A QUANTUM-CHEMICAL MAGNIFYING GLASS
FOR CHROMOPHORES IN PROTEINS

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Zusammenfassung

Die quantenmechanische Beschreibung großer Moleküle wird sehr aufwändig, wenn das gesamte System mit hoher Genauigkeit behandelt werden soll. Selektive Methoden ermöglichen den Zugang zu gezielten Informationen über räumlich begrenzte Teilsysteme oder über einen Teil von Freiheitsgraden und erlauben so eine Fokussierung auf die relevanten Aspekte einer Fragestellung. Dadurch reduzieren sie den nötigen Rechenaufwand und vereinfachen die Interpretation der Ergebnisse, also erleichtern sie die Behandlung komplexer Systeme.

Für die theoretische Resonanz-Raman-Spektroskopie von Chromophoren in Proteinen ist die Anwendung elektronischer Subsystem-Methoden in Verbindung mit einem einfachen und effizienten oder aber einem genauen und aufwendigen Ausdruck für die Raman-Intensitäten sehr vielversprechend. In dieser Arbeit werden lokale und selektive Techniken untersucht, die eine effiziente Berechnung von Resonanz-Raman-Spektren ermöglichen.

Elektronendichten, die mit Hilfe von Einbettungsverfahren mit eingefrorener Elektronendichte (frozen-density embedding), einer Subsystem-Formulierung der Dichtefunktionaltheorie, erhalten wurden, werden mit Kohn–Sham-Dichtefunktional-Ergebnissen verglichen, indem für Systeme, die durch Wasserstoffbrücken verknüpft sind, und für eine schwache koordinative Bindung in einem Molekül eine topologische Analyse der Dichte durchgeführt wird. Sowohl die topologischen Daten als auch Abbildungen der Differenzdichte zeigen, dass die Änderungen in der Dichte bei Bindungsbildung qualitativ reproduziert werden. Unter Verwendung der Erweiterung dieser Elektronenstruktur-Methode für angeregte Zustände kann der Einfluss der Umgebung auf die elektronischen Zustände in Resonanz beschrieben werden, wodurch sich der Ansatz für Resonanz-Raman-Spektroskopie eignet.


Näherungsansätze für Resonanz-Raman-Spektren erweisen sich häufig schon als zufriedenstellend, wenn die so berechneten Spektren mit zeitaufgelösten experimentellen Spektren in Lösung verglichen werden, da feine Unterschiede in den Intensitätsverteilungen nicht aufgelöst werden. Zur Untersuchung reaktiver Intermediate
Zusammenfassung

in der Photochemie von Nitroaromaten werden einfache Resonanz-Raman-Modelle angewendet und ihre Leistungsfähigkeit überprüft. Der Vergleich theoretischer und experimenteller Spektren unterstützt die Identifizierung und Charakterisierung der Intermediate, wodurch die Bedeutung dieser Näherungsmethoden aufgezeigt wird.

Abstract

The quantum-mechanical description of large molecules is very demanding if the complete system has to be treated with high accuracy. Selective methods give access to specific information on local subsystems or on subsets of degrees of freedom and thus allow one to focus on the relevant aspects of a problem. Thereby they save computational effort, simplify the interpretation of the results and hence facilitate the theoretical analysis of complex systems.

For theoretical resonance Raman spectroscopy on chromophores in proteins, the application of subsystem-based electronic-structure methods in combination with a simple, efficient or a sophisticated description of the vibrational part is very promising. In this thesis, local and selective techniques are examined, which permit the efficient calculation of resonance Raman spectra.

Densities obtained from frozen-density embedding, a subsystem formulation of density-functional theory, are compared to Kohn–Sham density-functional theory results by performing a topological analysis for hydrogen-bonded systems and a weak coordinative bond in a molecule. The topological data as well as difference density plots show that the density changes upon binding are qualitatively reproduced. Through the generalization of this electronic structure method for excited states, the influence of the environment on the resonating electronic states can be included, which makes the approach suited for resonance Raman spectroscopy.

For resonance Raman spectra which do not only account for the main Franck–Condon contribution but also consider scattering contributions which arise from vibronic coupling, Herzberg–Teller terms have to be considered. The implementation of Herzberg–Teller vibronic-coupling terms into the program DNR enables one to accurately describe resonance Raman spectra for different enhancement mechanisms of the Raman modes. Test calculations for the skatole molecule prove the relevance of Herzberg–Teller contributions also for modes, for which the dominant Franck–Condon contribution does not vanish.

Approaches which yield an approximate resonance Raman spectrum are often already sufficient when comparing to time-resolved experimental spectra in solution, since fine differences in intensity distributions are not resolved. For the study of reactive intermediates in the photochemistry of nitroarenes, simple resonance Raman models are applied and their performance is assessed. The comparison of theoretical and experimental spectra aids in the identification and characterization of the intermediates, which demonstrates the value of these approximate approaches.

Resonance Raman is inherently a selective technique. This can be reflected in efficient calculations of resonance Raman spectra, when a mode-selective approach is combined with an intensity criterion, so that intense modes in a spectrum are selectively determined. With this intensity-tracking algorithm, reference spectra can be reproduced while the computational effort is reduced.
1 Introduction

What a Magnifying Glass Does

Some things are so small that they are hard to see with our eyes. A magnifying glass makes these things look bigger so we can see them better.

Some things are easy to see with our eyes, but a magnifying glass lets us look more closely at details on those things.

Taken from “A Magnifying Glass” by Robyn Opie, Martin Smith; Wings, Flinders Park, S.A. 2004.

The function of the “magnifying glass” in the title of this thesis is described by the above excerpt taken from a children’s book as a tool, which enlarges small things and on the other hand can filter out details in a specific region. Thus, an examination with a magnifying glass is at once a sensitive and a selective method to study an object. For the elucidation of the structure of chromophores in proteins, resonance Raman spectroscopy constitutes such a sensitive and selective experimental method. This thesis deals with the theoretical description of such spectra using the methods of quantum chemistry, hence I chose the figure of speech of the “quantum-chemical magnifying glass”.

Vibrational spectroscopic methods in general, like infrared and Raman spectroscopy, are versatile tools to study the structure and properties of molecules. With increasing size of the molecules, however, the interpretation of the spectra is hampered by the large number of close-lying or even overlapping vibrational peaks. Resonance Raman spectroscopy has the advantage that certain peaks in the vibrational spectra are selectively enhanced. Through the change in the electronic structure upon excitation, the molecule starts to vibrate along modes which are related to the electronic structure change between ground and excited state. Thus the electronic resonance conditions act like a filter on the vibrational spectrum [1]. This selectivity in the enhancement and the sensitivity means that resonance Raman spectroscopy can be used as a probe for chromophoric sites in complex biological systems.

However, resonance Raman spectroscopy is a versatile method which can be used for a wide field of applications, which is not restricted to biomolecules. For small molecules, its selectivity is not the essential characteristic but the information it provides about the excited-state structure. It is used to elucidate the structure and dynamics of excited states in photochemical reactions of small molecules [2–4] or to characterize the excited-state properties of push-pull chromophores [5, 6]. Furthermore, it has been applied to identify and quantify traces of polyaromatic hydrocarbons [7]. Yet, the most prominent applications are indeed biological molecules,
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[8–10], e.g. proteins and light-harvesting systems [11–14]. For example, resonance Raman is a tool in the investigation of metalloproteins [15,16], e.g., the structure and function of heme in hemoglobin and myoglobin [17,18] or in general for porphyrin-containing systems [19,20], or for the photochemical mechanisms of visual pigments in rhodopsin [21]. Furthermore, purine and pyrimidine bases of nucleic acids [22–24] have been examined. Resonance Raman spectra of peptide backbone amide vibrations reveal information about the secondary structure [25]. A large number of resonance Raman investigations deal with the aromatic amino acid residues Tryptophan, Tyrosine and Phenylalanine, in particular with their enhancement mechanisms and dependence of vibrational frequencies on the environment [26–31].

Large molecules often exhibit crowded spectra with many close-lying vibrations. Despite their selective nature, even for resonance Raman spectra the relationship between structure and spectral features is not obvious in all cases as is, for instance, the case for reactive intermediates. It may be rather difficult to uniquely assign a structure to a vibrational spectrum. Then, quantum chemical predictions are indispensable. For the special case of resonance Raman spectroscopy, a number of algorithmic developments have been proposed in the past, e.g., Lee and Heller’s time-dependent approach [32] and the gradient approximation to it [33], as well as recent works such as methods based on generalized polarizability tensor derivatives [34]. In such theoretical investigations, the relation between spectrum and molecular structure is immediate. A problem with the quantum-mechanical calculation of vibrational spectra is the increase in computational effort for larger systems. This limits the size of a molecule which can be studied. Certain problems, however, suggest a selective description. In many cases only a subsystem is relevant for the experimental question, so that the development of methods focussing on these subsystems or subsets of degrees of freedom to be described is of high conceptional and practical value. If the electronic properties of the subsystem can be interpreted locally, embedding approaches provide a quantum-mechanical description of this fragment without neglecting the influence of the environment. Approaches have been developed, which describe only the subsystem quantum-mechanically while including the environment through empirical, classical terms using molecular mechanics (QM/MM approaches) [35–37]. Subsystem methods in the framework of density-functional theory aim at obtaining the exact ground-state electron density as a superposition of fragment densities. In the frozen-density embedding method [38], partitioning of the density into two fragments is employed: The optimum density \( \rho_1 \) of an active subsystem is determined in the presence of an effective embedding potential due to the fixed (frozen) electron density \( \rho_2 \) of the environment. Concerning the vibrational structure, the number of degrees of freedom which have to be accounted for in a calculation can be reduced significantly by employing mode-selective techniques [39–41]. This holds true especially for vibrations of mainly local character [40,41]. If such a mode-selective approach is connected with an intensity criterion, the experimental selectivity in resonance Raman spectroscopy can be put to advantage.
The aim of this thesis is to present selective methods for the electronic structure as well as the vibrational structure to yield an efficient theoretical treatment of resonance Raman spectra. To begin with, quantum-chemical methods which form the basis for the developments and results achieved within this thesis are introduced in Chapter 2. In Chapter 3, the topological analysis of electron densities obtained with frozen-density embedding for hydrogen-bonded systems and a weak coordination bond is described. Chapter 4 addresses the fundamentals of theoretical resonance Raman spectroscopy with special attention to the inclusion of vibronic coupling with Herzberg–Teller terms [42]. Moreover, methods to calculate Raman spectra are discussed. The implementation of Herzberg–Teller terms in the resonance Raman program DNR [43], which allows one to obtain accurate resonance Raman spectra, as well as first test calculation are presented in Chapter 5. In Chapter 6, the application of approximate resonance Raman approaches on the experimental problem of identifying photochemical intermediates is described, which allows for an assessment of the approximate methods. Lastly, Chapter 7 introduces an advance for the selective calculation of resonance Raman spectra by combining a mode-selective technique with intensity expression given in Ref. [33].
2 Quantum-Mechanical Description of Molecules and Molecular Assemblies

Molecules are many-particle systems, which are described by a wavefunction depending on electronic and nuclear coordinates. Spectroscopic techniques probe the electronic as well as the vibrational structure via frequencies and intensities. For a theoretical treatment of molecular spectra, the electronic as well as the vibrational structure have to be determined. Electronic and nuclear coordinates are dealt with separately: The solution of the electronic Schrödinger equation for a fixed nuclear configuration yields an electronic energy and thus allows one to determine the electronic ground-state structure, i.e., the nuclear configuration corresponding to the lowest energy. The vibrations around such a minimum configuration are obtained by the solution of the nuclear Schrödinger equation. In this chapter the methods to solve the electronic and vibrational structure of a molecule shall be introduced as far as they are pertinent to this thesis. For more detailed accounts the reader is referred to textbooks, for example to Ref. [44]. For large molecules these standard quantum-mechanical approaches can pose a challenge or at least become computationally demanding. Subsystem approaches try to overcome these problems by focussing on the relevant parts of a larger system. A subsystem formulation within density-functional theory will be discussed below following a general introduction into quantum-mechanical methods for chemistry.

2.1 Time-independent Schrödinger equation

For a quantum-mechanical description of molecules, the Schrödinger equation plays a key role, since its solution yields the molecular wavefunctions and energy eigenvalues. The Schrödinger equation is a function of the coordinates of the elementary particles which constitute the molecule, i.e., nuclei and electrons, and of time. For the scope of this thesis, we can restrict ourselves to non-relativistic quantum mechanics since the molecules considered contain no heavy elements. If the potentials describing the interactions between the particles are time-independent, time and coordinate variables can be separated. For these stationary states, the wavefunction \( \Psi_i \) of state \( i \) depending solely on nuclear and electronic coordinates is determined by the time-independent Schrödinger equation

\[
\hat{H}(r, R)\Psi_i(r, R) = E_i \Psi_i(r, R),
\]  

(2.1)
where \( r \) and \( R \) denote the coordinates describing the electrons and nuclei, respectively. The Hamiltonian \( \hat{H} \) (in the absence of external fields) consists of operators corresponding to the kinetic energy of the electrons, \( \hat{T}_e(r) \), and nuclei, \( \hat{T}_{\text{nuc}}(R) \), and of the potential-energy operators describing the interaction between the particles, which are the electron–electron repulsion, \( \hat{V}_{e,e}(r) \), the Coulomb attraction between electrons and nuclei, \( \hat{V}_{\text{nuc},e}(R,r) \), and the Coulomb repulsion between the nuclei, \( \hat{V}_{\text{nuc},\text{nuc}}(R) \):

\[
\hat{H}(r, R) = \hat{T}_e(r) + \hat{T}_{\text{nuc}}(R) + \hat{V}_{e,e}(r) + \hat{V}_{\text{nuc},e}(r, R) + \hat{V}_{\text{nuc},\text{nuc}}(R). \tag{2.2}
\]

### 2.2 Separation of electronic and nuclear coordinates

The motion of electrons and nuclei is coupled by \( \hat{V}_{\text{nuc},e}(R,r) \). For the treatment of most chemical problems, electronic and nuclear coordinates can be separated, apart from a few special cases, e.g., in spectroscopy when electronic states are very close in energy. The nuclei are much heavier than the electrons and thus they move much slower, so that it is an obvious approximation to calculate the motion of the electrons for a fixed configuration of the nuclei. The electrons are thought to follow immediately. The separation of the coordinates mathematically corresponds to a product ansatz of the total wavefunction \( \Psi_i \) as a product of a nuclear wavefunction \( \chi_{j,k}(R) \) and an electronic wavefunction \( \psi_j(r; R) \), which depends only parametrically on the nuclear coordinates, \( \Psi_i(r, R) = \chi_{j,k}(R)\psi_j(r; R) \). In order to obtain the electronic wavefunction, an electronic Hamiltonian, which does not contain the kinetic energy of the nuclei, is defined for a fixed nuclear configuration:

\[
\hat{H}_{\text{el}}(r; R) = \hat{T}_e(r) + \hat{V}_{e,e}(r, r) + \hat{V}_{\text{nuc},e}(r, R) + \hat{V}_{\text{nuc},\text{nuc}}(R). \tag{2.3}
\]

The solutions of the electronic Schrödinger equation,

\[
\hat{H}_{\text{el}}(r; R)\psi_j(r; R) = E_{\text{el},j}\psi_j(r; R), \tag{2.4}
\]

form a complete basis. For the solution of the nuclear Schrödinger equation,

\[
\hat{H}_{\text{nuc}}(R)\chi_{j,k}(R) = \left( \hat{T}_{\text{nuc}} + E_{\text{el},j} \right)\chi_{j,k}(R) = E_{\text{nuc},j,k}\chi_{j,k}(R), \tag{2.5}
\]

the electronic energy for a set of configurations \( \{R\} \) takes the role of a potential energy. The representation of the total wavefunction depending on electronic and nuclear coordinates as a single product constitutes an approximation. For the exact solution, the total wavefunction is expanded in the set of electronic wavefunctions (which is impractical since the complete set has to be known) and inserted in the total Schrödinger equation. When the matrix elements of the nuclear kinetic energy operator \( T_{\text{nuc}} \) are evaluated, terms coupling different electronic states arise. These non-adiabatic coupling terms prevent the use of a single-product wavefunction and
require a sum over all electronic wavefunctions. The treatment of these coupling terms yields different approximations: If the off-diagonal terms are neglected, the so-called adiabatic approximation results. In the Born–Oppenheimer approximation, additionally, the diagonal terms are left out, so that the vibrational motion takes place solely under the influence of the electronic potential. Thus, the concept of the potential energy surface (PES) arises out of the approximate description of the total wavefunction as a single product, which is justified since non-adiabatic corrections are in general small. In both cases, the sum collapses to one product of wavefunctions. The difference between the Born–Oppenheimer and the adiabatic approximation is in the nuclear wavefunctions, the electronic wavefunctions are the same for both approximations. Separating nuclear and electronic coordinates yields two equations, the nuclear and the electronic Schrödinger equation.

2.3 Nuclear Schrödinger equation

The nuclear Schrödinger equation determines the vibrational motion and its solution is therefore necessary to calculate vibrational spectra. Since even within the Born–Oppenheimer approximation, the complete PES can only be determined for a limited number of nuclear coordinates $\mathbf{R}$, usually analytical PES functions are used. For standard vibrational analyses, the electronic energy is expanded around a minimum of the PES to second-order terms for all nuclear coordinates. The second-order derivatives of the electronic energy are collected in the Hessian matrix $\mathbf{H}$. If the coordinates are mass-weighted and the set of coordinates found in which the Hessian takes a diagonal form, then in these normal coordinates $\mathbf{Q}$ the nuclear motion, i.e., the vibrations of the molecule, can be described as a set of decoupled harmonic oscillators:

$$
-\frac{\nabla^2 j}{2} + \frac{1}{2} H^{(Q)}_{jj} Q_j^2 \chi_{jk} = E_{\text{nuc},j,k} \chi_{jk},
$$

(2.6)

where $\nabla^2 j$ is defined with respect to the mass-weighted normal coordinate $Q_j$.

2.4 Electronic Schrödinger equation

Several ab initio electronic structure methods, i.e., methods for the solution of the electronic Schrödinger equation, exist of which most prominent in quantum chemistry are the wavefunction approaches and density-functional theory. Since for molecules the electronic Schrödinger equation cannot be solved exactly, approximate solutions have to be found. The variational principle, which states that the expectation value for a trial wavefunction is always higher than the exact eigenvalue, allows to search for the best electronic ground-state wavefunction using an energy criterion. For the wavefunctions an ansatz containing parameters is made. These parameters are subsequently optimized to find the best function within that approximate ansatz. Usually, a basis set expansion is employed, so that the expansion coefficients are optimized.
2 Quantum-Mechanical Description of Molecules and Molecular Assemblies

2.4.1 Single-determinantal methods

The electronic wavefunction is a function of the coordinates of all electrons (and parametrically, of the nuclei). The motion of the electrons is coupled by the operator for the electron–electron interaction: $\hat{V}_{e,e}(\mathbf{r},\mathbf{r})$, i.e., the electrons cannot be described independently of each other. However, again the simplest approximate ansatz consists of a product of one-particle wavefunctions, each depending on the coordinates of only one electron, the so-called Hartree product. An additional condition which has to be met by the ansatz is the fulfillment of the Pauli principle, which states that the wavefunction needs to be antisymmetric with respect to the exchange of two electrons. The Hartree product does not meet this criterion, however it can be anti-symmetrized and written as a determinant (the Slater determinant). Then so-called one-determinant methods result. By employing this product ansatz, the $N$-electron problem is reduced to $N$ effective (but coupled) one-electron problems. The Hartree–Fock (HF) method is an \textit{ab initio} ansatz to determine these one-particle functions, which are the molecular orbitals. In order to incorporate the electron spin in this description, the orbitals are described as a product of a spatial function and a spin function. Spatial orbitals as well as spin functions are orthonormal. The equations determining the orbitals $\phi_i$ can be written as a pseudo-eigenvalue equation, the canonical Hartree–Fock equation

$$\hat{f}\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}),$$  \hspace{1cm} (2.7)

where the Fock operator $\hat{f} = \hat{h} + \hat{J} - \hat{K}$ consists of the one-electron operator $\hat{h}$ which contains the kinetic energy of an electron as well as the interaction of the electron with all the nuclei, while the two-electron operators, the Coulomb operator $\hat{J}$ and the exchange operator $\hat{K}$, depend on the other orbitals and are defined as:

$$\hat{h} = -\frac{\nabla_i^2}{2} + \hat{V}_{\text{nuc},e,i},$$  \hspace{1cm} (2.8)

$$\hat{J} = \sum_j \hat{j}_j \text{ with } \hat{j}_j\phi_i = \langle \phi_j | r_{12} | \phi_j \rangle_2 \phi_i,$$  \hspace{1cm} (2.9)

$$\hat{K} = \sum_j \hat{k}_j \text{ with } \hat{k}_j\phi_i = \langle \phi_j | r_{12} | \phi_i \rangle_2 \phi_j.$$  \hspace{1cm} (2.10)

Because of the dependence of $\hat{J}$ and $\hat{K}$ on the other orbitals, these equations can only be iteratively solved in so-called self-consistent field calculations. The canonical Hartree–Fock equation can be written using a HF potential $v_{\text{HF}}$, which contains the electron–nuclear interaction and electron–electron interaction terms:

$$\left[-\frac{\nabla_i^2}{2} + v_{\text{HF}}(\mathbf{r})\right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}).$$  \hspace{1cm} (2.11)
2.4.2 Correlated methods

Even in a complete basis or if the HF equations are solved numerically, the HF eigenfunction and eigenvalue are still a crude approximation because of the way the electron–electron interaction is treated, i.e., in an averaged way. The HF wavefunction constitutes the best one-determinant wavefunction in a given basis. The difference to the correct, non-relativistic result is called correlation energy. There are three main approaches in quantum chemistry, namely configuration interaction (CI), many-body perturbation theory and coupled cluster (CC), which try to capture the electron–electron correlation, improving the wavefunction by including more parameters to increase the flexibility. Instead of a single Slater determinant, the electronic wavefunction can be expanded in the complete basis of Slater determinants, which are generated from the HF determinant $\Phi_{\text{HF}}$ by creating “excited” determinants through replacing occupied by virtual orbitals in the determinant. In this way, singly, doubly, triply, etc. excited determinants $\Phi_i$ emerge,

$$\psi_{\text{CI}} = a_0 \Phi_{\text{HF}} + \sum_{i=1} a_i \Phi_i.$$  \hfill (2.12)

This multi-determinantal ansatz, in which the expansion coefficients $a_i$ are calculated employing a variational approach, is called configuration interaction. If the complete basis is employed in the expansion (Full CI), the exact wavefunction (in the above mentioned non-relativistic framework) is obtained. However, this is feasible only for very small systems and small basis sets, so that in practice the expansion needs to be truncated after a few terms. This leads to a wealth of CI-methods, for example CISD, where singly and doubly excited determinants are included. For cases in which the description with one determinant is not even qualitatively sufficient the wavefunction can be described by several determinants, where not only the expansion coefficients but also the molecular orbitals are optimized. To this kind of multi-configuration self-consistent field (MCSCF) methods belongs the complete active space self-consistent field (CASSCF) approach. Molecular orbitals are divided into an active and an inactive space with restrictions on excitations, thus reducing the number of determinants for a full CI treatment within the active subspace. CASSCF energies are often improved on by employing a perturbative treatment to second order, which is called CASPT2.

In the alternative coupled-cluster approach, as in the CI method, excited determinants are employed, but the formalism leads to different results for truncated expansions. The coupled-cluster wavefunction is generated by the effect of an excitation operator $\hat{T}$ on the Slater determinant:

$$\psi_{\text{CC}} = e^{\hat{T}} \Phi_{\text{HF}},$$  \hfill (2.13)

where $\hat{T}$ is defined as the sum of excitation operators generating all possible singly excited determinants $\hat{T}_1$, all possible doubly excited determinants $\hat{T}_2$, all possible triply excited determinants $\hat{T}_3$, etc.: $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$. The Taylor series
expansion of the exponential function in Eq. (2.13),

\[ e^\hat{T} = 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \cdots \]  

(2.14)

results in higher excited determinants for truncated CC than for CI due to products of excitation operators, for example \( \hat{T}^2 \) giving quadruple excitations.

### 2.5 Density-Functional Theory

In density-functional theory (DFT) methods, the quantum-mechanical description of molecules and molecular properties is based on the electron density. In contrast to the wavefunction, the electron density is an observable and is defined as the probability of finding electrons as a function of (three) spatial coordinates. It is connected to the \( N \)-electron wavefunction depending on \( 3N \) spatial coordinates \( \{ r_i \} \) and \( N \) spin coordinates \( s_i \) by:

\[ \rho(r_1) = N \int \int \cdots \int |\psi(\{ r_i \}, \{ s_i \})|^2 d^3r_1 d^3r_2 \cdots d^3r_N ds_N. \]  

(2.15)

The ground-state energy is expressed as a functional of the electron density rather than obtained by the solution of the Schrödinger equation. The DFT description gives access to equivalent results to the wavefunction description. The position of the nuclei and their charge, which together determine the external potential, and the number of electrons have to be known in order to specify the Hamiltonian for a system.

The basis of DFT methods is formed by the Hohenberg–Kohn theorem [45]. The first part of the Hohenberg–Kohn theorem states that the external potential is determined within a constant by the electron density of the ground state. Moreover, the integral of the electron density over space yields the number of electrons, so that the Hamiltonian of the system can be fully specified, and thus the ground-state wavefunction is fixed. The energy can then be written as a functional of the ground-state density, \( E[\rho] \), (and likewise the ground-state wavefunction \( \psi[\rho] \)). The second part of the Hohenberg–Kohn theorem gives a variational principle for functionals of the density analogous to the one for wavefunctions. The energy is minimized under the condition that the density integrates to the correct number of electrons. Although the energy thus can in principle be expressed as a functional of the density, in practice an exact energy functional is still unknown. The description of electron correlation in DFT methods translates to a problem of defining accurate functionals. The standard approach to obtain approximations of the functionals is to split the energy functional in order to describe the known parts and then approximate the remaining parts. For parts of the energy, functional expressions in terms of the density are known, e.g., the Coulomb interaction between electron density and nuclei. The electron–electron interaction \( V_{ee}[\rho] \) is split into a (known) Coulomb part and
into a non-classical part:

\[ V_{ee}[\rho] = J[\rho] + V_{ee,\text{nonclass}}[\rho]. \]  

(2.16)

However, the kinetic energy and the non-classical electron interaction cannot be easily expressed in terms of the density, but only in terms of the wavefunction. Approximate kinetic-energy density functionals exist, but another approach is more successful, namely Kohn–Sham (KS) DFT.

### 2.5.1 Kohn–Sham DFT

For the kinetic energy \( T[\rho] \), a solution was proposed by Kohn and Sham [46], which led to the success of the DFT methods. The kinetic energy is calculated for a hypothetical system of non-interacting electrons, with an identical electron density to the system of interacting electrons. This non-interacting system can be exactly described by a single Slater determinant wavefunction. The orbitals are determined by solving one-particle equations analogous to the Hartree–Fock equations, cf. Eq. (2.11):

\[
\left(-\nabla_i^2 + v_s(r)\right) \phi_i(r) = \varepsilon_i \phi_i(r),
\]  

(2.17)

where \( v_s \) is the external potential of the non-interacting reference system. For this system, the exact kinetic energy can be calculated as a function of the orbitals \( \phi_i \). This kinetic energy for the non-interacting system is taken as an approximation for the kinetic energy of the interacting system. The residual kinetic-energy contribution must then be included in the approximate functionals for the non-classical electron-electron interaction, the so-called exchange–correlation functionals \( E_{xc} \):

\[
E[\rho] = T_s[\{\phi_i\}] + J[\rho] + V_{ne}[\rho] + E_{xc}[\rho].
\]  

(2.18)

Since the interacting and the non-interacting systems have by construction the same density, the density of the interacting system can be determined employing the one-particle equations for the non-interacting system (denoting the external potential as \( v_i^{\text{KS}} \)):

\[
\left(-\nabla_i^2 + v_i^{\text{KS}}\right) \phi_i = \varepsilon_i \phi_i,
\]  

(2.19)

with \( v_i^{\text{KS}}(r) = -\sum_k \frac{Z_k}{|r - R_k|} + \int \frac{\rho(r')}{|r - r'|} \, dr' + \frac{\delta E_{xc}[\rho]}{\delta \rho} \).  

(2.20)

The exact density is obtained as a sum over the squares of the occupied orbitals. The Slater-determinant wavefunction does not correspond to a wavefunction of the interacting system, though. The effective potential in the one-particle equations contains functional derivatives of the density functionals for the contributions to the total energy (kinetic energy, exchange–correlation energy, etc.). Thus, approximate
exchange–correlation functionals $E_{xc}$ are needed. A hierarchy of approximations has been and is continuously being developed. The most simple functionals belong to the Local Density Approximation (LDA), and depend on the local density of the system, for instance the VWN functionals [47]. In the Generalized Gradient Approximations (GGA), additionally the gradient of the density is considered, e.g., the BP86 functional [48,49]. If higher order derivatives of the density or the orbital kinetic-energy density are included, meta-GGA functionals result. Moreover, hybrid functionals, which contain exact HF exchange, have been formulated and successfully applied, e.g., the B3LYP functional [48,50].

For the calculation of excitation energies, a linear response formulation of the extension of DFT to time-dependent phenomena (time-dependent DFT, TDDFT) can be employed.

### 2.5.2 Frozen-Density Embedding

Most present-day applications of density-functional theory (DFT) use the Kohn–Sham approach [46] to optimize the electron density of molecular systems in connection with approximate functionals for the exchange–correlation contribution to the electronic energy. An alternative way was suggested in 1993 by Wesolowski and Warshel [38], which is based on earlier subsystem formulations of DFT [51]. It uses a partitioning of the total electron density into two contributions and optimizes one part of the total density while keeping the other one frozen [52]. The kinetic energy in this so-called frozen-density embedding (FDE) approach is expressed as the sum of the kinetic energies of the subsystems plus a non-additive contribution, which is evaluated in terms of approximate, density-dependent kinetic energy functionals (see, e.g., Ref. [53–56]).

The method has been generalized for excited states [57,58] and has widely been used to determine, e.g., interaction energies [59–65], equilibrium distances [66], excitation energies and electronic spectra [67–71], and molecular properties [70,72–75]. Moreover, solvation and free energy calculations [76–78] as well as activation free energy calculations in solution [79] have been presented, and molecular dynamics simulations based on such subsystem approaches have been carried out [78,80,81]. The FDE scheme may be extended to an arbitrary number of subsystems as presented in Ref. [81] for condensed-phase dynamics or in Ref. [58] for the calculation of coupled excitations. This generalized setup using many fragments is particularly suited for multilevel simulations [82], which was one of the main goals in the development of the FDE method from the very beginning [38]. For local properties of embedded molecules various approximations can be applied in order to enhance the efficiency of FDE, e.g., in calculations of solvent effects on molecular properties [68–70,73]. Also protein environments have been modeled by the embedding approach [83]. Similar DFT embedding techniques have been applied in connection with a wavefunction description of the embedded system [84–90]. Currently, FDE is mainly applied as an effective environmental method rather than as a different...
2.5 Density-Functional Theory

It can be regarded as a QM/QM hybrid method.

In the FDE approach, the system under investigation with electron density $\rho_{\text{tot}}$ is partitioned into two subsystems denoted as 1 (embedded system) and 2 (environment), each of which is defined by its density, $\rho_1$ and $\rho_2$, and the coordinates $\mathbf{R}_{A_1}$ and $\mathbf{R}_{A_2}$ as well as the charges $Z_{A_1}$ and $Z_{A_2}$ of its nuclei. By constructing a guess for the electron density of the environment, $\rho_2$, one can derive Kohn–Sham-like one-electron equations for the determination of the optimum density $\rho_1$ from the minimization of the energy functional $E = E[\rho_1 + \rho_2]$ w.r.t. $\rho_1$ while keeping $\rho_2$ fixed (“frozen”). In these one-electron equations for the orbitals $\phi_i^{(1)}$ of system 1, the effect of $\rho_2(\mathbf{r})$ is represented by an effective embedding potential $v_{\text{emb}}^{\text{eff}}(\mathbf{r})$,

$$\left[-\frac{\nabla^2}{2} + v_{\text{KS}}[\rho_1](\mathbf{r}) + v_{\text{emb}}^{\text{eff}}[\rho_1, \rho_2](\mathbf{r})\right]\phi_i^{(1)}(\mathbf{r}) = \varepsilon_i^{(1)}\phi_i^{(1)}(\mathbf{r}),$$

(2.21)

where $v_{\text{emb}}^{\text{eff}}[\rho_1, \rho_2](\mathbf{r})$ is given by

$$v_{\text{emb}}^{\text{eff}}[\rho_1, \rho_2](\mathbf{r}) = \sum_{A_2} \frac{Z_{A_2}}{\mathbf{r} - \mathbf{R}_{A_2}} + \int \frac{\rho_2}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \delta E_{xc}[\rho] \bigg|_{\rho = \rho_1} - \delta T_s[\rho] \bigg|_{\rho = \rho_1} + \delta E_{xc}[\rho] \bigg|_{\rho = \rho_{\text{tot}}} - \delta T_s[\rho] \bigg|_{\rho = \rho_{\text{tot}}}.$$

(2.22)

For exact exchange–correlation ($E_{xc}[\rho]$) and kinetic-energy ($T_s[\rho]$) functionals defined in the KS formulation of DFT, this approach would be exact provided that the exact $\rho_1 = \rho_{\text{tot}} - \rho_2$ is, for a given $\rho_2$, $v_s$-representable, which also implies that it is non-negative everywhere in space. In practice, the latter condition can be relaxed by using so-called freeze-and-thaw cycles [52], in which the role of $\rho_1$ and $\rho_2$ is iteratively exchanged until the energy is optimized as a bifunctional of both $\rho_1$ and $\rho_2$. In that case, the corresponding one-electron equations for the orbitals of system 2 are,

$$\left[-\frac{\nabla^2}{2} + v_{\text{KS}}[\rho_2](\mathbf{r}) + v_{\text{emb}}^{\text{eff}}[\rho_2, \rho_1](\mathbf{r})\right]\phi_i^{(2)}(\mathbf{r}) = \varepsilon_i^{(2)}\phi_i^{(2)}(\mathbf{r}),$$

(2.23)

where $v_{\text{emb}}^{\text{eff}}[\rho_2, \rho_1](\mathbf{r})$ is the equivalent of $v_{\text{emb}}^{\text{eff}}[\rho_1, \rho_2](\mathbf{r})$, in which the densities $\rho_1, \rho_2$ are exchanged and the Coulomb potential due to the nuclei $A_2$ in system 2 is replaced by the corresponding potential of the nuclei in system 1. Instead of an iterative improvement of $\rho_1$ and $\rho_2$, an approximate description of $\rho_2$ can be chosen for effective environmental methods.
The kinetic-energy part of $v_{\text{eff}}(r)$ is sometimes written as the functional derivative $\frac{\delta T_{\text{nadd}}[\rho_1, \rho_2]}{\delta \rho_1}$ of the non-additive kinetic-energy functional

$$T_{\text{nadd}}[\rho_1, \rho_2] = T_s[\rho_1 + \rho_2] - T_s[\rho_1] - T_s[\rho_2],$$

which, unless an exact kinetic-energy functional is known, constitutes an approximation to

$$T_{s}^{\text{nadd}} = T_s \left[ \{ \phi_i^{(1) + (2)} \} \right] - T_s \left[ \{ \phi_i^{(1)} \} \right] - T_s \left[ \{ \phi_i^{(2)} \} \right]$$

and is in practice the limiting factor to the general applicability of this approach.
3 Density Analysis for Frozen-Density Embedding

Frozen-density embedding (FDE) has been widely used as an effective environmental model. As an alternative formulation of density-functional theory (DFT), FDE should still lead to the exact density of a system if the exact kinetic and exchange–correlation energy functionals were known and the density to be optimized fulfilled certain criteria (see Chapter 2.5.2). In practice, approximate functionals for the kinetic-energy component have to be used, which limits the applicability of the FDE scheme to rather weakly interacting systems [61, 62, 72]. More strongly interacting subsystems, e.g., systems connected by a covalent bond, cannot be appropriately described by the presently available approximations. Schemes to overcome this problem have been devised. One example is the introduction of capping groups to describe proteins [91].

Most of the previous studies have assessed the accuracy of FDE calculations in an indirect way, i.e., by analyzing their accuracy for properties, energies, or structures. Brief analyses of the electron density deformation from FDE and supermolecular calculations have been presented for the FH···NCH complex in Ref. [77] and for the Li⁺–H₂O complex in Ref. [59], although the latter study apparently contained some numerical flaws [92].

In order to gain a more detailed understanding of factors affecting the accuracy of embedding calculations, a systematic analysis of the differences in the topology of electron densities obtained from FDE calculations and from Kohn–Sham (KS)-DFT calculations is necessary. For that purpose, a set of molecules with hydrogen-bonding interactions was investigated. These are the rather strongly bound systems HOH···F⁻, F⁻–H–F⁻, and the nucleic acid base pair adenine–thymine, which comprises a twofold hydrogen bond. It should be noted that topological analyses of hydrogen-bonded systems had been carried out before, but with a very different focus, for instance to develop criteria for the detection of hydrogen bonds [93], to investigate the distance dependence of the electron-density topology [94], or to study the relationship between the topology and energetic properties of hydrogen bonds [95]. These FDE calculations for hydrogen bonds are briefly compared to results for van der Waals-interactions and a coordinative bond. For coordinative bonds in solids, e.g., for MnF₆⁻ [96] lanthanide complexes [97, 98], and zinc complexes [99], subsystem calculations had been performed. However, such a description of donor–acceptor bonds is problematic. Therefore, here ammonia borane has been chosen as a first example due to its simple structure.

After introducing the methodology, different criteria for the assessment of densi-
ties from FDE calculations for the H$_2$O···F$^-$ complex are compared (Section 3.2). Since such a calculation involves both numerical approximations as well as more fundamental approximations concerning the energy functionals employed, the different factors that determine the performance of FDE in terms of their impact on the electron-density topology are analyzed (Section 3.3). The analysis is then extended to the symmetric hydrogen-bonded system F−H−F$^-$ and the DNA base pair adenine–thymine, before they are set against the van-der-Waals complex neon dimer and the coordinative bond in ammonia borane (Section 3.4). Conclusions on the factors influencing the FDE density are drawn in Section 3.5. After the analysis of the basic quantity of FDE, an illustrative example is given to demonstrate the usefulness of FDE for the spectroscopy of chromophores in biomolecules (Section 3.6).

3.1 Methodology

The superposition of isolated molecular densities already produces a density similar to that of the interacting complex in many cases. Therefore, difference (or deformation) densities as well as the negative Laplacian of the electron density are employed as more sensitive diagnostic tools. The ability to model the binding region between the subunits in the FDE calculations is furthermore analyzed by a topological analysis of the electron density according to the theory of atoms in molecules [100]. It provides detailed insight into the electronic structure of molecules and solids that in the past has been utilized for many different purposes [101], such as analyzing the bonding scenario in transition metal ethylene and acetylene complexes [102,103] and deriving a new concept to describe agostic interactions in early transition metal complexes [104]. The topology of an electron density distribution can be summarized by a characteristic set of critical (i.e. stationary) points [100]. The so-called bond critical point (BCP) is the saddle point found between two bound atoms in a molecule, i.e., it is the minimum on a line connecting the local maxima of the electron density which correspond to the atomic positions. A second type of critical point, the ring critical point (RCP), is found when atoms form a ring structure like in benzene. In the center of the benzene ring the electron density exhibits a minimum along two directions within the ring plane but a maximum in a third direction perpendicular to the ring. The value of the electron densities at these critical points can, together with the values of the negative Laplacian, be used to characterize a chemical bond. The negative Laplacian of the electron density, $L(r) = -\nabla^2 \rho(r)$, is a measure of the curvature of the electron density at a given point. These two topological parameters, $\rho(r)$ and $L(r)$ evaluated at the critical points, allow for a direct bond characterization. A positive value of $L(r)$, which indicates a local concentration of the electron density within the bonding region, is found for covalent bonds. For a closed-shell interaction, the value of $L(r)$ is negative at the BCP and $\rho(r)$ is small (of the order of 0.05 eÅ$^{-3}$). Analogously to $\rho(r)$, stationary points can also be identified and characterized in the topology of $L(r)$. Of special importance are the local maxima in the positive regions of the negative Laplacian, the so-called
local charge concentrations. In compounds containing only main group elements two types of local charge concentrations can be identified. The *bonding* charge concentrations are found in the valence regions of atoms connected by a covalent bond, while the *non-bonding* charge concentrations are observed at the positions where free electron pairs are located. In the following, the latter type of maxima will be referred to in short as “charge concentrations”. As the topological parameters at the critical points and the local charge concentrations can directly be used to detect even subtle changes in the electron density distribution as well as to characterize a chemical interaction, they are well suited for an assessment of the electron density distributions obtained from the FDE approach.

All calculations were performed using the Amsterdam Density Functional (ADF) package [105, 106]. The optimized structures of the hydrogen-bonded system were obtained employing the BP86 exchange–correlation functional [48, 49] and a TZP basis set from the ADF basis set library [105]. For the supermolecular KS-DFT calculations (i.e., KS calculations on the whole system consisting of several fragments) and for the FDE calculations on the subsystems the BP86 functional was used. In the latter case, the BP86 functional was also used for the exchange–correlation contribution to the embedding potential. If not mentioned otherwise, a gradient-dependent approximation for the non-additive kinetic energy contribution was used that is related to the exchange functional of Perdew and Wang [107], and which was reparameterized for the kinetic energy by Lembarki and Chermette [108]. This functional will be denoted as PW91k in the following.

During the study of coordination compounds, an inconsistency in the implementation of the PW91k functional for the spin-restricted case was detected. For details, see Ref. [109]. Exemplary calculations for the hydrogen-bonded complexes have been repeated. Changes in the electron densities and negative Laplacians are \( \sim 0.01 \, e\AA^{-3} \) and \( < 0.1 \, e\AA^{-5} \), respectively. The results for ammonia borane have been obtained with the corrected implementation.

For comparison, KS-DFT calculations within the local density approximation (LDA) using the Vosko–Wilk–Nusair correlation functional [47] in combination with the KS-LDA exchange functional were also performed.

The two subunits connected by hydrogen bonds were chosen as the fragments in the FDE calculations, i.e., the hydrogen bonding region forms the boundary between the subsystems. For the neon dimer and ammonia borane, the subsystem boundary is taken to be the region of the van der Waals interaction and the coordination bond, respectively. Both the density and \( L(\mathbf{r}) \) are linear, so that their values for a superposition of fragment densities can be obtained by adding up the corresponding values for the subsystems. The densities of the fragments and the supermolecule were obtained on the same grid for each complex under study. The electron density and the negative Laplacian \( L(\mathbf{r}) \) were obtained on a grid of points (step-size 0.01 Å) from a locally modified version of the DENSF-utility program of the ADF package. The search for stationary points in the electron density was performed with the program INTEGRITY [110]. The isocontour plots of the difference densities and \( L(\mathbf{r}) \) were prepared using MATHEMATICA [111, 112].
3.2 Criteria for the assessment of the FDE densities

In this section the criteria for assessing the quality of FDE densities will be applied to the hydrogen-bonded complex of water and a fluoride ion as an example. The BP86/TZP optimized structure of the complex is shown in Fig. 3.1. The H···F distance in this planar complex is 1.32 Å, the O–H···F angle is 177.9 degrees and the H–O–H angle is 101.1 degrees. There are two different O–H bond lengths, O–H1 = 0.97 Å and O–H2 = 1.11 Å.

Figure 3.1: Optimized (BP86/TZP) structure and coordinates in the grid of the H-bonded system H2O···F−.

Subsystem densities were obtained using a TZP basis set after three freeze-and-thaw cycles, (see Ref. [52] for details). A subsystem basis set was employed in each calculation in this section; note that this is an approximation, since a supermolecular basis set is in principle needed in order to provide full flexibility for a polarization of a subsystem density by the other subsystem. The choice of this type of basis set was motivated by the fact that actually most practical applications of FDE as an environmental model do, similarly to QM/MM hybrid methods, not use basis functions in the environmental region. The results in this section thus allow an assessment of the densities obtained in such calculations where FDE is used as an approximate environmental model. But it must be kept in mind that they do not allow an assessment of the limitations of this subsystem approach to reproduce the electron densities from supermolecular KS calculations in principle, which requires to carefully distinguish between purely technical approximations (basis sets, convergence of freeze-and-thaw cycles) and fundamental approximations in the energy functionals applied. These effects will be analyzed in Section 3.3. Note that the term “embedding densities” will be used in the following for the sum of the two subsystem densities obtained from the FDE calculations. As mentioned above, the
3.2 Criteria for the assessment of the FDE densities

BP86 functional for the exchange–correlation part of the embedding potential was used, while for the non-additive kinetic-energy contribution the PW91k functional was chosen as default. These settings correspond to a standard FDE calculation that often gives good results for molecular properties [68–70]. The effect of changes to these defaults will be investigated in the subsequent sections.

Probably the most obvious way to compare electron densities is to present them in a map, e.g., by plotting isodensity values in a plane. This is shown in Fig. 3.2 a) for the density in the molecular plane of H$_2$O···F$^-$, obtained in a KS-DFT calculation of the supermolecule (hereafter referred to as $\rho_{\text{super}}$). This map can then be compared to the densities obtained by summing up the subsystem densities from the embedding calculation, $\rho_{\text{emb}}$, or from the isolated fragments’ densities, $\rho_{\text{frag}}$. The fragments in this case are a H$_2$O molecule and a F$^-$ ion. The corresponding plots for $\rho_{\text{frag}}$ and $\rho_{\text{emb}}$ (see Fig. S1 in the Supplementary Material of Ref. [113]) are very similar to $\rho_{\text{super}}$, and no differences can be found upon visual inspection. Thus, this direct approach does not offer a sensitive criterion for the assessment of the differences in the density.

For a more detailed analysis of the FDE electron densities, deformation densities, i.e., the difference between $\rho_{\text{super}}$ and $\rho_{\text{frag}}$, or $\rho_{\text{emb}}$ and $\rho_{\text{frag}}$, were considered. These deformation densities show changes in the density upon formation of the H···F bond. Additionally, the difference densities $\rho_{\text{super}} - \rho_{\text{emb}}$ were studied. This offers the possibility to detect subtle deviations between the FDE and supermolecular KS electron densities in a locally resolved manner. In Figs. 3.2 b) to d) deformation and difference densities are depicted for H$_2$O···F$^-$. In part b) the deformation density upon formation of the hydrogen bond between the fluoride ion and the water molecule is presented for the supermolecular KS case. The difference density in the fluorine subsystem is positive in a ring around the fluorine ion perpendicular to the plotting plane, which originates from the electron lone pairs. It is also positive in the middle of the H···F connection line, while the remaining part in this subsystem is negative. In the water subsystem, the difference density is negative around hydrogen atom H2 and in a region perpendicular to the bond axis on the oxygen, but positive elsewhere. In comparison to the two isolated subsystems, the electron density around the oxygen atom and the fluorine ion appear to be polarized towards the connecting hydrogen atom in the hydrogen-bonded complex. The corresponding difference density for the embedding calculation is shown in Fig. 3.2 c). In this case, the two regions of positive difference densities around the fluorine ion are overlapping and less localized than in the supermolecular calculation. In particular, the density deformation is less directed towards the hydrogen bonding region. Nonetheless, the qualitative features of the deformation density plot agree with the supermolecular case, although it can be recognized from the data points included in Fig. 3.2 that quantitative differences remain. A direct comparison between $\rho_{\text{super}}$ and $\rho_{\text{emb}}$ is possible by analyzing their difference density shown in Fig. 3.2 d). The density $\rho_{\text{emb}}$ in the F···H2–O region is too low around atom H2, but too high towards the fluorine ion and too high on the O–H2 bond close to H2.
Figure 3.2: Density $\rho_{\text{super}}$ (a) and deformation densities $\rho_{\text{super}}-\rho_{\text{frag}}$ (b), $\rho_{\text{emb}}-\rho_{\text{frag}}$ (c) and difference density $\rho_{\text{super}}-\rho_{\text{emb}}$ (d) for H$_2$O···F$^-$. Contour lines are drawn at $\pm 2, 4, 8 \times 10^n$ eÅ$^{-3}$ with $n = -2, -1, 0, 1, 2, 3$ for the density and with $n = -4, -3, -2, -1, 0$ and for 0 eÅ$^{-3}$ for the difference densities. Positive (including zero) values and negative values are marked by solid and dashed lines, respectively. Atomic positions and bond critical points are marked by dots and open circles, respectively. Coordinates are given in units of Å.

Regarding the changes perpendicular to the bond axis at the atoms O and F, $\rho_{\text{emb}}$ is too high around O and too low around F. On the opposite side of the hydrogen bond at the fluorine ion, the difference density is negative close to the nucleus and positive further away, i.e., the density seems to be more strongly contracted to the fluorine atom in $\rho_{\text{emb}}$. Upon formation of the bond, density appears to be shifted from this region to the hydrogen bond. Although this shift is qualitatively captured by FDE, the detailed structure of the density in the bonding region is not
fully reproduced. At hydrogen atom H1 and around the oxygen atom, the difference density is negative. This means that not enough density is shifted from these regions towards the hydrogen bond by FDE. The embedding calculation can thus not fully reproduce the polarization of the water molecule and the fluorine atom upon bond formation.

A sensitive and locally resolved probe for the differences in electron densities is the negative Laplacian. In Fig. 3.3 the negative Laplacians $L_{\text{frag}}$, $L_{\text{emb}}$ and $L_{\text{super}}$ are depicted.

Figure 3.3: Negative Laplacian $L_{\text{frag}}$ (a), $L_{\text{emb}}$ (b) and $L_{\text{super}}$ (c) for H$_2$O···F$^-$. Contour lines are drawn at ±2, 4, 8 × 10$^n$ eÅ$^{-5}$ with $n = -4, -3, -2, -1, 0, 1, 2$ and additionally at 0, 70 and 158 eÅ$^{-5}$. Positive (including zero) values and negative values are marked by solid and dashed lines, respectively. Coordinates are given in units of Å.

In $L_{\text{frag}}$, the fluorine atom is spherically symmetric. Since the same geometric structure as in the hydrogen-bonded complex was used for the water molecule, the two O–H bonds are not equivalent, e.g., the bonding charge concentration on the O–H2 bond is smaller than on the O–H1 bond. In $L_{\text{emb}}$, the Laplacian in the region of hydrogen atom H2, region B in Fig. 3.3 c), looks similar to the unperturbed $L_{\text{frag}}$, but the region of local charge concentration descends steeper and does not extend as far to the fluorine atom as in $L_{\text{frag}}$ or $L_{\text{super}}$. In $L_{\text{super}}$, this local charge concentration descends more symmetrically to both sides of the F···H2–O connection line. Moreover, the bonding charge concentration on the oxygen atom towards H2, shown by an additional contour line at 70 eÅ$^{-3}$ in Fig. 3.3 c), region A, is higher than towards H1. Further maxima of the local charge concentration can be found on a ring perpendicular to the plotting plane around the fluorine atom (region C in Fig. 3.3 c)), shown by the contour lines at 158 eÅ$^{-3}$). In $L_{\text{emb}}$, this ring is much less pronounced and the bonding charge concentration in region A is much smaller, but still visible. The Laplacian plots thus show that certain characteristic effects of the
hydrogen-bond formation can be recognized in the FDE calculation, albeit they do not quantitatively agree with the reference plots.

While (difference-)density and Laplacian maps offer the possibility for a spatially resolved analysis, it is sometimes useful to employ representative indicators for the features of the electron density. Topological parameters at the BCPs (see Fig. 3.1) as listed in Table 3.1 can be utilized for this purpose.

Table 3.1: Coordinates $r_{BCP}$ (in units of Å) of the BCPs and values of $\rho(r)$ in $e\text{Å}^{-3}$ and $L(r)$ in $e\text{Å}^{-5}$ at the BCP of $\rho(H_2O\cdots F^-)$ calculated with different approximations (suprmolecular density $\rho_{\text{super}}$, embedding density $\rho_{\text{emb}}$ and superposition of the isolated fragment densities $\rho_{\text{frag}}$).

<table>
<thead>
<tr>
<th>BCP</th>
<th>XC</th>
<th>$r_x,BCP$</th>
<th>$r_y,BCP$</th>
<th>$\rho(r_{BCP})$</th>
<th>$L(r_{BCP})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\rho_{\text{super}}$</td>
<td>BP86</td>
<td>$-0.72$</td>
<td>$-0.15$</td>
<td>$2.32$</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>$-0.73$</td>
<td>$-0.15$</td>
<td>$2.27$</td>
<td>$-10.7$</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>BP86</td>
<td>$-0.72$</td>
<td>$-0.15$</td>
<td>$2.32$</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{frag}}$</td>
<td>BP86</td>
<td>$-0.73$</td>
<td>$-0.15$</td>
<td>$2.33$</td>
</tr>
<tr>
<td>2</td>
<td>$\rho_{\text{super}}$</td>
<td>BP86</td>
<td>$0.02$</td>
<td>$-1.14$</td>
<td>$1.52$</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>$0.02$</td>
<td>$-1.15$</td>
<td>$1.48$</td>
<td>$-5.27$</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>BP86</td>
<td>$0.02$</td>
<td>$-1.17$</td>
<td>$1.52$</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{frag}}$</td>
<td>BP86</td>
<td>$0.01$</td>
<td>$-1.11$</td>
<td>$1.63$</td>
</tr>
<tr>
<td>3</td>
<td>$\rho_{\text{super}}$</td>
<td>BP86</td>
<td>$0.01$</td>
<td>$-1.77$</td>
<td>$0.75$</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>$0.01$</td>
<td>$-1.76$</td>
<td>$0.74$</td>
<td>$0.60$</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>BP86</td>
<td>$0.01$</td>
<td>$-1.73$</td>
<td>$0.55$</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{frag}}$</td>
<td>BP86</td>
<td>$0.01$</td>
<td>$-1.79$</td>
<td>$0.72$</td>
</tr>
</tbody>
</table>

The most significant differences can be seen at BCP3, which is located on the hydrogen bond where the system is divided into subsystems for FDE. The approximate $\rho_{\text{emb}}$ obtained with the particular setup used here, i.e., without ghost basis functions in the environmental system, seems to yield worse results than $\rho_{\text{frag}}$ for the topological parameters, as the coordinates of BCP3 are too close to the hydrogen atom and values of the density and $L(r)$ show larger deviations from $\rho_{\text{super}}$ than those of $\rho_{\text{frag}}$. With increasing distance from the hydrogen bond, the differences in the topological parameters disappear. While at BCP2 the density is virtually the same for $\rho_{\text{super}}$ and $\rho_{\text{emb}}$ and only the negative Laplacians differ, at BCP1 both values are nearly identical for the two approaches. Therefore, further discussions concentrate on BCP2 and BCP3 only. Data for BCP1 may be found in Tables S1 and S2 of the Supplementary Material of Ref. [113].

Characteristic points can be found in the negative Laplacian outside the molecular plane of $H_2O\cdots F^-$. The maxima of the local charge concentration found at the free electron pairs of the oxygen atom are smaller in $L_{\text{super}}$ ($112 e\text{Å}^{-5}$) and $L_{\text{emb}}$ ($108 e\text{Å}^{-5}$) than in $L_{\text{frag}}$ ($130 e\text{Å}^{-5}$). In the vicinity of the fluorine atom, the maximal value of the local charge concentration decreases from $L_{\text{super}}$ ($168 e\text{Å}^{-5}$) to
3.3 Factors affecting the quality of the density

In this section, different factors which determine the overall accuracy of the electron density in frozen-density embedding calculations in comparison to supermolecular KS calculations are analyzed. First, the questions concerning the numerical approximations made in FDE that are of great relevance for practical applications will be addressed. These are the number of freeze-and-thaw cycles (if any) and the basis set employed. Second, the choice of the energy functionals employed for the embedding potential will be subject of study.

As far as the basis set is concerned, the most important factor for FDE calculations is not the quality of the atomic basis sets — as long as reasonably large basis sets (TZP or better) are employed — but the question whether or not a calculation for one subsystem requires the basis functions of the complementary system, i.e., whether a “monomer basis” or a “supermolecular basis” (ghost basis functions on the frozen subsystem) is needed [114]. This is an important question for the assessment of FDE as a competitive environmental model, as its efficiency for large environments critically depends on the fact that a subsystem basis set can be used.

Concerning the energy functionals or the potentials derived from them, the approximation for the exchange–correlation functional in the embedding potential can in practice be chosen differently from the one used within the subsystems. However, a restriction to a consistent choice of the same exchange–correlation potential for (i) the supermolecular KS calculation, (ii) the exchange–correlation potential within the subsystems, and (iii) the embedding potential in all cases will be applied. A brief analysis of the impact of different XC potentials on the density obtained from the supermolecular KS-DFT calculation will be carried out in order to provide an estimate for the sensitivity of the density on the choice of $E_{xc}$. As a criterion for the influence of the various parameters mainly the topological parameters at the BCPs will be considered, but in some cases also deformation density and difference density plots will be used.

3.3.1 Basis sets

FDE describes the polarization of densities under the influence of an environment, for which a flexible basis set is needed [114]. For the preceding results, only monomer (or subsystem) basis sets were considered, i.e., basis functions were only provided for the atoms in the non-frozen system. A remaining problem might therefore be that the basis is not flexible enough in the region of the frozen subsystem in order...
to allow for a sufficient transfer of electron density from one system to the other, so that a supermolecular basis set might be required for quantitative modeling.

In Table 3.2 the topological parameters at the BCPs for different basis sets and ghost basis sets are listed. As can be seen from these data, the coordinates of BCP2 and BCP3 hardly change when going from a DZP to a TZP or TZ2P (monomer) basis set. The density at the BCPs increases slightly, both in the FDE and in the supermolecular KS calculations. The changes in the Laplacian values do not show a clear trend. The increase in the basis set size does not lead to significant improvements in the agreement between FDE and supermolecular KS results.

A much more pronounced effect can be observed when a ghost basis on the frozen fragment is used, i.e., when effectively a supermolecular basis set is applied in the subsystem calculation. The densities obtained from such calculations are denoted as \( \rho_{\text{emb,gh}} \). Although the precise values of the topological parameters depend on the particular combination of basis set on the embedded fragment and ghost basis on the frozen fragment, the calculations employing ghost basis sets typically lead to much better results than any of the calculations with a monomer basis set. An exception is the density at BCP2, which is slightly underestimated by the calculations with ghost basis functions, whereas the results without ghost basis functions are in good agreement with the KS reference values. The value of the Laplacian at BCP3 is an instructive example: It changes from 2.20 \( e\AA^{-5} \) (TZP, monomer basis set) to 0.80 \( e\AA^{-5} \) (TZP plus TZP ghost basis, in the following denoted as TZP/TZP), thus reducing the deviation from the reference from 1.52 to 0.12 \( e\AA^{-5} \). The results also demonstrate that a DZP ghost basis is already sufficiently large, since the additional changes when going from a DZP to a TZP ghost basis are rather small.

To further analyze the effect of the ghost basis set the difference density between \( \rho_{\text{super}} \) (TZP) and \( \rho_{\text{emb,gh}} \) (TZP/TZP) was calculated, which is shown in Fig. 3.4 (see also Fig. S2 in the Supplementary Material of Ref. [113] for a plot of the difference density \( \rho_{\text{emb,gh}} - \rho_{\text{emb}} \)). Compared to Fig. 3.2 d) it can be seen that the absolute differences in the F···H−O bonding region are smaller than in the calculation without the ghost basis functions, with the exception of the maximum of the difference density near H2, which is slightly higher in \( \rho_{\text{super}} - \rho_{\text{emb,gh}} \) than in \( \rho_{\text{super}} - \rho_{\text{emb}} \) (0.42 \( e\AA^{-3} \) compared to 0.39 \( e\AA^{-3} \)). The size of the region around H2, in which the FDE electron density is too small, is decreasing, and the absolute values of the difference density are smaller in the region of negative difference density between H2 and the fluorine atom. Additionally, the region between H2 and the oxygen atom is described better, since also there the absolute differences are smaller than in the case of \( \rho_{\text{emb}} \). Moreover, the density close to the fluorine ion on the side opposite to the hydrogen bond is apparently better described. The ghost basis set obviously allows for a better transfer of charge from the F\(^{-}\) to the H\(_2\)O fragment. Although there are still pronounced differences between \( \rho_{\text{super}} \) and \( \rho_{\text{emb,gh}} \), the ghost basis set leads to a significant improvement of the density obtained in the FDE calculations.
### 3.3 Factors affecting the quality of the density

Table 3.2: Basis set dependence of the coordinates $r_{BCP}$ (in units of Å) of BCP2 and BCP3 in $H_2O \cdot \cdot F^-$ and of $\rho(r)$ in eÅ$^{-3}$ and $L(r)$ in eÅ$^{-5}$ at the BCPs obtained with different approximations ($\rho_{super}$, $\rho_{emb}$, $\rho_{emb,gh}$ and $\rho_{frag}$); ghost basis sets in the boundary region only are indicated by "(bd)". Three freeze-and-thaw cycles were used for $\rho_{emb}$ and $\rho_{emb,gh}$.

<table>
<thead>
<tr>
<th>BCP 2</th>
<th>$\rho_{super}$</th>
<th>$r_{x,BCP}$</th>
<th>$r_{y,BCP}$</th>
<th>$\rho(r_{BCP})$</th>
<th>$L(r_{BCP})$</th>
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<tbody>
<tr>
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<td>DZP</td>
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<td>-1.14</td>
<td>1.50</td>
<td>-5.17</td>
</tr>
<tr>
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<td>-8.37</td>
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<td>1.47</td>
<td>-7.39</td>
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<td></td>
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<td>1.48</td>
<td>-7.33</td>
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<td>-1.18</td>
<td>1.48</td>
<td>-8.13</td>
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<td>1.61</td>
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</tr>
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<td>2.14</td>
</tr>
<tr>
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<td>DZP/DZP</td>
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</tr>
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<td>-1.73</td>
<td>0.67</td>
<td>0.73</td>
</tr>
<tr>
<td>$\rho_{frag}$</td>
<td>DZP</td>
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<td>-1.79</td>
<td>0.71</td>
<td>2.10</td>
</tr>
<tr>
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<td>TZP</td>
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<td>-1.79</td>
<td>0.72</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>TZ2P</td>
<td>0.01</td>
<td>-1.79</td>
<td>0.73</td>
<td>1.71</td>
</tr>
</tbody>
</table>
Figure 3.4: Difference density $\rho_{\text{super}} - \rho_{\text{emb,gh}}$ (a), and deformation density $\rho_{\text{emb,gh}} - \rho_{\text{frag}}$ (b) for H$_2$O···F$^-$, using a TZP ghost basis and five freeze-and-thaw iterations in the FDE calculations. Contour lines are drawn at $\pm 2, 4, 8 \times 10^n$ eÅ$^{-3}$ with $n = -4, -3, -2, -1, 0$ and at 0 eÅ$^{-3}$. Positive (including zero) and negative values are marked by solid and dashed lines, respectively. Atomic positions are marked by dots. Coordinates are given in units of Å.

However, providing ghost basis functions on all atoms of the frozen fragment $\rho_2$ counteracts the advantages of a subsystem formalism, since it increases the basis set size for each subsystem calculation to that of the supersystem. Since the intention was to increase the flexibility of the basis to accurately describe the polarization of one subsystem by another one, it might be sufficient to provide ghost basis functions only in the boundary region between the two subsystems. This was tested by performing FDE calculations in which a minimal ghost basis was supplied, i.e., a DZP basis on the atom next to the boundary between the two subsystems only (F or H$_2$, respectively). The results for the topological parameters are shown in Table 3.2, $\rho_{\text{emb,gh}}$ TZP/DZP (bd); they are virtually the same as in the case of the full ghost basis. It must of course be noted that even the “minimal basis” in this case already represents a large part of the full ghost basis, especially in case of F$^-$ as the frozen system. Therefore, this issue will be analyzed again for a larger frozen system in Section 3.4. Nevertheless, the conclusion that the basis set in the frozen region may be of lower quality than the one in the embedded region can already be drawn.
3.3 Factors affecting the quality of the density

3.3.2 Freeze-and-thaw cycles

Another important factor for the quality of \( \rho_{\text{emb}} \) is the convergence with respect to the number of freeze-and-thaw cycles [52]. If no freeze-and-thaw cycles at all are used, it will make a difference which of the two fragments is treated as the frozen fragment. But since the relaxation of the densities within several freeze-and-thaw cycles applied here should lead to a converged total density, this problem will not be discussed in detail. A brief analysis can, however, be found in Section 2.1 of the Supplementary Material of Ref. [113]. The convergence of the densities w.r.t. the number of freeze-and-thaw cycles will be studied in the following. In principle this can be done in two different ways: (i) One iterative series of calculations is performed, in which after each cycle the total density is compared to the total density of the previous cycle. A cycle consists of two calculations, in which first system 2 and then system 1 is frozen. (ii) Two series of freeze-and-thaw iterations are performed, of which the first starts with system 2 frozen, whereas the second starts with system 1 frozen. Here, the total densities of the two series are compared to each other after each iteration. This second approach has the advantage that it can also confirm whether or not both series of calculations converge to the same total density, or if the choice of the initial embedded fragment has an influence on the converged total density. Therefore, results for protocol (i) are given in Fig. S4 of the Supplementary Material of Ref. [113], while the second approach is presented here.

In Fig. 3.5 a) and b), the difference densities resulting from freeze-and-thaw cycles starting with a frozen water fragment and from those starting with a frozen fluorine fragment are shown for three and four freeze-and-thaw cycles. After three cycles, the differences are in the order of \( 10^{-4} \) e\( \AA \)^{-3} and after four cycles below \( 10^{-4} \) e\( \AA \)^{-3}. I.e., the densities are very well converged. This is also confirmed by the analysis of densities of consecutive cycles within one series of freeze-and-thaw iterations as shown in Fig. S4 of the Supplementary Material of Ref. [113]. For calculations including ghost basis functions typically more cycles are needed. In Fig. 3.5 c) to e), the corresponding difference density plots are shown in which a TZP ghost basis was included. It can be seen that five cycles are needed to converge the densities to less than \( 10^{-4} \) e\( \AA \)^{-3}. The maximal difference after three cycles, which is the default in this study, is smaller than \( 10^{-2} \) e\( \AA \)^{-3} and thus below the accuracy for the topological parameters reported in this work. It should also be noted that more cycles do not change the qualitative appearance of difference plots as reported in this work.

Besides assessing the quality of embedding densities, a more fundamental question connected to FDE can be addressed by analyzing the difference density maps. In principle, FDE should, in the limit of exact functionals, be able to yield the correct total density provided that the sought-for density \( \rho_1 \), i.e., the density complementary to the frozen \( \rho_2 \), is non-negative everywhere. Whether this condition is fulfilled by the starting densities of the isolated fragments and the final embedding densities can be tested by subtracting the density of one fragment (isolated or embedded) from \( \rho_{\text{super}} \) (assuming \( \rho_{\text{super}} \) to be a sufficiently good approximation for the exact density).
Figure 3.5: Difference densities obtained from freeze-and-thaw calculations with reversed order of fragments (freeze-and-thaw cycles starting with frozen fluorine or with frozen water fragments, respectively) after 3 cycles (a) and after 4 cycles (b) for $\text{H}_2\text{O}\cdots\text{F}^-$ without ghost basis, and after 3 (c), 4 (d) and 5 cycles (e) with a TZP ghost basis. Contour lines are drawn at $\pm 2, 4 \times 10^{-4} \text{ eÅ}^{-3}$ and at $0 \text{ eÅ}^{-3}$. Positive (including zero) and negative values are marked by solid and dashed lines, respectively. Atomic positions are marked by dots. Coordinates are given in units of Å.

In Figure 3.6 the difference densities obtained by subtracting $\rho_{\text{frag}}(\text{F}^-)$, $\rho_{\text{emb}}(\text{F}^-)$, and $\rho_{\text{emb,gh}}(\text{F}^-)$ from $\rho_{\text{super}}$ are shown. A TZP ghost basis was employed in the calculation of $\rho_{\text{emb,gh}}(\text{F}^-)$ in combination with five freeze-and-thaw cycles. Starting with $\rho_{\text{frag}}(\text{F}^-)$ as the frozen density, the difference density is not non-negative everywhere in space, and consequently FDE cannot yield the correct density. This is not surprising, as the starting point was the density of an isolated fragment which is only an approximate description for the situation in the supermolecule. After three freeze-and-thaw iterations, a considerable improvement is achieved, since the areas in which $\rho_1$ would have to be negative are diminished, and the absolute values of the density in the areas where it is still negative are smaller than before. But even then, the condition $\rho_{\text{tot}} - \rho(\text{F}^-)$ is not fulfilled everywhere. The use of a TZP ghost basis leads to a further improvement in most regions, as can be seen from Figure 3.6 c).
3.3 Factors affecting the quality of the density

Figure 3.6: Difference densities $\rho_{\text{super}} - \rho_{\text{frag}}(F^-)$ (a), $\rho_{\text{super}} - \rho_{\text{emb}}(F^-)$ (b) and $\rho_{\text{super}} - \rho_{\text{emb,gh}}(F^-)$ (c) for H$_2$O···F$^-$. For the calculation of $\rho_{\text{emb,gh}}(F^-)$, a TZP ghost basis and five freeze-and-thaw iterations were used. Contour lines are drawn at $\pm 2, 4, 8 \times 10^3$ eÅ$^{-3}$ with $n = -4, -3, -2, -1$ and at 0 eÅ$^{-3}$. Positive (including zero) and negative values are marked by solid and dashed lines, respectively. Atomic positions are marked by dots. Coordinates are given in units of Å.

3.3.3 Exchange–correlation and kinetic-energy functionals

The investigation of the energy functionals started with a brief test on the influence of the exchange–correlation functional on the density. For this purpose, the BP86 data were compared to those from the LDA, which is a rather drastic change, in supermolecular calculations. From the data reported in Table 3.1, it can be seen that the results are very similar. The coordinates for the BCPs differ by only 0.01 Å, which is the accuracy of the grid used. The densities at the BCPs differ by 0.05 eÅ$^{-3}$ or less, and the Laplacian values typically agree within 0.08 eÅ$^{-5}$. The influence of the exchange–correlation functional is thus small though not completely negligible. But the approximations for the exchange–correlation functional are introduced in both supermolecular KS and FDE calculations and were made consistently in the following calculations, so that no in-depth analysis of the effects on the embedding potential was carried out.

More important for the differences between the two approaches is the choice of the (non-additive) kinetic-energy functional, since this only occurs within the FDE context. Several approximate functionals are available, and tests were performed for the following ones: The PW91k functional as described above, the Thomas–Fermi functional (TF) [115,116], the gradient-corrected TF functional in which 1/9 of the von Weizsäcker correction [117] was added (TF9W), and the functional by Thakkar (THAKKAR92) [53]. Additionally, the effect of a purely electrostatic embedding (i.e., exchange–correlation and kinetic-energy components of the embedding potential were switched off), which is denoted as COULOMB, was tested.
Table 3.3: Coordinates $r_{\text{BCP}}$ (in units of Å) of the BCPs in $\text{H}_2\text{O} \cdots \text{F}^-$ and values of $\rho(r)$
in $e\text{Å}^{-3}$ and $L(r)$ in $e\text{Å}^{-5}$ at BCP2 and BCP3 for the supermolecular density $\rho_{\text{super}}$, embedding densities obtained with different kinetic energy functionals or electrostatic embedding (COULOMB) without ($\rho_{\text{emb}}$) and with a TZP ghost basis on the frozen subsystem ($\rho_{\text{emb,gh}}$). In calculations without ghost basis, three freeze-and-thaw cycles were used, whereas five cycles were used in calculations with ghost basis.

<table>
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<th></th>
<th>$r_x,\text{BCP}$</th>
<th>$r_y,\text{BCP}$</th>
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<th>$L(r,\text{BCP})$</th>
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<td>-1.73</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$ TF</td>
<td>0.01</td>
<td>-1.73</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$ TF9W</td>
<td>0.01</td>
<td>-1.73</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$ THAKKAR92</td>
<td>0.01</td>
<td>-1.73</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$ COULOMB</td>
<td>0.01</td>
<td>-1.75</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The results obtained for the topological parameters of $\text{H}_2\text{O} \cdots \text{F}^-$ are listed in Table 3.3. For the calculations with supermolecular basis sets a TZP ghost basis and five freeze-and-thaw cycles were employed, whereas three cycles were applied in calculations without ghost basis sets. TF9W and THAKKAR92 yield data very similar to PW91k, also TF and PW91k data do not differ very much. The coordinates of the BCPs are virtually the same, the densities agree within 0.01 $e\text{Å}^{-3}$, and the Laplacian values are very similar for BCP3. Only at BCP2 the values for $L(r)$ from PW91k and TF without ghost basis functions differ by about 0.18 $e\text{Å}^{-5}$, but even that is small compared to the difference between KS and FDE calculations (about 2.8 $e\text{Å}^{-5}$ at BCP2 and 1.5 $e\text{Å}^{-5}$ at BCP3). As was already discussed in Section 3.3.1, the results obtained with a supermolecular basis are typically much
better than those without, which holds for all kinetic-energy functionals studied here. Only the Laplacian at BCP2 is not very well reproduced even when including a ghost basis. By comparing the $\rho_{\text{emb,gh}}$ (PW91k) data to those in Table 3.2 (TZP/TZP), it can furthermore be seen that the additional two freeze-and-thaw cycles hardly change the results.

The data obtained with purely electrostatic embedding must be interpreted with care. From the data in Table 3.3 it can be seen that the results for the density and the Laplacian are rather bad if the full supermolecular basis is used. The results at BCP3 are even qualitatively wrong, as the negative Laplacian value has a wrong sign. The reason for this is that the purely electrostatic embedding is lacking the repulsive non-additive kinetic-energy contribution close to the nuclei in the frozen system, so that electron density is transferred into the frozen region (see also the discussion in Refs. [59, 72, 92, 118]). This phenomenon is called the electron leak problem or electron spill-out effect and is also widely known in QM/MM electrostatic coupling schemes [119]. The data in Table 3.3 also show that the simple electrostatic embedding benefits from error cancellation effects if ghost basis functions in the environmental system are neglected. In that case, it leads to a better agreement with the KS reference calculations than the calculations with a kinetic-energy and exchange–correlation contribution, both for the density and the Laplacian at BCP3. At BCP2, the Coulombic embedding also results in a better agreement for the Laplacian, whereas the density is worse than with the full embedding potential. Note that even for subsystem basis sets charge leaking may become a problem if diffuse functions are included.

### 3.4 Densities from FDE in other types of complexes

Because of the limitations of the available approximate functionals for the non-additive kinetic-energy component of the potential, the quality of the results from FDE calculations depends on the molecules under study, in particular the kind (and strength) of interaction between the subsystems. For this purpose, FDE and supermolecular KS densities for different interaction types will be compared.

First, the focus lies on cases that pose greater challenges to FDE due to stronger hydrogen-bond interactions. The studied systems are on the one hand the symmetric hydrogen bond in $\text{F}^{-}\text{H}\text{F}^{-}$, starting from asymmetric fragments, and on the other hand the more complicated topology of the density in the DNA base pair adenine–thymine, in which the combined effect of two hydrogen bonds needs to be described. Since this section mainly focuses on the practical applicability of FDE, a DZP ghost basis in case of calculations using supermolecular basis sets and three freeze-and-thaw iterations in all calculations will be employed. These results for hydrogen-bonds are compared to the neon dimer and to ammonia borane.
3.4.1 F−H−F−

F−H−F−, which contains two equivalent H−F bonds, is considered to have one of the strongest hydrogen bonds. A reliable estimate for the dissociation energy $D_0$ in F− and HF is 44.4 ± 1.6 kcal/mol [120,121]. The experimental estimate for the F−F distance (2.278 Å) [122] is smaller than the van-der-Waals distance of two fluorine atoms (2.7 Å). This system has been subject to FDE studies in the context of proton transfer reactions before, where it was used as a test system for the evaluation of free energy calculations of chemical reactions in solution [123].

Figure 3.7: Optimized (BP86/TZP) structure and coordinates in the grid of the H-bonded system F−H−F−.

The BP86/TZP optimized structure of the molecule is shown in Figure 3.7. The H−F distance in this linear, symmetric molecule is 1.16 Å, so that the calculated F−F distance of 2.32 Å is in fair agreement with the experimental value. The density $\rho_{super}$ of the F−H−F− ion is symmetric, as can be seen in Figure 6 of the Supplementary Material of Ref. [113]. The H−F bond on which BCP1 is located was divided, so that a stretched HF and a fluoride ion were obtained as fragments. Consequently, the superposition of fragment densities is not symmetric, and also $\rho_{emb}$ does not show the required symmetry (see Figure 6 of the Supplementary Material of Ref. [113]).

If, however, ghost basis functions are added, the resulting $\rho_{emb,gh}$, shown in Figure 3.8 a), appears almost symmetric w.r.t. the horizontal mirror plane. Slight deviations from this symmetry can be detected in the plot of the difference density between the symmetric supermolecule density and $\rho_{emb,gh}$, Figure 3.8 b). This difference density plot also reveals that the agreement between $\rho_{super}$ and $\rho_{emb,gh}$ is not perfect, since alternating regions of positive and negative difference density can be observed. On an absolute scale, these deviations are rather small, as can be seen from the densities at the BCPs, where $\Delta \rho = 0.12 \, e\AA^{-3}$ at BCP1 and $\Delta \rho = 0.09 \, e\AA^{-3}$ at BCP2.

The coordinates of the BCPs in $\rho_{emb}$ are symmetrical w.r.t. the hydrogen atom, but the densities differ considerably ($|\rho(BCP1) − \rho(BCP2)| = 0.37 \, e\AA^{-3}$) and the sign of $L(r)$ at BCP1 is different from that at BCP2, see Table 3.4. FDE without ghost basis functions is thus qualitatively more similar to the isolated fragments than to the supermolecule for F−H−F−. This is partly remedied by ghost basis functions,
which do not improve the coordinates of the BCPs much, but considerably reduce
the asymmetry in the density (\( |\rho(BCP1) - \rho(BCP2)| = 0.03 \text{ e}\AA^{-3} \)). Furthermore,
\( L(r) \) has the same sign at both BCPs and shows a comparatively small deviation
of only 0.31 e\AA^{-5}. Hence, FDE yields a qualitatively correct description of this
complex even though the starting fragments are asymmetric and the interaction
strength is very large.

Figure 3.8: Density \( \rho_{\text{emb,gh}} \) (a), difference density \( \rho_{\text{super}} - \rho_{\text{emb,gh}} \) (b), and negative Laplacians \( L_{\text{frag}} \) (c), \( L_{\text{emb}} \) (d), \( L_{\text{emb,gh}} \) (e), and \( L_{\text{super}} \) for F−H−F−. A DZP ghost
basis was employed for \( \rho_{\text{emb,gh}} \) and \( L_{\text{emb,gh}} \); three freeze-and-thaw cycles were
 carried out in all cases. Contour lines are drawn at \( \pm 2, 4, 8 \times 10^n \text{ e}\AA^{-3} \) with
\( n = -2, -1, 0, 1, 2, 3 \) for the density, \( n = -4, -3, -2, -1, 0 \) and at 0 e\AA^{-3}
for the difference density, and with \( n = -4, -3, -2, -1, 0, 1, 2 \) and at 0 e\AA^{-5}
for the negative Laplacian. Positive (including zero) and negative values are
marked by solid and dashed lines, respectively. Atomic positions and bond
 critical points are marked by dots and open circles, respectively. Coordinates
are given in units of \( \text{Å} \).
3 Density Analysis for Frozen-Density Embedding

Table 3.4: Coordinates $r_{\text{BCP}}$ (in units of Å) of the BCPs in F–H–F– and values of $\rho(r)$ in $eÅ^{-3}$ and $L(r)$ in $eÅ^{-5}$ at the BCPs for $\rho_{\text{super}}$, $\rho_{\text{emb}}$, $\rho_{\text{emb,gh}}$ (obtained with a DZP ghost basis), and $\rho_{\text{frag}}$.

<table>
<thead>
<tr>
<th></th>
<th>$r_x,\text{BCP}$</th>
<th>$r_y,\text{BCP}$</th>
<th>$\rho(\text{BCP})$</th>
<th>$L(\text{BCP})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCP1 $\rho_{\text{super}}$</td>
<td>0.28</td>
<td>0.00</td>
<td>1.14</td>
<td>−1.68</td>
</tr>
<tr>
<td>$\rho_{\text{emb}}$</td>
<td>0.21</td>
<td>0.00</td>
<td>1.07</td>
<td>−5.68</td>
</tr>
<tr>
<td>$\rho_{\text{emb,gh}}$</td>
<td>0.23</td>
<td>0.00</td>
<td>1.02</td>
<td>−2.74</td>
</tr>
<tr>
<td>$\rho_{\text{frag}}$</td>
<td>0.30</td>
<td>0.00</td>
<td>1.30</td>
<td>−3.08</td>
</tr>
<tr>
<td>BCP2 $\rho_{\text{super}}$</td>
<td>−0.28</td>
<td>0.00</td>
<td>1.14</td>
<td>−1.68</td>
</tr>
<tr>
<td>$\rho_{\text{emb}}$</td>
<td>−0.22</td>
<td>0.00</td>
<td>0.71</td>
<td>1.92</td>
</tr>
<tr>
<td>$\rho_{\text{emb,gh}}$</td>
<td>−0.23</td>
<td>0.00</td>
<td>1.05</td>
<td>−2.80</td>
</tr>
<tr>
<td>$\rho_{\text{frag}}$</td>
<td>−0.29</td>
<td>0.00</td>
<td>0.96</td>
<td>1.70</td>
</tr>
</tbody>
</table>

In Figure 3.8 c) to f) also the plots of the negative Laplacian are shown. Whereas $L_{\text{frag}}$, part c), consists clearly of an independent, spherically symmetric fluorine fragment and a HF fragment, in $L_{\text{emb}}$, part d), one can already recognize local charge concentrations at atom F1 and a shift of charge concentration towards atom F1 at the hydrogen atom. $L_{\text{emb,gh}}$ in part e) is almost symmetric and already very similar to $L_{\text{super}}$, which is shown in part f). The negative Laplacian thus allows to quantitatively follow the improving description of the electron density from the asymmetric fragments via the fragments from the embedding approach without ghost basis to the FDE fragments including ghost basis functions, which do already capture the characteristic signatures of the supermolecule.

3.4.2 Hydrogen bonding in the DNA base pair adenine-thymine

As a last example, the DNA base pair adenine–thymine (AT) was studied, which comprises two different hydrogen bonds in the region between the two fragments, so that the total change in the density will be influenced by the combined effect of these interactions. Excited states of this system have been studied before with FDE and were found to be in good agreement with results from supermolecular time-dependent DFT calculations [67]. The BP86/TZP optimized structure of the base pair is shown in Figure 3.9. The H···O distance between the amino group of adenine and an oxygen on thymine is 1.82 Å and thus larger than the H···N distance of 1.73 Å, which constitutes the second hydrogen bond. For the FDE formalism adenine and thymine form the two subsystems. Plots of the electron densities and negative Laplacians for the molecular plane are shown in Figures S7 and S8 of the Supplementary Material of Ref. [113]. The topological parameters at BCP1, BCP2, BCP4, and BCP5, i.e., at the BCPs in the hydrogen-bonding region, are shown in Table 3.5. The data for the other BCPs and RCPs shown in Figure 3.9) can be found in Table S4 of the Supplementary Material of Ref. [113]. For these points the deviation of $\rho_{\text{emb}}$ and $\rho_{\text{emb,gh}}$ from $\rho_{\text{super}}$ in the coordinates is
as small as 0.01 Å or below, 0.01 \( e \AA^{-3} \) or below in the densities and 0.02 \( e \AA^{-5} \) or below in \( L(\mathbf{r}) \). Exceptions are BCP10 and BCP11, where \( L(\mathbf{r}) \) deviates by 0.03 and 0.05 \( e \AA^{-5} \), respectively, and RCP2, where the deviations in the coordinates are somewhat larger. The latter effect could be due to the small values of the density and its curvature in the region around RCP2. For BCP1 and BCP2, both \( \rho_{\text{emb}} \) and \( \rho_{\text{emb,gh}} \) work rather well, where \( \rho_{\text{emb,gh}} \) is again superior to \( \rho_{\text{emb}} \). At BCP1, which is part of the longer hydrogen bond, slightly better results can be achieved with \( \rho_{\text{emb}} \) than at BCP2, while \( \rho_{\text{emb,gh}} \) yields results of almost the same quality for both BCPs.

Figure 3.9: Optimized (BP86/TZP) structure of the DNA base pair AT with positions of the BCPs and RCPs.

The differences in the densities compared to the supermolecular reference calculation are 0.04 and 0.03 \( e \AA^{-3} \) for \( \rho_{\text{emb}} \) and \( \rho_{\text{emb,gh}} \), respectively, whereas they are slightly larger for \( \rho_{\text{emb}} \) (0.06 \( e \AA^{-3} \)) at BCP2 (for \( \rho_{\text{emb,gh}} \) the difference density is 0.03 \( e \AA^{-3} \)). A similar picture arises for the values of the Laplacian. This suggests that FDE works somewhat better for the weaker, longer hydrogen bonds. At BCP4 and BCP5, which are also directly affected by the hydrogen bond network, only small differences in densities (about 0.01 to 0.02 \( e \AA^{-3} \)) and in \( L(\mathbf{r}) \) (about 0.2 to 0.8 \( e \AA^{-5} \)) can be observed. For further distant BCPs the differences are even smaller, which means that FDE can accurately describe the topology of this complex.

As the influence of the FDE scheme is obviously limited to the bonds adjacent to the inter-subsystem boundary, it would be desirable if a ghost basis description of the frozen fragment could be confined to that region as well. For the base pair studied here, providing ghost basis functions only on the atoms of the other fragments taking part in the hydrogen bond yields results that are very close to those obtained with the full ghost basis set. For example, the value of the density at BCP2 increases
from 0.29 to 0.32 $e\text{-Å}^{-3}$ when adding ghost functions to the boundary region only (denoted as $\rho_{\text{emb,gh}}$ (bd) in Table 3.5), and remains constant when all other ghost basis functions are included as well. The negative Laplacian decreases by 0.17 $e\text{-Å}^{-5}$ from 0.99 to 0.82 $e\text{-Å}^{-5}$, whereas inclusion of the other ghost basis functions leads only to a small additional change of 0.03 $e\text{-Å}^{-5}$. This is important for calculations on systems embedded in larger environments for which both efficient and accurate descriptions of the topology of the density are needed, since it demonstrates that a very good approximation to the results obtained with a supermolecular basis can be achieved when ghost basis functions in the boundary region are provided. In particular in the ADF implementation of FDE, the use of a full molecular basis would lead to an enormous increase in computational effort, since not only the size of the Fock matrix, but also the numerical integration grid used to calculate the matrix elements would become much larger. This grid needs to be dense in regions where the values of the basis functions of the non-frozen system are not small [69].

Table 3.5: Coordinates $r_{\text{BCP}}$ (in units of Å) of the BCPs in the base pair AT and values of $\rho(r)$ in $e\text{-Å}^{-3}$ and $L(r)$ in $e\text{-Å}^{-5}$ at the BCPs and RCPs for $\rho_{\text{super}}$, $\rho_{\text{emb}}$, $\rho_{\text{emb,gh}}$ (obtained with a DZP ghost basis), and $\rho_{\text{frag}}$; calculations with ghost basis sets in the boundary region only are indicated by “(bd)”.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$r_{x,\text{BCP}}$</th>
<th>$r_{y,\text{BCP}}$</th>
<th>$\rho(r_{\text{BCP}})$</th>
<th>$L(r_{\text{BCP}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCP1</td>
<td>$\rho_{\text{super}}$</td>
<td>−0.24</td>
<td>1.97</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>−0.25</td>
<td>1.97</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$</td>
<td>−0.25</td>
<td>1.97</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$ (bd)</td>
<td>−0.25</td>
<td>1.97</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{frag}}$</td>
<td>−0.22</td>
<td>1.98</td>
<td>0.22</td>
</tr>
<tr>
<td>BCP2</td>
<td>$\rho_{\text{super}}$</td>
<td>0.37</td>
<td>−0.28</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
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<td>−0.27</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$</td>
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<td>−0.27</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$ (bd)</td>
<td>0.39</td>
<td>−0.27</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{frag}}$</td>
<td>0.36</td>
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<td>$\rho_{\text{emb}}$</td>
<td>1.12</td>
<td>0.07</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$</td>
<td>1.12</td>
<td>0.07</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$ (bd)</td>
<td>1.12</td>
<td>0.07</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{frag}}$</td>
<td>1.14</td>
<td>0.08</td>
<td>1.96</td>
</tr>
<tr>
<td>BCP5</td>
<td>$\rho_{\text{super}}$</td>
<td>−1.06</td>
<td>1.64</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>−1.06</td>
<td>1.64</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$</td>
<td>−1.06</td>
<td>1.64</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb,gh}}$ (bd)</td>
<td>−1.06</td>
<td>1.64</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{frag}}$</td>
<td>−1.07</td>
<td>1.64</td>
<td>2.12</td>
</tr>
</tbody>
</table>
3.4.3 Densities and difference densities for the neon dimer

Van der Waals-interactions are very weak interactions so that FDE is expected to work well. The bond distance in the BP86/TZP optimized structure of the neon dimer studied here is 3.32 Å. However, not surprisingly almost no differences can be found and even the densities of the isolated fragments are almost indistinguishable from the supermolecular results, see Fig. 3.10.

Figure 3.10: Density $\rho_{\text{frag}}$ (a), $\rho_{\text{emb}}$ (b), and $\rho_{\text{super}}$ (c) and difference density $\rho_{\text{super}} - \rho_{\text{emb}}$ for the neon dimer. Contour lines are drawn at $\pm 2, 4, 8 \times 10^n$ eÅ$^{-3}$ with $n = -3, -2, -1, 0, 1, 2, 3$ for the density and $n = -4, -3$ and at 0 eÅ$^{-3}$ for the difference density. Atomic positions and bond critical points are marked by dots and open circles, respectively. Coordinates are given in units of Å.

3.4.4 FDE electron densities for coordination bonds: Ammonia Borane

For ammonia borane, the electron densities of both subsystems were relaxed in five freeze-and-thaw cycles and, as mentioned above, the corrected implementation of the PW91k functional and a supermolecular basis was employed. The dative bond between the BH$_3$ and NH$_3$ fragments exhibits a bonding energy of 187.1 kJ/mol, which is comparable to F$-$H$-$F$^-$ with a bond energy of 185.9 kJ/mol, but here two uncharged fragments are involved. The optimized structure of ammonia borane is shown in Figure 3.11 a). The B–N distance is 1.66 Å (experimental value: 1.58 Å [124]).
Contour plots of the electron density for the supermolecular and the FDE calculation are shown in Figures 3.11 b) and c). The difference of the supermolecular density and the superposition of the isolated fragment densities is shown in Figure 3.11 d). Significant changes upon bond formation can be observed, which show similar characteristics to the \( \text{H}_2\text{O} \cdots \text{F}^- \) example: The electron density is increased in the bonding region and in the \( \text{BH}_3 \) moiety, whereas it is decreased around the nitrogen atom. An exception is a ring of increased electron density around the nitrogen atom that is perpendicular to the bonding axis (this corresponds to the ring around \( \text{F}^- \) ion in the \( \text{H}_2\text{O} \cdots \text{F}^- \) example). The difference of the supermolecular density and the density from the FDE calculation is shown in Figure 3.11 e). The differences on the bonding axis are smaller than in Figure 3.11 d), which means that FDE works qualitatively correct and shifts electron density towards the bonding axis, although there are still some deficiencies.

Figure 3.11: a) BP86/TZP optimized structure of ammonia borane (\( \text{BH}_3\text{NH}_3 \)). The double labeling of some atoms means that there are two atoms that differ only in their \( z \)-coordinate and are therefore overlaying in the picture. Note that the color change along the N–B bond is arbitrary and thus not related to the partitioning into subsystems. b) Supermolecular density, c) embedding density, d) deformation density \( \rho_{\text{super}} - \rho_{\text{frag}} \), e) difference density \( \rho_{\text{super}} - \rho_{\text{emb}} \).

The values for the electron density and the negative Laplacian at the BCPs are shown in Table 3.6. The difference of the supermolecular density and the superpo-
sition of the isolated fragment densities at BCP3, which is located at the border of the two subsystems, is $0.2753 \text{ eÅ}^{-3}$, which means that there are large changes upon the formation of the bond. By comparing the coordinates of BCP3, one notices that the \textit{x}-coordinate of BCP3 is shifted towards the nitrogen atom by the FDE scheme, whereas the other BCPs are almost unchanged. The shift of 0.07 Å for BCP3 is larger than the shifts that were observed in the analysis of the hydrogen-bonded systems. Regarding the difference density, one can observe that the value of the electron density from the FDE calculation is too low in the region around H3, whereas in the region around H6, it is too high.

The difference density at BCP3 is an order of magnitude larger than the difference density at BCP1 and BCP2, which are located in the center of their corresponding fragments. Compared to the superposition of the isolated fragment densities at BCP3 (0.4382 eÅ$^{-3}$), FDE works qualitatively correctly but overcorrects the density in this region. Also the error in the negative Laplacian at BCP3 differs considerably from the values of BCP1 and BCP2. Compared to the analysis of the hydrogen-bonded systems, the difference of the electron density in the boundary region of the two subsystems is not very large, but the discrepancies in the negative Laplacian are more pronounced. One would expect a positive sign for a covalent bond, but not for a coordination bond. The negative Laplacian at BCP3 is positive for FDE but negative for the supermolecular calculation, which means that the bonding region is not described entirely correctly. In summary, ammonia borane represents a more challenging system for FDE than the previously studied hydrogen bonded systems although qualitative changes in the electron density upon bond formation are described correctly. Hence, reasonable results can be obtained for weak dative bonds as in $\text{H}_3\text{N} \cdots \text{BH}_3$.

Table 3.6: Coordinates $r_{\text{BCP}}$ (in units of Å) of the BCPs and values of $\rho(r)$ in $\text{eÅ}^{-3}$ and $L(r)$ in $\text{eÅ}^{-5}$ at the bond critical points of ammonia borane.

<table>
<thead>
<tr>
<th>BCP</th>
<th>$r_{x,\text{BCP}}$</th>
<th>$r_{y,\text{BCP}}$</th>
<th>$\rho(r)$</th>
<th>$L(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\rho_{\text{super}}$</td>
<td>1.93</td>
<td>0.69</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>1.93</td>
<td>0.70</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{super}} - \rho_{\text{emb}}$</td>
<td>0.00</td>
<td>−0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>$\rho_{\text{super}}$</td>
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<td>−0.54</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>−0.14</td>
<td>−0.54</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{super}} - \rho_{\text{emb}}$</td>
<td>−0.01</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>$\rho_{\text{super}}$</td>
<td>0.53</td>
<td>0.00</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{emb}}$</td>
<td>0.60</td>
<td>0.00</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>$\rho_{\text{super}} - \rho_{\text{emb}}$</td>
<td>−0.07</td>
<td>0.00</td>
<td>−0.16</td>
</tr>
</tbody>
</table>

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3.5 Conclusions from the density analysis

Densities obtained in the FDE approach have been tested for different systems from the weakly interacting neon dimer and hydrogen bonds to the coordinative bond in ammonia borane. For the studied systems, the electron density could be described reasonably well. Among the considered factors influencing the FDE density, the choice of the particular approximation for the non-additive kinetic-energy functional $T_n^{\text{add}}$ had only a minor influence on the results. However, it turned out that monomer basis sets are often not sufficient to obtain reliable results. In case of a simple electrostatic embedding the restriction to a monomer basis set can lead to seemingly good results due to error cancellation effects. This changes drastically when a supersystem basis set is used also in the embedding calculation. In that case, an entirely electrostatic embedding leads to well-known charge-leaking problems, which have also been discussed within the FDE framework [59, 72, 92, 118]. The use of a supermolecular basis certainly limits the applicability of FDE as an effective model for large environments. Fortunately, we could show that a few additional basis functions in the boundary region are sufficient to obtain a comparable result.

A quantitative comparison of difference densities and the Laplacian of the densities as well as the topological parameters at the bond critical points reveals that there are some remaining problems in the FDE description of the density in the boundary region between the subsystems. These originate from the approximate nature of the non-additive kinetic-energy functional that only employs information about the density, but not about the orbitals of the subsystem, although it effectively replaces the non-orthogonality requirement of the subsystem orbitals. Therefore, the resulting electron density in the hydrogen-bonding region does not show the same directionality as obtained in supermolecular calculations. This could be the reason for some of the known problems related to FDE and similar subsystem-DFT approaches. In particular, it might be responsible for the fact that molecular dynamics simulations based on subsystem DFT are able to reproduce the radial distribution function for the first solvation shell around a water molecule in water, but not for the second solvation shell anymore [81]: Due to the lack of directionality, the second solvation shell will be less structured in these simulations, although the distances in the first solvation shell are accurately reproduced. A possible way to improve the FDE scheme for applications in which this directionality plays a major role may be the inclusion of terms depending on the overlap of the subsystem orbitals in the non-additive kinetic energy in some approximate manner.
3.6 Towards modeling environment: a chromophore in a protein environment

A correct description of the environment is not only important to describe ground-state properties, but especially so for excited-state properties, such as excitation energies and transition dipole moments. In order to describe spectra of chromophores in proteins correctly, the environment has to be included when calculating excitation energies and excited-state properties. For spectroscopic methods which depend on these properties, the inclusion is of course crucial, as e.g., for resonance Raman spectroscopy, which is a sensitive tool to study excited-state structures, and which depends sensitively on the value of excitation energies relative to the laser excitation, the form of the excited-state potential energy surfaces and on the transition dipole moments.

A very important chromophore in natural environments is the indole motif in the amino acid tryptophan (Trp). Due to the dependence of its excited-state properties on the environment, information on the conformation and solvent accessibility can be deduced from the resonance Raman spectra of Trp. The experimental UV absorption spectrum of indole shows basically three peaks in the region between 200 and 300 nm, which are denoted as \( L_b \) (at ca. 290 nm in Cyclohexan), \( L_a \) (ca. 277 nm), and \( B_b \) (ca. 220 nm), respectively [125]. The influence of hydrogen bonding at the NH moiety of the indole ring and hydrophobic interactions of the aromatic ring on the excited states and resonance Raman intensities of indole have been studied experimentally by Matsuno and Takeuchi [125]. It was found that Raman bands that are enhanced through resonance with the \( B_b \) transition become strongest when there is hydrogen-bonding to the indole ring in hydrophobic solvents, whereas Raman bands enhanced through resonance with the \( L_a \) transition are most intense when there is no hydrogen bonding. Hydrogen-bonding and hydrophobic interactions have an effect on the intensity and position (blue or red shift) of the bands, thus the polarity and proton accepting abilities of the solvent influence the absorption spectra of the Trp model compound skatole. For the \( L_a \) band, a pronounced blue shift in apolar, non-hydrogen-bonding solvents is observed, which is also known for other indole derivatives. However, the \( L_b \) band does not show such a blue shift. Since there is a further blue shift of the \( L_a \) band in the gas phase, the shift is usually attributed to the absence of hydrogen bonding [125].

The description of environment effects for excited-state properties using FDE can be illustrated for the example of a Trp containing substructure of the protein Im7 [29]. For a detailed account of subsystem-based approaches for spectra of biomolecules, see Ref. [126]. In order to calculate spectra for the Trp residue, models of the residue in its environment have to be chosen. Two factors might influence the spectra: the backbone and the residues in the local vicinity of the Trp. Excitation energies and oscillator strengths are calculated for three models of Trp in Im7. The influence of residues in the local vicinity has been studied using the FDE approach. Model A is the Trp molecule in the structure as it is found in the protein (Trp75),
but as a neutral amino acid. Model B corresponds to model A with an additional
environment, which consists of the fragments Asp49-Pro48-His47-Glu46 and Asn79,
cut from the protein structure and saturated at the cuts to free acid or base form.
Model C contains in addition to Trp75 the neighbouring amino acids Arg76 and
Glu74 with the same environment as in model B. The structures of the models are
depicted in Fig. 3.12.

All calculations were performed with ADF, using a TZP basis and the SAOP
functional [127] for the calculation of excitation energies. For model A, 50 excited
states were calculated. For the calculation of the excitation energies of model B (100
excited states) and model C (200 excited states), a FDE calculation with two freeze-
and-thaw cycles was used, with the LDA functional for the environment (“VWN”
[47] as implemented in ADF) and the SAOP functional for the Trp containing part.

For these models, the energies corresponding to the $E(L_b)$, $E(L_a)$ and $E(B_b)$
transitions are provided in Table 3.7. All intense excitations appear blue-shifted due
to the influence of the protein environment described in the FDE calculation (model
A compared to model B). Contrary to the observations by Matsuno et al. [125]
mentioned above, the $L_b$ band exhibits a stronger shift than the $L_a$ band. The $B_b$
band is shifted most strongly. Surprisingly, the elongation of the backbone in model
C shows a larger effect on the blue shifts for the $E(L_a)$ and $E(L_a)$ bands than the
inclusion of the environment. This can be observed as well in the absorption spectra
in Fig. 3.12. Since an increasing size of the embedded model affects the efficiency
and especially the interpretation, for strongly interacting fragments using capping
groups might be an alternative [91]. In addition to the protein environment and
the backbone, effects of solvent molecules would have to be included to explain the
experimental spectrum in detail. For hydrogen-bond accepting solvents red shifts are
expected. These observations illustrate that in order to obtain theoretical electronic
spectra of chromophores in proteins, several opposing effects need to be described
accurately.

Table 3.7: Excitation energies in eV for the $L_a$ and $L_b$ bands and $B_b$ band in the Trp
models A, B and C.

<table>
<thead>
<tr>
<th>model</th>
<th>$E(L_b)$</th>
<th>$E(L_a)$</th>
<th>$E(B_b)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.303</td>
<td>4.612</td>
<td>5.720</td>
</tr>
<tr>
<td>B</td>
<td>4.332</td>
<td>4.628</td>
<td>5.776</td>
</tr>
<tr>
<td>C</td>
<td>4.446</td>
<td>4.728</td>
<td>5.820</td>
</tr>
</tbody>
</table>
Figure 3.12: Absorption spectra of Trp models A, B and C. A Gaussian broadening of 0.4 eV was applied.
4 Selective Technique in Vibrational Spectroscopy: (Resonance) Raman spectroscopy

Raman spectroscopy is based on an inelastic scattering process: In a two photon-description, a photon is absorbed in a so-called virtual state and another photon emitted on returning to the initial state, see Fig. 4.1. The energy difference between incident and scattered light yields information on the energy levels of the studied molecule, since it corresponds to the energy of a molecular vibrational or vibronic transition. If vibrational excitation is combined with an electronic transition in vibrational spectroscopy, resonance variants can emerge, which often feature a specific selection of active vibrations and finally result in a spectrum with only few lines, ideally suited for structure elucidation and reaction control. Resonance Raman (RR) spectroscopy is of this type.

Figure 4.1: Schematic representation of Raman and resonance Raman scattering processes: On the left hand side, a Raman process is depicted. The molecule is excited to a “virtual” excited state, $\hbar \omega_1$ denotes the laser excitation energy and $\hbar \omega_s$ the energy of the scattered light. On the right hand side, Raman scattering under resonance conditions is shown, i.e., the laser excitation energy matches the energy of an excited state.
Apart from the selectivity it is the sensitivity which makes RR spectroscopy a valuable tool: the intensities of the modes are enhanced by up to six orders of magnitude. While Raman spectra contain information on the ground state in the vibrational frequencies, RR intensities have a clear relationship to the excited-state structure and therefore are a probe for the excited state. By combining these advantages, RR is especially suited to study species in low concentrations, such as photochemical intermediates, or, since the excited-state properties depend sensitively on the environment, focus on chromophores in biomolecules, e.g., aromatic amino acids in proteins or porphyrins [128]. In addition to information on the displacement of the excited state structure, information on the symmetry of the modes can be gained from the polarization of the scattered light.

From an experimental point of view, Raman spectroscopy has some practical advantages over infrared spectroscopy besides its selectivity and sensitivity: it is possible to work in aqueous solution in glass or silica cells and to study also the low frequency region. For RR, the availability of lasers with different excitation wavelengths developed since the 1960s has been of great importance.

The application of theoretical approaches to RR spectra [4, 33, 129–131] has become feasible for larger molecules in recent years due to the development of reliable methods for the calculation of ground-state vibrational modes and excited electronic states [6, 34, 132–135]. Specialized textbooks on Raman theory [136, 137] with a detailed treatment as well as numerous reviews, e.g., [129, 135, 138] reflect the interest in this subject. Ref. [24] contains an overview and comparison of state-of-the-art theoretical approaches. Especially Heller’s gradient approximation [33] offers a fast and — depending on the vibronically excited states — often quite accurate way to predict RR spectra [11, 134, 139]. An alternative similar to this approach, which is based on resonance polarizability derivatives, was presented by Jensen et al. [34]. Vibronic couplings are also of increasing importance in calculations on the vibrational structure of electronic spectra (see Ref. [140] for an example), and especially so for Raman spectroscopy.

### 4.1 Kramers–Heisenberg–Dirac equation

Different approaches to describe the interaction between light and a molecule in the scattering process exist. Treating both the molecule and light classically can already explain certain aspects of Raman scattering but does not take the specific properties of the molecule under study into account [136, 141]. Therefore, usually, a semi-classical approach is chosen, in which light is treated classically and the molecule quantum-mechanically. This yields a sufficient description and a quantum-electrodynamical treatment applying quantum mechanics to light and matter is not necessary for Raman spectroscopy.

A key property for the description of scattering processes are the oscillating electric and magnetic dipole and higher multipole moments induced by the incident light. For our case of (resonance) Raman spectroscopy, the electric dipole is most
4.1 Kramers–Heisenberg–Dirac equation

important. The dependence of the first-order induced electric dipole moment \( p^{(1)} \) on linear terms of the dynamic electric field \( E \) is given by the polarizability tensor \( \alpha \):

\[
p^{(1)} = \alpha \cdot E. \tag{4.1}
\]

For the induced electric dipole moment associated with the Raman scattering process, which effects a molecular transition with frequency \( \omega_M \), this can be specified to

\[
p_0(\omega_1 \pm \omega_M) = \alpha^{\text{Ram}}(\omega_M) \cdot E_0(\omega_1), \tag{4.2}
\]

where \( \alpha^{\text{Ram}}(\omega_M) \) is the polarizability tensor associated with the molecular frequency \( \omega_M \), and \( E_0 \) is the amplitude of the incident radiation of angular frequency \( \omega_1 \). In a component-wise form this reads:

\[
p^{(\rho)}_0(\omega_1 \pm \omega_M) = \sum_{\sigma} \alpha^{\text{Ram}}_{\rho\sigma}(\omega_M) \cdot E^{(\sigma)}_0(\omega_1), \tag{4.3}
\]

where \( \rho, \sigma \) can be \( \{x,y,z\} \).

The Raman polarizability tensor \( \alpha^{\text{Ram}} \) is often referred to as scattering tensor. Since we deal here only with Raman scattering, the superscript “Ram” will be dropped in the following. An expression for the scattering tensor elements \( \alpha_{\rho\sigma} \) can be derived using time-dependent perturbation theory, assuming a first-order perturbation by an electromagnetic wave of angular frequency \( \omega_1 \). This yields the Kramers–Heisenberg–Dirac equation \([142,143]\):

\[
(\alpha_{\rho\sigma})_{fi} = \frac{1}{\hbar \sum_{r \neq i,f}} \left\{ \frac{\langle f | \hat{p}_\rho | r \rangle \langle r | \hat{p}_\sigma | i \rangle}{\omega_{ri} - \omega_1 - i\Gamma_r} + \frac{\langle f | \hat{p}_\sigma | r \rangle \langle r | \hat{p}_\rho | i \rangle}{\omega_{rf} + \omega_1 + i\Gamma_r} \right\}. \tag{4.4}
\]

Here, \( \langle f | \hat{p}_\rho | r \rangle \) and \( \langle r | \hat{p}_\sigma | i \rangle \) denote transition matrix elements of the dipole operator components \( p_\rho, p_\sigma \), between wavefunctions of the final state \( |f\rangle \), intermediate state \( |r\rangle \) and initial state \( |i\rangle \). In the denominator \( \hbar \omega_{ri}, \hbar \omega_{rf} \) are the energy differences between the vibronic states and \( \Gamma_r \) is the homogeneous linewidth (also called damping factor), which is connected to the lifetime of the intermediate states \( |r\rangle \). The summation runs over all intermediate states \( |r\rangle \), excluding the final and initial states \( |f\rangle, |i\rangle \). The molecular frequency dependence is now conveyed by the indices \( fi \), since \( \omega_M = \omega_f - \omega_i \). The original equation by Kramers and Heisenberg \([142]\) was verified by Dirac, who added the damping factor in the denominator \([143]\), thus preventing an infinite expression for the exact resonance case. With respect to the sign of the damping factor in the two terms of Eq. (4.4) several forms exists (here, Placzek’s opposite-sign convention is followed \([144]\)) and there is an on-going discussion as to which sign convention is correct \([145–148]\). For the following considerations, wavefunctions are taken to be real, time-independent, and non-degenerate. One factor which has a large influence on the intensities and intensity distribution is the relative magnitude of the energy differences \( \hbar \omega_{ri} \) and \( \hbar \omega_{rf} \), and the angular frequency of the laser excitation \( \omega_1 \). Four cases can be distinguished:

1) The excitation frequency \( \omega_1 \) is much smaller than the frequency difference \( \omega_{ri} \) \( (\omega_1 \ll \omega_{ri}) \) for all intermediate states \( |r\rangle \) (assuming the intermediate states to be
4 Selective Technique in Vibrational Spectroscopy: (Resonance) Raman spectroscopy

higher in energy than the initial and final states). This situation is known as “normal” Raman scattering and one often talks about the absorption and emission of a photon by a virtual state. In the two-photon picture, the second term can be interpreted as a virtual process in which emission precedes absorption.

2) If the excitation frequency is similar to the frequency $\omega_{ri}$ between the initial state and some intermediate states, then these terms dominate the sum over intermediate states $|r\rangle$ (their intensity is enhanced), since the denominator of the first term of Eq. (4.4) becomes very small. This first term is called the resonance term. Usually the vibronic states belong to one specific excited electronic surface. This situation, where the excitation frequency is in resonance with discrete states, is called discrete RR scattering. The second, off-resonance term, is small compared to the resonance term, slowly varying and therefore often negligible.

3) For excitation frequencies approaching the frequency $\omega_{ri}$, an intensity increase for specific modes occurs. This situation between normal and resonance Raman is called pre-resonance Raman.

4) Another special case is the resonance enhancement of continuum states above the dissociation limit, which leads to continuum RR scattering. This will not be further discussed here.

Apart from the energy differences in the denominator, the products of electric transition dipole moment elements $\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle$ in the numerator determine the value of the scattering tensor elements. They are weighted by the energy denominators, so that for resonance conditions only a few, or one, electronic states with appreciable values of products of transition dipole elements contribute, while for normal Raman all electronic states with non-zero numerators participate. This makes RR spectroscopy a method to obtain information on the excited state, since the properties of one state, its lifetime and (ro)vibronic structure, can determine the RR spectra.

In practice, the most important approximation is the Born–Oppenheimer adiabatic approximation (see Section 2.2) to the real time-independent wavefunctions. Thus, a vibronic state $r$ with electronic quantum number $e^r$, vibrational quantum number $v^r$, and rotational quantum number $R^r$, $|r\rangle = |e^r v^r R^r\rangle$ is expressed as a product $|r\rangle = |e^r\rangle|v^r\rangle|R^r\rangle$, and its energy $\hbar\omega_r = \hbar\omega_{e^r v^r R^r}$ as a sum of electronic, vibrational and rotational energies $\omega_{e^r v^r R^r} = \omega_{e^r} + \omega_{v^r} + \omega_{R^r}$. The damping constant $\Gamma_{e^r v^r R^r}$ refers to a specific state $|r\rangle$.

Applying the Born–Oppenheimer approximation to Eq. (4.4) yields:

$$\alpha_{\rho\sigma} f_i = \frac{1}{\hbar} \sum_{e^r v^r R^r \neq e^f v^f R^f} \left\{ \frac{\langle R^f|\langle v^f|\langle e^f|\hat{p}_\rho|e^r\rangle|v^r\rangle|R^r\rangle}{\omega_{e^r} + \omega_{v^r} + \omega_{R^r} - \omega_1 - i\Gamma_{e^r v^r R^r}} \langle R^f|\langle v^f|\langle e^f|\hat{p}_\sigma|e^f\rangle|v^f\rangle|R^f\rangle \right\}.$$

Starting from this general equation all different types of Raman spectroscopy can be described. However, in order to deal with Eq. (4.5), knowledge of all (ro)vibronic
wavefunctions, energies and damping constants is required. Approximations can be made for specific cases, which reduces the necessary information considerably. The initial electronic state is taken to be the electronic ground state, $e^i = e^g$. As a simplifying step, closure over the rotational states $R$ shall be effected. Therefore, the $R$-dependent energy terms $\hbar \omega_{e^gR}, \hbar \omega_{e^gR^s}, i\hbar \Gamma_{e^g,e^gR}$ in the denominator have to be examined. If either $\omega_1$ is smaller than any vibronic absorption frequency $\omega_{e^g} + \omega_{e^g},$ or for $e^r = e^g,$ larger than the rovibrational frequency $\omega_{e^g} + \omega_{R^s,R}$, then $\omega_{R^s,R}$ is negligible. The damping constant $\Gamma_{e^g,e^gR}$ is small compared to the frequency terms and thus has been left out in this reasoning. Its dependency on $R$ is not strong, therefore it can be replaced by $\Gamma_{e^g,e^g},$ or subsequently by $\Gamma_{e^g}$, if the dependence on the vibrational states is neglected as well.

$$
(\alpha_{\rho\sigma})_{fi} = \frac{1}{\hbar} \sum_{e^g,v^r} \left\{ \frac{\langle R^f | \langle v^f | \langle \rho | e^r \rangle | v^r \rangle \langle v^r | \langle \sigma | e^g \rangle | v^i \rangle | R^i \rangle}{\omega_{e^g R^s} + \omega_{v^r,v^i} - \omega_1 - i \Gamma_{e^g}} + \frac{\langle R^f | \langle v^f | \langle \rho | e^r \rangle | v^r \rangle \langle v^r | \langle \sigma | e^g \rangle | v^i \rangle | R^i \rangle}{\omega_{e^g R^s} + \omega_{v^r,v^i} + \omega_1 + i \Gamma_{e^g}} \right\} 
$$

(4.6)

In order to resolve the rotational structure, the coordinates have to be transformed from space-fixed to molecule-fixed axes and the dependence on $|R^i$ can be separated. For pure vibrational (resonance) Raman scattering, i.e., if the rotational structure is not resolved, the scattering tensor elements can be calculated from Eq. (4.7), interpreting $\rho, \sigma$ as molecule-fixed coordinates, and the intensity can be calculated from isotropic averages.

$$
(\alpha_{\rho\sigma})_{fi} = \frac{1}{\hbar} \sum_{e^g,v^r} \left\{ \frac{\langle v^f | \langle e^f | \langle \rho | e^r \rangle | v^r \rangle \langle e^r | \langle \sigma | e^g \rangle | v^i \rangle | v^i \rangle}{\omega_{e^g R^s} + \omega_{v^r,v^i} - \omega_1 - i \Gamma_{e^g}} + \frac{\langle v^f | \langle e^f | \langle \rho | e^r \rangle | v^r \rangle \langle e^r | \langle \sigma | e^g \rangle | v^i \rangle | v^i \rangle}{\omega_{e^g R^s} + \omega_{v^r,v^i} + \omega_1 + i \Gamma_{e^g}} \right\} 
$$

(4.7)

### 4.2 Vibronic coupling and Raman spectroscopy

Because of the interaction between the motion of nuclei and electrons, a complete separation of electronic and nuclear coordinates is not possible. Terms describing this interaction are called vibronic coupling terms. The electronic Hamiltonian weakly depends on the nuclear coordinates, and thereby the vibrations of the molecule. In a zero-order approximation, i.e., when vibronic coupling is weak, separate equations can be formulated. However, there is an effect on molecular spectroscopy, which is pronounced in RR spectroscopy. In the Born–Oppenheimer
approximation, the vibronic coupling between the electronic and nuclear motion is neglected. To correct for that, Herzberg and Teller [42] expanded the electronic wavefunction of a state $|\psi\rangle$ as a function of the normal modes $Q_k$ in terms of electronic wavefunctions $|e^s\rangle$ at the equilibrium geometry $Q_0$:

$$|e^r(r, Q)\rangle = |e^r(r, Q_0)\rangle + \sum_{s \neq r} \sum_{k} a_s(Q_k)|e^s(r, Q_0)\rangle. \quad (4.8)$$

The expansion coefficients $a_s(Q_k)$ can be obtained by treating the dependence of the electronic Hamiltonian $\hat{H}_e$ on the nuclear coordinates as an expansion in normal coordinates to the linear term at the equilibrium position and using perturbation theory. The resulting coefficients contain the nuclear-coordinate dependence of the electronic part of the wavefunction

$$|e^r(r, Q)\rangle = |e^r(r, Q_0)\rangle + \frac{1}{\hbar} \sum_{s \neq r} \sum_{k} \frac{h_{e^se^r}^{k}}{\omega_{e^s} - \omega_{e^r} Q_k |e^s(r, Q_0)\rangle} \quad (4.9)$$

with the coupling integral

$$h_{e^se^r}^{k} = \left\langle e^s(r, Q_0) \left| \left( \frac{\partial \hat{H}_e}{\partial Q_k} \right)_0 \right| e^r(r, Q_0) \right\rangle. \quad (4.10)$$

Eq. (4.9) represents a correction to the adiabatic electronic wavefunction, and the term “vibronic coupling” in this context may be misleading, since it means coupling between electronic and vibrational wavefunction, which prevents the separation into a product. The total wavefunction is still an adiabatic wavefunction, where a correction to the electronic part was added to describe the dependence on the nuclear coordinates:

$$|e^r v^i(r, Q_k)\rangle = \left[ |e^r(r, Q_0)\rangle + \sum_{s \neq r} \sum_{k} a_s(Q_k)|e^s(r, Q_0)\rangle \right] |v^i(Q_k)\rangle. \quad (4.11)$$

This approach is valid only in case of weak vibronic coupling.

The transition electric dipole moments $\langle v^i | \langle e^f | \hat{p}_\rho(r) | e^r \rangle | v^r \rangle$ and $\langle v^r | \langle e^r | \hat{p}_\sigma(Q) | e^g \rangle | v^i \rangle$, depend on the nuclear coordinates through the electronic wavefunctions $|e^g\rangle, |e^f\rangle$ and $|e^r\rangle$. The electric dipole moment operator acts on both electronic and nuclear coordinates, $\hat{p}_\rho = \hat{p}_\rho(r) + \hat{p}_\rho(Q)$:

$$\langle v^f | \langle e^f | \hat{p}_\rho(r) + \hat{p}_\rho(Q) | e^r \rangle | v^r \rangle = \langle v^f | \langle e^f | \hat{p}_\rho(r) | e^r \rangle | v^r \rangle + \langle v^f | \langle e^f | \hat{p}_\rho(Q) | e^r \rangle | v^r \rangle$$

$$= \langle v^f | \langle e^f | \hat{p}_\rho(r) | e^r \rangle | v^r \rangle + \langle e^f | e^r \rangle \langle v^f | \hat{p}_\rho(Q) | v^r \rangle. \quad (4.12)$$

For transition dipole moments between different excited states, due to the orthogonality of electronic wavefunctions, only a matrix element between two vibrational
wavefunctions and the electronic part of the transition dipole moments (the “electronic transition moment” in contrast to the complete “vibronic transition moment”) remains:

\[ \langle v_f | \langle e_f | \hat{p}_p(r) | e_r \rangle | v_r \rangle = \langle v_f | (p_p)_{e_f e_r} | v_r \rangle. \]  

(4.13)

If the expressions for the perturbed electronic states are inserted, and quadratic terms in \( Q_k \) are neglected, the electronic transition moment elements become:

\[
(p_p)_{e_f e_r} = (p_p)_{e_f e_r}^0 + \frac{1}{\hbar} \sum_{e^e \neq e^r} \sum_k (p_p)_{e^e e^r}^0 \frac{h_{e^e e^r}}{\omega_{e^e} - \omega_{e^r}} Q_k \\
+ \frac{1}{\hbar} \sum_{e^e \neq e^r} \sum_k \frac{h_{e^e e^r}}{\omega_{e^e} - \omega_{e^r}} Q_k (p_p)_{e^e e^r}^0. 
\]  

(4.14)

An alternative approach to the Herzberg–Teller (HT) expansion of the electronic wavefunctions employs a direct expansion of the electronic transition dipole moment in the nuclear coordinates and has been first used for numerical calculations by Warshel and Dauber [149]:

\[
(p_p)_{e_f e_r} = (p_p)_{e_f e_r}^0 + \sum_k (p_p)_{e_f e_r}^k Q_k 
\]  

(4.15)

with \( (p_p)_{e_f e_r}^k = \left( \frac{\partial (p_p)_{e_f e_r}}{\partial Q_k} \right)_0. \)

(4.16)

The vibronic transition moment then becomes:

\[
\langle v_f | (p_p)_{e_f e_r} | v_r \rangle = (p_p)_{e_f e_r}^0 \langle v_f | v_r \rangle + \sum_k (p_p)_{e_f e_r}^k \langle v_f | Q_k | v_r \rangle 
\]  

(4.17)

or

\[
\langle v_f | (p_p)_{e_f e_r} | v_r \rangle = \langle p_p)_{e_f e_r}^0 \langle v_f | v_r \rangle \]

\[
+ \frac{1}{\hbar} \sum_{e^e \neq e^r} \sum_k (p_p)_{e^e e^r}^0 \frac{h_{e^e e^r}}{\omega_{e^e} - \omega_{e^r}} \langle v_f | Q_k | v_r \rangle \\
+ \frac{1}{\hbar} \sum_{e^e \neq e^r} \sum_k \frac{h_{e^e e^r}}{\omega_{e^e} - \omega_{e^r}} (p_p)_{e^e e^r}^0 \langle v_f | Q_k | v_r \rangle. 
\]  

(4.18)

In the Condon approximation, only the first term of Eqs. (4.17) and (4.18) is taken into account, i.e., the transition dipole moment corresponds to a product of the electronic transition moment and a vibrational overlap integral. When the Condon approximation breaks down, higher terms have to be considered, namely the “HT vibronic coupling” terms. When comparing Eqs. (4.14) and (4.15), the Taylor expansions of the dipole moment and of the Hamiltonian lead to the same terms, if one takes into consideration that [136]:

\[
(p_p)_{e_f e_r}^k = \frac{1}{\hbar} \left\{ \sum_{e^e \neq e^r} (p_p)_{e^e e^r}^0 \frac{h_{e^e e^r}}{\omega_{e^e} - \omega_{e^r}} + \sum_{e^e \neq e^r} \frac{h_{e^e e^r}}{\omega_{e^e} - \omega_{e^r}} (p_p)_{e^e e^r}^0 \right\}. 
\]  

(4.19)
4 Selective Technique in Vibrational Spectroscopy: (Resonance) Raman spectroscopy

Inserting the expression for the transition dipole moment of Eq. (4.18) into Eq. (4.7) and separating vibrational and electronic terms yields:

\[
(\alpha_{\rho\sigma})_{fi} = \frac{1}{\hbar} \sum_{e^v v' \neq e^v v'} \left\{ \frac{(p_p)_{e^v e^f}}{\omega_{e^v e^g}} + \frac{(p_\sigma)_{e^v e^g}}{\omega_{e^v e^f} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | v'' \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \left\{ \frac{(p_p)_{e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | Q_k | v'' \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \left\{ \frac{(p_\sigma)_{e^v e^g}}{\omega_{e^v e^f} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | v'' | Q_k \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \left\{ \frac{h_{k e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | Q_k | v'' \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \left\{ \frac{h_{k e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | v'' | Q_k \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \sum_{k'} \left\{ \frac{(p_p)_{e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | Q_k | v'' \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \sum_{k'} \left\{ \frac{(p_\sigma)_{e^v e^g}}{\omega_{e^v e^f} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | v'' | Q_k \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \sum_{k'} \left\{ \frac{h_{k e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | Q_k | v'' \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \sum_{k'} \left\{ \frac{h_{k e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | v'' | Q_k \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \sum_{k'} \left\{ \frac{h_{k e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | Q_k | v'' \rangle \langle v'' | v' \rangle
\]

\[
+ \frac{1}{\hbar^2} \sum_{e^v e^f} \sum_{k} \sum_{k'} \left\{ \frac{h_{k e^v e^f}}{\omega_{e^v e^g} + \omega_{v' v''} - \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''} + \omega_{e^v e^f} + \omega_{v' v''} + \omega_{e^v e^g} + \omega_{w' w''}} \right\} \langle v' | v'' | Q_k \rangle \langle v'' | v' \rangle
\]
The advantage of this explicitly written HT coupling lies in the interpretation: By coupling of states $e^r$ and $e^g$ with the states $e^s$ and $e^t$, intensity can be borrowed from the transitions $e^t : e^s$, $e^s : e^t$, $e^f : e^t$ and $e^s : e^t$. The coupling with states $e^s$ includes transitions, for which $p_{e^t,e^t}$ must be non-zero, which are allowed transitions from the state $e^t$ to $e^s$, whereas coupling with states $e^t$ involves transitions, where $p_{e^t,e^t}$ is non-zero. However, in the latter case the coupling is ineffective, unless $\omega_{e^f} = \omega_{e^t}$ or $\omega_{e^f} - \omega_{e^t}$ in the denominators are small. The three last terms in Eq. (4.20) contain a product of two coupling constants, where the denominators are $(\omega_{e^f} - \omega_{e^t})(\omega_{e^g} - \omega_{e^t})$, $(\omega_{e^f} - \omega_{e^t})(\omega_{e^g} - \omega_{e^t})$ and $(\omega_{e^f} - \omega_{e^t})(\omega_{e^g} - \omega_{e^t})$. Since the energy differences between states $e^t$ and $e^f, e^g$ are larger than $\omega_{e^r} - \omega_{e^t}$, the coupling is less effective and the resulting terms are smaller. These terms will be dropped in the following.

Inserting the direct expansion expression for the transition dipole moment Eq. (4.17) into Eq. (4.7) and separating vibrational and electronic terms yields a more useful form for computations:

$$
\begin{align*}
&= \frac{1}{\hbar} \sum_{e^t \neq e^s, e^f, e^g} \left\{ \left( \begin{array}{c} (p_{e^t})_{e^f,e^s} \\ (p_{e^t})_{e^f,e^g} \\ (p_{e^t})_{e^t,e^g} \\ (p_{e^t})_{e^t,e^s} \end{array} \right) \right\} \times
\langle v^f | v^r \rangle \langle v^r | v^t \rangle
+ \sum_k \left\{ \left( \begin{array}{c} (p_{e^t})_{e^f,e^s} \\ (p_{e^t})_{e^f,e^g} \\ (p_{e^t})_{e^t,e^g} \\ (p_{e^t})_{e^t,e^s} \end{array} \right) \right\} \times
\langle v^f | Q_k | v^r \rangle \langle v^r | v^t \rangle
+ \sum_{k,k'} \left\{ \left( \begin{array}{c} (p_{e^t})_{e^f,e^s} \\ (p_{e^t})_{e^f,e^g} \\ (p_{e^t})_{e^t,e^g} \\ (p_{e^t})_{e^t,e^s} \end{array} \right) \right\} \times
\langle v^f | v^r \rangle \langle v^r | Q_k | v^t \rangle
\end{align*}
\right)
\right. 
$$

The first term is called the Franck–Condon term since its nuclear terms consisting of products of overlap integrals between vibrational wavefunctions of the ground and excited states resemble the Franck–Condon factors which govern the intensity of vibronic transitions. The term “Franck–Condon factor” is sometimes used just for the vibrational overlap integral between ground state and excited state vibrational wavefunction (elsewhere called a “Franck–Condon integral” [150]) but usually means...
the square of that [151,152]. Here, in a wider sense the term will encompass also the
products of different vibrational overlap integrals between a ground and an excited-
state wavefunction, as they are met with for Raman scattering. The second, third
and fourth term resulting from the linear term in the Herzberg–Teller expansion are
the so-called Herzberg–Teller terms. Their nuclear terms contain overlap integrals
and matrix elements of the normal coordinates \( Q_k \) (“Herzberg–Teller integrals”).
The nuclear terms containing these matrix elements will be dubbed “Herzberg–
Teller factors” in analogy to the Franck–Condon factors.

4.3 Polarizability tensors for resonance Raman spectroscopy

In the following, we will only be concerned with vibrational RR scattering or pure vi-
brational Raman scattering, where initial and final vibrational state of the scattering
process belong to the same electronic state, the electronic ground state, \( e^i = e^f = e^g \).

There are several possibilities to calculate the polarizability tensor elements \( \alpha_{\rho\sigma} \)
for (pre-)resonance conditions. Here, we will be concerned with discrete RR scatter-
ing. In principle, Eq. (4.21) can be used for that purpose. In most cases, only the
Franck–Condon term is calculated. Furthermore, the second, off-resonance term in
the equations is small compared to the resonance term, slowly varying and therefore
often negligible. Since resonance conditions, i.e., a close matching of laser frequen-
cies and excitation energies, applies only to one or only very few excited states, the
sum over electronic states can be restricted to these states.

Overall, there are three main approaches to calculate RR polarizability tensor
elements: sum-over-state methods, transform theory methods and time-dependent
methods. All approaches require assumptions on the form of the electronic potential
energy surfaces (PES).

4.3.1 Potential energy surfaces

For the evaluation of the FC and HT factors in the Raman scattering tensor elements,
approximations for the potential energy surface to solve the nuclear Schrödinger
equation and obtain the vibrational wavefunctions, are needed. Usually, harmonic
potential energy surfaces are assumed for both the ground and excited states, which
may be displaced. In principle, the composition of the normal modes of ground and
excited states of polyatomics are not identical. They are related by a rotation, the
so-called Duschinsky rotation [153] that mixes the ground-state coordinates. But as
a first approximation, an identical composition of the normal modes can be assumed.
This allows the description of the multidimensional FC and HT factors as a product
of one-dimensional FC and HT factors for independent harmonic oscillators. In this
independent mode harmonic oscillator (IMDHO) model [154–156], see Fig. (4.2),
often also identical frequencies are assumed, although a frequency change can be
incorporated. This model is also called Gradient Franck–Condon or Linear Coupling
model. The displacements \( \Delta \) can be obtained from the gradients of the excited
states, see Eqs. (4.22) and (4.23):
4.3 Polarizability tensors for resonance Raman spectroscopy

Figure 4.2: Displaced harmonic oscillators with equal frequencies and displacement $\Delta_j^Q$.

\[ E_{\text{el}}^{\text{ex}}(Q_j) = E_{\text{el}}^{\text{ex}}(\Delta_j^Q) + \frac{1}{2} \omega_j^2 (Q_j - \Delta_j^Q)^2 \]  
(4.22)

\[ \left( \frac{\partial E_{\text{el}}^{\text{ex}}(Q_j)}{\partial Q_j} \right)_{Q_j=0} = \omega_j^2 (Q_j - \Delta_j^Q)_{Q_j=0} = -\omega_j^2 \Delta_j^Q. \]  
(4.23)

Sometimes reduced normal coordinates $q_j$ instead of mass-weighted normal coordinates $Q_j$ are used. Coordinates and displacements are related by:

\[ q_j = Q_j \sqrt{\frac{2\pi c \bar{\nu}_j}{\hbar}} = Q_j \sqrt{\frac{\omega_j}{\hbar}} \]  
(4.24)

\[ \Delta_j^q = \Delta_j^Q \sqrt{\frac{2\pi c \bar{\nu}_j}{\hbar}} = \Delta_j^Q \sqrt{\frac{\omega_j}{\hbar}}. \]  
(4.25)

More precise descriptions of the PES, e.g., considering anharmonic effects [157] can be included in the calculations.

4.3.2 Sum-over-states formalism

Sum-over-states methods employ Eq. (4.21) directly to calculate the polarizability tensor elements. However, the number of intermediate states increases exponentially with the number of modes, especially if they have considerable displacement. Moreover, if frequency changes, Duschinsky rotation or anharmonic potential are included, complicated multi-dimensional FC factors and HT factors result.
4.3.3 Transform theory methods

Transform theory methods \([156, 158–162]\) constitute a further approach, which is based on the Kramers–Kronig relations. They make use of a connection between polarizability tensor components and the absorption cross section. An advantage of this approach is the direct correlation between the Raman intensity of the mode of interest and its excited-state displacement, while less information is needed on the other modes. Frequency changes, Duschinsky rotation, anharmonicity and HT terms can be incorporated in the description, see references in \([129]\).

4.3.4 Time-dependent approach

The sum-over-states picture is not only computationally very demanding but also requires summing over all intermediate vibrational states. An alternative description are time-dependent approaches \([32,129,131,158,163]\), which explain important aspects of Raman scattering by wave-packet dynamics on the excited-state surface. A change from the sum-over-states picture to the time-dependent picture can be achieved by employing a half-Fourier transformation of the denominator in the sum-over-states expression. In the following, this will be shown for RR scattering tensor elements, assuming only one excited state in resonance, a negligible non-resonance term and the Condon approximation to be valid. Of course, this can be extended to encompass several excited states and HT terms. Starting from Eq. (4.21) and employing a half-Fourier transformation leads to:

\[
(\alpha_{\rho\sigma})_{fi} = \sum_{v'} \frac{(p_{\rho})^{0}_{e,f,v}(p_{\sigma})^{0}_{e,g,v}}{\omega_{v'eg} + \omega_{v'vi} - \omega_1 - i\Gamma_{e,v}} \times \langle v'|v^r\rangle\langle v^r|v^i\rangle
\]

\[
= (p_{\rho})^{0}_{e,f,v}(p_{\sigma})^{0}_{e,g,v} \times 
\int_0^{\infty} dt \sum_{v'} \langle v'|\exp\left(-i\frac{\hat{H}_{ex}}{\hbar}\right)|v^r\rangle \langle v^r|v^i\rangle \cdot \exp \left[ -i(\omega_{v'eg} + \omega_{v'vi} - \omega_1 - i\Gamma_{e,v})t \right].
\]

(4.26)

Writing the vibrational energy difference \(\omega_{v'vi} - \omega_{v'eg}\) explicitly as \(\omega_{v'} - \omega_{v'vi}\) and employing a spectral representation for the nuclear Hamiltonian of the excited-state surface

\[
\exp[-i(\omega_{v'} + \omega_{v'eg})] = \exp[-i\hat{H}_{ex}t/\hbar] v^r
\]

(4.27)

yields

\[
(\alpha_{\rho\sigma})_{fi} = (p_{\rho})^{0}_{e,f,v}(p_{\sigma})^{0}_{e,g,v} \times 
\int_0^{\infty} dt \sum_{v'} \langle v'|\exp(-i\hat{H}_{ex}t/\hbar)|v^r\rangle\langle v^r|v^i\rangle \cdot \exp \left[ i(\omega_{v'} + \omega_1) - \Gamma_{e,v}t \right].
\]

(4.28)
4.3 Polarizability tensors for resonance Raman spectroscopy

The sum over the intermediate vibrational states $|v^r\rangle$ can be removed by using the completeness relation $\sum_{v^r} |v^r\rangle\langle v^r| = 1$:

$$(\alpha_{\rho\sigma})_{fi} = (p_{\rho})_{v^r}^0 (p_{\sigma})_{e^r e^g}^0 \times \int_0^\infty dt \langle v^f| \exp(-i\hat{H}^{ex}t/\hbar)|v^i\rangle \cdot \exp [i(\omega_{v^f} + \omega_1) - \Gamma_{e^r}t].$$ (4.29)

Now the propagator acts on the initial wavefunction $|v^i\rangle$, $\exp[-i\hat{H}^{ex}t/\hbar]|v^i\rangle = |v^i(t)\rangle$ and a final equation with a time-dependent FC overlap integral $\langle v^f|v^i(t)\rangle$ results:

$$(\alpha_{\rho\sigma})_{fi} = (p_{\rho})_{v^r}^0 (p_{\sigma})_{e^r e^g}^0 \times \int_0^\infty dt \sum_{v^r} \langle v^f|v^i(t)\rangle \cdot \exp [i(\omega_{v^f} + \omega_1) - \Gamma_{e^r}t]$$

$$= (p_{\rho})_{v^r}^0 (p_{\sigma})_{e^r e^g}^0 \times i \int_0^\infty dt \langle v^f|v^i(t)\rangle \exp(i(\omega_{v^f} + \omega_1)t) \cdot \exp^{-\Gamma_{e^r}t}.$$ (4.30)

$|v^i(t)\rangle$ is the initial vibrational wave packet propagated on the excited-state potential energy surface, see Fig. 4.3. Here, $\Gamma_{e^r}$ has a specific meaning: it is connected to the finite excited-state lifetime, which must be taken into account under resonance conditions. A sum over more excited electronic states $e^r$ can be easily included. In this description, all information about vibrational eigenstates is contained in the Hamiltonian. It is possible to include anharmonic potentials or Duschinsky rotation [164]. It has to be stressed, that the time-dependent picture describes the same situation as the sum-over-states approach, only in a different language. Therefore, it is not a time-resolved description.

Figure 4.3: Illustration of the time-dependent picture of Raman scattering.
In many cases, the time integral is determined only by a short time after the excitation, so that short-time approximations have been derived [32, 33]. The reason for short propagation times can be traced back to several causes: on the one hand, the mismatch between external excitation energy \( \omega_1 \) and the energy of the excited state plays a role: The larger the mismatch, the shorter the propagation time, which is usually justified by an uncertainty principle argument [33]. This is why for prereonsonance and off-resonance Raman spectra HT terms are important, since the wave packet cannot evolve for a long enough time for modes with a large displacement to achieve a significant overlap with the ground-state wavefunction. Additionally, recurrences of the wave packet at larger times do in general not lead to significant contributions, since many modes with different frequencies lead to a cancelling in the multidimensional overlap integrals. Furthermore, the damping by the factor \( \exp(-\Gamma_e t) \) contributes to short propagation times. As a consequence of short propagation times the geometry of the excited states, i.e., mainly the gradient in the region of the minimum ground state structure plays the most important role. Starting from this point, approximate analytical expressions have been derived for Raman intensities by Heller et al. [33] in the Condon approximation. These are often given in the form of relative Raman intensities and will be referred to as “gradient approximation”,

\[
\frac{i_j}{i_k} = \left( \frac{V_j^q}{V_k^q} \right)^2,
\]

with \( V^q_j \) denoting the excited-state gradient with respect to normal mode \( j \) in reduced normal coordinates at the ground-state minimum structure,

\[
V_j^q = \left( \frac{\partial E_{el}^{ex}}{\partial q_j} \right)_{q_j=0}.
\]

In the IMDHO model, the excited-state gradient can be related to the normal mode displacement,

\[
\left( \frac{\partial E_{el}^{ex}}{\partial q_j} \right)_{q_j} = \omega_j \left( q_j - \Delta q_j \right) \bigg|_{q_j=0} = -\omega_j \Delta q_j,
\]

compare to Eq. (4.24).

This expression for the special case of the IMDHO model and equal frequency is identical to Savin’s rule [165]:

\[
\frac{i_j}{i_k} = \frac{\nu_j^2}{\nu_k^2} \left( \frac{\Delta q_j}{\Delta q_k} \right)^2.
\]
4.4 Placzek polarizability tensor

For pure vibrational scattering, Placzek introduced approximations which lead to a simple form and make the calculation with standard quantum chemistry software feasible.

The sum over intermediate states in Eq. (4.7) runs over all electronic states, including the ground state $e^g$. For the ground state, the damping constant can be set to zero, and $\omega_{e^r e^g} = 0$. If $\omega_1$ is much larger than any ground-state vibrational frequency difference $\omega_{v^r v^i}$, the electronic ground state can be neglected in the sum over the intermediate states, since its terms are small compared to the terms belonging to excited electronic states. For these terms, the vibrational frequency differences $\omega_{v^r v^i}$ and $\omega_{v^r v^f}$ as well as the damping constants can be neglected, if the excitation frequency $\omega_1$ is much smaller than any electronic excitation energy $\omega_{e^r e^g}$ and much larger than any vibrational frequency difference:

\[
\left(\alpha_{\rho \sigma}\right)_{e^r \neq e^g} = \frac{1}{\hbar} \sum_{e^r \neq e^g, v^r \neq v^i} \left\{ \frac{\langle v^f | (e^g | \hat{p}_\rho | e^r) | v^r \rangle \langle v^r | (e^r | \hat{p}_\sigma | e^g) | v^i \rangle}{\omega_{e^r e^g} - \omega_1} + \frac{\langle v^f | (e^g | \hat{p}_\sigma | e^r) | v^r \rangle \langle v^r | (e^r | \hat{p}_\rho | e^g) | v^i \rangle}{\omega_{e^r e^g} + \omega_1} \right\}. \quad (4.35)
\]

For the complete sets of vibrational states $v^r$ of each electronic state $e^r$ in the sum over the intermediate states, closure can be invoked,

\[
\left(\alpha_{\rho \sigma}\right)_{e^r \neq e^g} = \frac{1}{\hbar} \sum_{e^r \neq e^g} \left\{ \frac{\langle v^f | (e^g | \hat{p}_\rho | e^r) | e^r \rangle \langle e^r | \hat{p}_\sigma | e^g \rangle | v^i \rangle}{\omega_{e^r e^g} - \omega_1} + \frac{\langle v^f | (e^g | \hat{p}_\sigma | e^r) | e^r \rangle \langle e^r | \hat{p}_\rho | e^g \rangle | v^i \rangle}{\omega_{e^r e^g} + \omega_1} \right\}. \quad (4.36)
\]

Eq. (4.36) can be rewritten using the adiabatic dynamic polarizability $\hat{\alpha}_{\rho \sigma}(Q)$:

\[
\left(\alpha_{\rho \sigma}\right)_{e^r \neq e^g} = \langle v^f | \hat{\alpha}_{\rho \sigma}(Q) | v^i \rangle. \quad (4.37)
\]

The transition dipole moment elements in Eq. (4.36) depend on the nuclear coordinates $Q$. These are contained in the adiabatic dynamic polarizability of Eq. (4.37), which thus likewise is a function of the nuclear coordinates.

In practice, the matrix elements of the adiabatic dynamic polarizability are expanded in a Taylor series around $Q_0$ to linear terms in $Q_k$, so that the Placzek polarizability reads:

\[
\left(\alpha_{\rho \sigma}\right)_{e^r \neq e^g} = \langle v^f | \hat{\alpha}_{\rho \sigma}(Q) | v^i \rangle = \left(\alpha_{\rho \sigma}\right)_0 \langle v^f | v^i \rangle + \sum_k \left( \frac{\partial \alpha_{\rho \sigma}}{\partial Q_k} \right)_0 \langle v^f | Q_k | v^i \rangle. \quad (4.38)
\]
This expansion parallels the expansion of the electronic transition moment. Indeed, the same expression can be obtained from Eq. (4.21) when invoking closure, neglecting quadratic terms in $Q_k$ and applying appropriate approximations for the energy denominators. The overlap integral of the two orthogonal ground state vibrational wavefunctions $\langle v^f | v^i \rangle$ is zero, thus the first term disappears. In the Placzek approximation for the elements of the scattering tensor, polarizability derivatives need to be calculated. This matches the observation in the time-dependent picture that for non-resonance conditions and thus short propagation times vibrational coupling terms become important.

4.5 Raman intensities: calculations in practice

In order to compare with experiment, first the scattering tensor elements $\alpha_{\rho\sigma}$ have to be determined and from these, Raman intensities can be calculated. Besides the data taken from quantum chemical calculations, i.e., excitation energies, transition dipole moments, and harmonic vibrational frequencies, and the wavelength of the laser, the homogeneous linewidth $\Gamma$ is needed for resonance Raman scattering tensor elements. In principle, $\Gamma$ can be determined from comparisons of RR and absorption data. In practice, however, it is treated as a parameter in the order of a few $100 \text{ cm}^{-1}$ [166–168]. When calculating the intensities, the experimental setup has to be taken into account, which means among other parameters the correct scattering geometry. The scattering tensor elements of the arbitrarily oriented molecules refer to molecule-fixed axes, therefore a way has to be found to average over the orientations and correlate them to the laboratory-fixed coordinates used in recording the experiment. Solvent and environmental effects are assumed to be incorporated in the molecular properties and the homogeneous linewidth. Typically a $90^\circ$ scattering arrangement is used: the incident light falls in along the $X$ direction, where the capital letter denotes a laboratory-fixed coordinate, and the scattered light is detected along the $Y$ direction. The incident light is polarized along the $Z$ direction. The scattered light is analyzed with respect to its two polarization components: same polarization as the incident light ($Z$), which is called polarized scattered light ($I_{\parallel}$, $I_{ZZ}$, $I_{\text{pol}}$), or polarized in the $X$ direction, i.e., depolarized scattered light ($I_{\perp}$, $I_{XZ}$, $I_{\text{dep}}$). From these two components the depolarization ratio $\rho$ can be determined:

$$\rho = \frac{I_{\text{dep}}}{I_{\text{pol}}}.$$  \hspace{1cm} (4.39)

The scattered intensity is proportional to the differential cross section $d\sigma/d\Omega$, where $d\Omega$ is the solid angle of detection, which is the irradiance $I_s$ divided by the intensity of the incident light $I_0$,

$$\frac{d\sigma}{d\Omega} = \frac{I_s}{I_0}.$$  \hspace{1cm} (4.40)
The differential cross section contains the sum of polarized and depolarized components. The total cross section, i.e., the differential cross section integrated over all possible scattering angles can be calculated from 90° results, but is not necessary for the comparison with experiment. The relation between the differential cross section and the scattering tensor elements is given by [152]:

$$\left( \frac{d\sigma_{fi}}{d\Omega} \right)_{s,0} = \frac{\omega^3 \omega_0}{c^4} |\hat{e}_s \cdot \alpha_{fi} \cdot \hat{e}_0|^2,$$

where $\hat{e}_s$ and $\hat{e}_0$ signify the unit vectors along the polarization direction of scattered and incident light, and which project out the part of the induced polarization $\alpha$ into laboratory coordinates. To that end, the molecule-frame coordinates used for $\alpha_{\rho\sigma}$ have to be converted to laboratory coordinates. For a 90° scattering geometry $\alpha_{ZZ}$ and $\alpha_{XZ}$ are needed. Then, in principle, averaging over the randomly oriented molecules needs to be done, for which direction cosines or Wigner rotation matrices can be employed. Instead, the rotational invariants $\Sigma^0$, $\Sigma^1$ and $\Sigma^2$ defined in molecule-frame coordinates are calculated:

$$\Sigma^0 = \frac{1}{3} |\alpha_{xx} + \alpha_{yy} + \alpha_{zz}| \quad (4.42)$$

$$\Sigma^1 = \frac{1}{2} \left[ |\alpha_{xy} - \alpha_{yx}|^2 + |\alpha_{xz} - \alpha_{zx}|^2 + |\alpha_{yz} - \alpha_{zy}|^2 \right] \quad (4.43)$$

$$\Sigma^2 = \frac{1}{2} \left[ |\alpha_{xy} + \alpha_{yx}|^2 + |\alpha_{xz} + \alpha_{zx}|^2 + |\alpha_{yz} + \alpha_{zy}|^2 \right]$$

$$+ \frac{1}{3} \left[ |\alpha_{xx} - \alpha_{yy}|^2 + |\alpha_{xx} - \alpha_{zz}|^2 + |\alpha_{yy} - \alpha_{zz}|^2 \right]. \quad (4.44)$$

The RR intensity of a particular mode is then proportional to the invariants of the scattering tensor, which can be connected to the laboratory-frame coordinates, (see Refs. [129, 169–171] for details):

$$|\alpha_{ZZ}|^2 = \frac{1}{3} \Sigma^0 + \frac{2}{15} \Sigma^2 \quad (4.45)$$

$$|\alpha_{XZ}|^2 = \frac{1}{6} \Sigma^1 + \frac{1}{10} \Sigma^2. \quad (4.46)$$
5 Herzberg–Teller Terms in Resonance Raman Spectroscopy

The selective nature of resonance Raman (RR) spectroscopy, i.e., the fact that the intensity of certain modes is strongly enhanced in comparison to other modes, can be traced back to several aspects. The matching of the laser frequency and energies of the excited states determines which state(s) are in resonance, and whether resonance or preresonance conditions are met. Resonance with a certain excited state results in a local selectivity if the excited state is localized, i.e., if changes in the electron density are confined to a part of the molecule. The enhancement mechanism is determined further by the (approximate) symmetry of the Raman active modes, i.e., the modes which undergo a vibrational transition. The local change of electron densities can result in displacements of the structure along totally symmetric modes, resulting in Franck–Condon (FC) activity of these modes, for which large overtone progressions can be observed. These totally symmetric modes can be discerned from Raman active non-totally symmetric modes, which for symmetry reasons show no displacement between ground and excited state and therefore no FC activity. The difference in the electronic wavefunctions of ground and excited state here leads, qualitatively speaking, to a change of the transition dipole moment along a vibrational coordinate. This is valid for non-degenerate ground states. For degenerate ground states, a symmetry change in the excited state can allow a displacement also for non-totally symmetric modes, see, e.g., Ref. [136,138].

In order to understand the Raman activity of non-totally symmetric modes, vibronic coupling has to be taken into account via the dependence of the transition dipole moment on the nuclear coordinates, leading to Herzberg–Teller (HT) terms. No overtone progressions but only fundamental vibrational transitions and first overtones and combination bands occur in the low-temperature limit. The differences observed for totally symmetric and non-totally symmetric modes can be related to the expressions for the resonance Raman scattering tensors.

There are three important factors which determine the value of the scattering tensor element: (1) the product of the transition dipole moment components, (2) a nuclear term, i.e., the multi-dimensional FC and HT factors, and (3) the energy denominator. HT terms are important if either the transition dipole moment is very small or zero, and intensity can be borrowed from a neighbouring state with a large transition dipole moment by coupling via a mode of suitable symmetry (an “intensity promoting mode” [150]) or if the potential energy surfaces of the initial and final state are very similar, i.e., equal frequencies and small or no displacement and no Duschinsky rotation can be assumed, so that the vibrational wavefunctions
are practically orthogonal and thus only Rayleigh-scattering terms survive. It has been shown that the displacement is of greater importance than the frequency change to obtain vibrational overlap integrals different from zero, so that it is in most cases a good approximation to assume equal frequencies [138]. For totally symmetric modes with a very small displacement, which results in small FC overlap integrals, HT coupling may play a role. However, coupling by a totally symmetric mode concerns excited states of the same symmetry, which have to be close in energy for the coupling to be efficient, since the coupling terms are divided by the energy difference between the two states [136,138]. Usually, the FC term is larger than the HT contribution, however, e.g., in the Soret-band excited resonance Raman spectra of cytochrome-c the non-Condon contribution was shown to be important even for totally symmetric modes [16]. For non-totally symmetric modes, HT coupling plays a significant role. Non-totally symmetric modes can couple electronic states of different symmetry, or components of two degenerate states of the same symmetry. The importance of FC and HT terms in preresonance and resonance enhancement is discussed in Ref. [138].

5.1 Herzberg–Teller terms in vibrationally resolved optical spectra

In practical calculations, HT terms are in most cases taken into account by the expansion of the transition dipole moment in normal coordinates (Eq. 4.15). The main task when calculating vibrationally resolved optical spectra is the calculation of the multi-dimensional FC and HT factors. Formulae for multi-dimensional Franck–Condon integrals, some of them including the Duschinsky rotation in polyatomic molecules have been published already in the 1950s and 1960s, e.g., in Refs. [172,173] and have later been elaborated on or complemented by other approaches (Refs. [150,151], and references therein). The relevance of vibronic coupling for vibrationally resolved optical spectra and the influence of different approximations has been subject of studies already in the 1970s. In this time period several papers with formulae for Herzberg–Teller integrals were published, e.g., Ref. [151]. The development of efficient methods to calculate FC and HT factors has been of continued interest, see Ref. [174] and references therein. In recent years, several implementations in general-purpose computer programs allow the computation of vibrationally resolved spectra, e.g., Gaussian09 [175,176], including Herzberg–Teller terms [177,178] and even finite-temperature effects [179].

Presently, explicit and recursive formulae for the vibrational overlap integrals for displaced harmonic oscillators (including frequency changes or the special case of equal frequencies) can be found in various articles [151,172], in some cases recursive formulae for products of the vibrational overlap integrals, i.e., the FC factors needed for absorption, Raman fundamentals and Raman overtones are directly given [129,180]. Formulae for the overlap integrals for HT terms, i.e., overlap integrals containing the nuclear coordinate, are found less commonly (in explicit form [154] or as a function of the FC overlap integrals [177,178]).
5.1 Herzberg–Teller terms in vibrationally resolved optical spectra

In the IMDHO model (cf. Section 4.3.1) only formulae for the calculation of one-dimensional factors are needed. This model is also known as the Linear Coupling Model LCM [177, 178, 181–183] or Gradient Franck–Condon (GFC) model. This approach neglects the Duschinsky rotation, which was argued to be “theoretically inconsistent” for Herzberg–Teller terms due to interferential features (see Ref. [179]). Studies including the Duschinsky effect for electronic spectra and even for RR spectra have been performed early on, see, e.g., Ref. [149, 184]. Comments on the neglect of the Duschinsky effect for vibronic intensity calculations and its advantages were made by Macak [177]. The Duschinsky effect can be large even when differences between the frequencies are small [185], however, for stiff molecules, a strong Duschinsky effect is unlikely [186]. Although less rigorous, employing the IMDHO model has the advantage that only the gradient of the excited state at the ground-state minimum and the ground-state frequencies are needed. In order to include the Duschinsky effect, optimization and frequency analysis of the excited state have to be performed (or at least the mixed second-order excited-state derivatives at the ground-state minimum have to be determined for an approximate treatment). Besides RR spectroscopy, HT terms are often discussed for absorption and emission spectroscopy, especially to explain deviations from the mirror symmetry between them. In this context, the importance of including the Duschinsky rotation for the description was stressed [185, 187].
5.2 Resonance Raman scattering tensor elements including Herzberg–Teller terms

If HT terms are taken into account by a Taylor expansion of the transition dipole moment in terms of the normal coordinates, the scattering tensor elements for pure vibrational RR are calculated according to Eqs. (5.1) (cf. Section 4.2 for the introduction of all occurring quantities),

\[
\frac{1}{\hbar} \sum_{v'} \left[ \left( \frac{\langle \alpha_{p\sigma} \rangle_{e^0v',e^0v'} (p_\sigma)_{e^0e'} (p_\sigma)_{e'e^0}}{\omega_{e'e^0} + \omega_{v'v} - \omega_1 - i\Gamma_{e'e^0}} + \frac{(p_\sigma)_{e^0e'} (p_\sigma}_{e'e^0} \right) \right] \times \langle v' | v' \rangle \langle v' | v' \rangle \\
+ \sum_k \left[ \left( \frac{(p_\sigma)_{e'e^0} (p_\sigma)}{\omega_{e'e^0} + \omega_{v'v} - \omega_1 - i\Gamma_{e'e^0}} + \frac{(p_\sigma)_{e'e^0} (p_\sigma)}{\omega_{e'e^0} + \omega_{v'v} + \omega_1 + i\Gamma_{e'e^0}} \right) \right] \times \langle v' | v' \rangle \langle v' | v' \rangle \\
+ \sum_{k,k'} \left[ \left( \frac{(p_\sigma)_{e'e^0} (p_\sigma)}{\omega_{e'e^0} + \omega_{v'v} - \omega_1 - i\Gamma_{e'e^0}} + \frac{(p_\sigma)_{e'e^0} (p_\sigma)}{\omega_{e'e^0} + \omega_{v'v} + \omega_1 + i\Gamma_{e'e^0}} \right) \right] \times \langle v' | v' \rangle \langle v' | v' \rangle . \tag{5.1}
\]

The multidimensional FC and HT factors are in the IMDHO model calculated as products of one-dimensional factors:

\[
\langle v' | v' \rangle \langle v' | v' \rangle = \prod_j \langle v'_j | v'_j \rangle \langle v'_j | v'_j \rangle, \tag{5.2}
\]

\[
\langle v' | Q_k | v' \rangle \langle v' | v' \rangle = \langle v'_k | Q_k | v'_k \rangle \langle v'_k | v'_k \rangle \prod_{j \neq k} \langle v'_j | v'_j \rangle \langle v'_j | v'_j \rangle, \tag{5.3}
\]

\[
\langle v' | v' \rangle \langle v' | Q_k | v' \rangle = \langle v'_k | v'_k \rangle \langle v'_k | Q_k | v'_k \rangle \prod_{j \neq k} \langle v'_j | v'_j \rangle \langle v'_j | Q_k | v'_j \rangle, \tag{5.4}
\]

\[
\langle v' | Q_k | v' \rangle \langle v' | Q_k | v' \rangle = \langle v'_k | Q_k | v'_k \rangle \langle v'_k | Q_k | v'_k \rangle \prod_{j \neq k} \langle v'_j | v'_j \rangle \langle v'_j | Q_k | v'_j \rangle \tag{5.5}
\]

\[
\langle v' | Q_k | v' \rangle \langle v' | Q_k | v' \rangle = \langle v'_k | Q_k | v'_k \rangle \langle v'_k | Q_k | v'_k \rangle \prod_{j \neq k} \langle v'_j | v'_j \rangle \langle v'_j | Q_k | v'_j \rangle. \tag{5.6}
\]
In Eq. (5.1), the sum over $k$ extends over all modes, so that HT factors are contained for Raman active and Raman inactive modes. In the case of RR intensities, for the coupling via normal modes $Q_k$, the summation over all $k$ is often restricted to a single $k$ in the second and third term of Eq. (5.1), and a pair of $k$ and $k'$ in the fourth term, as in e.g., Ref. [136,138]. This rests on the assumption that Herzberg–Teller terms are important only for non-totally symmetric modes with $\Delta = 0$. This can be taken into consideration when evaluating the HT factors: For integrals with identical modes in the ground and excited state, formulae can be found in textbooks, e.g., Ref. [152] or can be derived using ladder operators for the harmonic oscillator in second quantization notation:

$$Q = \sqrt{\frac{\hbar}{2\omega}}(b + b^+), \quad (5.7)$$

$$\langle v_f | Q | v_i \rangle = \sqrt{\frac{\hbar}{2\omega}} \langle v_f | b + b^+ | v_i \rangle$$

$$= \sqrt{\frac{\hbar}{2\omega}} \left[ \sqrt{v_i} \langle v_f | v_i - 1 \rangle + \sqrt{v_i + 1} \langle v_f | v_i + 1 \rangle \right], \quad (5.8)$$

$$\langle v_f | Q^2 | v_i \rangle = \frac{\hbar}{2\omega} \langle v_f | (b + b^+)(b + b^+) | v_i \rangle$$

$$= \frac{\hbar}{2\omega} \left[ \sqrt{v_i} \sqrt{v_i - 1} \langle v_f | v_i - 2 \rangle + \sqrt{v_i + 1} \sqrt{v_i + 2} \langle v_f | v_i + 2 \rangle \right.$$

$$\left. + (2v + 1)\langle v_f | v_i \rangle \right], \quad (5.9)$$

$$\langle v_f | Q | v_i \rangle = \begin{cases} (v_i + 1)^{\frac{3}{2}} \sqrt{\frac{\hbar}{2\omega}} & \text{for } v_f = v_i + 1 \\ (v_i)^{\frac{3}{2}} \sqrt{\frac{\hbar}{2\omega}} & \text{for } v_f = v_i - 1 \\ 0 & \text{otherwise,} \end{cases} \quad (5.10)$$

$$\langle v_f | Q^2 | v_i \rangle = \begin{cases} (v_i + 2)^{\frac{3}{2}}(v_i + 1)^{\frac{1}{2}} \frac{\hbar}{2\omega} & \text{for } v_f = v_i + 2 \\ (v_i)^{\frac{3}{2}}(v_i - 1)^{\frac{1}{2}} \frac{\hbar}{2\omega} & \text{for } v_f = v_i - 2 \\ (2v_i + 1) \frac{\hbar}{2\omega} & \text{for } v_f = v_i \\ 0 & \text{otherwise.} \end{cases} \quad (5.11)$$
In the low-temperature limit, only contributions of the HT factors for the Raman active modes and HT terms corresponding to first overtones and combination bands, and one Rayleigh-term contribution remain,

$$\langle v'_k | Q_k | v''_k \rangle \langle v'_k | v''_k \rangle \rightarrow \langle 1_k | Q_k | 0_k \rangle \langle 0_k | 0_k \rangle = \langle 1_k | Q_k | 0_k \rangle, \quad (5.12)$$

$$\langle v'_k | v''_k | Q_k | v'_k \rangle \rightarrow \langle 1_k | 1_k | Q_k | 0_k \rangle = \langle 1_k | Q_k | 0_k \rangle, \quad (5.13)$$

$$\langle v'_k | Q_k | v''_k \rangle \langle v'_k | Q_k | v''_k \rangle \rightarrow \langle 2_k | Q_k | 1_k | Q_k | 0_k \rangle, \quad (5.14)$$

$$\langle 1_k | Q_k | 0_k \rangle \langle 0_k | 0_k \rangle \cdot \langle 1_k | 1_{k'} | Q_{k'} | 0_{k'} \rangle \rightarrow \langle 1_k | Q_k | 0_k \rangle \cdot \langle 1_{k'} | Q_{k'} | 0_{k'} \rangle, \quad (5.15)$$

$$\langle v'_k | Q_k | v''_k \rangle \langle v'_k | Q_k | v''_k \rangle \rightarrow \langle 0_k | Q_k | 1_k | Q_k | 0_k \rangle = \langle 1_k | Q_k | 0_k \rangle^2. \quad (5.16)$$

If the latter is neglected, Herzberg–Teller coupling is only needed for the Raman active modes. Neglecting overtones and combination bands yields:

$$\frac{\langle \alpha_{\rho\sigma} \rangle_{e\rho e'\sigma e', e'\sigma}}{\hbar} \sum_{e'} \left\{ \frac{(p_{\rho})_{e\rho e'}(p_{\sigma})_{e'\sigma}}{\omega_{e\rho e} + \omega_{e'\sigma} - \omega_1 - i\Gamma_{e'\sigma}} + \frac{(p_{\sigma})_{e\rho e'}(p_{\rho})_{e'\sigma}}{\omega_{e\rho e} + \omega_{e'\sigma} + \omega_1 + i\Gamma_{e'\sigma}} \right\} \prod_j \langle v'_j | v'_j \rangle \langle v''_j | v''_j \rangle \times \langle 1_k | Q_k | 0_k \rangle \langle 0_k | 0_k \rangle \cdot \prod_{j \neq k} \langle v'_j | v'_j \rangle \langle v''_j | v''_j \rangle \times \langle 1_k | 1_k | Q_k | 0_k \rangle \langle 0_k | Q_k | 0_k \rangle \cdot \prod_{j \neq k} \langle v'_j | v'_j \rangle \langle v''_j | v''_j \rangle \right) \cdot (5.17)$$

Using the selection rules given in Eq. (5.10), the integrals have the following values:

$$\langle 1_k^0 | Q_k | 0_k^0 \rangle = \sqrt{\frac{\hbar}{2\omega_k}}, \quad (5.18)$$

$$\langle 2_k | Q_k | 1_k \rangle \langle 1_k | Q_k | 0_k \rangle = \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{2\omega_k}} \sqrt{\frac{\hbar}{2\omega_k}} = \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{2\omega_k}}, \quad (5.19)$$

$$\langle 1_k | Q_k | 0_k \rangle \langle 0_k | 0_k \rangle \langle 1_k' | 1_k' \rangle \langle 1_k' | Q_{k'} | 0_{k'} \rangle = \sqrt{\frac{\hbar}{2\omega_k}} \sqrt{\frac{\hbar}{2\omega_{k'}}}. \quad (5.20)$$
The picture behind this simplification is that the excited state in resonance couples only with one other electronic state, and that this coupling is mediated by one specific normal mode, for which the “intensity is borrowed”.

However, there is no apparent (formal) reason why the Rayleigh term contributions $\langle 0_k | v_k | Q_k | 0_k \rangle$ and $\langle 0_k | Q_k | v_k | 0_k \rangle$ which are 0 for $\Delta = 0$, but are non-negligible for larger values of $\Delta$, and HT terms for Raman active modes with a non-zero displacement can be generally dropped. Possibly, for these modes the transition dipole moment derivatives are very small. The HT factor $\langle 0_k | Q_k | 1_k \rangle \langle 1_k | Q_k | 0_k \rangle$, which has a significant value even for $\Delta = 0$, might, however, be of no importance since it is multiplied by a product of two transition dipole moment element derivatives. But this reasoning would also hold against the intensities of overtones of non-totally symmetric modes.

In order to judge whether the neglect of Herzberg–Teller terms for totally symmetric modes is a sound assumption, scattering tensor elements calculated using Eqs. (5.1) and (5.17) should be analyzed. Additionally, for totally symmetric modes exhibiting a displacement, the scattering tensor calculated according to Eq. (5.17), which was derived for modes without a displacement, should be tested as an approximate method.

**5.3 Resonance Raman calculation with DNR**

The program DNR [43] allows the computation of various vibrationally resolved optical spectra, i.e., not only RR spectra, but also Raman profiles, vibrational resonance Raman optical activity, and absorption spectra.

The Franck–Condon term Eq. (5.1) had already been implemented in DNR. In the current version of DNR, the Duschinsky effect is neglected. If the Duschinsky effect is included in the calculation, the multi-dimensional overlap integrals needed for the calculation of the scattering tensor elements cannot be decomposed into products of one-dimensional overlap integrals any more. In this work, the existing implementation in DNR was first extended to include Herzberg–Teller terms assuming ground-state and excited-state normal modes as well as the frequencies to be identical. Both approaches, i.e., HT terms for all terms or only two HT contributions for Raman active modes, have been implemented. The computation of HT contributions to RR scattering tensors largely parallels that of the FC terms. Mainly, one-dimensional HT factors had to be added, and some changes in the order of the subroutines were necessary. Before describing the implementation of the HT terms for RR calculations within DNR, first the existing implementation as far as it is relevant shall be described. The DNR program is constructed in a modular way and thus allows to select different routines in which different approaches and approximations to resonance Raman spectra are implemented. Implementing the HT terms is most straightforward (and unfortunately, most computationally demanding) in the sum-over-states ansatz. Therefore, this approach was chosen in connection with the GFC model for the potential energy surfaces.
Figure 5.1: DNR program — flow chart of a GFC model sum-over-states (GFC-SOS) RR calculation

**DNR**
- set input for the program
- determine type of calculations:
  - absorption spectrum
  - resonance Raman spectrum
  - Raman profile

**Input**
- options for type of calculation
- number of vibrational modes
- general options:
  - thresholds, flags etc.
- ground and excited-state data:
  - frequencies, transition moments, energies, mode displacements, damping constants
- number of HT active modes
- trans. dipole moment derivatives
- options for HT calculation

**CalcRRIntensity**
- loop over excited states:
  - add tensor contributions for modes
  - calculate rotational invariants
  - calculate total polarization factor
  - calculate mode-dependent prefactor
  - calculate RR intensity

**MakeResRamanSpectrum**
- loop over ext. perturbation frequencies:
- calculate resonance Raman spectrum
- PlotSpectrum(spectrum(i))

**CalcResRamanSpectrum**
- module selection: module = e.g., GFC
- loop over excited states:
  - calculate contribution of excited state to scattering tensor
  - select type of RR calculation
- loop over modes:
  - calculate RR intensities

**SimpleGFCResRaman**
1. calculate 1D overlap factors (GFC-SOS)
2. loop over modes:
   - calculate FC contribution to scattering tensor elements
   - loop over modes:
     - calculate $3 \times 3$ tensors

for HT terms:
- loop over HT active modes $Q_k, Q_{k'}$:
  - select type of HT calculation
  - loop over modes:
    * calculate HT contribution
    * calculate and add $3 \times 3$ tensors
- add HT contribution to FC scattering tensor

**CalcScatTensor**
- calculate products of dip. moment elements
  for HT terms: dip. moment derivatives
- calculate real and imag. parts of $\alpha$
5.3 Resonance Raman calculation with DNR

Figure 5.2: DNR program — subroutines needed for the GFC-SOS RR calculation

**FCOverlap1D**
- loop over modes i:
  - calculate 1D overlap factors including HT factors
  - determine total number of states
- calculate maximal overlap needed for threshold

**CalcSumOfVibstates_bruteforce**
- loop over intermediate vibrational states:
  - calculate products of 1D overlap factors
    - `vstate%pfc` for vibrational states
  - calculate energy for this vib. state
  - calculate denominators
    - for (off-)res. term
    - calculate tensor contribution
- set tensor contribution

**CalcSumOfVibstates_bruteforce_ht**
- loop over intermediate vibrational states:
  - calculate products of 1D overlap factors
    - `vstate%pfc`, `vstate%phtQm`, `vstate%phtmQ`, `vstate%phtQmQ`
  - calculate energy for this vib. state
  - calculate denominators
    - for (off-)res. term
    - calculate tensor contributions
- set tensor contributions

**QuantaCheck1m0**
- calculate 1D overlap factors
  - `⟨0|v⟩⟨v|0⟩` and `⟨1|v⟩⟨v|0⟩`
  - and determine `v_{max}`

**QuantaCheck1m0_ht**
- calculate 1D overlap factors
  - `⟨0|v⟩⟨v|0⟩`, `⟨1|v⟩⟨v|0⟩` ...
  - and `⟨0|v⟩⟨v|Q|0⟩`, `⟨1|v⟩⟨v|Q|0⟩` ...
  - and determine common `v_{max}`
An outline of the RR calculation can be found in Figs. 5.1 and 5.2. If only FC terms are considered, the transition dipole moments can be moved before the summation over the intermediate vibrational states, which is possible since final and initial electronic state are identical for pure vibrational Raman scattering. The bottleneck of the calculation is the computation of and summation over the nuclear part, i.e., the multi-dimensional FC factors. Planck’s constant is included in the calculation of the energy differences in the denominator. In DNR, the damping term in the denominator of the Kramers–Heisenberg–Dirac expression is substracted from the other terms, following the description in e.g., Ref. [129],

\[
\left(\alpha_{\rho\sigma}\right)_{e^g v^f, e^g v^i} = \left(p_\rho\right)^0_{e^g v^f}\left(p_\sigma\right)^0_{e^g v^i} \times \\
\sum_{v^r} \left\{ \frac{\langle v^f | v^r \rangle \langle v^r | v^i \rangle}{\hbar \omega^{e^g v^f} + \hbar \omega^{v^r v^i} + \hbar \omega_1 - i \hbar \Gamma^{e^g v^f}} + \frac{\langle v^f | v^r \rangle \langle v^r | v^i \rangle}{\hbar \omega^{e^g v^i} + \hbar \omega^{v^r v^f} + \hbar \omega_1 - i \hbar \Gamma^{e^g v^i}} \right\}.
\]

At the beginning of a DNR calculation, the keywords necessary for the run and ground and excited state data are read from the input file \texttt{dnr.control} and saved in specifically defined data types. In the main program, the type of calculation (absorption spectrum, Raman profile or RR) is determined and the corresponding routines are called. For a RR calculation, this is \texttt{MakeResRamanSpectrum}, in which the routine for the calculation of RR spectra is called \texttt{(CalcResRamanSpectrum)} and subsequently the spectra are plotted for a number of excitation frequencies. There are several options in \texttt{CalcResRamanSpectrum} which stand for different approximations to the potential energy surfaces. Here, the simplest, \texttt{SimpleGFCResRaman} is chosen. This implements the GFC model. The task of computing the nuclear part is split into calculating first the one-dimensional overlap integrals, and then the multidimensional overlap integrals are calculated as products for the intermediate vibrational states. Since for each mode a number of vibrational states on the excited state potential energy surface have to be taken into account and multidimensional overlap integrals for all possible combinations have to be considered, the number of multidimensional overlap integrals is huge. For these intermediate vibrational states, the energy difference between ground state \(e^g v^f\) or \(e^g v^i\) and excited state \(e^r v^r\) is calculated as sum of the electronic energy difference and vibrational energy difference: \(\omega^{e^r v^r} + \omega^{v^r v^i}\) or \(\omega^{e^r v^r} + \omega^{v^r v^i}\).

Due to the damping constant \(\Gamma\) in the denominator, there are real and imaginary parts to the resonance and off-resonance terms, which are calculated separately and saved in a \((4 \times 4)\) array. Treating these contributions separately is possible when rewriting the denominator (\(a\) denotes the energy terms) as

\[
\frac{1}{a - i\Gamma} = \frac{a + i\Gamma}{(a - i\Gamma)(a + i\Gamma)} = \frac{a + i\Gamma}{a^2 - i^2\Gamma^2} = \frac{a + i\Gamma}{a^2 + \Gamma^2} = \frac{a}{a^2 + \Gamma^2} + i \frac{\Gamma}{a^2 + \Gamma^2}.
\]

(5.22)
These contributions from the denominator are multiplied by the multidimensional overlap integrals and summed up for all intermediate vibrational states. Subsequently, they are multiplied by the products of the elements of the transition dipole moment to yield the scattering tensor elements. From these, RR intensities are calculated.

Several aspects are important for the calculation of the multidimensional Franck–Condon and Franck–Condon-Herzberg–Teller (FC-HT) factors. On the one hand, the number of vibrational states for the one-dimensional FC or HT factors has to be determined. In principle, the number of intermediate vibrational states $v_k^r$ in a one-dimensional Franck–Condon factor for harmonic vibrational wavefunctions is infinitely large. However, using the completeness relation in Eq. (5.23),

$$\sum_{v_k^r} |v_k^r\rangle\langle v_k^r| = 1,$$

(5.23)

the number of vibrational states $v_{k_{\text{max}}}^r$ can be determined, beyond which further states do not have a significant contribution (in practice, this contribution has to be defined by a threshold $\text{thres1D}$):

$$\sum_{v_k^r=0}^{v_{k_{\text{max}}}^r} \langle 0 | v_k^r \rangle \langle v_k^r | 0 \rangle = 1 - \text{thres1D},$$

(5.24)

$$\sum_{v_k^r=0}^{v_{k_{\text{max}}}^r} \langle 1 | v_k^r \rangle \langle v_k^r | 0 \rangle = \text{thres1D} \quad \text{Raman active mode,}$$

(5.25)

$$\sum_{v_k^r=0}^{v_{k_{\text{max}}}^r} \langle 2 | v_k^r \rangle \langle v_k^r | 0 \rangle = \text{thres1D} \quad \text{overtones.}$$

(5.26)

On the other hand, even a limited number of states in the one-dimensional factors leads to an enormous number of possible combinations for the multidimensional FC (or FC-HT) factors. However, a large part of these factors does not contribute significantly, which calls for a screening of these factors to reduce computational cost. Besides the straightforward brute-force approach to calculate all the factors a prescreening which renders the calculation of very small contributions unnecessary is implemented in Dnr. This is based on the fact that a large number of similar multidimensional FC factors are calculated. For a given mode $j_{\text{min}}$ in the multidimensional factor, the product of the one-dimensional factors for the remaining modes $j_{\text{min}} + 1$ to $j_{\text{max}}$ with a specific combination of quantum numbers can be evaluated. If this partial result is already below the threshold for the complete multidimensional factor, then all factors containing this sequence can be discarded. For an example of eight modes, when $j_{\text{min}}$ equals 1, and when $\prod_{j=2}^{8} \langle 0 | k_j \rangle \langle k_j | 0 \rangle$ is below the threshold for the multidimensional factors, all factors containing $\prod_{j=2}^{8} | k_j \rangle = |0123456\rangle$ are
Table 5.1: Influence of the threshold on the RR intensity for two stilbene modes for $E_{\text{exc}}=4.62$ eV with an external excitation wavelength of 288 nm (4.31 eV). The same value was chosen for the one-dimensional and multi-dimensional thresholds thres1D and thresND in the sum-over-states DNR calculation. Stilbene data from Ref. [3].

<table>
<thead>
<tr>
<th>$\nu$/cm$^{-1}$</th>
<th>thres E-06</th>
<th>thres E-07</th>
<th>thres E-08</th>
<th>thres E-09</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>4.322E-02</td>
<td>4.625E-02</td>
<td>4.640E-02</td>
<td>4.642E-02</td>
</tr>
<tr>
<td>1629</td>
<td>4.269E-01</td>
<td>4.358E-01</td>
<td>4.359E-01</td>
<td>4.360E-01</td>
</tr>
</tbody>
</table>

neglected, i.e., $\langle 00000000|10123456\rangle$, $\langle 00000000|20123456\rangle$, $\langle 00000000|30123456\rangle$ ··· are set to zero.

Of course, the results will depend on the thresholds applied for the one- and multidimensional factors and one has to make sure that results are converged (see Table 5.1). If the multi-dimensional threshold thresND is not given explicitly, it is defined as a function of the one-dimensional threshold thres1D, the number of modes $n_{\text{mod}}$ and the product of the largest absolute $\langle 0|\nu\rangle\langle \nu|0 \rangle$ FC factors $f_{\text{max}}$ of each mode:

$$\text{thresND} = \text{thres1D} \cdot \frac{f_{\text{max}}^2}{n_{\text{mod}}^2}.$$ (5.27)

With Eq. (5.27), a much tighter threshold results (1.656 E-15 with thres1D= E-06 for the stilbene example), so that it can be advantageous to specify a separate thresND-keyword. In those cases, however, convergence of the results should be tested.

5.4 Implementation of Herzberg–Teller terms in DNR

For the calculation of HT terms, the program flow for the FC terms could be adapted with only small modifications. In the input section, keywords for the different HT options (calculation according to Eq. (5.1) or Eq. (5.17), the number of the HT active modes and transition dipole moment derivative data were added. For the computation of the FC factors, the subroutine $\text{QuantaCheck1m0}$ was extended by the calculation of HT factors and placed separately in $\text{QuantaCheck1m0_ht}$. The same value thres1D is used for the determination of the maximum number of vibrational states for a mode $v_{\text{max}}$ as for the FC terms. If a HT keyword is present, then the HT version is used, so that a common $v_{\text{max}}$ and thus the same intermediate vibrational states for FC and HT terms are obtained. In contrast to the calculation of the FC terms, for the HT terms the multiplication with the transition dipole elements and their derivatives cannot be done as the last step, but has to be done...
within the summation over $k$. In principle, two ways of ordering the sums over intermediate vibrational states $v_r$ and the sums over the HT modes $k$ and $k'$ are possible, i.e., 1) the outer sum over $v_r$ and the inner sum(s) over $k, k'$ as is formulated in Eq. (5.1) or 2) the outer sum over $k, k'$ and the inner sum over $v_r$. The latter way was chosen, since this can be better integrated into the existing program structure. For the HT terms, in the subroutine SimpleGFCResRaman loops over the $k, k'$ were added, within which the scattering tensor contributions for a certain combination of Raman active mode and HT active modes $k, k'$ were calculated, i.e., the sum over $v_r$ for the multi-dimensional FC-HT factors divided by the energy denominator. These have to be multiplied by a product of transition dipole moment elements (derivatives) and then all contributions for one specific Raman active mode are summed up. Several subroutines exist for the computation of the scattering tensor contributions (CalcSumOfVibstates): a full HT term calculation following Eq. (5.1) (in a bruteforce sum-over-states or prescreen version) or using approximations given in Eq. (5.17) with prescreening. In Fig. 5.2, only the bruteforce variant for the HT factors is given. The HT prescreen versions work analogously to the FC routine. In contrast to the bruteforce HT calculation, each HT scattering contribution ($vstate\%phtQm, vstate\%phtmQ, vstate\%phtQmQ$) is calculated separately. For the FC-HT factors, the multi-dimensional thresholds $\text{thresND}$ were multiplied once with $\hbar/\omega$ for FC-HT factors containing one mass-weighted normal coordinate $Q_k$ and twice if they contain $Q_k$ and $Q_{k'}$.

### 5.4.1 One-dimensional Herzberg–Teller factors

If HT terms shall be included for RR spectra (with overtones possible) then the following HT factors are needed: $\langle 0\vert v\vert Q\vert 0 \rangle = \langle 0\vert Q\vert v\vert 0 \rangle$, $\langle 1\vert v\vert Q\vert 0 \rangle$, $\langle 2\vert v\vert Q\vert 0 \rangle$, $\langle 1\vert Q\vert v\vert 0 \rangle$, and $\langle 2\vert Q\vert v\vert 0 \rangle$. For the fourth term of Eq. (5.1), if $k = k'$, the following integrals are needed: $\langle 0\vert Q\vert v\vert Q\vert 0 \rangle$, $\langle 1\vert Q\vert v\vert Q\vert 0 \rangle$, and $\langle 2\vert Q\vert v\vert Q\vert 0 \rangle$.

For the FC term, only FC factors are needed. In DNR, recursive formulae were implemented according to a review by Myers et al. [129] and an article by Chinsky et al. [180], who used formulae derived by Manneback [172] and Inagaki et al. [154], respectively. In the latter article, explicit formulae for the calculation of FC integrals and HT integrals are given. These can be used to compare recursive formulae for the expressions for the HT factors given above, which have to be derived to make their computation for larger quantum numbers $v$ feasible. The explicit formulae contain factorials of $v$, which give rise to problems for larger $v$. 

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Explicit formulae for HT factors

Explicit formulae for integrals between the harmonic vibrational ground state $|i\rangle$ and the excited state $|v\rangle$ displaced by $\Delta$ (in reduced normal coordinates $q$) according to Inagaki et al. [154] are:

- Franck–Condon integrals:

  \begin{align*}
  \langle i | v \rangle &= (2^{i+v} i!v!)^{\frac{1}{2}} e^{-\frac{\Delta^2}{\hbar \omega}} \times K \\
  \text{with } K &= \sum_{k} (-1)^{v-k} 2^k \left[ \frac{i!v!}{(i-k)!(v-k)!} \right] \Delta^{i+v-2k}.
  \end{align*}

  The summation over $k$ runs from $k = 0$ to $\min(i, v)$.

  For $i \in \{0, 1, 2\}$ this results in:

  \begin{align*}
  \langle 0 | v \rangle &= (2^v v!)^{\frac{1}{2}} e^{-\frac{\Delta^2}{\hbar \omega}} \times (-1)^v \Delta^v \\
  \langle 1 | v \rangle &= (2^{v+1} v!)^{\frac{1}{2}} e^{-\frac{\Delta^2}{\hbar \omega}} \times \left[ (-1)^v \Delta^{v+1} + (-1)^{v-1} 2v \Delta^{v-1} \right] \\
  \langle 2 | v \rangle &= (2^{v+2} 2v!)^{\frac{1}{2}} e^{-\frac{\Delta^2}{\hbar \omega}} \times \left[ \Delta^{v+2} + (-1)^{v-1} 4v \Delta^v + (-1)^{v-2} 4v(v-1) \Delta^{v-2} \right].
  \end{align*}

- Herzberg–Teller integrals:

  For the integrals containing a normal coordinate, Inagaki et al. use dimensionless normal coordinates $q$ for the integration of the harmonic eigenfunctions. For the integrals this yields the following relation:

  \begin{align*}
  \langle i | Q | v \rangle &= \langle i | q | v \rangle \sqrt{\frac{\hbar}{\hbar \omega}}.
  \end{align*}

  The general formula is given by

  \begin{align*}
  \langle i | q | v \rangle &= \langle i | v \rangle \frac{\Delta}{2} + (2^{i+v} i!v!)^{\frac{1}{2}} e^{-\frac{\Delta^2}{\hbar \omega}} \times (L_1 - L_2) \\
  \text{with } L_1 &= \sum_{k} (-1)^{v-k} 2^k \left[ \frac{i!v!}{(i-1-k)!(v-k)!} \right] \Delta^{i+v-1-2k} \\
  \text{and } L_2 &= \sum_{k} (-1)^{v-k} 2^k \left[ \frac{i!v!}{(i-k)!(v-1-k)!} \right] \Delta^{i+v-1-2k}.
  \end{align*}

  The summation over $k$ runs from $k = 0$ to $\min(v, (i-1))$ for $L_1$ and for $L_2$ to $\min(i, (v-1))$. For $i = 0, L_1 = 0$ and for $v = 0, L_2 = 0$. 

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For $i \in \{0, 1, 2\}$ this results in:

$$
\langle 0 \vert q \vert v \rangle = (2^v v!)^{-\frac{1}{2}} e^{-\frac{\Delta^2}{4}} (-1)^v \Delta^{v-1} \cdot \left[ \frac{\Delta}{2} - v \right] \quad (5.34)
$$

$$
\langle 1 \vert q \vert v \rangle = (2^{v+1} v!)^{-\frac{1}{2}} e^{-\frac{\Delta^2}{4}} (-1)^v \cdot \left[ \frac{\Delta v^2}{2} - 2v \Delta^v + \Delta^v + 2v(v-1) \Delta^{v-2} \right] \quad (5.35)
$$

$$
\langle 2 \vert q \vert v \rangle = (2^{v+3} v!)^{-\frac{1}{2}} e^{-\frac{\Delta^2}{4}} (-1)^v \cdot \left[ \frac{\Delta^v+3}{2} + 2\Delta^{v+1} - 3v \Delta^{v+1} - 4v \Delta^{v-1} + 6v(v-1) \Delta^{v-1} \right]. \quad (5.36)
$$

### Recursion formulae for HT factors

The normal coordinate $Q$ can be expressed in terms of raising and lowering operators of the harmonic oscillators, see Eq. (5.7). Thus, the Herzberg–Teller integrals can be calculated as a linear combination of Franck–Condon integrals [151, 177, 178]:

$$
\langle i \vert Q \vert v \rangle = \sqrt{\frac{h}{2\omega}} \left( \sqrt{i}(i - 1\vert v) + \sqrt{i + 1}(i + 1\vert v) \right). \quad (5.37)
$$

Eq. (5.37) can be employed to derive formulae for products of FC integrals and HT integrals, the HT factors, in terms of FC factors. Direct recursion formulae for HT factors have not yet been derived.

For the HT integrals $\langle i \vert Q \vert v \rangle$ with $i = 0, 1, 2$ this yields:

$$
\langle 0 \vert Q \vert v \rangle = \sqrt{\frac{h}{2\omega}} \langle 1 \vert v \rangle, \quad (5.38)
$$

$$
\langle 1 \vert Q \vert v \rangle = \sqrt{\frac{h}{2\omega}} \left( \sqrt{1}(0\vert v) + \sqrt{2}(2\vert v) \right), \quad (5.39)
$$

$$
\langle 2 \vert Q \vert v \rangle = \sqrt{\frac{h}{2\omega}} \left( \sqrt{2}(1\vert v) + \sqrt{3}(3\vert v) \right). \quad (5.40)
$$

Using Eqs. (14) and (15) in the review by Myers et al. [129], recursion formulae can be derived for FC factors, which had not yet been implemented in DNR but are needed for the HT terms. Note the sign error in the recursion formulae Eqs. (14) and (15) for the overlap integrals in the review by Myers. These equations read (with an added factor of $(-1)^v$ to obtain the correct sign):

$$
\langle i + 1 \vert v \rangle = \left( \frac{v}{i + 1} \right)^{\frac{1}{2}} \langle i \vert v - 1 \rangle - \frac{\Delta}{\sqrt{2}(i + 1)} \langle i \vert v \rangle \cdot (-1)^v, \quad (5.41)
$$

$$
\langle i \vert v + 1 \rangle = \left( \frac{i}{v + 1} \right)^{\frac{1}{2}} \langle i - 1 \vert v \rangle + \frac{\Delta}{\sqrt{2}(v + 1)} \langle i \vert v \rangle \cdot (-1)^v. \quad (5.42)
$$
With Eqs. (5.38)–(5.40) and (5.41)–(5.42), all needed HT factors mentioned above can be computed from FC factors, for some of which recursion formulae have recently been implemented. An overview is given in Table 5.2.

- $\langle 0|v\rangle\langle v|Q|0 \rangle$: Using Eq. (5.38), this HT factor reduces to a FC factor, which had already been implemented, multiplied by the factor $\sqrt{\frac{\hbar}{2\omega}}$:

$$\langle 0|v\rangle\langle v|Q|0 \rangle = \frac{\hbar}{2\omega} \langle 1|v\rangle\langle v|0 \rangle.$$ (5.43)

- $\langle 1|v\rangle\langle v|Q|0 \rangle$: Applying Eq. (5.38), this HT factor reduces to a FC factor, which had not been implemented:

$$\langle 1|v\rangle\langle v|Q|0 \rangle = \sqrt{\frac{\hbar}{2\omega}} \langle 1|v\rangle\langle v|1 \rangle.$$ (5.44)

Using Eqs. (5.41) and (5.42) for the FC integral $\langle 1|v\rangle\langle v|1 \rangle$, the FC factor $\langle 1|v\rangle\langle v|1 \rangle$ can be expressed in terms of an implemented FC factor for $v - 1$:

$$\langle 1|v\rangle\langle v|1 \rangle = \frac{1}{2} e^{-\frac{\Delta^2}{2}} \Delta^2.$$ (5.46)

- $\langle 2|v\rangle\langle v|Q|0 \rangle$: This HT factor reduces to a linear combination of FC factors for $v - 1$, which had already been implemented:

$$\langle 2|v\rangle\langle v|Q|0 \rangle = \sqrt{\frac{\hbar}{2\omega}} \langle 2|v\rangle\langle v|1 \rangle,$$ (5.47)

$$\langle 2|v\rangle\langle v|1 \rangle = \left( \frac{v}{\sqrt{2}} - \frac{\Delta^2}{\sqrt{2^3}} \right) \langle 1|v - 1\rangle\langle v - 1|0 \rangle - \left[ \frac{1}{v} \frac{\Delta^5}{2^3} + ((-1)^v - 1) \frac{\Delta^3}{2^2} - v \frac{\Delta}{2} (-1)^v \right] \times$$

$$\langle 0|v - 1\rangle\langle v - 1|0 \rangle,$$ (5.48)

with $\langle 2|0\rangle\langle 0|1 \rangle = \frac{1}{4} e^{-\frac{\Delta^2}{2}} \Delta^3$. 

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5.4 Implementation of Herzberg–Teller terms in Dnr

• \( \langle 1 | Q | v \rangle \langle v | 0 \rangle \): This HT factor reduces to a linear combination of FC factors, which had already been implemented:

\[
\langle 1 | Q | v \rangle \langle v | 0 \rangle = \sqrt{\frac{\hbar}{2\omega}} \left( \langle 0 | v \rangle + \sqrt{2} \langle 2 | v \rangle \right) \langle v | 0 \rangle
\]
\[
= \sqrt{\frac{\hbar}{2\omega}} \left( \langle 0 | v \rangle \langle v | 0 \rangle + \sqrt{2} \langle 2 | v \rangle \langle v | 0 \rangle \right) . \quad (5.49)
\]

• \( \langle 2 | Q | v \rangle \langle v | 0 \rangle \): This HT factor reduces to a linear combination of FC factors, which had already been implemented:

\[
\langle 2 | Q | v \rangle \langle v | 0 \rangle = \sqrt{\frac{\hbar}{2\omega}} \left( \sqrt{2} \langle 1 | v \rangle + \sqrt{3} \langle 3 | v \rangle \right) \langle v | 0 \rangle
\]
\[
= \sqrt{\frac{\hbar}{2\omega}} \left( \sqrt{2} \langle 1 | v \rangle \langle v | 0 \rangle + \sqrt{3} \langle 3 | v \rangle \langle v | 0 \rangle \right) . \quad (5.50)
\]

• \( \langle 0 | Q | v \rangle \langle v | Q | 0 \rangle \): This HT factor reduces to the FC factor Eq. (5.46):

\[
\langle 0 | Q | v \rangle \langle v | Q | 0 \rangle = \frac{\hbar}{2\omega} \langle 1 | v \rangle \langle v | 1 \rangle . \quad (5.51)
\]

• \( \langle 1 | Q | v \rangle \langle v | Q | 0 \rangle \): This HT factor reduces to a linear combination of a FC factor already implemented and one described above (see Eq. 5.48):

\[
\langle 1 | Q | v \rangle \langle v | Q | 0 \rangle = \frac{\hbar}{2\omega} \left[ \langle 1 | v \rangle \langle v | 0 \rangle + \sqrt{2} \langle 2 | v \rangle \langle v | 1 \rangle \right] . \quad (5.52)
\]

• \( \langle 2 | Q | v \rangle \langle v | Q | 0 \rangle \): The linear combination for this HT factor requires the FC factor \( \langle 3 | v \rangle \langle v | 1 \rangle \):

\[
\langle 2 | Q | v \rangle \langle v | Q | 0 \rangle = \frac{\hbar}{2\omega} \left[ \sqrt{2} \langle 1 | v \rangle \langle v | 1 \rangle + \sqrt{3} \langle 3 | v \rangle \langle v | 1 \rangle \right] , \quad (5.53)
\]
\[
\langle 3 | v \rangle \langle v | 1 \rangle = \left[ \sqrt{\frac{3}{2}} \frac{\Delta^2}{\sqrt{3}} + \frac{1}{\sqrt{\nu^2}} \Delta^4 \right] \langle 2 | v - 1 \rangle \langle v - 1 | 0 \rangle
\]
\[
+ \left[ \frac{1}{\sqrt{4v}} \frac{\Delta^4}{\sqrt{3}} (-1)^v - \frac{\Delta}{\sqrt{3}} (-1)^v \right] \langle 1 | v - 1 \rangle \langle v - 1 | 0 \rangle , \quad (5.54)
\]

with \( \langle 3 | 0 \rangle \langle 0 | 1 \rangle = \frac{1}{4\sqrt{6}} e^{-\Delta^2} \Delta^4 \).

It can be calculated from implemented FC factors for \( v - 1 \).
Table 5.2: Overview of the HT factors and the FC factors they are calculated from. Underlined FC factors had already been implemented in DNR.

<table>
<thead>
<tr>
<th>HT factor</th>
<th>FC factors</th>
<th>FC factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle 0</td>
<td>v\rangle\langle v</td>
<td>Q</td>
</tr>
<tr>
<td>$\langle 1</td>
<td>v\rangle\langle v</td>
<td>Q</td>
</tr>
<tr>
<td>$\langle 2</td>
<td>v\rangle\langle v</td>
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<td>$\langle 2</td>
<td>v\rangle\langle v</td>
</tr>
<tr>
<td></td>
<td>$\langle 2</td>
<td>Q</td>
</tr>
<tr>
<td></td>
<td>$\langle 3</td>
<td>v\rangle\langle v</td>
</tr>
<tr>
<td></td>
<td>$\langle 0</td>
<td>Q</td>
</tr>
<tr>
<td></td>
<td>$\langle 1</td>
<td>Q</td>
</tr>
<tr>
<td></td>
<td>$\langle 2</td>
<td>v\rangle\langle v</td>
</tr>
<tr>
<td></td>
<td>$\langle 2</td>
<td>Q</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\langle 3</td>
</tr>
</tbody>
</table>

5.4.2 Sum rules for Herzberg–Teller integrals

In order to determine the maximum number of vibrational states for one mode, $v_{\text{max}}$, required in the sum in Eq. (5.1), such that the completeness relation is fulfilled to within a threshold, sum rules for the HT factors have to be exploited:

\[
\sum_v \langle 1|v\rangle\langle v|Q|0\rangle = \langle 1_g|Q|0_g\rangle = \sqrt{\frac{\hbar}{2\omega}}, \quad (5.55)
\]

\[
\sum_v \langle 1|Q|v\rangle\langle v|0\rangle = \langle 1|Q|0\rangle = \sqrt{\frac{\hbar}{2\omega}}, \quad (5.56)
\]

\[
\sum_v \langle 0|v\rangle\langle v|Q|0\rangle = \langle 0|Q|0\rangle = 0, \quad (5.57)
\]

\[
\sum_v \langle 0|Q|v\rangle\langle v|0\rangle = \langle 0|Q|0\rangle = 0, \quad (5.58)
\]

\[
\sum_v \langle 2|Q|v\rangle\langle v|0\rangle = \langle 2|Q|0\rangle = 0, \quad (5.59)
\]

\[
\sum_v \langle 2|Q|v\rangle\langle v|Q|0\rangle = \langle 2|Q|0\rangle = 0, \quad (5.60)
\]

\[
\sum_v \langle 0|Q|v\rangle\langle v|Q|0\rangle = \langle 0|Q^2|0\rangle = \frac{\hbar}{2\omega}, \quad (5.61)
\]

\[
\sum_v \langle 1|Q|v\rangle\langle v|Q|0\rangle = \langle 1|Q^2|0\rangle = 0, \quad (5.61)
\]

\[
\sum_v \langle 2|Q|v\rangle\langle v|Q|0\rangle = \langle 2|Q^2|0\rangle = \sqrt{2}\frac{\hbar}{2\omega}. \quad (5.62)
\]
The resulting integrals after invoking closure contain two wavefunctions on the same potential energy surface.

Currently, $v_{\text{max}}$ for each mode is determined during the calculation of the one-dimensional FC and HT factors. For every $v$, it is tested whether the condition given in Eqs. (5.24–5.26) for FC factors, or conditions analogously defined for HT factors according to Eqs. (5.55–5.62), are fulfilled. There is only one $v_{\text{max}}$ per mode, which is the largest among those obtained from different FC and HT factors, so that for one mode, the same number of intermediate states is taken into account for all FC and HT factors. However, in the current implementation, if the first term for a HT factor is very small or if, e.g., for $\Delta = 2n$, the first terms cancel exactly, a wrong $v_{\text{max}}$ can result. This problem should be circumvented by determining $v_{\text{max}}$ values in dependence of the $\Delta$ value. $v_{\text{max}}$ for all relevant FC and HT factors. For different FC factors, $v_{\text{max}}$ values for $\Delta$ values up to 10.0 are shown in Fig. 5.3. Similar plots are obtained for the HT factors. Judging from these plots, the relation between $v_{\text{max}}$ and the FC or HT factors is not linear, but one could define two regions for a fit. Such a fit has not been implemented yet, which makes it necessary that results are checked with respect to the $v_{\text{max}}$ values. However, since the $v_{\text{max}}$ value is not determined separately for the FC and HT factors but for every $v$ the termination conditions are tested for all relevant factors, no problems should occur in practice. Using a fit would make the calculation a little bit faster, though.

Figure 5.3: Maximum quantum number $v_{\text{max}}$ for the factors $\langle X|v\rangle\langle v|0\rangle$ with $X=0,1,2,3$ and a threshold of $10^{-8}$ in dependence of the displacement $\Delta$. 

![Figure 5.3](image-url)
5.4.3 Tests for the FC factors

The newly implemented formulae for \( \langle 1|v\rangle\langle v|1 \rangle \), \( \langle 2|v\rangle\langle v|1 \rangle \) and \( \langle 3|v\rangle\langle v|1 \rangle \) have to be checked. Because of the sign error for the overlap integrals in Eqs. (14) and (15) in the review by Myers et al. [129], which were used to derive the formulae for the integral products, these overlap integrals were checked first and compared against the explicit formulae given by Inagaki et al. [154] and Minaev et al. [178], see Tables 5.3–5.5. With the corrected sign, identical values result. The products of integrals given by Chinsky et al. [180] yield the same results as direct multiplication of the Inagaki integrals, as do the formulae derived for \( \langle 1|v\rangle\langle v|1 \rangle \), \( \langle 2|v\rangle\langle v|1 \rangle \) and \( \langle 3|v\rangle\langle v|1 \rangle \) using the sign corrected recursion formulae, see Tables 5.6–5.8. For the tests, a value of 0.4 was used for \( \Delta \).

Table 5.3: Overlap integrals \( \langle 0|v\rangle \) obtained by formulae given by Inagaki [154], Minaev [178] and Myers [129]. The * denotes that the formula was multiplied by \((-1)^v\).

<table>
<thead>
<tr>
<th>( v )</th>
<th>Inagaki</th>
<th>Minaev</th>
<th>Myers</th>
<th>Myers*</th>
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</tr>
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</tr>
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<td>0.00000000</td>
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</tbody>
</table>

Table 5.4: Overlap integrals \( \langle 1|v\rangle \) obtained by formulae given by Inagaki [154], Minaev [178] and Myers [129]. The * denotes that the second term of the formula was multiplied by \((-1)^v\).

<table>
<thead>
<tr>
<th>( v )</th>
<th>Inagaki</th>
<th>Minaev</th>
<th>Myers Eq. (14)*</th>
<th>Myers Eq. (15)*</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-0.36894314</td>
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</tr>
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<td>-0.01739577</td>
<td>-0.01739577</td>
</tr>
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<td>0.00276174</td>
<td>0.00276174</td>
</tr>
<tr>
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</table>
5.4 Implementation of Herzberg–Teller terms in DNR

Table 5.5: Overlap integrals $\langle 2|v \rangle$ obtained by formulae given by Inagaki [154], Minaev [178] and Myers [129]. The * denotes that the second term of the formula was multiplied by $(-1)^v$.

<table>
<thead>
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<th>Myers</th>
<th>Myers Eq. (14)*</th>
<th>Myers Eq. (15)*</th>
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</thead>
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</tr>
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</tr>
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</tr>
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Table 5.6: Franck–Condon factors $\langle X|v \rangle \langle v|0 \rangle$ for $X = 0, 1, 2$ obtained by recursive formulae given by Chinsky [180] and by products of overlap integrals given by Inagaki [154].

<table>
<thead>
<tr>
<th>$v$</th>
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<th>Inagaki</th>
<th>Chinsky</th>
<th>Inagaki</th>
<th>Chinsky</th>
<th>Inagaki</th>
</tr>
</thead>
<tbody>
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<td>v \rangle \langle v</td>
<td>0 \rangle$</td>
<td>$\langle 0</td>
<td>v \rangle \cdot \langle 0</td>
<td>v \rangle$</td>
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<td>0.26109673</td>
<td>0.26109673</td>
<td>0.05221935</td>
<td>0.05221935</td>
</tr>
<tr>
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<td>-0.24020899</td>
<td>-0.24020899</td>
<td>-0.10026114</td>
<td>-0.10026114</td>
</tr>
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<td>-0.02005223</td>
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<td>0.04403135</td>
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<td>0.00000000</td>
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Table 5.7: Franck–Condon factors $\langle X | v \rangle \langle v | 1 \rangle$ for $X = 1, 2$ obtained by the recursive formulae Eqs. (5.46) and (5.48) and by products of overlap integrals given by Inagaki [154]. The terms have been summed up to check the convergence to the closure relation value.

<table>
<thead>
<tr>
<th>$v$</th>
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<th>Inagaki</th>
<th>$\sum_v$</th>
<th>Eq. (5.48)</th>
<th>Inagaki</th>
<th>$\sum_v$</th>
</tr>
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</tr>
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</tr>
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<td>0.0015828</td>
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<tr>
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<td>0.0000428</td>
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<td>0.0000000</td>
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<tr>
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<td>0.0000000</td>
<td>0.0000000</td>
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<td>0.0000000</td>
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<tr>
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<td>0.0000000</td>
</tr>
</tbody>
</table>

Table 5.8: Franck–Condon factors $\langle X | v \rangle \langle v | 1 \rangle$ for $X = 3$ obtained by the recursive formulae Eq. (5.54) and by products of overlap integrals given by Inagaki [154]. The terms have been summed up to check the convergence to the closure relation value.

<table>
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<th>$\sum_v$</th>
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</thead>
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</tr>
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<td>0.00000001</td>
<td>0.00000000</td>
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<tr>
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<tr>
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<td>0.00000000</td>
<td>0.00000000</td>
</tr>
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</table>
5.5 Exemplary calculations for a $C_s$-symmetric skatole structure

As a test system for calculations including HT terms in Raman spectra, the $C_s$ symmetric molecule skatole has been chosen (see Fig. 5.4). On the one hand, skatole is the basic structural motif determining the RR spectra of the amino acid Trp, where HT terms are discussed to play a role for some excited states [26]. On the other hand, skatole as a $C_s$ symmetric molecule allows one to study modes separately according to their symmetry and establish the importance of HT terms for totally and non-totally symmetric modes. With 51 vibrational modes, it is of a size which is still feasible for a calculation including all HT terms, but can be assumed large enough, so that effects resulting from approximations or applied screening thresholds can be observed.

Figure 5.4: B3LYP/TZVP optimized structure of skatole ($C_s$).

5.5.1 Numerical derivatives of the transition dipole moment elements and excited-state displacements $\Delta$

Derivatives of the transition dipole moment elements can be determined numerically in a straightforward manner. The data for the DNR test calculations for the HT terms were obtained from TURBOMOLE and SNF calculations. Frequencies and normal modes for a B3LYP/TZVP optimized $C_s$ symmetric skatole were calculated, and structures displaced by 0.01 $\sqrt{\text{amu}}$ · bohr along the 17 $a''$-symmetric mass-weighted normal modes were generated. For these and the minimum energy structure the first ten excited states were obtained with B3LYP/TZVP. For the numerical derivatives of the transition dipole moment elements, a three-point formula was used. The sign of the transition dipole matrix elements and their derivatives has to be handled with care: These signs are not uniquely defined. However, as long as both transition dipole matrix element (derivatives) in the numerator of the sum-over-states expressions Eq. (5.1) and Eq. (5.17) follow the same sign convention, the sign of the product will not be affected. Another sign issue occurs in the numerical
Herzberg–Teller Terms in Resonance Raman Spectroscopy

determination of the derivative. When comparing transition dipole moments for two structures, the sign can switch in three places. The pairs of molecular orbitals involved in the transition and the coefficients in the excited-state calculation can change their sign. For all displaced structures, the sign had to be determined in relation to the minimum structure, so that the correct derivative was yielded. The definition of the normal mode itself is only defined up to an arbitrary sign. As long as the same sign is used for the displaced structures and in the determination of the displacement $\Delta q$, signs will be consistent. This is guaranteed, as the displacements have been calculated with the program transgrad [188] using the normal modes from the SNF output file, along which the structures have been displaced. All data for the skatole molecule can be found in Table 5.10. Another possibility, which is more practicable for middle-sized to large molecules, would be to extract the numerical derivatives with respect to normal modes directly from output files of the VIBRON program [189] implemented in the ADF program package.

For the numerical derivatives, the accuracy depending on step size, integration grid and SCF convergence criteria were tested, see Table 5.9. Differences are of the order of $10^{-4}$ a.u./$\sqrt{\text{amu-bohr}}$. It appears that choosing a step size of 0.01 $\sqrt{\text{amu-bohr}}$ with standard SCF convergence criteria for calculations on excited states (scfconv 7, $1 \cdot 10^{-7}$ for the energy) and a standard integration grid ("M3") is reasonable. For smaller step sizes, the last digit will show larger deviations, for larger step sizes, one has to ensure to be still in the harmonic region. The results obtained with the larger integration grid M4 and stricter SCF convergence criteria surprisingly fail more often to reproduce the value of 0.0000 $\sqrt{\text{amu-bohr}}$, which is given by symmetry.

Table 5.9: Influence of step size, integration grid and SCF convergence criteria on numerical transition dipole moment element derivatives for the first three excited states of skatole and the $a''$-symmetric mode $\nu_{20} = 916 \text{ cm}^{-1}$. Derivatives of the transition dipole moment elements are given in a.u./$\sqrt{\text{amu-bohr}}$.

<table>
<thead>
<tr>
<th>state</th>
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<th>grid M4</th>
<th>scfconv 8</th>
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</thead>
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<td>0.01 0.02</td>
<td>0.01 0.02</td>
</tr>
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<td></td>
</tr>
<tr>
<td></td>
<td>y 0.0000 0.0000 0.0000</td>
<td>0.0001 0.0004</td>
<td></td>
</tr>
<tr>
<td></td>
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<tr>
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<tr>
<td></td>
<td>y 0.0000 0.0000 0.0000</td>
<td>-0.0002 0.0004</td>
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</tr>
<tr>
<td></td>
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<td></td>
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<td>0.0117 0.0121</td>
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<td></td>
<td>z 0.0000 0.0000 0.0000</td>
<td>0.0000 0.0000</td>
<td></td>
</tr>
</tbody>
</table>

Since the transition dipole moment element derivatives are obtained in the unit a.u./$\sqrt{\text{amu-bohr}}$, they have to be converted to a.u./$\sqrt{\text{kg-m}}$, in order to be consistently used with transition dipole moment elements in a.u. and HT terms expressed using $\sqrt{\hbar/\omega}$ in SI units.

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5.5 Exemplary calculations for a $C_s$-symmetric skatole structure

Table 5.10: Data for test calculations on skatole: frequencies $\nu_k$, excited-state displacements $\Delta q_k^*$ and transition dipole moment derivatives for the $a'$ and $a''$ symmetric modes. For the $a'$ symmetric modes, the $z$ component of the transition dipole moment derivative is zero, while for the $a''$ symmetric modes the $x$ and $y$ components as well as $\Delta q_k^*$ are zero.

<table>
<thead>
<tr>
<th>$\nu_k$/cm$^{-1}$</th>
<th>$\Delta q_k^*$</th>
<th>$(p)_k$</th>
<th>$\nu_k$/cm$^{-1}$</th>
<th>$(p)_k$</th>
</tr>
</thead>
<tbody>
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<td>$a'$</td>
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<td>$y$</td>
<td>$a''$</td>
<td>$z$</td>
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<td>0.00815</td>
<td>0.01135</td>
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<tr>
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<td>0.00660</td>
<td>154.4</td>
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5.5.2 DNR test calculations

The DNR test calculations have been performed for the first excited state at 4.62 eV with a laser excitation frequency of 266 nm (4.66 eV) and Γ = 50 cm$^{-1}$. A small subset of the modes, including 5 $a''$ symmetric and 8 $a'$ symmetric modes in the range of 700 cm$^{-1}$ and 1200 cm$^{-1}$, was employed to investigate physical as well as technical aspects: For these modes, the relevance of off-resonance terms will be studied first. Furthermore, the different routines for the calculation of the multi-dimensional FC-HT factors, i.e., bruteforce (bruteforce) and prescreen (prescreen) sum-over-states calculation according to Eq. (5.1) and prescreen sum-over-states calculation according to Eq. (5.17) and Eq. (5.18) (dubbed htsimp) will be compared to a calculation of only FC terms and the contributing terms will be analyzed. Additionally, a modified version of the prescreen routine, which omits the second-order HT terms is tested. In order to verify whether the spectrum for a subset of modes is related to the information of the spectrum for the complete set of modes, the influence of the number of $a'$ and $a''$ symmetric modes included in the calculation will be studied. For the complete set of modes of the skatole molecule, FC and different approximate HT spectra will be presented.

Relevance of off-resonance terms

For resonance Raman spectra, the off-resonance terms are often dropped. Relative intensities obtained from bruteforce calculations, including off-resonance terms or neglecting them, are given in Table 5.11.

Table 5.11: Relative intensities with and without off-resonance terms calculated for the 1$^1A$ state of the skatole molecule for a subset of modes, with HT terms included for $a'$ and $a''$ modes in bruteforce calculations. For comparison, intensities are scaled such that the highest intensity is 1.00000.

<table>
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5.5 Exemplary calculations for a \( C_s \)-symmetric skatole structure

As can be seen, the change in the scaled intensities is of the order of \( 10^{-4} \), that is, the relative intensities are nearly identical, independent of the inclusion of off-resonance terms. Therefore, in the following, off-resonance terms will not be considered.

Comparison of different approaches to resonance Raman spectra including HT terms

In Table 5.12, the different approaches for the calculation of RR intensities including HT terms in \( D_{nr} \) are compared for a subset of 5 \( a'' \) symmetric modes and 8 \( a' \) symmetric modes of skatole. For comparison, the FC term intensities are also given.

Table 5.12: Relative RR intensities obtained for a subset of 5 \( a'' \) and 8 \( a' \) symmetric modes of skatole. Results for the FC terms only, HT terms for only \( a'' \) symmetric modes, and HT terms for all modes using different approximations. In the modified \texttt{prescreen*} routine, the second-order HT terms are omitted. \texttt{prescreen} results are compared to a \texttt{bruteforce} calculation.

<table>
<thead>
<tr>
<th>( \nu / \text{cm}^{-1} )</th>
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<tr>
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</tr>
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</table>

The first point noted concerns a merely technical issue: The results obtained with the \texttt{bruteforce} and \texttt{prescreen} routine, taking into account HT terms for all 13 modes should yield the same results. This holds true for the \( a' \) symmetric modes. For the \( a'' \) symmetric modes, the results differ. The largest difference is \( 4 \cdot 10^{-3} \), which shows that the applied threshold for the prescreening of the HT
Herzberg–Teller Terms in Resonance Raman Spectroscopy

terms yields results which are not as accurate as for the FC terms. The large number of small HT terms sets a limit to the accuracy if the computation should still lead to results in a reasonable time. On the same workstation computer, the bruteforce calculation takes nearly nine days compared to less than two minutes for the prescreen calculation. Since both give close results, and the bruteforce routine is not feasible for larger molecules, the bruteforce routine shall be reserved to generate reference results to determine the prescreening thresholds. HT terms are often considered to be important only for non-totally symmetric modes which do not exhibit FC term activity, in this case the $a''$ symmetric modes. Taking the HT terms into account only for these $a''$ symmetric modes could therefore be a good approximation. All routines applying prescreening exhibit the same relative intensities for the $a''$ symmetric modes, the intensities for the $a'$ modes however show differences. These will be discussed in more detail below, according to an analysis of the output of the calculation.

For $a''$ symmetric modes, HT contributions are all of first order in $Q_k$ and arise only if $Q_k$ is the raman active mode. These terms are calculated in all routines, which is why the contributions for $a''$ modes are identical for routines using prescreening, see Table 5.12. First-order HT contributions for Raman active $a'$ modes result, if $Q_k$ is the Raman active mode, i.e., terms where the Raman active mode effects HT coupling. Furthermore, contributions to Raman active $a'$ modes arise either from Rayleigh-type second-order HT terms, if $Q_k = Q_{k'}$ is an $a''$ symmetric mode or for any combination of $a'$ modes $Q_k$ and $Q_{k'}$ (first and second-order terms). All of these terms are included in the prescreen calculation. The differences between the htsimp and the full prescreen HT contributions can be of positive or negative sign, so that they could also diminish the relative intensity compared to the FC term calculation.

If HT terms are only calculated for $a''$ symmetric modes using the htsimp and prescreen routine, the $a'$ mode intensities differ by the second-order Rayleigh term HT contributions caused by the $a''$ modes included in the latter routine. The increase or decrease in intensity is in this example $1.5 \times 10^{-4}$ for the most intense mode ($\tilde{\nu} = 1000.5 \text{ cm}^{-1}$), in general the qualitative difference is small. The htsimp routine has been employed as an approximate method for HT terms for both $a'$ and $a''$ symmetric modes. Differences in the intensities can be attributed to the missing second-order terms and the fact that the HT contributions were derived for non-totally symmetric modes with zero displacement. Comparing the $a'$ mode intensities to the prescreen calculation, differences appear in the first position after the decimal point, which corresponds to a factor of two for the least intense mode ($\tilde{\nu} = 719.3 \text{ cm}^{-1}$). On the other hand, significant changes (cf. $\tilde{\nu} = 890.5 \text{ cm}^{-1}$ and $\tilde{\nu} = 1091.6 \text{ cm}^{-1}$) are reproduced. Thus, this constitutes still a better approximation to the full calculation than the htsimp calculation including only HT contributions from $a''$ symmetric modes. In the studied example, the HT second-order tensor elements are as large as $-3.06$ compared to $-223.1$ for the most intense FC mode. For molecules with a large number of modes, the missing terms can possibly add up to a large contribution. However, since the contributions which are added up have different signs they cancel to large extent, so that the main discrepancy can be traced back to the approximation of identical modes for displaced modes. Indeed, when
the prescreen routine is modified so that only first-order HT terms are computed (prescr. in Table 5.12), the differences to the prescreen results reduce to $7 \cdot 10^{-2}$ at most for this example. This approximation comes with the great advantage that it still scales linearly with the number of HT modes, so that it is feasible for larger molecules.

In Fig. 5.5, the resulting spectra are presented. The comparison of the spectra clearly shows that contrary to the textbook wisdom that HT terms are most important for non-totally symmetric modes, apparent changes are connected to the totally symmetric modes in this example ($\tilde{\nu} = 890.5 \text{ cm}^{-1}$ and $\tilde{\nu} = 1091.6 \text{ cm}^{-1}$). The only $a''$ symmetric mode which is visible if only HT contributions for $a''$ modes are considered, is the vibration at $\tilde{\nu} = 947.4 \text{ cm}^{-1}$.

Figure 5.5: RR spectra obtained for a subset of 5 $a''$ and 8 $a'$ symmetric modes of skatole. Results for the FC terms only, HT terms for only $a''$ symmetric modes and HT terms for all modes using different approximations. The highest intensity in each spectrum was scaled to 1.
Effect of the number of FC and HT modes on the RR spectra

For molecules with a large number of vibrations, a calculation including all modes becomes computationally demanding. Often, the relevant part of the spectrum is confined to a specific wavenumber region. If the calculation can be restricted to only a part of the modes, the effort will be reduced considerably. In order to test whether such a reduction to a subset of modes gives reasonable results, the subset considered before was modified by removing two \( a' \) symmetric modes, or one \( a'' \) symmetric mode, see Fig. 5.6.

Figure 5.6: RR spectra obtained for subsets of 5 \( a'' \) and 6 \( a' \) symmetric modes (a) and (d)), 4 \( a'' \) and 8 \( a' \) symmetric modes, (b) and (e)) and 5 \( a'' \) and 8 \( a' \) symmetric modes (c) and (f)) of skatole. Results for the FC terms only, and FC and HT terms for all modes using the prescreen routine are shown. The highest intensity in each spectrum was scaled to 1.

Decreasing the number of \( a' \) symmetric modes by two drastically changes the relative intensity (cf. Fig. 5.6, panel a) to c) and panel d) to f)): For FC term intensities as well as HT term intensities, the enhancement pattern changes. The vibrations at \( \tilde{\nu} = 774.5 \text{ cm}^{-1} \) and \( \tilde{\nu} = 890.5 \text{ cm}^{-1} \) gain, whereas the modes above 1100 cm\(^{-1}\) lose intensity.
Removing an $a''$ symmetric mode from the subset, on the other hand, does not have such a strong impact on the spectra. In a pure FC term calculation (cf. Fig. 5.6, panel b) to c) and panel e) to f)), the number of $a''$ modes does not have any influence, while in the HT calculation, there is a change for the totally symmetric modes, too, due to the Rayleigh term contribution of the $a''$ modes. However, this difference is negligibly small.

Hence if a subset of modes has to be chosen for a RR calculation including HT terms, it must necessarily contain all totally symmetric modes, whereas the non-totally symmetric modes can be selectively chosen.

**FC-HT Resonance Raman Spectra of Skatole**

As shown above, meaningful RR calculations must contain the complete set of totally symmetric modes. For skatole, calculations for the complete set of modes were performed. All calculations for the subsets of modes presented before had been performed with the arbitrarily chosen damping constant value of $\Gamma = 50 \text{ cm}^{-1}$. For such a small value of $\Gamma$, a strong dependence of relative intensities on the laser excitation frequency could be observed. The more reasonable value of $\Gamma = 500 \text{ cm}^{-1}$ was therefore used for the calculations on the full set of modes, which compares better with other calculated spectra. The skatole molecule with its 51 vibrational modes already poses a challenge if no approximations are applied to the HT term calculation: employing the prescreen routine takes more than two months on a workstation.

Among the approximate approaches, the modified prescreen routine (i.e., without second-order terms), the htsimp routine as well as calculations including HT contributions only for the $a''$ modes were performed. The relative intensities are presented in Table 5.13 (for $a''$ symmetric modes) and Table 5.14 (for $a'$ symmetric modes), the resulting spectra are shown in Fig. 5.7.

As noted for the small subsystem of 13 modes, the same intensities of $a''$ symmetric modes are obtained independent of the routine. The highest intensity among the $a''$ symmetric modes is observed for $\tilde{\nu}=947.4 \text{ cm}^{-1}$ and $\tilde{\nu}=795.2 \text{ cm}^{-1}$. On close inspection, these two peaks can be detected in the spectra shown in the panels b) to d) in Fig. 5.7. Yet, these peaks can hardly be regarded as distinctive for the appearance of the spectrum. Accordingly, the spectrum calculated including HT terms for the $a''$ symmetric modes using the htsimp routine looks very similar to the FC spectrum, since the $a'$ symmetric modes are represented by their FC term intensities. The same holds for the prescreen routine, applied to the $a''$ symmetric modes. The second-order terms have merely a small influence on the $a'$ symmetric modes, see Table 5.14, but correspond to a significant increase in computer time. In principle, the symmetry can be taken into account in the implementation such that second-order contributions to $a'$ symmetric modes need only be calculated for $Q_k(a') = Q_k(a')$ and a linear scaling results. Yet the marginal differences compared to the htsimp results do not justify this additional effort. Spectra which do not neglect the HT contribution to totally symmetric modes are shown in panel c) and d) of Fig. 5.7, and were obtained by the htsimp routine and the modified...
prescreen\textsuperscript{*} routine applied to all modes. Intensities from the prescreen routine including the second-order terms cannot be presented yet, since the calculation takes approximately three months. Judging by the results for the subsystem (cf. Table 5.12), the modified prescreen\textsuperscript{*} intensities will be more similar to the complete prescreen than to the htsimp results. Both routines scale linearly but the htsimp is obviously faster (in this example of the order of one hour compared to two days), which can at least partly be attributed to differences in the implementation.

Figure 5.7: RR spectra for skatole obtained with different approaches to calculate HT contributions, the FC term spectrum and the difference between modified prescreen\textsuperscript{*} HT and FC spectrum are given for comparison.
5.5 Exemplary calculations for a $C_\text{s}$-symmetric skatole structure

By comparing the intensities obtained with the modified prescreen$^*$ routine to the FC intensities, an estimate for the magnitude of the HT effect for the $a'$ symmetric modes can be made (see Fig. 5.7, panel e)). For these results, the HT contributions are positive for all modes. The largest HT contribution appears for the peak at $\tilde{\nu} = 1658.2$ cm$^{-1}$, followed by the peak at $\tilde{\nu} = 1616.6$ cm$^{-1}$. This corresponds to the largest transition dipole moment derivatives in Table 5.10. A similar observation can be made for the other modes with large HT contributions. In general, the transition dipole moment derivatives are of comparable magnitude as the transition dipole moments and cannot justify the neglect of terms. If one compares the overall appearance of the RR spectrum including HT terms shown in Fig. 5.7, panel d) to the FC spectrum in panel a), the most striking differences are the changed intensity patterns of the three peaks around 1600 cm$^{-1}$ and the two peaks below 1200 cm$^{-1}$, and the additional peak below 900 cm$^{-1}$. The characteristic features of the RR spectrum are determined by the FC spectrum, but for an accurate description including HT terms is necessary.

Table 5.13: Relative intensities (without off-resonance term, $\Gamma = 500$ cm$^{-1}$) calculated for the $1^1A$ state of the skatole molecule, with HT terms included for $a''$ modes only and $a'$ and $a''$ modes in a full and an approximative (htsimp) calculation. Intensities for $a'$ modes.

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<th>HT terms: $a'$ and $a''$ modes</th>
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Table 5.14: Relative intensities (without off-resonance term, $\Gamma = 500\text{cm}^{-1}$) calculated for the $1^1A$ state of the skatole molecule, with HT terms included for $a''$ modes only and $a'$ and $a''$ modes in a full and an approximative (htsimp) calculation. Intensities for $a'$ modes.

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<th>HT terms: $a'$ and $a''$</th>
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5.6 Conclusions for Herzberg–Teller terms with DNR

The sum-over-states implementation for resonance Raman spectra in DNR has been extended to calculate HT terms within the IMDHO model. For that purpose, one-dimensional HT factors have been implemented and the existing prescreen and bruteforce routines for the computation of the FC factors have been modified to include HT terms. Since the bruteforce routine does not allow the treatment of anything but very small systems, it is only of use to produce reference data and to determine the screening thresholds. Even the prescreen routine, which comprises second-order terms and therefore scales quadratically with the number of modes, is for middle-sized molecules such as skatole not feasible within a reasonable time. For these cases, a modified prescreen* routine without second-order terms has been devised. Furthermore, an approximate expression often mentioned when discussing HT terms, in which the HT treatment is restricted to linear terms and non-totally symmetric modes, was implemented and dubbed htsimp. Selecting all modes or only a subset of a specific symmetry for the HT calculation, combined with the three implemented routines, defines a hierarchy of approximations to treat HT terms. These have been evaluated for a test case, the RR spectrum for the first excited state of the $C_s$ symmetric skatole. For the HT terms of $a'$ symmetric modes no approximations are necessary, all approaches yield the same intensities. If only these terms are of interest, the htsimp routine is sufficient. As an approximate approach it is of value also for the computation of HT contributions for $a''$ modes due to its high efficiency. For middle-sized systems, HT for non-totally symmetric modes can be obtained with the prescreen* routine, which scales linearly and is a good compromise between accuracy and efficiency. The prescreen routine represents the best possible treatment but due to its unfavourable scaling it is only applicable to small molecules.

The wide-spread belief that HT contributions are mainly important for non-totally symmetric modes and negligible for totally symmetric modes could not be verified. On the contrary, for the studied RR spectrum of skatole the opposite is the case. Qualitatively, HT terms are crucial for non-totally symmetric modes since they are zero in the Condon approximation, but quantitatively, the HT contributions for totally symmetric modes determine the intensity pattern of the spectrum. Following the textbook argument that efficient HT coupling for totally symmetric modes requires close-lying excited states of the same symmetry [136], an explanation for the large HT terms for totally-symmetric modes in skatole might be that the next totally-symmetric excited state with a high oscillator strength is close in energy, that is 4.616 eV to 4.865 eV (obtained with B3LYP/TZVP). Whether skatole is a special case or totally symmetric modes must generally be accounted for in a HT treatment, has to be determined in further studies.

In practice, the classification of the modes according to symmetry and accordingly a differentiated treatment is often not possible, since the studied systems such as biomolecules are predominantly of $C_1$ symmetry. For the application to these cases, restrictions using the approximate local symmetry could be useful.
6 Simple Resonance Raman Models for the Photochemistry of Nitroarenes

6.1 Simple resonance Raman approaches

For an accurate description of resonance Raman (RR) intensities, formulae derived from the Kramers–Heisenberg–Dirac equation including information on the vibronic levels of the system, and additionally including vibronic coupling terms, are needed. However, especially for the application to biomolecules, where resonance Raman spectroscopy shows its strength, the computational cost rapidly becomes prohibitively large for such a procedure. Even a limitation to Franck–Condon terms still requires expensive calculations, unless very simple models for the potential energy surfaces are applied and the sum-over-states formalism is replaced by a time-dependent description. Heller’s gradient approximation [33] (see Section 4.3.4, Eq. (4.31)) provides an even easier way to obtain RR intensities, which has been shown to work especially well for large molecules. In Ref. [33] it is stated that this approximation is valid for preresonance conditions, and even for resonance conditions if many modes and large displacements are involved. This approximation has found wide-spread use for the calculation of relative RR intensities due to its comparative simplicity and reliable results [11,19,24,190–193]: In order to obtain a RR spectrum, only the minimum structure, ground-state frequencies and the (Cartesian) gradient of the excited state in resonance are necessary. The damping constant Γ and excited-state energy are not needed, which has been considered a deficiency in comparison to transform theory formulations for RR intensities [168]. In practice one is confronted with the problem of the accurate determination of excitation energies in order to identify the excited state in resonance. This is of great importance, since the approximation regards (pre-)resonance with one single excited electronic state, although schemes to apply it to several excited states have been devised [190,194]. We employed both the time-dependent formalism (see Section 4.3.4) in combination with the Gradient Franck–Condon model, i.e., using the independent mode harmonic oscillator (IMDHO) approximation for the potential energy surfaces (see Section 4.3.1) and the gradient approximation to study photoproducts of ortho-nitrobenzaldehyde (NBA) and ortho-nitrotoluene (oNT). For the excitation energies and excited-state properties, time-dependent density-functional theory (TDDFT) calculations were performed. For oNT, we set out to verify these results by more
involved wavefunction methods, i.e., a coupled cluster method (RICC2) and complete active space self-consistent field (CASSCF) calculations followed by a second-order perturbation treatment (CASPT2). These theoretical results were compared to experimental femtosecond stimulated Raman spectroscopy (FSRS) results. Several prototypical nitroarenes and their photoreactions, among them NBA and oNT, have been investigated in the group of P. Gilch at the LMU in Munich in order to study the mechanism and the kinetics of the photoreactions of nitroarenes, using femtosecond infra-red, transient absorption spectroscopy and FSRS [139, 195–197]. FSRS can be considered a time-resolved, resonant variant of Raman spectroscopy.

For the theoretical description of the Raman spectra, first the influence of the excitation energy, and the value of the damping constant $\Gamma$, for which usually an empirical value is used, are studied for NBA, using the implementation of the time-dependent RR intensity formalism in the computer program Dnr [198] before such a spectrum is compared against one obtained using the sum-over-states formalism and one within Heller’s gradient approximation. The spectra in Fig. 6.1 a) show that the value of the damping constant $\Gamma$ influences the absolute intensity of the peaks, while the relative intensities remain similar. An excitation energy mismatch of 0.2 eV, which is a tolerable error for TDDFT excitation energies, does not change the intensities significantly for this (large) value of $\Gamma$ (see the spectrum for $E_{\text{exc}} = 3.195$ eV in panel b) compared to the red spectrum in panel a). On closer inspection, for the lower excitation energy, the peaks at about 800 cm$^{-1}$ and below exhibit slightly higher intensities, while for peaks with higher wavenumbers the intensities are larger for the excitation energy $E_{\text{exc}} = 3.4$ eV. For large values of $\Gamma$, the relative intensities mainly depend on the vibrational overlap integrals, which are determined by the values of the normal mode displacement $\Delta$ (see Section 4.3.1). These are the same for both calculations, so that the relative intensities change only slightly. The observations concerning the excitation energy mismatch and the variation of the value of $\Gamma$ cannot be generalized for other molecules though, since the combination of these values influences the resonance enhancement of particular vibrations. The sum-over-states formalism in Dnr differs from the time-dependent formalism in the implementation so that the obtained intensities are not directly comparable. The relative intensities, however, are consistent to the time-dependent formalism results (see panel c)). The gradient approximation yields virtually the same results for NBA as the time-dependent formalism, so that the approximation can be employed for the study of photoproducts if there is only one state in resonance (see panel d)).
6.1 Simple resonance Raman approaches

Figure 6.1: Raman spectra assuming resonance with the $3^1A$ state of NBA (intensities are given in arbitrary units, the off-resonance term was neglected in DNR calculations). In panel a), the damping constant $\Gamma$ was varied from 500 cm$^{-1}$ (red) to 50 cm$^{-1}$ (blue, dotted) for the spectra calculated for the excitation energy obtained in TDDFT calculation (3.4 eV). In panel b), the spectrum calculated for the experimental (3.195 eV, blue) value of the excitation energy is shown (for a value of $\Gamma$=500 cm$^{-1}$). Panel c) depicts the spectrum for the TDDFT excitation energy using the sum-over-states formalism ($\Gamma$=500 cm$^{-1}$) and d) the gradient approximation spectrum. In the latter two cases, the intensity of the most intense peak was scaled to equal the intensity of this peak in the red spectrum of panel a).
6.2 Photoproducts of \( o \)-nitrobenzaldehyde

The photochemistry of nitroarenes has been of interest for several reasons: nitroarenes have appeared as photolabile protective groups for synthetic organic reactions, and have found application for so-called caged compounds [199].

Mechanism and kinetics of the reaction have been studied in the 1980s and early 1990s by Yip et al., who performed picosecond transient absorption experiments on various nitroarenes [200–204]. They could determine an upper boundary for the formation time of the primary photoproducts of the order of \( \sim 30 \) ps. Schwörer and Wirz [205] performed experiments with a higher time-resolution on the phototautomerisation of nitrotoluene. Yet, their paper does not focus on the primary processes. As early as 1901 Silber and Ciamician [206] reported that when illuminated NBA transforms into nitrosobenzoic acid. Time-resolved experiments by Yip and Sharma [202] and by Laimgruber et al. [195] have given evidence that this transformation involves several elementary steps. It is assumed [207] that the primary step in \textit{ortho}-substituted nitroarenes is a hydrogen transfer from the substituent to the nitro group. For NBA this transfer should result in the formation of a ketene (see Figure 6.2) [195,202,208,209], which could be cryo-trapped in an argon matrix [209]. In a femtosecond IR experiment [195] the \( \sim 2100 \) cm\(^{-1}\) resonance characteristic for a ketene [210] was seen to emerge in \( \sim 400 \) fs. The characterization of the ketene intermediate and the kinetics of its formation has been subject of a combined theoretical and experimental study, employing transient absorption spectroscopy of NBA in acetonitrile, and femtosecond stimulated Raman spectroscopy (FSRS) addressing the structure of the ketene intermediate. Experimental details and results are described in Ref. [139] together with the supporting TDDFT calculations. The latter will be discussed in the following.

Figure 6.2: Schematic representation of the photochemistry of NBA. Photo-excitation triggers a hydrogen transfer process which results in a ketene intermediate. Subsequent reactions yield the final nitroso product.
6.2 Photoproducts of o-nitrobenzaldehyde

Since the experimental spectra are subject to a resonance enhancement, one can expect that normal Raman calculations are not appropriate since Placzek’s polarizability theory for Raman scattering [136, 144, 211] breaks down in this case. Therefore, resonance Raman calculations based on Heller’s time-dependent approach (see, e.g., [33, 130, 131, 134, 135, 212, 213]) were carried out, for which electron–phonon coupling constants from TDDFT calculations were employed, which usually provide reliable results for resonance Raman intensities.

FSRS is a time-resolved Raman technique established during the last decade [214–217]. Its principle and various applications have recently been reviewed by Kukura et al. [218]. The set-up used in the present study has been detailed in Ref. [217]. A more accurate, but more involved theoretical description has been given by Lee and coworkers [219, 220]. The FSRS set-up was also used to record transient absorption data. For experimental details, see Ref. [139].

DFT calculations were carried out using the program package ADF [105, 106]. We employed the Becke–Perdew exchange–correlation functional, dubbed BP86 [49, 221], for ground-state structure optimizations and frequency analyses. For the TDDFT calculations we applied ADF’s RESPONSE module [222]. We used the SAOP potential (statistical averaging of (model) orbital potentials) [127, 223, 224] with the adiabatic local density approximation (ALDA) for the exchange–correlation kernel in combination with the triple-ζ plus polarization (TZP) basis sets from the ADF basis set library [105] to calculate vertical excitation energies. Excited-state gradients were obtained by numerical differentiation along the normal coordinates using ADF’s VIBRON module [140]. For comparison, also TDDFT calculations using the B3LYP functional [48, 50] were performed with the program TURBOMOLE [225], employing Heller’s gradient approximation for the RR spectra.

Within Heller’s framework the Franck–Condon contribution to the scattering tensor elements $[\alpha_{\sigma,\rho}]_{\beta\iota}$, which is usually the dominant contribution in resonance Raman spectra, is obtained from the half Fourier-transform integral Eq. (4.30). The time-dependent wave-packet overlap can be evaluated analytically for the IMDHO model, in which it is assumed that both the ground- and the excited-state potential energy surface can be approximated by a harmonic potential with the same normal modes and frequencies. This requires the displacements of the excited-state equilibrium structure along the normal coordinates relative to the ground-state equilibrium structure, which are — within the IMDHO model — proportional to the excited-state gradients along the normal coordinates. The time-integral can then be evaluated numerically where the upper limit for the integration can be chosen on the basis of the damping constant $\Gamma$. This has been implemented in the program DNR, and tested against sum-over-state evaluations of the scattering tensor (see Fig. 6.1 c), which can also be performed with DNR but which are much less efficient for molecules with many vibrational modes. The damping constant enters the calculation as a parameter; typical values used in resonance Raman calculations are in the range of 100 to 1600 cm$^{-1}$ [134, 226]. Preliminary tests have shown that the choice of $\Gamma$ within this range mainly affects the absolute intensities, whereas the relative intensities reported here are not much changed (cf. Fig. 6.1 a). Therefore, we applied a uniform damping constant of 400 cm$^{-1}$ in all calculations.
6 Simple Resonance Raman Models for the Photochemistry of Nitroarenes

6.2.1 Transient absorption spectroscopy and FSRS experiments

The absorption spectrum of NBA (Fig. 6.3) in the near UV region consists of various overlapping bands [139]. For an approximate description of these bands the spectrum was decomposed into Gaussian contributions. The oscillator strength \( f_i \) of each contribution \( i \) was calculated according to Ref. [227]

\[
f_i = 4.32 \cdot 10^{-9} \int \epsilon(\tilde{\nu}) d\tilde{\nu}.
\]  

(6.1)

\( \epsilon(\tilde{\nu}) \) is the extinction coefficient in units of M\(^{-1}\)cm\(^{-1}\) as a function of the wavenumber \( \tilde{\nu} \) in units of cm\(^{-1}\). The results of the decomposition (also for NBA in cyclohexane) are compiled in Table 1 and will be addressed together with the TDDFT calculations. The decomposition shows that absorption of the actinic pump light (258 nm) promotes NBA to an upper singlet state. The results for NBA in ethanol [195] suggest that the excited-state decay partially recovers the NBA ground state and partially results in the formation of the ketene. Either species will be vibrationally excited. Based on the lifetime of 20 ns reported earlier [202] one would expect a constant ketene absorption in our time window.

Figure 6.3: Absorption spectrum of NBA dissolved in acetonitrile (black line) and its decomposition into Gaussian components (blue lines). The sum of all components is given by the red line. For the decomposition a linear energy scale was used and therefore the Gaussians are somewhat asymmetric in the linear wavelength representation shown. The dashed lines symbolize the wavelength of the actinic (A) and Raman (B) pump light.
6.2 Photoproducts of o-nitrobenzaldehyde

Figure 6.4: Comparison of experimental (solid, black) and computed (SAOP/TZP) Raman spectra (dotted, colored). Lower graph stationary Raman spectrum of NBA with solvent contribution subtracted, stars mark artifacts of this subtraction. Upper graph ketene intermediate spectrum obtained by summing all spectra recorded after 20 ps. Intensities are given in arbitrary units. To reproduce the experimental linewidth the theoretical stick spectra were convoluted with Gaussian line shape functions with a width of 25 cm$^{-1}$. For NBA resonance with the first excited state and for the ketene resonance with the second one was assumed.

In the spectral region covered in the FSRS experiment (1000 – 2200 cm$^{-1}$) Raman resonances of the acetonitrile solvent and the NBA solute are located. The wavelength of the Raman pump (388 nm) causes a pre-resonance Raman enhancement of the NBA modes [217] responsible for the high relative intensity of the solute modes. The most intense Raman mode of NBA is located at 1353 cm$^{-1}$. Intense resonances in that region are characteristic for nitroarenes and are assigned to the symmetric stretch vibration of the NO$_2$ group [228]. By comparison of the Raman signature of the first occurring intermediate with results from TDDFT calculations (see Fig. 6.4) the assignment of the transient absorption spectrum to a ketene structure can be further substantiated. For this comparison all the experimental spectra recorded from 20 ps onwards were averaged. After 20 ps the spectra do not change in shape and by virtue of this averaging the signal-to-noise ratio is increased. This averaged difference spectrum is then transformed into the spectrum of the ketene intermediate by adding a scaled Raman spectrum of NBA to the difference spectrum. The determination of the scaling factor was based on the constraints that the retrieved spectrum must not contain negative peaks and that no peaks of the NBA parent compounds appear. The scaling factor was taken to be 0.008 ± 50%. Pronounced characteristics of the spectrum corrected for the bleach (Fig. 6.4) are a triplet of bands with an intense central band at 1521 cm$^{-1}$ and a weaker band at 2105 cm$^{-1}$. This spectrum will now be analyzed relying on TDDFT calculations.
6.2.2 TDDFT calculations

In this section we will first validate the TDDFT approach by analyzing the resonance Raman spectrum of NBA, for which an experimental steady-state spectrum is available. Subsequently, we will use the same approach for the transient ketene intermediate and compare the theoretical findings with the FSRS spectra.

The structure of the NBA reactant is a good starting point for the computational studies since its molecular structure is well known from diffraction experiments [229, 230]. The diffraction studies show that in the solid state the nitro- and the aldehyde substituent are by $\sim 30^\circ$ out of co-planarity with the benzene ring. The twist angles of both substituents have the same sign. The hydrogen atom of the aldehyde function points in the direction of the nitro group. In the DFT-optimized structure of NBA these general features are reproduced, although the twist angles are slightly smaller (see Fig. 6.5).

Figure 6.5: Optimized (BP86/TZP) structure of NBA.

For this optimized structure electronic excitations were calculated seeking states which contribute to a (pre-)resonance Raman enhancement. Two factors are decisive for this issue: (i) the excitation energy to the state in resonance must match the frequency of the incident light beam, and (ii) the transition must show a significant oscillator strength. The second point is due to the fact that the cross section of the Franck–Condon type resonance Raman scattering, which dominates most resonance Raman spectra by far and is the only term considered here, depends on the fourth power of the electronic transition dipole moment. In the following, we will first identify the important excited states in the experimental spectrum. Then, we will compare the calculated SAOP excitation energies and oscillator strengths to those from B3LYP calculations, so that we can finally map the calculated states to those experimental transitions for which resonance conditions are fulfilled. Note that an assessment of the oscillator strengths obtained from different density functional schemes can be found in Ref. [231]. A comparison with the experimental absorption spectrum of NBA shows that the laser wavelength of 388 nm corresponds to an excitation into the long-wavelength tail of the spectrum. Based on the decomposition
6.2 Photoproducts of o-nitrobenzaldehyde

of the experimental absorption spectrum (see Fig. 6.3 and Table 6.1) the state most likely in resonance should be the first excited singlet state with a maximum at 343 nm in acetonitrile, which was assigned to a \( n\pi^* \) transition. This state, however, has a rather low oscillator strength of \( 5.2 \times 10^{-3} \). It might thus be possible that also the second excited state plays a role for the resonance enhancement. This state is experimentally found at 297 nm in acetonitrile and was assigned to a \( \pi\pi^* \) transition. Although it is much higher in energy, it could still be important since the absorption band is broad and it has a higher oscillator strength of 0.0306 (in the experiment).

Table 6.1: Experimental positions of the bands based on a convolution of six Gaussians (in eV; see Fig. 6.3).

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<th>Number</th>
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<th>( f ) MeCN</th>
<th>( E_{ex} ) cyclohexane</th>
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Table 6.2 shows the calculated excitation energies, oscillator strengths, and the dominant orbital transitions obtained from the SAOP calculation. In this calculation, the lowest unoccupied molecular orbital (LUMO) of NBA is a \( \pi^* \) orbital located on the nitro group (see Figure 6.6). Hence, transitions from the occupied \( \pi \) orbitals of the benzene ring to the LUMO are expected to suffer from the general problem of TDDFT to describe charge-transfer (CT) excitations. Although this does not mean a complete failure as in the case of so-called long-range charge-transfer excitations [232–238], it is well-known that such excitation energies in nitrobenzenes are underestimated by TDDFT [239, 240]. In order to identify problems related to the CT character of certain transitions, we also calculated excitation energies using the B3LYP hybrid functional for a structure optimized with B3LYP and a triple-\( \zeta \) valence plus polarization (TZVP) basis set as implemented in TURBOMOLE [225]. The resulting excitations were mapped to the SAOP results on the basis of the orbital transitions involved (see Table 6.2). An additional low-lying state with small oscillator strength (not shown in Table 6.2), which corresponds to a HOMO \( \rightarrow \) LUMO+1 orbital transition, was found at 3.64 eV (SAOP) and 4.12 eV (B3LYP). This state is not considered to be important for the resonance Raman scattering because of its low intensity and relatively high excitation energy.

Since the B3LYP calculations partly (though not sufficiently) correct for the failure in case of CT transitions of the ALDA kernel applied in connection with SAOP TDDFT calculations, we expect significant shifts for those excitations that are of CT type. By comparing the SAOP and B3LYP data in Table 6.2 it can be seen that there are large differences for the first and second excited-state energies of the SAOP calculation in comparison to B3LYP. The reason for the deviation in case of
the $\pi\pi^*$ (CT) excitation is certainly its CT character, and CASSCF/CASPT2 calculations on the corresponding transitions in nitrobenzene suggest typical excitation energies of 4.99 eV [241]. CASSCF/CASPT2 calculations by Leyva et al. [242] for NBA exhibit an excitation with charge-transfer character at 4.45 eV. In contrast to this, the discrepancy for the $n\pi^*$ transition occurring within the NO$_2$ group is not obvious in terms of the orbital transitions. For the third excited state, which is of $\pi\pi^*$ type and which also shows a partial CT contribution, SAOP and B3LYP are in much better agreement with a deviation of only 0.21 eV. The calculated excitation energies from both calculations are much lower than the ones determined on the basis of a Gaussian decomposition of the experimental absorption spectrum in acetonitrile. An additional calculation using the approximate coupled cluster doubles model CC2 and Dunning’s correlation consistent valence triple-$\zeta$ basis with polarization functions (cc-pVTZ) with the RICC2 program of the TURBOMOLE suite [243] resulted in an excitation energy for this $\pi\pi^*$ (CT) state of 4.71 eV and is thus in accordance with the experimental results. However, it turned out that this coupled-cluster approach does not provide a reliable reference wavefunction for NBA based on the so-called D1 diagnostic proposed in Ref. [244], so that also the RICC2 excitation energies are not fully trustworthy.

Table 6.2: Calculated (SAOP/TZP and B3LYP/TZVP) excitation energies $E_{\text{ex}}$ (in eV) and oscillator strengths $f$ for NBA. Experimental values deduced from the decomposition of the absorption spectrum of for NBA (see Fig. 6.3) in acetonitrile are given for comparison.

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<th>$f$</th>
<th>$E_{\text{ex}}$</th>
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<td>0.0006</td>
<td>3.61</td>
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<tr>
<td>$\pi\pi^*$ (CT)</td>
<td>HOMO $-1$ $\rightarrow$ LUMO</td>
<td>3.40</td>
<td>0.0165</td>
<td>4.26</td>
<td>0.0133</td>
<td>4.73</td>
<td>0.1012</td>
</tr>
<tr>
<td>$\pi\pi^*$</td>
<td>HOMO $-2$ $\rightarrow$ LUMO</td>
<td>3.54</td>
<td>0.0280</td>
<td>3.75</td>
<td>0.0168</td>
<td>4.17</td>
<td>0.0306</td>
</tr>
</tbody>
</table>

Figure 6.6: Isosurface plots of the molecular orbitals (SAOP/TZP) involved in the lowest electronic excitations of NBA.

The values of the experimental excitation energies are of course also subject to uncertainties. They were obtained assuming Gaussian line shapes and a certain number of Gaussian components. Either assumption can be questioned. Nevertheless, large discrepancies between the TDDFT calculations and experiment remain. The
assignment of the excited states to be considered for the resonance enhancement, i.e., the \( n\pi^* \) and the \( \pi\pi^* \) state identified on the basis of the experimental absorption spectrum, is less complicated. Apparently, the first transition \((n\pi^*)\) from the SAOP calculation fits best to the applied laser energy of 3.20 eV (388 nm) if we take into account that the SAOP excitation energies are too small. The second excited state obtained with SAOP is severely affected by the CT problem and should appear at much higher energies, so that the third excited state \((\pi\pi^*)\) in the SAOP calculation (or the second excited state in the B3LYP calculation) corresponds to the broad experimentally observed state at 4.17 eV (297 nm). These two states will thus be considered in the following.

In spite of the problems of TDDFT to reproduce the correct vertical excitation energies, the derivatives of the excitation energies along the normal coordinates as needed for the calculation of resonance Raman intensities will be much less affected, since they will — to a large extent — be determined by the change in the energies of the orbitals involved in the transition. Since neither SAOP nor B3LYP are able to reproduce the vertical excitation energies accurately, we restrict ourselves to the discussion of the SAOP results for the resonance Raman spectra. It was shown previously that non-hybrid exchange-correlation functionals yield reliable resonance Raman intensities under similar conditions [11].

We calculated the resonance Raman intensities for the lowest excited states of NBA with SAOP/TZP based on Heller’s time-dependent formalism. In order to analyze the importance of the two excited states that we identified as potentially important for the resonance Raman scattering of NBA \((n\pi^* \text{ and } \pi\pi^*)\), we compare the spectra obtained when considering (i) only the first excited state \((n\pi^*)\), (ii) only the third excited state (in the SAOP calculation; second excited state in experiment, \(\pi\pi^*)\), and (iii) both of these states simultaneously in Fig. 6.7. Intensities are not in general additive in case of several excited states in resonance, since each excited state gives a contribution to the scattering tensor, which must be squared to give the total intensity [169,245]. Another difficulty for several states in or close to resonance is that the energy gap between the excited states can play a crucial role for the total intensity. Since the vertical excitation energies from the TDDFT calculations turned out not to be fully reliable for NBA, we simulated the resonance Raman spectrum with the combined effect of both states assuming the experimentally determined excitation energies of 3.61 and 4.17 eV, and a laser wavelength of 388 nm.

All spectra shown in Fig. 6.7 are normalized, so that their absolute intensities are not directly comparable. The \(\pi\pi^*\) transition has a larger contribution on an absolute scale than the \(n\pi^*\) transition due to its much larger transition moment, so that the features of the spectrum obtained for the third excited state in resonance also dominate the spectrum in which both states were considered. In comparison to the experimental spectrum in Fig. 6.4 we note that all three calculated spectra reproduce the intense feature for the NO\(_2\) stretch vibration. The calculated wavenumber of 1296 cm\(^{-1}\) underestimates the experimental one at 1350 cm\(^{-1}\) considerably, which is rather unusual for frequency analyses based on the BP86 functional [246]. The peaks above 1350 cm\(^{-1}\) up to 1700 cm\(^{-1}\) in the experimental spectrum apparently agree best with the features in the computed spectrum where the first excited state \((n\pi^*)\) is assumed to be in resonance (see Fig. 6.4). This could mean that either
the ratio of the calculated transition moments for the \( n\pi^* \) transition in comparison to the one obtained for the \( \pi\pi^* \) transition is too small, or that inaccuracies in the experimental decomposition affect the outcome of the resonance Raman calculation. At the present stage, the best strategy to decide which state is in resonance appears to be a comparison of experimental and calculated spectra (see also Ref. \[190\]).

Figure 6.7: Calculated (SAOP/TZP; intensities in arbitrary units) resonance Raman spectra for NBA using Heller’s time-dependent formalism. Lower panel: resonance assumed for the first excited state (\( n\pi^* \)); middle panel: resonance assumed for the third excited state (\( \pi\pi^* \); second excited state in experiment); upper panel: both states included in the calculation. All spectra are normalized. Stick spectra were convoluted with Gaussian line shape functions with a width of 25 cm\(^{-1}\).

The ketene intermediate is formed in a hydrogen transfer process from the aldehyde substituent to the nitro group. It is most likely that after transfer the hydrogen atom is bonded to the oxygen of the nitro group next to the (former) aldehyde function (\( Z \)-form). The optimized structure of this \( Z \)-form is planar, the hydrogen atom attached to the nitro group points away from the ketene function and this function is slightly tilted (Fig. 6.8). The SAOP/TZP calculation yields three transitions in the spectral range of interest which are located at 2.12 eV (oscillator strength \( f = 3.5 \cdot 10^{-5} \)), 2.61 eV (\( f = 0.0804 \)), and 4.10 eV (\( f = 0.0802 \)). The dominant orbital transitions in this case are the \( HOMO \rightarrow LUMO+1 \), \( HOMO \rightarrow LUMO \), and \( HOMO \rightarrow LUMO+2 \), respectively (see Fig. 6.8). Again, a B3LYP/TZVP calculation carried out for comparison yields larger excitation energies, but the disagreement is only about 0.2 eV for the first two transitions (2.31 eV, \( f = 3.1 \cdot 10^{-5} \) and 2.84 eV, \( f = 0.1125 \)) and about 0.4 eV for the third one (4.51 eV, \( f = 0.1180 \)). Hence, the deviation is much smaller than in case of NBA.

The first transition is not observed in the experimental spectrum assigned to the ketene intermediate. This could very well be due to its low oscillator strength. The second transition, which is predicted to be more intense and to peak at 2.61 eV (480 nm, SAOP/TZP), is in line with the experimental spectrum which features
a band peaking at 440 nm. The experimental spectrum hints to a further intense transition at \(\sim 300\) nm (4.13 eV) again in accordance with the SAOP/TZP calculation.

Figure 6.8: Ketene intermediate: Optimized (BP86/TZP) structure (left) and isosurface plots of the molecular orbitals (SAOP/TZP) involved in the lowest electronic excitations (right).

The wavelength of the Raman pump pulse is within the envelope of the 445 nm transition and so this transition will be dominantly responsible for the resonance Raman enhancement. The resonance Raman spectrum computed for this transition is in good agreement with the experimental one (Fig. 6.4). In both the experimental and the theoretical spectrum a weak resonance at \(\sim 2100\) cm\(^{-1}\) is observed. The resonance is due to the stretch vibration of the central carbon atom in the ketene function. Because of the lower signal-to-noise ratio of the set-up employed in the foregoing experimental study [195] this mode was not observed by Raman spectroscopy heretofore. In that study we took advantage of the large IR cross section of this mode and recorded its IR signature. Improvements described in Ref. [217] now enable us to detect this resonance also by means of FSRS. The next resonance in the theoretical spectrum, which is accompanied by a very weak peak at its low frequency edge, is located at 1639 cm\(^{-1}\). These two bands might correspond to the experimental band at 1600 cm\(^{-1}\) which is broader than the other resonances pointing at overlapping bands. The 1639 cm\(^{-1}\) mode has a large N–C stretch contribution. Its high frequency points to a double bond between the nitrogen atom of the nitro group and the ring. In both the theoretical and the experimental spectrum, the most intense band is located at \(\sim 1520\) cm\(^{-1}\). This mode can be described as an in-phase motion of the two formal double bonds in the ring. The good agreement for these three stretch vibrations strongly support the valence bond structure of the ketene intermediate depicted in Fig. 6.2. The other modes at lower frequencies have mostly hydrogen in-plane deformation character. Also for them the agreement with the experimental data is reasonable. Since they are not so informative in terms of structure we will refrain from an in-depth description of these modes. For a spectrum recorded in the solvent 2-butanol, the comparison with the RR spectrum calculated using Heller’s gradient approximation allowed the identification of a solvent peak, see Fig. 6.9.
6 Simple Resonance Raman Models for the Photochemistry of Nitroarenes

Figure 6.9: Comparison of an experimental (lower panel; solvent 2-butanol) and calculated (upper panel) resonance Raman spectra for the ketene intermediate. The calculated stick spectrum was convoluted with Gaussian line shape functions with a width of 10 cm\(^{-1}\). Both spectra are normalized, intensities are given in arbitrary units.

6.2.3 Conclusions for the photoproducts of NBA and the time-dependent formulation of resonance Raman

The combination of FSRS data and TDDFT calculations has been used to characterize the first ground-state intermediate in the photochemistry of NBA. This intermediate is a ketene which is formed via a hydrogen transfer from the aldehyde to the nitro-substituent. Evidence for the population of the electronic ground state of the ketene comes from two sources. First, the transient absorption spectrum of this intermediate (see Ref. [139]) closely resembles the one obtained by matrix isolation spectroscopy [209]. Since the latter experiment relied on steady-state spectroscopy, the ketene had to be in its electronic ground state. Second, the experimental Raman spectrum could be well reproduced in the TDDFT-based resonance Raman calculations, which have been performed for the ground state of the ketene intermediate. The experimental and computed Raman spectra feature resonances which are very characteristic for the single-double bond pattern of the ketene intermediate. If the ketene were in an electronically excited state the respective bond orders should be different and thereby the Raman spectrum.

The reliability of the time-dependent formulation using the Gradient Franck–Condond model for RR intensities was confirmed for the steady-state spectrum of \(\alpha\)-NBA, in spite of the problems for the vertical excitation energies. Subsequently, the comparison of the time-resolved experimental spectra with the calculated resonance Raman signatures allowed the identification of the intermediate.
6.3 Photoproducts of ortho-nitrotoluene

A further reaction studied in the context of the photodeprotection of ortho-nitrobenzyl protective groups is the photochemical reaction of ortho-nitrotoluene (oNT), the simplest compound of this type (see Fig. 6.10). The first step common to the photoreactions [201, 205, 247], a hydrogen transfer from the alkyl group to the nitro group, leads to the formation of a ground-state intermediate, an aci-nitro tautomer. Although this fact has been known since the 1960s [248, 249], mechanistic and kinetic details on the formation and decay of the aci-nitro tautomer obtained in later studies [200, 205] do not yield an unambiguous picture. In contrast to the reaction of NBA, for oNT the reaction to the aci-nitro form is partially reversible, the final product is likely an ortho-nitrosobenzyl alcohol. For the reaction of NBA, intermediates with non-aromatic bonding patterns, as the ketene intermediate, have been shown to give rise to ethylenic stretch vibrations which feature a high Raman intensity. Therefore, the aci-nitro tautomers should, due to their structural similarity concerning the single–double bond pattern, be suited for FSRS experiments, thus avoiding difficulties in assignment found in the earlier transient spectroscopic studies in the UV and visible range [200, 205]. For the FSRS experiments, the same setup as for NBA was used [197].

The aci-nitro-tautomer can occur as a syn- or anti-conformer for both tautomeric forms (E and Z). Electronic structure calculations have been carried out for oNT and the different forms of the tautomer, in order to support the assignment of the spectra. Here, we pay special attention to the calculation of the excitation energies for oNT, where TDDFT are compared to RICC2 and CASSCF/PT2 results. For the TDDFT and RICC2 calculations for ground-state structures, excitation energies and excited-state gradients the TURBOMOLE suite was used. For vibrational Raman spectra, the SNF program [211] was employed.

Figure 6.10: Schematic representation of the photochemistry of oNT. Photo-excitation triggers a hydrogen transfer process which results in an aci-nitro tautomer. Subsequent reactions yield the final nitroso product.
6 Simple Resonance Raman Models for the Photochemistry of Nitroarenes

6.3.1 oNT ground-state structure

For the ground-state structure and frequencies of oNT, DFT calculations using the B3LYP and BP86 functionals and the CC2 and MP2 methods have been employed, see Fig. 6.11 for the B3LYP/TZVP structure. The structures differ mainly in the dihedral angle spanned by the atoms O2-N-C1-C6, which varies in a range from $-132^\circ$ (RICC2/TZVP, RIMP2/TZVP) to $-166^\circ$ (BP86/TZP). With a cc-pVTZ basis, the RICC2 and RIMP2 dihedral angles shift to $-146^\circ$ and $-144^\circ$, respectively. In order to systematically study the dependence of the energy on this dihedral angle, a relaxed scan for values between $-125^\circ$ and $-175^\circ$ in steps of $5^\circ$ was performed using BP86/TZ2P. The minimum energy with respect to this dihedral angle was found at $-155^\circ$. When this angle is varied to $-145^\circ$ or $-175^\circ$, the resulting energy difference amounts to only 0.5 kJ/mol and 0.4 kJ/mol, respectively. Even for $-125^\circ$, the energy difference is only 4.1 kJ/mol. Thus it is very likely that at ambient temperatures distortion of this angle has to be taken into consideration. The influence of this rotation on the resonance Raman spectra was studied for three structures of the scan, at dihedral angles of $-135^\circ$, $-155^\circ$ and $-175^\circ$. The resonance Raman spectra revealed that the influence of changes in this angle on the spectra is not very large. An experimental study using gas phase electron diffraction yielded a dihedral angle of $-142^\circ$ [250]. Among the theoretical methods employed here, the RICC2/cc-pVTZ calculation leads to the best agreement with experiment with a dihedral angle of $-146^\circ$. Therefore, this structure was chosen for the CASSCF/CASPT2 calculations for the excited states.

Figure 6.11: (B3LYP/TZVP) optimized structure of oNT
6.3 Photoproducts of ortho-nitrotoluene

Excitation energies and absorption spectrum

Excitation energies for oNT were calculated using the B3LYP/TZVP, SAOP/TZP (for the BP86/TZP structure) and RICC2/cc-pVTZ methods. The results, including transition dipole moments and oscillator strengths obtained with B3LYP/TZVP, can be found in Table 6.3. Graphical representations of the B3LYP/TZVP molecular orbitals involved in the lowest transitions are depicted in Fig. 6.12. Note that for the SAOP results, the order of the first two excited states is reversed with respect to the B3LYP results. The description of the lowest energy state obtained in the SAOP calculation (3.30 eV) is dominated by the HOMO→LUMO transition (92 %), HOMO and LUMO being comparable to those of the B3LYP calculation. This transition has therefore partial charge-transfer character and is probably affected by the problems connected with TDDFT and charge-transfer transitions and thus resulting in too low energies. The B3LYP excitation dominated by the HOMO→LUMO transition (4.21 eV) compared to the corresponding RICC2 transition (4.86 eV) is still more than 0.6 eV lower. An absorption spectrum is plotted for the (B3LYP/TZVP) excitations in Fig. 6.13. The computed absorption spectrum of oNT has a maximum at 257 nm, which in comparison to the experimental value of 250 nm [242] corresponds to a shift of +0.14 eV.

Table 6.3: Calculated excitation energies, dominant orbital transitions, transition dipole moments $\mu_t$ and oscillator strengths for oNT. SAOP and RICC2 energies are given for the transitions belonging to corresponding orbital transitions.

<table>
<thead>
<tr>
<th>state</th>
<th>transition</th>
<th>$E$ / eV</th>
<th>$\mu_t$ / a.u.</th>
<th>$f$</th>
<th>$E$ / eV</th>
<th>$E$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^1A$</td>
<td>34a→37a (48%), 35a→37a (46%)</td>
<td>3.78</td>
<td>0.36</td>
<td>1.18E-02</td>
<td>3.67</td>
<td>3.78</td>
</tr>
<tr>
<td>$3^1A$</td>
<td>36a→37a (86%)</td>
<td>4.21</td>
<td>0.47</td>
<td>2.31E-02</td>
<td>3.30</td>
<td>4.86</td>
</tr>
<tr>
<td>$4^1A$</td>
<td>33a→37a (83%)</td>
<td>4.35</td>
<td>0.26</td>
<td>6.98E-03</td>
<td>4.07</td>
<td>4.34</td>
</tr>
<tr>
<td>$5^1A$</td>
<td>35a→37a (45%), 34a→37a (42%)</td>
<td>4.82</td>
<td>1.08</td>
<td>1.37E-01</td>
<td>4.14</td>
<td>5.59</td>
</tr>
<tr>
<td>$6^1A$</td>
<td>35a→38a (48%), 36a→39a (36%)</td>
<td>5.76</td>
<td>0.18</td>
<td>4.44E-03</td>
<td>5.26</td>
<td>6.18</td>
</tr>
</tbody>
</table>

Figure 6.12: B3LYP/TZVP molecular orbitals involved in the lowest electronic transitions of oNT. H denotes the highest occupied molecular orbital (HOMO) and L the lowest unoccupied molecular orbital (LUMO).
Figure 6.13: Absorption spectrum obtained with B3LYP/TZVP for the ground state of oNT generated from the lowest 20 excitations with a Gaussian broadening of 0.3 eV.

Raman and resonance Raman spectra

In the FSRS experiment an excitation wavelength of 388 nm was applied [197], which corresponds to 3.20 eV. Calculations yield higher first excitation energies: 3.78 eV (B3LYP/TZVP and RICC2/TZVP). It is therefore not certain that resonance conditions should be applied to describe the experiment. Though Heller’s gradient approximation assumes resonance with a defined excited state, it should also give a reasonable description for preresonance conditions. However, results have to be interpreted with caution. Excitation energies to the second excited state are 0.4-0.5 eV higher in energy (3.67 eV for SAOP/BP86/TZVP, 4.21 eV for B3LYP/TZVP and 4.34 eV for RICC2/cc-pVTZ). Higher-lying excited states beyond the second excited state have not been considered for the interpretation of this experiment, because the excitation energies are too high in comparison to the experimental excitation energy.

In Fig. 6.14, an experimental spectrum in panel a) is compared to calculated spectra: b) and c) show (B3LYP/TZVP) Raman spectra calculated using dynamic and static polarizabilities. (B3LYP/TZVP) resonance Raman spectra for the two lowest excited states are shown in d) and e). The effect of the transition from off-resonance conditions to resonance conditions can be observed in the Raman spectra going from static over dynamic polarizabilities to the resonance Raman spectrum in Figs. 6.14 b) to d) and e). In comparison to the spectrum calculated with static polarizabilities, the Raman spectrum calculated with dynamic polarizabilities for an excitation wavelength of 388 nm features a mode at 1362 cm\(^{-1}\) (a symmetric stretch vibration of the nitro group) that is enhanced, whereas the C-H stretch vibrations in the region above 3000 cm\(^{-1}\) compared to the other modes are less intense. This effect is even more pronounced in the B3LYP/TZVP Raman spectrum assuming resonance with the first excited state, which is strongly dominated by the mode at 1362 cm\(^{-1}\).
A vector representation of the nitro group stretch vibration is plotted in f). On comparison of the experimental spectrum with the calculated ones, the best match is the spectrum in panel c), calculated using dynamic polarizabilities for an excitation wavelength of 388 nm but assuming off-resonance conditions. This is understandable as the excitation energy of 3.20 eV is about 0.6 eV below the excitation energies calculated with B3LYP and RICC2. In the experimental spectrum of oNT, besides the most intense peak at \( \sim 1350 \text{ cm}^{-1} \), there are several peaks of lower intensity: at \( \sim 1200 \text{ cm}^{-1} \), \( \sim 1480 \text{ cm}^{-1} \) and \( \sim 1580 \text{ cm}^{-1} \). While in the resonance Raman spectrum assuming resonance with the first excited state, there are only few peaks of very low intensity between \( \sim 1000 \text{ cm}^{-1} \) and \( \sim 1600 \text{ cm}^{-1} \), there are more peaks of low intensity in the spectrum assuming resonance with the second excited state which can be brought in agreement to the experimental spectrum. However, the excitation energy for this state is 1 eV higher than the experimental value and the relative intensities in the off-resonance Raman spectrum calculated for 388 nm are a better match.

Figure 6.14: Comparison of the experimental spectrum to calculated B3LYP/TZVP spectra: a) experimental FSRS spectrum (388 nm) in deuterated acetonitrile [197]. Solvent peaks are marked by asterisks. b) (off-resonance) Raman spectra for oNT calculated using static polarizabilities (limit \( \lambda \to \infty \)) c) (off-resonance) Raman spectra for oNT calculated for an excitation wavelength of 388 nm. d) and e) resonance Raman spectra assuming resonance with the 3\(^1\)A or 2\(^1\)A state. f) Graphical representation of the nitro group stretch vibration.
6.3.2 aci-nitro tautomers

For the two $C_s$ symmetric syn-aci-nitro tautomers ($E$ and $Z$ conformer) and the $C_1$- symmetric anti-$Z$-conformer, relative energies were calculated with the B3LYP functional and TZVP and TZVPP basis sets. For the anti-$E$-conformation no minimum structure was found. The syn-$E$-tautomer is the most stable tautomer of the three, the energy obtained with a TZVPP basis being 14.1 kJ/mol more stable than the one of the syn-$Z$-tautomer and 36.2 kJ/mol more stable than that of the anti-$Z$-tautomer (see Fig. 6.15). The energy differences between the three tautomers calculated here are in accordance with the energy differences calculated by Dunkin [247] (syn-$Z$: 12.2 eV, anti-$Z$: 32.7 eV) using B3PW91/6-31G(d).

Figure 6.15: B3LYP/TZVP optimized structures of the aci-nitro tautomers and calculated relative energies in kJ/mol for TZVP and TZVPP basis sets.

<table>
<thead>
<tr>
<th>method</th>
<th>syn-$E$</th>
<th>syn-$Z$</th>
<th>anti-$Z$</th>
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<tbody>
<tr>
<td>B3LYP/TZVP</td>
<td>0</td>
<td>14.18</td>
<td>38.74</td>
</tr>
<tr>
<td>B3LYP/TZVPP</td>
<td>0</td>
<td>14.08</td>
<td>36.21</td>
</tr>
</tbody>
</table>

For the two energetically lowest lying conformers, the syn-$E$- and syn-$Z$-nitro tautomers excitation energies have been calculated using B3LYP/TZVP, SAOP/TZP (for a BP86/TZP structure) and RICC2/cc-pVTZ for the twenty lowest states. The NBA ketene intermediate and the aci-nitro tautomers are structurally similar. Therefore, the calculated absorption spectrum of the NBA ketene intermediate has been plotted for comparison together with the calculated (B3LYP/TZVP) spectra for the syn-$E$- and syn-$Z$-tautomer in Fig. 6.16. The tautomers and the ketene intermediate exhibit similar absorption spectra. The excitation energies and oscillator strengths for the lowest five excited states can be found in Table 6.4. More elaborate data on the excitation energies for the tautomers comparing different methods are listed in Tables 6.5 and 6.6. For both tautomers, the differences between the different methods are similar: SAOP/TZP yields an energy, which is $\sim$0.25 eV lower, while the RICC2/cc-pVTZ value is 0.3 eV higher than the B3LYP/TZVP value.
6.3 Photoproducts of ortho-nitrotoluene

Table 6.4: Calculated excitation energies and oscillator strengths for the syn-\(E\)- and syn-\(Z\)-tautomer and the NBA ketene intermediate (B3LYP/TZVP).

<table>
<thead>
<tr>
<th>state</th>
<th>(E)/eV</th>
<th>(f)</th>
<th>state</th>
<th>(E)/eV</th>
<th>(f)</th>
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<th>(f)</th>
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<td>1.51E-01</td>
<td>(2^1A')</td>
<td>3.00</td>
<td>1.70E-01</td>
<td>(\text{NBA ketene}^\text{state})</td>
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<td>2.31</td>
</tr>
<tr>
<td>(1^1A'')</td>
<td>4.35</td>
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<td>7.37E-03</td>
<td>(3^1A)</td>
<td>2.84</td>
<td>1.13E-01</td>
</tr>
<tr>
<td>(3^1A')</td>
<td>4.43</td>
<td>6.65E-03</td>
<td>(1^1A'')</td>
<td>4.40</td>
<td>2.40E-05</td>
<td>(4^1A)</td>
<td>4.51</td>
<td>1.18E-01</td>
</tr>
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<td>(4^1A')</td>
<td>4.76</td>
<td>8.50E-03</td>
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<td>6.67E-05</td>
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<td>1.02E-03</td>
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Table 6.5: Calculated excitation energies, dominant orbital transitions and corresponding transition dipole moments \(\mu_t\) for the syn-\(E\)-tautomer.

<table>
<thead>
<tr>
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<th>transition</th>
<th>(E)/eV</th>
<th>(\mu_t) / a.u.</th>
<th>(E)/eV</th>
<th>(E)/eV</th>
<th>(E)/eV</th>
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</thead>
<tbody>
<tr>
<td>(2^1A')</td>
<td>6a&quot;→7a&quot; (96%)</td>
<td>3.09</td>
<td>1.41</td>
<td>2.84</td>
<td>3.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1^1A'')</td>
<td>30a’→7a'' (98%)</td>
<td>4.35</td>
<td>0.01</td>
<td>4.13</td>
<td>4.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3^1A')</td>
<td>5a&quot;→7a&quot; (54%), 6a&quot;→8a&quot; (40%)</td>
<td>4.43</td>
<td>0.25</td>
<td>3.88</td>
<td>4.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4^1A')</td>
<td>6a&quot;→9a&quot; (37%), 4a&quot;→7a&quot; (34%)</td>
<td>4.76</td>
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<td>4.27</td>
<td>4.86</td>
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</tr>
<tr>
<td>(5^1A')</td>
<td>6a&quot;→8a&quot; (39%), 4a&quot;→7a&quot; (34%)</td>
<td>5.19</td>
<td>0.66</td>
<td>4.94</td>
<td>5.50</td>
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Table 6.6: Calculated excitation energies, dominant orbital transitions and corresponding transition dipole moments \(\mu_t\) for the syn-\(Z\)-tautomer.

<table>
<thead>
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<th>state</th>
<th>transition</th>
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<th>(\mu_t) / a.u.</th>
<th>(E)/eV</th>
<th>(E)/eV</th>
<th>(E)/eV</th>
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</thead>
<tbody>
<tr>
<td>(2^1A')</td>
<td>6a&quot;→7a&quot; (95%)</td>
<td>3.00</td>
<td>1.52</td>
<td>2.76</td>
<td>3.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3^1A')</td>
<td>5a&quot;→7a&quot; (65%), 6a&quot;→8a&quot; (33%)</td>
<td>4.29</td>
<td>0.26</td>
<td>3.77</td>
<td>4.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1^1A'')</td>
<td>30a’→7a'' (98%)</td>
<td>4.40</td>
<td>0.01</td>
<td>4.14</td>
<td>4.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4^1A')</td>
<td>6a&quot;→9a&quot; (36%), 4a&quot;→7a&quot; (36%)</td>
<td>4.76</td>
<td>0.32</td>
<td>4.23</td>
<td>4.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5^1A')</td>
<td>6a&quot;→8a&quot; (45%), 4a&quot;→7a&quot; (25%)</td>
<td>5.09</td>
<td>0.74</td>
<td>4.88</td>
<td>5.29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Figure 6.16: Absorption spectra obtained with B3LYP/TZVP for the \textit{syn-E-} (red line) and \textit{syn-Z-}tautomer (blue line), and for comparison, the NBA ketene intermediate (black line). The lowest 20 excitations were plotted with a Gaussian broadening of 0.3 eV.

The lowest excitation energy for both tautomers is close enough to the experimental excitation value (3.19 eV) to assume resonance conditions. The spectra obtained with B3LYP/TZVP are displayed in Fig. 6.17, together with an experimental difference spectrum. The experimental difference spectra recorded in acetonitrile were summed up between 5 ps and 3 ns and exhibit an intense peak at \(\sim 1515 \text{ cm}^{-1}\), and a further (positive) peak at \(\sim 1250 \text{ cm}^{-1}\) beside negative peaks resulting from the oNT bleaching. The interpretation of the spectra is hampered by the fact that only one peak can be unambiguously assigned in comparison with the experimental spectrum. This corresponds to the vibration of the \textit{cis}-butadiene motif (ethylene stretch vibration) in both tautomers. For vibrational wavenumbers, harmonic BP86 frequencies have proven to be reliable because of a fortunate error cancellation [246, 251–253], so that we focus on the BP86/TZVP results for comparison of the two tautomers. For the \textit{syn-E-}tautomer, BP86 yields a wavenumber of 1519 cm\(^{-1}\) in comparison to 1538 cm\(^{-1}\) for the \textit{syn-Z-}tautomer, which suggests that the \textit{syn-E-}tautomer is the intermediate. B3LYP/TZVP wavenumbers confirm the relative position of this peak in both intermediates, thus giving the same qualitative result. Additionally, the second most intense peak in the \textit{syn-E-}tautomer spectrum (1242 cm\(^{-1}\)) is close to the experimental value of the second peak. However, the question of which tautomer is generated in experiment cannot be answered on the basis of the resonance Raman spectra alone.
6.3 Photoproducts of ortho-nitrotoluene

Figure 6.17: B3LYP/TZVP Resonance Raman spectra for the lowest excited states of the syn-E- and syn-Z-tautomer and an experimental difference spectrum in acetonitrile (23 spectra summed up between 5 ps and 3 ns).

6.3.3 CASSCF/CASPT2 calculations for oNT

Since the DFT and CC2 results for oNT given in Table 6.3 yield not only large differences in excitation energy but also in the ordering of the states, CASSCF/CASPT2 calculations for the excitation energies and transition dipole moments were carried out using the program package Molcas 7.3 [254]. Unfortunately, CASSCF calculations require iterative testing of several parameters in this case. The RICC2/cc-pVTZ structure was chosen for the calculations on the excited states since it is similar to the experimental structure [250]. In order to obtain excited-state energies and transition properties, state-averaged CASSCF calculations were performed on several roots, followed by multi-state CASPT2 calculations. Oscillator strengths were obtained with the RASSI (Restricted active space state interaction) module of Molcas. The following issues have to be considered [242,255]: 1) Since the energy of the virtual orbitals depends strongly on the basis set, a good basis is crucial for the active space selection. Inclusion of Rydberg-type diffuse basis functions can be necessary to avoid mixing of Rydberg character into valence orbitals which can affect the description of the excited states. 2) The choice of the active space is the key for
an appropriate description of excited states. 3) In order to deal with intruder states level shifts are applied in the CASPT2 calculation \[256\]. Increasing the level shift comes along with loss of dynamical correlation and higher excitation energies.

For the related compound NBA CASSCF/CASPT2 calculations have been published \[242\], which were taken into consideration when choosing the basis set and active space as shall be discussed now:

**Basis set**

Gonzalez and coworkers used in their calculations for NBA \[242\] an ANO-L basis (contraction \((14s9p4d3f)/[4s3p2d]\) for C, N and O and \((8s4p3d)/[3s2p]\) for H), which according to the MOLCAS manual is a basis set which gives reliable results. Since the larger basis sets (contraction \((14s9p4d3f)/[5s4p3d2f]\) for C,N and O and \((8s4p3d)/[3s2p1d]\) for H) are still affordable and are expected to yield even better results, the CAS calculations will be performed using this basis set.

**Selection of the Active Space**

Leyva et al. describe the selection of the active space for calculations on NBA in detail \[242\]. A calculation with an active space which contains all double bonds, lone pairs and the non-bonding \(p\)-orbital of the nitro group is possible neither for NBA nor for oNT, since the required active spaces of \((24,17)\) and \((18,13)\) are computationally not feasible (cf. Fig. 6.18 for the determination of the complete active spaces). Therefore, several restricted active spaces had been employed for NBA \[242\]. In order to test whether an analogous procedure is possible for oNT, a CAS calculation for NBA using one of the active spaces mentioned in Ref. \[242\], namely \((12,11)\) in combination with an ano-L basis set (contraction as described above), was performed. This restricted active space was described as excluding all lone pairs, while containing all \(\pi, \pi^*\) pairs on the benzene moiety. However, the molecular orbitals obtained do not match with the line of thought followed in Ref. \[242\], which is evident by the fact that the totally bonding and antibonding combination of the \(\pi\) orbitals of the ring are missing in the active space. Our attempt to derive restricted active spaces from molecular orbitals of an extended Hückel calculation was not effective. Thus, various restricted active spaces based on Hartree–Fock orbital energy differences were tested in this work.
As a first test for oNT, we chose a (10,9) active space, since in the SCF calculation these orbitals are separated by energy gaps from the next orbitals (this corresponds to the smallest (12,11) active space chosen for NBA by Leyva et al. [242]). Additionally, calculations on a (14,11) and (14,14) active space were performed. The state-averaged CAS calculations were performed for five roots of equal weight, followed by a MS-CASPT2 calculation. For the CASPT2 calculation, a level shift of 0.3 a.u. was applied (analogous to the calculations for NBA). The resulting energies are given in Table 6.7.

For all calculations, the reliability of the results has to be checked. Among other criteria for the reliability, in the CASPT2 calculation the reference weight of the CASSCF wavefunction for the excited states should be of comparable magnitude as the reference weight of the CASSCF wavefunction for the ground state. To identify corresponding excited states in the CAS calculations employing different active spaces, the CI coefficients of the state and their weights have to be studied closely. Comparing the results from the (10,9) active space to the (14,11) active space, there appears at least one excited state to be missing in the first calculation. Even the (14,11) active space may not be large enough, since there is an additional excited state in the energy range between 4-5 eV in the DFT and RICC2 calculations. Rydberg states may appear at energies above 5 eV and can therefore occur in the calculations. In the CASSCF results, they are shifted to lower energies relative to valence states due to a different amount of correction required from dynamical correlation. Therefore, the inclusion of a larger number of states might be necessary so that the relevant (valence) states are present at the CASSCF level. Another issue is the mixing of Rydberg-type orbitals with valence orbitals, which can influence the CASPT2 results. In order to prevent this, three diffuse Rydberg basis functions (1 s-type, 1 p-type and 1 d-type) following the scheme described in the MOLCAS manual were added [257,258].
Table 6.7: MS-CASSCF/CASPT2 energies for the lowest five states of oNT calculated for three different active spaces and a level-shift of 0.3 a.u. Energies given in eV.

<table>
<thead>
<tr>
<th>state</th>
<th>(10,9)</th>
<th>(14,11)</th>
<th>(14,14)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 roots</td>
<td>5 roots</td>
<td>5 roots</td>
</tr>
<tr>
<td>1(^1)A</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2(^1)A</td>
<td>3.77</td>
<td>3.64</td>
<td>3.94</td>
</tr>
<tr>
<td>3(^1)A</td>
<td>5.24</td>
<td>4.15</td>
<td>4.47</td>
</tr>
<tr>
<td>4(^1)A</td>
<td>5.72</td>
<td>5.17</td>
<td>5.31</td>
</tr>
<tr>
<td>5(^1)A</td>
<td>6.90</td>
<td>5.81</td>
<td>5.82</td>
</tr>
</tbody>
</table>

Table 6.8: MS-CASSCF/CASPT2 energies obtained for the lowest eight states of oNT calculated for the (14,11) active space. The influence of additional Rydberg-type basis functions and the level-shift (in a.u.) has been studied. Energies given in eV.

<table>
<thead>
<tr>
<th>state</th>
<th>without Rydberg basis</th>
<th>with Rydberg basis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>level shift 0.3</td>
<td>level shift 0.3</td>
</tr>
<tr>
<td></td>
<td>8 roots</td>
<td>imag. level shift 0.2</td>
</tr>
<tr>
<td>1(^1)A</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2(^1)A</td>
<td>3.72</td>
<td>3.62</td>
</tr>
<tr>
<td>3(^1)A</td>
<td>4.29</td>
<td>4.18</td>
</tr>
<tr>
<td>4(^1)A</td>
<td>4.99</td>
<td>4.85</td>
</tr>
<tr>
<td>5(^1)A</td>
<td>5.37</td>
<td>5.15</td>
</tr>
<tr>
<td>6(^1)A</td>
<td>5.58</td>
<td>5.56</td>
</tr>
<tr>
<td>7(^1)A</td>
<td>6.95</td>
<td>6.84</td>
</tr>
<tr>
<td>8(^1)A</td>
<td>7.16</td>
<td>7.14</td>
</tr>
</tbody>
</table>

The number of states was increased to eight in these calculations and different level-shift values and an imaginary level-shift were applied. The CASPT2 calculation for the (14,14) active space and a level-shift of 0.2 a.u. did not converge. Since already for the calculation for five states the (14,11) active space yielded lower energies, the calculations including the Rydberg basis functions were performed for this active space. The energies obtained in these calculations are given in Table 6.8. These results show that the inclusion of the Rydberg-type basis functions significantly lowers the energies. A level shift value of 0.3 a.u. and an imaginary level shift of 0.2 a.u. yield similar results; the latter leads to slightly lower excitation energies for the lowest five excited states. Therefore, for further comparison the energies obtained with the imaginary level shift will be used.
6.3.4 Comparison of calculated excitation energies for oNT

The energies obtained in DFT calculations with two different functionals and in RICC2 and CASSCF/CASPT2 calculations cannot be related by a simple shift, because they differ in the relative energies of the excited states. Moreover, it is not guaranteed that all relevant states are obtained in the calculation. Therefore, a mapping of the states is not easily possible. The oscillator strength is not suited for an unambiguous assignment, since there is only a qualitative agreement at best. Usually a directional information on the transition is given in form of the transition dipole moment components, transition strength, or in case of MOlCAS, components of Einstein coefficients. Unfortunately, these are not directly comparable, since it is not obvious which definitions form the basis of the calculated values.

Table 6.9: Energies of excited states in eV and oscillator strengths obtained with CASSCF/CASPT2 (imaginary level shift 0.2 a.u., eight roots, including Rydberg basis functions), RICC2 and B3LYP calculations.

<table>
<thead>
<tr>
<th>state</th>
<th>CASSCF/CASPT2</th>
<th>RASSI</th>
<th>RICC2/cc-pVTZ</th>
<th>B3LYP/TZVP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E / eV</td>
<td>f</td>
<td>E / eV</td>
<td>f</td>
</tr>
<tr>
<td>1^1A</td>
<td>0.00</td>
<td>0.00</td>
<td>3.78</td>
<td>0.10E-01</td>
</tr>
<tr>
<td>2^1A</td>
<td>3.60</td>
<td>0.29E-01</td>
<td>4.34</td>
<td>0.95E-04</td>
</tr>
<tr>
<td>3^1A</td>
<td>4.18</td>
<td>0.23E-02</td>
<td>4.86</td>
<td>0.17E-02</td>
</tr>
<tr>
<td>4^1A</td>
<td>4.78</td>
<td>0.82E-01</td>
<td>5.59</td>
<td>0.16</td>
</tr>
<tr>
<td>5^1A</td>
<td>5.05</td>
<td>0.29</td>
<td>6.18</td>
<td>0.32E-01</td>
</tr>
<tr>
<td>6^1A</td>
<td>5.50</td>
<td>0.17</td>
<td>6.41</td>
<td>0.16</td>
</tr>
<tr>
<td>7^1A</td>
<td>6.93</td>
<td>0.83E-02</td>
<td>6.66</td>
<td>0.51E-01</td>
</tr>
<tr>
<td>8^1A</td>
<td>7.32</td>
<td>0.18E-01</td>
<td>6.66</td>
<td>0.51E-01</td>
</tr>
</tbody>
</table>

When comparing the CASSCF/CASPT2 calculations with the (14,11) active space with eight roots, and including Rydberg basis functions with the RICC2/cc-pVTZ and B3LYP/TZVP results given in Table 6.9, and taking into account energies, oscillator strength and relative magnitude of x, y and z contributions to the transition dipole moment, the first excited state appears to be the same state in all three calculations. For this state, comparable excitation energies and oscillator strengths are obtained. For the second excited state, the energies are similar, but as could already be seen in Table 6.3, the B3LYP HOMO—LUMO transition appears at too low energy (4.21 eV), which corresponds to the transition at 4.86 eV in the RICC2 calculation. The first four excited states of the CASSCF/PT2 and RICC2 calculations might correspond to the same states, although oscillator strengths and relative magnitudes of the transition dipole moment components do not match accurately. For higher excited states, a mapping of states becomes increasingly difficult. In view of the sensitive dependence of resonance Raman spectra on the relative energies of excited states, these deviations in the results and especially the wrong ordering in DFT calculations are problematic.
6.3.5 Conclusions for the photoproducts of oNT, excitation energies and Heller’s gradient approximation

For the photoproducts of oNT, we focussed on the theoretical description of the excitation energies. For oNT, the calculated excitation energies as well as the comparison of theoretical (resonance) Raman spectra to the experimental spectra result in an off-resonance description of the oNT spectra. For the aci-nitro tautomer intermediate, different methods and density functionals do not agree in the vertical excitation energy. The qualitative picture obtained with all methods, however, suggests a resonance Raman description for the intermediates. Although the comparison of experimental and calculated spectra does not allow to distinguish between possible intermediates, the theoretical spectra obtained using the gradient approximation do not contradict the experimental spectrum, rather do they show an intensity pattern which can be brought in accordance with experiment for both possible intermediates (syn-Z and syn-E). The reliability of the harmonic wavenumbers is in this context more important than the model applied for the RR intensities. As regards the vertical excitation energies, neither RICC2 nor CASSCF/CASPT2 can be considered as the final solution to this problem.
7 Algorithmic Advances to Exploit the Intrinsic Selectivity of Resonance Raman Spectra

The selectivity of resonance Raman spectroscopy allows one not only to identify different species in a mixture, but even different instances of the same aromatic amino acid residue on different parts within a protein [27, 259]. This turns it into a method to probe a molecule locally: ground-state vibrations in the region where the electronic structure of the excited state changes compared to the ground state, i.e., where the excited state is localized, are enhanced. Thus, though still representing an aspect of the complete molecule, the RR spectrum is determined by intense vibrations on a specific part of the molecule. For the theoretical description of RR spectra, at least the normal modes of the ground state as well as the excited-state gradient have to be calculated to yield intensities in the framework of Heller’s gradient approximation. Frequency analyses based on density-functional theory are very efficient [211] and yield harmonic frequencies that are usually in very good agreement with fundamental frequencies as obtained in experiment [246, 260], so that intricate features in complicated vibrational spectra can be clarified [252, 261, 262]. An analysis on the basis of experimental information alone would be much more difficult in many cases, if possible at all. Conventional methods for the determination of frequencies and intensities describe all vibrations on the same footing, irrespectively of their intensity. This becomes increasingly demanding for larger molecules and is, moreover, not efficient, if one knows in advance that the spectrum is determined by only a small number of frequencies. The development of the mode-tracking algorithm [39, 263, 264], which allows the selective calculation of a subset of pre-defined normal modes, made it possible to restrict the theoretical frequency analyses to subsets of the Hessian eigenvectors, which are of relevance for a particular problem under study. A necessary condition for an efficient application of the mode-tracking algorithm is that at least a rough guess for the normal modes to be optimized can be provided. Various ways to obtain such a guess have been employed [24, 40, 263, 265–270]. For a recent review, see Ref. [264].

While it is sometimes known which vibrations in a Raman spectrum will get enhanced under resonance conditions, this may not be true in general for more complicated molecules, e.g., transition metal compounds [271]. In this chapter the possibility to use an algorithm based on the mode-tracking principle together with the information on the excited-state gradient in order to directly determine only
the intense vibrations in a resonance Raman spectrum will be explored. The approximate relative intensity of a vibration within Heller’s gradient (or short-time) approximation \cite{33} is related to the projection of the excited-state gradient vector onto that normal mode. The method presented in this chapter uses this gradient vector as a guess vector in a mode-tracking calculation and subsequently focuses on vibrational normal modes with a large overlap with that vector. Of major importance for the efficiency of the method are the criteria according to which the intense modes are chosen and their convergence is assessed. The algorithm applied here is thus very different from, e.g., the approach presented in Ref. \cite{261}, in which the intensities were calculated in a mode-wise way after the vibrational frequencies and normal modes had been determined.

This intensity-tracking algorithm can be applied very generally to the calculation of vibrational spectra, provided that a suitable starting distortion and an expression to identify the intense modes during the intensity-tracking calculation are available. For its application to infrared and Raman spectroscopy, see \cite{272,273}. Here in particular its application for resonance Raman investigations on (models for) proteins is studied, since the structure elucidation of proteins as well as of other biomolecules is an important field of application for experimental resonance Raman spectroscopy \cite{274,275}. By analyzing the amide vibration wavenumbers and intensities \cite{25,276,277}, the secondary structure of proteins can be probed. If the excitation wavelength is tuned to energies at which bands of the aromatic amino acids tryptophan (Trp), tyrosine (Tyr), and phenylalanine (Phe) are selectively enhanced, information about hydrogen bonds and hydrophobicity of the environment and orientation of these chromophores can be obtained \cite{21,27,30,276,278}. Resonance Raman spectroscopy is also a valuable method to aid the study of protein folding, as shown, e.g., in the investigation of variants of the E colicin-binding immunity protein Im7 and their different conformational states \cite{29}.

In the following, the underlying theory and details of the algorithm and implementation (Section 7.1) will be presented before the approach is employed for the calculation of resonance Raman intensities of uracil in Section 7.2. An application to models of the protein Im7 follows in Section 7.3 as well as further local approximations. Conclusions on the intensity-tracking algorithm for RR spectra are listed in Section 7.4.

### 7.1 Theoretical Background

In order to appreciate the algorithmic structure of the intensity-tracking approach, which focuses exclusively on the determination of high-intensity modes, a brief review on the algorithmically related, though conceptually very different mode-tracking protocol is given, which is solely based on the form of the collective motion provided as a guess.
7.1 Theoretical Background

7.1.1 Mode-tracking Algorithm

The full details of the original mode-tracking algorithm have been presented in previous work [39, 263, 264]. An outline of the main steps is given in the following. In the mode-tracking algorithm the eigenvalues $\lambda_i$ of the Hessian matrix are determined by employing a subspace iteration method like the Lanczos [279] or Davidson method [280]. In each iteration, approximate solutions for a subset of eigenvectors $L_i$ are obtained. This procedure can be applied to solve for a certain pre-selected mode (or, when using a block-Davidson method, several pre-selected modes), where the iterative algorithm will be carried out until the approximations of the selected eigenvectors are converged. Thus the diagonalization of the full mass-weighted Hessian $H^{mw}$,

\[(H^{mw} - \lambda_i) L_i = 0 \quad (7.1)\]

is formally replaced by solving,

\[(H^{mw} - \lambda_i^{(k)}) L_i^{(k)} = r_i^{(k)}, \quad (7.2)\]

where $r_i^{(k)}$ is the residuum vector for the approximate eigenvector $L_i^{(k)}$ in iteration $k$. The elements of the residuum vector have the same unit as the elements of the mass-weighted Hessian and are given in the following in units of hartree/[amu $\times$ bohr$^2$], where amu is the atomic mass unit ($1.66056 \cdot 10^{-27}$ kg). The exact eigenvectors of the Hessian provide the unitary transformation matrix from mass-weighted Cartesian ($R^{mw}$) to mass-weighted normal coordinates ($Q$) according to

\[Q = LR^{mw}, \quad R^{mw} = L^\dagger Q. \quad (7.3)\]

The eigenvectors $L_i$, i.e., the columns of the matrix $L$, describe the normal modes of the molecule.

At the beginning of the mode-tracking calculation, an approximation $b_i$ for each eigenvector to be optimized has to be chosen. These “guess vectors” represent the first basis vectors in which the approximate eigenvectors are expanded. In the following step, the vectors $\sigma_i$ are determined,

\[\sigma_i := H^{mw} b_i, \quad (7.4)\]

which are calculated numerically as directional derivatives of the gradient of the electronic energy with respect to the basis vectors. The vectors $\sigma_i$ are used for the calculation of the elements of the small Davidson matrix $\tilde{H}$,

\[\tilde{H}_{ji} = b_j^T H^{mw} b_i = b_j^T \sigma_i. \quad (7.5)\]

By diagonalization of the Davidson matrix, approximate eigenvalues $\lambda_i^{(k)}$ and eigenvectors $L_i^{(k)}$ of the full Hessian can be constructed. Subsequently the residuum vectors $r_i^{(k)}$ are calculated for all $L_i^{(k)}$ according to Eq. (7.2).
Afterwards, the root-homing step is carried out, in which those approximate eigenvectors from the full set \( \{ L^k_i \} \) are determined, which correspond to the sought-for vibrations and shall thus be further optimized. This is typically done on the basis of the overlap with either the initial guess vector(s) or the approximate eigenvector(s) selected in the previous iteration.

In a subsequent convergence check it is tested whether the approximate normal modes are already sufficiently accurate. If not, new basis vectors are constructed according to

\[
b_{n_b}^{(k) + j} = X r_i^{(k)},
\]

where \( n_b^{(k)} \) is the number of basis vectors in iteration \( k \), \( j \) runs from 1 to the number of approximate eigenvectors selected for further optimization, and \( X \) is a preconditioner. In previous investigations, it turned out that even without preconditioning, i.e., by formally choosing \( X^{(k)} = 1 \), the algorithm can be applied very efficiently (cf. Ref. [263]).

### 7.1.2 Intensity Tracking

Intensities for vibrational spectra can be calculated reliably within the double harmonic approximation for infrared and non-resonant Raman spectra. Under resonance conditions, the situation is more complicated, but often an estimate of relative intensities is possible on the basis of the gradient of the excited-state potential energy surface [33]. In those cases, the calculation of relative intensities is even simpler (though less generally applicable) than the calculation of off-resonance Raman intensities [11, 24, 190–193].

The mode-tracking algorithm as described above aims at finding those eigenvectors of the Hessian which resemble most closely the pre-defined collective motion. In contrast to that, intensity tracking aims at the determination of all normal modes of considerable intensity without an intuitive guess for how these vibrations may look like. In order to obtain the intense modes, a hypothetical vibration which represents a superposition of the most intense modes weighted by their intensities is needed as a starting distortion. This idea should in principle work for any kind of vibrational spectroscopy for which an intensity expression in terms of the normal modes can be derived in closed form. In the following Heller’s gradient approximation will be shown to offer a way for such an intensity-driven approach for the case of resonance Raman spectroscopy since it can selectively provide information about the movement of the atoms in the intense vibrational modes.

The expression for the relative intensities \( i_j \) and \( i_k \) in the framework of the gradient approximation in terms of mass-weighted normal coordinates \( Q_j \) reads (cf. Eq. (4.31))

\[
\frac{i_j}{i_k} = \frac{\tilde{\nu}_k}{\tilde{\nu}_j} \left( \frac{V_j^Q}{V_k^Q} \right)^2,
\]

where

\[
V_j^Q = \left( \frac{\partial E^{\text{el}}}{\partial Q_j} \right)_{Q=0}.
\]
The expression for relative intensities contains the wavenumbers and the gradient of the excited-state energy with respect to the mass-weighted normal coordinates. Although wavenumbers and normal modes of the spectrum are unknown before a vibrational calculation, the excited-state gradient with respect to Cartesian coordinates can be calculated analytically with a single calculation with many excited-state electronic structure methods, e.g., configuration interaction with singly-substituted determinants (CIS) [281], time-dependent density-functional theory (TDDFT) [282–286], the approximate second-order coupled-cluster model CC2 [287], or the complete active space self-consistent field (CASSCF) method [288].

The expression for $V_{ij}^Q$ can be explicitly written in terms of mass-weighted coordinates as,

$$V_{ij}^Q = \sum_i \frac{\partial R_{ij}^{mw}}{\partial Q_j} \left( \frac{\partial E_{el}^{ex}}{\partial R_{ij}^{mw}} \right)_{R=0} = \sum_i L_{ij} g_{ij}^{mw} = L_{ij} \cdot g^{mw}, \quad (7.9)$$

where the mass-weighted gradient vector $g^{mw}$ has been introduced,

$$g_{ij}^{mw} = \left( \frac{\partial E_{el}^{ex}}{\partial R_{ij}^{mw}} \right)_{R=0}, \quad (7.10)$$

and used Eq. (7.3) to determine

$$\frac{\partial R_{ij}^{mw}}{\partial Q_j} = L_{ij}. \quad (7.11)$$

Eq. (7.9) thus shows that the excited-state derivative along a normal coordinate is equal to the corresponding expansion coefficient of the mass-weighted excited-state gradient vector in terms of normal coordinates, i.e., its projection onto the Hessian eigenvector. Because the intensity is proportional to $(V_{ij}^Q)^2$, intense modes will have a larger overlap with the excited-state gradient vector, so that the gradient resembles a particular normal coordinate the more closely the more intense it is. The excited-state gradient is thus a suitable guess vector for the mode-tracking of intense modes.

Since the present approach tries to select and optimize all normal modes that carry a significant percentage of the total intensity, irrespective of the type of motion, the root-homing procedure, i.e., the selection of eigenvector approximations for further optimization, has to be adapted in order to choose the most intense modes. However, all eigenvectors are improved by the expansion in a growing basis, thus not only the eigenvectors which were selected for optimization are well described after convergence of the algorithm, but in the ideal case a reasonable approximation for the less intense features in the spectrum is obtained as well.

During the intensity-tracking iterations, only approximate normal mode vectors are available at the beginning. An expression for the approximate relative intensity
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of mode \( j \) can be derived from Eqs. (7.7) and (7.9),

\[
i_{j,\text{rel}} = \frac{1}{\tilde{\nu}_j} \cdot \left(V_j^Q\right)^2 = \frac{1}{\tilde{\nu}_j} \cdot (L_j \cdot g^{\text{mw}})^2,
\]

(7.12)

where the eigenvectors \( L_j \) and wavenumbers \( \tilde{\nu}_j \) have to be replaced by their current approximations.

Modes which according to Eq. (7.12) have a high approximate (relative) intensity are selected for further optimization. There are several possible schemes to implement such a root-homing procedure, of which the following were tested: (i) the selection of the \( N \) most intense modes in each iteration, and (ii) the selection of a certain number of modes in such a way that their relative intensities sum up to a certain percentage of the total intensity. The subsequent steps, i.e., convergence check and construction of new basis vectors, follow the standard mode-tracking procedure. The description of the most intense modes is iteratively improved until they are converged, so that an approximate resonance Raman spectrum is obtained which is accurate with respect to the most intense modes. The gain in efficiency compared to a conventional calculation of the resonance Raman spectrum should thus be the larger the more low-intensity modes are present in the spectrum, since these modes will be automatically discarded in the intensity-tracking calculation.

In Fig. 7.1 the iterative improvement of modes by an increasing basis selected for the intense modes is visualized. The qualitative difference between mode-tracking and intensity-tracking calculations is illustrated in Fig. 7.2: Whereas the primary goal of mode-tracking is to determine the exact normal mode and frequency of a specific vibration for which an intuitive guess was supplied, the aim of intensity tracking is an iterative refinement of an entire spectrum based on an unspecific guess that corresponds to a hypothetical vibration carrying the entire intensity. They are distinctly different in their start and end points, as intensity tracking neither requires a guess distortion close to a converged vibrational motion for the start nor does it aim at producing only a few vibrations but instead the complete structure-characteristic fingerprint.

7.1.3 Technical details

DFT ground-state structure optimizations and calculations of excitation energies, excited-state gradients as well as raw-data calculations of energy gradients needed for the intensity-tracking approach were performed with the hybrid functional B3LYP [48, 50, 221, 289] and the Becke–Perdew (BP86) functional [49, 221] employing the TZVP basis sets implemented in TURBOMOLE [225, 290]. In case of BP86 the resolution-of-the-identity (RI) approximation was applied. Note that only one excited-state gradient calculation at the ground-state equilibrium position is needed for resonance-Raman calculations within Heller's gradient approximation. Mode-tracking and intensity-tracking calculations were carried out with a modified version of the program AKIRA [39]. If not specified otherwise, standard AKIRA convergence
Figure 7.1: First steps of an intensity-tracking calculation for tryptophan: in the first iteration, basis vectors $b_1$ and approximate eigenvector $L^{(1)}_1$ are identical. In the following iterations $k$, more basis vectors $b_j$ (in blue boxes) are generated to specifically improve the approximate eigenvectors $L^{(k)}_i$ (red boxes) of high intensity. New modes of low intensity emerge. Each approximate eigenvector $L^{(k)}_i$ is a linear combination of all basis vectors available in iteration $k$. 
Figure 7.2: Schematic comparison of mode tracking (left) and intensity tracking (right). In the former case, a guess for a specific normal mode of the molecule under study is created, which is iteratively refined to get the exact normal mode and vibrational frequency. In contrast to this, intensity-tracking starts with an unspecific guess for a hypothetical collective motion that contains the entire intensity in the resonance Raman spectrum. A guess for the entire spectrum is then iteratively refined. The intermediate spectra shown on the right are taken from a B3LYP/TZVP resonance Raman calculation on uracil, assuming resonance with the $2^1 A'$ state.
criteria and an intensity threshold of 80% of the total intensity for root-homing were applied (see below). For comparison, excited-state gradients were projected onto normal modes calculated by a complete frequency calculation with the SNF program [211]. These spectra are dubbed “conventional gradient spectra”. All resonance Raman spectra are plotted applying a Gaussian broadening with a half-width of 10 cm\(^{-1}\).

## 7.2 Validation: intensity-tracking for uracil

In order to validate the intensity-tracking algorithm, the resonance Raman spectrum for the \(2^1 A'\) state of uracil was calculated, which has been well studied with various theoretical methods [24, 168]. Uracil is a planar molecule and, within Heller’s gradient approximation, resonance Raman active vibrations must be in that plane (\(a'\) symmetry). The mode-tracking implementation used here does not explicitly consider the molecular symmetry for the calculations, but allows the creation of an orthogonal subspace against which new basis modes are orthonormalized. The optimized \(C_s\) symmetric uracil structure, see Fig. 7.3, was obtained using B3LYP/TZVP and the gradient of the \(2^1 A'\) state at 5.25 eV. Since uracil is a planar molecule with 12 atoms, there are \(12 \times 2 = 24\) degrees of freedom in the \(xy\)-plane. Two of them represent translations and one is a rotation, so that there are 21 degrees of freedom for vibrational motion relevant for the current test.

Figure 7.3: B3LYP/TZVP optimized structure of uracil (\(C_s\) symmetry) and molecular orbitals (B3LYP/TZVP) dominating the transition to the \(2^1 A'\) state of uracil.

One can expect the intensity-tracking algorithm to work best for electronic transitions localized on a small part of a larger molecule with localized vibrational modes, since a smaller number of basis vectors will be needed for their description. The decrease in computing time of the intensity-tracking calculation compared to a full semi-numerical calculation of the vibrational spectrum [211] is given by the ratio of the number of basis vectors needed in comparison with the total number of vibrational degrees of freedom of the molecule, since for both methods there is a linear correlation between the number of basis vectors and the computing time needed. Intermediate intensity calculations and the root-homing procedure produce only a small overhead.
Uracil does not at all fulfill this prerequisite, since the molecular orbitals involved in the electronic transition under study are basically delocalized over the entire molecule (see Fig. 7.3). Therefore, this small molecule represents the most critical test case for the convergence behavior of the intensity-tracking algorithm since the mode construction cannot benefit from intensity selection. This is reflected in the current example by the necessity to include all 21 basis vectors in order to converge the spectrum if rather strict convergence criteria are applied. The intermediate and final spectra are depicted in Fig. 7.2. The spectrum in the first iteration contains the intensity of all modes concentrated in one peak, which corresponds to the collective motion given by the excited-state gradient vector. Note that its approximate eigenvalue is already quite close to the frequency of the most intense mode in the converged spectrum. In the following iterations, the intensity is distributed to more and better approximations of the normal modes (note that in Fig. 7.2 only vibrations between 500 and 2000 cm\(^{-1}\) are shown). Enlarging the basis leads to a shift in the wavenumbers and appearance of new modes. New approximate normal modes which carry a substantial fraction of the intensity are selected for further optimization in the root-homing step. Such modes may split up in subsequent iterations (cf. Fig. 7.2, iteration 4 to iteration 5). After a few iterations the most important features are obtained, i.e., the approximate frequencies of the intense peaks and their relative intensities do not change anymore. For example, the two most intense peaks already appear at approximately correct positions after three iterations. The spectrum in iteration 8 represents already a good approximation to the final spectrum. Several modes which are not converged according to the applied criteria hardly change when compared to the subsequent iteration. This suggests that the applied convergence criteria are too strict. Another important aspect for the convergence behaviour of the spectra is the choice of the selected modes and thus the root-homing procedure, which will be analyzed in the next section. In a complete basis, the converged intensity-tracking spectrum and the conventional gradient spectrum are virtually identical, see Fig. 7.4. The tiny remaining deviations are due to the fact that the numerical differentiations applied in both types of calculations make use of different basis vectors, so that they are affected by numerical noise in slightly different ways.
7.3 Resonance Raman spectra of Im7-based models

Intensity-tracking is expected to be most valuable in cases of large molecules with a comparatively small number of intense vibrations. In the following, it will be shown how the iterative refinement of signatures in a resonance Raman spectrum can be optimized if these requirements are fulfilled. As an example, models derived from the Im7 protein are studied that all contain the skatole motif from the tryptophan residue.

This investigation requires several steps: First, the excited states of the core chromophore, i.e., the skatole moiety of the Trp residue, will be investigated in order to identify possible states in resonance, and its conventional gradient spectra are determined. Second, a mapping of the excited states for Im7-based models to those of skatole in order to identify the resonant states for UV resonance Raman spectroscopy is done. After these steps have been carried out, it has to be determined which convergence criteria are necessary in order to obtain reliable spectral features, and how the convergence behavior can be controlled and steered in such a way that it allows fast access to the characteristic signatures. Finally, the criteria obtained from these investigations are applied in a model calculation of the resonance Raman spectrum for a large fragment of the Im7 protein.
7.3.1 Preparatory calculations: Identification of resonating states

The calculation of resonance Raman spectra in Heller’s gradient approximation requires as a first step the identification of the excited state responsible for the resonance enhancement. The criteria that can be used for this purpose are the requirements that (i) the resonance condition with the incident light beam is fulfilled for the excited state and that (ii) the transition dipole moment for the corresponding transition is large. For the larger Im7-based models considered here, TDDFT is the only applicable first-principles method for excited states since it offers a good compromise between accuracy and computational cost, in particular for the valence excited states that are studied in this chapter. However, it is well known that TDDFT suffers from several problems that lead to an underestimation of certain types of excitation energies (see, e.g., Chapter 6 and Refs. [68, 238, 291], and references therein). The number of low-lying excited states is thus artificially increased in such calculations, and the oscillator strength of intense electronic transitions may be distributed over several close-lying excitations by spurious mixings [238]. This clearly hampers the identification of excited states that are relevant for the resonance Raman spectrum.

Therefore, two models of different sizes for that part of the Im7 protein that contains the Trp fragment were chosen and their excited states mapped to those of the bare skatole chromophore. Note that the full Im7 protein also contains three tyrosine residues that are important for the total resonance Raman spectrum, which was ignored in this study in order to set up model compounds in which one particular chromophore can be assumed to be responsible for the intensity pattern to be tracked.

In Fig. 7.5, the optimized structures of skatole as a zeroth-order model for Trp in Im7 (in a C\textsubscript{s} symmetric minimum structure) and of the Im7-based models 1 and 2 are shown. For the optimization of the ground-state structures, frequency analyses, excitation energies and excited-state gradients of skatole and model 1, B3LYP/TZVP was employed, whereas for the larger model 2, BP86 was used for the ground-state structures and frequency analysis for efficiency reasons. The implications of using different functionals for ground and excited states will be discussed below.

The small Im7-based model 1 comprises 35 atoms and consists of the amino acid Trp, capped by an aldehyde group at the N-terminus and a glycine fragment (instead of the arginine residue) connected to the C-terminus, see Fig. 7.5. Model 2 consists of the amino acid sequence Ile–Lys–Glu–Trp–Arg–Ala–Ala–Asn–Gly (151 atoms), in which Lys and Arg are included in their neutral form. The structures of both models were fully optimized.

In Table 7.1 excitation energies, transition dipole moments and dominant orbital transitions are presented. In the wavelength regime between 250 and 280 nm (energy range from 4.4 to 5.0 eV), which was assumed for the excitation wavelength, one obtains two excited states for skatole, which are denoted as $L_a$ ($2^1A$) and $L_b$ ($3^1A$).
7.3 Resonance Raman spectra of Im7-based models

Figure 7.5: B3LYP/TZVP optimized structures of skatole ($C_s$) and model 1 as well as the BP86/TZVP optimized structure of model 2. Also shown are the molecular orbitals (B3LYP/TZVP) involved in the lowest electronic excitations of skatole.

Note that in this DFT study the order of these two states is reversed in comparison to, e.g., the study on the corresponding states in indole in Ref. [255] and the experimental findings mentioned there. This problem has been discussed in detail for other aromatic compounds [292]. The $2^1A$ state is dominated by the HOMO→LUMO orbital transition (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital), while a combination of the HOMO→1→LUMO and HOMO→LUMO+1 orbital transitions is dominant for the $3^1A$ state. Isosurface plots of the orbitals involved are shown in Fig. 7.5. Since the $2^1A$ and $3^1A$ state are only 0.25 eV apart in energy for B3LYP and 0.37 eV for BP86, they can both be expected to contribute to a resonance Raman spectrum with an excitation energy in that range. The experimental excitation energies for both states are somewhat smaller, but similarly close ($4.31$ eV and $\sim 4.77$ eV [293], respectively). A detailed theoretical study of the excited states of the underlying indole motif can be found in Ref. [255].
Table 7.1: Calculated excitation energies, dominant orbital transitions and corresponding transition dipole moments $\mu_t$ for skatole and models 1 and 2. The applied functionals are denoted in parentheses. Where two different functionals are denoted, the first one was used for the ground state structure and frequencies and the second one for excitation energies and the excited-state gradient. Note that the transition mentioned in the first column always refers to the corresponding transition in skatole; H: HOMO; L: LUMO.

<table>
<thead>
<tr>
<th>transition</th>
<th>molecule</th>
<th>state</th>
<th>transition</th>
<th>$E_e$/eV</th>
<th>$\mu_t$/a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H→L</td>
<td>skatole (B3LYP)</td>
<td>$2^1A'$</td>
<td>$6a''-7a''$ (89%)</td>
<td>4.62</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>skatole (BP86 )</td>
<td>$2^1A'$</td>
<td>$6a''-7a''$ (88%)</td>
<td>4.20</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>model 1 (B3LYP)</td>
<td>$4^1A$</td>
<td>$72a-74a$ (89%)</td>
<td>4.64</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>model 1 (BP86/B3LYP)</td>
<td>$4^1A$</td>
<td>$72a-74a$ (86%)</td>
<td>4.58</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>model 1 (BP86)</td>
<td>$8^1A$</td>
<td>$72a-74a$ (78%)</td>
<td>4.17</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>model 2 (BP86/B3LYP)</td>
<td>$15^1A$</td>
<td>$283a-288a$ (65%)</td>
<td>4.59</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>model 2 (BP86)</td>
<td>$92^1A$</td>
<td>$279a-288a$ (46%)</td>
<td>4.26</td>
<td>0.46</td>
</tr>
<tr>
<td>H→1→L</td>
<td>skatole (B3LYP)</td>
<td>$3^1A'$</td>
<td>$5a''-7a''$ (60%)</td>
<td>4.87</td>
<td>0.42</td>
</tr>
<tr>
<td>+H→L+1</td>
<td>skatole (BP86)</td>
<td>$3^1A'$</td>
<td>$6a''-8a''$ (37%)</td>
<td>4.57</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>model 1 (B3LYP)</td>
<td>$6^1A$</td>
<td>$71a-74a$ (61%)</td>
<td>4.87</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>model 1 (BP86)</td>
<td>$12^1A$</td>
<td>$71a-74a$ (45%)</td>
<td>4.57</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Within Heller’s gradient approximation, it is assumed that only one excited state is in resonance, which is clearly a simplification in the present case. In principle, the approach could also be applied to identify the most important modes for two or more close-lying states. Once these vibrations are identified, more sophisticated treatments taking interference effects into account could be applied subsequently in the restricted set of normal modes. For this pilot study of the intensity tracking algorithm, however, the approximation is made that either the $L_a$ or the $L_b$ state alone determine the spectrum.

For model 1, the identification of these states is straightforward by comparing the excitation energies, transition dipole moments, and orbital transitions involved in the excitations to those of skatole (see Table 7.1). The situation for model 2 is more complicated and not unambiguous due to the problems outlined above for TDDFT calculations on large systems. But the choice of the resonating states made here can
be assessed by comparing the final resonance Raman spectra to those of the smaller structural motifs, which will be done in Section 7.3.5.

Figure 7.6: Resonance Raman spectra of skatole for resonance with the \(2^1A'\) or \(3^1A'\) state obtained by a conventional gradient calculation using B3LYP/TZVP. Also shown are the spectra for the corresponding states of Im7-based model 1 obtained either in a converged intensity-tracking calculation (ITC) or as conventional gradient spectra (CGS). Wavenumbers of important vibrations are given in units of cm\(^{-1}\).
While the state corresponding to the $2^1A$ state of skatole was investigated for both models, the excited state corresponding to the $3^1A$ state of skatole was only examined for model 1 in order to test convergence criteria and root-homing options. As will be shown below, the intensity distribution for this state is distinctly different from that of the $2^1A$ state, so that the requirements for the intensity-tracking algorithm to converge quickly can be tested on a broader basis.

The B3LYP/TZVP resonance Raman spectrum obtained within Heller’s gradient approximation by assuming resonance with the $2^1A'$ state of skatole is shown in Fig. 7.6. It is dominated by the peak at 1617 cm$^{-1}$, and two further intense peaks appear at 775 cm$^{-1}$ and 1371 cm$^{-1}$. The corresponding normal modes are visualized in Fig. 7.7. In the spectrum obtained from the $3^1A$ state, the modes at 775, 1035, and 1371 cm$^{-1}$ dominate the spectrum, and several other modes of considerable intensity are present. The enhancement is thus less selective for resonance with this state, and consequently intensity-tracking should be more beneficial for the $2^1A$ state.

### 7.3.2 Convergence criteria for intensity tracking

In the original mode-tracking approach, the residuum vector is a measure for the convergence of the sought-after normal mode and its frequency. When studying the convergence of an intensity-tracking calculation, however, two aspects have to be taken into consideration: The first is the selection of reliable criteria for the convergence of the vibrational peaks chosen for optimization in comparison to a conventional calculation. The second concerns the questions of how many and which modes should be selected for the iterative refinement, which also has direct consequences on the overall convergence of the spectrum, since convergence is only tested for the selected modes. This point will be discussed in Section 7.3.3.

The goal of this section is to determine reliable convergence criteria which yield approximate resonance Raman spectra that are in good agreement with a full calculation of the spectrum with the smallest possible number of basis vectors (bv). For model 1, a complete basis consists of $35 \times 3 - 6 = 99$ basis vectors. In the following, the convergence is tested in dependence of the threshold value for the maximum absolute component of the residuum vector ($r_{\text{max}}^{\text{thres}}$).

For model 1 of the Im7 protein, resonance Raman spectra calculated for two excited states, $4^1A$ and $6^1A$, which correspond to the $2^1A'$ and $3^1A'$ states of skatole, were studied. Using strict convergence criteria, the intensity-tracking calculation requires a full basis, and the results of the conventional gradient calculations can be reproduced (see Fig. 7.6) apart from small numerical deviations. A note in passing: the resonance Raman spectrum of the $4^1A$ state is very similar to the $2^1A'$ spectrum of skatole with respect to the intensity distribution and wavenumbers of the modes.
The wavenumbers of the intense modes exhibit only very small shifts, e.g., from 1371 cm$^{-1}$ to 1369 cm$^{-1}$, and the vibrations are mainly localized on the skatole moiety. In Fig. 7.7, graphical representations of the normal modes are compared to the corresponding skatole modes. The spectrum of model 1 exhibits further modes in the region of 1000 to 1400 cm$^{-1}$ carrying small percentages of the intensity, but the additional 64 vibrational degrees of freedom compared to skatole do not alter the spectrum significantly. In Fig. 7.8 several intermediate spectra during the intensity-tracking iterations with a convergence criterion of $r_{\text{thres}}^{\text{max}} = 5 \cdot 10^{-4}$ for the third excited state are shown. This leads to a converged spectrum with an almost complete basis of 91 basis vectors and only minor deviations compared to the conventional gradient spectrum. Although a large percentage of the full set of basis vectors is required for formal convergence, the most important features of the resonance Raman spectrum are already obtained with good accuracy in iteration 15 with 44 basis vectors. The convergence criteria are thus obviously too tight if only an approximate spectrum is desired. Several different values of $r_{\text{max}}^{\text{thres}}$ were tested, for which the spectra are shown in Fig. 7.9.
Figure 7.8: Convergence of the modes during B3LYP/TZVP intensity-tracking iterations (It.) with standard convergence criteria ($\eta_{\text{max}}^{\text{thres}} = 0.0005$) for the resonance Raman spectrum for the $4^1A$ state of model 1 (Converged: black; not converged: red). The total number of basis vectors (bv) is given on the right hand side. The relative intensities have the same scale, only the results for iterations 15, 19 and 22 are magnified by a factor of 2.
7.3 Resonance Raman spectra of Im7-based models

Figure 7.9: Converged spectra (B3LYP/TZVP) for the 4\(^1\)A (left) and 6\(^1\)A (right) state of model 1 for different convergence criteria. The total number of basis vectors (bv) and of converged modes (conv) is given for each spectrum.

Applying a value as strict as \(5 \cdot 10^{-4}\) or \(1 \cdot 10^{-3}\) requires a rather large number of basis vectors for convergence (94 bv and 79 bv for 4\(^1\)A, 99 or 95 bv for 6\(^1\)A), yielding spectra in very good agreement with the conventional one. \(r_{\text{thres}}^\text{max}\) values of \(5 \cdot 10^{-3}\) or larger result in crude approximations to the spectrum. For the 6\(^1\)A spectrum, where the intensity is distributed to more modes, a larger number of basis vectors is needed to get an equally good description. The tests showed that spectra featuring the most significant bands and some additional details can be obtained with an intermediate value for \(r_{\text{thres}}^\text{max}\) of \(3 \cdot 10^{-3}\) (46 bv for 4\(^1\)A and 55 bv for 5\(^1\)A), leading to a reduction in computational effort to 46% and 56%, respectively.

In conclusion, the maximum element of the residuum vector should not be larger than 0.003 in order to get a reasonable approximation to the spectrum. If additionally the norm of the residuum vector is considered, the maximum element can be chosen to be 0.005 if the norm is as small as 0.0001. The number of converged modes is in general not well suited to assess the degree of convergence of the overall spectrum.

7.3.3 Root-homing

In the preceding tests, reasonable spectra required the convergence of a rather large number of modes. This is caused by the fact that too many modes are selected with the root-homing criteria initially applied, especially when the most intense modes are already obtained. The algorithm hence tries to optimize also many lower-intensity modes that may not be relevant for the characteristic features of a spectrum. This
results in an almost simultaneous convergence of all selected modes as the basis approaches completeness. A smart root-homing should, on the contrary, lead to a directed convergence of the most intense features of the spectrum and not construct too many new basis vectors per iteration, so that a smooth development of the spectrum can be expected.

Two possible types of root-homing are tested here: (A) selecting the most intense modes to be optimized so that their cumulative intensity exceeds a threshold percentage of the total intensity $I_{\text{thres}}$, or (B) choosing the integer number of $N_{\text{sel}}$ most intense modes.

The converged spectra for the third ($4^1 A$) and fifth ($6^1 A$) excited state are depicted in Fig. S2 in the Supplementary Material to Ref. [294]. The dependence of the final spectrum on the root-homing option is less pronounced than for the convergence criteria. The tightest threshold considered for each of the three options naturally results in a larger number of basis vectors and a spectrum which agrees better with the conventional gradient spectrum, since more approximate normal modes are chosen for further optimization. With option (A) and a threshold value of 80% for $I_{\text{thres}}$, a (nearly) complete basis is needed for a converged spectrum. But even a rather small value of 50% still yields good approximate spectra for this molecule while reducing the number of basis vectors to 64 bv for $4^1 A$ and 89 bv for $6^1 A$.

Again, it can be seen that the intensity-tracking algorithm works better for the $4^1 A$ spectrum, which contains only a small number of intense bands. With the option to optimize the 5 most intense modes, i.e., option (B) with $N_{\text{sel}} = 5$, the spectrum is well converged for the most important features, and even for $N_{\text{sel}} = 3$ the results are only slightly worse.

It should be noted that options (A) and (B) show somewhat complementary features in the tests. Option (B) works well if there is a particular interest in a small number of high-intensity modes, as is the case in the $4^1 A$ spectrum. In the $6^1 A$ spectrum, however, several modes of considerable intensity in the wavenumber range between 1100 and 1350 cm$^{-1}$ are only approximately converged or still missing. Nevertheless, the most dominant bands are clearly converged with option (B), and this option will thus be the preferred one for spectra of larger molecules with only a few significant bands. Option (A) on the other hand guarantees that also those parts of the spectrum are converged in which a considerable part of the total intensity is distributed over a number of modes. However, this often leads to the selection of a large number of approximate modes for further optimization.

In addition to the two root-homing options presented here, a third root-homing option (C) was tested, in which modes carrying a relative intensity exceeding a threshold value $i_{\text{thres}}$ are selected. The results for root-homing option (C) are contained in Fig. S2 of the Supplementary Material to Ref. [294]. The smallest number of basis vectors for formal convergence is needed when using option (C) for the root-homing with threshold value of $i_{\text{thres}} = 0.2$. However, these settings also lead to the least accurate approximation to the total spectrum and were therefore not considered in more detail.
Figure 7.10: Converged spectra for the $4^1A$ (left) and $6^1A$ (right) state of model 1 for a combination of different root-homing options. A wavenumber selection criterion as mentioned in the main text was applied in all cases. $N_{\text{max}}$ indicates for how many of the modes selected by the intensity criterion new basis vectors were created. The total number of basis vectors (bv) and of converged modes (conv) is given for each spectrum.

In order to avoid these disadvantages in cases where more than just very few modes need to be converged, a combination of different root-homing criteria was also tried. In particular, (i) a wavenumber criterion was applied to all calculations, i.e., only vibrational modes in the range between 500 and 2000 cm$^{-1}$ were chosen for further optimization and (ii) the modes to be converged were selected according to criterion (A), but new basis vectors were created only for at most $N_{\text{max}}$ selected modes in each iteration. The results of these calculations are shown in Fig. 7.10. It can be seen that in particular for the $4^1A$ spectrum a significantly smaller number of basis vectors is needed, e.g., 43 basis vectors for the combination $I_{\text{thres}} = 0.5$, $N_{\text{max}} = 5$ and the wavenumber test instead of 64 basis vectors when only the $I_{\text{thres}} = 0.5$ criterion is applied. For the $6^1A$ spectrum the reduction in computational cost is less good, which is most probably related to the fact that a relatively large percentage of the normal modes carry substantial intensity in the spectrum, so that it is very hard to reduce the number of basis vectors.
7.3.4 Approximations for intense normal modes from small basis sets

A further possible scheme for an enhanced efficiency will be discussed, i.e., the utilization of calculations with very small basis sets as a guess for the actual calculation employing a larger basis. All tests will be performed for model 1. The resonance Raman spectra for the \(4^1A\) state of model 1 calculated with B3LYP and three basis sets of increasing size, SV(P), TZVP and TZVPP, yield very similar results, differing mainly in the peak positions, see Fig. 7.11. The agreement between intensity-tracking spectra and conventional gradient spectra is well for all three basis sets.

Figure 7.11: Resonance Raman spectra for the \(4^1A\) state of model 1 using B3LYP and different basis sets calculated by intensity tracking and a conventional gradient spectrum. The total number of basis vectors (bv) and converged modes (conv) is given on the right hand side.
7.3 Resonance Raman spectra of Im7-based models

Figure 7.12: Resonance Raman intensities for 3 (top) and 6 (bottom) modes of the $4^1A$ excited state of model 1 calculated by a B3LYP/TZVPP mode-tracking calculation starting from SV(P) normal modes. Intensities were obtained using the B3LYP/TZVPP gradient of the $4^1A$ state energy.

Standard mode-tracking applications show that normal modes obtained with smaller basis sets can be very good approximations to the normal modes obtained using a larger basis set [263]. Accordingly, intense normal modes of a resonance Raman spectrum can be determined by an intensity-tracking calculation using a small basis set and subsequently be refined by a standard mode-tracking calculation in a larger basis set. In doing so, only the frequencies in the higher-quality basis will be obtained. In order to get also the intensities, the excited-state gradient has to be calculated for the larger basis as well. This procedure has been applied on the one hand to the three most intense modes of the SV(P) intensity-tracking spectrum for the $4^1A$ state of model 1 at 782.44 cm$^{-1}$, 1404.02 cm$^{-1}$ and 1637.91 cm$^{-1}$ and on the other hand to the 6 intense modes between 1400 cm$^{-1}$ and 1650 cm$^{-1}$ (1404.02 cm$^{-1}$, 1468.72 cm$^{-1}$, 1498.15 cm$^{-1}$, 1537.28 cm$^{-1}$, 1613.10 cm$^{-1}$ and 1637.91 cm$^{-1}$) in a mode-tracking calculation using a TZVPP basis. The relative intensities of these modes are depicted in Fig. 7.12. The root-homing during the mode-tracking run was performed on the basis of the overlap with the initial SV(P) normal modes. For the calculation with 6 modes the alternative root-homing by comparison to the modes of the preceding iteration works as well. But it can show the problem that the calculation drifts to another mode than the one originally sought for. In the calculation with this root-homing option for three modes, convergence problems arise for the mode starting from 1404.02 cm$^{-1}$. The reasons are that the overlap between the SV(P) and the converged TZVPP mode is smaller than for the other modes, and that there are several intense modes in that region with near-degenerate wavenumbers.
In this case, the optimized TZVPP mode is not the mode showing the largest overlap with the guess modes from the SV(P) calculation. Convergence to that mode can be enforced by performing the roothoming by measuring the overlap with the initial guess. 43 basis vectors are needed for that calculation, which is a comparatively large number compared to the 46 basis vectors for the six modes in one region. Nevertheless, a substantial fraction of the computational effort can be saved if only a small number of high-intensity modes is desired.

7.3.5 Intensity tracking for Im7-based model 2

For large models of the Im7 protein, TDDFT yields a multitude of artificially low-lying excited states which mix with the excited states relevant to describe the experimentally observed spectra as can be seen from the data in Table 7.1. These data also show that B3LYP at least partly remedies this problem, since the state corresponding to the $2^1A$ state of skatole is the $15^1A$ state of model 2 with B3LYP, whereas it is the $92^1A$ state in case of BP86. I.e., 77 more low-lying states are found in the BP86 calculation, and it would thus be advantageous to use B3LYP for the entire calculation, as was done for the previous models. However, the pure density functional BP86 leads to an enormous increase in efficiency for large molecules, and furthermore gives harmonic vibrational frequencies that are typically in better agreement with experimental fundamental frequencies than B3LYP data [246]. In earlier work [11], a hybrid approach was successfully tested, in which the excitation energies and excited-state gradients were calculated with B3LYP, whereas BP86 was used for the frequency analysis.

In order to test the effect of this hybrid approach for the class of systems studied here, the resonance Raman spectrum for the $4^1A$ state of the smaller model 1 obtained with a combination of B3LYP and BP86 was compared to the spectra in which either functional was used consistently in Fig. 7.13. The main features are identical for all three spectra, whereas the intensity distribution and frequencies of the intense modes change. Comparing the B3LYP/B3LYP spectrum to the BP86/B3LYP spectrum, all intense modes are shifted to lower wavenumbers in the latter calculation while the intensity distribution appears to be roughly the same. Below 1400 cm$^{-1}$, the intensity pattern seems to be changed. However, a closer inspection reveals that the mode at 1388 cm$^{-1}$ in the B3LYP calculation is shifted to 1346 cm$^{-1}$ in the BP86 calculation, which leads to the slightly different appearance. Further notable differences are the additional intense modes at about 1720 cm$^{-1}$ in the BP86/B3LYP calculation. Deviations in the intensity distribution between the BP86/B3LYP calculation and the pure BP86 calculation can be observed for the modes at 759 cm$^{-1}$, at about 1350 cm$^{-1}$ and at about 1720 cm$^{-1}$. Overall, the most intense features of the two spectra are sufficiently consistent, so that the BP86/B3LYP hybrid approach will be used in the following for the large model 2.
7.3 Resonance Raman spectra of Im7-based models

Figure 7.13: Resonance Raman spectra of model 1 assuming resonance with the $4^1A$ state ($8^1A$ in case of BP86/BP86/TZVP) obtained by conventional gradient calculations using different functionals. The first of two given functionals was used for the ground-state structure and frequencies and the second for excitation energies and the excited-state gradient. Wavenumbers of intense vibrations are given in units of cm$^{-1}$.

This hybrid approach was employed for the intensity-tracking calculations on the excited electronic states of model 2. This model consists of 151 atoms, so that there are 453 degrees of freedom in total, and a complete vibrational basis comprises 447 basis vectors. An intensity-tracking calculation with root-homing scheme (B) and a selection criterion of $N_{\text{sel}} = 5$ was performed. Additionally, the wavenumber criterion $500 \text{ cm}^{-1} < \tilde{\nu} < 2000 \text{ cm}^{-1}$ was applied. The approximate spectra for different iterations are shown in Fig. 7.14. It can clearly be seen that the most intense band at $\sim 1570 \text{ cm}^{-1}$ is practically converged already in the first intermediate spectrum shown, which utilizes 79 basis vectors. In the next spectrum, based on 129 basis vectors, all features in the range between 1500 and 1800 cm$^{-1}$ with appreciable intensity are virtually converged. Formal convergence is achieved with 197 basis vectors, and by comparison with the conventional gradient spectrum it can be seen that indeed all the intense bands, which are located between $\sim 1350$ and $1800 \text{ cm}^{-1}$, are very well reproduced by the intensity-tracking calculation. Furthermore, the overall impression of the intensity distribution in the lower-wavenumber range is also qualitatively correct. A better agreement with the reference spectrum can be obtained, e.g., by applying the hybrid root-homing procedure outlined in the last section, but the selection criterion of $N_{\text{sel}} = 5$ offers a good compromise between accuracy and efficiency. Only 44% of the full number of basis vectors are needed to
accurately reproduce the intense features in the spectrum, which also means that the cpu time in comparison with a full semi-numerical calculation of the vibrational spectrum is reduced to roughly 44%.

Figure 7.14: Convergence of the spectra during BP86/TZVP intensity-tracking iterations (It.) for model 2, starting from the (B3LYP/TZVP) gradient of the 15^1A state. The total number of basis vectors is given on the right hand side. Lowest panel: conventional (reference) gradient spectrum.
7.3.6 Approximate spectra using a local subsystem gradient

As the resonance Raman intensities of chromophores like Trp are determined by localized excited states, it can be assumed that a subset of the gradient components limited to the chromophore will have the largest contributions and already give a good approximation to the spectrum using the complete gradient. In Fig. 7.15, such approximate spectra for the $15^1A$ state of model 2 obtained with the gradient of the skatole substructure in model 2, are shown. The above described hybrid approach for the density functionals was used, and for the calculation of the excited-state gradient, the skatole fragment was capped with a hydrogen atom.

Figure 7.15: Approximate resonance Raman spectra of model 2 employing the excited-state gradient (resonance with the $2^1A'$ state is assumed) of a skatole substructure for the calculation of intensities and as a guess in an intensity-tracking calculation (ITC). For the ITC, the total number of basis vectors (bv) is given. For comparison, the conventional gradient spectra (CGS) obtained with the skatole gradient and the complete model 2 gradient (resonance with $15^1A$ state assumed) are shown. For the frequency calculations (BP86/TZVP) and for the excited-state gradient (B3LYP/TZVP) was used.

The intensity-tracking spectrum obtained with the same root-homing scheme as for the model 2 calculation shown in Fig. 7.14 converges using 196 bv (i.e., as efficient as the calculation for the complete gradient) and reproduces the gradient spectrum well. Compared to the spectrum for the complete gradient, the main differences are the missing C-O-stretch and N-H bending vibrations of the backbone in the region above 1620 cm$^{-1}$. Between 1350-1620 cm$^{-1}$, the relative intensities are slightly
different and below 1320 cm$^{-1}$ there are more peaks. However, the main features are very well reproduced. Thus, combining excited-state information restricted to a subsystem of the molecule under study with a method to selectively calculate relevant ground-state frequencies yields a RR spectrum with correct frequencies and approximate relative intensities. In practice, applications are limited to cases where the corresponding excited states can be identified.

### 7.4 Conclusions for resonance Raman intensity tracking

In this chapter, it was shown that calculations with an intensity-driven algorithm can reproduce conventional gradient spectra very well if strict convergence criteria are applied, which is a necessary condition for a successful application of this algorithm. Subsequently, different root-homing procedures for the selection of modes for further optimization were demonstrated to control the convergence behavior of the calculation. It turned out that root-homing option (B), in which a fixed number of intense modes is chosen in each iteration, gives fast access to the most intense features in the resonance Raman spectrum. In contrast to this, the option in which a threshold for the cumulative intensity is applied (A) allows to quickly determine which wavenumber range is covered by intense vibrations in the spectrum. Option (B) is thus favorable in typical applications of large molecular systems with only a few intense vibrations in the resonance Raman spectrum. This was confirmed in the example of the resonance Raman spectrum of Im7 models, in which the Trp residue shows characteristic peaks. A possible problem with option (A) is that too many new basis vectors are constructed in each iteration, so that a rather sudden convergence is achieved, which typically requires a comparatively large percentage of the total number of possible basis vectors. This problem can be solved by restricting the maximum number of new basis vectors in order to achieve a smooth convergence behavior.

As far as the efficiency is concerned, which can directly be measured as the ratio of the number of basis vectors needed for convergence and the full number of vibrational degrees of freedom, it must be noted that the convergence in intensity-tracking calculations is intrinsically more difficult than in typical mode-tracking applications for specific vibrations [24,40,295]. The reasons for this behavior are that intensity-tracking calculations (i) target several vibrations, the exact number of which is unknown at the beginning, (ii) start with an unspecific guess for the type of collective motion, and thus typically require more basis vectors for correction, and (iii) may partially comprise very unspecific modes that easily couple to other vibrations in the molecule, which affects the convergence behaviour. In view of these problems, the methodology outlined here is quite successful in providing insight into the dominant features of the RR spectrum of large molecules at reduced cost, since the only alternative is a full frequency analysis.
8 Conclusion and Perspective

The results described in the preceding chapters of this work have been presented with theoretical resonance Raman spectroscopy of proteins as the thread leading through this work. In the following, conclusions and perspectives are detailed for the individual parts. The value of the obtained results is of course not confined to this special application, but the conclusions drawn apply more generally.

• Density Analysis for Frozen-Density Embedding
  Frozen-density embedding (FDE) has proven to be an efficient model for environmental effects on molecular properties. In this thesis, the more fundamental question whether or not FDE also provides reasonable total electron densities when used with the available approximate functionals was investigated. It was demonstrated that FDE is able to reproduce the qualitative changes in the electron-density topology upon hydrogen bonding of two subsystems and for a simple coordinative bond compared to Kohn–Sham density-functional theory (KS-DFT) calculations.

  The type of the basis set, i.e., a monomer or a supermolecular basis, proved to be more important than the choice of the approximate non-additive kinetic energy functional. However, it could be demonstrated that typically only a few additional basis functions in the hydrogen-bonding region are sufficient to obtain a significant improvement of the electron-density description, which is comparable with the one obtained with a full supermolecular basis set. If this procedure is applied, FDE will still be much more efficient than supermolecular calculations but at the same time allow for a more accurate description of the density in the bonding region. The remaining differences reveal a lack of directionality in the bonding region, which arises from accounting for the other fragment only by its density. This became also apparent in test calculations on an acetone–water system [296] in which the dependence of excitation energies in supermolecular and FDE calculations on the angle of the second O–H bond with respect to the hydrogen-bond plane was analyzed. In these results a similar problem surfaced: The FDE excitation energies did not reproduce the angular dependence found in the KS-DFT excitation energies, which is related to the supermolecular orbitals by the description through dominant orbital transitions. Taking the orbital-overlap depending terms in the boundary region into account could help to reduce such problems.

  In spite of the problems to reproduce the exact KS-DFT density of a system it must be noted that FDE and related subsystem approaches offer the major
advantages that the electrostatic interaction of a system with its environment does not suffer from problems related to the discretization of the Coulomb potential in a low-order multipole expansion, and that non-classical effects are included in the potential. These factors may be more important in the simulation of hydrogen-bonded systems under “real” conditions than the rigorous requirement of reproducing supermolecular densities to high accuracy.

FDE has been shown in this work to reproduce the characteristics of the density in the bonding region even in such systems such as the F−H−F− molecule and for an example of a weak coordinative bond. Bonds with a more polar character, as in TiCl4, or more covalent bonding contributions as in chromium hexacarbonyl, have been examined in a following study [109]. The occurring problems due to oppositely charged fragments or the covalent bonding character could be partly remedied with a long-distance correction introduced in Ref. [118].

- **Herzberg–Teller terms in resonance Raman spectroscopy**

  The resonance Raman routines of the program Dnr have been extended by Herzberg–Teller (HT) terms. To that end, formulae for one-dimensional HT terms within the independent-mode displaced harmonic oscillator model have been worked out. This implementation allows to calculate resonance Raman spectra going beyond the Condon approximation for the transition dipole moment and thus including vibronic coupling terms. So far, only fundamental transitions in the low-temperature limit can be calculated, but the inclusion of combination bands, overtones and finite temperature effects is straightforward. Going beyond the most simple approximation for the potential energy surfaces by either including frequency changes or taking into account the Duschinsky effect should be considered in future work. While frequency changes can be incorporated into the existing implementation with minor changes, the Duschinsky rotation would require a much larger effort, since the multi-dimensional HT integrals do not factorize into one-dimensional integrals. It should, however, be examined whether an approximate treatment using analytical formulae for small rotations can more easily be incorporated.

  In addition to calculating first as well as second-order HT terms for all modes, different approximate approaches have been tested for the first excited state of the C3v symmetric skatole. The HT contributions for skatole have been analyzed according to their symmetry. As to the relevance of HT contributions, the results show that they cannot be neglected for totally symmetric modes from the outset, as for skatole they are far more important than the contributions arising from non-totally symmetric modes. Skatole might represent a special case, though, since the existence of a close-lying totally symmetric excited state with a high oscillator strength might be responsible for the strong HT contributions. This second excited state should likewise borrow intensity from the first state and exhibit strong HT contributions for totally symmetric
modes. In order to compare with experimental resonance Raman spectra, for skatole and derived systems both energetically close-lying states are important, so that also the second state should be studied closely. The general question of the relevance of HT terms can only be settled by analyzing a range of different molecules. Porphyrins might pose an obvious choice, since they are an important basic structure for biologically important molecules like hemoglobin, and a characterization for HT terms according to symmetry can be employed for symmetric model compounds. DNR now allows a HT treatment up to linear terms even for these middle-sized to large systems.

- **Simple resonance Raman models for the photochemistry of nitroarenes**

Simple resonance Raman models, which were derived for Franck–Condon resonance Raman intensities, namely a time-dependent description in connection with simple harmonic potential energy surfaces (Gradient Franck–Condon) and Heller’s gradient approximation, have been applied to study photochemical products of nitroarenes. Moreover, excitation energies from different electronic structure methods have been compared. The ortho-nitrobenzaldehyde ground-state structure was characterized as well as the first intermediate of the reaction, a ketene. Comparison with the experimental intensities showed that the Gradient Franck–Condon together with the time-dependent formalism yields reliable resonance Raman intensities. For ortho-nitrotoluene, the ground-state structure and the aci-nitro tautomer intermediates have been examined using Heller’s gradient approximation. The ortho-nitrotoluene spectrum has to be characterized by normal Raman scattering, whereas the aci-nitro tautomer spectra can be simulated by resonance Raman approaches. It is unfortunately not possible to identify unambiguously which tautomeric form occurs in the reaction on the basis of the comparison of the experimental time-resolved spectra. However, comparisons of sum-over-states calculations, the Gradient Franck–Condon time-dependent approach and Heller’s gradient approach for resonance Raman spectra of ortho-nitrobenzaldehyde show that reliable results are obtained for the latter.

For ortho-nitrotoluene, in addition to time-dependent density-functional theory, the coupled cluster approach RICC2 and complete active space self-consistent field calculations followed by a second-order perturbative treatment have been employed to obtain excitation energies. The vertical excitation energies obtained from the different methods cannot be unambiguously mapped beyond the first excited state.
8 Conclusion and Perspective

- **Algorithmic advances to exploit the intrinsic selectivity of resonance Raman spectra**
  The possibility to efficiently obtain the characteristic features of a resonance Raman spectrum on the basis of a new intensity-driven algorithm was investigated. In this way, one can exploit the selectivity that is inherent to experimental resonance Raman spectroscopy also within a theoretical framework. Two steps are essential for this purpose: (i) the construction of a guess vector for a hypothetical collective motion that contains the entire intensity in the resonance Raman spectrum, and (ii) the iterative refinement of approximate normal modes which potentially carry a high intensity. The first step can be addressed by taking advantage of Heller’s gradient approximation for relative resonance Raman intensities. For the second part, several selection procedures within an algorithm analogous to the mode-tracking scheme were developed and tested. The examples discussed demonstrate that intensity tracking is a smart and versatile method to obtain approximate resonance Raman spectra. It should be noted that even in those cases where Heller’s gradient approximation is not reliable the present approach can be of great help, since the modes obtained are those with the highest Franck–Condon activity. They will thus also be the most important ones for more sophisticated methods for theoretical resonance Raman spectroscopy, e.g., based on sum-over-states or time-dependent approaches. With modified or additional guess vectors, it should also be possible to address cases in which Herzberg–Teller active modes or several excited states play a role. The latter point will be important for reliable predictions of resonance Raman spectra of Trp-containing systems under experimental conditions due to the two close-lying intense transitions of the skatole motif. Since these modifications of the intensity-tracking scheme may introduce additional vibrations with significant intensity, the guess vectors and the root-homing procedure should be carefully tested for such more sophisticated schemes in order to optimize the convergence behaviour.

  Further improvements in the convergence control might be possible by defining different convergence criteria for modes of different intensities, for example in such a way that tight convergence is only requested for those parts of the spectrum that stand out very sharply due to their high intensity, or by regarding the wavenumber changes. Another open question that should be addressed in future work is how efficient preconditioning schemes can be designed for intensity-tracking calculations, i.e., how the construction of new basis vectors can be optimized for the search of intense normal modes.

A recurring prototypical model system in this thesis has been the amino acid tryptophan, or the skatole motif as its basic constituent. In the course of this work, frozen-density embedding has been shown to yield reliable densities for weakly interacting subsystems. Extensions to proteins, and including the influence of an environment on electronic spectra exist, so that it can be used as an effective environmental model for the electronic structure part of resonance Raman calculations. This is due
to the fact that FDE facilitates a locally selective description of the chromophore in a protein. For this chromophore, resonance Raman approximations of different accuracy can be applied, from the simple gradient approximation by Heller, the gradient Franck–Condon time-dependent approach to sum-over-states calculations including vibronic coupling terms. The experimental selectivity of resonance Raman spectroscopy can be fully exploited by the intensity-tracking approach, which allows a selective description of the vibrational modes according to their intensities. Thus we have assembled the steps leading to a selective subsystem quantum chemical description of resonance Raman spectroscopy of chromophores in proteins, e.g., of the tryptophan in the Im7 protein — the figurative magnifying glass for chromophores in proteins.
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