., in the bands about 1120 cm\(^{-1}\), compared to the one gained with the usual finite-field guess or the reference spectrum because 101 basis vectors instead of the full number of vibrational normal modes (105 basis vectors) were calculated. The results employing a breathing mode as the initial guess are also given in Table 4.2. Obviously, the intensity-tracking does not behave significantly different for \( r^{\text{thres}} = 0.001 \) if the breathing-mode guess is employed instead of the one obtained with the finite-field method. This is illustrated for \( I_{\min} = 0.1 \) and \( N = 5 \) in the spectra of Fig. 4.4. However, a remarkable discrepancy may exist if \( r^{\text{thres}} = 0.005 \) is chosen (except for the \( N = 5 \) criterion). The calculations corresponding to the selection criteria \( I_{\text{sum}} = 0.8, I_{\min} = 0.1, \) and \( I_{\min} = 0.2 \) led to spectra that were not converged and terminated after choosing not more than ten basis vectors with the breathing mode as the initial guess.

As is presented in Fig. 4.4 for \( I_{\min} = 0.1 \), only intense normal modes at about 3000 and 3380 cm\(^{-1}\) were optimized and converged, whereas in the calculation employing the initial guess from the finite-field method also the vibrations at lower wavenumbers were obtained.

Regarding the computational efficiency, the lowest number of basis vectors was determined for \( N = 5 \) requiring about 40\% (for \( r^{\text{thres}} = 0.005 \)) and 60\% (with \( r^{\text{thres}} = 0.001 \)) of the basis vectors compared to the full calculation. Spectra of similar quality (setting \( r^{\text{thres}} = 0.005 \)) were found for \( I_{\text{sum}} = 0.8 \) with 63 basis vectors and \( I_{\min} = 0.1 \) with 89 basis vectors.

Table 4.2: Results of the intensity-tracking calculations [number of basis vectors (vectors), iterations, and converged normal modes (conv.)] for \( \Delta(\delta\delta\delta)\)-tris(ethylene-diaminato)cobalt(III) (6) (total number of normal modes: 105) with the initial guess obtained by the finite-field method employing different selection procedures and values for the maximum component of the residuum vector; the values in parentheses show the results obtained with a breathing mode as the initial guess.

<table>
<thead>
<tr>
<th>( r^{\text{thres}} )</th>
<th>( I_{\text{sum}} = 0.8 )</th>
<th>( I_{\min} = 0.1 )</th>
<th>( I_{\min} = 0.2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N = 5 )</td>
<td>42 (44)</td>
<td>63 (9)</td>
<td>89 (10)</td>
</tr>
<tr>
<td>( I_{\text{sum}} = 0.8 )</td>
<td>18 (16)</td>
<td>17 (7)</td>
<td>12 (7)</td>
</tr>
<tr>
<td>( I_{\min} = 0.1 )</td>
<td>29 (32)</td>
<td>58 (5)</td>
<td>88 (5)</td>
</tr>
<tr>
<td>( I_{\min} = 0.2 )</td>
<td>61 (32)</td>
<td>13 (7)</td>
<td>51 (2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( r^{\text{thres}} )</th>
<th>( I_{\min} = 0.1 )</th>
<th>( I_{\min} = 0.2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N = 5 )</td>
<td>61 (62)</td>
<td>83 (85)</td>
</tr>
<tr>
<td>( I_{\min} = 0.1 )</td>
<td>20 (20)</td>
<td>15 (12)</td>
</tr>
<tr>
<td>( I_{\min} = 0.2 )</td>
<td>28 (34)</td>
<td>32 (29)</td>
</tr>
</tbody>
</table>
Figure 4.4: Calculated IR spectra (BP86/RI/TZVP) of $\Delta(\delta\delta\delta)$-tris(ethylene-diaminato)cobalt(III) (6); the first spectrum at the top is the reference spectrum, while the other intensity-tracking spectra were obtained by applying $N = 5$ or $I_{\text{min}} = 0.1$ with $r_{\text{thres}} = 0.001$ and $r_{\text{thres}} = 0.005$, respectively. Three different initial guesses were employed: two employing the finite-field method, calculated via Eq. (4.35) (“finite field”) and Eq. (3.274) (“finite-field EV”), respectively, and one employing a breathing mode, indicated by “breathing mode”. The reference spectrum at the top was obtained by a calculation of the complete set of normal modes.

For $r_{\text{thres}} = 0.001$, the full number of basis vectors was obtained for both of these selection procedures in contrast to the choice $N = 5$. Compared to the other selection criteria and the corresponding spectra, the criterion of $I_{\text{min}} = 0.2$ appears to be too high resulting in less converged high-intensity normal modes than the selection procedure with $N = 5$ despite the higher number of basis vectors (61 and 83 for $r_{\text{thres}} = 0.005$ and $r_{\text{thres}} = 0.001$, respectively).

4.2.2.3 Purpose-driven optimization of high-intensity normal modes

In practical applications, often only a part of the spectrum or a special type of vibration is of interest. Such information can, in addition to the intensity, be employed for the optimization of the approximate normal modes which thus requires a combination of intensity- and mode-tracking algorithms.
The frequency as an additional selection parameter  For optimizing only special normal modes, the intensity-tracking algorithm was modified in such a way that the desired wavenumber serves as a selection parameter besides the IR intensity. As an example, the results of the intensity-tracking calculations of $\Delta(\delta\delta\delta)$-tris(ethylenediaminato)cobalt(III) for a wavenumber range of 500 to 1750 cm$^{-1}$ are given in Table 4.3. The number of basis vectors is reduced compared to the calculation without the frequency selection criterion, e.g., 36, 62, and 34 instead of 42, 89 and 61 basis vectors, respectively, for $r^\text{thres} = 0.005$ (see the values in the row “500 – 1750 cm$^{-1}$” in Table 4.3).

If only the two most intense normal modes in this wavenumber range are of interest, these combinations are a good choice because the calculations finished with the two highest-intensity normal modes at about 1000 and 1600 cm$^{-1}$ being converged. Only a small decrease and even an increase of the number of basis vectors was obtained for $r^\text{thres} = 0.001$ and $N = 5$ since the approximate normal modes in that wavenumber range do not converge as rapidly as the ones in the range from 2500 to 3500 cm$^{-1}$. An option to improve on the convergence in this wavenumber region could be to employ a more advanced way of preconditioning based on, for instance, Hessians from more approximate methods (see Ref. [387] for preconditioning in the context of mode-tracking). Taking the breathing mode as the initial guess in the intensity-tracking which employs $N = 5$ or $I^\text{min} = 0.1$ only four basis vectors were obtained. These were all converged and correspond to the intense band at about 3350 cm$^{-1}$, a very weak normal mode at 437 cm$^{-1}$, and two medium-intensity normal modes at 1410 and 3011 cm$^{-1}$, which represents of course an insufficient approximation to the IR spectrum.

For all-(S)-decaalanine, a decrease in the number of the calculated basis vectors was found, e.g., for a wavenumber range of 1000 to 1750 cm$^{-1}$ (see Table 4.4) in combination with $I^\text{min} = 0.1$ and $I^\text{min} = 0.2$, respectively. Only ten and 16 basis vectors were obtained with five and eight normal modes being converged, respectively, which include the most intense normal mode in that wavenumber range at about 1650 cm$^{-1}$. Although only normal modes between 1000 and 1750 cm$^{-1}$ were systematically optimized in this calculation, we still also obtained converged normal modes between 3300 and 3500 cm$^{-1}$.

Optimization of local high-intensity normal modes  If we look closer at the convergence behaviour, we find that certain normal modes at wavenumbers lower than 500 cm$^{-1}$ and higher than 3000 cm$^{-1}$ converge fast. These rapidly converging normal modes mainly correspond to localized vibrations in the molecule, in which only a few atoms move. Since many of such “local” normal modes (not to be confused with the hypothetical “localized” modes introduced in section 3.5.3) exist in the wavenumber ranges mentioned (e.g., particular hydrogen stretching vibrations in the higher wavenumber region), the bands in these ranges are easily found and converge quickly, even if they are
Table 4.3: Results of the intensity-tracking calculations [number of basis vectors (vectors), iterations (it.), and converged normal modes (conv.)] for $\Delta(\delta\delta\delta)$-tris-ethylenediaminato)cobalt(III) (6) with the initial guess obtained by the finite-field method employing different selection procedures and values for the maximum component of the residuum vector; the values in parentheses are the results obtained with a breathing mode as the initial guess.

<table>
<thead>
<tr>
<th>$r_{\text{thres}}$</th>
<th>0.005</th>
<th>0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vectors</td>
<td>it.</td>
</tr>
<tr>
<td>$N = 5$:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 – 1750 cm$^{-1}$:</td>
<td>36 (4)</td>
<td>12 (4)</td>
</tr>
<tr>
<td>non-H atoms:</td>
<td>16 (7)</td>
<td>9 (6)</td>
</tr>
<tr>
<td>H atoms:</td>
<td>3 (37)</td>
<td>3 (15)</td>
</tr>
<tr>
<td>single atom:</td>
<td>13 (12)</td>
<td>6 (7)</td>
</tr>
<tr>
<td>H atoms,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 – 1750 cm$^{-1}$:</td>
<td>7 (10)</td>
<td>7 (7)</td>
</tr>
<tr>
<td>non-H atoms,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 – 1750 cm$^{-1}$:</td>
<td>8 (22)</td>
<td>6 (10)</td>
</tr>
<tr>
<td>$I_{\min} = 0.1$:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 – 1750 cm$^{-1}$:</td>
<td>62 (4)</td>
<td>19 (4)</td>
</tr>
<tr>
<td>non-H atoms:</td>
<td>6 (13)</td>
<td>6 (8)</td>
</tr>
<tr>
<td>H atoms:</td>
<td>10 (67)</td>
<td>7 (20)</td>
</tr>
<tr>
<td>single atom:</td>
<td>25 (4)</td>
<td>7 (4)</td>
</tr>
<tr>
<td>H atoms,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 – 1750 cm$^{-1}$:</td>
<td>14 (29)</td>
<td>8 (17)</td>
</tr>
<tr>
<td>non-H atoms,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 – 1750 cm$^{-1}$:</td>
<td>8 (85)</td>
<td>6 (14)</td>
</tr>
<tr>
<td>$I_{\min} = 0.2$:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 – 1750 cm$^{-1}$:</td>
<td>34</td>
<td>18</td>
</tr>
<tr>
<td>non-H atoms:</td>
<td>69</td>
<td>13</td>
</tr>
<tr>
<td>H atoms:</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>single atom:</td>
<td>39</td>
<td>9</td>
</tr>
<tr>
<td>H atoms,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 – 1750 cm$^{-1}$:</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>non-H atoms,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 – 1750 cm$^{-1}$:</td>
<td>8</td>
<td>7</td>
</tr>
</tbody>
</table>

not selected for optimization. By contrast, many “delocalized” normal modes appear in the wavenumber range of 1000 to 1500 cm$^{-1}$ which converge slowly. Under certain circumstances, it may be useful to focus on the localized normal modes, e.g., if it is known that stretching vibrations dominate the spectrum.
Table 4.4: Results of the intensity-tracking calculations [number of basis vectors (vectors), iterations, and converged normal modes (conv.)] for all-(S)-decaalanine (5) with the initial guess evaluated by the finite-field method employing different selection procedures and values for the maximum component of the residuum vector.

<table>
<thead>
<tr>
<th>( r_{\text{thres}} )</th>
<th>( 0.005 )</th>
<th>( 0.001 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vectors</td>
<td>iterations</td>
</tr>
<tr>
<td>( N = 5: )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 – 1750 cm(^{-1}):</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>non-H atoms:</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>H atoms:</td>
<td>27</td>
<td>15</td>
</tr>
<tr>
<td>single atom:</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>( I_{\text{min}} = 0.1: )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 – 1750 cm(^{-1}):</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>non-H atoms:</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>H atoms:</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>single atom:</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>( I_{\text{min}} = 0.2: )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 – 1750 cm(^{-1}):</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>non-H atoms:</td>
<td>37</td>
<td>22</td>
</tr>
<tr>
<td>H atoms:</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>single atom:</td>
<td>10</td>
<td>7</td>
</tr>
</tbody>
</table>

In order to optimize only such localized normal modes, the contribution of every atom to the norm of the approximate normal modes was calculated (compare section 4.2.1.2). If this contribution exceeds a given threshold, the normal mode will be optimized. For our calculations, a contribution of at least 30% to the norm of the normal mode turned out to be useful. As can be seen in Tables 4.3 and 4.4 (compare row “single atom”), this criterion in combination with the three intensity-tracking variants led in most cases to a remarkable reduction of the number of required basis vectors. In general, the normal modes up to about 500 cm\(^{-1}\) were converged as well as the ones at 3000 cm\(^{-1}\) and higher. In extreme cases like for \( \Delta(\delta\delta\delta)-\text{tris(ethylenediaminato)cobalt(III)} \) with \( I_{\text{min}} = 0.1 \) only two normal modes were converged (the ones with the lowest and highest wavenumber for \( r_{\text{thres}} = 0.005 \) and two at about 3360 and 3400 cm\(^{-1}\) for \( r_{\text{thres}} = 0.001 \)).

Selection of intense normal modes with large contribution from specified atoms Another typical application of vibrational spectroscopy is to find the vibrational normal modes of a particular atom or group of atoms. This is the case, for example, for metal centers in enzymes and small ligands connected to them [393]. A third criterion which we combined with intensity-tracking is
thus the directed optimization of intense normal modes showing large contributions from a certain atom or group of atoms. This possibility was applied to the cobalt complex and to all-(S)-decaalanine, compare Tables 4.3 and 4.4. For example, all normal modes for which the hydrogen atoms provide at least 70% to the norm of the normal mode (compare section 4.2.1.2) were optimized if they also fulfilled the intensity criterion (see the results in the row “H-atoms” of the Tables 4.3 and 4.4). For some cases, the selection parameters are too tight. For example, $r_{\text{thres}} = 0.005$ together with $N = 5$ yielded only three basis vectors with one converged normal mode at 3355 cm$^{-1}$ for the cobalt complex. Similarly, only three converged normal modes resulted from the calculation from nine and seven basis vectors, respectively, for all-(S)-decaalanine if $I_{\text{min}} = 0.1$ or $I_{\text{min}} = 0.2$ was applied. By contrast, only ten basis vectors were determined for ∆(δδδ)-tris(ethylenediaminato)cobalt(III) employing $I_{\text{min}} = 0.1$. The five converged normal modes yield a quite good IR spectrum since they contain the highest-intensity normal modes from the wavenumber range about 1400 to 3600 cm$^{-1}$. The results for analogous calculations in which the contribution of the non-hydrogen atoms to the normal mode norm is larger than 70% are also given in Tables 4.3 and 4.4 (row “non-H atoms”). In this case, especially normal modes in the range from 500 to 1500 cm$^{-1}$ were optimized.

The three presented mode-based selection criteria can easily be combined. This is demonstrated for ∆(δδδ)-tris(ethylenediaminato)cobalt(III) in Table 4.3, where normal modes providing a large contribution (again at least 70% to the norm of the normal mode) from hydrogen and non-hydrogen atoms, respectively, and satisfying the frequency range of 900 to 1750 cm$^{-1}$ were optimized (see rows “H atoms, 900 – 1750 cm$^{-1}$” and “non-H atoms, 900 – 1750 cm$^{-1}$” in Table 4.3), if the IR intensity was high enough to fulfill the intensity-tracking criterion. It is worth mentioning the result from choosing a large hydrogen atom contribution and a frequency range of 900 to 1750 cm$^{-1}$: only ten basis vectors were found with seven being converged if $I_{\text{min}} = 0.2$ was set. Among the converged ones are the most important bands at about 1000, 1600, and 3300 cm$^{-1}$ although the latter does not satisfy the selected frequency range. In the other calculations, not all intense peaks were found due to the strict selection procedure. This shows that efficiency can be improved with additional selection criteria, albeit more input knowledge has to be at hand to be sure that all important spectral features are obtained.

For comparison, calculations with a breathing mode as the initial guess were also performed and are given in Table 4.3. This initial guess mostly led to approximate IR spectra of low quality for $r_{\text{thres}} = 0.005$ because the calculations finished too quickly so that not all important normal modes were obtained. We can thus conclude that a very unspecific guess can easily lead to bad convergence or early termination of the intensity-tracking algorithm and should thus be avoided.
4.2.2.4 Intensity-tracking in practice: Schrock’s dinitrogen molybdenum complex

One important field of application of IR spectroscopy is the clarification of reaction mechanisms. But if the molecules under study are too large, conventional theoretical approaches become unfeasible and intensity-tracking can offer a way for fast routine assignment of intense characteristic normal modes. A prototypical example is the catalytic reduction of dinitrogen to ammonia [407–410] via Schrock’s molybdenum complex (see Fig. 4.1). The dinitrogen stretching vibration can be employed as an indicator for the charge state of the dinitrogen complex. It has been found [410] that the \( \text{N}_2 \) stretching vibration appears at 2255 cm\(^{-1} \) when the complex carries a positive charge whereas the neutral species gives rise to a vibration at about 1990 cm\(^{-1} \) and the anion shows a peak at 1855 cm\(^{-1} \). This information can be used to elucidate the structure of intermediates in the reduction mechanism.

The dinitrogen metal complex is quite large (280 atoms) and the calculation of the full spectrum requires the determination of 834 normal modes, which is computationally unfeasible for routine vibrational analyses. Fortunately, a complete IR spectrum for the Schrock complex is already available [416, 417] and can serve as a reference for the intensity-tracking calculation. However, not the whole spectrum is of interest since only the intense vibrations involving the metal center, at which the reactions take place, are important for monitoring the reaction process. For such a problem, intensity-tracking combined with the condition that the metal atom and its surrounding atoms (especially the \( \text{N}_2 \) ligand) participate in the normal mode is the optimum choice.

We chose the neutral dinitrogen complex and performed intensity-tracking calculations with \( r_{\text{thres}} = 0.001 \). In order to optimize only the intense normal modes involving the metal center, we employed the additional condition that the contribution of the metal atom and the nitrogen atoms directly bound to it (including the whole \( \text{N}_2 \) ligand and additionally the carbon atoms directly connected to Mo-ligating nitrogen atoms) to the norm of the normal mode is at least 25%. Employing \( N = 5 \), the calculation finished with 80 converged basis vectors and a total number of 126 basis vectors, which led to the determination of only 15% of the total number of normal modes. The evaluations for each displaced structure took about 11.5 hours on one core of an AMD opteron 270 processor so that a non-parallelized calculation would take about 11.5 \( \cdot \) 126 \( \cdot \) 2 = 2898 hours. In contrast to that, a standard full semi-numerical calculation on one such core would last about 280 \( \cdot \) 6 \( \cdot \) 11.5 = 19320 hours. Of course, we employed parallelization techniques in both cases so that the wall clock time for the calculations was much smaller.

The spectra from the intensity-tracking and full calculations are shown in Fig. 4.5. In the spectrum of the full calculation (see top of Fig. 4.5), the normal mode at 1988 cm\(^{-1} \) shows the highest relative intensity followed by vibrations at about 1560 cm\(^{-1} \) and 950 cm\(^{-1} \). The \( \text{N}_2 \) stretching vibration is easily identifiable.
because no other peaks occur in the region from 1600 to 2500 cm\(^{-1}\).

In the intensity-tracking calculation, the normal mode at 1984 cm\(^{-1}\) shows the highest intensity comparable to the one at 1988 cm\(^{-1}\) in the full calculation (see bottom of Fig. 4.5). It was already converged in the eleventh iteration involving 40 basis vectors; the deviation of 4 cm\(^{-1}\) to the full calculation can be attributed to the convergence threshold applied and noise in the semi-numerical algorithm employed here. For comparison, the vector representations of this normal mode obtained from the intensity-tracking and from the full calculation are shown in Fig. 4.6. Obviously, both vibrations can be assigned to N\(_2\) stretching vibrations. The bands at about 1560 cm\(^{-1}\) are intense both in the intensity-tracking and in the full calculation. They correspond to C–C stretching vibrations, which do not significantly involve the metal center. Although they were not selected for

Figure 4.5: IR spectra (BP86/RI/TZVP) of Schrock’s dinitrogen molybdenum complex (7) obtained by a calculation of the complete set of normal modes (top; spectrum taken from Ref. [417]) and by an intensity-tracking calculation employing \(N = 5\) in combination with the condition of large contributions from the metal center (bottom).
Figure 4.6: Vector representation of normal modes of Schrock’s dinitrogen molybdenum complex (7) obtained from a calculation of the complete set of normal modes (left-hand side) and from an intensity-tracking calculation (right-hand side).

948 cm$^{-1}$

940 cm$^{-1}$

1562 cm$^{-1}$

1559 cm$^{-1}$

1988 cm$^{-1}$

1984 cm$^{-1}$
optimization in the intensity-tracking run, they were converged quite fast. As an example, the vector representations of such a vibration are given in Fig. 4.6 and the normal modes obtained from the intensity-tracking and from the full calculation agree well. The intense band at about 949 cm$^{-1}$ in the spectrum of the full calculation corresponds to two near-lying delocalized normal modes at 948 and 949 cm$^{-1}$, respectively, containing many unspecific distortions which also involve the metal center. These two normal modes show a sufficiently high intensity to fulfill the intensity criterion accompanied with a large contribution from the metal atom and its neighbors. One comparable normal mode was found in the intensity-tracking calculation at 940 cm$^{-1}$ (compare Fig. 4.6). The intensity of the corresponding band in the spectrum is thus lower than in the full calculation, since the band in the latter calculation is a superposition of the two close-lying normal modes. The converged normal mode at 940 cm$^{-1}$ corresponds to a metal center vibration, which is similar to the normal mode at 948 cm$^{-1}$ from the full calculation. Some deviations, especially in the vibrational motion of the ligands, occur due to the fact that we used a threshold value $r_{\text{thres}} = 0.001$. In order to increase the accuracy of the wavenumber and normal mode, a smaller threshold can be chosen, which would lead to an increased computational effort. In contrast to that, a reduction in computational time can be obtained with $r_{\text{thres}} = 0.005$ resulting, of course, in larger deviations of the normal modes. For example, employing $I_{\text{min}} = 0.1$ and $r_{\text{thres}} = 0.005$ together with the condition of large contributions from the metal center (compare above), the nitrogen stretching vibration was found at 1969 cm$^{-1}$ and a vibration fulfilling the condition of large contributions from the metal center at 1020 cm$^{-1}$ with a total number of only 13 basis vectors.

If one is only interested in the intensity of the nitrogen stretching vibration, it is of course easier to take such a kind of normal mode already as the initial guess in a standard mode-tracking calculation which leads to a converged normal mode with corresponding intensity after only a few iteration steps. But the absolute value of the intensity is not very helpful if it cannot be compared to the intensities of other bands in the spectrum in order to estimate its relative importance. An intensity-tracking calculation with $I_{\text{min}} = 0.3$ and $r_{\text{thres}} = 0.005$ stopped after evaluating only twelve basis vectors with nine being converged corresponding to a reduction in the number of calculated normal modes of more than 98%. Although only the nitrogen and some hydrogen stretching vibrations were optimized, where the former was found at 1969 cm$^{-1}$, this calculation has the advantage that relative intensities can be estimated. It may thus be assessed how intense the N$_2$ stretching vibration is compared to other vibrations in the spectrum.

A first impression of the spectrum can also be obtained with other root-homing options. Worth mentioning are the intensity-tracking calculations without any additional mode-based selection parameter and $r_{\text{thres}} = 0.005$, which also led to rapid convergence. If the five most intense normal modes were optimized ($N = 5$), the calculation stopped with 26 approximate normal modes, of which
18 are converged. A spectrum of similar quality is obtained with $I_{\text{sum}} = 0.8$ employing 24 basis vectors with 19 converged normal modes. Compared to the spectrum obtained with $I_{\text{min}} = 0.1$ in combination with the large contributions from the metal atom and its surrounding atoms (see above), more intense vibrations in the wavenumber ranges from 1000 to 1600 cm$^{-1}$ and 2900 to 3200 cm$^{-1}$ were found and converged. Although there are still some deviations from the reference, the approximate spectrum is good enough in order to locate frequency regions with high-intensity vibrations.

### 4.2.3 Raman and Raman optical activity intensity-tracking

Tryptophan is an essential building block of proteins, whose structures have been explored by means of ROA spectroscopy [342, 418]. Its W3 vibration is usually well visible in the ROA spectrum at around 1550 cm$^{-1}$ and a detailed ROA study can be found in section 6.3.

Figure 4.7: Approximate Raman spectra (BP86/RI/TZVP) of L-tryptophan obtained by the intensity-tracking calculation (bottom and middle) and the reference conventional full calculation (top).

The results of the Raman intensity-tracking calculation for L-tryptophan are given in Fig. 4.7. They were obtained with a convergence criterion of $I_{\text{thres}} = \ldots$
0.001 and the selection criterion $I_{\text{min}} = 0.1$. In addition, solely the approximate normal modes with a wavenumber between 1000 and 2000 cm$^{-1}$ were optimized. As can be easily seen, the number of basis vectors increases with each iteration. In the sixth iteration, for example, twelve basis vectors were employed and 30 in the ninth iteration. The first basis vectors were converged in the twelfth iteration (43 basis vectors) leading to converged normal modes at 1565 and 1744 cm$^{-1}$. In the 14-th iteration, the very intense normal mode at 1540 cm$^{-1}$ and the intense following ones (at 1568, 1612, and 1746 cm$^{-1}$) were converged. The calculation finished with a total number of 69 basis vectors, among them 47 being converged. The agreement with the spectrum of the calculation employing the full set of normal modes is very good. Small deviations occur for less intense bands, which is due to the fact that in the intensity-tracking calculation six basis vectors less than in a full conventional calculation were determined. Other convergence and selection parameter can, of course, lead to a smaller number of basis vectors and, as a consequence, to larger savings in computational effort. The ROA intensity-tracking calculation together with the reference calculation, in which all normal modes were evaluated, is given in Fig. 4.8.

Figure 4.8: Approximate ROA spectra (BP86/RI/TZVP) of $L$-tryptophan obtained with a ROA intensity-tracking calculation (bottom and middle) and the conventional full calculation (top).
As a convergence threshold for the normal modes, we employed $r_{\text{thres}} = 0.003$. Every (approximate) normal mode was optimized if its relative ROA intensity was larger than 0.1 ($I_{\text{min}} = 0.1$) and its wavenumber lay between 1000 and 2000 cm$^{-1}$. The first converged normal mode occurred in the eighth iteration and corresponds to a stretching vibration at 3609 cm$^{-1}$. In the following iteration, the normal modes with the low wavenumbers of 275 and 300 cm$^{-1}$ were also converged. This agrees with the findings in section 4.2.1.2, in which it has been observed that especially (local) normal modes at very low and high wavenumbers converge fast. In the tenth iteration, eleven out of 51 basis vectors were converged.

Among them is the characteristic, intense W3 vibration, which is of most interest for the interpretation of the experimental spectra. The calculation finished with a total number of 63 basis vectors (and 46 converged ones). The obtained spectrum features all important intense bands in the spectrum although deviations occur due to the rather large threshold of 0.003 for the maximum component of the residuum vector. The reduction in computational effort is about 16%, but can be maximized by applying other intensity- and mode-based selection criteria and a different convergence threshold. Furthermore, L-tryptophan is a comparatively small molecule (27 atoms) and it can be expected that the savings in computational effort will increase with the number of atoms like it has been found in the case of IR intensity-tracking calculations.
5. Prediction of Raman Optical Activity Spectra for Chiral Transition Metal Complexes

Chiral molecules occur nowadays as functional materials in many fields of biological, chemical, and physical sciences. This leads to a need of efficient synthetic methods, which often employ molecular auxiliaries. An important class in this regard are chiral metal complexes catalyzing stereoselective reactions (for details, we refer, e.g., to Ref. [419]).

For the characterization of such complexes, VCD spectroscopy, which measures the difference in absorption of left- and right-circularly polarized infrared radiation for molecular vibrational transitions [413, 420–435], has often been applied. Yet, to our knowledge no measured ROA spectra of chiral metal complexes are available. Motivated by the VCD measurements and the expectation that ROA measurements will follow, the first ROA calculations of chiral metal complexes (see Fig. 5.1) were calculated in course of this work [225] and are presented in sections 5.1 and 5.2. Since it may be expected that the density-functional dependence of the property tensors is more pronounced in the case of metal complexes than in the case of organic molecules, this topic is investigated in section 5.1 together with a study of different basis sets, followed by a discussion of the ROA spectra in section 5.2. Section 5.3 contains a survey about the influence of the degree of ligand substitution, ligand chirality, and geometrical isomerism on ROA spectra by means of cobalt complexes containing chiral 3-acetylcamphorato ligands [436].

5.1 Basis-set and density-functional dependence

For the investigation of the influence of basis sets and density functionals on ROA spectra of metal complexes, calculations with the SVP, SVPP, TZVP, and TZVPP basis sets and the density functionals BP86 and B3LYP were performed. For the latter, the coordinate and gauge origin was set to the center of mass in order to keep the gauge-origin dependence of the pure length representation as small as possible.

We compare the spectra obtained with the $\beta(G')^2$ invariant and the $G'$ tensor in the length and velocity representation because the difference between these representations is a measure of the incompleteness and, therefore, of the quality of the basis set (compare section 3.3.1). As an example, the spectra of $\Lambda$-tris(acetylacetonato)rhodium(III) are given in Fig. 5.2.
As expected, the spectra obtained with the distinct representations become the more similar the larger the basis set. This is most obvious for the doublet at 1534/1546 cm$^{-1}$, which shows a very large absolute intensity in the case of the pure length representation and the SVP basis set whereas the corresponding one calculated with $\beta(G')^2$ in the velocity form has a much smaller value. However, if the basis set is changed to TZVP and TZVPP, the absolute intensities increase with the size of the basis set and are almost the same in magnitude as the ones from the pure length representation. Hence, in the case of Λ-tris(acetylacetonato)rhodium(III), at least the TZVP basis set should be employed for a qualitative picture of the spectra. In order to have a more accurate description of the intensities, the TZVPP basis set is needed. It provides more polarization functions than the TZVP and SVP basis sets. Interestingly, the spectra obtained in the length representation show very small changes when going from the SVP to the TZVP and TZVPP basis sets, which also demonstrates the negligible gauge-origin dependence. In contrast to that, the spectra
employing the $\beta(G')^2$ invariant in the velocity form change remarkably. This shows the slower basis set convergence of the velocity representation.

Figure 5.2: Calculated ROA spectra (property tensors: BP86/RI/SVP, BP86/RI/TZVP, BP86/RI/TZVPP, B3LYP/TZVP; force field: BP86/RI/TZVPP; backscattering direction) of Λ-tris(acetylacetonato)rhodium(III) $(3)$: “length” and “velocity” indicate that the $\beta(G')^2$ values were calculated in the length and velocity representation, respectively.
The B3LYP spectrum is only available for the pure length representation. The signs of the intensities are quite well reproduced. However, the absolute intensity values show noticeable differences when compared to the ones obtained with the BP86 density functional. The error induced by the RI approximation in the calculations employing the non-hybrid density functional is usually negligible (for optical rotation it is less than 2% [377]) and hence, this might not be the reason for such a distinct behaviour. Significant deviations were also observed between the spectra obtained with the BP86 and B3LYP density functionals for Λ-tris(acetylacetonato)rhodium(III) and Δ(δδδ)-tris(ethylendiaminato)cobalt(III), but we detected negligible deviations for dichloro(sparteine)zinc(II). This is an indication for the well-known fact that present-day density functionals face difficulties when transition metal atoms are involved. Only zinc as a late transition metal atom is different in this respect and the results obtained for the Zn complex are in agreement with those obtained for organic molecules [47]. We compared the values of the $\alpha$, $G'$, and $A$ tensors evaluated with BP86 and B3LYP for Λ-tris(acetylacetonato)rhodium(III) and found non-negligible deviations. It has already been observed in optical rotation calculations that the values obtained with the hybrid density functional B3LYP differ from the ones obtained from non-hybrid density functionals. It was assumed that this is due to the fact that excitation energies of valence states are underestimated by B3LYP [376, 437]. However, the derivatives of the tensors with respect to the normal coordinates are necessary for the ROA invariants, not the tensor values alone. Therefore, it is possible that the differences in the tensor values obtained by BP86 and B3LYP vanish upon differentiation. However, this is not found and the differences do not cancel. In order to demonstrate the importance of polarization functions, which have already been proven to be important for ROA intensities in the case of organic molecules [438], the spectra of Δ(δδδ)-tris(ethylendiaminato)cobalt(III) were calculated employing the SVP, SVPP, TZVP, and TZVPP basis sets (see Fig. 5.3). The limit of a complete basis set is more or less reached with the TZVPP basis set since the differences between the spectra obtained with the $G'$ tensor in the length and velocity form vanish. It is obvious that basis set convergence is faster in the case of the length representation. The role of polarization functions becomes apparent in the comparison between the spectra from calculations with the SVPP and TZVPP basis sets and the ones obtained with the SVP and TZVP basis sets. The spectrum of the pure length form maintained by the SVPP basis set is already very similar to the one from the triple-zeta valence TZVPP basis set although the first one is only a single valence basis set. However, the SVPP basis set contains the same polarization functions as the TZVPP basis set which leads to the high similarity of both spectra for the pure length representation. In contrast to this, the spectrum calculated with the $G'$ tensor in the velocity representation and the SVPP basis set does not resemble the spectra obtained with the TZVPP basis set to such a large extent because of the slower basis
set convergence of the velocity form.

Figure 5.3: Calculated ROA spectra (property tensors: BP86/RI/SVP, BP86/SVPP, BP86/RI/TZVP, BP86/RI/TZVPP; force field: BP86/RI/TZVPP; backscattering direction) of $\Delta(\delta\delta\delta)$-tris(ethylendiaminato)cobalt(III) (2); “length” and “velocity” indicate that the $G'$ tensor values were calculated in the length and velocity representation, respectively.
5.2 Discussion of the spectra

The spectra of the cobalt complexes are shown in Fig. 5.4. The spectrum of $\Lambda$-tris(acetylacetonato)cobalt(III) is quite sparse. In the region from 150 to 425 cm$^{-1}$, deformational (bending, rocking, twist) vibrations of the oxygen atoms arise, whereas the Co–O stretching modes exist at 612 and 643 cm$^{-1}$. The largest bands of the spectra at 1253 and 1258 cm$^{-1}$ correspond to symmetric and antisymmetric combinations of symmetric C–C stretching vibrations. At 1541 cm$^{-1}$, a carbonyl stretching vibration can be found where two ligands show an in-phase symmetric stretching vibration, the third ligand being out-of-phase (compare Fig. 5.5). The totally in-phase combination is evaluated with a wavenumber of 1554 cm$^{-1}$.

At higher wavenumbers, C–H stretching modes occur in different combinations of (anti)symmetric vibrations of the CH$_3$ and C–H groups. In the case of $\Delta(\delta\delta\delta)$-tris(ethylenediaminato)cobalt(III), the wavenumber region from around 200 to 1300 cm$^{-1}$ provides a lot of characteristic peaks, whereas only three bands of C–H stretching vibrations (symmetric and antisymmetric vibrations in distinct combinations) can be found between 2900 and 3200 cm$^{-1}$. The N–H stretching vibrations show up at higher wavenumbers. Deformational vibrations of the nitrogen atoms occur for example at 243 cm$^{-1}$ and stretching vibrations at 324 cm$^{-1}$. N–H$_2$ rocking modes give rise to the bands at 651 and 673 cm$^{-1}$, C–H$_2$ rocking modes to the peak at 839 cm$^{-1}$. At 1015 and 1122 cm$^{-1}$, C–C stretching and C–H$_2$ rocking vibrations arise. The large negative intensity at 1298 cm$^{-1}$ belongs to a twist mode delocalized over the C–H$_2$ and N–H$_2$ groups. The doublet at 1606/1614 cm$^{-1}$ corresponds to N–H$_2$ bending modes. No significant similarity exists between the spectra of the two cobalt complexes in Fig. 5.4.

The spectra of $\Lambda$-tris(acetylacetonato)rhodium(III) and dichloro(sparteine)zinc(II) are given in Fig. 5.6. Comparing the spectra of the first with the ones of the cobalt analog in Fig. 5.4, similar intensities in the region from 2900 to 3200 cm$^{-1}$ can be found, but very different intensities in the region from 100 to 1800 cm$^{-1}$. The wavenumbers, however, deviate not much from the ones obtained for $\Lambda$-tris(acetylacetonato)cobalt(III). Therefore, the normal modes of $\Lambda$-tris(acetylacetonato)rhodium(III) occur at similar wavenumbers like the ones of $\Lambda$-tris(acetylacetonato)cobalt(III). Worth mentioning is the doublet at 1244/1246 cm$^{-1}$, which corresponds to the symmetric and antisymmetric combination of symmetric C–C stretching modes. These modes show the largest absolute intensities in the spectra of $\Lambda$-tris(acetylacetonato)cobalt(III). Contrary to that, the largest peak in the $\Lambda$-tris(acetylacetonato)rhodium(III) spectra is found at 1534 cm$^{-1}$, which belongs to the already mentioned out-of-phase combination of carbonyl stretching modes of the ligands, the negative band at 1546 cm$^{-1}$ belonging to the in-phase combination. These two modes feature much smaller intensities in the case of $\Lambda$-tris(acetylacetonato)cobalt(III), but the out-of-phase motion appears also at lower wavenumbers than the in-phase
Figure 5.4: Calculated ROA spectra (backscattering direction; BP86/RHlock/TZVPP) of $\Lambda$-tris(acetylacetonato)cobalt(III) (1) (top) and $\Delta(\delta\delta\delta)$-tris(ethylenediaminato)-
cobalt(III) (2) (bottom); the upper part of each spectrum shows the plot without
the $A$ tensor contribution, the lower panel provides the full reference spectrum.

combination. Interestingly, the same has been encountered by Sato et al. [431]
for the VCD-active carbonyl stretching vibrations of the open-shell complexes
$\Delta$-tris(acetylacetonato)chromium(III) and $\Delta$-tris(acetylacetonato)rhenium(III),
whereas they found a reversed order of the carbonyl stretching vibrations for the
closed-shell complexes $\Delta$-tris(acetylacetonato)cobalt(III) and $\Delta$-tris(acetylacetonato)rhodium(III).

The spectra of dichloro(sparteine)zinc(II) feature many signals, the ones with the largest absolute intensities occurring at about 800 – 1400 cm$^{-1}$. N–C stretching vibrations appear, e.g., at 1022 cm$^{-1}$, deformational vibrations of the hydrogen atoms from 1039 to 1434 cm$^{-1}$, followed by the C–H stretching vibrations in the wavenumber region from 2800 to 3100 cm$^{-1}$.

As is obvious on the basis of these spectra, ROA experiments would be a reliable tool for studying the stereochemistry of chiral metal complexes. Since the spectra of the $\Lambda$-tris(acetylacetonato)rhodium(III) and $\Lambda$-tris(acetylacetonato)cobalt(III) complexes show significant differences despite the same ligand structure it is to expect that ROA measurements will be sensitive to the metal atoms employed.

Figure 5.5: Vector representation of the normal mode of $\Lambda$-tris(acetylacetonato)cobalt(III) (1) at 1541 cm$^{-1}$.

Magnitude of the electric-dipole–electric-quadrupole contribution The there has been some discussion in the literature about the importance of the electric-dipole–electric-quadrupole tensor for ROA intensities (compare section 3.5.1). It has been found to be small for most vibrations in case of organic molecules, except for C–H stretching vibrations where the contribution can be very large [324]. Now the question arises if the same holds for ROA spectra of metal complexes, i.e., for a completely different type of molecules. In order to investigate this, we plotted the spectra with and without $A$ tensor contribution in Figs. 5.4 and 5.6. For all four molecules, similar patterns can be recognized: in the wavenumber region below 2500 cm$^{-1}$, no noteworthy difference between the spectrum with
and without the $\beta(A)^2$ calculation appears, the $A$ tensor contribution is negligible. At higher wavenumbers, some remarkable deviations in the intensities exist. An inversion of the sign of a peak, visible at 3031 cm$^{-1}$, exists in the spectra of $\Lambda$-tris(acetylacetonato)rhodium(III) and $\Lambda$-tris(acetylacetonato)cobalt(III).

Figure 5.6: Calculated ROA spectra (backscattering direction; BP86/RI/TZVPP) of $\Lambda$-tris(acetylacetonato)rhodium(III) (3) (top) and dichloro(sparteine)zinc(II) (4) (bottom); the upper part of each spectrum shows the plot without the $A$ tensor contribution, the lower panel provides the full reference spectrum.
This band is a superposition of several peaks. It should be noted that no sign inversion can be found for a single intensity if one compares the intensity values for each peak of this band obtained with and without $A$ tensor contribution. The overall differences due to neglect of the $\beta(A)^2$ values are small and do not lead to such remarkable sign inversions of the peaks belonging to C–H stretching vibrations like in the case of organic molecules [324]. As a consequence, the omission of the $A$ tensor contribution does not lead to a significant change of the spectrum.

### 5.3 Influence of chiral ligands on the spectra

Another class employed as molecular auxiliaries in chemical syntheses are chiral organic molecules (for a recent review, see, for instance, Ref. [439]). An example is camphor, which is commercially available and provides the basic molecular structure for diverse molecules utilized for a variety of reactions [439–441].

Figure 5.7: The possible isomers for the $\Delta$ configuration; A–A indicates the acetylacetonato ligand and C–O the 3-acetylcamphorato ligand, which can be present as $(+)$- or $(-)$-enantiomer.

In order to investigate the influence of chiral ligands on ROA spectra, the acetylacetonato (acac) ligands in the tris(acetylacetonato)cobalt(III) complexes are stepwise replaced by chiral $(+)$- or $(-)$-3-acetylcamphorato (acam) ligands. Complexes containing a mixture of $(+)$- and $(-)$-acam ligands are not considered. This leads for each of the $(+)$- and $(-)$-forms of the camphor to
six different isomers for the $\Delta$ and the $\Lambda$ configuration of the complex, respectively [435]. They are depicted in Fig. 5.7 for the $\Delta$ configuration and the structure of $\Delta$-Co((+)-acam)(acac)$_2$ is presented as an example in Fig. 5.8. The complexes containing two acac ligands and one acam ligand can adopt the $\Delta$ and $\Lambda$ configuration. If two acac ligands are substituted by acam ligands, three different isomers for the $\Delta$ and $\Lambda$ enantiomers, respectively, are possible, where two are trans isomers and the third one is a cis isomer. The $\Delta$, $\Lambda$-tris((+)-3-acetylcamphorato)cobalt(III) and $\Delta$, $\Lambda$-tris((−)-3-acetylcamphorato)cobalt(III) complexes can occur as fac and mer stereoisomers whose stereoselectivity regarding their formation was subject of discussion in the literature [442, 443]. This systematical replacement of the ligands allows us to study the effects of the ligand chirality, of the geometrical isomerism, of the $\Lambda/\Delta$ configuration as well as of the number of chiral ligands on ROA spectra.

Figure 5.8: The optimized molecular structure (BP86/RI/TZVP) of $\Delta$-Co((+)-acam)(acac)$_2$ (left-hand side) and the corresponding Lewis structure (right-hand side).

5.3.1 Degree of ligand substitution

First, the dependence of ROA spectra on the number of chiral ligands is studied. The chiral (+)-acam ligand is considered, which is introduced into the $\Delta$-Co(acac)$_3$ complex by substitution of the non-chiral acac ligands. The spectrum of (+)-3-acetylcamphor is shown in Fig. 5.9 together with the one of the (+)-acam ligand, which is obtained by removal of one proton. The spectra show weak peaks in the low wavenumber region up to 600 cm$^{-1}$. Two negative bands around 700 cm$^{-1}$ and two positive ones around 800 cm$^{-1}$ can be found in the spectra both of the neutral ligand and the anion although their height differs. The two negative bands at 879 and 901 cm$^{-1}$ in the spectrum of the neutral ligand correspond to overall deformational vibrations, followed by a large positive-negative pair, which also contains C–C stretching vibrations.
Figure 5.9: The backscattering ROA spectra (BPS86/RI/TZVPP) of (+)-3-acetylcamphor (top, left-hand side), (+)-acam (top, right-hand side), \( \Delta \text{-Co(acac)}_3 \) (middle, left-hand side), \( \Delta \text{-Co((+)-acam)}_2 \) (middle, right-hand side), \( \text{trans(I)-\Delta-} \text{-Co((+)-acam)}_2 \) (bottom, left-hand side), and \( \text{mer-\Delta-Co((+)-acam)}_3 \) (bottom, right-hand side).

A similar pattern is observed in the spectrum of the anion with wavenumbers shifted slightly to higher values. The remaining parts of the spectrum mostly differ, e.g., the positive band at around 1430 cm\(^{-1}\) in the spectrum of the neutral ligand is only half as intense as in the spectrum of the anion and a different pattern is obtained for the surrounding bands. The antisymmetric and symmetric combinations of the carbonyl stretching vibrations give rise to very intense peaks at 1700 and 1750 cm\(^{-1}\), respectively, in the spectrum.
5.3. Influence of chiral ligands on the spectra

Interestingly, these combinations are observed in the same order in the spectrum of the anion, but the antisymmetric combination shows a negligible positive intensity. The symmetric combination leads to a positive peak, contrary to the neutral species. The corresponding vibrations are significantly shifted to lower wavenumbers due to the structural difference between the neutral and the negatively charged ligand. These findings are contrary to the ones obtained from the VCD spectra, in which the carbonyl stretching vibrations were not observed for the free ligands [435].

The spectrum of $\Delta\text{-Co(acac)}_3$ is also given in Fig. 5.9. Replacing one acac ligand by the (+)-acam ligand considerably increases the number of peaks with strong intensity. This is seen in the ROA spectrum of $\Delta\text{-Co}((+)-acam)(\text{acac})_2$ in Fig. 5.9 and is especially obvious in the region from 700 to 1200 cm$^{-1}$. In this wavenumber range, the acam ligand induces many bands, which is in accordance with the ROA spectrum of the isolated ligand molecule, although the intensities change due to binding to the metal complex. Easily detected are the two negative bands and the positive band between 200 and 500 cm$^{-1}$, which also occur in the spectrum of $\Delta\text{-Co(acac)}_3$. The acam ligand slightly participates in the corresponding normal modes. The intense negative band, existing in the spectrum of the $\Delta\text{-Co(acac)}_3$ complex at around 600 cm$^{-1}$, can be found in the spectrum of $\Delta\text{-Co}((+)-acam)(\text{acac})_2$ close to another negative band belonging to deformational vibrations involving all ligands. In the region from 1250 to 1510 cm$^{-1}$, the intensities are more or less the same in both spectra. In contrast to that, the positive band around 1250 cm$^{-1}$ shows a diminished height if the chiral ligand is present. It corresponds to a C–C stretching vibration and carries a similar intensity as in the spectrum of $\Delta\text{-Co(acac)}_3$, but the overlap with a negative close-lying normal mode, localized mainly on the acam ligand, instead of a positive band as in the spectrum of $\Delta\text{-Co(acac)}_3$ leads to the reduced intensity. The out-of-phase and in-phase combinations of carbonyl stretching vibrations of the acac ligands are found at 1548 and 1555 cm$^{-1}$ in the same order like for $\Delta\text{-Co(acac)}_3$ and again with small negative intensities. The carbonyl stretching vibration of the acam ligand occurs at 1579 cm$^{-1}$ with a positive intensity.

As an example for a ROA spectrum of a complex with two acam ligands, the one of trans(I)-$\Delta\text{-Co}((+)-acam)_2(\text{acac})$ is given in Fig. 5.9. The two negative bands and the positive band between 200 and 500 cm$^{-1}$, which have already been observed in the $\Delta\text{-Co}((+)-acam)(\text{acac})_2$ spectrum, are again easily recognizable. The following part of the spectrum is similar to the one of $\Delta\text{-Co}((+)-acam)(\text{acac})_2$ up to about 1500 cm$^{-1}$ although the intensity of the bands partly differs. An exception is the positive band around 1250 cm$^{-1}$ observed in the spectrum of $\Delta\text{-Co(acac)}_3$ with a very high intensity and in the one of $\Delta\text{-Co}((+)-acam)(\text{acac})_2$ with an already reduced intensity. In the complex with two acam ligands it is no longer observable with high intensity due to the negative bands caused by the acam ligands. The carbonyl stretching vibration of the acac ligand leads to a very weak negative peak at 1508 cm$^{-1}$. The intense
positive peak at 1565 cm$^{-1}$ belongs to the out-of-phase and the negative one at 1575 cm$^{-1}$ to the in-phase combination of the carbonyl stretching vibrations of the acam ligands, respectively, which is, of course, different from the spectrum of $\Delta$-Co((+)-acam)(acac)$_2$.

If the remaining acac ligand is substituted by the (+)-acam ligand, the mer-$\Delta$-Co((+)-acam)$_3$ complex is obtained, whose ROA spectrum is presented in Fig. 5.9. It shows many similarities (although the intensities are partly higher) in the region from 700 to 1400 cm$^{-1}$ compared to the one of trans(I)-$\Delta$-Co((+)-acam)$_2$(acam) since this region has already been dominated by the acam ligands in the $\Delta$-Co((+)-acam)(acam)$_2$ and trans(I)-$\Delta$-Co((+)-acam)$_2$(acam) spectra. Obviously, the spectra differ around 400 cm$^{-1}$ since the negative band and the following intense positive band, in which the acam ligand participates only slightly and which mainly originate from normal modes localized on the acac ligand, occur with very small absolute intensities. Furthermore, intense negative bands around 600 cm$^{-1}$ are observed, in contrast to the spectrum of trans(I)-$\Delta$-Co((+)-acam)$_2$(acam). Noticeable differences are also observed from 1400 up to 1600 cm$^{-1}$ due to the missing contributions of the acac ligands. The most intense peaks in the region belong to the carbonyl stretching vibrations. The out-of-phase combinations belong again to a positive intensity and the in-phase one gives rise to a large negative intensity. The out-of-phase vibrations are found at lower wavenumbers in analogy to the spectrum of trans(I)-$\Delta$-Co((+)-acam)$_2$(acam).

### 5.3.2 Ligand chirality

As a next step, the importance of the ligand chirality for ROA intensities is investigated. This can be accomplished by inspecting the spectra of the complexes, studied in the previous section for the (+)-acam ligand, employing now the (−)-enantiomer of the acam ligand.

The spectra of $\Delta$-Co(−-acam)(acam)$_2$ and $\Delta$-Co((+)-acam)(acam)$_2$ given in Fig. 5.10 comprise many similarities. The bands from 100 cm$^{-1}$ to around 700 cm$^{-1}$ are almost the same, except of the small peaks around 550 cm$^{-1}$. The situation is different for the wavenumbers of about 750 to 1250 cm$^{-1}$ since the bands occur with a reversed sign. This shows the influence of the acam ligand because the (−)- instead of the (+)-form is employed giving rise to ROA intensities with inverted signs. The intense positive-negative pair around 1250 cm$^{-1}$ is present in both spectra due to the dominating participation of the acac ligands (especially in the normal mode belonging to the positive band), even though with differing intensity values. The out-of-phase and in-phase combinations of the carbonyl stretching vibrations of the acac ligands show both for $\Delta$-Co((+)-acam)(acam)$_2$ and $\Delta$-Co(−-acam)(acam)$_2$ very weak negative intensities. The sign of the intensity of the carbonyl stretching vibration of the acam ligand is, as expected, reversed. However, the band is more intense in the case of $\Delta$-Co(−-acam)(acam)$_2$ ($-0.05 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$) than for $\Delta$-Co((+)-
5.3. Influence of chiral ligands on the spectra

acam)(acac)₂ (0.02 · 10⁻⁶ Å⁴ a.m.u.⁻¹). So, the Δ configuration together with the (−)-enantioinety of the acam ligand appears to slightly enhance the intensity of the acam carbonyl stretching vibration.

Analogous observations are made when comparing the spectra of trans(I)-Δ-Co((+)-acam)₂(acac) and trans(I)-Δ-Co((−)-acam)₂(acac). The low wavenumber parts are largely similar, especially the intense bands caused by the acac ligand. Noteworthy is the enhancement of the negative band around 1620 cm⁻¹ for the (−)-acam-containing complex, which belongs to a mixture of stretching and in-plane deformational vibrations delocalized over the whole molecule. The part of the spectra with higher wavenumbers mainly consists of bands with opposite sign. Some deviations occur, e.g., between 1300 and 1500 cm⁻¹ due to the influence of the acac ligand or the Δ configuration. The carbonyl stretching vibration of the acac ligand in trans(I)-Δ-Co((−)-acam)₂(acac) at 1553 cm⁻¹ corresponds, like in the case of trans(I)-Δ-Co((+)-acam)₂(acac), to a negative intensity, however with a smaller absolute value. The out-of-phase and in-plane combinations localized on the acam ligands give rise to bands with inverted signs.

The ROA spectrum of mer-Δ-Co((−)-acam)₃ shows, compared to the one of mer-Δ-Co((+)-acam)₃, some differences, e.g., around 450 cm⁻¹, but the important two negative bands at around 600 cm⁻¹ are similar in both spectra. The bands at higher wavenumbers show mostly opposite signs. Noticeable is that the by far most intense peak is the in-phase carbonyl stretching vibration with a large negative value. Compared to that, the out-of-phase combinations show a small positive and negative value so that they are not visible in the spectrum.

5.3.3 Geometrical isomers

Since the chiral acam ligand is employed, several geometrical isomers are possible (compare Fig. 5.7). The trans(II)-Δ-Co((+)-acam)₂(acac) complex is one example, its ROA spectrum is presented in Fig. 5.10. Obviously, there are differences compared to the spectrum of trans(I)-Δ-Co((−)-acam)₂(acac). The negative band around 370 cm⁻¹ in the spectrum of the latter does not occur in the one of the trans(II) isomer. Most remarkable is the negative-positive pair around 500 cm⁻¹ which is observed for the trans(II) isomer whereas relatively weak positive bands can be found in the spectrum of the trans(I) analog. In addition, the intensities of several peaks vary, as, for example, the ones of the three negative bands centered at around 650 cm⁻¹. Some minor sign changes are visible (see, for example, the region around 1400 cm⁻¹). Interestingly, all carbonyl stretching vibrations carry a positive intensity, contrary to the trans(I) isomer, for which a negative-positive-negative pattern is obtained.

The spectrum of the cis isomer shows larger similarities with the spectrum of trans(I)-Δ-Co((+)-acam)₂(acac) than the trans(II) isomer. The most obvious difference is the increase of the positive band at 220 cm⁻¹ in the spectrum of the cis isomer. The negative band at around 370 cm⁻¹ is also found, contrary
to the spectrum of the trans(II) isomer. The intensity of this normal mode is dominated by the contribution of the $\beta(G')^2$ invariant, for which a value of $-488 \cdot 10^{-6} \text{ A}^4 \text{ a.m.u.}^{-1}$, $67 \cdot 10^{-6} \text{ A}^4 \text{ a.m.u.}^{-1}$, and $-507 \cdot 10^{-6} \text{ A}^4 \text{ a.m.u.}^{-1}$ is calculated for the trans(I), trans(II), and cis isomers, respectively.

Figure 5.10: The backscattering ROA spectra (BP86/RI/TZVPP) of $\Delta$-Co(−)-acam)(acac)$_2$ and $\Delta$-Co(+)acam)(acac)$_2$ (top, left-hand side), trans(I)-$\Delta$-Co(−)-acam)$_2$(acac) and trans(I)-$\Delta$-Co(+)acam)$_2$(acac) (top, right-hand side), mer-$\Delta$-Co(−)-acam)$_3$ and mer-$\Delta$-Co(+)acam)$_3$ (middle, left-hand side), trans(II)-$\Delta$-Co(−)-acam)$_2$(acac) and trans(I)-$\Delta$-Co(+)acam)$_2$(acac) (middle, right-hand side), cis-$\Delta$-Co(−)-acam)$_2$(acac) and trans(I)-$\Delta$-Co(+)acam)$_2$(acac) (bottom, left-hand side), and fac-$\Delta$-Co(−)-acam)$_3$ and mer-$\Delta$-Co(+)acam)$_3$ (bottom, right-hand side).
Figure 5.11: Group coupling matrices for the $\beta(G')^2$ invariant of the normal mode at 371 cm$^{-1}$ for trans(I)-$\Delta$-Co((+)-acam)$_2$(acac) (top; left-hand side), trans(II)-$\Delta$-Co((+)-acam)$_2$(acac) (top; middle), and cis-$\Delta$-Co((+)-acam)$_2$(acac) (top; right-hand side); “Ac” denotes the acac ligand, “L1” and “L2” the (+)-acam ligands, and “M” the cobalt atom; a graphical representation of the normal mode is given at the bottom.

<table>
<thead>
<tr>
<th>trans1</th>
<th>trans2</th>
<th>cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>Ac</td>
<td>Ac</td>
</tr>
<tr>
<td>L1</td>
<td>L1</td>
<td>L1</td>
</tr>
<tr>
<td>L2</td>
<td>L2</td>
<td>L2</td>
</tr>
<tr>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
</tbody>
</table>

A picture of the normal mode is given in Fig. 5.11 together with group coupling matrices [340] (compare section 3.5.2) of the three isomers for the $\beta(G')^2$ invariant. The negative band in the spectra of the trans(I) and cis isomers mainly originates from the coupling of the ligands between each other leading to large negative contributions since negative contributions from the metal atom are found for all three isomers. For the trans(II) isomer, only small positive contributions are obtained.

A remarkable negative band around 480 cm$^{-1}$ solely exists in the spectrum of the trans(II) isomer, for which remarkably negative $\beta(G')^2$ values of $-511 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$ and $-443 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$ are evaluated for the normal modes at 450 cm$^{-1}$ and 489 cm$^{-1}$. The corresponding values for the trans(I) isomer are $-4 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$ and $227 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$, respectively, and $-154 \cdot 10^{-6}$
Å$^4$ a.m.u.$^{-1}$ and $-3 \cdot 10^{-6}$ Å$^4$ a.m.u.$^{-1}$ for the cis isomer. The contributions of the $\beta(A)^2$ invariant are small. The group coupling matrices and a picture of the normal mode at 450 cm$^{-1}$ are shown in Fig. 5.12.

Figure 5.12: Group coupling matrices for the $\beta(G')^2$ invariant of the normal mode at 450 cm$^{-1}$ for trans(I)-$\Delta$-Co((+)-acam)$_2$(acac) (top; left-hand side), trans(II)-$\Delta$-Co((+)-acam)$_2$(acac) (top; middle), and cis-$\Delta$-Co((+)-acam)$_2$(acac) (top; right-hand side); “Ac” denotes the acac ligand, “L1” and “L2” the (+)-acam ligands, and “M” the cobalt atom; a graphical representation of the normal mode is given at the bottom.

As can be seen, the decisive point for the much more negative intensity in the case of the trans(II) isomer is the coupling of the acam ligands with the acac ligands causing significant negative contributions (also in the case of the cis isomer, but with a smaller magnitude).

The situation is different for the normal mode at 489 cm$^{-1}$, where the large negative contributions arising from the acam ligands themselves are responsible for the negative intensity found in case of the trans(II) isomer (see Fig. 5.13). Only small negative contributions are calculated for the trans(I) isomer so that
the positive value arising from the coupling of the acam ligands dominates. For the cis isomer, a mixture of negative and positive contributions is evaluated leading to a very small negative $\beta(G')^2$ value.

Figure 5.13: Group coupling matrices for the $\beta(G')^2$ invariant of the normal mode at 489 cm$^{-1}$ for trans(I)-$\Delta$-Co((+)-acam)$_2$(acac) (top; left-hand side), trans(II)-$\Delta$-Co((+)-acam)$_2$(acac) (top; middle), and cis-$\Delta$-Co((+)-acam)$_2$(acac) (top; right-hand side); “Ac” denotes the acac ligand, “L1” and “L2” the (+)-acam ligands, and “M” the cobalt atom; a graphical representation of the normal mode is given at the bottom.

The positive band observed at around 520 cm$^{-1}$ in the spectrum of the cis isomer is as intense as in the spectrum of the trans(I) analog and not as high as for the trans(II) isomer. Comparing the cis and trans isomers, some varieties in the peak height are observed in the region around 650 cm$^{-1}$, but they are quite small. The acac carbonyl stretching vibration of the cis isomer at 1544 cm$^{-1}$ leads to a small negative band, which is in analogy to the trans(I) isomer. The carbonyl stretching combinations of the acam ligands of cis-$\Delta$-Co((+)-acam)$_2$(acac) at 1566 cm$^{-1}$ and 1575 cm$^{-1}$ give rise to positive peaks.
in accordance to the trans(II) isomer.

In order to demonstrate that these three geometrical isomers also exhibit distinguishable ROA spectra in the case of hybrid density functionals, the ROA spectra obtained with B3LYP are shown in Fig. 5.14.

Figure 5.14: The backscattering ROA spectra (property tensors: B3LYP/TZVP; force field: BP86/RI/TZVPP) of trans(I)-∆-Co((+)-acam)\(_2\) (acac) and trans(II)-∆-Co((+)-acam)\(_2\) (acac) (left-hand side), and trans(I)-∆-Co((+)-acam)\(_2\) (acac) and cis-∆-Co((+)-acam)\(_2\) (acac) (right-hand side).

The calculation with this density functional yields in parts quite different ROA intensities compared to the ones calculated with the pure density functional BP86. However, as in the case of BP86, the regions from 100 to around 400 cm\(^{-1}\) and from about 600 to 700 cm\(^{-1}\) comprise bands which show noticeably different bands for the trans(I), trans(II), and cis isomers. The similarity between the spectra of trans(I)-∆-Co((+)-acam)\(_2\) (acac) and cis-∆-Co((+)-acam)\(_2\) (acac), however, is not so pronounced as in the spectra of Fig. 5.10 obtained with the BP86 density functional. The acac carbonyl stretching vibration corresponds to a small negative intensity in the spectrum of the trans(I) isomer and to positive ones in the spectra of the other two isomers. The out-of-phase combination of the carbonyl stretching vibration of the acam ligands leads to a weak negative band in case of the cis isomer and to positive ones for the trans isomers. For the in-phase combination, a positive ROA intensity is calculated for all three isomers.

The laser wavelengths in ROA measurements are usually lower than the one employed in our ROA calculations (900 nm) for the metal complexes. These may, however, cause (pre)resonance effects in the ROA spectrum of the metal complexes. For example, the first three electronic excitations were evaluated to have wavelengths of 603, 586, and 584 nm for trans(I)-∆-Co((+)-acam)\(_2\) (acac), 604, 585, and 583 nm for trans(II)-∆-Co((+)-acam)\(_2\) (acac), and 603, 587, and 584 nm for cis-∆-Co((+)-acam)\(_2\) (acac) with the B3LYP density functional. The next electronic transitions were calculated to be at wavelengths below 461 nm. The three mentioned excitation wavelengths lead to transitions mainly from
the highest occupied molecular orbital (HOMO) and lower occupied ones to the lowest unoccupied molecular orbital (LUMO) and to the LUMO+1. The molecular orbitals with large contributions to the three considered electronic transitions in the case of \textit{cis-\Delta-}\textit{Co}((+)-acam)\textsubscript{2}(acam) are shown in Fig. 5.15.

**Figure 5.15:** Molecular orbitals (B3LYP/TZVP) of \textit{cis-\Delta-}\textit{Co}((+)-acam)\textsubscript{2}(acam) involved in the three electronic transitions considered in this work.

The RROA spectra considering resonance with these three energetically lowest electronic transitions were calculated. The left-hand side of Fig. 5.16 shows the spectra obtained by setting the excitation wavelength to 603 nm for \textit{trans(I)-\Delta-}\textit{Co}((+)-acam)\textsubscript{2}(acam) and \textit{cis-\Delta-}\textit{Co}((+)-acam)\textsubscript{2}(acam), and to 604 nm for \textit{trans(II)-\Delta-}\textit{Co}((+)-acam)\textsubscript{2}(acam). Since these wavelengths correspond to the excitation wavelengths of the first excited electronic state, the obtained spectra are typical monosignate RROA spectra due to resonance with only a single excited electronic state [223, 224, 226] (see section 3.4). Remarkable differences between the spectra of the \textit{trans(I)} and \textit{trans(II)} isomers are found for the wavenumbers of the bands around 140 cm\textsuperscript{-1}, as has already been observed in the corresponding off-resonance spectra in Fig. 5.10. Moreover, especially the intense bands show a significant different intensity values whereby the ones of the \textit{trans(I)} isomer are mostly more intense. In general, the RROA spectra from around 1100 to 1500 cm\textsuperscript{-1} show only some small bands, which is in contrast to
Figure 5.16: The RROA spectra (B3LYP/TZVP) considering the first three excited electronic states of \textit{trans}(I)-\Delta-Co((+)-acam)\textsubscript{2}(acac) and \textit{trans}(II)-\Delta-Co((+)-acam)\textsubscript{2}(acac) (top), and of \textit{trans}(I)-\Delta-Co((+)-acam)\textsubscript{2}(acac) and \textit{cis}-\Delta-Co((+)-acam)\textsubscript{2}(acac) (bottom); the excitation wavelength for the spectra was set to the wavelength of the first excited electronic state of the molecule on the left-hand side and to 584 nm for the spectra on the right-hand side.

Interestingly, the RROA spectra for the excitation wavelength of 584 nm are again monosignate (see the spectra on the right-hand side of Fig. 5.16). Some vibrations show negative intensities, but their values are negligibly small so that they are not recognizable in the broadened spectra. In contrast to the RROA spectra obtained in resonance with the first excited electronic state, the by far most intense band is now the one around 1570 cm\textsuperscript{-1}. The \textit{trans}(I) isomer gives primarily rise to more intense bands than the \textit{trans}(II) isomer and the most obvious deviation in the band position is again detected for the bands between...
100 and 200 cm\(^{-1}\). The RROA spectrum of the cis isomer consists of bands, which are in general also less intense than the ones of the trans(I) isomer, but more intense than the corresponding bands of the trans(II) isomer.

The geometrical isomers of the $\Delta$-Co((+)-acam)$_3$ complex are the fac and mer isomers, whose ROA spectra are given in Fig. 5.10. The characteristic pattern is pretty much the same although the height of the bands is slightly different for most bands. However, there are some smaller bands, which even carry an opposite sign. For example, the deformational vibrations of the hydrogen atoms emerging around 1400 cm\(^{-1}\) have ROA bands with varying signs. The negative band surrounded by positive bands around 500 cm\(^{-1}\) in the spectrum of the mer isomer is due to a deformational vibration of the carbon and oxygen atoms and is positive in the case of fac-$\Delta$-Co((+)-acam)$_3$.

### 5.3.4 $\Delta$ versus $\Lambda$ configuration

As a last aspect, the influence of the $\Lambda$ and $\Delta$ configurations on the ROA spectra is investigated. This is achieved by comparison of the spectra of $\Delta$-Co((+)-acam)(acac)$_2$ and $\Lambda$-Co((+)-acam)(acac)$_2$ (see Fig. 5.17). The part from 100 to 700 cm\(^{-1}\) contains bands whose signs are opposite for the $\Delta$ and $\Lambda$ configurations whereas the following peaks mainly carry the same sign. This is due to the equal chirality of the acam ligands. Exceptions are the reversed bands between about 900 and 1000 cm\(^{-1}\) where the acac ligands play a major role (compare the spectrum of $\Delta$-Co(acac)$_3$ in Fig. 5.9). The $\Lambda$ configuration is again dominating for the bands with wavenumbers higher than approximately 1220 cm\(^{-1}\) leading to reversed signs of the corresponding bands. However, the absolute intensity values partly vary remarkably. The carbonyl stretching vibration of the acam ligands is an exclusion because it belongs to a positive band in both spectra. As described above, the intensity is very small for the $\Delta$ isomer. The $\Lambda$ stereoisomer, nevertheless, leads to a much more intense band.

Figure 5.17: The backscattering ROA spectra (BP86/RI/TZVPP) of $\Lambda$-Co((+)-acam)(acac)$_2$, $\Delta$-Co((+)-acam)(acac)$_2$ (left-hand side) and fac-$\Lambda$-Co((+)-acam)$_3$ and fac-$\Delta$-Co((+)-acam)$_3$ (right-hand side).
Another example is the Co((+)-acam)$_3$ complex. The ROA spectrum of the \textit{fac} isomer in the $\Lambda$ configuration is given in Fig. 5.17. Comparing it to the spectrum of \textit{fac-$\Delta$}-Co((+)-acam)$_3$, again the opposite signs of most bands up to 700 cm$^{-1}$ are obvious but, in addition, the characteristic patterns are different. The bands at higher wavenumbers are similar for the $\Lambda$ and $\Delta$ isomers, at least up to 1400 cm$^{-1}$. The remaining part of the spectrum appears to be a mixture of bands with intensities having equal and opposite sign, i.e., neither the $\Lambda / \Delta$ nor the ligand configuration totally dominates these normal modes, mainly featuring hydrogen deformational and antisymmetric carbonyl stretching vibrations. The out-of-phase and in-phase combinations of the carbonyl stretching vibrations at 1574/1575 cm$^{-1}$ occur with opposite bands in the spectra, which means that the $\Lambda / \Delta$ isomery primarily determines their ROA intensity. Worth mentioning is the relatively weak negative band of the out-of-phase combination for the $\Lambda$ isomer.
6. Raman Optical Activity Investigation of Biomolecules

The ROA spectra discussed in section 5 concerned chiral metal complexes, for which, however, experimental data is lacking. In contrast to this, a plethora of measured ROA spectra is available for organic molecules, ranging from sugar molecules to proteins and viruses (see, e.g., Refs. [4,26,28–31,48,314,317,334,418,444–459]). The focus of the theoretically predicted ROA spectra in the remaining part of this thesis lies therefore on different types of biomolecules. The comparison to experimental data allows then the assessment of solvent effects on ROA spectra and the determination of typical ROA signatures. The first examples presented in this chapter deal with quite small molecules, namely the analgesic naproxen (section 6.1), the anhydro sugar 1,6-anhydro-\(\beta\)-D-glucopyranose (section 6.2), and the amino acid tryptophan (section 6.3). Secondary structure elements of \(\alpha\)-, \(\beta\)\(_{10}\)-helices, and \(\beta\) turns are investigated in sections 6.4 and 6.5 by means of model helices and a metallothionein protein. These are the by far largest molecules for which \textit{ab initio} ROA calculations have been carried out up to date [460,461].

6.1 Resonance Raman optical activity study of naproxen

The first (and only) experimental observation of RROA was reported in 1998 for the analgesic naproxen [133], which is structurally similar to the pain reliever ibuprofen. A theoretical RROA approach was presented by Jensen \textit{et al.} based on TD-DFT that is suitable also in cases of several close-lying excited electronic states in resonance [301]. It is well-known that under such circumstances peculiar features can appear in RR spectra which are known as anti-resonance Raman scattering or RR deenhancement. Such an effect was first observed by Stein \textit{et al.} in 1976 [462] for a series of transition metal complexes, followed by a series of experimental and theoretical investigations [463–467]. Although the approach presented in Ref. [301] can in principle deal with such effects, it neglects the vibronic details of the electronic state in resonance. While this is often an excellent approximation, especially in molecules with unstructured absorption bands, the vibronic structure can have an important impact in molecules where pronounced vibronic details can be recognized in the UV-VIS spectrum. Many molecules exhibit more than just one absorption band in the UV-VIS. Due to inaccuracies in calculated excitation energies, it may thus be difficult to decide from a theoretical point of view alone which of the electronic states is (or are)
in resonance in an experimental set-up [152, 388, 397, 398, 468–472].

In this thesis, the first RROA calculations including vibronic details of the considered excited electronic states are presented employing the IMDHO model (compare section 3.4 and appendix A.3) [226]. As examples, (S)-(+)naproxen and its ester (S)-(+)naproxen-OCOCD$_3$ were chosen. Their structures are shown in Fig. 6.1. There exist several conformers of (S)-(+)naproxen and the conformer which resembles the lowest energy conformer found in Ref. [473] was taken for the calculations. In the following, calculated RROA and RR spectra as well as off-resonance spectra of the ester conformer are compared with the experimental ones given in Ref. [133]. Furthermore, changes of the RROA and RR intensities which are due to the consideration of resonance with the second excited electronic state are investigated for (S)-(+)naproxen.

Figure 6.1: Optimized structures (B3LYP/TZVP) (top) and graphical representation (bottom) of (S)-(+)naproxen (left-hand side) and (S)-(+)naproxen-OCOCD$_3$ (right-hand side).

6.1.1 Comparison to experimental spectra

The experimental spectra of (S)-(+)naproxen-OCOCD$_3$ were measured in the DCPI set-up with an excitation wavelength of 514.5 nm. Although the maximum of the absorption band was found in experiment near 325 nm, the excitation wavelength was found to lie within the low-frequency tail of this absorption band [133]. Therefore, we employed the formulae of the DCPI experimental set-up [compare Eqs. (3.215) and (3.217)] for the calculation of the RROA and RR spectra (which was done for a laser wavelength of 302 nm since this is the calculated excitation wavelength of the first excited electronic state) and for the ROA and Raman spectra, which were calculated in the far-from-resonance approximation [23] employing the same laser wavelength as in the experiment (514.5 nm). The recorded ROA spectrum (see Fig. 6.2) shows mostly negative
bands. A monosignate spectrum with negative intensities is predicted by theory if resonance with one excited electronic state is considered (compare section 3.4).

Figure 6.2: top: The experimental RROA (left-hand side) and RR (right-hand side) spectra of \((S)-(\pm)-naproxen-OC\), which were reproduced from the data given in Ref. [133]; middle: the calculated DCPI RROA (left-hand side) and RR (right-hand side) spectra (B3LYP/TZVP) of \((S)-(\pm)-naproxen-OC\) obtained with an excitation wavelength of 302 nm; bottom: the off-resonance DCPI ROA (bottom; left-hand side) and Raman (bottom; right-hand side) spectra of \((S)-(\pm)-naproxen-OC\) obtained with a laser wavelength of 514.5 nm.
As can be seen in Fig. 6.2, the calculated RROA spectrum is monosignate, containing only negative intensities, which is in accordance with the positive value of the calculated rotatory strength. Comparing the RR spectrum simulated with the same laser wavelength in Fig. 6.2, similar bands are found except that the intensities are all positive, again confirming the theory that the bands are the same in the RR and RROA spectra, having at most different signs. As mentioned before, the ROA and Raman spectra for the 514.5 nm laser wavelength are evaluated in the far-from-resonance approximation, which is usually applied in ROA calculations [19, 40, 43, 46, 47, 49–51, 53, 54, 225, 322–324, 342, 460, 474–476]. It is obvious in Fig. 6.2 that the (off-resonance) ROA spectrum shows a mixture of positive and negative bands as it is expected for non-resonance ROA spectra. If one compares the calculated spectra with the experimental one, it is obvious that the band at around 1380 cm\(^{-1}\) is, related to other bands in the spectrum, intense in the experimental spectrum as well as in the theoretically predicted ROA and RROA spectra, where the most intense normal mode is obtained at 1400 cm\(^{-1}\) involving C–C stretching and hydrogen in-plane deformatonal vibrations (see Fig. 6.3). The slightly positive band around 1330 cm\(^{-1}\) in the experimental spectrum may correspond to the positive band around 1310 cm\(^{-1}\) in the off-resonance spectrum, similarly the other positive band in the experimental spectrum around 1390 cm\(^{-1}\), which may be found in the ROA spectrum around 1415 cm\(^{-1}\). Furthermore, the bands in the region from 1470 to 1540 cm\(^{-1}\) can be recognized in the calculated ROA spectrum. In spite of that, only the one around 1520 cm\(^{-1}\), which belongs to a normal mode dominated by in-plane deformational vibrations of the hydrogen atoms at the benzene rings and wagging motions of methyl groups (compare Fig. 6.3), shows a non-negligible intensity in the calculated RROA spectrum. The negative band around 1615 cm\(^{-1}\) in the RROA spectrum (the corresponding normal mode is also shown in Fig. 6.3) might correspond to the one slightly shifted to higher wavenumbers in the experimental spectrum or to the one found at around 1670 cm\(^{-1}\) in the calculated ROA spectrum.

Figure 6.3: Graphical representation of the normal modes at 1400 cm\(^{-1}\), 1520 cm\(^{-1}\), and 1611 cm\(^{-1}\).
The on- and off-resonance Raman spectra are given on the right-hand side of Fig. 6.2. The doublet around 1410 cm$^{-1}$ is similar in the calculated RROA and ROA spectra and agrees well with the ones obtained in the experiment. The region from 1450 to 1540 cm$^{-1}$ is, compared to the experimental spectrum, again better described by the calculated Raman than the RR spectrum. The intense band experimentally observed around 1630 cm$^{-1}$ may correspond to the band around 1615 cm$^{-1}$, which is obtained with a small relative intensity in the Raman spectrum and a higher intensity in the RR spectrum, or, alternatively, to the intense band in the Raman spectrum around 1670 cm$^{-1}$.

6.1.2 Effect of the second excited electronic state

Often, there are close-lying electronic states in a molecule so that the obtained resonance spectra originate not only from resonance with a single electronic state. In the following, this phenomenon for the case of two close-lying excited electronic states is discussed and (S)-(+-)-naproxen is taken as the example molecule (see Fig. 6.1 for a graphical representation of the molecular structure). Its excitation profile is given in Fig. 6.4.

Figure 6.4: The simulated (B3LYP/TZVP) DCPI ROA excitation profile of (S)-(+-)-naproxen considering the first two excited electronic states.

The excitation for the first electronic state, which is mainly determined by an excitation from the HOMO to the LUMO (see Fig. 6.5 for molecular orbital plots), is found at 302 nm with an oscillator strength of 0.0428 (in the length representation of the electric-dipole operator) and 0.0423 (in the velocity representation of the electric-dipole operator; compare section 3.3.1). The rotatory strength is obtained with a value of $9 \times 10^{-5}$ atomic units (a.u.) in the length representation and $8 \times 10^{-5}$ a.u. in the velocity representation. The next electronic state is excited at 279 nm with a smaller oscillator strength of
0.014 (length representation) and 0.015 (velocity representation). The rotatory strength is similar to the first excited electronic state with \(9 \times 10^{-5}\) a.u. both in the length and velocity representations. This excitation involves electronic transitions from the HOMO−1 to the LUMO and from the HOMO to the LUMO+1 molecular orbitals (compare Fig. 6.5). The excitation wavelength of the third electronic state, which is not considered here, was calculated as 243 nm.

Figure 6.5: The molecular orbitals (B3LYP/TZVP) of \((S)-(+)-\text{naphoxen}\) involved in the two electronic excitations considered.

The effects in the RROA spectra due to changes in the excitation wavelength can be seen in Fig. 6.4, where the RROA spectra for laser wavelengths from about 310 to 270 nm (thus, including the first two electronic states) are shown. The RROA spectra in this region are very sensitive to the excitation wavelength. Around 300 nm, the spectra are monosignate with negative intensities, which is expected if only one electronic state is considered. However, positive RROA intensities are observed around an excitation wavelength of 290 nm which is an indication that the approximation of resonance with a single excited electronic state breaks down. Applying a laser wavelength lower than 280 nm gives again
rise to purely negative intensities since the second excited electronic state is dominating.

We investigate the vibration at 1611 cm\(^{-1}\) (for the graphical representation of the normal mode, see Fig. 6.3) in more detail in order to demonstrate how the intensity may change due to interference of two electronic states. The excitation profile considering solely the first excited electronic state is given at the top of Fig. 6.6. The most intense bands are obtained at wavelengths of about 300 and 315 nm, with the largest contribution coming from the imaginary part of the line shape function given in Eq. (A.10). Negligible intensities are found for wavelengths smaller than 280 nm. The second excited electronic state causes several bands from about 290 to 260 nm (see the middle part of Fig. 6.6), where the intense one at about 288 nm is again dominated by the part containing the imaginary contribution from the line shape function. Contrary to that, a large value of the real part is observed for the second intense one at around 276 nm. The excitation profile considering the two excited electronic states is given at the bottom of Fig. 6.6. The parts of the spectrum from about 330 to 300 nm and 280 to 250 nm are very similar to the spectra where only one excited electronic state is considered and more or less simply the sum of the contributions of the first and second excited electronic states. A large unusual effect, however, is found at about 288 nm. The spectra of the single excited electronic states, both the first and second one (at the top and the middle of Fig. 6.6, respectively), show a negative intensity due to the part originating from the imaginary line shape contributions. In spite of that, calculating the two excited electronic states at once, i.e., adding the tensor elements of the first and second excited electronic states and evaluating the invariants and the intensity afterwards, results in a positive band (see the bottom of Fig. 6.6), which even carries a larger absolute intensity than the sum of the bands obtained from the SES spectra, again coming from the large value evoked by the imaginary line shape contribution. This change, which not only alters the height of the band but also its sign, is due to the terms in the invariants that contain a tensor element belonging to one excited electronic state and the other tensor element corresponding to the other excited electronic state, e.g., \(\alpha_{\text{state1}} G_{\text{state2}}\), \(\alpha_{\text{state2}} G_{\text{state1}}\), \(\alpha_{\text{state1}} A_{\text{state2}}\), and \(\alpha_{\text{state2}} A_{\text{state1}}\). Further sign inversions can be found, for example, for the weak bands from 288 to about 275 nm since the contributions raised from the imaginary line shape part show positive values. An intensity deenhancement can be observed for the band around 295 nm, mainly because the real-line-shape part leads to a positive contribution in contrast to the negative ones calculated for the SES spectra.

The DCPI RROA intensity [see Eq. (3.215)] consists of two invariants, the \(\beta(G)^2\) invariant containing the magnetic-dipole part and \(\beta(A)^2\) comprising electric-quadrupole contributions. As discussed in section 3.4, the latter vanishes in the limit of resonance with one electronic state. This is obvious in the upper plot of Fig. 6.7, where the values for \(\beta(A)^2\) are found to be negligibly small, both for resonance with the first and second excited electronic states, respectively.
Figure 6.6: The calculated (B3LYP/TZVP) DCPI RROA excitation profiles of the normal mode at 1611 cm$^{-1}$ of (S)-(+)naproxen considering the first (top), the second (middle), and both electronic states (bottom); “real” indicates the contribution containing the real, “imag” containing the imaginary part of the line shape function to the total (“both”) RROA intensity.
6.1. Resonance Raman optical activity study of naproxen

Figure 6.7: The calculated (B3LYP/TZVP) DCPI RROA excitation profiles of the 1611 cm$^{-1}$ normal mode of (S)-(+-)naproxen obtained from the $\beta(A)^2$ (top and middle) and the $\beta(G)^2$ (bottom) invariants considering the first (“first state”), second (“second state”), and both (“both states”) electronic states.
Figure 6.8: The calculated (B3LYP/TZVP) DCPI RR excitation profiles of the 1611 cm\(^{-1}\) normal mode of (S)-(+)/naproxen considering the first (top), the second (middle), and both electronic states (bottom): “real” indicates the contribution arising from the real, “imag” from the imaginary parts of the line shape function to the total (“both”) RR intensity.
This picture changes completely if both states are considered at once (see middle of Fig. 6.7). Their interference leads to remarkably large $\beta(A)^2$ values, which are mostly positive. The $\beta(A)^2$ contributions of the SES spectra only give rise to a line around zero since they are so small compared to the result obtained from the calculation considering both excited electronic states at once. The behaviour of the $\beta(G)^2$ invariant, which is responsible for the RROA intensity in the SES limit [compare Eq. (3.238)], is also presented in Fig. 6.7. The regions from 320 to 295 nm and 280 to 255 nm are more or less the same, no matter whether both excited electronic states are considered or whether the SES approximation is employed. However, in the wavelength area in between, the negative contributions are almost cancelled due to destructive interference effects and even reversed to a small positive contribution at around 288 nm. So, the significant modifications in the RROA intensities in the region between resonance of the first and second excited electronic state are partly caused by the $\beta(G)^2$ invariant since its contribution is only small and negative or even positive due to interference. However, the large positive values obtained from the $\beta(A)^2$ invariant are the main reason for the intense positive band around 288 nm observed in the spectrum given at the bottom of Fig. 6.6.

Interference effects can also be observed in the calculated RR excitation profiles in Fig. 6.8. The ones obtained from the SES limit calculations for the first and second excited electronic state, respectively, show a very similar pattern compared to the corresponding RROA profiles, also in view of the contributions originating from the real and imaginary parts of the line shapes. Solely the absolute intensity values as well as their signs differ, which is in accordance with the predictions of the SES theory (see section 3.4). Considering resonance with the two excited electronic states, deenhancement effects are observed especially between excitation wavelengths of 280 and 296 nm. This result agrees with the observation of RROA interference effects at wavelengths lying between the excitation wavelengths of the first and second excited electronic states. Analysis in terms of the real and imaginary parts of the Raman scattering cross section, as was performed, e.g., in Ref. [463], is not straightforward in our case since the employed intensity formula in Eq. (3.217) contains sums and differences of tensor elements, making a general statement difficult. Even more involved is such an analysis in the case of the ROA invariants, which consist of tensor elements from different polarizability tensors.

### 6.2 Calculated Raman optical activity spectra of 1,6-anhydro-β-D-glucopyranose

A class of molecules for which a number of ROA spectra are available are carbohydrates [446–448,450–452,456,457]. Among them, a special kind of sugar derivatives are anhydro sugars which formally emerge by water elimination of aldoses and ketoses. Their reactivity depends on the size of the cyclic sugar
structure [477] and they are utilized as starting reagents for different types of syntheses, which do not necessarily only involve carbohydrate molecules. In 1917, the very first anhydro sugar was discovered, namely for the molecule \(D\)-altro-heptulose [478]. Another example for an anhydro sugar is 1,6-anhydro-\(\beta\)-D-glucopyranose (AGP), which can be formed by dry distillation of \(D\)-glucose [479]. Aqueous acid easily leads to hydrolysis of this anhydro sugar to glucose [480], which makes it a valuable reagent for, e.g., the preparation of glucose derivatives and polymerization reactions [479, 481].

Treating \(D\)-glucose with aqueous acids, the resulting equilibrium mixture contains AGP solely in small amounts so that it remained undiscovered for a long time [482]. Nevertheless, NMR [483–485], kinetic [486], and optical rotation [487, 488] experiments as well as molecular mechanics simulations [489, 490] were performed, demonstrating that the \(\text{1}_{\text{C}}\text{4}\) chair conformation is the dominant conformation. This was also found in crystal structures [479, 491]. The experimental ROA spectrum was published in 1991 [446]. In contrast to the numerous ROA measurements of sugar molecules, only two theoretical investigations have been performed [458, 492] showing that the conformational flexibility of the sugar molecules and solvent effects have to be explored in order to obtain calculated spectra agreeing well with the experimental ones. As a consequence, the number of structures to be considered is in principle quite large already for these small molecules, but it can be significantly reduced by dealing solely with the low-energy conformers. In this thesis, the ROA spectrum of AGP, which is a relatively rigid molecule, is studied. The conformers for the chair and boat conformations are examined, which results in 54 different structures [493].

Solvation is essential for polar functional groups as present in sugar molecules, but it is also the most difficult effect to model in calculations. For the calculation of vibrational spectra, a reliable, but also efficient solvation model is required. Continuum solvation is a first step toward this. As a continuum model, COSMO [494] with the standard settings as implemented in TURBOMOLE is employed. It can be anticipated that such a model is not well suited if directed weak contacts (hydrogen bonds) are built up from solvent molecules to the solute molecule, and hence microsolvated solute structures are an essential part of the modelling process (see, for example, Ref. [495] for a detailed study of water-microsolvation of a solute molecule). The optimum quantum-chemical model is then a combination of continuum- and micro-solvation. It is important to note that continuum solvation effects are not incorporated in the calculation of the property tensors, but they indirectly influence the Raman and ROA intensities via the COSMO-modified normal modes. They also affect the relative energies of conformers, their molecular structures, their vibrational frequencies, and thus also the Gibbs enthalpies.

In principle, each hydrogen atom of the hydroxyl groups of AGP has several possibilities to orient itself with respect to the ring. Gauche (g+ and g−, respectively, depending on the sign of the torsional angle) and trans (t) orientations are considered. This orientation is described by dihedral angles, which we define
as H(20)-O(11)-C(6)-C(2) for hydrogen atom H(20), as H(19)-O(9)-C(7)-C(6) for H(19), and as H(21)-O(10)-C(8)-C(4) for hydrogen atom H(21) (see Fig. 6.9 for the numbering of the atoms). The conformations are denoted by an abbreviation, in which the first part refers to the dihedral angle corresponding to hydrogen atom H(20), the second one referring to H(19), and the last one to H(21). For example, g+g−t denotes the conformation with a positive gauche dihedral angle of H(20), a negative gauche torsional angle of H(19), and a trans dihedral angle of H(21).

6.2.1 Influence of conformation and solvent

In the following, the influence of the different conformations and solvent effects on the calculated ROA spectra is demonstrated by some examples.

6.2.1.1 Chair versus boat conformation

As an initial step, we examine the differences in the ROA intensities for the $^1C_4$ chair and the $B_{0,3}$ boat conformations (for details about the notation, we refer to Ref. [496]). As an example, the ROA spectra of the chair and boat conformation of the g−g+t rotamer are given in Figs. 6.9 and 6.10, respectively. In the spectrum of the chair conformation, the band at 681 cm$^{-1}$ corresponds to a bending vibration, mainly of the ring atoms, and the negative band at 805 cm$^{-1}$ to a C–C stretching vibration followed by a deformational vibration of the whole molecule at 832 cm$^{-1}$. A mixture of C–C stretching and deformational vibrations of the hydrogen atoms gives rise to the positive peak at 914 cm$^{-1}$ and mainly deformational vibrations of the methylene groups of the ring lead to the negative band at about 950 cm$^{-1}$. The vibration at 981 cm$^{-1}$ contains some stretching vibrations of the C(4) and O(3) atoms as well as deformational vibrations. Each band at 1018, 1039, and 1042 cm$^{-1}$ involves a C–O stretching vibration of one of the three hydroxyl groups, respectively. The following intense bands involve deformational vibrations, mainly of the hydrogen atoms, in different variants. The normal mode at 1178 cm$^{-1}$, for example, includes a large movement of the H(21) hydrogen atom, while the negative one at 1319 cm$^{-1}$ features bending especially of the H(21) and H(14) hydrogen atoms, and the other negative mode at 1351 cm$^{-1}$ shows mainly bending of the H(19) hydrogen atom.

The ROA spectrum of the boat conformation of the g−g+t rotamer (compare Fig. 6.10) agrees partly with the one of the chair conformation. This is most obvious in the region up to 1100 cm$^{-1}$, in which the intensity values differ, but the signs are (mostly) the same. In addition, some vibrations are shifted to higher wavenumbers, but the corresponding bands of the ROA spectrum of the chair conformation can be assigned. Significant differences are observed at higher wavenumbers. The strong negative bands at around 1200 cm$^{-1}$ were not found in the spectrum of the chair conformation, only a few weak ones.
These normal modes are again bending vibrations, particularly of the hydrogen atoms. The intense negative peak at about 1379 cm\(^{-1}\) also corresponds to a bending vibration, which involves especially the hydroxyl group at C(8). Worth mentioning are the different signs of the band at around 1450 cm\(^{-1}\). It is negative in the case of the chair conformation and positive for the boat conformer. The underlying normal mode is a bending vibration of the two hydrogen atoms H(16) and H(17) of the methylene group in the ring. Although the motion of the atoms is quite similar, the corresponding intensities differ in sign since the magnetic-dipole-containing invariant, \(\beta(G')\), shows either a large positive or negative contribution for the boat and chair conformations, respectively, whereas the other invariant containing electric-quadrupole contributions is small. A local decomposition according to the proposal of Hug [340] (see section 3.5.2) showed that the H(17) hydrogen atom always gives a negative contribution to the \(\beta(G')\) invariant, which is the dominant one in the chair conformation. However, the H(16) hydrogen atom and its coupling to the H(17) and C(5) atoms contribute a large positive amount in the boat conformation so that the \(\beta(G'')\) invariant and the overall intensity are positive. This demonstrates how difficult it is to understand the origins of ROA intensities.

6.2.1.2 Influence of the orientation of the hydrogen atoms in hydroxyl groups

As mentioned above, the hydrogen atoms of the hydroxyl groups can assume many different orientations since they can rotate almost freely. In the case of sugar molecules, the most common orientations are the gauche and trans orientations. Several spectra of conformers differing in this regard are shown in
6.2. Raman optical activity spectra of 1,6-anhydro-\(\beta\)-D-glucopyranose

Fig. 6.10. The tg+t rotamer differs from the g-g+t rotamer by the orientation of the H(20) hydrogen atom. The corresponding spectra are very similar in the lower wavenumber region, in which mainly vibrations involving the carbon atoms occur. The largest differences occur at around 1200 cm\(^{-1}\), where an intense negative peak is found for the tg+t conformer, whereas such a band occurs at about 1235 cm\(^{-1}\) in the spectrum of the g-g+t rotamer. Changing the orientation of the H(20) hydrogen atom from a positive to a negative gauche torsional angle, the g-g-t conformer is obtained. Comparing its spectrum in Fig. 6.10 to the one of the g-g+t rotamer in Fig. 6.9, a similar pattern is found from 600 to 900 cm\(^{-1}\). However, the positive and negative bands between 900 and 1000 cm\(^{-1}\), which correspond to a mixture of stretching and deformational vibrations, show a reversed sign. The most conspicuous differences are again observed for the region from about 1150 to 1400 cm\(^{-1}\) since mainly hydrogen deformational vibrations occur in this range. Around 1200 cm\(^{-1}\), several ROA intensities differ significantly and sign inversions lead to a different appearance of the spectrum from 1250 to 1400 cm\(^{-1}\).

The ROA spectra are also sensitive to changes of the orientation of the H(21) hydrogen atom. This is demonstrated in Fig. 6.10 for the g-g+g- conformer in comparison to the ROA spectrum of the g-g+t conformer (Fig. 6.9). Significant differences are already detected for wavenumbers higher than 900 cm\(^{-1}\), although some similarities can be found in the peak pattern from about 1300 to 1400 cm\(^{-1}\) since the sign of the intensities are the same although the absolute values are different. Without going into more detail, it can be easily seen that already small changes in the orientation of the hydrogen atoms of the hydroxyl groups have a large effect on the ROA intensities.

6.2.1.3 Solvent effects

Two approximations were investigated in order to include solvent effects. The first one is the application of the COSMO continuum model which affects the energy, the molecular geometry, and the molecular Hessian (i.e., vibrational frequency) calculation, whereas no COSMO corrections were included in the KS equations for the calculation of the property tensors (see section 4.1). In Fig. 6.11, the ROA backscattering spectrum of the g-g+t conformer is presented as obtained with COSMO. There are only small differences compared to the spectrum calculated without any solvent (see Fig. 6.9). The values of the intensities differ, which is especially obvious for the large negative band at about 1300 cm\(^{-1}\). In contrast to this, the changes in the wavenumbers are small, and the overall pattern is thus quite similar. However, also a few sign changes are observed, particularly in the region from 1000 to 1050 cm\(^{-1}\), which correspond to C-O stretching vibrations of the hydroxyl groups, and for the small peak at about 1180 cm\(^{-1}\). However, the most remarkable pattern of the spectrum is not influenced by the intensities with reversed sign. Hence, the influence of the COSMO model is in total quite small compared to the
spectrum calculated without the continuum model.

Figure 6.10: Calculated backscattering ROA spectra (BP86/RI/TZVPP) of AGP in the \(tg+t\) (top; right-hand side), \(g−g−t\) (bottom; left-hand side), and \(g−g+g−\) (bottom; right-hand side) rotamers in the chair conformation and of the \(g−g+t\) (top; left-hand side) rotamer in the boat conformation; the line spectra have been scaled by 0.05.

As a second approximation, the continuum model was employed and, in addition, each hydroxyl group was solvated with one water molecule in such a way that the hydrogen atoms of the hydroxyl groups interact with the oxygen atoms of the water molecules (see Fig. 6.11). There are many changes in the corresponding spectrum compared to the one obtained solely with COSMO although the shifts in the wavenumbers are small for the comparable normal modes. Even in the low wavenumber region, in which the skeletal vibrations occur, remarkable differences exist. For instance, the only positive band at about 700 cm\(^{-1}\) in the spectrum without water molecules splits into two positive bands involving stretching vibrations of, e.g., the C–O bonds in the rings, affecting the water molecule interacting with the H(19) hydrogen atom. The negative-positive-negative pattern between 815 and 859 cm\(^{-1}\) shows distinct intensities since they also involve the water molecules through some deformational vibrations of the hydroxyl groups. In the region between 900 and 1000 cm\(^{-1}\), solely positive bands are observed in contrast to the spectrum without solvent molecules, demonstrating the large influence of the water molecules on the ROA intensities.
6.2. Raman optical activity spectra of 1,6-anhydro-\(\beta\)-D-glucopyranose

All vibrations at higher wavenumbers are more or less strongly modified due to the presence of the water molecules. Interestingly, the small positive peak around 1180 cm\(^{-1}\) in the spectrum obtained with COSMO and no explicit solvation is changed to a negative one if the water molecules are present and thus shows again the same sign as in the spectrum calculated without any solvent effect (Fig. 6.9). In contrast, the intense positive mode at around 1200 cm\(^{-1}\) is found in all spectra whether or not solvent effects are incorporated.

Figure 6.11: Calculated backscattering ROA spectra (BP86/RI/TZVPP) of the \(g-g+t\) conformer of AGP in the chair conformation obtained by employing the continuum model COSMO (left-hand side) and by explicit solvation with water molecules and COSMO (middle); the line spectra have been scaled by 0.05; the optimized (BP86/RI/TZVPP) structure of the explicitly solvated \(g-g+t\) conformer is shown on the right-hand side.

6.2.2 Comparison of calculated and experimental spectra

A construction of Raman and ROA spectra from the calculated spectra of the different conformers is desirable for the comparison to experimental data. Since the latter were obtained at room temperature, the population of the conformers at that temperature has to be examined as the conformers are usually not equally stable.

6.2.2.1 Populations of the conformers

First, all structures in the chair conformation were optimized without considering solvent effects. Minima were found for the conformers listed in Table 6.1. The one with the lowest electronic energy is the \(g-g+t\) conformer, which is shown in Fig. 6.9, followed by the \(tg+g+\) and \(tg-g+\) conformers with a about 2 kJ/mol higher electronic energy than the \(g-g+t\) conformer. A slightly higher electronic energy was found for the \(g-g+g-\) rotamer. Considering also the \(g-g+g+\) and \(g+g+g+\) rotamers, which are about 4 kJ/mol higher in electronic energy, these six conformers represent about 95% of the total population evaluated by a Boltzmann distribution. Considering the Gibbs enthalpy (evaluated for a temperature of 298.15 K), the results are similar, although the most stable one is now the \(g-g+g+\) rotamer, followed by the \(g-g+t\) rotamer. The Gibbs
enthalpy differences are not so large for the six mentioned conformers as the electronic energy differences, but, nevertheless, their population sums up to about 73% of the total population. The remaining 27% mainly correspond to ten conformers contributing between 1.6 and 3.0% (see Table 6.1). The g−g+t conformation has already been determined to be the most abundant one by employing Gibbs energy differences from molecular mechanics simulations [490], which may be due to favorable hydrogen bonding interactions of H(20) and H(19) with the oxygen atoms of the rings. Interestingly, the second most abundant conformation was found to be the g−g−t conformation in Ref. [490], which is not the case in our calculations. However, the tg+g+ conformer, which Straathof et al. noted to be the one with the third highest population [490], is also found in our calculations with a high population. Furthermore, they found the g−g+g−, tg−g+, and g+g+g+ conformations with population fractions of 6.6%, 6.1%, and 3.6%, respectively, which are in general lower than our population fractions (10.7%, 12.3%, and 9.8%, respectively). The g−g−g−, ttg+, g+tg+, and g+g−g+ conformers show no significant population, in contrast to Ref. [490]. It is notable that only conformations including a trans orientation of a hydroxyl hydrogen atom show a non-vanishing population if this hydrogen atom is the H(20) atom, which may be due to favorable hydrogen bonding interactions with the oxygen atom of the ring. For the conformations ttt, ttg−, tg−t, g+t, g+g+t, and tg+g−, no electronic energy minima were obtained.

The electronic energy differences and the corresponding populations obtained with the COSMO continuum model given in Table 6.1 differ from the ones obtained without COSMO (compare Table 6.1). The most stable conformer is again the g−g+t conformer, although its population is evaluated to be 23% instead of 37%. The g−g+g−, tg+g+, and g+g+g+ conformers are also estimated to be quite abundant. However, the population of tg−g+ is found to be 3% instead of 16% without the continuum model. No energy minimum was found for the g+g−g− and ttt rotamers. The populations obtained with the Gibbs enthalpies at 298.15 K reflect in most cases the results found by the electronic energy differences although the absolute values may differ. Obviously, there is no population with less than 1% contrary to the ones obtained from the electronic energy differences. Furthermore, the tg+t, g+g+g−, g+g+t, and tg+g− conformers are predicted to be higher populated (4% – 5%), whereas negligible values were calculated for the populations when considering only the electronic energy differences.

Inspecting the populations evaluated with the electronic energy differences considering only the boat conformers (with COSMO) in Table 6.2, relatively large populations were calculated for the g+g−t (13%), ttg− (9%), tg+t (8%), g−g−t (7%), and g+tg− (7%) rotamers. The remaining conformers are populated to at least 1%. However, comparing the energies with the ones of the chair conformations, the population of the g+g−t conformer is only 3%, which is in
Table 6.1: The electronic energy (E) and Gibbs enthalpy (G) (298.15 K) differences with respect to the conformer with the lowest energy/enthalpy value obtained for the conformers of AGP without including any solvent effect (left-hand side) and by employment of the continuum model COSMO (right-hand side) in the chair conformation; the values in brackets give the population in percentage obtained by a Boltzmann distribution (298.15 K).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>g−g+t</td>
<td>0.00 (36.66)</td>
<td>0.18 (13.29)</td>
<td>0.00 (23.00)</td>
<td>0.06 (9.82)</td>
</tr>
<tr>
<td>tg+g+</td>
<td>2.07 (15.89)</td>
<td>0.35 (12.41)</td>
<td>1.33 (13.47)</td>
<td>0.00 (10.06)</td>
</tr>
<tr>
<td>tg−g+</td>
<td>2.07 (15.88)</td>
<td>0.37 (12.31)</td>
<td>4.75 (3.38)</td>
<td>3.87 (2.11)</td>
</tr>
<tr>
<td>g−g+g−</td>
<td>2.97 (11.05)</td>
<td>0.73 (10.65)</td>
<td>0.78 (18.62)</td>
<td>0.35 (8.74)</td>
</tr>
<tr>
<td>g−g+g+</td>
<td>3.55 (8.75)</td>
<td>0.00 (14.30)</td>
<td>5.76 (2.26)</td>
<td>1.66 (5.15)</td>
</tr>
<tr>
<td>g+g+g+</td>
<td>4.06 (7.14 )</td>
<td>0.97 (9.67)</td>
<td>2.58 (8.12)</td>
<td>0.72 (7.53)</td>
</tr>
<tr>
<td>g−g−t</td>
<td>8.71 (1.09 )</td>
<td>4.69 (2.16)</td>
<td>4.19 (4.25)</td>
<td>3.77 (2.20)</td>
</tr>
<tr>
<td>g−g−g+</td>
<td>9.90 (0.67 )</td>
<td>5.43 (1.60)</td>
<td>7.36 (1.18)</td>
<td>3.57 (2.38)</td>
</tr>
<tr>
<td>g−g−g−</td>
<td>9.94 (0.66 )</td>
<td>4.55 (2.28)</td>
<td>4.75 (3.39)</td>
<td>3.82 (2.16)</td>
</tr>
<tr>
<td>tg−g−</td>
<td>9.98 (0.65 )</td>
<td>5.36 (1.65)</td>
<td>10.58 (0.32)</td>
<td>5.33 (1.17)</td>
</tr>
<tr>
<td>g+g−g+</td>
<td>10.63 (0.50 )</td>
<td>4.58 (2.25)</td>
<td>5.29 (2.72)</td>
<td>3.97 (2.03)</td>
</tr>
<tr>
<td>ttg+</td>
<td>11.97 (0.29)</td>
<td>3.86 (3.01)</td>
<td>4.35 (3.98)</td>
<td>2.92 (3.10)</td>
</tr>
<tr>
<td>g−tg+</td>
<td>12.51 (0.24)</td>
<td>5.13 (1.81)</td>
<td>7.07 (1.33)</td>
<td>3.19 (2.78)</td>
</tr>
<tr>
<td>g+tg+</td>
<td>12.56 (0.23)</td>
<td>4.35 (2.47)</td>
<td>4.92 (3.17)</td>
<td>3.05 (2.94)</td>
</tr>
<tr>
<td>g−tg−</td>
<td>13.75 (0.14)</td>
<td>4.26 (2.56)</td>
<td>4.42 (3.87)</td>
<td>3.03 (2.96)</td>
</tr>
<tr>
<td>g−tt</td>
<td>14.17 (0.12)</td>
<td>4.14 (2.69)</td>
<td>3.79 (4.99)</td>
<td>2.81 (3.24)</td>
</tr>
<tr>
<td>tg+t</td>
<td>21.62 (0.01)</td>
<td>4.05 (2.79)</td>
<td>8.78 (0.67)</td>
<td>1.46 (5.58)</td>
</tr>
<tr>
<td>g+g+g−</td>
<td>25.57 (0.00)</td>
<td>6.86 (0.90)</td>
<td>10.50 (0.33)</td>
<td>1.55 (5.39)</td>
</tr>
<tr>
<td>g+g−g−</td>
<td>28.95 (0.00)</td>
<td>13.38 (0.06)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>g+tg−</td>
<td>31.52 (0.00)</td>
<td>8.18 (0.53)</td>
<td>10.74 (0.30)</td>
<td>3.11 (2.87)</td>
</tr>
<tr>
<td>g+g−t</td>
<td>26.63 (0.00)</td>
<td>7.84 (0.60)</td>
<td>10.62 (0.32)</td>
<td>4.62 (1.56)</td>
</tr>
<tr>
<td>ttg−</td>
<td>—</td>
<td>—</td>
<td>10.29 (0.36)</td>
<td>2.77 (3.29)</td>
</tr>
<tr>
<td>tg−t</td>
<td>—</td>
<td>—</td>
<td>10.09 (0.39)</td>
<td>5.44 (1.12)</td>
</tr>
<tr>
<td>g+tt</td>
<td>—</td>
<td>—</td>
<td>10.00 (0.41)</td>
<td>3.06 (2.93)</td>
</tr>
<tr>
<td>g+g+t</td>
<td>—</td>
<td>—</td>
<td>9.67 (0.47)</td>
<td>1.87 (4.73)</td>
</tr>
<tr>
<td>tg+g−</td>
<td>—</td>
<td>—</td>
<td>9.45 (0.51)</td>
<td>2.20 (4.14)</td>
</tr>
</tbody>
</table>

acccordance with Ref. [490], where the populations were calculated from Gibbs energy differences obtained via molecular mechanics simulations. The populations for the tg+t, g−g−t, and g+tg− rotamers lie between 1% and 2%. Employing Gibbs enthalpies, the populations are more equally spread over the different conformers, the smallest one obtained for the g−g+g− conformer with 3%. Interestingly, the largest population is found for the g−g+t conformer (7% instead of 4% derived from the electronic energy differences).
the largest population \((g+g-t)\) employing the electronic energy differences is obtained with a population of only 5%

The electronic energy differences of the conformers containing three water molecules, which solvate the hydroxyl groups in addition to the continuum model, are also given in Table 6.2. The by far largest populations were obtained for the \(g-\text{tt}\) (77%) and \(tg-g+\) (18%) rotamers, where the water molecules are oriented in such a way that they can interact with the hydrogen and the oxygen atoms of different hydroxyl groups. The other conformers show negligible populations. Only the populations evaluated with the Gibbs enthalpies for these conformers, for which no imaginary frequency was found, are given because only these represent an energetic minimum. Again, a very high population of 78% is evaluated for the \(g-\text{tt}\) conformer, followed by the \(g+g+g+,\) \(tg+g+\), and \(g-g+g-\) conformers with 6% – 5%. However, these values must not be overinterpreted since the solvation with only three water molecules is, of course, not sufficient for a complete solvation of the whole molecule.

6.2.2.2 Construction of spectra and comparison to experiment

As was shown in the previous section, there is not only one conformer with a considerable population. This implies that the measured ROA spectrum is a superposition of the ROA spectra of certain conformers. As a consequence, the ROA intensities of the different conformers were multiplied by the population fractions calculated from the Gibbs enthalpy differences (indicated in the spectra by “G”) or from the electronic energy differences (denoted by “E” in the corresponding spectra) (compare section 6.2.2.1) for the conformations being considered. These individual ROA intensities were then summed up to generate the full ROA spectrum.

As a first test, the ROA spectrum of all chair conformers obtained without solvent effects was calculated. Weighting the spectra according to the populations given in Table 6.1 for the Gibbs enthalpy differences, the spectrum given in Fig. 6.12 is obtained. The experimental spectrum, taken from Ref. [446], is shown in Fig. 6.14. Since no significant bands were recorded for wavenumbers higher than about 1250 cm\(^{-1}\), only the region from 600 to 1250 cm\(^{-1}\) is plotted. The positive band at about 700 cm\(^{-1}\) as well as the negative-positive pattern at around 840 cm\(^{-1}\) are found both in the experimental and calculated spectra. In the experimental spectrum, two negative bands are observed at approximately 900 cm\(^{-1}\), which are reproduced in the calculated spectrum although being more separated with a weak negative and positive band in-between. The three positive bands from about 950 to 1050 cm\(^{-1}\) in the experimental spectrum are also found in the calculated spectrum. A difference is obvious for the region from 1100 to 1200 cm\(^{-1}\) because a positive intensity is calculated at around 1100 cm\(^{-1}\), followed by a negative band at roughly 1170 cm\(^{-1}\), which does not fit to the experimental data with a negative band at around 1100 cm\(^{-1}\) and a positive band at about 1150 cm\(^{-1}\). The two intense bands centered at about
1200 cm\(^{-1}\) exist in the experimental and in the calculated spectrum. Weighting the here considered conformer spectra by the populations evaluated from the electronic energy differences given in Table 6.1 does not lead to a better agreement with the experimental spectrum.

The corresponding construction of the Raman spectrum is presented in Fig. 6.13. The agreement with the experimental spectrum in Fig. 6.14 is very good although the absolute intensity values differ and the wavenumbers are shifted in some cases. The band at roughly 680 cm\(^{-1}\) is found in the calculated spectrum as well as the intense band near 810 cm\(^{-1}\). Even the following weak band is reproduced in the calculated spectrum. The positions of the three bands between 850 and 1000 cm\(^{-1}\) match the experimental spectrum, yet the peak height differs and they occur at higher wavenumbers. The broad band around 1100 cm\(^{-1}\) is also found but slightly shifted to lower wavenumbers compared to the experimental spectrum. The doublet at about 1200 cm\(^{-1}\) also fits the experimental data well.

Incorporating solvent effects, the ROA spectrum was built by the spectra of the chair conformers which were calculated with the COSMO continuum model, again with the weighting obtained from the Gibbs enthalpy populations in Table 6.1. There are some changes, compared to the overlap spectra calculated without the continuum model. The two negative bands around 900 cm\(^{-1}\) are better reproduced when comparing to the experimental spectrum. However, the positive and negative bands between about 1100 and 1270 cm\(^{-1}\) do not reproduce the negative-positive order of the experimental spectrum. Furthermore, the two positive peaks around 1200 cm\(^{-1}\) are plotted as one broad band, which, however, can be modified by choosing another width for the Gaussian band shapes (see the discussion in Ref. [46]).

Taking the boat conformers into account, the overlap spectrum changes slightly. Two weak negative bands are more visible near 1000 cm\(^{-1}\), which does not match the experimental spectrum. In addition, the band at about 1160 cm\(^{-1}\) shows a less negative value. However, this peak is not observed in the experimental spectrum at all. Taking the populations obtained from the electronic energy differences in Tables 6.1 and 6.2, only minor modifications, e.g., in the 1100 – 1170 cm\(^{-1}\) region are found but the agreement with the experimental spectrum is not significantly improved. The Raman spectrum evaluated by superimposing the spectra from chair and boat conformers (calculated with COSMO) and weighting according to the Gibbs enthalpy populations (see Tables 6.1 and 6.2) does not provide a significant better agreement with the experimental spectrum. Weak bands around 640 and 760 cm\(^{-1}\) appear to be too high in comparison with the experimental spectrum. Noteworthy is the small modification in the intensities of the three dominating bands between 850 and 1000 cm\(^{-1}\) in the calculated spectrum matching the heights in the experimental spectrum slightly better.
Table 6.2: The electronic energy (E) and Gibbs enthalpy (G) (298.15 K) differences compared to the conformer with the lowest electronic energy/enthalpy obtained employing COSMO for the conformers of AGP in the boat (left-hand side) conformation; the values on the right-hand side correspond to conformers in the chair conformation using COSMO and explicit solvation ("expl.solv.") with three water molecules; the values in brackets give the population in percentage obtained by a Boltzmann distribution (298.15 K).

<table>
<thead>
<tr>
<th>conformer</th>
<th>$\Delta E$ [kJ/mol]</th>
<th>$\Delta G$ [kJ/mol]</th>
<th>$\Delta E$ [kJ/mol]</th>
<th>$\Delta G$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(boat) (COSMO)</td>
<td>(boat) (COSMO)</td>
<td>(chair) (COSMO+ expl.solv.)</td>
<td>(chair) (COSMO+ expl.solv.)</td>
</tr>
<tr>
<td>$g-g+t$</td>
<td>3.10 ( 3.79)</td>
<td>0.00 ( 7.05)</td>
<td>11.69 ( 0.69)</td>
<td>15.74 ( 0.14)</td>
</tr>
<tr>
<td>$g-g+g-$</td>
<td>6.23 ( 1.07)</td>
<td>2.54 ( 2.53)</td>
<td>12.62 ( 0.47)</td>
<td>6.72 ( 5.22)</td>
</tr>
<tr>
<td>$tg+g+$</td>
<td>4.27 ( 2.36)</td>
<td>2.04 ( 3.09)</td>
<td>12.48 ( 0.50)</td>
<td>6.64 ( 5.39)</td>
</tr>
<tr>
<td>$g+g+g+$</td>
<td>5.79 ( 1.28)</td>
<td>1.25 ( 4.26)</td>
<td>13.76 ( 0.30)</td>
<td>6.67 ( 5.32)</td>
</tr>
<tr>
<td>$g-\overline{t}$</td>
<td>1.46 ( 7.33)</td>
<td>1.22 ( 4.31)</td>
<td>11.31 ( 0.80)</td>
<td>13.83 ( 0.30)</td>
</tr>
<tr>
<td>$tg+$</td>
<td>2.05 ( 5.78)</td>
<td>0.88 ( 4.94)</td>
<td>12.24 ( 0.55)</td>
<td>—</td>
</tr>
<tr>
<td>$g-\overline{t}g-$</td>
<td>2.67 ( 4.50)</td>
<td>0.90 ( 4.90)</td>
<td>12.31 ( 0.53)</td>
<td>13.25 ( 0.37)</td>
</tr>
<tr>
<td>$g-g-g-$</td>
<td>3.90 ( 2.74)</td>
<td>1.14 ( 4.45)</td>
<td>12.66 ( 0.46)</td>
<td>—</td>
</tr>
<tr>
<td>$tg-g+$</td>
<td>—</td>
<td>—</td>
<td>3.62 (17.80)</td>
<td>10.60 ( 1.09)</td>
</tr>
<tr>
<td>$g+tg+$</td>
<td>2.70 ( 4.46)</td>
<td>0.79 ( 5.12)</td>
<td>12.65 ( 0.47)</td>
<td>20.30 ( 0.02)</td>
</tr>
<tr>
<td>$g+g-g+$</td>
<td>3.09 ( 3.79)</td>
<td>1.35 ( 4.09)</td>
<td>13.39 ( 0.35)</td>
<td>—</td>
</tr>
<tr>
<td>$g-g+g+$</td>
<td>7.52 ( 0.64)</td>
<td>1.40 ( 4.01)</td>
<td>23.02 ( 0.01)</td>
<td>8.41 ( 2.64)</td>
</tr>
<tr>
<td>$g-\overline{t}g+$</td>
<td>3.78 ( 2.88)</td>
<td>0.74 ( 5.23)</td>
<td>24.36 ( 0.00)</td>
<td>21.20 ( 0.02)</td>
</tr>
<tr>
<td>$g-g-g+$</td>
<td>4.80 ( 1.91)</td>
<td>0.92 ( 4.86)</td>
<td>23.12 ( 0.01)</td>
<td>16.04 ( 0.12)</td>
</tr>
<tr>
<td>$tg+t$</td>
<td>1.13 ( 8.38)</td>
<td>0.60 ( 5.53)</td>
<td>27.08 ( 0.00)</td>
<td>18.89 ( 0.04)</td>
</tr>
<tr>
<td>$tg+g-$</td>
<td>3.29 ( 3.51)</td>
<td>1.08 ( 4.56)</td>
<td>27.38 ( 0.00)</td>
<td>18.90 ( 0.04)</td>
</tr>
<tr>
<td>$g+g+t$</td>
<td>1.95 ( 6.02)</td>
<td>0.17 ( 6.58)</td>
<td>28.51 ( 0.00)</td>
<td>20.43 ( 0.02)</td>
</tr>
<tr>
<td>$g+tt$</td>
<td>—</td>
<td>—</td>
<td>17.16 ( 0.08)</td>
<td>12.96 ( 0.42)</td>
</tr>
<tr>
<td>$tg-t$</td>
<td>2.92 ( 4.07)</td>
<td>0.88 ( 4.94)</td>
<td>17.52 ( 0.07)</td>
<td>—</td>
</tr>
<tr>
<td>$ttg-$</td>
<td>0.96 ( 8.96)</td>
<td>1.68 ( 3.58)</td>
<td>28.44 ( 0.00)</td>
<td>—</td>
</tr>
<tr>
<td>$g+g+g-$</td>
<td>4.88 ( 1.85)</td>
<td>1.49 ( 3.86)</td>
<td>27.84 ( 0.00)</td>
<td>21.42 ( 0.01)</td>
</tr>
<tr>
<td>$g+g-t$</td>
<td>0.00 (13.22)</td>
<td>1.00 ( 4.71)</td>
<td>29.07 ( 0.00)</td>
<td>—</td>
</tr>
<tr>
<td>$tg-g+$</td>
<td>—</td>
<td>—</td>
<td>17.52 ( 0.07)</td>
<td>13.41 ( 0.35)</td>
</tr>
<tr>
<td>$g+tg-$</td>
<td>1.74 ( 6.56)</td>
<td>1.17 ( 4.40)</td>
<td>29.12 ( 0.00)</td>
<td>26.13 ( 0.00)</td>
</tr>
<tr>
<td>$g+g-g-$</td>
<td>2.45 ( 4.92)</td>
<td>2.10 ( 3.02)</td>
<td>29.59 ( 0.00)</td>
<td>28.04 ( 0.00)</td>
</tr>
<tr>
<td>$ttt$</td>
<td>—</td>
<td>—</td>
<td>21.37 ( 0.01)</td>
<td>—</td>
</tr>
</tbody>
</table>
6.2. Raman optical activity spectra of 1,6-anhydro-β-D-glucopyranose

Figure 6.12: ROA spectra of the backscattering direction (BP86/RI/TZVPP) constructed by overlapping the spectra of all chair conformers (top), calculated without considering solvent effects (left-hand side) and with the continuum model COSMO (right-hand side), and of chair and boat conformers (middle) calculated with COSMO; the spectra on the bottom have been obtained from the spectra of the chair conformers and employing COSMO and solvation with water molecules. “E” and “G” indicate weighting according to the populations evaluated from the electronic energy and Gibbs enthalpy differences, respectively; the line spectra have been scaled by 0.1.
As a final step, the ROA spectrum was constructed from the ROA spectra obtained from the AGP conformers with three water molecules in addition to the use of the COSMO model. As was shown above, the influence of the spectra of the boat conformers on the overlap spectrum obtained with COSMO has been very small, mainly due to their very small populations. It is expected that a similar situation may be found for the solvated boat conformers and, therefore, the ROA spectra of the boat rotamers solvated with water molecules were not calculated. The spectra of the solvated chair conformers were weighted according to the percentages given in Table 6.2. The spectrum obtained when considering the Gibbs enthalpy differences is presented at the bottom of Fig. 6.12 on the left-hand side and the one taking the electronic energy differences into account on the right-hand side. The former provides the most remarkable patterns although a single negative band instead of the doublet around 880 cm\(^{-1}\) is found and the following positive band occurs already at wavenumbers lower than 900 cm\(^{-1}\). The region from 1050 to 1200 cm\(^{-1}\) contains again a strong positive band, followed by a negative one, which does not agree with the negative doublet and the positive band observed in the experimental spectrum. The spectrum calculated with respect to the populations from the electronic energy differences (see Fig. 6.12 and Table 6.2) is also a satisfactory approximation to the experimental one. This is in agreement with optical rotation studies, for which the populations evaluated from the electronic energy differences turned out to be a good choice (without considering solvent effects) [497]. Since only a couple of conformers show a significant population, the weighting factors were omitted and the spectrum was constituted by superimposing the spectra of all chair conformers (see Fig. 6.14). The resulting spectrum is in quite good agreement with the experimental one. The broad negative band around 880 cm\(^{-1}\) corresponds to two narrow bands in the experimental spectrum. A
similar result is found for the broad band at approximately 1200 cm\(^{-1}\). The positive bands in the region from 900 to 1050 cm\(^{-1}\) are easily visible. One disagreement with the experimental spectrum is again the positive peak between the negative bands around 1070 cm\(^{-1}\), which is not observed in the experimental spectrum. The negative band at roughly 1180 cm\(^{-1}\), which was observed in most of the calculated spectra, does not occur. The analogously constructed Raman spectrum is also given in Fig. 6.14. The agreement with the experimental spectrum is essentially as good as found for the spectra in Fig. 6.13.

Figure 6.14: Raman (top) and ROA (bottom) spectra of the backscattering direction (BP86/RI/TZVPP) obtained by overlapping the spectra of all explicitly solvated chair conformers (left-hand side) and the experimental spectra (right-hand side; reproduced from Ref. [446]); the line spectra have been scaled by 0.1.

6.3 Raman optical activity signatures of tryptophan side chains

Most bands in the ROA spectra of proteins are assigned to the peptide backbone. However, some bands are related to the conformation of specific side chains. For example, Blanch et al. [418] suggested by comparing the ROA backscattering spectra of different viral coat proteins that a ROA band at \(\approx 1550\) cm\(^{-1}\), which is assigned to the W3 vibration of the indole ring in tryptophan, can be used to determine the absolute stereochemistry of the tryptophan side chain. While
Figure 6.15: Structure of N-acetyl-(S)-tryptophan-\(N'\)-methylamide and definition of the torsional angles \(\chi^{2,1}\) and \(\chi^{1}\). \(\chi^{2,1}\) is defined by the atoms \(C_2-C_3-C^\beta-C^\alpha\), the torsional angle \(\chi^{1}\) is defined by the atoms \(C_3-C^\beta-C^\alpha-N\) (for further details, we refer to Ref. [500]).

It had been shown earlier in an analysis of the Raman spectra of different crystalline tryptophan derivatives [498, 499] that the wavenumber of this W3 vibration correlates with the magnitude of the \(\chi^{2,1}\) torsional angle (see Fig. 6.15 for the definition of this angle), they infer that its sign can be deduced from the sign of the corresponding ROA band. From the positive W3 ROA signal of hen lysozyme in solution and the observation that its crystal structure shows a positive sign of \(\chi^{2,1}\) for four of the six tryptophan residues, they conclude that a positive W3 ROA signal corresponds to a positive sign of \(\chi^{2,1}\). Additional support for this assignment is given by an observed increase of the magnitude of the W3 ROA signal for a complex of hen lysozyme with the trimer of \(N\)-acetylglucosamidine in which, according to its crystal structure, five out of six tryptophans show a positive sign of \(\chi^{2,1}\).

However, there are a number of uncertainties in this assignment which could not be resolved by experiment. The sign and the magnitude of the W3 ROA signal might depend not only on \(\chi^{2,1}\) (Blanch et al. assumed a \(\sin \chi^{2,1}\) dependence of the magnitude of the ROA intensity), but could also be influenced by other structural parameters such as the \(\chi^1\) torsional angle. This would complicate the comparison of the W3 ROA signal observed in hen lysozyme to the crystal structure, which contains six tryptophan residues in different conformations. Furthermore, it is not certain that the conformation of the tryptophan side chains in solution is the same as in the crystal.

In order to obtain a deeper insight into the influence of the torsional angles \(\chi^{2,1}\) and \(\chi^1\) on the intensity of the W3 ROA signal, calculations with
6.3. Raman optical activity signatures of tryptophan side chains

Table 6.3: Torsional angles $\chi^{2,1}$ and $\chi^1$ of different conformers of $N$-acetyl-(S)-tryptophan-$N'$-methylamide, relative energies of the different conformers $E_{rel}$ (in kJ mol$^{-1}$) with respect to the minimum energy conformer ($2^+$), as well as wavenumbers $\nu$ (in cm$^{-1}$) and ROA intensity $I_R - I_L$ (in Å$^4$ a.m.u.$^{-1}$) of the W3 vibration.

<table>
<thead>
<tr>
<th></th>
<th>$\chi^{2,1}$</th>
<th>$\chi^1$</th>
<th>$E_{rel}$</th>
<th>$\nu$</th>
<th>$I_R - I_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1+)</td>
<td>+113.7</td>
<td>-47.1</td>
<td>8.0</td>
<td>1538.8</td>
<td>0.2434</td>
</tr>
<tr>
<td>(2+)</td>
<td>+79.4</td>
<td>+45.6</td>
<td>0.0</td>
<td>1530.6</td>
<td>0.2916</td>
</tr>
<tr>
<td>(3+)</td>
<td>+91.6</td>
<td>-156.4</td>
<td>12.9</td>
<td>1535.6</td>
<td>0.1804</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$\chi^{2,1}$</th>
<th>$\chi^1$</th>
<th>$E_{rel}$</th>
<th>$\nu$</th>
<th>$I_R - I_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1−)</td>
<td>-81.6</td>
<td>-48.8</td>
<td>7.0</td>
<td>1539.0</td>
<td>-0.1168</td>
</tr>
<tr>
<td>(2−)</td>
<td>-102.2</td>
<td>+30.1</td>
<td>7.8</td>
<td>1530.7</td>
<td>-0.2806</td>
</tr>
<tr>
<td>(3−)</td>
<td>-86.1</td>
<td>-164.5</td>
<td>5.7</td>
<td>1538.2</td>
<td>-0.3034</td>
</tr>
</tbody>
</table>

$N$-acetyl-(S)-tryptophan-$N'$-methylamide as model system (see Fig. 6.15) were performed [342], which is the simplest model that, in addition to the tryptophan side chain, also contains the main structural features of the peptide backbone. This structural model allows for an extrapolation of the results to extended peptide chains and proteins because it is reasonable to assume that the normal mode responsible for the W3 signal is localized on the tryptophan side chain and does not couple with normal modes on other parts of the protein. In addition, it can be expected that the ROA intensity is not significantly influenced by contributions of other chiral residues that are not included in the model.

The structures of six different conformers of $N$-acetyl-(S)-tryptophan-$N'$-methylamide were optimized, which differ in the torsional angles $\chi^{2,1}$ (for which two different orientations, corresponding to a positive and a negative torsional angle, are possible) and $\chi^1$ (for which three different orientations are possible). The values of these angles and the relative energies of these conformers are summarized in Table 6.3. All conformers fall into an energy range of only 13 kJ mol$^{-1}$. Therefore, in larger proteins the conformation of the backbone and the protein environment may change the energy ordering of the conformers, and all orientations of the torsional angles can be realized.

The calculated ROA spectra of the six conformers are depicted in Fig. 6.16. In all spectra, the W3 ROA band at $\approx1540$ cm$^{-1}$ can be clearly identified as the one with the highest absolute ROA intensity. For the conformers ($1^+$) to ($3^+$), this band has a positive sign, while it is negative for the conformers ($1^-$) to ($3^-$). In the other parts of the spectrum, no clear similarities of the spectra of the different conformers can be identified. The wavenumbers and the ROA intensity of the W3 mode of all conformers are collected in Table 6.3.

From the calculated ROA spectra, it is easily seen that a positive $\chi^{2,1}$ torsional angle corresponds to a positive W3 ROA signal whereas a negative $\chi^{2,1}$ angle corresponds to a negative W3 ROA signal, irrespective of the torsional angle $\chi^1$ or other structural parameters. Thus, our calculations confirm the experimental
Figure 6.16: Calculated backscattering ROA spectra (BP86/RI/TZVP) of different conformers of N-acetyl-(S)-tryptophan-N'-methylamide.
assignment. No correlation between the magnitude of the W3 ROA signal and the magnitude of $\chi^{2,1}$ was found. In particular, the sin $\chi^{1,2}$-dependence suggested earlier [418] cannot be confirmed. It is worth noting that for the backbone ROA bands of the model compounds considered here, in particular the amide I, II, and III regions, large differences between the spectra of the different conformers are observed, even though the conformation of the backbone is identical. Similar results have been obtained for different diastereomers of trialanine [54] for which a large influence of the side chains on the amide ROA bands was found.

Further insight into the origin of the W3 ROA signal can be gained by analyzing the associated normal mode, which is shown in Figure 6.17. The normal mode is a combination of an in-plane vibration of the indole ring, a deformation of the C$^\beta$H$_2$ group, and an in-plane N–H deformation of an amide group in the backbone. For the conformers with different sign of $\chi^{2,1}$, the orientation of the indole ring with respect to the C$^\beta$H$_2$ group differs and, therefore, the relative phase of the indole and the C$^\beta$H$_2$ vibrations. Furthermore, a different backbone N–H deformation is involved for different conformers, and the amplitude of this backbone N–H deformation differs.

However, these differences in the normal modes are not responsible for the varying sign of the ROA signal. This can be seen by analyzing the contributions of these different groups (i.e., the indole ring, the C$^\beta$H$_2$ group, and the backbone) to the ROA signal according to the local decomposition analysis proposed by Hug [340] (compare section 3.5.2). The group coupling matrices shown in Figure 6.17 clearly demonstrate that the main contribution to the ROA signal is generated by those distortions in the normal mode that originate from the (achiral) indole ring. Also the change of the sign is governed by the contribution of the indole ring. At the indole ring, the normal modes of the different conformers are almost identical. Therefore, the change of the sign of the ROA signal must be caused by a change of the derivatives of the electric-dipole–electric-dipole tensor $\alpha$ and the electric-dipole–magnetic-dipole tensor $G'$ with respect to nuclear displacements of the atoms in the indole ring (the electric-quadrupole contribution is negligible). This change of property tensor derivatives is due to the different local chirality at the C$^\beta$ atom in conformers with opposite sign of $\chi^{2,1}$, which affects the total wave function from which the property was calculated and which is probed by the nuclear displacements of the atoms in the non-chiral indole ring. In contrast to that, the vibration of the C$^\beta$H$_2$ group (or its coupling with the vibration of the indole ring) only gives a small contribution to the ROA intensity.

This shows that the ROA intensity of the tryptophan W3 band at approximately 1540 cm$^{-1}$ reflects the absolute conformation with respect to the $\chi^{2,1}$ torsional angle of the tryptophan side chain and confirms the earlier experimental assignment that a positive W3 ROA signal corresponds to a positive $\chi^{2,1}$ torsional angle and a negative signal to a negative $\chi^{2,1}$.
Figure 6.17: W3 normal mode of different conformers of N-acetyl-(S)-tryptophan-N'-methylamide and associated group coupling matrices of the ROA invariant $\beta(G')^2$ for this normal mode.
6.4 Investigation of secondary structure elements of α- and 3_{10}-helices

ROA spectroscopy has been applied in many studies to gain information on the secondary structure of polypeptides and proteins [37, 457, 501, 502]. It can provide information on the solution structure that is not accessible otherwise. For instance, it has been shown that ROA spectroscopy can be used to distinguish hydrated and unhydrated α-helices [29], to discriminate different β-sheets structures [28], and to study polypeptides and proteins adopting poly-(L-)proline II helical structures in solution [49, 503].

These informations have to be extracted from the measured vibrational frequencies and intensities. Therefore, it is crucial to understand how the measured vibrational spectra are determined by the structure of the investigated protein, and how changes in the secondary structure influence the positions and intensities of the bands in the vibrational spectra. To relate protein structure and vibrational spectra, dedicated experimental studies on model peptides as well as detailed theoretical investigations are necessary [112]. One particular example where such a link could be established is the discrimination of α-helix and 3_{10}-helix by means of IR and VCD spectroscopy. Using a combination of experiment and theory, Keiderling and coworkers showed that the two conformations can be clearly distinguished by a specific VCD pattern in the amide I and amide II regions [504]. An example for ROA spectroscopy is the absolute conformation of tryptophan side chains (see section 6.3).

For a detailed understanding of the relation between secondary structure and vibrational spectra, ab initio calculations are extremely useful [112]. They allow it to study well defined structural models that can be varied in a controlled way. This makes it possible to isolate the secondary structure changes from other effects, thus providing insight that is not available from experimental studies, where changes in secondary structure always go along with other changes, such as, e.g., changes of the primary structure or of the solvent.

In this thesis, the ROA signatures of α-helical and 3_{10}-helical secondary structure elements in proteins are investigated, for which model polypeptides are constructed exhibiting these specific structural features. Alanine polypeptides have been chosen since alanine represents the smallest chiral amino acid. In order to support an α-helix and a 3_{10}-helix, rather large polypeptides containing twenty amino acid residues are required, since for smaller helices distorted helices have been observed [46]. Therefore, a polypeptide consisting of twenty (S)-alanine residues, denoted as (Ala)_{20}, is employed as a model system.

The optimized structures of the polypeptides under investigation are shown in Fig. 6.18 and were obtained from a full geometry optimization. The backbone dihedral angles of the central residues are approximately $\phi = -63^\circ$ and $\psi = -42^\circ$ for the α-helix and $\phi = -60^\circ$ and $\psi = -19^\circ$ for the 3_{10}-helix, i.e., the two conformers differ in the backbone dihedral angle $\psi$ (the N–C–C–N torsional angle), while $\phi$ (the C–N–C–C torsional angle) is almost identical in both
Figure 6.18: Optimized structures (BP86/RI/TZVP) of (Ala)$_{20}$ in the conformation of (a) an $\alpha$-helix and (b) a $3_{10}$-helix.

Conformers. At the termini, both helices are slightly distorted, and in the case of the $\alpha$-helix, the termini tend to resemble a $3_{10}$-helix. All spectra presented in section 6.4.1 are calculated for isolated molecules. Solvation effects are discussed in section 6.4.2 for $\alpha$-helical (Ala)$_{20}$.

ROA calculations for polypeptide model systems have so far only been used as a “fingerprint technique” (i.e., calculated spectra of different structural models have been compared to experimental data or to each other). Therefore, these studies have so far not led to detailed insight into the generation of the ROA signals in proteins. Such an understanding of the origin of ROA bands in proteins would make it possible to rationalize how structural changes affect the observed spectra and how spectral signatures of secondary structure elements arise. This is also a prerequisite for developing reliable “rules of thumb” for the prediction of ROA spectra of proteins and would make it possible to develop simplified empirical models on the basis of parameters extracted from ab initio calculations on realistic model systems. In particular, one would like to know
6.4. Investigation of secondary structure elements of $\alpha$- and $3_{10}$-helices

(a) which vibrations are responsible for the observed ROA bands, (b) what determines the signs and the intensities of these bands, and which groups of atoms are responsible for the observed ROA signals, and (c) what determines the observed band shapes, in particular whether a single peak, a couplet, or a more complicated band shape is found.

While all this information is in principle directly available from the calculations, its interpretation is more difficult. The vibrational spectra of polypeptides and proteins consist of many bands, with a large number of close-lying normal modes contributing to each band. However, these individual normal modes are usually not resolved in experiment. In ROA spectroscopy, the situation is further complicated by the fact that in many cases the individual normal modes contributing to one band show a rather irregular intensity pattern with positive and negative intensities for close-lying normal modes which may cancel each other. In addition, the normal modes are mostly delocalized over the whole system, which additionally hampers the analysis.

To overcome the latter problem, an analysis of calculated vibrational spectra in terms of rigorously defined localized vibrations [343, 460, 505] has been carried out [505], which — in contrast to the delocalized normal modes — are in general dominated by a vibration on a single residue. Localized modes on different but homologous residues are found to be very similar. Therefore, these localized modes simplify the interpretation of calculated vibrational spectra of large molecules and make it possible to analyze them in terms of vibrational frequencies and intensities of localized modes and the couplings between them.

6.4.1 Analysis of the Raman optical activity spectra

The calculated backscattering ROA spectra for both the $\alpha$-helical and the $3_{10}$-helical (Ala)$_{20}$ in the region from 1100 to 1800 cm$^{-1}$, which comprises the bands commonly used for the investigation of polypeptides and proteins, are shown in Figs. 6.19a and 6.20a. The eight considered bands, the corresponding wavenumber ranges, and the maxima and minima of these bands are listed in Table 6.4.

In general, the amide I modes are dominated by C=O stretching vibrations, with smaller contributions of N–H bending and C$\alpha$–H bending vibrations. The amide II modes comprise the out-of-phase combination of the N–H bending and the C–N stretching vibrations of the amide group. The modes denoted as C$\alpha$–H bending and those denoted as amide III modes are usually jointly referred to as “extended amide III region” since all these modes consist of coupled N–H bending and C$\alpha$–H bending vibrations [506]. C$\alpha$–H bending (I) modes mainly feature a bending vibration of the C$\alpha$–H group, where the direction of the bending vibration is along the N–C$\alpha$ bond while those for the C$\alpha$–H bending (II) band are dominated by a C$\alpha$–H bending vibration that is perpendicular to the N–C$\alpha$ bond.
Figure 6.19: (a) Calculated backward scattering ROA spectra (BP86/RI/TZVP) of α-helical (left) (Ala)_{20}; individual peaks have been included as a line spectrum scaled by 0.04; (b) assignment of the individual modes to characteristic bands; (c) band-averaged ROA spectra; the heights of the rectangular peaks indicate the total intensities of the bands.
6.4. Investigation of secondary structure elements of $\alpha$- and $3_{10}$-helices

Figure 6.20: (a) Calculated backward scattering ROA spectra (BP86/RI/TZVP) of $3_{10}$-helical (right) $(\text{Ala})_{20}$; individual peaks have been included as a line spectrum scaled by 0.04; (b) assignment of the individual modes to characteristic bands; (c) band-averaged ROA spectra; the heights of the rectangular peaks indicate the total intensities of the bands.
Table 6.4: Wavenumber ranges (“range”), band maxima or minima (“max./min.”), total ROA intensity (“ROA int.”), and ROA band shapes (“band shape”) for the characteristic bands in the ROA spectra of α-helical and 3_{10}-helical (Ala)_{20}; for the band shapes, “+” indicates a positive, “−” a negative band; “+/−” represents a couplet that is positive at low wavenumbers and negative at high wavenumbers while “−/+” indicates a couplet that is negative at low and positive at high wavenumbers.

<table>
<thead>
<tr>
<th></th>
<th>range [cm(^{-1})]</th>
<th>max./min. [cm(^{-1})]</th>
<th>ROA int. [10(^{-3}) Å(^4) a.m.u.(^{-1})]</th>
<th>band shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-helix</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>amide I</td>
<td>1633–1681</td>
<td>1644, 1664</td>
<td>−48.1</td>
<td>−/+</td>
</tr>
<tr>
<td>amide II</td>
<td>1468–1515</td>
<td>1513</td>
<td>−118.6</td>
<td>−</td>
</tr>
<tr>
<td>C(^{2})H(_{3}) asymm. bend</td>
<td>1446–1466</td>
<td>1449, 1461</td>
<td>−52.2</td>
<td>−/+</td>
</tr>
<tr>
<td>C(^{2})H(_{3}) symm. bend</td>
<td>1356–1373</td>
<td>1370</td>
<td>61.2</td>
<td>+</td>
</tr>
<tr>
<td>C(^{α})-H bending (I)</td>
<td>1304–1334</td>
<td>1311, 1326</td>
<td>−81.5</td>
<td>−/+</td>
</tr>
<tr>
<td>C(^{α})-H bending (II)</td>
<td>1257–1290</td>
<td>1273, 1289</td>
<td>402.8</td>
<td>+ +</td>
</tr>
<tr>
<td>amide III</td>
<td>1184–1260</td>
<td>1253</td>
<td>−110.9</td>
<td>−</td>
</tr>
<tr>
<td>skeletal C(^{α})-N stretch</td>
<td>1103–1156</td>
<td>1138, 1151</td>
<td>−153.6</td>
<td>+/−</td>
</tr>
<tr>
<td>3_{10}-helix</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>amide I</td>
<td>1631–1674</td>
<td>1636, 1648</td>
<td>38.6</td>
<td>+/−</td>
</tr>
<tr>
<td>amide II</td>
<td>1474–1515</td>
<td>1484, 1516</td>
<td>−171.4</td>
<td>− −</td>
</tr>
<tr>
<td>C(^{2})H(_{3}) asymm. bend</td>
<td>1447–1457</td>
<td>1448</td>
<td>−69.2</td>
<td>−</td>
</tr>
<tr>
<td>C(^{2})H(_{3}) symm. bend</td>
<td>1357–1369</td>
<td>1367</td>
<td>100.9</td>
<td>+</td>
</tr>
<tr>
<td>C(^{α})-H bending (I)</td>
<td>1304–1334</td>
<td>1314, 1324</td>
<td>−116.6</td>
<td>−/+</td>
</tr>
<tr>
<td>C(^{α})-H bending (II)</td>
<td>1268–1282</td>
<td>1271</td>
<td>90.0</td>
<td>+</td>
</tr>
<tr>
<td>amide III</td>
<td>1183–1259</td>
<td>1254</td>
<td>96.4</td>
<td>−/+</td>
</tr>
<tr>
<td>skeletal C(^{α})-N stretch</td>
<td>1124–1159</td>
<td>1149</td>
<td>−125.5</td>
<td>−</td>
</tr>
</tbody>
</table>

Figs. 6.19b and 6.20b show the calculated ROA spectra, in which the assignment of normal modes to characteristic bands is indicated by boxes. The band shapes for each of the bands are included in Table 6.4. Positive and negative peaks can cancel each other so that the band shapes found in the calculated spectra not only sensitively depend on the positions of the individual vibrational transitions but also on the line broadening that is applied to visualize the spectra. Therefore, these total band intensities can be expected to be less sensitive to inaccuracies in the computational methodology. Since it was not clear whether these errors, in particular the employment of the harmonic approximation, are homogeneous for close-lying peaks, it was suggested to interpret ROA spectra of large molecules in terms of the total intensities of characteristic bands [46]. To visualize these total band intensities, Figs. 6.19c and 6.20c contain the calculated ROA spectra of (Ala)\(_{20}\) using rectangular peaks indicating the total intensities of the bands.
6.4. Investigation of secondary structure elements of α- and 310-helices

6.4.1.1 Comparison to experimental spectra

In order to identify which features of experimental ROA spectra are reproduced correctly by our calculations and for which an improved theoretical description might be necessary, the calculated ROA spectrum of α-helical (Ala)$_{20}$ are compared to available experimental spectra in Fig. 6.21. Since short alanine polypeptides do not adopt the idealized α-helical structure in solution, but are instead frayed at the termini [507], spectra measured for (all-S)-polylanine are taken for the comparison. Alanine polypeptides usually do not adopt a 310-helical conformation in solution, and only one experimental spectrum of a 310-helical heptapeptide in aqueous solution is available in the literature [508]. However, this heptapeptide consists of Cα-tetrasubstituted residues with rather complex side chains, which alter the ROA spectrum with respect to the one that could be expected for peptides containing standard amino acids so that we do not employ this experimental one.

In Fig. 6.21, the calculated ROA spectrum of α-helical (Ala)$_{20}$ is shown together with the experimental solution spectra of (all-S)-polylanine in dichloracetic acid (DCA) and in a mixture of 30% DCA and 70% chloroform. The spectra measured in the two solvents are very similar, the only notable exceptions are the different relative intensities of the peaks at 1304 cm$^{-1}$ and at 1338 cm$^{-1}$. The weak negative peak at 1215 cm$^{-1}$ in the spectrum with 30% DCA/70% CH$_3$Cl is related to the solvent [29].

The couplet, negative at low and positive at high wavenumbers, found for the amide I band between 1640 and 1670 cm$^{-1}$ in our calculations is also observed in the experimental spectra, even though the negative part is very weak in the experimental (all-S)-polylanine spectra. However, a more pronounced amide I couplet is observed in the experimental ROA spectra of other α-helical polypeptides and proteins, and has been identified earlier as a signature of α-helices [37]. As in the calculated spectrum, the amide II band (between 1470 and 1520 cm$^{-1}$) is absent in the experimental ROA spectrum. Furthermore, the couplet centered at ca. 1455 cm$^{-1}$ obtained for the asymmetric CH$_3$ bending band in the calculated ROA spectrum agrees very well with the couplet in the experimental spectra at the same position. Similarly, the weak positive symmetric CH$_3$ bending evaluated at 1370 cm$^{-1}$ in the calculations is in accordance with the weak positive band observed experimentally at 1385 cm$^{-1}$. Finally, also the negative peak observed experimentally at 1165 – 1170 cm$^{-1}$ for the skeletal Cα–N stretching band is reproduced correctly by the calculations.

The agreement is not that good for the bands in the extended amide III region. According to our assignment, the positive peak at 1338 cm$^{-1}$ in the experimental spectra corresponds to the Cα–H bending (I) band, for which a couplet, centered at ca. 1320 cm$^{-1}$ is obtained in the calculated spectrum. The positive peak at 1304 cm$^{-1}$ in the experimental spectra corresponds to the Cα–H bending (II) band, for which a strong positive peak at 1273 cm$^{-1}$, together with a weaker one at 1289 cm$^{-1}$ is found in the calculations. The negative peak at
Figure 6.21: Comparison of (a) the calculated ROA spectrum (BP86/RI/TZVP) of \( \alpha \)-helical (Ala)\(_{20} \) with experimental spectra measured for \( \alpha \)-helical (all-S)-polyalanine in dichloroacetic acid (DCA) (b) and in 30\% DCA/70\% \( \text{CH}_3\text{Cl} \) (c); experimental spectra have been reproduced after Ref. [29].
1278 cm\(^{-1}\) in the experimental spectra can be identified with the amide III band, for which a weak negative peak at 1253 cm\(^{-1}\) is calculated. While for the C\(^{\alpha}\)-H bending (I) band neither the band shape nor the total intensity obtained from the calculations resembles the experimental spectra, the calculated C\(^{\alpha}\)-H bending (II) and amide III bands qualitatively agree with experiment. However, the relative ROA intensities of the different peaks are also not described well in the calculations, the amide III band at 1278 cm\(^{-1}\) is much stronger in the experimental spectra than in the calculated one.

### 6.4.1.2 Identifying signatures of \(\alpha\)- and \(3_{10}\)-helices

While \(\alpha\)-helical structures have been studied in detail by ROA spectroscopy and several signatures of \(\alpha\)-helical structures have been identified [29], only little is known about spectral signatures of \(3_{10}\)-helices. An early assignment of a peak at ca. 1340 cm\(^{-1}\) to a \(3_{10}\)-helix [509] had to be revised later [37]. By comparing the ROA spectra calculated for \(\alpha\)-helical and for \(3_{10}\)-helical (Ala)\(_{20}\), it is possible to extract signatures that might be used to discriminate \(\alpha\)-helix and \(3_{10}\)-helix. Notable differences occur for the amide I and II bands as well as for the bands in the extended amide III region. While differences are also observed for the asymmetric CH\(_3\) bending band, this band is related to the alanine side chains and is not present in other amino acids so that it is not generally useful.

In the amide I region, a couplet, which is negative at low and positive at high wavenumbers, is found for the \(\alpha\)-helical (Ala)\(_{20}\). Such a couplet has been identified earlier as a signature of \(\alpha\)-helices by comparing experimental spectra of polypeptides and proteins containing \(\alpha\)-helical secondary structure elements [29,501]. In contrast, the opposite couplet, positive at low and negative at high wavenumbers is obtained for the \(3_{10}\)-helical (Ala)\(_{20}\). These couplets can be explained by the different vibrational coupling constants (compare section 3.5.3) for the two conformers obtained from the analysis in terms of localized modes [460], which are directly related to the backbone structure. Even though these vibrational coupling constants have been extracted from the calculations on the full systems [460], for the amide I band the different pattern can be qualitatively explained by a transition dipole coupling model [343,510]. For the \(\alpha\)-helix, amide C=O groups of nearest-neighbor residues are oriented in parallel so that a large positive nearest-neighbor coupling constant is obtained. For the \(3_{10}\)-helix, the nearest-neighbor coupling constant is smaller, and the coupling with the vibration of the C=O group of the second-nearest-neighboring residue, which has a negative sign, is dominating. This can be understood since, for the \(3_{10}\)-helix, this second-nearest-neighbor coupling corresponds to one complete turn of the helix, and the fact that the opposite couplet is obtained for the \(3_{10}\)-helix is thus directly related to the different number of residues within one turn of the helix. Therefore, this amide I ROA couplet might be used to discriminate \(\alpha\)-helical and \(3_{10}\)-helical structures. However, in proteins containing both \(\alpha\)-helical and \(3_{10}\)-helical secondary structure elements, the different
couplets might overlap and thus partly cancel.

A second signature can be identified for the amide II band. In the $\alpha$-helix calculation the amide II band is not visible in the plotted spectra. This agrees with the experimental observation that the amide II band is absent in the ROA spectra of $\alpha$-helical polypeptides and proteins [29,501]. In contrast, the amide II band appears in the calculated spectra of $3_{10}$-helical (Ala)$_{20}$. This agrees with the calculation of the Raman spectrum [343], which also shows an increased intensity for the $3_{10}$-helical structure. In both cases, the increased intensity can be traced back to increased intensities of the amide II localized modes that are due to changes in the electronic structure. Our calculations predict that the amide II band in $3_{10}$-helices is split into two peaks. This splitting is due to the structure of the amide II intensity coupling matrix, in which the nearest-neighbor coupling terms are negligible while the second-nearest-neighbor coupling terms are significantly larger in magnitude [460]. These intensity coupling terms depend on the orientation of the different amide groups with respect to each other so that this band shape can directly be related to the secondary structure.

Several differences between the calculated spectra of the two conformers are also found in the extended amide III region. In particular, the amide III band is negative in $\alpha$-helical (Ala)$_{20}$ and positive in $3_{10}$-helical (Ala)$_{20}$. However, the total intensities of this band sensitively depend on the degree of mixing between the classical amide III and the C$^\alpha$–H bending vibrations. This not only depends on the secondary structure, but its accurate description might also require an adequate treatment of solvent effects. Therefore, the case of an explicitly hydrated $\alpha$-helix is discussed in the following section.

### 6.4.2 Effect of explicit solvation on the spectrum of the $\alpha$-helix

A ROA study of $\alpha$-helices in polypeptides, supplemented by X-ray crystal structure data, has suggested that ROA spectroscopy can distinguish between hydrated and unhydrated $\alpha$-helices [29]. The positive band around 1300 cm$^{-1}$ has been supposed to belong to the unhydrated form whereas the band around 1340 cm$^{-1}$ has been assumed to dominate if the $\alpha$-helix is hydrated. For the investigation of this hydration effect, it is necessary to include the solvent environment into the calculation. The simplest way is the employment of a continuum solvation model [511,512]. In order to test the significance of continuum solvation effects on the calculated ROA spectrum of the $\alpha$-helical (Ala)$_{20}$ model, we performed calculations with the continuum model COSMO [494,513].

Employing the continuum model in the calculation affects the molecular structure, the corresponding normal modes, and in this way the ROA intensities (compare also section 6.2). As is obvious in Fig. 6.22, the inclusion of continuum solvation effects does not change the ROA spectrum remarkably.
6.4. Investigation of secondary structure elements of $\alpha$- and $3_{10}$-helices

Figure 6.22: Calculated backscattering ROA spectra (BP86/RI/TZVP) of (Ala)$_{20}$ in the $\alpha$-helical conformation obtained without considering solvent effects (“gas phase”), by employment of the continuum model COSMO (“COSMO”), and by use of explicit solvation with water molecules and COSMO (“COSMO + expl. solv.”).

This is also reflected in the structure obtained from the optimization with COSMO which has $\phi$ and $\psi$ angles of about $-64^\circ$ and $-43^\circ$, which is comparable to $\phi = -63^\circ$ and $\psi = -42^\circ$ obtained from the optimization without considering any solvent effects. Most obvious is the shift of the amide I bands around 1650 cm$^{-1}$ to higher wavenumbers and the missing positive band around 1330 cm$^{-1}$. The quite small ROA intensities of the amide II bands around 1500 cm$^{-1}$ also differ partly in the intensities. The bands from about 1250 to 1350 cm$^{-1}$ are a bit shifted to higher wavenumbers. The two positive bands in the extended amide III region, which have been observed with maxima at 1304 and 1338 cm$^{-1}$ in experiment and at 1273 and 1289 cm$^{-1}$ in the gas-phase calculation (compare Fig. 6.21), are obtained in the COSMO calculation around 1277 and 1300 cm$^{-1}$ with intensities comparable to the ones of the calculation without the continuum model. Thus, all qualitative features compared to the spectrum obtained without considering solvent effects are preserved.

A continuum solvation model cannot be expected to yield an accurate description of specific solvent effects (i.e., of hydrogen bonds between solvent molecules and the solute), as has already been found for the sugar molecule in section 6.2, and it can only be considered as a first estimate. In order to study the effect of hydration on the ROA spectrum of $\alpha$-helices, more sophisticated solvent models that explicitly include the molecular structure of the environment are required [468, 514–516]. Therefore, a calculation of $\alpha$-helical (Ala)$_{20}$ explicitly solvated with water molecules in addition to the employment of COSMO was performed [513]. The water molecules were included in such a way that one water molecule forms a hydrogen bond to one carbonyl group already engaged in an intrachain hydrogen bonding to an amide group. This type of hydration has been termed external hydration [29]. The optimized structure is given in Fig. 6.23. The backbone angles are found to be approximately $\phi = -66^\circ$ and $\psi = -40^\circ$. This is in accordance with experimental results that the mean values
of the φ angle and ψ angle are about \( \phi = -66^\circ \) and \( \psi = -41^\circ \), respectively, for α-helices having hydrogen bonds to water or hydrophilic side chains. In contrast to that, mean values of \( \phi = -59^\circ \) and \( \psi = -44^\circ \) have been determined for α-helices without such hydrogen bonds [517]. This resembles the observation made in the calculation that the absolute values of the φ angle increases and the one of the ψ angles decreases if explicit solvation is included.

Figure 6.23: The optimized structure (BP86/RI/TZVP; COSMO) of (Ala)\(_{20}\) in the α-helical conformation solvated with water molecules.

Comparing the spectrum calculated with COSMO and explicit solvation and the one evaluated solely by employment of COSMO, some significant differences are visible. The amide I bands around 1650 cm\(^{-1}\), which are shifted to lower wavenumbers if COSMO is employed in the ROA calculation, occur at even lower wavenumbers in case of explicit solvation and COSMO. This trend does not fit to experimental data since already a good agreement has been found between the gas-phase calculation spectrum and the experimental ones (see Fig. 6.21), which may, of course, be due to a fortunate error cancellation. The positive band around 1460 cm\(^{-1}\) corresponding to CH\(_3\) bending vibrations gives rise to a very high intensity in the calculation including water molecules, which is, however, not so intense in the experimental spectra in Fig. 6.21. Differences due to the inclusion of the water molecules into the calculation emerge also for the quite small bands around 1350 and 1500 cm\(^{-1}\). Of most interest are the positive amide III bands. The one at lower wavenumbers is very similar to the ones observed in the spectra of the gas-phase and COSMO calculation (compare above) with a band maximum at 1272 cm\(^{-1}\). The other positive band at about 1295 cm\(^{-1}\), nevertheless, shows a higher intensity. This is the band which is supposed to be enhanced if hydration of the α-helix is existent. Therefore, the observed increase of this band in the ROA spectrum of the solvated model supports this assumption. However, more detailed experimental and theoretical studies are necessary for the validation of this assumption. A better agreement with experiment is also observed for the negative amide III
Metallothioneins: proteins with irregular structure

Metallothioneins are cysteine-rich proteins, which have been known since 1957 [518]. They have the ability to bind heavy metals, mainly zinc, but also others like cadmium, copper, mercury, silver, and arsenic [519]. Their metabolic role is still not totally clear [518] and their functions in organisms have been discussed extensively in the literature (for an overview, see, e.g., Refs. [518, 520, 521]). For instance, metallothioneins play an important role in zinc-transfer processes and corresponding redox reactions [522–524]. Moreover, they quench reactive oxygen and nitrogen molecules causing oxidative stress and they have been investigated in the context of diseases like diabetes, rheumatoid arthritis, and atherosclerosis as well as Parkinson, Creutzfeldt–Jacob, and Alzheimer [518, 525–527].

Four different forms have been identified in mammals, which all contain 20 cysteine and at least five lysine residues. The amino acids histidine, phenylalanine, tyrosine, and tryptophan have not been found. As a consequence, metallothioneins do not adsorb radiation around 280 nm, which is usually applied in routine methods of protein detection [518]. X-ray and NMR studies have revealed that metallothioneins consist of an α and a β domain, the first containing eleven cysteine residues with four metal atoms and the other binding three metal ions with the help of nine cysteine residues [528–533]. The dominating secondary structure elements are β turns, which consist of four amino acid segments.

Vibrational spectroscopy provides information about the structure of metallothioneins in their natural environment. The spectra, however, are often difficult to understand so that, in addition, theoretical investigations are required. This combined approach has already facilitated the interpretation of experimental IR, Raman, and VCD spectra of metallothioneins (see, for instance, Ref. [534]). There is one ROA spectrum available, measured by Smyth et al. from the rabbit metallothionein [454]. This spectrum contains some interesting bands, which could not be assigned with certainty to the structural features and the corresponding normal modes. Here, a calculation can yield deeper insights, clarifying the origin of these bands. In course of this work, the ROA spectra for the β domain of rat metallothionein were calculated, for which already a MD study has been presented [535]. The rat metallothionein has been chosen since a refined X-ray structure is available [531] and a graphical representation of the optimized structure is shown in Fig. 6.24. The metal ions clustered by the cysteine residues are two zinc and one cadmium ion, which are given in grey and orange, respectively, and the sulfur atoms are indicated by yellow. The overall structure contains in total more than 400 atoms with 31 amino acid residues. This molecule has an irregular structure and is therefore an example for a system to which computationally cheaper, approximate theoretical approaches
Figure 6.24: Graphical representation of the optimized structure (BP86/RI/TZVP) of the $\beta$ domain of rat metallothionein employed in the calculations.

for ROA spectra calculations employing results of smaller fragments for the extrapolation to larger molecular systems [41] cannot be applied. After a detailed discussion of the model structure in section 6.5.1, the ROA spectrum is analyzed in section 6.5.2 and compared to experimental data in section 6.5.3.

6.5.1 Comparison of the crystal and the model structure

The starting coordinates for the structure optimization were taken from the X-ray structure of rat metallothionein (PDB code 4mt2) [528,529,531,532] by omitting the $\alpha$-domain part. In order to assess how much the structure employed in the spectra calculation deviates from the $\beta$ domain of the rat metallothionein crystal structure, a superposition of the backbone trace of the optimized and the crystal structure is shown in Fig. 6.25. The backbone of the optimized structure is quite similar to the one of the crystal structure. Some larger deviations are obvious, especially at the ends of the backbone. The only secondary structure elements found in the $\beta$ domain of the crystal structure are $\beta$ turns, which are defined by four sequential amino acid residues. Employing the backbone torsional angles $\phi$ and $\psi$, several types of turns have been defined: type I is classified by ideal angles of $\phi_{i+1} = -60^\circ$ and
ψ_{i+1} = -30° on residue \( i + 1 \) and \( φ_{i+2} = -90° \) and \( ψ_{i+2} = 0° \) angles on residues \( i + 2 \), where \( i \) denotes the first atom constituting the turn. Type II is defined by \( φ_{i+1} = -60°, ψ_{i+1} = 120°, φ_{i+2} = 80° \), and \( ψ_{i+2} = 0° \), type VIII by \( φ_{i+1} = -60°, ψ_{i+1} = -120°, φ_{i+2} = 120° \), and \( ψ_{i+2} = 0° \), type I’ by \( φ_{i+1} = 60°, ψ_{i+1} = -30°, φ_{i+2} = -120° \), and \( ψ_{i+2} = 120° \), type II’ by \( φ_{i+1} = 60°, ψ_{i+1} = 30°, φ_{i+2} = -120° \), and \( ψ_{i+2} = 0° \). Type IV contains all turns which are excluded from these categories (for further details, we refer to Refs. [536–539]). A β turn of type I is found for residues ASP2 – PRO3 (\( φ = -58°, ψ = -36° \)) – ASN4 (\( φ = -86°, ψ = -14° \)) – CYS5 and the sequence CYS26 – THR27 (\( φ = -71°, ψ = -12° \)) – SER28 (\( φ = -79°, ψ = -10° \)) – CYS29. The residues CYS15 – ALA16 (\( φ = 33°, ψ = 63° \)) – GLY17 (\( φ = 77°, ψ = 6° \)) – SER18 and CYS21 – LYS22 (\( φ = -76°, ψ = -45° \)) – GLN23 (\( φ = -146°, ψ = 75° \)) – CYS24 form a β turn of type I’ and IV, respectively. The dominating secondary structure elements in the α domain of the rat metallothionein (not shown) are also β turns, where several turns of type I and one of type IV are detected in addition to one inverse γ turn.

Figure 6.25: Graphical representation of the backbone trace of the β domain crystal structure (PDB code: 4mt2) in blue and of the optimized structure (BP86/RI/TZVP) in orange.

Similar results are obtained for the optimized structure. The turns of type I are found with angles of \( φ = -85° \) and \( ψ = 10° \) for PRO3, \( φ = -106° \) and \( ψ = -7° \) for ASN4, as well as \( φ = -81° \) and \( ψ = 2° \) for THR27 and \( φ = -100° \)
and $\psi = 1^\circ$ for SER28. The $\Gamma'$ $\beta$ turn shows now angles of $\phi = 52^\circ$ and $\psi = 44^\circ$ for ALA16 and $\phi = 88^\circ$ and $\psi = 2^\circ$ for GLY17. The sequence giving rise to a IV $\beta$ turn in the crystal structure forms a $\beta$ turn of type IV in our optimized structure with $\phi = -109^\circ$ and $\psi = -57^\circ$ for LYS22 and $\phi = -132^\circ$ and $\psi = 97^\circ$ for GLN23. In addition, a type IV $\beta$ turn is determined for the residues PRO3 – ASN4 ($\phi = -106^\circ$; $\psi = -7^\circ$) – CYS5 ($\phi = -133^\circ$; $\psi = 92^\circ$) – SER6. As in the $\alpha$ domain of the crystal structure, an inverse $\gamma$ turn is ascertained constituted by ALA8 – THR9 ($\phi = -87^\circ$; $\psi = 78^\circ$) – ASP10.

Ramachandran plots [540] of the $\beta$ domain of both the crystal structure and the optimized structure are presented in Fig. 6.26. In both structures, almost all amino acid residues show $\phi$- and $\psi$-angles in the favored regions. The number of residues in the $\alpha$ region, which contains values of about $\psi = 40^\circ$ to $\psi = -60^\circ$ and in which the $\alpha$- and $3_{10}$-helices are found, is more or less as high as the quantity of amino acids in the $\beta$ regions belonging to higher $\psi$ values. One residue (except for the glycine residues) carries a positive $\phi$ value in the left-handed helix region. These results demonstrate that the optimized structure shows all important secondary structure elements as the corresponding crystal structure, although the latter may, of course, deviate from the structure occurring in solution. A similar disordered structure and $\psi/\phi$-angle distribution is found for the $\alpha$ domain of the crystal structure. Therefore, we only take the $\beta$ domain into account for our calculations, which results also in a lower computational effort.

6.5.2 Analysis of the calculated spectrum

The calculated ROA spectrum of the $\beta$ domain of rat metallothionein is presented in Fig. 6.27. The most intense bands occur in the region from about 1180 to 1420 cm$^{-1}$. A number of mostly positive bands is obvious at low wavenumbers, where skeletal vibrations occur. The one at around 750 cm$^{-1}$ arises due to deformational vibrations of the carbon atoms with a large contribution of an out-of-plane motion of the hydrogen atoms bound to the nitrogen atoms, especially of the cysteine residues. These out-of-plane modes together with the backbone vibrations give also rise to positive ROA intensities around 800 cm$^{-1}$ including the hydrogen atoms from other amino acids like the hydroxyl hydrogen atoms of threonin and serine residues. Deformational hydrogen vibrations, in particular of the methyl and methylene groups, distributed over the whole molecule and coupled with stretching vibrations of the backbone result in the positive band at 851 cm$^{-1}$. The small negative band at 883 cm$^{-1}$ is mainly due to the normal mode at 884 cm$^{-1}$, which features an in-plane deformational vibration of two cysteine residues bound to a zinc atom (see Fig. 6.28) whereas the positive band around 910 cm$^{-1}$ contains an important contribution of, e.g., lysine C–N stretching vibrations. The negative contributions around 950 cm$^{-1}$ arise from delocalized C–C stretching vibrations, e.g., at 953 cm$^{-1}$ from the GLY11 residue. A significant negative ROA intensity shows the normal mode
Figure 6.26: Ramachandran plots of the glycine residues (right-hand side) and the remaining amino acids (left-hand side); \( \phi \) is the C–N–C\(^\alpha\)–C and \( \psi \) the N–C\(^\alpha\)–C–N dihedral angle; the upper part belongs to the \( \beta \) domain of the crystal structure (PDB code: 4mt2) and the lower one to the corresponding optimized structure (BP86/RI/TZVP); the light blue lines indicate favored and the violet lines allowed regions of the \( \phi/\psi \) dihedral angle combinations.

at 1022 cm\(^{-1}\), which is more or less located on CYS13 with a strong C–C stretching vibration between the carbon atom of the methylene group and C\(^\alpha\). Contrary to that, the stretching between C–O of SER14 at 1032 cm\(^{-1}\) as well as the serine vibration at 1046 cm\(^{-1}\) (see Fig. 6.28) and the C–C stretching modes of CYS21 at 1037 cm\(^{-1}\) and LYS20 at 1059 cm\(^{-1}\) contribute remarkable positive ROA intensities. The C–C and C–O stretching vibrations of the serine
residues give rise to positive and negative contributions at 1070 and 1071 cm$^{-1}$, respectively. A large part to the negative band observed around 1110 cm$^{-1}$ is provided by the backbone stretching and hydrogen wagging and twisting vibrations of LYS30 and LYS31 at 1072 cm$^{-1}$ and of LYS20 at 1115 cm$^{-1}$ (compare Fig. 6.28). The most negative ROA intensity, which also brings about the most negative band in the broadened spectrum in Fig. 6.27, is found for the normal mode of CYS19 at 1189 cm$^{-1}$ shown in Fig. 6.28. It is dominated by the amide III vibration, i.e., by the bending vibration of the hydrogen atom on the nitrogen and C$^\alpha$ atom, together with methylene twist motions. A local decomposition of this normal mode depicted by a group coupling matrix as proposed by Hug [340] (see section 3.5.2) is shown in Fig. 6.29 for the $\beta(G''_{2})^2$ invariant, for which a large negative value was calculated. For the electric-quadrupole-containing invariant, solely a negligibly small negative intensity value was evaluated so that its contribution to the backscattering ROA intensity can safely be neglected. The rows and columns of the matrix in Fig. 6.29 correspond to atoms or groups of atoms. The magnitude of their contribution is represented by the area of circles, which are filled if the sign of the contribution is positive and empty if negative. As can be seen in Fig. 6.29, the large negative intensity found for this normal mode is basically due to the contributions from the hydrogen atom bound to the nitrogen atom. Not only the hydrogen atom itself provides a remarkable negative value, but also its coupling to the neighboring hydrogen atoms and the remaining molecule. Smaller negative contributions are evaluated especially for one hydrogen atom of the methylene group, whereas the hydrogen atom of C$^\alpha$ gives rise to predominantly, yet comparatively small, positive contributions.
6.5. Metallothioneins: proteins with irregular structure

Figure 6.28: Characteristic normal modes of structural fragments; the numbers indicate the corresponding wavenumbers in cm$^{-1}$.
Figure 6.29: Group coupling matrix for the $\beta(G')^2$ invariant of the normal mode at 1189 cm$^{-1}$ for the $\beta$ domain of rat metallothionein; “H1” and “H2” denote the hydrogen atoms of the methylene group, and “H3” and “H4” the hydrogen atoms bound to $C\alpha$ and the nitrogen atom of CYS19, respectively. The contributions of the remaining atoms of the molecule are summarized in “R”.

Significant positive ROA intensities are found for the amide III modes of, e.g., SER6 at 1207 cm$^{-1}$, LYS30 and TYR27 at 1214 cm$^{-1}$, ASP2 at 1219 cm$^{-1}$, and LYS30 and LYS31 at 1236 cm$^{-1}$. In contrast to that, negative intensity values are calculated, for instance, for THR27 and CYS26 at 1185 cm$^{-1}$, CYS7 at 1202 cm$^{-1}$, LYS20 and CYS21 at 1231 cm$^{-1}$, and ASP10, GLY11, and SER12 at 1234 cm$^{-1}$. Twist motions of PRO3 at 1232 cm$^{-1}$ (see Fig. 6.28) and 1252 cm$^{-1}$ also show nonnegligible positive and negative ROA intensities, respectively. The broad band with maximum at 1308 cm$^{-1}$ and the small minimum at 1358 cm$^{-1}$ in Fig. 6.27 encompass more or less $C\alpha$–H bending vibrations. Two different types can be distinguished: one with a motion of the hydrogen atom perpendicular to the direction of the $C\alpha$–N bond, designated as $C\alpha$–H(II), occurring from about 1250 to 1300 cm$^{-1}$ and one with the hydrogen atom moving along this bond, indicated by $C\alpha$–H(I), observed in the region from about 1300 to 1330 cm$^{-1}$ [343,460,505]. Negative contributions from such modes originate, for example, from GLY11 at 1257 cm$^{-1}$, GLY17 and SER18 at 1262 cm$^{-1}$, CYS29 at 1292 cm$^{-1}$, and lysine residues at 1303 and 1328 cm$^{-1}$ (see Fig. 6.28). Positive contributions are worth to be mentioned from CYS13 and SER14 at 1254 cm$^{-1}$, CYS19 at 1288 cm$^{-1}$, SER12 at 1301 cm$^{-1}$, LYS20 and LYS22 at 1305 and 1330 cm$^{-1}$, respectively. The highest ROA intensity calculated in the plotted wavenumber range in Fig. 6.27 shows the normal mode at 1258 cm$^{-1}$, which is dominated by the $C\alpha$–H(II) normal mode of SER28 and contributions from methylene wagging vibrations mainly of the cysteine residues (see Fig. 6.28). It does, nevertheless, not lead to the most intense band due to overlap with bands of other (negative) ROA intensities. Thus, the maximum is observed at 1308 cm$^{-1}$ in the calculated spectrum, mainly due to the $C\alpha$–H(II) modes of the lysine residues.
Bending vibrations, especially from the methyl group in combination with the hydroxyl hydrogen atom of LYS22, lead to a remarkable negative ROA intensity at 1414 cm$^{-1}$ whereas the methylene bending modes of, e.g., LYS30 at 1414 cm$^{-1}$, several cysteine residues at 1422 cm$^{-1}$ (see Fig. 6.28), and ASP2 at 1424 cm$^{-1}$ provide positive contributions so that in total a positive band at around 1420 cm$^{-1}$ is observed. The reason for the negative band around 1460 cm$^{-1}$ are in particular the negative ROA intensities from LYS20 methylene bending and LYS30 amino group wagging modes. The LYS22 methylene bending and LYS20 wagging vibration at 1474 and 1490 cm$^{-1}$, respectively, comprise, however, a large positive ROA intensity. Typical amide II modes, i.e., a strong bending of the hydrogen atom bound to the nitrogen atom as well as C–N stretching, is observed at 1480 cm$^{-1}$ for LYS30 and LYS31, and at 1502 cm$^{-1}$ for LYS20 with a remarkable negative intensity. Contrary to that, SER14 together with CYS13 and CYS15 show amide II modes with a nonnegligible positive value at 1510 cm$^{-1}$ and ALA16 in combination with SER14 and CYS15 an even more intense one at 1527 cm$^{-1}$. Positive contributions are also found at, e.g., 1538 and 1545 cm$^{-1}$ from amide II modes of SER6 and CYS21, respectively, so that a small positive band at around 1531 cm$^{-1}$ in Fig. 6.27 is obtained despite the large negative ROA intensity provided at 1524 cm$^{-1}$ (compare the line spectrum at the right-hand side of Fig. 6.27) from the CYS29, ALA16, and GLY17 amide II modes. Quite few normal modes are obtained in the region from about 1550 to 1620 cm$^{-1}$. The by far largest (negative) ROA intensity comprises the mode at 1574 cm$^{-1}$, which is dominated by C–N and carbonyl stretching vibrations of LYS20 and wagging vibrations of SER18. A graphical representation of this normal mode can be found in Fig. 6.28. The remaining normal modes up to 1800 cm$^{-1}$ are either wagging vibrations of the LYS NH$_3$ groups or typical amide I vibrations, which are characterized by carbonyl stretching motions with smaller contributions from N–H and C$\alpha$–H bending modes. Significant positive ROA intensities are, for example, obtained for LYS25 and LYS20 wagging modes at 1641 (see Fig. 6.28) and 1660 cm$^{-1}$ while LYS22 and LYS25 at 1642 cm$^{-1}$ and LYS22 wagging modes at 1660 cm$^{-1}$ lead to remarkable negative intensities. Noteworthy positive contributions from amide I modes are calculated for, e.g., LYS25 and CYS26 at 1677 cm$^{-1}$, CYS13 and SER14 at 1669 cm$^{-1}$, and MET1 and ASP2 at 1676 cm$^{-1}$. Nevertheless, the negative contributions prevail and occur for amide I modes for instance at 1654 cm$^{-1}$ for ALA8 and THR9, at 1662 cm$^{-1}$ for CYS24 and GLN23, at 1687 cm$^{-1}$ for GLY11, at 1691 cm$^{-1}$ for ALA16, and at 1709 cm$^{-1}$ for CYS21 and LYS22 (see Fig. 6.28 for a graphical representation of the vibration).

6.5.3 Comparison to experimental data

As a final step, we compare our calculated spectra to the measured ROA and Raman spectra of rabbit metallothionein presented in Ref. [454]. It is expected
that there will be some differences since our calculation considers the $\beta$ domain of rat metallothionein in the gas phase whereas the experiment has been performed for the rabbit metallothionein, which has the same amino acid sequence as rat metallothionein, but contains seven cadmium metal atoms instead of two zinc and five cadmium atoms, in a pH=8 buffer solution. In addition, the cadmium ions are kinetically labile which easily leads to dimerization of the metallothionein in the sample. As a consequence, 28% dimer were found after the ROA measurement of the rabbit metallothionein in the solution [454]. Comparing the lower wavenumber part of the experimental and calculated ROA spectra shown in the upper part of Fig. 6.30, some similarities are visible. A positive band in the experimental spectrum at around 750 cm$^{-1}$ is also found in the calculated spectrum as well as the following minimum. The doublet around 1000 cm$^{-1}$ in our calculated spectrum, originating mainly from backbone stretching modes, agrees with the one in the experimental spectrum with maxima at 974 and 1016 cm$^{-1}$. The most obvious bands in the experimental spectrum are the negative band at 1201 cm$^{-1}$ and the positive one with maximum at 1313 cm$^{-1}$. These are astonishingly well reproduced in our calculation.
As has been shown in the previous section, the sharp negative band is due to vibrations of cysteine residues, which has not totally been clear from analyzing the experimental spectrum only [454]. The positive band in the experimental spectrum, which has a slightly broader shoulder at the lower wavenumber side, was assumed to exist due to residues with $\psi$ and $\phi$ angles in the $\alpha$ region of the Ramachandran plot whereas $\beta$ structures were supposed to be absent due to missing negative ROA bands in the 1220 to 1260 cm$^{-1}$ region [454]. The corresponding band in our calculation is broadened to the lower wavenumber region since it contains two types of vibrations: amide III modes at lower wavenumbers and $C^\alpha$–H bending vibrations at higher ones. Looking at significant contributions to the intensity with respect to the different amino acids (compare the previous section) and the corresponding $\phi$ and $\psi$ angles, no relation between the sign of the intensity and these angles is obvious. As a consequence, no general statement about the sign of the band and the occurrence of particular amino acids and backbone angles can be made. However, since our model structure contains turns as the only secondary structure elements, these two bands may be considered as signatures for turns, especially for $\beta$ turns. A quite similar doublet was also observed, for instance, for the peptide L-PRO-L-LEU-GLY-NH$_2$ [541], which shows a $\beta$ turn of type II [542, 543]. Moreover, this wavenumber region has already been found in Raman spectra to be characteristic for $\beta$ turns [534].

The remaining part of the calculated spectrum does not agree well with the experimental one. For instance, the intense positive band around 1420 cm$^{-1}$ in the calculated spectrum is, if at all, found with a quite weak positive intensity around 1400 cm$^{-1}$ in experiment. The subsequent negative band has its minimum at around 1460 cm$^{-1}$ in the calculated spectrum. In the experimental one, two negative bands around 1435 cm$^{-1}$ are obtained. These may originate from methyl out-of-plane deformational vibrations, for which negative intensity values are evaluated in our calculation in this wavenumber range. The negative band at about 1575 cm$^{-1}$ in the calculated spectrum is not observed in the experimental one. As described in the previous section, this band is due to the combination of LYS20 C–N and C=O stretching vibrations and hydrogen deformational vibrations of SER18. It should be noted that the positions of these two residues in our model structure deviate remarkably from the ones in the crystal structure where the distance between these residues is larger. Thus, this vibration may not necessarily exist in such a way in ROA measurements, possibly also due to solvent effects. The positive band at 1652 cm$^{-1}$ in the experimental ROA spectrum is not found in our calculated spectrum. Indeed, several normal modes show positive intensities in the calculated spectrum but they overlap with other negative bands leading in total to a negative band, which is broadened to the lower wavenumber side. The minimum at 1708 cm$^{-1}$ mainly stems from the amide I mode of CYS21 and LYS22 whereas especially NH$_3$ wagging modes from the LYS residues contribute around 1650 cm$^{-1}$. Since these LYS residues occur at the outer sphere of the metallothionein, their ROA intensities may significantly be changed if explicit solvation is considered (as
has been found, for instance, for the sugar molecules in section 6.2).

Looking at the experimental and calculated Raman spectra at the bottom of Fig. 6.30, a good agreement between both spectra is apparent. Although the relative intensities differ, the characteristic patterns are easily visible. The two bands in the region from 600 to 800 cm\(^{-1}\) are found in both spectra as well as the minimum around 820 cm\(^{-1}\) and the following band, at about 890 cm\(^{-1}\) in the measured and around 840 cm\(^{-1}\) in the calculated spectrum. The two bands centered around 1000 cm\(^{-1}\) are observed in the experimental measurement with a higher Raman intensity for the one at lower wavenumbers, whereas the band with higher wavenumbers gives rise to a more intense band in our calculation. The remaining part of the experimental spectrum with bands at around 1240 cm\(^{-1}\) (which is broadened to the higher wavenumber range), 1440 cm\(^{-1}\), and 1650 cm\(^{-1}\) is also obtained in our calculation, although the relative intensity of the band at 1650 cm\(^{-1}\) is smaller than in the measured spectrum.
7. Summary and Outlook

Many different topics of theoretical spectroscopy have been tackled in this work. On the one hand, the theoretical basis for the calculation of molecular properties in the quasi-relativistic DKH approach has been developed. Further theoretical work has concerned the gauge dependence of ROA invariants, the treatment of electronic resonances in ROA spectroscopy, and the concept of intensity-carrying modes in IR, Raman, and ROA spectroscopy. On the other hand, an efficient calculation of IR, Raman, and, in particular, ROA spectra has been made possible by the implementations made in the course of this thesis. This had been the prerequisite for the calculation of the presented vibrational spectra, which have been investigated for a variety of molecules, ranging from metal complexes to large biomolecules. The main achievements are summarized in the following.

Efficient treatment of magnetic properties in Douglas–Kroll–Hess theory  All options for the treatment of magnetic vector potentials in the DKH procedure were investigated employing a unified notation without unnecessary additional assumptions (like a specific choice for the parameterization of the unitary transformation). One possibility for the incorporation of the magnetic vector potential into the fpFW transformation is the replacement of the momentum operator by the mechanical momentum operator so that the fpFW transformation can again be written in closed form. This transformation led to quite complicated expressions, which could not easily be classified with respect to the orders in the external potential $V$ and the magnetic vector potential $A$ and which would be rather clumsy for the calculation of magnetic properties. So, it was advantageous to start with a magnetic-field-independent fpFW transformation which resulted in well-defined odd and even terms in the potentials. In order to decouple the $A$-dependent terms in subsequent DKH transformations, the expansion parameters had to be chosen such that they remove the odd $A$-containing terms in a successive manner, which gave rise to para- and diamagnetic contributions in the final Hamiltonian. Furthermore, general procedures for decoupling up to infinite order in both the scalar and the magnetic vector potential were discussed by extension of the analytical decoupling scheme [209] and of the numerical procedure very recently presented by Matveev et al. [214]. For the evaluation of first-order properties via perturbation theory, only the unperturbed wave function is needed. As a consequence, only a decoupling with respect to $V$ had to be performed, which led to simpler expressions and
to a smaller computational effort than the simultaneous decoupling of \( V \) and \( A \). For second-order properties, the first-order perturbed wave function has to be calculated. This can only be obtained in a two-component framework if the full Dirac Hamiltonian with the magnetic vector potential is decoupled, i.e. the elimination of odd \( V \)- and \( A \)-containing terms had to be carried out. In order to avoid the calculation of the first-order perturbed wave function, the second-order (and in principle, of course, also the first-order) properties can alternatively be evaluated variationally. This, however, necessitates also the decoupling with respect to both potentials.

The application of transformations which depend linearly on the magnetic vector potential yielded additional para- and diamagnetic contributions compared to the case of magnetic-field-independent transformations. As was shown with the help of perturbation theory, these additional terms cancel each other, i.e., one can create para- and diamagnetic contributions by adding and subtracting terms from the corresponding second-order energy. The separation into para- and diamagnetic contributions depends on the chosen perturbation-dependent transformation.

**Theory and calculation of Resonance Raman optical activity spectra**

A theory for RROA spectroscopy, both in the sum-over-states and the time-dependent approaches, was presented. After the general ansatz, for which electric-dipole, electric-quadrupole, and magnetic-dipole contributions have to be considered, the property tensors were simplified by applying the Condon approximation. In the limit of resonance with one excited electronic state, the contribution from the electric-quadrupole-containing invariant vanishes (as has already been found by Nafie [223]) so that the magnetic-dipole-containing invariants give rise to the RROA intensity. Furthermore, the case of resonance with two excited electronic states was discussed in the most straightforward way by addition of the contributions of the two states.

Spectra were calculated for \((S)-(+)\)-naproxen-OCD\(_3\) and it could be shown that the experimental spectra contain elements of both the simulated off-resonance and in-resonance spectra. In addition, it was demonstrated that RROA spectra can be remarkably affected by interference of electronically excited states, which is even more involved than in RR spectra since not only enhancement and deenhancement of the bands can occur but in addition their sign can be reversed.

**Intensity-carrying modes in IR, Raman, and Raman optical activity spectroscopy**

The theoretical foundations for the determination of modes carrying maximum IR, Raman, and ROA intensity were devised. The obtained ICMs are hypothetical modes, which, in general, do not exactly resemble normal modes. However, they provide a way for visualizing the nuclear (atomic) movements in the molecule which give rise to high intensities.

IR and Raman ICMs of several small molecules were presented. Moreover, ICMs for different ROA experimental set-ups were evaluated in case of the
Selective calculation of normal modes with high intensity  An intensity-tracking algorithm was implemented which selectively calculates normal modes with high IR, Raman, or ROA intensity. For this quantum chemical scheme, ICMs are the optimum guess for a starting mode. The algorithm successively refines approximate Hessian eigenvectors involving displacements of atomic positions which correspond to large (absolute) intensities. Different intensity-based selection procedures, which can be custom-made for a given problem, and various convergence criteria were tested. In addition, mode-based criteria were applied. The reduced computational effort was the larger the more constraints were applied in terms of the selection criteria. This made the calculation of (approximate) IR, Raman, and ROA spectra possible for systems whose full spectra can only be obtained with prohibitively high computational costs. Moreover, the intensity-tracking protocol is well suited for obtaining a quick glance on special spectroscopic features of large molecules.

Efficient calculation of Raman optical activity spectra  An efficient implementation for the calculation of ROA spectra was presented. The employment of density-fitting techniques for the ROA property tensor evaluation, carried out with the program package TURBOMOLE, in combination with the massively parallel and restart-friendly methodology of SnF was the prerequisite for the ROA spectra calculations presented in this work. With this set-up, it was possible to routinely obtain consistent force fields and ROA spectra of large molecules with large basis sets. Gauge-origin independence was assured by calculating \( \beta(G')^2 \) in the velocity representation of the electric-dipole operator, which is available for pure density functionals.

Raman optical activity spectra of chiral metal complexes  The first ROA spectra of metal complexes were calculated in the course of this work. In contrast to the ROA intensities of organic molecules, a significant density-functional dependence was found for the rhodium and cobalt complexes. Our calculations suggest that ROA spectroscopy is not only sensitive to the metal atoms employed but additionally to the chirality of the ligands. As could be shown for cobalt complexes with chiral 3-acetylcamphorato ligands, ROA spectra are distinguishable for complexes containing a varying number of chiral ligands and even for geometrical isomers. Moreover, the influence of the \( \Lambda/\Delta \) configuration on the ROA spectra was remarkable.

Raman optical activity investigation of biomolecules  Besides the analgesic naproxen, whose spectra were investigated with emphasis on resonance
effects, ROA spectra of other organic molecules were studied in the far-from-
resonance approximation. The first example was the anhydro sugar 1,6-anhydro-
$\beta$-D-glucopyranose, for which the ROA spectra of 54 different rotamers were
calculated. It was demonstrated that the change from the boat to the chair
conformation results in remarkable modifications in the corresponding ROA
spectra, which were also sensitive to the different rotamers. Solvent effects were
included by the continuum model COSMO and explicit solvation of water
molecules resulting in remarkable modifications in the ROA spectra compared
to the ones obtained without considering solvent effects. The final spectra were
constructed by superimposing spectra of different conformers leading to a good
agreement with experimental spectra.

For the chiral amino acid $L$-tryptophan, it was shown that the ROA intensity
of the W3 band at about 1540 cm$^{-1}$ reflects the absolute conformation with
regard to the $\chi^2$ torsion angle of the tryptophan side chain confirming earlier
experimental assignments.

Secondary structure signatures of $\alpha$- and $3_{10}$-helices were investigated by ana-
lyzing the calculated ROA spectra and comparing them to experimental data.
The amide I couplet, negative at low and positive at high wavenumbers, which
has already been found in experiment, could be confirmed as a signature of
$\alpha$-helices. Moreover, the calculations suggest that the opposite amide I couplet
could serve as a signature of $3_{10}$-helices.

Finally, the first ROA spectrum of a metalloprotein, the $\beta$ domain of rat metal-
lothionein, was presented. This protein has turns as the only secondary structure
elements and is the by far largest molecule, for which a full $ab\ initio$ calculation
has been performed up to date. In accordance to experimental ROA data, an
intense negative and positive band was found at around 1200 and 1300 cm$^{-1}$,
respectively, which may serve as a ROA signature for $\beta$ turns.

**Outlook** The results presented in this work have demonstrated that theoretical
vibrational spectroscopy is an indispensable tool for the interpretation and
prediction of vibrational spectra, especially in the case of large molecules. Work
in the future may include the following extensions of the presented theoretical
and implementational achievements and their applications:

- The DKH implementations may be extended in order to include magnetic-
field-dependent transformations so that the calculation of second-order
properties like NMR shielding tensors, hyperfine coupling tensors, and $g$-
tensors will be possible. This may be achieved by an extension of the
already existing analytical decoupling scheme up to infinite order. In
addition, a comparison to the analogous numerical procedure would be of
interest. Very recently, an alternative evaluation of the DKH Hamiltonian
has been proposed, which remarkably reduces the computational cost and
allows for a polynomial scaling [544]. This approach may be worth to be investigated with respect to magnetic-field-dependent properties.

- The implementation for the calculation of ROA spectra may be extended in such a way that a continuous transition from the resonance to the far-from-resonance case is possible. This may be achieved by inclusion of a finite lifetime for the excited electronic states (compare Ref. [301]). In addition, the near-resonance theory as described by Nafie [224] may be implemented and studied with respect to the importance of the different levels of approximations. Since work on the DNR program package regarding higher-order (Herzberg–Teller) terms is underway, RROA calculations including these contributions will be straightforward. The extension of the current implementation for RROA calculations to the employment of the time-dependent ansatz, for which the underlying theory has been presented in this work, may also be accomplished in the future.

- The concept of the intensity-carrying modes can easily be extended to other spectroscopies involving derivatives of property tensors with respect to normal coordinates like, e.g., VCD spectroscopy. The corresponding ICMs may then serve as initial guesses for intensity-tracking calculations, to which the current implementation may be extended without much effort.

- The present implementation for the evaluation of ROA invariants assures gauge-origin dependence by employing the velocity representation of the electric-dipole moment operator for the calculation of the magnetic-dipole-containing invariant. The calculation of this velocity form is only available for pure density functionals in the program package TURBOMOLE since it can be computed essentially with the same computational effort as the corresponding length form in this case. Because the density-functional dependence is negligible for organic molecules, the pure density functional BP86, for which additionally density-fitting techniques are available, has been employed for all corresponding calculations. For the chiral metal complexes, nevertheless, a remarkable difference between the ROA spectra obtained with the BP86 and B3LYP density functionals has been detected. In order to find out whether hybrid density functionals give better results for metal complexes than pure density functionals, experimental data are needed. Then, the current TURBOMOLE implementation may be extended in order to provide origin-independent results also in the case of hybrid density-functional calculations. One way is to enable the calculation of the velocity form of the electric-dipole moment operator for hybrid density functionals. Another way is the implementation of LAOs, which is probably more favorable since it may be expected that the property tensors calculated with LAOs show a better basis set convergence than the ones obtained with the velocity form of the electric-dipole moment operator.
• Currently, the derivatives of the ROA property tensors with respect to normal coordinates are evaluated numerically employing the massively parallel implementation of Snf. An alternative way are analytical derivatives, which may, especially for spectra calculations of large molecules, lead to a reduced computational effort. Analytical derivatives for the electric-dipole–electric-dipole property tensor have already been available in TURBOMOLE [374, 405]. In an analogous way, analytical derivatives for the electric-dipole–magnetic-dipole and electric-dipole–electric-quadrupole tensors needed for ROA spectroscopy may be implemented.

• In course of our study of secondary structure elements of biomolecules, other kinds of helices and $\beta$-sheets are worth to be investigated. Furthermore, a systematic investigation of the dependence of the ROA intensities on the backbone angles is lacking. This may lead to a deeper insight about the generation and appearance of the different bands in the ROA spectra. In this way, it may also be shown whether ROA spectroscopy is able to discriminate different types of turns.

• In order to get appropriate starting structures for molecules adopting different conformations in solution, MD or Monte-Carlo simulations can be employed, which may be particularly important for, e.g., ROA spectra calculations of sugar molecules (see Ref. [492]). In this way, solvent effects are already considered if solvent molecules are included into the simulations. First-principles MD simulations [545, 546] as well as quantum-mechanical/molecular-mechanical approaches [547] may be a route to even more accurate calculations of such effects on Raman and ROA spectra.

• The Snf interface for the program package NWChem enables the study of highly accurate Raman spectra obtained from CC polarizability tensors. As a first step, the influence of diverse central difference formulae employed for the numerical differentiation by Snf and of higher CC excitations for the Raman tensor calculation, carried out by NWChem, may be investigated. Of special interest is the comparison to experimental gas-phase Raman data. This may give a hint about the magnitude of the errors introduced by the employment of Placzek’s theory for the Raman intensity calculations. The comparison to Raman spectra obtained from DFT calculations is also worth to be carried out. In this context, the variety of density functionals available in NWChem may be assessed.
A. Implementations

In order to make the calculations presented in sections 3.6, 4.2, 5, and 6 possible, several implementations had been necessary. In the following, we briefly summarize the main achievements.

A.1 The program package Snf

For the calculation of full vibrational spectra, the program package Snf [96,548] was employed. This program acts as meta-program, i.e., it collects raw data provided by other quantum chemical program packages like Adf [549,550], Gaussian [551,552], Dalton [553], Molpro [554], and Turbomole [555, 556]. Since the calculations are performed in the harmonic approximation (see section 1.3), the evaluation of the Hessian [compare Eq. (1.13)] containing the second derivatives of the electronic energy with respect to the Cartesian nuclear coordinates is required. These differentiations can be done analytically, but they would need a new implementation for each electronic structure method. That is why a semi-numerical differentiation scheme is employed in Snf. The first derivatives of the electronic energy with respect to the Cartesian nuclear coordinates, the electronic energy gradients, are calculated analytically by the quantum chemical program packages mentioned above. The second derivatives with respect to the Cartesian nuclear coordinates are then evaluated numerically and normal modes are calculated. This has the advantage that new interfaces to Snf can be added quite easily.

The derivatives of a property tensor element $T_{12}$ with respect to the normal coordinates, which are necessary for the intensity calculations, are evaluated numerically by Snf via

$$\left(\frac{\partial T_{12}}{\partial Q_k}\right)_0 = \sum_{i=1}^{M} \left(\frac{\partial T_{12}}{\partial R_{i\alpha}}\right)_0 L_{ki\alpha} \quad (A.1)$$

with the Cartesian derivative obtained via

$$\frac{\partial T_{12}}{\partial R_{i\alpha}} = \frac{T_{12}(R_{i\alpha} + s(R_{i\alpha})) - T_{12}(R_{i\alpha} - s(R_{i\alpha}))}{2s(R_{i\alpha})} \quad (A.2)$$

$s(R_{i\alpha})$ is the step size for the distortion of atom $i$ from the given structure into the $\alpha$ direction. The distorted structures are created by Snf and the
corresponding property tensors are calculated by the quantum chemical program packages like TURBOMOLE or DALTON. The differentiation and intensity calculation is then performed by SNF.

Because of its efficiency, TURBOMOLE was employed for all electronic energy gradient and property tensor calculations described in this work (except of the spectra shown in section 3.5.1 which employed ROA property tensors obtained from DALTON). For ROA calculations in the far-from-resonance approximation, the electric-dipole–electric-dipole, electric-dipole–magnetic-dipole, and electric-dipole–electric-quadrupole property tensors are needed (compare section 3.3). Since the $A$ tensor calculation was not available in TURBOMOLE and the $G'$ tensor only indirectly via the rotatory dispersion tensor [225, 376, 377], the missing parts for the calculation of the three ROA tensors were implemented into TURBOMOLE’s ESCF module [375–378, 557]. This implementation, for which density-fitting techniques can be employed in the case of pure density functionals [378] (compare section 4.1), enables now a fast calculation of ROA tensors. Only the combination of the efficient evaluation of property tensors by TURBOMOLE and the massively parallel and restart-friendly methodology of SNF made the ROA calculations of the metal complexes in section 5 and the large biomolecules in section 6 possible.

In addition to the extension of SNF’s TURBOMOLE interface, an interface for the program package NWChem [558, 559] was written, which enables the very accurate calculation of Raman spectra with the CC method [560].

A.2 The program package AKIRA

The program package AKIRA [386, 561] allows for the selective calculation of normal modes via mode-tracking [386, 387, 389, 394–396] (see section 4.2.1.1). The program structure is quite similar to the one of SNF, also with regard to the parallelization and restart facilities. AKIRA creates structures distorted along the basis vectors of interest, for which the electronic energy gradients are calculated by the quantum chemical packages like TURBOMOLE. After collecting these gradients, the differentiation with respect to the basis vectors is performed in order to obtain the desired (approximate) normal mode. In course of this work, the existing implementation of AKIRA was extended to IR-, Raman-, and ROA intensity-tracking (see section 4.2). In contrast to the pure mode-tracking implementation, it is now possible to converge more than one normal mode in a calculation, for which the intensities of interest are evaluated in each iteration step. The raw data (the electronic energy gradients and the required property tensors) were evaluated with TURBOMOLE. In addition, diverse selection criteria (compare section 4.2.1.2) were implemented.

The determination of the ICMs for IR-, Raman-, and ROA-spectroscopy was also implemented into AKIRA.
A.3 The program package DNR

The RROA spectra in sections 6.1 and 5.3 were carried out with the program package DNR [562], which is designed for the calculation of RR spectra and was extended to RROA calculations in course of this work. In DNR, the IMDHO approximation (see section 3.4.1) in the sum-over-states ansatz is applied. A tensor element $T_{12}$, considering one excited electronic state $|e_j\rangle$, the Raman active transition from $v_{i,1}$ to $v_{f,1}$ and a common line width $\Gamma$, are calculated for a non-linear molecule according to [563]

$$T_{12}(\omega_L) = \frac{1}{\hbar} \phi_{1,0}^{\text{el}} \phi_{2,0}^{\text{el}} \sum_{v_j} \frac{\langle v_f|v_j\rangle \langle v_j|v_i\rangle}{\omega_{v_jv_i} - \omega_L - i\Gamma}$$

$$= \frac{1}{\hbar} \phi_{1,0}^{\text{el}} \phi_{2,0}^{\text{el}} \sum_{v_j,1} \cdots \sum_{v_{j,M-6}} \infty \infty \frac{\langle v_{f,1}|v_{j,1}\rangle \langle v_{j,1}|v_{i,1}\rangle \Pi_{k=2}^{3M-6} |\langle v_{j,k}|v_{i,k}\rangle|^2}{\omega_{e_j\epsilon_0} + \sum_{k=1}^{3M-6} v_{j,k}\omega_k - \omega_L - i\Gamma} \quad (A.3)$$

with

$$\omega_{v_jv_i} = \omega_{e_j\epsilon_0} + \sum_{k=1}^{3M-6} v_{j,k}\omega_k. \quad (A.4)$$

$\omega_{e_j\epsilon_0}$ is the energy difference between the zeroth vibrational levels of the excited and ground electronic states, respectively. The total wave functions $|i\rangle$, $|f\rangle$, and $|j\rangle$ for the initial, final, and excited states are given in BO approximation (skipping the rotational and translational contributions) as a product ansatz for the nuclear wave function,

$$|i\rangle = |\epsilon_0\rangle \Pi_{k=2}^{3M-6} |v_{i,k}\rangle, \quad (A.5)$$

$$|f\rangle = |\epsilon_0\rangle \Pi_{k=2}^{3M-6} |v_{f,k}\rangle, \quad (A.6)$$

$$|j\rangle = |e_j\rangle \Pi_{k=2}^{3M-6} |v_{j,k}\rangle, \quad (A.7)$$

where the total wave functions have explicitly been written in terms of the electronic wave functions $|\epsilon_0\rangle$ and $|e_j\rangle$ and of the vibrational wave functions $|v_{f,k}\rangle$, $|v_{i,k}\rangle$, $|v_{j,k}\rangle$ corresponding to the final, initial, and excited electronic states, respectively. $\omega_k$ and $v_{j,k}$ are the vibrational angular frequency and vibrational quantum number, respectively, corresponding to normal mode $L_k$.

It is assumed that no hot bands occur so that only one initial state with vibrational wave functions $|v_{i,1}v_{i,2}\cdots v_{i,3M-6}\rangle$ has to be considered and that the vibrational energies of the ground state can be taken for all Raman-inactive normal modes at the beginning and at the end.

Employing the intensity shift function [564,565]

$$S(\omega_L - v_{j,1}\omega_1) := \sum_{v_{j,2}} \cdots$$

$$\sum_{v_{j,3M-6}} \frac{\Pi_{k=2}^{3M-6} |\langle v_{j,k}|v_{i,k}\rangle|^2 \cdot \Gamma}{(\omega_{\epsilon_0\epsilon_0} - (\omega_L - v_{j,1}\omega_1) + \sum_{k=2}^{3M-6} v_{j,k}\omega_k)^2 + \Gamma^2} \quad (A.8)$$
and its Kramers–Kronig transform [564, 565]

\[ T(\omega_L - v_{j,1}\omega_1) = \sum_{v_{j,2}} \cdots \]

\[
\sum_{v_{j,3M-6}} \Pi_{k=2}^{3M-6} |\langle v_{j,k}|v_{i,k}\rangle|^2 \left( \omega_{e_j,e_0} - (\omega_L - v_{j,1}\omega_1) + \sum_{k=2}^{3M-6} v_{j,k}\omega_k \right) \]

\[
(\omega_{j0} - (\omega_L - v_{j,1}\omega_1) + \sum_{k=2}^{3M-6} v_{j,k}\omega_k)^2 + \Gamma^2, \quad (A.9)
\]

the property tensor elements in real and imaginary parts are obtained as

\[
T_{12}(\omega_L) = \frac{1}{\hbar} \langle v_{f,1}\rangle_{v_{j,1}} \sum_{v_{i,1}} \langle v_{j,1}|v_{i,1}\rangle [T(\omega_L - v_{j,1}\omega_1) - iS(\omega_L - v_{j,1}\omega_1)]. \quad (A.10)
\]

The Franck–Condon integrals needed in the IMDHO model (see section 3.4) can be obtained from the normal-mode displacements \( \Delta_k \) of the excited-state equilibrium structure [564, 566]

\[
|\langle v_{j,k}|v_{i,k}\rangle|^2 = \frac{\Delta_{2v_{j,k}}^2}{2v_{j,k}v_{j,k}!} \exp \left( -\frac{\Delta_k^2}{2} \right), \quad (A.11)
\]

\[
\langle v_{j,k}|v_{j,k}\rangle \langle v_{j,k}|v_{i,k}\rangle = \Delta_k \sqrt{2} \left[ \frac{\Delta_{2v_{j,k}}^2}{2v_{j,k}v_{j,k}!} - \frac{2v_{j,k}\Delta_k^2}{2v_{j,k}v_{j,k}!} \right] \exp \left( -\frac{\Delta_k^2}{2} \right). \quad (A.12)
\]

\( \Delta_k \) is determined from the derivative of the excited-state energy \( E^j \) of the excited electronic state \( |e_j\rangle \) with respect to normal coordinate \( Q_k \) and corresponding angular frequency \( \omega_k \):

\[
\left( \frac{\partial E^j}{\partial Q_k} \right)_{Q_k=0} = \omega_k^2 (Q_k - \Delta_k)_{Q_k=0} = -\omega_k^2 \Delta_k. \quad (A.13)
\]
B. Computational Methodology

DFT was the method of choice for all calculations presented in this work due to the comparatively large size of the molecules under study and the reliability of the results [108]. Because of its efficient implementation, TURBOMOLE [555,556] was employed for all structure optimization, electronic energy gradient, and property tensor calculations (except for the property tensor evaluation in section 3.5.1). The BP86 density functional [122,123] and Ahlrichs' TZVP basis set [567] were utilized for the structure optimizations. For Schrock's molybdenum complex in section 4.2, whose structure was taken from Ref. [568], the SVP basis set [569] was employed for the carbon and hydrogen atoms and for the small sugar molecules in section 6.2 even the larger TZVPP basis set [567,570] due to the small number of atoms. The RI density-fitting technique (see section 4.1) employing the Karlsruhe auxiliary basis functions [571] was employed for all TURBOMOLE calculations with the BP86 density functional. Exceptions are the finite-field calculations, which were performed without the RI approximation (employing the TZVP basis set and the BP86 density functional) in section 4.2 for the initial guess of the intensity-tracking calculations because the errors due to the RI approximation are difficult to assess in this case. Various external electric-field strengths and self-consistent field convergence criteria for the electronic energy were tested for the calculation of this first guess vector. It turned out by comparison to full spectra calculations that an external electric field of 0.001 a.u. gives reliable results which is in accordance with the literature [572,573]. Additionally, a self-consistent field convergence criterion of at least $10^{-8}$ a.u. for the total electronic energy was necessary in order to obtain reliable results. The IR intensity-tracking guess was obtained via a three-point central difference formula with external electric fields into the $x$, $-x$, $y$, $-y$, $z$, and $-z$ directions. In an analogous way, the diagonal elements of the Cartesian polarizability for the Raman intensity-tracking guess, which was also applied for the ROA intensity-tracking, were evaluated while four-point backward difference formulae [402] were adapted for the off-diagonal ones.

The full vibrational spectra shown in this work were obtained with Snf [96,548] (see section A.1 for details). A three-point central differences formula was applied for the numerical differentiation leading to the determination of $6M$ distortions of a molecule with $M$ atoms. The step length in the numerical differentiation was set to 0.01 bohr. Since our local version of TURBOMOLE's Escf module for the ROA tensor calculations had not been available at that time yet, DALTON was used for the ROA tensor calculations presented in section 3.5.1.
employing LAOs \cite{278} for origin independent results. Because of the less efficient implementation in \textsc{Dalton} compared to \textsc{Turbomole}, Zuber and Hug’s rDPS:3-21G basis set \cite{438} was employed for the property tensor calculations, which is a small basis set especially designed for ROA spectra calculations. It contains the 3-21+G basis set \cite{574} augmented by one diffuse $p$-type polarization function on every hydrogen atom. For all other ROA calculations, our local version of \textsc{Turbomole}’s \textsc{Escf} module was used (compare section A.1) where the origin independence was assured by taking the velocity form of the electric-dipole operator for the $\beta (G')^2$ invariant (see section 3.3.1). Since only the length form is available for hybrid density functionals, the center of mass of the molecules was set to the gauge origin in the ROA calculations with B3LYP in order to make the origin dependence negligibly small.

In general, the TZVP basis set was found to be sufficient for the calculations of organic molecules so that this basis set was employed for all IR-, Raman-, and ROA-calculations (additionally the effective core potential as provided by \textsc{Turbomole} was applied for the cadmium atom of the metalloprotein in section 6.5 in order to account for scalar-relativistic effects). Exceptions are the sugar molecules in section 6.2 and propane-1,3-dione (and its anion) in section 3.6, for which even the larger TZVPP basis set was applied due to the small size of the molecules.

For the metal complexes in section 5, the TZVPP basis set \cite{567, 570} was required in order to obtain reliable results (for the rhodium atom, the TZVP basis set with the corresponding effective core potential basis set was applied due to the lack of a TZVPP basis set). For the investigation of the basis set dependence of ROA intensities, also the SVP and SVPP basis sets were tested (see section 5.1). The latter additionally contains the polarization functions, which are contained in the TZVPP basis set and described in Ref. \cite{570}. This SVPP basis set was used without the RI approximation due to the absence of the corresponding auxiliary basis set. Vibrational frequencies in section 5 were taken from the calculations with TZVPP and BP86.

A remarkable density functional dependence was found for the metal complexes, in contrast to the organic molecules for which the dependence is negligible \cite{47}. Therefore, always the pure density functional BP86 was employed for the latter profiting of the RI density-fitting technique.

The intensity-tracking calculations in section 4.2 were performed with \textsc{Akira} and \textsc{Turbomole} as raw data source. As no particular preconditioner was available, a unit matrix was employed \cite{387}, which typically does not affect the convergence behaviour. The ICMs in section 3.6 were evaluated with \textsc{Akira} using Cartesian derivatives from full spectra calculations with \textsc{Snf} and \textsc{Turbomole}.

The RR and RROA calculations in sections 5.3 and 6.1 were performed with the program package \textsc{Dnr} (see appendix A.3). The vibrational frequencies were obtained from \textsc{Snf} calculations employing \textsc{Turbomole} with the BP86 density functional. The TZVP basis set was applied in section 6.1 and the TZVPP basis
set in section 5.3. The Cartesian excited-state energy gradients were obtained from TURBOMOLE with B3LYP and TZVP. The damping parameter was set to 0.0002 a.u.

The Gibbs enthalpies in section 6.2 were calculated with Snf in the particle-in-a-box–rigid-rotor–harmonic-oscillator approximation employing the same density functional and basis set as for the structure optimizations. Although this standard approximation is not particularly well suited for obtaining Gibbs enthalpies in condensed phase, we may assume that the approximation is sufficient — mostly because the translational and rotational partition functions hardly matter for the entropy in this approximation since all molecular comparisons rely on a constant number of particles (one molecule at a time), and hence these contributions basically drop out because of the equal masses and very similar moments of inertia.

For all calculations with the solvent continuum model COSMO, the standard settings as provided by TURBOMOLE were applied.

The analysis of the helix spectra in section 6.4 was accomplished with an add-on package to Snf written in the PYTHON programming language [575]. The NUMPY package [576] was used for efficient linear algebra operations. For managing the geometric coordinates and for the assignment of atoms to individual residues and atom types in the investigated polypeptide, the OPENBABEL library [577,578] was employed. Plots of vibrational spectra in section 6.4.1 were produced using the MATPLOTLIB package [579]. The group-coupling matrices in sections 5.3, 6.3, and 6.5 were obtained with SPECPLOT [580].

Molecular structures and pictures of normal modes were visualized using the program JMOl [581]. The excitation wavelength for the Raman and ROA calculations was set to the standard wavelengths of 488 nm for the organic molecules in section 3.5.1, the zinc complex in section 5.2, and the cobalt complex in section 5.1 and to 514.5 nm in sections 6.2, 6.3, and for the calculations for L-tryptophan in sections 3.6 and 4.2. In order to avoid resonance with an excited electronic state, a laser wavelength of 799.3 nm was taken for the remaining calculations in sections 3.6, 5, and 6.4. For the protein in section 6.5, a wavelength of 1800 nm was chosen. The excitation wavelength for the RR and RROA spectra are given in the corresponding sections.

The total ROA intensity of a vibration is broadened to simulate the effect of an environment in such a way that the integration over the band yields the calculated total ROA intensity. Consequently, after this artificial line broadening the units should be Å\(^4\)/(a.m.u. · cm\(^{-1}\)). However, the usual convention with Å\(^4\)/a.m.u. as units was employed keeping in mind that the full area of a band is referred to. The vibrational spectra in sections 3.5.1, 5, 6.2, 6.4.2, and 6.5 were plotted using a Gaussian bandshape with a full width at half maximum (FWHM) of 15 cm\(^{-1}\) and the ones in sections 4.2 and 6.1 with a FWHM of 10 cm\(^{-1}\). For the vibrational spectra in sections 6.3 and 6.4.1, a Lorentzian bandshape with a FWHM of 15 cm\(^{-1}\) was employed. The excitation profiles in section 6.1 were plotted with a FWHM of 2.5 cm\(^{-1}\). The programs MOLDEN [582], GNUPLOT,
XMGRACE, XFIG, and PyMOL [583] were employed for making the plots. The Ramachandran plots were produced with the Protein Structure Validation Suite [584] employing MolProbity [585].
C. Notation

In general, tensors are printed in bold-face, i.e., also vectors and matrices. Greek indices represent the spatial coordinates $x$, $y$, and $z$. If not indicated otherwise, summation over Greek indices is implied. Dot products of quantities are usually written as $A \cdot B$ or, if appropriate, as $A_\alpha B_\alpha$ employing summation over Greek indices. The superscripts ‘*’ and ‘T’ indicate complex conjugated and transposed quantities, respectively. Derivatives with respect to time are marked by a dot over the regarding quantity. Operators are not explicitly indicated by a hat since it should be obvious from the context which quantity is an operator and which not. SI units are employed throughout this work. The only exception is section 2 containing the relativistic part of this work where Gaussian units have been chosen, that is, $4\pi\epsilon_0 = 1$ and $\epsilon_0$ is dimensionless. This is due to the reason that relativistic theories employ series expansions in powers of $1/c$ for the study of non-relativistic limits, which is more easily seen in Gaussian units. A general overview on the Dirac equation in different systems of units can be found in Ref. [56].

Some often employed symbols are enumerated in the following:

\begin{align*}
\delta_{\alpha\beta} & \quad \text{component of the Kronecker delta} \\
\epsilon_{\alpha\beta\gamma} & \quad \text{component of the Levi–Civita tensor} \\
T_e & \quad \text{electronic kinetic-energy operator} \\
T_{\text{nuc}} & \quad \text{nuclear kinetic-energy operator} \\
e & \quad \text{elementary charge} \\
|e\rangle & \quad \text{electronic wave function} \\
|v\rangle & \quad \text{vibrational wave function} \\
|\chi\rangle & \quad \text{nuclear wave function} \\
R_{\text{mw}} & \quad \text{mass-weighted nuclear coordinates} \\
R_{\text{nuc}} & \quad \text{nuclear coordinates} \\
R_k & \quad \text{coordinates of nucleus } k \\
r_e & \quad \text{electronic coordinates} \\
L_k & \quad \text{normal mode } k \\
Q_k & \quad \text{normal coordinate } k \\
m_e & \quad \text{electron mass} \\
m_k & \quad \text{mass of particle } k \\
e & \quad \text{electron charge} \\
q_k & \quad \text{charge of particle } k \\
Z_k & \quad \text{charge of nucleus } k 
\end{align*}
\[ |\Psi^S\rangle \] small component of the 4-component wave function
\[ |\Psi^L\rangle \] large component of the 4-component wave function
\[ A \] magnetic vector potential
\[ B \] magnetic field in free space
\[ E \] electric field in free space
\[ \tilde{E}^{(0)} \] complex amplitude of the electric field \( E \)
\[ E^{(0)} \] real amplitude of the electric field \( E \)
\[ \tilde{B}^{(0)} \] complex amplitude of the magnetic field \( B \)
\[ B^{(0)} \] real amplitude of the magnetic field \( B \)
\[ \Phi \] scalar potential
\[ \Pi \] mechanical momentum operator
\[ \sigma \] Pauli vector
\[ \beta, \alpha \] Pauli matrices
\[ p \] momentum operator
\[ t \] time
\[ \hbar \] Planck's constant divided by 2\( \pi \)
\[ c \] speed of light
\[ \varepsilon_0 \] permittivity in free space
\[ \mu_0 \] permeability in free space
\[ \epsilon \] dielectric constant in material
\[ \mu \] permeability in material
\[ \rho \] charge density
\[ \rho^{KS} \] Kohn–Sham density
\[ J \] current density
\[ n \] propagation vector
\[ \kappa \] wave vector
\[ \omega \] angular frequency
\[ \omega_L \] angular frequency of the incident light
\[ \omega_d \] angular frequency of the scattered light
\[ v \] speed of the electromagnetic wave
\[ \lambda \] wavelength
\[ \nu \] frequency
\[ \tilde{\nu} \] wavenumber
\[ \mu_\alpha \] \( \alpha \) component of the electric-dipole moment operator
\[ \theta_{\alpha\beta}^\gamma \] \( \alpha\beta \) component of the electric-quadrupole moment operator
\[ \theta_{\alpha\beta} \] \( \alpha\beta \) component of the electric-quadrupole moment operator in the traceless form
\[ m_\alpha \] \( \alpha \) component of the magnetic-dipole moment operator
\[ G \] number of particles
\[ M \] number of nuclei
\[ N_e \] number of electrons
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{\text{thres}}$</td>
<td>maximum element of the residuum vector in an intensity-tracking calculation</td>
</tr>
<tr>
<td>$N$</td>
<td>number of (approximate) normal modes selected for further optimization in an intensity-tracking calculation</td>
</tr>
<tr>
<td>$G_{ij}$</td>
<td>derivative of the electronic energy with respect to nuclear coordinate $R_{ij}$</td>
</tr>
<tr>
<td>$\alpha_{\alpha\beta}$</td>
<td>$\alpha\beta$ component of the electric-dipole–electric-dipole tensor</td>
</tr>
<tr>
<td>$G'_{\alpha\beta}$</td>
<td>$\alpha\beta$ component of the electric-dipole–magnetic-dipole tensor</td>
</tr>
<tr>
<td>$A_{\alpha\beta\gamma}$</td>
<td>$\alpha\beta\gamma$ component of the electric-dipole–electric-quadrupole tensor</td>
</tr>
</tbody>
</table>
## D. List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>Adiabatic Franck–Condon</td>
</tr>
<tr>
<td>ALA</td>
<td>Alanine</td>
</tr>
<tr>
<td>ASN</td>
<td>Asparagin</td>
</tr>
<tr>
<td>ASP</td>
<td>Aspartic acid</td>
</tr>
<tr>
<td>BLYP</td>
<td>Becke–Lee–Yang–Parr</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke three parameter Lee–Yang–Parr</td>
</tr>
<tr>
<td>BO</td>
<td>Born–Oppenheimer</td>
</tr>
<tr>
<td>BP86</td>
<td>Becke Perdew 1986</td>
</tr>
<tr>
<td>CC</td>
<td>Coupled-Cluster</td>
</tr>
<tr>
<td>CI</td>
<td>Configuration Interaction</td>
</tr>
<tr>
<td>CP</td>
<td>Circularly polarized</td>
</tr>
<tr>
<td>CYS</td>
<td>Cysteine</td>
</tr>
<tr>
<td>DCA</td>
<td>Dichloracetic acid</td>
</tr>
<tr>
<td>DCP</td>
<td>Dual circularly polarized</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DKH</td>
<td>Douglas–Kroll–Hess</td>
</tr>
<tr>
<td>fpFW</td>
<td>Free-particle Foldy–Wouthuysen</td>
</tr>
<tr>
<td>FW</td>
<td>Foldy–Wouthuysen</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GFC</td>
<td>Gradient Franck–Condon</td>
</tr>
<tr>
<td>GLN</td>
<td>Glutamine</td>
</tr>
<tr>
<td>GLY</td>
<td>Glycine</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree–Fock</td>
</tr>
<tr>
<td>HFC</td>
<td>Hessian Franck–Condon</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ICM</td>
<td>Intensity-carrying mode</td>
</tr>
<tr>
<td>ICP</td>
<td>Incident circularly polarized</td>
</tr>
<tr>
<td>IMDHO</td>
<td>Independent mode, displaced harmonic oscillator</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn–Sham</td>
</tr>
<tr>
<td>LAO</td>
<td>London atomic orbital</td>
</tr>
<tr>
<td>LEU</td>
<td>Leucine</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>LYS</td>
<td>Lysine</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>MP</td>
<td>Møller–Plesset perturbation theory</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>NESC</td>
<td>Normalized elimination of the small component</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
<tr>
<td>PRO</td>
<td>Proline</td>
</tr>
<tr>
<td>QED</td>
<td>Quantum electrodynamics</td>
</tr>
<tr>
<td>rDPS:3-21G</td>
<td>Reduced diffuse polarization function and shell augmented 3-21G</td>
</tr>
<tr>
<td>RI</td>
<td>Resolution-of-the-identity</td>
</tr>
<tr>
<td>ROA</td>
<td>Vibrational Raman optical activity</td>
</tr>
<tr>
<td>RR</td>
<td>Resonance Raman</td>
</tr>
<tr>
<td>RROA</td>
<td>Resonance Raman optical activity</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
</tr>
<tr>
<td>SCP</td>
<td>Scattered circularly polarized</td>
</tr>
<tr>
<td>SER</td>
<td>Serine</td>
</tr>
<tr>
<td>SES</td>
<td>Single excited electronic state</td>
</tr>
<tr>
<td>SVP</td>
<td>Split valence plus polarization</td>
</tr>
<tr>
<td>SVPP</td>
<td>Split valence double polarization</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time-dependent density functional theory</td>
</tr>
<tr>
<td>TDKS</td>
<td>Time-dependent Kohn–Sham</td>
</tr>
<tr>
<td>THR</td>
<td>Threonine</td>
</tr>
<tr>
<td>TZVP</td>
<td>Triple-zeta valence polarization</td>
</tr>
<tr>
<td>TZVPP</td>
<td>Triple-zeta valence double polarization</td>
</tr>
<tr>
<td>VCD</td>
<td>Vibrational circular dichroism</td>
</tr>
<tr>
<td>VFC</td>
<td>Vertical Franck–Condon</td>
</tr>
<tr>
<td>ZORA</td>
<td>Zeroth order regular approximation</td>
</tr>
</tbody>
</table>
E. List of Publications and Invited Talks

Publications originated from this work:


**Additional publications:**


**Invited Talks:**

1. *Towards the calculation of Raman optical activity spectra for large molecules 2007*, Deep Computing Seminar, IBM Research Laboratory Rüschlikon, Switzerland.


F. Acknowledgements

First of all, I thank Prof. Dr. Markus Reiher for being an excellent supervisor and giving me the opportunity to work on the field of spectroscopy including so many different aspects of this topic. His enthusiasm and openness for ideas were always very encouraging. Furthermore, he gave me the possibility to work without time pressure and to attend many international conferences, even as far away as Australia. Discussions about the job-related future after this thesis are also gratefully acknowledged as well as showing me understanding every time when I needed (short-time) holidays due to my ill parents.

I would also like to thank Prof. Dr. Neugebauer for providing immediate and competent help whenever I needed some. He was always open for discussions and had the basic ideas for the projects we worked together. Furthermore, I am very grateful for giving me the possibility for a research stay at the University of Leiden, which was a great experience.

Moreover, I thank Dr. Christoph Jacob for the cooperation on the ROA papers of tryptophan and the helices as well as developing and performing the analysis with respect to the localization of modes. He was always a great source of ideas.

In addition, I would like to thank Dr. Irina Malkin-Ondík for the collaboration and the related discussions on the relativistic part of this work as well as Dr. Jeff Hammond, now at the Argonne National Laboratory, for the cooperation on Coupled-Cluster Raman spectra calculations.

For a lot of helpful discussions regarding my ROA papers I would like to thank Prof. Dr. Kenneth Ruud of the University of Tromsø.

Special thanks go to Dr. Stephan Schenk who takes care of the computer cluster, provided me so with excellent working conditions, and who was always open for questions.

For the excellent support regarding the administrative work, I am very indebted to Romy Isenegger, Veronika Sieger, and Veronika Siegrist. In addition, I gratefully acknowledge the great support of Prof. Dr. Wilfred F. van Gunsteren who convinced me to stay at the ETH when I was an exchange student as well as his secretary Daniela Kalbermatter.

Furthermore, I am grateful to the Stipendiumstelle of the ETH Zurich for providing me with fellowships for the travels to the summer school in Palermo and the conferences in Manchester and Helsinki. Thanks go to the Kontaktgruppe für Forschungsfragen of Ciba, Novartis, Roche, Merk Serono, and Syngenta for the grant, which made the visit of the WATOC conference in Sydney possible.
as well as PD Dr. Hans Peter Lüthi-Diploudis for the support.
Last but not least, I would like to thank the working group for the nice and
friendly atmosphere. Moreover, I am indebted to my room mate Dr. Remigius
Mastalerz for reading parts of this manuscript, supplying me with a lot of
sweets, particularly during the last months of this thesis, helping me with the
plots, and innumerable discussions about the work and life in general.
Bibliography


[132] Ganzmüller, G., Berkaine, N., Fouqueau, A., Casida, M. E., Reiher, M., Comparison of density functionals for differences between the high- ($^5T_{2g}$) and low- ($^1A_{1g}$) spin states of iron(II) compounds IV. Results for the ferrous complexes [Fe(L)(‘NHS$_4$’)], *J. Chem. Phys.*, **122** (2005) 234321.


[151] Sinnecker, S., Rajendran, A., Klamt, A., Diedenhofen, M., Neese, F., Calculation of Solvent Shifts on Electronic g-Tensors with the Conductor-Like Screening Model (COSMO) and Its Self-Consistent Generalization


[461] Luber, S., Reiher, M., Theoretical Raman optical activity study of the β domain of rat metallothionein, 2009, DOI: 10.1021/jp909483q.


BIBLIOGRAPHY


[536] Venkatachalam, C. M., Stereochemical criteria for polypeptides and proteins. IV. Conformation of a system of three linked peptide units, Biopolymers, 6 (1968) 1425–1436.


[553] DALTON, a molecular electronic structure program, Release 2.0 (2005), URL: http://www.kjemi.uio.no/software/dalton/dalton.html.
BIBLIOGRAPHY  283


[561] Neugebauer, J., Herrmann, C., Reiher, M. AKIRA — the program for the purpose-driven calculation of pre-selected molecular vibrations, URL: http://www.theochem.ethz.ch/software/akira.
[562] Neugebauer, J. DNR 1.1.0 — a program for resonance Raman and vibronic structure calculations.


[580] Herrmann, C., Luber, S. Specplot, a tool for visualizing snf output.


