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Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation

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HRS 001

Prepared for Handbook of High-Resolution Spectroscopy,
M. Quack and F. Merkt,
Wiley, Chichester 2010

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“The language of spectra, a true atomic music of the spheres”

Sommerfeld (1919), as translated and cited by Pais (1991)
# 1 Introduction

The aim of this first chapter is to introduce the basic experimental and theoretical concepts underlying molecular spectroscopy. At a purely empirical level, human color vision can be considered to be a basic form of spectroscopy, although the relation between the observed “colour” and the electromagnetic spectrum of light is not simple. In that sense, auditory perception can be considered to be a better frequency analyzer, although this would be considered a spectroscopy of sound rather than electromagnetic radiation. The relation of spectroscopy to music has been addressed in the words of Sommerfeld, which themselves contain a reference to the earliest days of human science.

Early spectroscopic experiments leading later to applications in chemistry can be followed in history from Newton’s spectrum, the observation of the “Fraunhofer lines” in the solar spectrum as appearing on the cover of the handbook, infrared spectra observed by the Herschels (father and son), UV photochemistry observed by Ritter, and finally the start of chemical, analytical and astronomical spectroscopy with the work of Bunsen and Kirchhoff in the 19th century. The “mathematical harmony” of the spectral lines of the hydrogen atom was found by Balmer (1885a, b). The key to modern spectroscopy arises, however, from quantum theory, starting with an understanding of the intensity distribution of black body radiation on the basis of quantization by Planck (1900b, a), the understanding of the photoelectric effect with the photon concept due to Einstein (1905) and most directly the understanding of the spectrum of the hydrogen atom on the basis of the “old” quantum theory as introduced by Bohr (1913a, b, c, d) including also Bohr’s condition for spectroscopic transitions between energy levels \( E_i \) and \( E_f \) connected by the absorption or emission of photons with frequency \( \nu_{fi} \) and Planck’s constant \( h \)

\[
|\Delta E_{fi}| = |E_f - E_i| = h\nu_{fi}
\]  

This equation together with Bohr’s theory of the hydrogen atom as a dynamical system having a quantized energy level structure forms the basis of the use of line resolved high-resolution spectroscopy in understanding the dynamics of atomic and molecular, later also nuclear systems. The underlying quantum dynamical theory of such microscopic systems was then completed by introducing “modern” quantum theory in the work of Heisenberg (1925); Schrödinger (1926a, b, c, d, e); Dirac (1927, 1929). In essence, current high-resolution molecular spectroscopy relies on the use of this theoretical framework in its application to furthering our knowledge on the fundamental aspects of molecular quantum dynamics as well as in its numerous practical applications in science and technology.

The outline of this introductory chapter to the Handbook of High-Resolution Spectroscopy is thus briefly as follows. In section 2 we shall introduce some basic equations of quantum mechanics as needed for spectroscopy. Section 3 treats the quantum dynamics of coherent radiative transitions. Section 4 discusses the basic concepts underlying spectroscopic experiments. Section 5 gives a brief introduction into the characteristics of molecular energy levels, section 6 discusses molecular symmetry and basic group theory as relevant to spectroscopy, and section 7 deals with radiationless transitions and line
shapes for high-resolution spectroscopy.

2 Quantum Mechanics and Spectroscopy

Quantum mechanics provides the underlying theory for molecular spectroscopy. It is dealt with in much detail in relevant text books by Messiah (1961); Cohen-Tannoudji et al. (1973); Sakurai (1985); Landau and Lifshitz (1985). For the historical background one can also consult Dirac (1958) and Heisenberg (1930), which remain of interest for the fundamental concepts. The aim of the present section is to introduce some of the basic concepts and definitions. This can obviously not replace a more detailed introduction into quantum mechanics, which can be found in the textbooks cited as well as in numerous other books on this topic.

2.1 Classical mechanics and quantum mechanics

Many systems in both classical and quantum mechanics can be described by the motion of interacting point particles, where the physical “particles” are replaced by points of mass \( m_k \) with position at the center of mass of the particle. For planetary systems, the “particles” would be the sun and planets with their moons (plus planetoids and artificial satellites, etc). For atomic and molecular systems the “point particles” can be taken to be the nuclei and electrons to within a good approximation.

In classical dynamics one describes such an \( N \) particle system by a point in the mathematical phase space, which has dimension \( 6N \) with \( 3N \) coordinates (for instance Cartesian coordinates \( x_k, y_k, z_k \) for each particle “\( k \)” and \( 3N \) momenta \( p_{x_k}, p_{y_k}, p_{z_k} \)). Such a point in phase space moving in time contains all mechanically relevant information of the dynamical system. In the 19th century Hamiltonian formulation of classical mechanics, one writes the Hamiltonian function \( H \) as sum of the kinetic \( (T) \) and potential \( V \) energy

\[
H = T + V
\]

in terms of generalized coordinates \( q_k \) and their conjugate momenta \( p_k \) (Landau and Lifshitz 1966; Goldstein 1980; Iro 2002). Following Hamilton one obtains the canonical Hamiltonian differential equations of motion accordingly

\[
\frac{dq_k}{dt} = \dot{q}_k = \left( \frac{\partial H}{\partial p_k} \right) \tag{3}
\]

\[
\frac{dp_k}{dt} = \dot{p}_k = - \left( \frac{\partial H}{\partial q_k} \right) \tag{4}
\]

The dynamics of the classical system is thus obtained from the solution of \( 6N \) coupled differential equations. Provided that one knows some exact initial condition for one point in phase space, all future and past states of the system in terms of the set \( \{q_k(t), p_k(t)\} \) can be calculated exactly. Further considerations arise, if the initial state is not known exactly, but we shall not pursue this further.

One approach to quantum dynamics replaces the functions \( H, p_k, q_k \) by the corresponding quantum mechanical operators (\( \hat{H}, \hat{p}_k, \hat{q}_k \)) or their matrix representations (\( \mathbf{H}, \mathbf{p}_k, \mathbf{q}_k \)) resulting in the
Heisenberg equations of motion

\[ \frac{d\hat{q}_k}{dt} = \frac{2\pi}{i\hbar} \left[ \hat{q}_k, \hat{H} \right] \]  
(5)

\[ \frac{d\hat{p}_k}{dt} = \frac{2\pi}{i\hbar} \left[ \hat{p}_k, \hat{H} \right] \]  
(6)

which involve now Planck’s quantum of action (or constant) \( \hbar \), and \( i = \sqrt{-1} \). Following Dirac (1958), these equations are the quantum mechanical equivalent of the Poisson-bracket formulation of classical mechanics and one can in fact derive the corresponding classical equations of motion from the Heisenberg equations of motion, if one uses quantum mechanics as the more fundamental starting point (see Sakurai (1985), for instance). The equations (5) and (6) contain the commutator of two operators \( \hat{A} \) and \( \hat{B} \) in general notation

\[ \left[ \hat{A}, \hat{B} \right] = \hat{A}\hat{B} - \hat{B}\hat{A} \]  
(7)

As quantum mechanical operators and their matrix representations do not in general commute, this introduces a new element into quantum mechanics as compared to classical mechanics. For instance, in Cartesian coordinates the coordinate operator \( \hat{x}_k \) is simply multiplicative, while the momentum operator \( \hat{p}_{x_k} \) is given by the differential operator

\[ \hat{p}_{x_k} = \frac{\hbar}{2\pi i} \frac{\partial}{\partial x_k} \]  
(8)

leading to the commutator

\[ [\hat{x}_k, \hat{p}_{x_k}] = i\hbar/(2\pi) \]  
(9)

and the corresponding Heisenberg uncertainty relation (Messiah 1961)

\[ \Delta x_k \Delta p_{x_k} \geq \hbar/(4\pi) \]  
(10)

where \( \Delta x_k \) and \( \Delta p_{x_k} \) are defined as the root mean square deviations of the corresponding ideal measurement results for the coordinates \( x_k \) and momenta \( p_{x_k} \). Similar equations apply to \( y_k, z_k \) with \( p_{y_k}, p_{z_k}, \) etc for all particles labelled by their index \( k \). It is thus impossible in quantum mechanical systems to know experimentally the position of the “point in phase space” to better than allowed by the Heisenberg uncertainty relation in a quantum mechanical state. In classical mechanics, on the other hand, the \( x_k \) and \( p_{x_k} \), etc commute and the point in phase space can be defined and measured with arbitrary accuracy, in principle.

A somewhat more complex reasoning leads to a similar “fourth” uncertainty relation for energy \( E \) and time \( t \)

\[ \Delta E \Delta t \geq \hbar/(4\pi) \]  
(11)

We note that Eqs. (10) and (11) are strictly inequalities, not equations in the proper sense. Depending on the system considered the uncertainty can be larger than what would be given by the strict equation. If the equal sign in Eqs. (10) and (11) applies, one speaks of a “minimum-uncertainty state
or wavepacket” (see below). The commutators in Eqs. (5) and (6) are readily obtained from the form of the kinetic energy operator in Cartesian coordinates

\[ \hat{T} = \frac{1}{2} \sum_{k=1}^{N} \left( \hat{p}_{xk}^2/m_k + \hat{p}_{yk}^2/m_k + \hat{p}_{zk}^2/m_k \right) \]  

(12)

and

\[ \hat{H} = \hat{T} + \hat{V} \]  

(13)

if the potential energy \( \hat{V} \) is a multiplicative function of the coordinates of the particles (for instance with the Coulomb potential for charged particles).

While this so called Heisenberg representation of quantum mechanics is of use for some formal aspects and also certain calculations, frequently the “Schrödinger representation” turns out to be useful in spectroscopy.

2.2 Time-dependent and time-independent Schrödinger equation

2.2.1 Time-dependent Schrödinger equation

In the Schrödinger formulation of quantum mechanics ("wave mechanics") one introduces the “wave function” \( \Psi(x_1, y_1, z_1, \ldots, x_N, y_N, z_N, \ldots, t) \) depending on the particle coordinates and time and satisfying the differential equation (time-dependent Schrödinger equation)

\[ \frac{i \hbar}{2\pi} \frac{\partial \Psi(x_1, y_1, z_1, \ldots, x_N, y_N, z_N, \ldots, t)}{\partial t} = \hat{H} \Psi(x_1, y_1, z_1, \ldots, x_N, y_N, z_N, \ldots, t) \]  

(14)

The physical significance of the wave function \( \Psi \) (also called state function) can be visualized by the probability density

\[ P(x_1, y_1, z_1, \ldots, x_N, y_N, z_N, \ldots, t) = |\Psi(x_1 \ldots z_N, t)|^2 \]  

(15)

\( P \) is real, positive or zero, whereas \( \Psi \) is, in general, a complex-valued function.

\( P(x_1, y_1, z_1, \ldots, z_N, t) \, dx_1 dy_1 dz_1 \ldots d z_N \) gives the probability of finding the quantum mechanical system of point particles in the volume element \( dx_1 \ldots d z_N \) at position \( x_1 \ldots z_N \) at time \( t \).

The differential operator in Eq. 14 is sometimes called energy operator \( \hat{E} \)

\[ \hat{E} = \frac{i \hbar}{2\pi} \frac{\partial}{\partial t} \]  

(16)

thus one can write

\[ \hat{E} \Psi(r, t) = \hat{H} \Psi(r, t) \]  

(17)

where we introduce the convention that \( r \) represents in general a complete set of space (and spin) coordinates and includes the special case of systems depending only on one coordinate which then can be called \( r \).
The solution of Eq. 14 has the form
\[ \Psi(r,t) = \hat{U}(t,t_0)\Psi(t_0) \] (18)

The time evolution operator \( \hat{U}(t,t_0) \) operating on \( \Psi(r,t_0) \) produces the function \( \Psi(r,t) \). \( \hat{U} \) satisfies the differential equation
\[ i\hbar \frac{\partial \hat{U}(t,t_0)}{\partial t} = \hat{H}\hat{U}(t,t_0) \] (19)

Thus, in general, one has to solve this differential equation in order to obtain \( \hat{U}(t,t_0) \). If, however, \( \hat{H} \) does not depend upon time, \( \hat{U}(t,t_0) \) is given by the equation
\[ \hat{U}(t,t_0) = \exp\left[ -\frac{2\pi i}{\hbar}\hat{H} \cdot (t - t_0) \right] \] (20)

The exponential function of an operator \( \hat{Q} \) as a matrix representation of this operator is given by Eq. 21
\[ \exp(\hat{Q}) = \sum_{n=0}^{\infty} \frac{\hat{Q}^n}{n!} \] (21)

One of the most important properties of \( \Psi \) is that it satisfies the principle of linear superposition. If \( \Psi_1(r,t) \) and \( \Psi_2(r,t) \) satisfy Eq. (14) as possible representations of the dynamical state of the system, then the linear superposition
\[ \Psi(r,t) = c_1\Psi_1(r,t) + c_2\Psi_2(r,t) \] (22)

is also a possible dynamical state satisfying Eq. (14), as is readily shown, given that \( \hat{H} \) is a linear operator and \( c_1, c_2 \) are complex coefficients. However, \( \Psi(r,t) \) in general is not an eigenstate of \( \hat{H} \).

### 2.2.2 Special case of stationary states and time-independent Schrödinger equation

We assume that \( \hat{H} \) does not depend on time. We consider the special case where \( \Psi_k(r,t) \) is an eigenfunction of \( \hat{H} \) with eigenvalue \( E_k \), thus

\[ \hat{H}\Psi_k(r,t) = E_k\Psi_k(r,t) \] (23)

The solution for this special case is given by Eq. (24)
\[ i\hbar \frac{\partial \Psi_k(r,t)}{\partial t} = E_k\Psi(r,t) = E_k\psi(r) \exp(-2\pi iE_k t / \hbar) \] (24)

\( \hat{H} \) being independent of time, one can divide in Eq. (23) by \( \exp(-2\pi iE_k t / \hbar) \) and obtains

\[ \hat{H}\psi_k(r) = E_k\psi_k(r) \] (25)

The eigenfunctions of \( \hat{H} \) are called stationary states

\[ \Psi_k(r,t) = \psi_k(r) \exp(-2\pi iE_k t / \hbar) \] (26)

The name for stationary states is related to the time independence of the probability density
\[ P(r,t) = \Psi_k(r,t)\Psi_k^*(r,t) = |\Psi_k(r,t)|^2 = |\psi_k(r)|^2 \] (27)

The time-independent Schrödinger equation (25) is thus derived as a special case from the time-dependent Schrödinger equation.
2.2.3 General time-dependent states

Making use of the superposition principle (Eq. (22)), the general solution of the Schrödinger equation results as

\[ \Psi(r,t) = \sum_k c_k \psi_k(r) \exp(-2\pi i E_k t/h) = \sum_k c_k \Psi_k(r,t) \]  

(28)

If \( \hat{H} \) does not depend on time, such as for isolated atomic and molecular systems, the coefficients \( c_k \) are time independent, generally complex coefficients. According to the principle of spectral decomposition, the probability to measure an energy \( E_k \) in the time-dependent state given by Eq. (28) is

\[ p_k(E_k) = |c_k|^2 = c_k c_k^* \]  

(29)

Thus with time-independent \( \hat{H} \), the \( p_k \) are independent of time as is also the expectation value of the energy

\[ \langle E_k(t) \rangle = \sum |c_k|^2 E_k \]  

(30)

Fig. 1 illustrates the spectral decomposition for two types of spectra. High-resolution spectroscopy providing the \( E_k \) and \( \psi_k \), Eq. (28) provides the basis for constructing a general time-dependent state from high-resolution spectroscopic results. The energy in a time-dependent state is therefore not a well defined quantity, it is only defined by means of a statistical distribution given by the \( p_k \). The distribution satisfies the uncertainty relation given by Eq. (11).

![Figure 1](image_url)

Figure 1: Spectral decomposition schemes: Illustration of spectral decomposition of a time-dependent state. \( p_k(E_k) = |c_k|^2 \) is the probability to measure the eigenvalue \( E_k \) in the time-dependent state given by \( \Psi(r,t) \). a) irregular spectrum and distribution, b) harmonic oscillator with a Poisson distribution.

2.3 Time-evolution operator formulation of quantum mechanics

Equation (19) can be made the starting point of a general formulation of quantum mechanics. \( \hat{U} \) does not only provide the solution of the Schrödinger equation according to Eq. (18), but also of the time
dependence for the density operator (see, for instance, Messiah (1961); Sakurai (1985))

$$\hat{\rho}(t) = \sum_n p_n |\Psi_n\rangle \langle \Psi_n|$$  \(\text{(31)}\)

satisfying the Liouville-von Neumann equation

$$i \hbar \frac{d\hat{\rho}(t)}{dt} = [\hat{H}, \hat{\rho}(t)]$$  \(\text{(32)}\)

by means of the solution

$$\hat{\rho}(t) = \hat{U}(t, t_0) \hat{\rho}(t_0) \hat{U}^\dagger(t, t_0)$$  \(\text{(33)}\)

This equation is of particular importance for statistical mechanics.

Furthermore, the Heisenberg equations of motion (5,6) for the operators \(\hat{p}_k\) and \(\hat{q}_k\) as for any generalized operator \(\hat{Q}\) corresponding to the dynamical observable \(Q\) are solved by means of the equation

$$\dot{\hat{Q}}(t) = \hat{U}^\dagger(t, t_0) \dot{\hat{Q}}(t_0) \hat{U}(t, t_0)$$  \(\text{(34)}\)

This equation is of importance for time-resolved spectroscopy, where one might, for instance, observe the time-dependent electric dipole moment \(\vec{M}(t)\) described by the dipole operator \(\hat{\mu}\). We note the difference in sign of Eq. (32) and the Heisenberg equations of motion, with resulting differences for the solutions given by Eqs. (33) and (34). This is no contradiction, as the density operator \(\hat{\rho}\) does not correspond to a dynamical variable (observable) of the quantum system.

Given a complete orthonormal basis \(\varphi_k\), which can also be the eigenstate basis \(\psi_k\), one can define matrix representations of the various operators

$$Q_{jk} = \langle \varphi_j | \hat{Q} | \varphi_k \rangle = \int_{-\infty}^{+\infty} \varphi_j^* \hat{Q} \varphi_k dr$$  \(\text{(35)}\)

where, consistent with our definitions above, the notation \(r\) stands either for the relevant coordinate in a one-dimensional system and the integration is carried out over the range of definition for \(r\), or else \(r\) represents the set of all coordinates and the integration corresponds to a multiple integral over the space of all coordinates. The equations given above for operators remain valid for the corresponding matrix representations replacing the operators \(\hat{Q}\) by the matrices \(Q\).

2.4 Time-dependent perturbation theory and matrix representation of the Schrödinger equation

We consider a decomposition of the Hamiltonian \(\hat{H}\) according to a zero-order Hamiltonian \(\hat{H}_0\) (which might be useful, if \(\hat{H}_0\) has a simple analytical solution such as a collection of harmonic oscillators) and a “perturbation” operator \(\hat{V}\) needed to complement \(\hat{H}_0\) in order to describe the complete Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}$$  \(\text{(36)}\)
We assume $\hat{H}_0$ and $\hat{V}$ to be time independent, although many of the following steps can be carried out similarly with time-dependent Hamiltonians and “perturbations” $\hat{V}$. The perturbation might sometimes be small, but this is not necessary. We assume the solution of the Schrödinger equation to be known with $\hat{H}_0$

$$\hat{H}_0 \varphi_k(r) = E_k \varphi_k(r) \quad (37)$$

The $\varphi_k$ form a complete basis and the general wavefunction is given by

$$\Psi(r, t) = \sum c_k(t) \varphi_k(r) \exp(-2\pi i E_k t / \hbar) \quad (38)$$

Here the coefficients $c_k(t)$ depend explicitly upon time because the $\varphi_k$ are not eigenfunctions of $\hat{H}$. If the $\varphi_k(r)$ and $E_k$ are known, the time dependence of the $c_k(t)$ provides in essence the solution of the Schrödinger equation with the complete Hamiltonian including the perturbation $\hat{V}$. Inserting $\Psi(r, t)$ into the time-dependent Schrödinger equation (14) with $\hat{H} = \hat{H}_0 + \hat{V}$ and simplifying the equations by means of the matrix representation of the operator $\hat{V}$ (Eq. (35))

$$V_{jk} = \langle \varphi_j | \hat{V} | \varphi_k \rangle \quad (39)$$

defining a set of coupled differential equations

$$i \hbar \frac{d}{dt} c_j(t) = \sum_k \exp(i\omega_{jk} t) V_{jk} c_k(t) \quad (40)$$

where we use the abbreviations

$$\omega_{jk} = \omega_j - \omega_k = \frac{2\pi E_j}{\hbar} - \frac{2\pi E_k}{\hbar} \quad (41)$$

Defining a matrix element of some kind of Hamiltonian matrix

$$\tilde{H}_{jk} = \exp(i\omega_{jk} t) V_{jk} \quad (42)$$

the set of equations defined by Eq. (40) can be written in matrix notation

$$i \hbar \frac{d}{dt} c(t) = \tilde{H}(t) c(t) \quad (43)$$

In this matrix representation, $\tilde{H}(t)$ depends on time. However, one can make the substitution

$$a_k = \exp(-i\omega_k t) c_k \quad (44)$$

and obtains

$$i \hbar \frac{d}{dt} a_j = \left( \sum_k V_{jk} a_k \right) + \frac{h}{2\pi} \omega_j a_j \quad (45)$$

Defining the diagonal matrix

$$E_{Diag} = \{ E_j = h\omega_j/(2\pi) \} \quad (46)$$

one obtains

$$i \hbar \frac{d}{dt} a(t) = \{ E_{Diag} + \mathbf{V} \} a = \mathbf{H}^{(o)} a(t) \quad (47)$$
where \( a \) is the column matrix of coefficients \( a = (a_1, a_2, \ldots, a_k \ldots a_n)^T \) and \( H^{(a)} \) is a time-independent matrix representation of the Hamiltonian as defined above.

Equation (47) is thus a matrix representation of the original Schrödinger equation which makes the influence of the perturbation \( \hat{V} \) explicit. The corresponding time-independent Schrödinger equation is obtained following section 2.2.2, and we do not repeat the corresponding equations. The solution of Eq. (47) is given by the matrix representations of Eq. (18) – (20), thus

\[
a(t) = U^{(a)}(t, t_0) a(t_0)
\]  

(48)

with

\[
U^{(a)}(t, t_0) = \exp(-2\pi i H^{(a)}(t - t_0)/\hbar)
\]  

(49)

These equations are generally useful for numerical computation, provided that the basis functions \( \varphi_k \) and the \( E_k \) are known and the matrix elements \( V_{jk} \) needed in Eq. 47 can be computed accordingly. Eqs. (48) and (49) are equivalent to the original Schrödinger equation. Approximations arise from the truncation of the generally infinite matrices at finite size and from errors introduced by the numerical algorithms used for the calculations of matrix elements and in the calculations of the various matrix operations.

3 Quantum dynamics of spectroscopic transitions under excitation with coherent monochromatic radiation

3.1 General aspects

While traditional spectroscopy in the optical domain has used weak, incoherent (quasithermal) light sources (see also section 4), present-day spectroscopy frequently uses high power coherent laser light sources allowing for a variety of phenomena ranging from coherent single-photon transitions to multiphoton transitions of different types. Figure 2 provides a summary of mechanisms for such transitions.

While excitation with incoherent light can be based on a statistical treatment (section 4), excitation with coherent light can be handled by means of quantum dynamics as outlined in section 2. Intense, coherent laser radiation as also electromagnetic radiation in the radiofrequency domain used in NMR spectroscopy (Ernst et al. (1987)) can be treated as a classical electromagnetic wave satisfying the general wave equations (50, 51) resulting from Maxwell’s theory

\[
\nabla^2 \vec{E} = \mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2}
\]  

(50)

\[
\nabla^2 \vec{B} = \mu_0 \varepsilon_0 \frac{\partial^2 \vec{B}}{\partial t^2}
\]  

(51)

\( \vec{E} \) is the electric field vector and \( \vec{B} \) the magnetic field vector (magnetic induction), \( \mu, \mu_0, \varepsilon, \varepsilon_0 \) are the normal field constants (Stohner and Quack 2010), with \( \varepsilon = \mu = 1 \) in vacuo. The Nabla operator \( \nabla \) is
defined by Eq. (52)

\[ \nabla = \vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z} \]  

(52)

where \( \vec{e}_x, \vec{e}_y, \vec{e}_z \) are the unit vectors in a right-handed Cartesian coordinate system. The classical electromagnetic wave can be understood as the coherent state description of the quantum field in the limit of very large average number \( \langle n \rangle \) of quanta per field mode (Glauber 1963a,b; Perelomov 1986). Coherent laser radiation as also radiofrequency radiation is frequently characterized by \( \langle n \rangle > 10^{10} \), thus the classical approximation to the electromagnetic field is excellent. The situation of weak thermal light sources in the optical domain is very different (\( \langle n \rangle < 1 \)), requiring a quantum statistical
We shall consider here for simplicity the special case of a classical $z$-polarized electromagnetic wave propagating in vacuo in the $y$-direction with slowly varying (or constant) field amplitudes $E_0(t)$ and $B_0(t)$, thus (see Fig. 3)

$$E_z(y,t) = |E_0(t)| \cos(\omega t + \eta' - k_\omega y) \quad (53)$$

$$B_x(y,t) = |B_0(t)| \cos(\omega t + \eta' - k_\omega y) \quad (54)$$

$\omega = 2\pi\nu$ is the angular frequency, $k_\omega = 2\pi/\lambda$ the angular wavenumber, $\nu = c/\lambda$ the ordinary frequency and $\lambda$ the wavelength. At a given position $y$ the phase $\eta'$ can be combined with the phase $-k_\omega y$ to an overall phase $\eta = k_\omega y - \eta'$.

![Image of a monochromatic wave](image)

Figure 3: Schematic representation of a monochromatic wave

The extension to more general cases is straightforward (see also Quack (1998)). The intensity of the radiation is in general

$$I(y,t) = |E_z(y,t)|^2 \sqrt{\frac{\varepsilon\varepsilon_0}{\mu\mu_0}} \quad (55)$$

and averaging over time with $\langle \cos^2 x \rangle = 1/2$. One has from Eqs. (53), (55)

$$I(t) = \frac{1}{2} |E_0(t)|^2 \sqrt{\frac{\varepsilon\varepsilon_0}{\mu\mu_0}} \quad (56)$$

For the speed of light, one has in some medium with refractive index $n_m$

$$c_m = (\mu_0\varepsilon_0)^{-1/2} = c/n_m \quad (57)$$

and in vacuo ($\mu = \varepsilon = 1$)

$$c = (\mu_0\varepsilon_0)^{-1/2} \quad (58)$$

We can mention here some practical equations for calculating electric and magnetic field strengths when irradiating with monochromatic radiation of given intensity $I$

$$\left| \frac{E_0}{V \text{cm}^{-1}} \right| \simeq 27.44924\sqrt{\frac{I}{W \text{cm}^{-2}}} \quad (59)$$

$$\left| \frac{B_0}{T} \right| \simeq 9.156 \cdot 10^{-6} \sqrt{\frac{I}{W \text{cm}^{-2}}} \quad (60)$$
A further quantity characterizing the irradiation over some period of time \( t \) is the fluence \( F(t) \) defined by Eq. (61)

\[
F(t) = \int_0^t I(t')dt'
\]  

(61)

For wavelengths \( \lambda > 100 \text{ nm} \) one can assume \( E \) and \( B \) to be constant over the extension of the atomic or molecular system at any given time \( (\Delta y > 1 \text{ nm}) \), which leads to the dipole approximation for the interaction energy between molecule and field

\[
\hat{V}_{\text{el.dipole}} = -\mu_{\text{el}} \vec{E}
\]

(62)

where \( \mu_{\text{el}} \) is the electric dipole vector given by Eq. (63)

\[
\mu_{\text{el}} = \sum q_i \vec{r}_i
\]

(63)

Similarly one has the interaction energy with a magnetic dipole \( \mu_{\text{magn}} \)

\[
\hat{V}_{\text{magn.dipole}} = -\mu_{\text{magn}} \vec{B}
\]

(64)

For the present quantum dynamical treatment of coherent excitation, we restrict our attention to electric dipole transitions in a field given by Eq. (53), therefore we can write with the \( z \)-component \( \mu_z \) of the electric dipole operator (and abbreviating \( \eta = k_\omega y - \eta' \))

\[
\hat{V}_{\text{el.dipole}} = -\mu_z E_z(y,t) = -\mu_z |E_0(t)| \cos(\omega t - \eta)
\]

(65)

The extension to magnetic dipole transitions is straightforward. We give here only a brief summary and refer to Quack (1978, 1982, 1998) for more detail.

### 3.2 Time-dependent quantum dynamics in an oscillatory electromagnetic field

We consider now the time-dependent Schrödinger equation (14) with a time-dependent Hamiltonian

\[
\hat{H}(t) = \hat{H}_{\text{Mol}} - \mu_z |E_0(t)| \cos(\omega t - \eta)
\]

(66)

which is of the form of Eq. (36), with \( \hat{H}_{\text{Mol}} \) being the time-independent Hamiltonian for the isolated molecule in the absence of fields and the interaction Hamiltonian \( \hat{V} \) is now a time-dependent, oscillatory function. We assume the solution of the time-independent Schrödinger equation for the isolated molecule to be given by Eq. (67) \( (\hbar = \hbar/2\pi) \)

\[
\hat{H}_{\text{Mol}} \varphi_k = E_k \varphi_k = \hbar\omega_k \varphi_k
\]

(67)

and write the solution of the time-dependent Schrödinger equation in the basis \( \varphi_k \) of molecular eigenstates with time-dependent coefficients

\[
\Psi(r,t) = \sum_k b_k(t) \varphi_k(r)
\]

(68)
Inserting this into Eq. (14) we obtain a set of coupled differential equations

\[ i\hbar \frac{db_j}{dt} = \sum_k H_{jk} b_k(t) \]  

(69)

or in matrix notation

\[ i\hbar \frac{d\mathbf{b}(t)}{dt} = \mathbf{H}(t)\mathbf{b}(t) \]  

(70)

This is again in essence a matrix representation of the original Schrödinger equation (see section 2). Assuming molecular states of well defined parity, the diagonal electric dipole matrix elements vanish and we have the diagonal elements of \( \mathbf{H}(t) \)

\[ H_{ii} = E_i = \langle \varphi_i | \hat{H}_{\text{Mol}} | \varphi_i \rangle \equiv \hbar \omega_i \]  

(71)

For other situations such as for chiral molecules or if parity violation were important (Quack 2010) one would have also a diagonal contribution from the electric dipole interaction energy. Disregarding here such cases, the electric dipole interaction energy leads to off-diagonal matrix elements

\[ H_{kj} = \langle \varphi_k | \hat{V}_{\text{cl.dipole}}(t) | \varphi_j \rangle \]  

(72)

Dividing \( H_{kj} \) by \( \hbar \cos(\omega t - \eta) \) we obtain a matrix element \( V_{kj} \), which is independent of time, if we can assume \( |E_0(t)| \) to be sufficiently slowly varying in time that it can be taken constant for the time period under consideration, as we shall do replacing \( E_0(t) \) by \( E_0 \)

\[ V_{kj} = H_{kj} / [\hbar \cos(\omega t - \eta)] = -\langle \varphi_k | \hat{\mu}_z | \varphi_j \rangle |E_0| / \hbar = V'_{jk} \]  

(73)

We then obtain a set of coupled differential equations in matrix notation

\[ i\hbar \frac{d\mathbf{b}(t)}{dt} = \{ \mathbf{W} + \mathbf{V} \cos(\omega t - \eta) \} \mathbf{b}(t) \]  

(74)

where we have defined the diagonal matrix \( \mathbf{W} \) by the matrix elements \( W_{kk} \equiv \omega_k \).

This is still a practically exact representation of the original time-dependent Schrödinger equation for the physical situation considered here. Because of the essential time dependence in \( \mathbf{V} \cos(\omega t - \eta) \), there is no simple closed expression in the form of the exponential function analogous to Eqs. (18, 20) or (48, 49). Apart from numerical, stepwise solutions discussed in Quack (1998), one can make use of series expansions such as the Magnus expansion. This solves Eq. 70 by means of the following series for \( \mathbf{U}(t, t_0) \)

\[ \mathbf{b}(t) = \mathbf{U}(t, t_0) \mathbf{b}(t_0) \]  

(75)

\[ \mathbf{U}(t_0, t_0) = 1 \]  

(76)

\[ \mathbf{U}(t, t_0) = \exp \left( \sum_{n=0}^{\infty} \frac{\mathbf{C}_n}{n!} \right) \]  

(77)

The first two terms are given by the following expressions

\[ i\hbar \mathbf{C}_0 = \int_{t_0}^{t} \mathbf{H}(t') dt' \]  

(78)
Higher terms contain more complex combinations of commutators of the type \([H(t'), H(t'')]\). From this one recognizes that the series terminates after the first term given by Eq. 78, if \(H(t')\) and \(H(t'')\) commute at all \(t', t''\), which is true if \(H\) does not depend on time resulting in the exponential solutions already discussed. There are other (rare) cases of time-dependent \(H(t)\), but with \([H(t'), H(t'')]\) = 0.

One can, however, also make use of the periodicity of the field using Floquet’s theorem Quack (1978, 1998).

### 3.3 Floquet solution for Hamiltonians with strict periodicity

With \(H = \hbar \{W + V \cos(\omega t - \eta)\}\) from Eq. (74) one has obviously

\[
H(t + \tau) = H(t)
\]

with period \(\tau = 2\pi/\omega\).

Making use of the Floquet theorem (or Floquet-Liapounoff theorem, see Quack (1978, 1998) for the historical references) one has the following form for the time-evolution matrix (with some integer \(n\))

\[
U(t, t_0) = F(t, t_0) \exp(A(t - t_0))
\] (81)

\[
F(t_0, t_0) = 1
\] (82)

\[
F(t + n\tau) = F(t)
\] (83)

\[
A(t') = A(t'') \quad \text{(all } t', t''\text{)}
\] (84)

It is then sufficient to integrate numerically over one period \(\tau\) and then obtain the evolution for all times by matrix multiplications according to Eqs. (81 – 84). In particular at multiples of the period \(\tau\) one finds (with \(t_0 = 0\))

\[
U(\tau) = \exp(A\tau)
\] (85)

\[
U(n\tau) = [U(\tau)]^n
\] (86)

There has been considerable literature making use of Floquet’s theorem for the treatment of coherent excitation and there exist computer program packages (see Quack (1998)). We shall discuss here a further useful approximation.

### 3.4 Weak-field quasiresonant approximation (WF-QRA) for coherent monochromatic excitation

We consider a level scheme for coherent excitation with levels near to the resonance as shown in Fig. 4. One can then associate with each molecular level of energy \(E_k = \hbar\omega_k\) an integer photon number.
for near-resonant excitation such that

$$\omega_k = n_k \omega + x_k$$  \hfill (87)\]

where \(x_k\) is a frequency mismatch for exact resonance at the best choice of \(n_k\).
\[ a_k = \exp(i m_k \omega t) b_k \]  

resulting in the set of differential equations

\[ i \frac{d a_k}{d t} = x_k a_k + \frac{1}{2} \sum_{j \neq k} V_{kj} a_j \]  

or in matrix form (with the diagonal matrix \( X \) and \( X_{kk} = x_k \))

\[ i \frac{d a}{d t} = \left\{ X + \frac{1}{2} V' \right\} a \]  

One can interpret this equation by means of an “effective Hamiltonian”

\[ H_{\text{eff}}^{(a)} = \hbar \left\{ X + \frac{1}{2} V' \right\} \]  

and the corresponding effective time-evolution matrix

\[ U_{\text{eff}}^{(a)}(t, t_0) = \exp \left[ -2 \pi i \frac{H_{\text{eff}}^{(a)}(t - t_0)}{\hbar} \right] \]

\[ = \exp \left[ -i \left( X + \frac{1}{2} V' \right)(t - t_0) \right] \]

\[ a(t) = U_{\text{eff}}^{(a)}(t, t_0) a(t_0) \]  

This is quite a remarkable result as it corresponds to replacing the molecular energies \( E_k \) by new effective energies \( \hbar X_{kk} \) and the couplings \( V_{kj} \) by new effective couplings \( (V_{kj}/2) \) for near-resonant levels (and implicitly by zero for far off-resonant levels). We can therefore use \( V'/2 \) rather than \( V/2 \) for the general matrix. This is graphically shown in Fig. 5 for the same level scheme as in Fig. 4, but with effective energies which are “on the same energy shell” and thus effective couplings between levels of similar effective energy. We note the close analogy to the dressed atom (dressed molecule picture by Cohen-Tannoudji which uses, however, a different derivation (Cohen-Tannoudji et al. (1992)). We note that the quasiresonant transformation as given in Quack (1978, 1998) can be written in matrix notation

\[ a = Sb \]  

with the diagonal matrix

\[ S_{kk} = \exp(i n_k \omega t) \]  

Similarly, a transformation for the density matrix \( P^{(a)} \) from \( P^{(b)} \) can be derived in this approximation, resulting in the solution of the Liouville-von Neumann equation for \( P(t) \) by

\[ P^{(a)}(t) = SP^{(b)} \left\{ S^\dagger \right\} \]  

\[ P^{(a)}(t) = U_{\text{eff}}^{(a)}(t, t_0) P^{(a)}(t_0) U_{\text{eff}}^{(a)}(t, t_0)^\dagger \]  

For details we refer to Quack (1978, 1982, 1998) and we turn now to a simple application to the special case of coherent radiative excitation connecting just two quantum states.
3.5 Coherent monochromatic excitation between two quantum states

If only two quantum states are considered, one obtains a scheme for the coherent monochromatic radiative excitation as shown in Fig. 6.

![Figure 6: Two level scheme for coherent radiative excitation with frequency ω](image)

Eq. (70) simplifies to the set of just two coupled differential equations

\[ i \frac{db_1}{dt} = \omega_1 b_1 + V_{12} \cos (\omega t - \eta) b_2 \]  \hspace{1cm} (98)

\[ i \frac{db_2}{dt} = V_{21} \cos (\omega t - \eta) b_1 + \omega_2 b_2 \]  \hspace{1cm} (99)

One might think that this rather simple set of coupled differential equations has a simple solution, but in fact it seems that until today no simple general analytical solution in form of a closed expression is known (see the discussion in Quack (1978, 1998) for special cases). Of course, one can write down formal series expansions (sections 3.2 and 3.3.) or solve the equations numerically quite easily.

However, following the discussion of section 3.4, an analytical solution in the form of a closed expression can be derived in the weak-field quasiresonant approximation. The most general solution in terms of the time evolution matrix \( U^{(a)}_{\text{eff}} \) is given by the matrix elements omitting the index “eff” to simplify the notation and taking a real \( V_{12} = V_{21}^* = V \) as parameter

\[ U^{(a)}_{11} = \exp(-i\lambda_1 t) \left[ x^2 + y^2 \exp(i\omega_R t) \right] \]  \hspace{1cm} (100)

\[ U^{(a)}_{22} = \exp(-i\lambda_1 t) \left[ y^2 + x^2 \exp(i\omega_R t) \right] \]  \hspace{1cm} (101)

\[ U^{(a)}_{12} = U^{(a)*}_{21} = \exp(-i\lambda_1 t)xy \left[ 1 - \exp(i\omega_R t) \right] \]  \hspace{1cm} (102)

where we have used the following parameters as abbreviations

\[ \omega_R = (\lambda_1 - \lambda_2) = \sqrt{V^2 + D^2} = \frac{2\pi}{\tau_R} \]  \hspace{1cm} (103)

\[ \lambda_1 = \frac{1}{2} \left( D + \sqrt{V^2 + D^2} \right) \]  \hspace{1cm} (104)
\[ \lambda_2 = \frac{1}{2}\left( D - \sqrt{V^2 + D^2} \right) \] (105)

\[ x = \left[ \frac{1}{2} - \frac{D}{2\omega_R} \right]^{1/2} \] (106)

\[ y = \left[ \frac{1}{2} + \frac{D}{2\omega_R} \right]^{1/2} \] (107)

We note that in Quack (1998) some of the expressions were misprinted and are corrected here. We also give the explicit form of the effective Hamiltonian corresponding to Eq. (91)

\[ \frac{H_{eff}^{(a)}}{\hbar} = \begin{pmatrix} 0 & 0 \\ 0 & D \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} \] (108)

\[ = X + \frac{1}{2} V \] (109)

In the two-level case the distinction between \( V \) and \( V' \) is not necessary.

\[ U_{eff}^{(a)}(t - t_0) = Z \exp \left[ -i\Lambda(t - t_0) \right] \] (110)

While these general equations can be used to derive numerous properties of the coherent monochromatic excitation in the two-level problem, we conclude here with the result for the time-dependent population of the excited level \( p_2(t) \), if initially at time zero only the ground state is populated \((p_1(t = 0) = 1)\).

One obtains Eq. (112) for the population of the upper level

\[ p_2(t) = |b_2(t)|^2 = \frac{V^2}{V^2 + D^2} \left[ \sin \left( \frac{1}{2} \sqrt{V^2 + D^2} \right) \right]^2 = 1 - p_1(t) \] (112)

This is a periodic exchange of population between ground and excited state with a period

\[ \tau_R = \frac{2\pi}{\sqrt{V^2 + D^2}} \] (113)

This period is called Rabi period, with \( \omega_R \) being the Rabi frequency, as these equations were derived on the basis of the so-called rotating wave approximation by Rabi (1937) (see also Rabi et al. (1938)) in the context of early nuclear magnetic resonance experiments (in beams, with a magnetic dipole transition matrix element \( V \), of course).

The rotating wave approximation becomes identical with the quasiresonant approximation for the special case of a two level problem. Eq. (112) is frequently called “Rabi formula”.

Fig. 7 shows the time-dependent level populations for a fairly typical case. With increasing resonance mismatch \( D \) the amplitude of the oscillation decreases, but the frequency of oscillation increases. The initial time evolution is independent of the resonance mismatch as is readily seen from the series expansion of the \( \sin(x) \) function for small arguments \( x \) \((\sin x = x + \ldots)\) giving at sufficiently small times

\[ p_2(t) \simeq V^2 t^2/4 \quad (\text{small } t) \] (114)
Figure 7: Two level problem level populations. The population $p_2$ of the upper level in the scheme of Fig. 6 are shown with different resonant defects $D = (0, 2, 3, 4, 5) \times 10^{12} \text{ s}^{-1}$ for an electric dipole transition (1 Debye) and $\nu = 1000 \text{ cm}^{-1}$ for the laser wavenumber.

One can also consider the time-averaged population $\langle p_2(\omega) \rangle_t$ as a function of the exciting laser frequency $\omega$ at fixed resonance frequency $\omega_{12} = \omega_2 - \omega_1$. Because $\langle \sin^2 x \rangle = 1/2$, one has

$$\langle p_2(\omega) \rangle_t = \frac{1}{2} \frac{V^2}{V^2 + (\omega - \omega_{12})^2}$$

(115)

$\langle p_2(\omega) \rangle$ is proportional to the average absorbed energy as a function of frequency $\omega$, so that one can interpret this expression as the effective absorption line shape under intense coherent excitation. Indeed, Eq. (115) corresponds to a Lorentzian line shape with full width at half maximum $\Gamma_{\text{FWHM}} = 2V$. This effect is called “power broadening” because $V \propto \sqrt{I}$ (cf. Eqs. (59) and (73), sometimes “intensity broadening” is used as well). We have neglected here effects from spontaneous emission or collisions, as is obviously appropriate for the time scales applicable to Fig. 6, but not necessarily always so.

We may finally conclude with an estimate of errors arising, when the conditions of the WF-QRA are not fulfilled. The special case of the degenerate two level problem has been solved exactly (Quack 1978). In this case one has $\omega_1 = \omega_2$ and therefore $D^2 = \omega^2$. The Rabi formula Eq. (112) thus would give

$$p_2^{\text{Rabi}}(t) = \frac{V^2}{V^2 + \omega^2} \left[ \sin \left( \frac{t}{2} \sqrt{V^2 + \omega^2} \right) \right]^2$$

(116)

The exact solution Quack (1978) is

$$p_2^{\text{ex}}(t) = \left\{ \sin \left( \frac{V}{\omega} \sin (\omega t) \right) \right\}^2$$

(117)

One can consider the limit $|V| \ll \omega$, because this must be assumed for the validity of the Rabi formula, and considering this limit, one obtains

$$p_2^{\text{Rabi}}(t) \approx \frac{V^2}{\omega^2} \left[ \sin (\omega t/2) \right]^2$$

(118)
Thus the exact solution gives the same amplitude as the Rabi formula, but the period differs by a factor of 2. Of course the second condition for the validity of the WF-QRA is not satisfied, as one cannot have \(|D| \ll \omega\) (rather by definition of the special case one has \(|D| = \omega\)). If \(|D| \ll \omega\), the Rabi formula gives a very good approximation, as one can show numerically. We may note here that closed analytical expressions for the solutions are available for the excitation of the harmonic oscillator both with the exact treatment (Eq. 70) and within the WF-QRA (Eq. 90), taking an infinite number of levels into account, which may seem perhaps surprising. The derivation has been given by Marquardt and Quack (1989) and leads to a further estimate of the ranges of validity and uncertainties introduced by the WF-QRA, in this case for a many level system.

4 Basic concepts of experimental spectroscopy

4.1 General remarks

Spectroscopy is the main experimental method to obtain quantitative information on, and study fundamental properties of, molecular systems. Molecular systems obey the law of quantum mechanics, as summarized in Section 2. Quantitative information must be acquired through reproducible experiments carried out under specified experimental conditions. In the case of molecular systems and other quantum systems, the outcome of experiments can be described statistically. Repeating the same measurement of an observable twice does not always give the same result, but the outcomes of a sufficiently large set of identical measurements are characterized by a probability distribution.

Molecules are mechanical systems which can be influenced by external forces applied by an experimentalist. Electromagnetic forces, because they are long-range forces and easily applied, are of particular importance in the study of molecular systems. Classically, the behavior of a particle of charge \(q\) in an electromagnetic field \((\vec{E}(\vec{r}, t), \vec{B}(\vec{r}, t))\) is described by the Lorentz force:

\[
\vec{F} = q(\vec{E} + \vec{v} \times \vec{B}).
\]  

(120)

By varying \(\vec{E}\) and \(\vec{B}\), the experimentalist varies \(\vec{F}\) and thus acts on the particle according to Newton’s second axiom:

\[
\vec{F}(t) = \frac{d(m\vec{v}(t))}{dt}.
\]  

(121)

In quantum mechanics, one describes the Hamiltonian of the system in terms of the vector potential \(\vec{A}(\vec{r}, t)\) and the scalar potential \(\phi(\vec{r}, t)\):

\[
\vec{B}(\vec{r}, t) = \text{rot}(\vec{A}(\vec{r}, t))
\]  

(122)

\[
\vec{E}(\vec{r}, t) = -\text{grad}(\phi(\vec{r}, t)) - \frac{\partial \vec{A}(\vec{r}, t)}{\partial t}.
\]  

(123)
For a single free particle of mass $m$ and charge $q$, the Hamiltonian takes the form

$$H(t) = \frac{1}{2m} \left( p - q\vec{A}(\vec{Q},t) \right)^2 + q\phi(\vec{Q},t).$$

(124)

However, in most spectroscopic studies described in the literature, $\vec{E}$ and $\vec{B}$ are used as primary parameters.

A quantum system under the influence of external time-dependent electromagnetic fields (which we call external perturbations) is described by a time-dependent Hamilton operator $\hat{H}(t)$

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t),$$

(125)

where $\hat{H}_0$ is the time-independent Hamilton operator of the system without external perturbation and

$$\hat{V}(t) = -\sum_n b_n(t) \hat{B}_n$$

(126)

is an operator representing the effects of the external forces applied by the experimentalist. In all practical cases, $\hat{V}(t)$ is a sum of contributions $-b_n(t) \hat{B}_n$, where $\hat{B}_n$ is a time-independent hermitian operator and $b_n(t)$ is a real function of time.

---

**Example: Interaction of light with molecular systems in the dipole approximation:** (see also previous sections) A monochromatic electromagnetic wave of wavelength $\lambda$ propagating along the $y$ axis of a suitably chosen laboratory coordinate system is schematically represented in Fig. 3. The interaction of a molecular system with an electromagnetic wave can be described by the interaction of the electric and magnetic dipole moments with the electric and magnetic fields, respectively, of the electric and magnetic quadrupole moments with the electric and magnetic field gradients, etc. The dipole approximation to describe the interaction of electromagnetic radiation with a molecular system consists of neglecting all interactions other than that between the dipoles and the fields. The approximation is valid as long as the electric or magnetic field strength does not change over the size $d$ of the molecular system, i.e., as long as $\lambda >> d$, because then the interactions involving the quadrupole and higher moments, which require a variation of the field strength in the immediate vicinity of the molecule, are negligible.

In the dipole approximation, the interaction operator with a monochromatic field of frequency $\omega$ can be written as:

$$\hat{V}(t) = \hat{V}_{\text{el}}(t) + \hat{V}_{\text{magn}}(t),$$

(127)

with

$$\hat{V}_{\text{el}}(t) = -\hat{\mu}_{\text{el}} \cdot E = -\left( \sum_i q_i \vec{r}_i \right) \cdot E_0 \cos(\omega t - \eta)$$

(128)

and

$$\hat{V}_{\text{magn}}(t) = -\hat{\mu}_{\text{magn}} \cdot \vec{B} = -\hat{\mu}_{\text{magn}} \cdot \vec{B}_0 \cos(\omega t - \eta),$$

(129)

where $\hat{\mu}_{\text{el}} = (\sum_i q_i \vec{r}_i)$ and $\hat{\mu}_{\text{magn}}$ are the electric and magnetic dipole operators of the molecular system, respectively. One sees immediately that Eqs. (128) and (129) have the general form of Eq. (126). If $d \approx \lambda$, the electric and magnetic field strengths vary over the size of the molecular system, and one must also consider the interaction of the electromagnetic fields with the quadrupoles, octupoles, etc. of the molecules. The electric dipole interaction is the dominant interaction in the microwave, infrared, visible and ultraviolet ranges of the electromagnetic spectrum.
(λ large). The magnetic dipole interaction is used in spectroscopies probing the magnetic moments resulting from the electron or nuclear spins such as EPR and NMR, and it is also important in optical spectroscopy if the electric dipole transition is forbidden. At short wavelength, i.e., for X- and γ-rays, the dipole approximation breaks down because \( \lambda \leq d \).

The art of experimenting consists of a) choosing a suitable interaction operator \( \hat{B}_n \), b) designing functions \( b_n(t) \) (called experimental “stimuli”) so as to act on the system under investigation, and finally c) detecting and analyzing the response of the system to the stimulus. Many tools are at the disposal of the experimentalist to generate the external perturbations such as microwave synthesizers, lamps, electromagnets, masers, lasers, etc. In many spectroscopic experiments, the sample consists of molecules in thermal equilibrium, and the external perturbation induces transitions between the energy levels of the molecules in the system, causing a departure from thermal equilibrium. In analyzing the response of the system to the stimulus, it is necessary to also consider possible interactions of the system under investigation with its environment. These interactions, e.g., the collisions with foreign gas particles or with the walls of an apparatus, or the interaction with the vacuum radiation field, lead to the relaxation of the system to thermal equilibrium. The distinction between the system under investigation and its environment is sometimes difficult to make and a given choice has implications on the way the results of an experiment are analyzed.

We now turn to an introductory description of the relationship between an experimental stimulus and the response of a system induced by this stimulus in the realm of response theory.

### 4.2 An introduction to response theory

A spectroscopic experiment can be viewed as an information transfer in which the system, here a molecular quantum system, gives a response to a stimulus, here a classical electromagnetic field. In general, it is advisable, in an experiment that aims at looking at the properties of a system, to disturb the system as little as possible during the measurement, so that the intrinsic properties of the system are highlighted. In the extreme case where the perturbation \( \hat{V}(t) \) is very much larger than \( \hat{H}_0 \), one risks to primarily get information on the experimental perturbation, the properties of the system becoming negligible. This consideration justifies a restriction of the discussion to the linear response of the system.

The response \( x(t) \) of a system to a stimulus \( y(t) \) can be described mathematically by the transformation

\[
x(t) = R y(t),
\]

(130) where \( R \) represents the response operator. In a spectroscopic measurement, the system may be viewed as the sample probed in the experiment, the stimulus as the radiation field(s) used to perturb the system, and the response as a signal emitted by the sample and collected by the measurement device.
The response operator is thus the characteristic property of the system and represents the quantity to be derived from an analysis of the response to the stimulus. The response operator can be determined by discrete sampling of \( y(t) \) and \( x(t) \), e.g., using a digital oscilloscope, at the times \( t_n = t_0 + n\Delta t \), with \( n = 0, 1, 2, \ldots, N \), as illustrated by Fig. 8. The response \( x_n = x(t_n) \) at time \( t_n \) can be viewed as being caused by the stimulus \( y_m = y(t_m) \) at all times between \( t_0 \) and \( t_N \):

\[
x_n = R_n(y_0, y_1, \ldots, y_N),
\]

where \( n = 0, 1, \ldots, N \), and \( R_n \) has the form \( R_n \rightarrow R \). A Taylor expansion around the point \( y_0, y_1, \ldots y_N = 0 \) gives for well-behaved systems:

\[
x_n = R^{(0)}(t) + \sum_{i=0}^{N} R^{(1)}_{n,i} y_i + \frac{1}{2!} \sum_{i=0}^{N} \sum_{j=0}^{N} R^{(2)}_{n,i,j} y_i y_j + \ldots,
\]

where \( R^{(1)}_{n,i} = \frac{\partial R_n(y_0, y_1, \ldots, y_N)}{\partial y_i} \bigg|_{y_i \neq y_{n,i}} \), \( R^{(2)}_{n,i,j} = \frac{\partial^2 R_n(y_0, y_1, \ldots, y_N)}{\partial y_i \partial y_j} \bigg|_{y_k \neq y_{n,i}, y_{n,j}} \), etc. For \( \Delta t \to 0 \), one can replace the sum by an integral and obtains a so-called Volterra expansion:

\[
x(t) = R^{(0)}(t) + \int_{-\infty}^{t} R^{(1)}(t, s) y(s) ds + \frac{1}{2!} \int_{-\infty}^{t} \int_{-\infty}^{t} R^{(2)}(t, s, s') y(s) y(s') ds ds' + \ldots.
\]

The parameters describing the system under study remain constant with time, the system is said to be time-invariant. The systems studied spectroscopically are often time-invariant (counter-examples would be a system undergoing a chemical reaction, or a system exposed to varying stray
fields), and in these systems the response functions show the behavior described by Fig. 9. The response \( x_T(t) = x(t + T) \) to a time-shifted stimulus \( y_T(t) = y(t + T) \) stands in the same relationship to \( y_T(t) \) as the response \( x(t) \) to the stimulus \( y(t) \). By replacing \( t \) by \( t + T \) in the Volterra expansion (133) one obtains:

\[
x_T(t) = x(t + T) = R^{(0)}(t + T) + \int_{-\infty}^{\infty} R^{(1)}(t + T, s) y(s) ds + \frac{1}{2!} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R^{(2)}(t + T, s, s') y(s) y(s') ds ds' + \ldots \quad (135)
\]

\[
x_T(t) = R^{(0)}(t) + \int_{-\infty}^{\infty} R^{(1)}(t, s) y_T(s) ds + \frac{1}{2!} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R^{(2)}(t, s, s') y_T(s) y_T(s') ds ds' + \ldots \quad (136)
\]

\[
x_T(t) = R^{(0)}(t) + \int_{-\infty}^{\infty} R^{(1)}(t, s - T) y(s) ds + \frac{1}{2!} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R^{(2)}(t, s - T, s' - T) y(s) y(s') ds ds' + \ldots \quad (137)
\]

Comparing Eqs. (135) and (137) term by term, one gets

\[
R^{(0)}(t + T) = R^{(0)}(t) = \phi^{(0)} \quad (138)
\]

and

\[
R^{(1)}(t + T, s) = R^{(1)}(t, s - T). \quad (139)
\]

One sees from Eq. (139) that \( R^{(1)} \) only depends on the time difference between stimulus and response, and therefore

\[
R^{(1)}(t, s) = \phi^{(1)}(t - s). \quad (140)
\]

Inserting Eqs. (138) and (140) into Eq. (133) leads to the following expression describing the response of a time-invariant system:

\[
x(t) = \phi^{(0)} + \int_{-\infty}^{\infty} \phi^{(1)}(t - s) y(s) ds + \ldots
\]

\[
= \phi^{(0)} + \int_{-\infty}^{\infty} \phi^{(1)}(s) y(t - s) ds + \ldots, \quad (141)
\]

Figure 9: Stimulus and response in a time-invariant system
where the second line was obtained by making the substitution \( s' = t - s \). The response of time-invariant causal systems, for which \( s \leq t \), i.e., for which \( s' \geq 0 \) (see above), can therefore be obtained from Eq. (141) by changing the integration range

\[
x(t) = \phi^{(0)} + \int_0^\infty \phi^{(1)}(s')y(t-s')ds' + \ldots.
\]

As expected, the background is constant in a time-invariant system (see Eq. (138)). If one only considers the linear response in such a system, one can write \( \phi^{(1)}(s) = \phi(s) \). After background subtraction, the response of a time-invariant linear system can finally be written as

\[
x(t) = \int_{-\infty}^\infty \phi(s)y(t-s)ds.
\]

The linearity of the system implies the following superposition principle: The response \( x(t) \) to a sum of stimuli \( y(t) = \sum_i y_i(t) \) is the sum \( x(t) = \sum_i x_i(t) \) of the responses \( x_i(t) \) to the stimuli \( y_i(t) \). In spectroscopy, one often uses oscillatory stimuli (for instance \( E_0 \cos(\omega t) \)). The superposition principle enables one to avoid using trigonometric functions. Indeed, the response \( x(t) \) to the stimulus \( y_0 e^{-i\omega t} \) can be expressed as \( \Re(x(t)) - i\Im(x(t)) \) where the real part \( \Re(x(t)) \) is the response to the stimulus \( y_0 \cos(\omega t) \) and the imaginary part \( \Im(x(t)) \) is the response to the stimulus \( y_0 \sin(\omega t) \).

4.3 Time-resolved vs. frequency-resolved spectroscopy

In this section we briefly discuss the responses to two special stimuli that are of particular importance in spectroscopy, Dirac’s delta function \( y(t) = \delta(t) \) and an oscillatory function \( y(t) = e^{-i\omega t} \). The former stimulus plays a special role in time-resolved spectroscopy, in which the response of a system is monitored following exposure to a very short impulsion, for instance an ultrashort laser pulse. The latter stimulus plays a special role in frequency-resolved spectroscopy in which the response of the system to a monochromatic electromagnetic wave is monitored as a function of the frequency.

a) Response to an impulsion \( \delta(t) \)

In the limit of an infinitely short experimental perturbation \( y(t) = \delta(t) \), where \( \delta(t) \) represents Dirac’s delta function,

\[
\delta(t) = \begin{cases} 
0 & \text{for } t \neq 0 \\
\infty & \text{for } t = 0,
\end{cases}
\]

which is the derivative of the Heaviside function \( H(t) \)

\[
H(t) = \begin{cases} 
0 & \text{for } t \leq 0 \\
1 & \text{for } t > 0.
\end{cases}
\]

Two important properties of the delta function \( \delta(t) \) are given by Equations (146) and (147):

\[
\delta(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{\pm i\omega t} d\omega
\]
\[ \int_{-\infty}^{\infty} f(t)\delta(t - t_0)dt = f(t_0). \]  

Using Equation (143), the linear response to the delta function can be determined to be

\[ x(t) = \int_{-\infty}^{\infty} \phi(s)\delta(t - s)ds = \phi(t), \]

which implies that the response function \( \phi(t) \), which characterizes the linear response to any stimulus, is simply the response to \( \delta(t) \). Experimentally, delta functions can only be realized approximately by a short impulsion, e.g., an ultrashort laser pulse (today femtosecond (fs) pulses are easily generated and the first laser systems producing attosecond pulses are becoming available (Brabec and Krausz 2000, Gallmann and Keller 2010, see also Wörner and Corkum 2010). In a spectroscopic experiment using one such short impulsion as stimulus, one monitors, in real time, the response of the system to the impulsion and one uses the term “time-resolved” spectroscopy. The response, called a free induction decay in nuclear magnetic resonance spectroscopy (NMR, Ernst et al. 1987), electron paramagnetic resonance (EPR, Schweiger and Jeschke 2001) and Fourier-transform microwave spectroscopy (see Bauder 2010; Jäger and Xu 2010; Grabow 2010 in this handbook), is the response function which, by means of a Fourier transformation, can be converted in the power spectrum of the system (see b below). Several important spectroscopic techniques rely on this principle, such as, for instance, Fourier-transform microwave spectroscopy, Fourier-transform NMR, EPR and microwave spectroscopy, and fs laser spectroscopy.

b) Response to an oscillatory function \( e^{-i\omega t} \)

Three types of oscillatory stimulus can be used:

\[ y_1(t) = e^{-i\omega t} = \cos(\omega t) - i \sin(\omega t) \]

\[ y_2(t) = \cos(\omega t) = \Re \{ e^{-i\omega t} \} \]

\[ y_3(t) = \sin(\omega t) = -\Im \{ e^{-i\omega t} \}. \]

Because of the superposition principle discussed above, it is advantageous to determine the response to \( y_1(t) \) from which the response to either \( y_2(t) \) or \( y_3(t) \) may be derived. One gets from Equation (143)

\[ x(t) = \int_{-\infty}^{\infty} \phi(s)e^{-i\omega (t-s)}ds \\
= \int_{-\infty}^{\infty} \phi(s)e^{i\omega s}ds e^{-i\omega t} \\
= \chi(\omega)e^{-i\omega t}, \]  

where

\[ \chi(\omega) = \int_{-\infty}^{\infty} \phi(s)e^{i\omega s}ds. \]

Formulating this result starting from Equation (130)

\[ x(t) = R_y(t) = Re^{-i\omega t} = \chi(\omega)e^{-i\omega t}, \]
one sees that the functions $e^{-i\omega t}$ are the eigenfunctions of the response operator $R$ for any linear system with complex eigenvalues $\chi(\omega)$. Depending on the magnitude of the eigenvalue $\chi(\omega)$ the system responds more or less strongly to the stimulus, i.e., it is more or less susceptible to it. The eigenvalue $\chi(\omega)$ is therefore called the susceptibility of the system. It is a function of the angular frequency of the stimulus and it represents the power spectrum of the system. Equation (153) shows that $\chi(\omega)$ is the Fourier transform of the response function.

---

**Fourier transformations:**

Combining Equations (146) and (147), one gets the so-called Fourier identity:

\[
 f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} ds \, e^{-i\omega(t-s)} f(s) \\
 = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} d\omega \int_{-\infty}^{\infty} e^{i\omega s} f(s) ds.
\]

(155)

With the Fourier transform

\[
 f(\omega) = \int_{-\infty}^{\infty} e^{i\omega s} f(s) ds,
\]

(156)

one can define the inverse Fourier transform from Equation (155)

\[
 f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \hat{f}(\omega) d\omega.
\]

(157)

By analogy, and with Equation (153), we can write the response function $\phi(t)$ as inverse Fourier transform of the susceptibility

\[
 \phi(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \chi(\omega) d\omega.
\]

(158)

Consequently, if one knows the susceptibility $\chi(\omega)$ at all frequencies $\omega$ one can determine the response function $\phi(t)$ by inverse Fourier transformation. To obtain the complete response behaviour of a linear system using oscillatory stimuli, one must measure $\chi(\omega)$ at each angular frequency $\omega$. Such a determination can be made either by sweeping the frequency of a tunable monochromatic radiation source (lasers, microwaves, ...) or, equivalently, by dispersing a white light source into its spectral components using a grating or a prism. Spectroscopic experiments carried out in the frequency domain are called frequency-resolved experiments.

Whether one measures $\chi(\omega)$ as a function of $\omega$ in a frequency-resolved experiment, or $\phi(t)$ as a function of $t$ in a time-resolved experiment, the same information is obtained. $\chi(\omega)$ can be converted into $\phi(t)$ by means of an inverse Fourier transformation, and vice versa. Time- and frequency-resolved spectroscopy are thus two sides of the same medal. Whether time-resolved or frequency-resolved spectroscopy is used to extract the spectrum of a sample depends on experimental convenience and on the availability of suitable sources of short pulses or monochromatic radiation. Another spectroscopic technique which relies on Fourier transformations is interferometric Fourier-transform spectroscopy, which is related, but not identical to time-resolved spectroscopy. The principles and applications of interferometric Fourier-transform spectroscopy are described in Albert *et al.* (2010).
4.4 The radiation field

This subsection describes the properties of the radiation field in a perfectly evacuated container, the walls of which are held at a temperature $T$, and contains a derivation of Planck’s radiation law. It is a prerequisite to introduce Einstein’s treatment of transitions induced by radiation in the next subsection.

The radiation field in an empty volume (for instance, the empty volume $V = L^3$ of a cubic container of side length $L$, see Fig. 10) in thermal equilibrium with a container at temperature $T$ can be viewed as a superposition of standing harmonic waves (also called oscillators or modes in this context).

![Figure 10: Empty volume, taken here as the interior of a cubic container with side length $L$](image)

a) The mode density

The waves are solutions of the wave equation

$$\Delta \Psi_{\vec{r},t} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi_{\vec{r},t} = 0.$$  \hspace{1cm} (159)

Taking into account the boundary conditions

$$\Psi(x = 0, y, z, t) = \Psi(x = L, y, z, t) = 0,$$  \hspace{1cm} (160)

and analogous conditions for the $y$ and $z$ dimensions, the solutions of Eq. (159) have the form

$$\Psi(\vec{r},t) = A(t) \sin(k_1 x) \sin(k_2 y) \sin(k_3 z) = A(t)B(x,y,z)$$  \hspace{1cm} (161)

with $\sin(k_i L) = 0$ from which follows $k_i L = n_i \pi$ for $i = 1, 2, 3$ and $n_i = 1, 2, \ldots$ Inserting Eq. (161) in Eq. (159), one obtains:

$$- \left( n_1^2 + n_2^2 + n_3^2 \right) \frac{\pi^2}{L^2} A(t)B(x,y,z) - \frac{1}{c^2} B(x,y,z) \frac{\partial^2}{\partial t^2} A(t) = 0,$$  \hspace{1cm} (162)

from which follows:

$$A(t) = A_0 \cos(\omega t) + \phi \quad \text{with} \quad \omega^2 = \frac{c^2 \pi^2}{L^2} \left( n_1^2 + n_2^2 + n_3^2 \right).$$  \hspace{1cm} (163)
The number of modes with angular frequency between 0 and $\omega$ is

$$N(\omega) = \int_0^\omega g(\omega) d\omega,$$

(164)

where $g(\omega) = \frac{dN(\omega)}{d\omega}$ represents the number density of oscillators which corresponds to all combinations of $n_1, n_2$ and $n_3$ which fulfill the equation

$$n_1^2 + n_2^2 + n_3^2 \leq \frac{\omega^2 L^2}{c^2 \pi^2}.$$

(165)

Eq. (165) is the equation of a sphere (see Fig. 11) with radius

$$r = \sqrt{n_1^2 + n_2^2 + n_3^2} = \frac{\omega L}{c\pi}.$$

(166)

Figure 11: Schematic diagram representing the possible combinations $(n_1, n_2, n_3)$ describing the modes of the radiation field with angular frequency $\leq \omega$

$n_1, n_2, n_3$ are positive and therefore

$$N(\omega) = \frac{1}{8} \left( \frac{4}{3} \pi \frac{\omega^3 L^3}{c^3 \pi^3} \right) = \frac{\omega^3 V}{6c^3 \pi^2}. $$

(167)

Since $\omega = 2\pi \nu$, one obtains from Eq. (167):

$$N(\nu) = \frac{8\pi^3 \nu^3 V}{6c^3 \pi^2}. $$

(168)

The mode density for a given polarization is therefore

$$g(\nu) = \frac{dN(\nu)}{d\nu} = 4\pi \nu^2 V; \quad g(\omega) = \frac{dN(\omega)}{d\omega} = \frac{1}{2} \frac{\omega^2 V}{c^3 \pi^2}. $$

(169)

Since two polarization directions have to be considered for each mode, the mode density is twice larger than given by Eq. (169) and amounts to

$$g(\nu) = \frac{8\pi \nu^2}{c^3} V. $$

(170)
b) The energy density

In classical electrodynamics, each mode has an energy $kT$ and the energy of the radiation field in a volume $V$ at temperature $T$ and between frequency $\nu$ and $\nu + d\nu$ is:

$$U(\nu)d\nu = g(\nu)kTd\nu = \frac{8\pi}{c^3}\nu^2VkTd\nu.$$  \hspace{1cm} (171)

The energy density (i.e., the energy per unit volume) is therefore given by

$$\rho(\nu) = \frac{U(\nu)}{V} = \frac{8\pi}{c^3}\nu^2kT,$$ \hspace{1cm} (172)

a relation known as Rayleigh-Jeans’ law. The expression (172) is valid for $kT \gg h\nu$ but incorrect for $\nu \to \infty$, as it predicts that in this case the energy density should become infinite. This physically incorrect property of Eq. (172) would lead to what has been termed “UV catastrophe”.

Planck’s radiation law is derived by assuming that each radiation mode can be described by a quantized harmonic oscillator with energy

$$E'_v = h\nu(v + \frac{1}{2}) \quad v = 0, 1, 2, \ldots$$ \hspace{1cm} (173)

Referencing the energy of each oscillator to the ground state ($v = 0$) of the oscillators

$$E_v = E'_v - E'_{v=0} = vh\nu,$$ \hspace{1cm} (174)

one can determine the average energy of an oscillator using statistical mechanics:

$$\langle E(\nu) \rangle = \sum_{v=0}^{\infty} vh\nu \frac{e^{-vh\nu/kT}}{\sum_{v=0}^{\infty} e^{-vh\nu/kT}}$$ \hspace{1cm} (175)

with $vh\nu$ the energy of the oscillator and $\frac{e^{-vh\nu/kT}}{\sum_{v=0}^{\infty} e^{-vh\nu/kT}}$ the probability ($\leq 1$) that the oscillator has the energy $vh\nu$ (Boltzmann factor).

Making the substitution $x = e^{-vh\nu/kT}$ in Eq. (175) leads to

$$\langle E(\nu) \rangle = h\nu \sum_{v=0}^{\infty} \frac{x^v}{1-x} = h\nu \frac{x}{1-x},$$

$$= h\nu \frac{e^{-vh\nu/kT}}{1-e^{-vh\nu/kT}} = h\nu \frac{1}{e^{vh\nu/kT} - 1}. \hspace{1cm} (176)$$

The energy density is the product of the mode density per unit volume and the average energy of the modes and is therefore given by (Planck 1900a)

$$\rho(\nu) = \frac{g(\nu)}{V} \langle E(\nu) \rangle = \frac{U(\nu)}{V} = \frac{8\pi}{c^3} \nu^3 \frac{1}{e^{vh\nu/kT} - 1},$$ \hspace{1cm} (177)

a relation known as Planck’s law for the energy density of the radiation field. The total energy $U/V$ per unit volume is
where $\sigma_s = \frac{2\pi^2k^4}{15c^4} = 5.67 \cdot 10^{-5}\text{gs}^{-3}\text{K}^{-4}$ represents the Stefan-Boltzmann constant. The heat capacity of free space can be determined to be

$$\left(\frac{\partial U^T_V}{\partial T}\right)_V = \nu \cdot \frac{16}{c}\sigma_s T^3.$$  

At high $T$, $U^T_V$ becomes very large and eventually sufficiently large that electron-positron pairs can be formed, at which point vacuum fills with matter and antimatter, first by spontaneous generation of electrons and positrons.

### 4.5 Kinetics of absorption and emission of incoherent, quasi-thermal radiation

This subsection presents Einstein’s theory of absorption and emission kinetics in a thermal radiation field and introduces the main processes detected in a spectroscopic experiment, the absorption and emission of photons (Einstein 1916b,a, 1917). By absorbing or emitting radiation, a quantum system makes a transition from an initial state $|1\rangle$ to a final state $|2\rangle$. Three processes must be considered:

1. absorption
2. spontaneous emission
3. stimulated emission (Fig. 12).

![Figure 12: Processes arising from the interaction of a two-level system with a radiation field](image)

The resonance condition (energy conservation) requires that

$$E_2 - E_1 = h\nu_{12}.$$  

We consider a system in thermal equilibrium with the radiation field at temperature $T$, where $N_1$, $N_2$ are the populations per unit volume in states $|1\rangle$ and $|2\rangle$, respectively. The rate equations for processes 1 - 3 are:
1. \[ \frac{dN_1}{dt} = B_{21} \rho(\nu_{12}) N_1 \] second order kinetics \hspace{1cm} (181)

2. \[ \frac{dN_1}{dt} = A_{12} N_2 \] first order kinetics \hspace{1cm} (182)

3. \[ \frac{dN_1}{dt} = B_{12} \rho(\nu_{12}) N_2 \] second order kinetics, \hspace{1cm} (183)

where \( \rho(\nu_{12}) \) represents the radiation energy density (Eq. (172)). The conditions for thermal equilibrium are that:

- \( N_1 \) and \( N_2 \) remain constant, which leads to the following equations:

\[
\frac{dN_1}{dt} = A_{12} N_2 + \rho(\nu_{12})(B_{12} N_2 - B_{21} N_1) = 0
\]

or

\[
A_{12} N_2 + B_{12} \rho(\nu_{12}) N_2 = B_{21} \rho(\nu_{12}) N_1. \hspace{1cm} (184)
\]

- the populations in the levels are described by Boltzmann’s distribution:

\[
\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT} = e^{-h\nu_{12}/kT}. \hspace{1cm} (185)
\]

Eqs. (184) and (185) are valid for all \( T \). For \( T \to \infty \), \( N_2 = N_1 \) and \( \rho(\nu_{12}) = \infty \) (see Eq. (177)). Because \( A_{12} \) and \( B_{12} \) are constants (i.e., are independent of \( T \)) and, in this case, \( B_{12} \rho(\nu_{12}) \gg A_{12} \), one can write:

\[
B_{12} \rho(\nu_{12}) + A_{12} \cong B_{12} \rho(\nu_{12}). \hspace{1cm} (186)
\]

From Eqs. (184), (186) and the condition \( N_2 = N_1 \) for \( T \to \infty \), one can derive the following results:

\[
B_{12} = B_{21} \Rightarrow A_{12} N_2 = B_{12} \rho(\nu_{12})(N_1 - N_2) \hspace{1cm} (187)
\]

and

\[
\rho(\nu_{12}) = \frac{A_{12}}{B_{12}} \left( \frac{N_1 - N_2}{N_2} \right) \hspace{1cm} (188)
\]

with

\[
\frac{N_1 - N_2}{N_2} = e^{h\nu_{12}/kT} - 1,
\]

where the last equality was obtained from Eq. (185). Equation (188) can serve as a starting point to derive Planck’s radiation law without involving quantized oscillators, as follows:

In the limit \( T \to \infty, \nu \to 0 \), Rayleigh-Jeans’ law (Eq. (172)) is valid, so that:

\[
\rho(\nu) = \frac{8\pi}{c^2} \nu^2 kT. \hspace{1cm} (189)
\]

Since, in this limit, \( kT \gg h\nu, \frac{h\nu}{kT} \ll 1 \), one can approximate \( e^{h\nu/kT} \) by the first two terms of a power series expansion:
\[ e^{\frac{\hbar \nu}{kT}} = 1 + \frac{\hbar \nu}{kT} + \ldots \]  

Inserting Eq. (190) into Eq. (188) and comparing with Eq. (189) one obtains

\[ \rho(\nu_{12}) = \frac{A_{12}}{B_{12}} \left( \frac{1}{1 + \frac{\hbar \nu_{12}}{kT} - 1} \right) = \frac{A_{12}}{B_{12}} \frac{kT}{\hbar \nu_{12}} = \frac{8\pi}{c^3} \nu_{12}^2 kT \]

\[ \Rightarrow \frac{A_{12}}{B_{12}} = \frac{8\pi}{c^3} \nu_{12}^3. \]  

Since \( A_{12} \) and \( B_{12} \) are constants, Eq. (191) is valid for all temperatures and for any frequency \( \nu_{12} \).

Inserting Eq. (191) into Eq. (188), one obtains Planck’s radiation law (Eq. (177)):

\[ \rho(\nu_{12}) = \frac{8\pi}{c^3} \nu_{12}^3 \left( \frac{1}{e^{\frac{\hbar \nu_{12}}{kT}} - 1} \right). \]  

\( A_{12} \) is thus related to \( B_{12} \), so that a single parameter suffices to describe radiative transitions between the quantum states 1 and 2, or more generally between states i and f (i for initial, f for final). In the electric dipole approximation, the Einstein coefficients can be expressed as

\[ A_{fi} = \frac{64\pi^4 \hbar^3}{3hc^3(4\pi\epsilon_0)} \langle f|\vec{\mu}_{el}|i \rangle^2, \]

\[ B_{fi} = \frac{8\pi^3}{3h^2(4\pi\epsilon_0)} \langle f|\vec{\mu}_{el}|i \rangle^2. \]  

One can combine all rate processes (Eqs. 181 - 183 and 193, 194 in the presence of a thermal (black body) radiation field at \( T \) into one rate coefficient for generalized first order kinetics (see Quack and Troe 1998).

\[ K_{fi} = A_{fi} \frac{\text{sign}(E_f - E_i)}{\exp[-\frac{(E_f - E_i)}{kT}] - 1} \]  

Einstein’s derivation does not rely on Planck’s description of the radiation field in terms of quantized oscillators, but it made use of the mode density from Rayleigh-Jeans’ law. The energy density corresponds to the product of the mode density and the energy per mode and can be used to derive the average number of photons per mode \( n(\nu) \):

\[ U(\nu) d\nu = V \rho(\nu) d\nu = g(\nu) \hbar \nu n(\nu) d\nu \]

with \( g(\nu) \) the mode density, \( \hbar \nu \) the photon energy, and \( n(\nu) \) the average number of photons per mode. From Eq. (176) one obtains:

\[ n(\nu) = \frac{\langle E(\nu) \rangle}{\hbar \nu} = \frac{1}{e^{\frac{\hbar \nu}{kT}} - 1}. \]  

Of course, the number of photons in a mode must be an integer (0, 1, 2, \ldots) and \( n(\nu) < 1 \) refers to an average number of photons. In the high temperature limit, \( e^{\frac{\hbar \nu}{kT}} \to 1 \) and the number of photons
per mode becomes very large. Depending on the value of $e^{\frac{\hbar \nu}{kT}}$ the average number of photons per mode can be larger or smaller than 1:

$$e^{\frac{\hbar \nu}{kT}} = 2 \Rightarrow n(\nu) = 1 \quad \text{and} \quad \frac{\hbar \nu}{kT} = \ln 2,$$

$$e^{\frac{\hbar \nu}{kT}} < 2 \Rightarrow n(\nu) > 1,$$

$$e^{\frac{\hbar \nu}{kT}} > 2 \Rightarrow n(\nu) < 1.$$  \hspace{1cm} (198)

4.6 The quantities in quantitative absorption spectroscopy

This subsection provides a short summary of the physical quantities used in the literature to quantify the interaction of light with matter. The measurement of the strength of this interaction can be used to determine the concentration of particles in a given sample, with applications in analytical chemistry, or to model the radiative processes taking place in a certain system with applications, e.g., in atmospheric chemistry.

The generic spectroscopic experiment is depicted in Fig. 13, which illustrates the attenuation of a radiation beam as it traverses a sample.

$I_0$ and $I$ represent the energy flow per unit surface and time, i.e., the intensity (with SI unit of W/m$^2$) of the radiation beam before and after traversing the sample. Instead of the intensity, one can also use the flow of photons per unit surface and time $I_{\text{ph,0}}$ and $I_{\text{ph}}$ because of the relation

$$I = I_{\text{ph}}h\nu.$$  \hspace{1cm} (199)

The flow of photons per unit surface and time can be expressed as

$$I_{\text{ph}} = c \cdot C_{\text{ph}},$$  \hspace{1cm} (200)

where $c$ represents the speed of light and $C_{\text{ph}}$ the photon concentration in the light beam as a particle density.
The number of absorbed photons per unit length $dx$ is proportional to the concentration $C_i$ of absorbing particles (as particle density) and to the intensity, so that

$$-dI = \sigma_\text{f} C_i dx,$$

(201)

where $\sigma_\text{f}$ is the molecular absorption cross section associated with the transition from state $i$ to state $f$. $\sigma_\text{f}$ depends on the frequency, and one sees from Eq. (201) that $\sigma_\text{f}$ must have the unit of $m^2$ or, as often used, $cm^2$. $\sigma_\text{f}$ can be interpreted as the surface of a completely absorbing disc which has the same absorption effect as the atom or molecule under investigation. Integrating Eq. (201) over the sample length one obtains:

$$-\int_{I_0}^I \frac{dI}{T} = \int_0^L \sigma_\text{f} C_i dx.$$

(202)

The result of the integration

$$\ln \left( \frac{I_0}{I} \right) = \sigma_\text{f} C_i L$$

(203)

is the well-known Lambert-Beer law. The quantity $\ln \left( \frac{I_0}{I} \right)$ is known as the Napierian absorbance. Another form of Lambert-Beer law is

$$\lg \left( \frac{I_0}{I} \right) = \varepsilon_\text{f} c_i L$$

(204)

where $\lg \left( \frac{I_0}{I} \right)$ is the decadic absorbance, $\varepsilon$ the molar extinction coefficient usually expressed in $dm^3/(cm \cdot mol)$, and $c_i$ the concentration in mol/$dm^3$.

Absorption can be viewed as a bimolecular process between a photon and an atom or a molecule:

$$-\frac{dC_{ph}}{dt} = k_{\text{bim}}^\text{f} C_{ph} C_i,$$

(205)

With $c = \frac{dC}{dt}$ and using Eq. (200), Eq. (205) can be rewritten as

$$-\frac{dI_{ph}}{dx} = -\frac{d(c \cdot C_{ph})}{dx} = -\frac{dC_{ph}}{dt} = k_{\text{bim}}^\text{f} C_{ph} C_i.$$

(206)

with $k_{\text{bim}}^\text{abs} = \sigma_\text{f} c \cdot C_{ph}$ the effective first-order kinetics rate constant. Comparing this expression with Eq. (181) one obtains ($C_i = N_i$)

$$-\frac{dN_i}{dt} = B_{\text{f}} \rho(\nu_i) N_i = k_{\text{bim}}^\text{abs} N_i$$

(207)

with

$$k_{\text{bim}}^\text{abs} = B_{\text{f}} \rho(\nu_i) = \sigma_\text{f} c \cdot C_{ph}(\nu_i).$$

(208)

In general, $C_{ph}(\nu)$ depends on the light source, and $C_{ph}(\nu)d\nu$ represents the concentration of photons with frequency lying in the interval between $\nu$ and $\nu + d\nu$ (see Fig. 14). $\sigma_\text{f}$ also depends on $\nu$, and often
has maxima at the positions where the frequency $\nu$ corresponds to the frequency $\nu_{fi}$ of a transition between two quantum states of the system under investigation (see Fig. 15). Section 7 presents the factors determining the lineshapes of the transitions in more detail.

To take the frequency dependence of $\sigma_{\text{fi}}$ and $C_{\text{ph}}$ into account, Eq. (208) can be rewritten as

$$k_{\text{abs}}^{\text{fi}} = c \int_0^\infty \sigma_{\text{fi}}(\nu)C_{\text{ph}}(\nu) d\nu. \quad (209)$$

Because the energy density $\rho(\nu) = h\nu n_{\text{ph}}(\nu)$, the concentration of photons can be expressed as

$$C_{\text{ph}}(\nu) = \frac{\rho(\nu)}{h\nu}, \quad (210)$$

and the bimolecular rate constant introduced in Eq (205) becomes

$$k_{\text{abs}}^{\text{fi}} = \frac{c}{h} \int_0^\infty \frac{\rho(\nu)\sigma_{\text{fi}}(\nu)}{\nu} d\nu. \quad (211)$$
If $\rho(\nu)$ does not vary over the absorption line, which is the case if the radiation source does not have too narrow a bandwidth or if the line associated with the transition $i \rightarrow f$ is narrow, then

$$k_{fi}^{\text{abs}} = \frac{c}{\hbar} \rho(\nu_i) \int_0^\infty \frac{\sigma_{fi}(\nu)}{\nu} d\nu = \frac{c}{\hbar} \rho(\nu_i) G_{fi},$$

with $G_{fi}$ the integrated absorption cross section. With Eq. (208), $G_{fi}$ can be related to the Einstein coefficient $B_{fi}$

$$B_{fi} = \frac{c}{\hbar} G_{fi},$$

and thus represents an intrinsic property of the transition between the states $i$ and $f$. One sees that $B_{fi}$ is $T$-independent, as assumed by Einstein (see subsection 4.5). Experimentally, one can determine the line strength $S_{fi}$ as the integral of the spectral intensity over the line profile (Fig. 16):

$$S_{fi} = \int_0^\infty \sigma_{fi}(\nu) d\nu.$$  \hspace{1cm} (214)

Figure 16: Line strength $S_{fi}$ as integral of the spectral intensity over the line profile

If the line is narrow, the function $\frac{1}{\nu}$ does not vary significantly over the line profile and can be approximated by $\frac{1}{\nu_{i,\text{max}}}$, so that the integrated absorption cross section $G_{fi}$ is proportional to the line strength $S_{fi}$

$$G_{fi} = \int_0^\infty \frac{\sigma_{fi}(\nu)}{\nu} d\nu \simeq \frac{1}{\nu_{i,\text{max}}} \int_0^\infty \sigma_{fi}(\nu) d\nu = \frac{S_{fi}}{\nu_{i,\text{max}}}. \hspace{1cm} (215)$$

The treatment outlined above suggests the following experimental procedure to characterize the transition between $i$ and $f$:

1) For given values of $L$ and $c_i$, measure the spectrum of the transition $f \leftarrow i$.
2) Determine $S_{fi}$ with Eq. (214).
3) Determine $G_{fi}$ with Eq. (212)
4) Determine $B_{fi}$ with Eq. (213).
5) Determine $A_{fi}$ with Eq. (191):

$$A_{fi} = \frac{8\pi}{c^3} \hbar \nu_i B_{fi} = \frac{8\pi}{c^3} \hbar \nu_i G_{fi}.$$  

(216)

One can also use the transition moment $M_{fi} = \langle f | \vec{M} | i \rangle$ instead of $B_{fi}$ (see Eq. (194))

$$B_{fi} = \frac{8\pi^3}{3h^2(4\pi\epsilon_0)} |M_{fi}|^2 \Rightarrow$$

(217)

$$|M_{fi}|^2 = \frac{3h^2(4\pi\epsilon_0)}{8\pi^3} B_{fi} = \frac{3h^2(4\pi\epsilon_0)c}{8\pi^3h} G_{fi}.$$  

(218)

where the transition dipole moment $M_{fi}$ is expressed in the SI unit system. $M_{fi}$ is often given in Debye (cgs unit; 1 Debye = 1 D = 3.33564 · 10^{-30} Cm) or in atomic units making use of the Bohr radius $a_0$ and the elementary charge $e$ (1 a.u. (dipole moment) = $ea_0 = 2.54175$ D). A useful approximate relation between $G_{fi}$ in pm$^2$ and $M_{fi}$ in Debye is

$$\left( \frac{G_{fi}}{\text{pm}^2} \right) \simeq 41.624 \left| \frac{M_{fi}}{\text{D}} \right|^2.$$  

(219)

In electronic spectroscopy, one often uses the oscillator strength, a number without dimension (unitless):

$$f_{fi} = \frac{(4\pi\epsilon_0)m_e c}{8\pi^2 e^2} \lambda_i A_{fi}$$

$$= 1.4992 \cdot 10^{-14}(A_{fi}/\text{s}^{-1})(\lambda/\text{nm})^2.$$  

(220)

The use of oscillator strengths in electronic spectroscopy is justified by a sum rule, which states that the sum of all oscillator strengths equals the number of electrons.

Another possibility to determine the transition probability is to measure the time-dependent decay of excited states with concentration $C_2$ (using labels of Fig. 7), satisfying Eq. 221 in the absence of external fields

$$C_2(t) = C_2(t_0) \exp(-A_{12}t)$$  

(221)

This determines also $B_{12}$, and $G_{21}$ by means of Eqs. 216 and this provides a route quite independent of absorption spectroscopy to determine these quantities.

More information on unit systems and recommended conventions to label physical quantities are provided in chapter hrs005 of this handbook (Stohner and Quack 2010).

### 4.7 Light scattering, Raman effect and Raman spectroscopy

If the electric dipole transition moments $\Gamma_f$, for direct transitions are zero, for instance by symmetry for rotational and vibrational transitions in homonuclear diatomic molecules, one still can observe the
relevant spectra by Raman scattering spectroscopy, which is illustrated in Fig. 17. Generally light is scattered by molecules as by other particles. If the scattered light has the same frequency \( \nu \) as the incoming light, one speaks of elastic or Rayleigh-scattering. However, the frequency of the scattered light may also change according to the equation for the scattered frequency \( \nu' \)

\[
h\nu' = h\nu \pm \Delta E
\]

(222)

where \( \Delta E \) is a quantum energy interval of the scattering molecule (or atom etc). Here one speaks of inelastic or Raman scattering. The effect was predicted theoretically by Smekal, Kramers and Heisenberg in the early 1920’s and observed experimentally by C. V. Raman (1928) (the history is briefly discussed by Weber (2010). The frequency is shifted according to Eq. (222) by quantized amount leading to sharp lines in the spectrum of scattered light. If \( h\nu' < h\nu \), then one speaks of “Stokes” lines and if \( h\nu' > h\nu \), one speaks of “Anti-Stokes” lines.

Figure 17: Top: Generic Raman spectroscopic experiment. Bottom: Schematic representation of the processes involved in Raman scattering. The thin arrows correspond to the incident \((h\nu)\) and scattered \((h\nu' = h\nu \pm \Delta E)\) radiation. The thick arrows represent rotational Raman transitions involving the \( J = 0 \) ground state.

The energy difference \( \Delta E \) is either deposited in the molecule (Stokes) or provided by the molecule (Anti-Stokes), as illustrated in the scheme of Fig. 17 for a rotational Raman transition in a homonuclear diatomic molecule (see section 5). While weak population transfer is in principle possible with off resonant monochromatic radiation by direct dipole coupling, as discussed in section 3 (the near degenerate Rabi problem would be an extreme example), the mechanism of Raman scattering is really very different, more closely related to the Goeppert-Mayer two photon absorption scheme of Fig. 2 involving coupling matrix elements to intermediate levels, which may, however, be very far off resonance,
as is illustrated in Fig. 18. This scheme allows us to understand the selection rule

$$\Delta J = 0, \pm 2$$  \hspace{1cm} (223)

The Raman scattering cross section can be calculated approximately from Eq. 224

$$\sigma_{fi}(\nu, \nu') \simeq \alpha(\nu')^4 \left| \sum_r \left( \frac{\langle f | \hat{\mu}_{el} | r \rangle \langle r | \hat{\mu}_{el} | i \rangle}{E_r - E_i - h\nu + i\Gamma_r} + \frac{\langle r | \hat{\mu}_{el} | i \rangle \langle f | \hat{\mu}_{el} | r \rangle}{E_r - E_f + h\nu + i\Gamma_r} \right) \right|^2$$  \hspace{1cm} (224)

$\alpha$ is a constant of proportionality. The matrix elements $\langle f | \hat{\mu}_{el} | r \rangle$ and $\langle r | \hat{\mu}_{el} | i \rangle$ have an angular momentum selection rule $\Delta J = \pm 1$ each (see below), thus for the products in Eq. 224 one obtains a combined selection rule $\Delta J = 0, \pm 2$. The parity of the molecular levels must also be the same, when connected by a Raman transition if parity is well defined (see Quack 2010).

![Figure 18: Stokes Raman transition between an initial state $i$ and a final state $f$. The frequency of the incident and scattered radiation is detuned from resonance with excited states $r$ by the detuning $\Delta E_r$.](image)

In the normal Raman effect, none of the intermediate levels $r$ in the scheme of Fig. 18 satisfies the Bohr resonance condition. The states $| r \rangle$ are never populated appreciably during the scattering process, which is instantaneous. If one of the states $| r \rangle$ matches the Bohr resonance condition for an intermediate level, then $E_r - E_i = h\nu$, and one denominator in the sum becomes small (and imaginary, $i\Gamma_r$ with $\Gamma_r$ being the full width at half maximum from the lifetime for that level, see section 7).

In this case the intermediate level gains an appreciable population, and one speaks of “resonance Raman scattering” and also of resonance fluorescence, if the process can be considered as absorption followed by spontaneous emission (fluorescence). These resonance processes have much larger cross sections leading to very high sensitivity in this type of spectroscopy. Otherwise very similar selection rules apply to the spectroscopic transitions viewed as scattering to obtain accurate molecular energy intervals $\Delta E_r$, including intervals relevant to a variety of molecular processes such as tunnelling splittings (Quack and Stockburger 1972; Stockburger 1973). Using laser radiation for excitation of the fluorescence, this process of laser induced fluorescence (LIF) has been introduced and exploited as the basis for one of the most sensitive spectroscopic techniques (Sinha et al. 1973).

More generally, the Raman scattering cross section can be further related to molecular polarizibility. Details of high resolution Raman spectroscopy are discussed in the article by Weber (2010),
5 Molecular energy levels

Spectroscopic measurements provide informations on the sample under study encoded in the form of line positions, line intensities and line shapes. The line positions can be used to extract information on the energy level structure of molecules. One must realize, however, that a line position (i.e., its frequency $\nu_i$) is only a measure of an energy difference $\Delta E_i = E_f - E_i = h\nu$ between two quantum states $i$ and $f$. To obtain the absolute positions of the energy levels, one can rely on existing knowledge on the energy positions $E_i$ or $E_f$ of one of the two states involved in the transition. One can also derive additional information on the energy level structure by determining so-called combination differences, i.e., by taking the differences between the positions of two lines originating from, or terminating on, a common energy level, as illustrated in Fig. 19.

Figure 19: Combination differences method. In a), the energy difference between states $|1\rangle$ and $|2\rangle$ can be determined from the measured position $h\nu_{13}$ and $h\nu_{23}$ of transitions from levels $|1\rangle$ and $|2\rangle$ to a common level $|3\rangle$ by building the initial-state combination difference $h\nu_{12} = h\nu_{13} - h\nu_{23}$. In b), the energy difference between states $|2\rangle$ and $|3\rangle$ can be determined from the measured positions $h\nu_{12}$ and $h\nu_{13}$ of transitions from level $|1\rangle$ to levels $|2\rangle$ and $|3\rangle$ by building the final state combination difference $h\nu_{23} = h\nu_{13} - h\nu_{12}$.

The purpose of this chapter is to briefly review the most general aspects of the energy level structure of atoms and molecules that are essential for the interpretation and the analysis of spectral positions in the rotational, vibrational and electronic spectra of molecules. Much more detailed information and many more examples can be found in subsequent articles of this handbook. In particular, the articles including many examples and also further scattering processes such as CARS (coherent anti-Stokes Raman scattering) and DFWM (degenerate four wave mixing).
hrs002 (Bauder 2010), hrs003 (Albert et al. hrs 003 2010) and hrs069 (Wörner and Merkt (2010)) provide treatments of the rotational, vibrational and electronic energy level structures of molecules, respectively, and of the corresponding spectroscopies.

5.1 Time-independent Schrödinger equation and stationary states

For a system of \( N \) particles with coordinates \( \vec{q}_i = (x_i, y_i, z_i) \) with \( i = 1, \ldots, N \), the time-independent Schrödinger equation is

\[
\hat{H} \Psi_n(x_1, y_1, z_1, \ldots, x_N, y_N, z_N) = E_n \Psi_n(x_1, y_1, z_1, \ldots, x_N, y_N, z_N)
\]  

(225)

with

\[
\hat{H} = \hat{T} + \hat{V} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m_i} + \hat{V}(x_1, y_1, z_1, \ldots, x_N, y_N, z_N) = \hat{H}(\vec{p}_i, \vec{q}_i)
\]  

(226)

where \( \vec{p}_i = (\hat{p}_{x_i}, \hat{p}_{y_i}, \hat{p}_{z_i}) \), \( \vec{p}_x = -ih \frac{\partial}{\partial x}, \hat{p}_{y_i} = -ih \frac{\partial}{\partial y}, \vec{p}_z = -ih \frac{\partial}{\partial z} \), \( \vec{p}_i^2 = -\hbar^2 \frac{\partial^2}{\partial x_i^2}, \vec{q}_i = (\vec{x}_i, \vec{y}_i, \vec{z}_i) \), \( \vec{x}_i = x_i, \vec{y}_i = y_i, \vec{z}_i = z_i \).

\( \Psi_n(x_1, y_1, z_1, \ldots, x_N, y_N, z_N) \) are the eigenfunctions of \( \hat{H} \) and \( E_n \) their energies. 

\(|\Psi_n(x_1, \ldots, z_N)|^2 dx_1 dy_1 dz_1 \cdots dz_N \) is the probability that, in state \( n \), particle 1 is located between \( x_1, y_1, z_1 \) and \( x_1 + dx_1, y_1 + dy_1, z_1 + dz_1 \), particle 2 between \( x_2, y_2, z_2 \) and \( x_2 + dx_2, y_2 + dy_2, z_2 + dz_2 \), etc. Here \( n \) represents a label (a quantum number or a set of quantum numbers) for the state. The eigenstates (\( \Psi_n, E_n \)) are stationary states. Usually, but not always, one uses the convention \( E_1 = 0 \), where \( \Psi_1 = |1\rangle \) represents the lowest energy eigenstate of the system.

5.2 Exact (and approximate) separability of the Schrödinger equation

The solution of the eigenvalue equation (225) is simplified if the Hamiltonian \( \hat{H}(\vec{p}_i, \vec{q}_i) \) can be written as a sum of two or more operators that act on distinct sets of variables,

\[
\hat{H}(\vec{p}_i, \vec{q}_i) = \hat{H}_a(\vec{p}_j, \vec{q}_j) + \hat{H}_b(\vec{p}_k, \vec{q}_k)
\]  

(227)

where \( i \) runs from 1 to \( z \), \( j \) from 1 to \( m \) and \( k \) from \( m + 1 \) to \( z \) in steps of 1. The eigenfunctions \( \Psi_n(\vec{q}_i) \) can, in this case, be written as products

\[
\Psi_n(\vec{q}_i) = \varphi_{a,n_a}(\vec{q}_j)\varphi_{b,n_b}(\vec{q}_k)
\]  

(228)

and their energies as sums

\[
E_n = E_{n_a} + E_{n_b}
\]  

(229)

whereby

\[
\hat{H}_a\varphi_{a,n_a}(\vec{q}_j) = E_{n_a}\varphi_{a,n_a}(\vec{q}_j) \quad \text{and}
\]

\[
\hat{H}_b\varphi_{b,n_b}(\vec{q}_k) = E_{n_b}\varphi_{b,n_b}(\vec{q}_k)
\]  

(230)
Example: the particle in a two-dimensional box. The potential energy is

\[ V(x, y) = \begin{cases} 
  0 & \text{for } 0 < x < L_a \text{ and } 0 < y < L_b, \\
  \infty & \text{otherwise.} 
\end{cases} \]  

(31)

In the box, \( V(x, y) = 0 \) and thus

\[ \hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \hat{V} \]  

(32)

Inserting the ansatz:

\[ \Psi(x, y) = \varphi_{a,n_a}(x)\varphi_{b,n_b}(y) \]  

(33)

into Eq. (32) gives

\[ \hat{H} \varphi_{a,n_a}(x)\varphi_{b,n_b}(y) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} \varphi_{a,n_a}(x) - \varphi_{a,n_a}(x) \left( \frac{\partial^2}{\partial y^2} \varphi_{b,n_b}(y) \right) \right) = \varphi_{a,n_a}(y)E_{a,n_a}(x) + \varphi_{b,n_b}(y)E_{b,n_b}(x) \]  

(34)

Dividing Eq. (34) by \( \varphi_{a,n_a}(x)\varphi_{b,n_b}(y) \) gives:

\[ E_n = -\frac{1}{\varphi_{a,n_a}(x)} \left( \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \varphi_{a,n_a}(x) \right) - \frac{1}{\varphi_{b,n_b}(y)} \left( \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \varphi_{b,n_b}(y) \right). \]  

(35)

We have therefore the following solution:

\[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \varphi_{a,n_a}(x) = E_{a,n_a}\varphi_{a,n_a}(x) ; \quad -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \varphi_{b,n_b}(y) = E_{b,n_b}\varphi_{b,n_b}(y); \]  

(36)

\[ \varphi_{a,n_a}(x) = \sqrt{\frac{2}{L_a}} \sin \left( \frac{na\pi x}{L_a} \right) ; \quad \varphi_{b,n_b}(y) = \sqrt{\frac{2}{L_b}} \sin \left( \frac{nb\pi y}{L_b} \right); \]  

(37)

\[ E_n = E_{a,n_a} + E_{b,n_b} = \frac{\hbar^2}{2m} \left( \frac{na^2}{L_a^2} + \frac{nb^2}{L_b^2} \right) ; \quad \Psi_{a,n_a,b,n_b}(x,y) = \varphi_{a,n_a}(x)\varphi_{b,n_b}(y). \]  

(38)

5.3 Separation of the center-of-mass motion

In atoms and molecules in free space the motion of the center of mass is exactly separable from the internal motion, because the potential \( V(q_i) \) in Eq. (226) only depends on the distances \( r_{ij} \) between the nuclei and electrons:

\[ \hat{H} = \hat{H}_{\text{cm}}(\hat{P}_{\text{cm}}, \hat{q}_{\text{cm}}) + \hat{H}_{\text{int}}(\hat{\rho}^{\text{int}}, \hat{\xi}^{\text{int}}), \]  

(39)

where \( \hat{\rho}^{\text{int}} \) and \( \hat{\xi}^{\text{int}} \) describe the internal motion and \( \hat{P}_{\text{cm}}, \hat{Q}_{\text{cm}} \) the center-of-mass motion.

Eq. (39) fulfills the condition for exact separability:

\[ E_n = E_{\text{cm}} + E_{\text{int}} \]  

(40)

\[ \hat{H}_{\text{cm}} = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial X_{\text{cm}}^2} + \frac{\partial^2}{\partial Y_{\text{cm}}^2} + \frac{\partial^2}{\partial Z_{\text{cm}}^2} \right] + V(X_{\text{cm}}, Y_{\text{cm}}, Z_{\text{cm}}) \]  

(41)
with $M = \sum_{i=1}^{N} m_i$. The overall translational motion of the atom/molecule can be treated as that of a free particle of mass $M$ in a three dimensional box. For a particle in a 3D box:

$$
\Psi_{\text{cm},n_{\text{cm}}}(X_{\text{cm}}, Y_{\text{cm}}, Z_{\text{cm}}) = \frac{2^{3/2}}{\sqrt{L_a L_b L_c}} \sin\left( \frac{n_a \pi X_{\text{cm}}}{L_a} \right) \sin\left( \frac{n_b \pi Y_{\text{cm}}}{L_b} \right) \sin\left( \frac{n_c \pi Z_{\text{cm}}}{L_c} \right)
$$

(242)

with $n_a, n_b, n_c = 1, 2, \ldots$ and $E_{\text{cm},n} = \frac{\hbar^2 n^2}{2M} \left( \frac{n_a^2}{L_a^2} + \frac{n_b^2}{L_b^2} + \frac{n_c^2}{L_c^2} \right)$.

In spectroscopy, one studies the transitions between the energy levels associated with the internal motion of atoms and molecules and concentrates on a problem of reduced dimensionality $3N - 3$:

$$
\hat{H}_{\text{int}}(\hat{p}^{\text{int}}, \hat{q}^{\text{int}}) \phi^\text{int}_n(\hat{q}^{\text{int}}_i) = E_n \phi^\text{int}_n(\hat{q}^{\text{int}}_i).
$$

(243)

5.4 Near-separability

In many instances, the Schrödinger equation is almost perfectly separable:

$$
\hat{H}(\hat{\vec{p}}_i, \hat{\vec{q}}_i) = \hat{H}_a(\hat{\vec{p}}_j, \hat{\vec{q}}_j) + \hat{H}_b(\hat{\vec{p}}_k, \hat{\vec{q}}_k) + \hat{H}'(\hat{\vec{p}}_i, \hat{\vec{q}}_i)
$$

(244)

with $i = 1, 2, \ldots, z$, $j = 1, 2, \ldots, m$ and $k = (m + 1), (m + 2), \ldots, z$, and the expectation value of $\hat{H}'$ is much smaller than those of $\hat{H}_a$ and $\hat{H}_b$. The functions $\phi_{a,n_a}(\hat{q}_j)\phi_{b,n_b}(\hat{q}_k)$, where $\phi_{a,n_a}(\hat{q}_j)$ and $\phi_{b,n_b}(\hat{q}_k)$ are the eigenfunctions of $\hat{H}_a$ and $\hat{H}_b$, respectively, are very similar to the eigenfunctions of $\hat{H}$ and can serve as zero-order approximations of the eigenfunctions of $\hat{H}$ in a perturbation theory treatment.

5.5 Hierarchy of motions and energies in molecules

The different types of motion in a molecule (electronic, vibrational, rotational, \ldots) take place on different time scales and are associated with different contributions to the total energy.

<table>
<thead>
<tr>
<th>Motion</th>
<th>Typical period</th>
<th>Typical energy interval/($\hbar c$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic</td>
<td>$\sim 1$ fs</td>
<td>$&gt; 5000$ cm$^{-1}$</td>
</tr>
<tr>
<td>Vibrational</td>
<td>10-100 fs</td>
<td>300-3000 cm$^{-1}$</td>
</tr>
<tr>
<td>Rotational</td>
<td>0.1 ps - 10 ps</td>
<td>1-100 cm$^{-1}$</td>
</tr>
</tbody>
</table>

This hierarchy of time scales implies the approximate separability of the corresponding motions that lies behind the so-called Born-Oppenheimer approximation: The nuclei appear immobile to the fast moving electrons, and hardly any rotation takes place during a vibrational period. The vibrational motion can thus be viewed as taking place in an “average” electronic cloud, and the rotational motion at a nuclear configuration corresponding to an average over the vibrational motion. The approximate separability can be expressed as:

$$
\hat{H}_{\text{int}} = \hat{H}_e(\hat{q}_i) + \hat{H}_v^{(e)}(\hat{Q}_n) + \hat{R}_r^{(ev)}(\theta, \phi, \chi) + \hat{R}_n^{(evr)}
$$

(245)

$$
E = E_e + E_v^{(e)} + E_r^{(ev)} + E_n^{(evr)}
$$

(246)

$$
\Psi = \varphi_e(\hat{q}_i, \hat{R}_n)\varphi_v^{(e)}(\hat{Q}_n)\varphi_r^{(ev)}(\theta, \phi, \chi)\phi_n^{(evr)}
$$

(247)
where e, v, r and ns stand for electronic, vibrational, rotational and nuclear spin, respectively, and the superscripts indicate which motion is averaged out and leads to an implicit dependence of the relevant quantity. The separability enables one to reduce a problem of high dimensionality to several problems of reduced dimensionality. It also justifies the chemist’s description of molecules in terms of “rigid” geometries. $\vec{Q}_\alpha$ and $\vec{q}_i$ are the position vectors of the nuclei ($\alpha = 1, 2, \ldots, N_k$) and the electrons ($i = 1, 2, \ldots, N_e$), respectively, and $\theta, \phi, \chi$ are the Euler angles describing the orientation of the molecule axis system in the lab frame. $\vec{R}_\alpha$ is used in equation (247) instead of $\vec{Q}_\alpha$ to indicate a parametric dependence (see below).

5.6 The Born-Oppenheimer approximation

The Born-Oppenheimer (BO) approximation enables the separation of electronic and nuclear degrees of freedom in a molecule. The Hamilton operator of a molecule with $N_k$ nuclei and $N_e$ electrons has the form

$$\hat{H}(\hat{\vec{Q}}_\alpha, \hat{\vec{q}}_i, \hat{\vec{P}}_\alpha, \hat{\vec{p}}_i) = \hat{T}_k + \hat{T}_e + V(\vec{Q}_\alpha, \vec{q}_i) \quad \alpha = 1, \ldots, N_k, i = 1, \ldots, N_e,$$

and the Schrödinger equation

$$\hat{H} \Psi_n(\vec{Q}_\alpha, \vec{q}_i) = E_n \Psi_n(\vec{Q}_\alpha, \vec{q}_i) \quad (n : \text{set of quantum numbers designating the eigenstates})$$

involves $3(N_k + N_e)$ coordinates. By making the BO approximation one reduces the dimensionality of the problem and solves an equation of $3N_e$ variables for the electronic motion and an equation of $3N_k$ variables for the nuclear motion. Separating the center-of-mass translational motion (see chapter 5.3) and the overall rotation of the molecule enables the reduction of the number of nuclear degrees of freedom by 6 for nonlinear molecules and by 5 for linear molecules.

In the BO treatment, $\Psi_n(\vec{Q}_\alpha, \vec{q}_i)$ is represented as a product

$$\Psi_n(\vec{Q}_\alpha, \vec{q}_i) = \varphi_m^{(n)}(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{Q}_\alpha)$$

of a nuclear wavefunction $\varphi_m^{(n)}(\vec{Q}_\alpha)$ and an electronic wavefunction $\phi_n(\vec{q}_i, \vec{Q}_\alpha)$ (separability). The treatment exploits the fact that the nuclei hardly move during a period of the electronic motion. The index $m$ is needed to distinguish different states of the nuclear motion (e.g. vibrational, rotational) associated with a given electronic state $n$.

The BO treatment consists of two steps:
Step 1: The nuclei are frozen at a given geometry $\vec{R}_\alpha : \vec{Q}_\alpha \rightarrow \vec{R}_\alpha$. As a result $\hat{T}_k = 0$ and the first term of Eq. (249) becomes constant. A purely electronic Schrödinger equation is then solved (the nuclear coordinates are treated as parameters, not as variables):

$$\hat{H} \rightarrow \hat{H}_e = \hat{T}_e + \hat{V}(\vec{q}_i, \vec{R}_\alpha).$$  \hspace{1cm} (252)

Inserting Eqs. (251) and (252) in Eq. (250) we obtain:

$$\left[\hat{T}_e + \hat{V}(\vec{q}_i, \vec{R}_\alpha)\right] \varphi_m^{(n)}(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{R}_\alpha) = V_n \varphi_m^{(n)}(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{R}_\alpha).$$  \hspace{1cm} (253)

Because neither $\hat{T}_e$ nor $\hat{V}$ act on the nuclear coordinates $\vec{Q}_\alpha$, $\varphi_m^{(n)}(\vec{Q}_\alpha)$ cancels out in Eq. (253):

$$\left[\hat{T}_e + \hat{V}(\vec{q}_i, \vec{R}_\alpha)\right] \phi_n(\vec{q}_i, \vec{R}_\alpha) = V_n \phi_n(\vec{q}_i, \vec{R}_\alpha).$$  \hspace{1cm} (254)

The solutions of Eq. (254) are sets of electronic wavefunctions $\phi_n(\vec{q}_i, \vec{R}_\alpha)$ and energies $V_n(\vec{R}_\alpha)$, where $n = 1, 2, \ldots$ and $n$ corresponds to a label for the electronic states.

Determining $V_n(\vec{R}_\alpha)$ for a large number of possible configurations $\vec{R}_\alpha$, one obtains the so-called BO potential hypersurface, which represents the dependence of the electronic energy on the nuclear coordinates. The dimensionality of the BO hypersurface is $3k - 5$ for linear molecules and $3k - 6$ for nonlinear molecules and equals the number of internal degrees of freedom $f$. $V_n(\vec{R}_\alpha)$ does not depend on the mass of the nuclei and is therefore isotope independent.

---

**Example:** Rough estimate of the error in the dissociation energy of $H_2^+$ associated with the BO approximation.

$H_2^+, f = 1$.

Figure 20: Schematic representation of the potential energy curve of the $X \ 2\Sigma_g^+$ ground electronic state of $H_2^+$ $(n = 1)$

At $R \rightarrow \infty$, $H_2^+$ dissociates in $H^+ + H(1s)$. The dissociation energies $D_e$ of $H_2^+$ and $D_2^+$ are identical within the BO approximation (see Fig. 20) and amount to $D_e \approx 22500 \text{ cm}^{-1}$. Extremely precise ab initio calculations have been
performed of the dissociation energies of \( \text{H}_2^+ \) and its deuterated isotopomers, including adiabatic and nonadiabatic corrections (Moss 1993b,a; 1996; Korobov 2006, 2008) and the calculations of rovibronic energy levels of these ions agree with precise spectroscopic measurements (see for instance Carrington et al. (1993); Leach and Moss (1995); Liu et al. (2010)).

The order of magnitude error of the BO approximation on the dissociation energy of \( \text{H}_2^+ \) can be estimated to be \( \approx 30 \, \text{cm}^{-1} \) (i.e. 0.13 %) because the ionization energies \( E_l \) of H and D differ by \( \approx 30 \, \text{cm}^{-1} \): \( \frac{E_l}{\text{cm}}(\text{H}) = R_H = 109677 \, \text{cm}^{-1} \) and \( \frac{E_l}{\text{cm}}(\text{D}) = R_D = 109706 \, \text{cm}^{-1} \).

Assuming that at least 10 points must be calculated per internal degree of freedom, Eq. (254) must be solved 10 times for a diatomic molecule \( (f = 1) \), 1000 times for a nonlinear triatomic molecule \( (\text{H}_2\text{O}, f = 3) \) and \( 10^{10} \) times for \( \text{C}_8\text{H}_6 \) \( (f = 30) \), if one wants to determine the complete potential hypersurface.

Stable molecular configurations correspond to local minima on the BO hypersurface and adiabatic isomerization reactions can be viewed as trajectories connecting two local minima on the Born-Oppenheimer hypersurface.

**Step 2:** The Schrödinger equation describing the nuclear motion on the \( n \)-th potential hypersurface is solved. Inserting Eq. (254) with the solution \( \varphi_m^{(n)}(\vec{Q}_a) \) and \( \phi_n(\vec{q}_i, \vec{Q}_a) \) in Eq. (248) leads to an equation describing the nuclear motion

\[
\hat{H}_N \phi_n(\vec{q}_i, \vec{Q}_a) \varphi_m^{(n)}(\vec{Q}_a) = \left[ \hat{T}_N + \hat{T}_e + \hat{V}(\vec{q}_i, \vec{Q}_a) \right] \phi_n(\vec{q}_i, \vec{Q}_a) \varphi_m^{(n)}(\vec{Q}_a) = \left[ \hat{T}_N + V_n(\vec{Q}_a) \right] \phi_n(\vec{q}_i, \vec{Q}_a) \varphi_m^{(n)}(\vec{Q}_a)
\]

(255)

with

\[
\hat{T}_N = -\sum_{\alpha}^{k} \frac{\hbar^2}{2Ma} \Delta_{\alpha} = -\sum_{\alpha}^{k} \frac{\hbar^2}{2Ma} \frac{\partial^2}{\partial Q_{\alpha}^2}.
\]

(256)

The notation in Eq. (256) implies:

\[
\frac{\partial}{\partial Q_{\alpha}} \phi_n(\vec{q}_i, \vec{Q}_a) \varphi_m^{(n)}(\vec{Q}_a) = \phi_n(\vec{q}_i, \vec{Q}_a) \frac{\partial}{\partial Q_{\alpha}} \varphi_m^{(n)}(\vec{Q}_a) + \varphi_m^{(n)}(\vec{Q}_a) \frac{\partial}{\partial Q_{\alpha}} \phi_n(\vec{q}_i, \vec{Q}_a) = \phi_n \varphi_m^{(n)r} + \varphi_m^{(n)} \phi_n'
\]

(257)

and

\[
\frac{\partial^2}{\partial Q_{\alpha}^2} \phi_n \varphi_m^{(n)} = \phi_n \varphi_m^{(n)rr} \underbrace{+ 2 \phi_n \varphi_m^{(n)r}}_{T_1} + \varphi_m^{(n)} \underbrace{\phi_n' \varphi_m^{(n)}}_{T_2} + \varphi_m^{(n)} \underbrace{\phi_n' \varphi_m^{(n)}}_{T_3}.
\]

(258)

Using Eq. (256) and Eq. (258), Eq. (255) can be rewritten as

\[
\hat{H}_N \phi_n \varphi_m^{(n)} = \left[ -\sum_{\alpha=1}^{k} \frac{\hbar^2}{2Ma} [T_1 + T_2 + T_3] + V_n(\vec{Q}_a) \right] \phi_n \varphi_m^{(n)} = E_m \phi_n \varphi_m^{(n)}.
\]

(259)

Term \( T_1 \) is the direct contribution to the nuclear kinetic energy. Terms \( T_2 \) and \( T_3 \) are indirect contributions to the kinetic energy of the nuclei which originate from the dependence of the electronic wavefunction on the nuclear coordinate. In low electronic states for which the BO hypersurfaces
are usually well separated, this variation is smooth and these terms can be neglected to a good approximation.

We thus get, when neglecting $T_2$ and $T_3$:

$$\hat{H}_N \phi_n(\vec{q}_i, \vec{Q}_\alpha) \varphi_m^{(n)}(\vec{Q}_\alpha) = -\sum_{\alpha=1}^{k} \frac{\hbar^2}{2M_\alpha} \phi_n(\vec{q}_i, \vec{Q}_\alpha) \Delta_\alpha \varphi_m^{(n)}(\vec{Q}_\alpha) + V_n(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{Q}_\alpha) \varphi_m^{(n)}(\vec{Q}_\alpha)$$

$$= E_n^m \phi_n(\vec{q}_i, \vec{Q}_\alpha) \varphi_m^{(n)}(\vec{Q}_\alpha).$$  \hspace{1cm} (260)

Dividing both sides of Eq. (260) by $\phi_n(\vec{q}_i, \vec{Q}_\alpha)$ enables one to eliminate the electron coordinates $\vec{q}_i$ and to obtain the equation describing the nuclear motion:

$$\hat{H}_N \varphi_m^{(n)}(\vec{Q}_\alpha) = \left[ -\sum_{\alpha=1}^{k} \frac{\hbar^2}{2M_\alpha} \Delta_\alpha + V_n(\vec{Q}_\alpha) \right] \varphi_m^{(n)}(\vec{Q}_\alpha) = E_n^m \varphi_m^{(n)}(\vec{Q}_\alpha). \hspace{1cm} (261)$$

This equation has the usual form for a Schrödinger equation and consists of a kinetic energy term (first term in the square brackets) and a potential energy term $V_n(\vec{Q}_\alpha)$. The equation can be solved numerically and $E_n^m$ represents the total (rovibronic) energy and $\varphi_m^{(n)}$ the nuclear wavefunction. For further discussion of the Born-Oppenheimer approximation we refer also to Bauder (2010).

To make this procedure less abstract we consider in the next subsection, the simplest case of diatomic molecules. This illustration will enable us to visualize the nuclear motion as consisting of a vibrational and a rotational motion.

### 5.7 Nuclear motion of a diatomic molecule

In the Born-Oppenheimer approximation, the nuclear motion of a diatomic molecule in electronic state $n$ is described by

$$\hat{H}_N = \frac{\hat{p}_2^2}{2M_1} + \frac{\hat{p}_2^2}{2M_2} + V_n(|\vec{Q}_2 - \vec{Q}_1|) = \frac{1}{2M} \hat{p}_{\text{CM}}^2 + \frac{1}{2\mu} \hat{p}_{\text{int}}^2 + V_n(|\vec{Q}_2 - \vec{Q}_1|)$$  \hspace{1cm} (262)

with $M = M_1 + M_2$ and $\mu = \frac{M_1 M_2}{M_1 + M_2}$.

The internal motion can be described by that of a fictive particle of mass $\mu$ and position $\vec{Q} = \vec{Q}_2 - \vec{Q}_1$, where $|\vec{Q}| = Q (= R)$ represents the internuclear distance.

$$\hat{H}_N \varphi_m^{(n)}(\vec{Q}) = -\frac{\hbar^2}{2\mu} \Delta_Q \varphi_m^{(n)}(\vec{Q}) + V_n(Q) \varphi_m^{(n)}(\vec{Q}) = E_n^m \varphi_m^{(n)}(\vec{Q}).$$  \hspace{1cm} (263)

Expressing $\Delta_Q$ in polar coordinates, one gets

$$\Delta_Q = \frac{\partial^2}{\partial Q^2} + \frac{2}{Q} \frac{\partial}{\partial Q} - \frac{1}{\hbar^2 Q^2} \hat{j}^2$$  \hspace{1cm} (264)

with

$$\hat{j}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi^2} \right).$$  \hspace{1cm} (265)
Figure 21: Born-Oppenheimer potential energy hypersurfaces of two electronic states of a diatomic molecule. In diatomic molecules, the hypersurfaces reduce to one-dimensional potential energy functions ($f = 1$).

Figure 22: Representation of the nuclear motion of diatomic molecule using polar coordinates ($Q = R, \varphi, \theta$) whereby $\hat{J}$ is the rotational angular momentum operator. Inserting Eqs. (264) and (265) in Eq. (263) leads to

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial Q^2} + \frac{2}{Q} \frac{\partial}{\partial Q}\right) + \frac{1}{2\mu Q^2} \hat{J}^2 + V_n(Q) - E_n^m\right] \varphi_m^{(n)}(Q) = 0.$$  

(266)
Since only $\hat{J}^2$ acts on $\theta$ and $\phi$, the equation is separable:

$$\varphi_m^{(n)}(Q, \theta, \phi) = F(Q)Y_{JM}(\theta, \phi) = \frac{1}{Q}G(Q)Y_{JM}(\theta, \phi). \quad (267)$$

In Eq. (267), $Y_{JM}(\theta, \phi)$ are the spherical harmonics that are the eigenfunctions of the angular momentum operators $\hat{J}^2$ and $\hat{J}_z$:

$$\hat{J}^2 Y_{JM}(\theta, \phi) = \hbar^2 J(J+1)Y_{JM}(\theta, \phi). \quad (268)$$

$$\hat{J}_z Y_{JM}(\theta, \phi) = \hbar MY_{JM}(\theta, \phi). \quad (269)$$

The reason for writing $F(Q)$ as $\frac{1}{Q}G(Q)$ in Eq. (267) is to simplify the algebra in later steps of the derivation.

Because

\[
\begin{align*}
\frac{\partial}{\partial Q} \left( \frac{G(Q)}{Q} \right) &= -\frac{1}{Q^2}G + \frac{1}{Q}G' \\
\frac{\partial^2}{\partial Q^2} \left( \frac{G(Q)}{Q} \right) &= \frac{2}{Q^3}G - \frac{2}{Q^2}G' + \frac{1}{Q}G''.
\end{align*}
\]

Eq. (266) can be rewritten as:

\[
\begin{align*}
-\frac{\hbar^2}{2\mu} \left[ \frac{2}{Q^2}G - \frac{2}{Q^2}G' + \frac{1}{Q}G'' \right] Y_{JM}(\theta, \phi) \\
+ \frac{1}{2\mu Q^2} \hbar^2 J(J+1)Y_{JM}(\theta, \phi) + (V_n(Q) - E_m^n) \frac{G(Q)}{Q} Y_{JM}(\theta, \phi) &= 0. \quad (271)
\end{align*}
\]

Simplifying and multiplying each remaining term of Eq. (271) by $\frac{Q}{Y_{JM}}$ one obtains:

\[
\begin{align*}
-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} G(Q) + \frac{\hbar^2}{2\mu R_e^2} J(J+1)G(Q) + (V_n(Q) - E_m^n) G(Q) &= 0. \quad (272)
\end{align*}
\]

This one-dimensional differential equation can be solved numerically to obtain the vibration-rotation energy levels. To illustrate the meaning of the different terms in Eq. (272) we make further approximations.

We consider only the region of $V_n(Q)$ close to the minimum $Q_{\text{min}} = R_e$ and write $Q = R_e + \rho$. We then make a Taylor series expansion of $V_n(Q)$ and $\frac{1}{Q^2}$ around $R_e$.

$$V_n(Q) = V_n(R_e) + \left( \frac{\partial V_n(Q)}{\partial Q} \right)_{R_e} \cdot \rho + \frac{1}{2} \left( \frac{\partial^2 V_n(Q)}{\partial Q^2} \right)_{R_e} \cdot \rho^2 + \cdots, \quad (273)$$

$$\frac{1}{Q^2} = \frac{1}{R_e} - \frac{2}{R_e^3} \cdot \rho + \cdots. \quad (274)$$

The second term on the right-hand side of Eq. (273) is zero because $V_n(Q)$ reaches a minimum at $R_e$. Keeping only the first term of Eq. (274) and the first two nonzero terms of Eq. (273) (harmonic oscillator approximation and rigid rotor approximation, respectively) and inserting into Eq. (272), one gets:

\[
\begin{align*}
-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} G(\rho) + \frac{\hbar^2}{2\mu R_e^2} J(J+1) G(\rho) + V_n(R_e) G(\rho) + \frac{1}{2} \kappa \rho^2 G(\rho) &= E_m^n G(\rho) \quad (275)
\end{align*}
\]
with \( k = \frac{\partial^2 U(Q)}{\partial Q^2} \mid_{R_e} \). This equation can be rewritten as
\[
\left( -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} + \frac{1}{2} k \rho^2 \right) G(\rho) = \left[ E^m_n - V_n(R_e) - E^J_{\text{rot}} \right] G(\rho).
\]
(276)
The operator in square brackets on the left-hand side of Eq. (276) can easily be recognized as the Hamilton operator of a harmonic oscillator and we can also write
\[
\left( -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} + \frac{1}{2} k \rho^2 \right) G(\rho) = h\nu_{\text{osc}}(v + \frac{1}{2}) G(\rho).
\]
(277)
Comparing the right-hand sides of Eq. (276) and Eq. (277), one can see that the total energy \( E^m_n \) is a sum of an electronic, a vibrational and a rotational energy:
\[
E^m_n = V_n(R_e) + E^v_{\text{vib}} + E^J_{\text{rot}} = V_n(R_e) + h\nu_{\text{osc}}(v + \frac{1}{2}) + h\nu_{\text{rot}}(J + 1).
\]
(278)

Figure 23: Schematic representation of the rovibronic energy levels of a diatomic molecule

One obtains a better approximation of the exact solution of Eq. (272) by
- keeping the higher terms in Eq. (273). The potential becomes anharmonic and therefore
\[
\frac{E^v_{\text{vib}}}{\hbar c} = w_e(v + \frac{1}{2}) - w_ex_e(v + \frac{1}{2})^2 + w_ey_e(v + \frac{1}{2})^3 + \cdots.
\]
(279)
(Note: The constants \( w_e, w_ex_e \) and \( w_ey_e \) are wavenumbers usually given in \( \text{cm}^{-1} \).)

- keeping higher terms in Eq. (274). One then can account for the lengthening of the average internuclear distance caused by the anharmonic vibrational motion
\[
B_v = B_e - \alpha_e(v + \frac{1}{2}) + \cdots,
\]
(280)

- taking into account centrifugal distortion (which corresponds to an elongation of the bond as the rotational motion gets faster, i.e. at increasing \( J \) values)
\[
E_{\text{rot}} = B_v J(J + 1) - D_v J^2(J + 1)^2 + \cdots.
\]
(281)
The constants $w_e, w_e x_e, w_e y_e, B_e, \alpha_e$, etc. are tabulated for many electronic states of many diatomic molecules (see Huber and Herzberg (1979); Bernath and McLeod (2001)) and can be used to calculate the rovibronic energies of a diatomic molecule. Nowadays efficient ways (and good programs) are available to solve Eq. (272) numerically. For further discussion of spectra and spectroscopic parameters of diatomic molecules as well as the extension to polyatomic molecules we refer to Albert et al. (hrs 003 2010).

6 Introduction to group theory and application to molecular spectroscopy

Group theory is an important tool for spectroscopy. It enables one to classify wavefunctions according to their symmetry properties and to determine selection rules in a straightforward manner. Formal introductions to group theory tend to be abstract. Instead of presenting such an introduction, we have selected topics particularly relevant to spectroscopy, which we illustrate by simple examples. Our hope is that such a presentation will help the reader to rapidly get acquainted with the main aspects of group theory as a tool for spectroscopists. This introductory approach should also facilitate the study of almost all chapters of this handbook, but does not replace a comprehensive presentation of group theory. Articles hrs073 (Schnell 2010), hrs074 (Oka 2010), hrs077 ((Quack 2010)) and hrs069 ((Wörner and Merkt 2010)) provide a more rigorous introduction and more detailed information on group theory and its applications to molecular physics and spectroscopy. They also contain many references to further articles and textbooks on group theory.

6.1 Symmetry Groups and symmetry operations

A group describing the symmetry properties of molecules can be viewed as a set of operations $\hat{S}_i$ which commute with the Hamiltonian $\hat{H}$ describing the molecules, i.e., which do not affect the energy spectrum

$$\left[ \hat{S}_i, \hat{H} \right] = 0.$$  \hspace{1cm} (282) 

$\hat{H}$ and $\hat{S}_i$ thus have a common set of eigenfunctions and the eigenvalues of $\hat{S}_i$ can be used as labels for the eigenfunctions. In molecular physics and molecular spectroscopy, two types of groups are particularly important, the point groups and the permutation-inversion groups. Point groups are widely used to label the energy levels of rigid or semi-rigid molecules whereas permutation-inversion groups, in particular the complete permutation-inversion (CNPI) and the molecular symmetry (MS) groups are generally employed to label the energy levels of nonrigid molecules, i.e. molecules in which the nuclear framework undergoes large-amplitude motions. The permutation-inversion groups and their use in the treatment of the spectroscopic properties of nonrigid molecules are the object of Chapter hrs073 (Schnell, 2009). This section provides an elementary-level introduction to group theory.
with emphasis on point groups. The general aspects, however, are also valid for permutation-inversion groups.

A) Point group operations and point group symmetry

\( E \): Identity (no operation).

\( C_n \): Rotation by \( \frac{2\pi}{n} \). The symmetry axis with highest \( n \) is chosen as principal \( z \) axis (see examples in Fig. 24).

![Figure 24: Examples of \( C_n \) point-group rotations in \( H_2O \) (\( n = 2 \)) and \( CH_3 \) (\( n = 3 \))](image)

Improper symmetry operations:

\( \sigma \): Reflection through a plane:

\( \sigma_v \): vertical planes (contains symmetry \( z \) axis);

\( \sigma_h \): horizontal plane (is \( \perp \) to symmetry \( z \) axis).

\( i \): Inversion. Inversion of all coordinates through the inversion center (see example in Fig. 25).

\( S_n \): Rotation-reflection: rotation by \( \frac{2\pi}{n} \) around the \( z \) axis followed by a reflection through the plane perpendicular to the rotation axis (see example in Fig. 26).

A molecule having an improper operation as symmetry operation cannot be optically active (chiral).

![Figure 25: Example of a molecule (here ethylene) with an inversion center indicated as a dot](image)

![Figure 26: Example of a molecule (here allene) with an \( S_4 \) symmetry operation](image)
B) Permutation-inversion operations

These operations are at the origin of the complete nuclear permutation-inversion group and the molecular symmetry group (see Bunker and Jensen (1998); Longuet-Higgins (1963) and also Mills and Quack (2002) for a historical review).

(ij): Permutation of the coordinates of two identical nuclei i and j.

(ijk): Cyclic permutation of the coordinates of three identical nuclei i, j, and k.

*: Inversion of all coordinates of all particles through the center of the lab-fixed frame.

(ij)*: Permutation followed by inversion of all coordinates of all particles.

(ijk)*: Cyclic permutation followed by inversion of all coordinates of all particles.

Permutation-inversion operations leave $\hat{H}$ unchanged.

---

Example 1: CH$_2$: C: 1, H: 2,3.

![Methylene molecule](image)

Figure 27: Methylene molecule in which the nuclei have been labeled 1, 2 and 3

$$\hat{H} = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 - \frac{\hbar^2}{2m_3}\Delta_3 + \sum_{i=1}^{8} -\frac{\hbar^2}{2m_e}\Delta_i + \frac{e^2}{4\pi\epsilon_0} \left( \frac{6}{r_{12}} + \frac{6}{r_{13}} + \frac{1}{r_{23}} \right) - \sum_{k=1}^{3} \sum_{i=1}^{8} \frac{Z_k e^2}{4\pi\epsilon_0 r_{ki}} + \sum_{i=1}^{8} \sum_{j>i}^{8} \frac{e^2}{4\pi\epsilon_0 r_{ij}}.$$ (283)

The coordinates only come “squared” in Eq. (283) and the operation * leaves $\hat{H}$ unchanged. One can also readily verify that the operation (23) which exchanges $r_2$ with $r_3$ does not change $\hat{H}$.

---

6.2 Definition of a group and important concepts

A group is a set of objects, called elements, A, B, C, ... (e.g., permutations, transformations, ...) which are connected by a combination rule (written as a product) $A \cdot B = C$ such that the result of the combination is also an element of the group. Three conditions must be fulfilled:

1. The combination rule must be associative.
   $$A \cdot (B \cdot C) = (A \cdot B) \cdot C.$$ 

2. There must be an element, the identity $E$, such that $E \cdot R = R \cdot E = R$ for all elements $R$ of the group.
3. Each element $R$ must have an inverse $R^{-1}$ which is also a group element such that
\[ R \cdot R^{-1} = R^{-1} \cdot R = E. \]

The order of a group is equal to the number of elements in the group. While many groups used to describe the symmetry properties of molecules have a finite number of elements, infinite groups, i.e., groups with an infinite number of elements, also exist, examples being the $C_{\infty v}$ and $D_{\infty h}$ point groups of linear molecules and the $K_h$ group used for atoms. The use of infinite groups is illustrated by several examples in Wörner and Merkt (2010). In this introductory article, only finite groups are used as illustrations.

The connection between symmetry operation $\hat{S}_i$ discussed above and group theory comes from the fact that if $\hat{S}_i$ and $\hat{S}_j$ leave $\hat{H}$ unchanged when applied individually, they must also leave $\hat{H}$ unchanged when applied in succession $\Rightarrow \hat{S}_i \cdot \hat{S}_j$ must be a symmetry operation if $\hat{S}_i$ and $\hat{S}_j$ are symmetry operations. Note: The notation $\hat{S}_i \cdot \hat{S}_j$ must be understood in the following way: $\hat{S}_j$ acts first, $\hat{S}_i$ second.

---

Example 2: the point group of $\text{H}_2\text{O}$: $C_{2v}$ group ($E, C^z_2, \sigma^{xz}, \sigma^{yz}$)

![C2v group operations](image)

Figure 28: $C_{2v}$ group operations and their effect on a water molecule. The dot indicates schematically the coordinates $(x, y, z)$ of an electron

From Fig. 28 one can see that the successive application of any two operations of the $C_{2v}$ point group is equivalent to the application of a third group operation. For instance,
\[ \sigma^{xz} \sigma^{yz} = C^z_2 \]
\[ \sigma^{xz} \sigma^{yz} = E \]
\[ C^z_2 \sigma^{xz} = \sigma^{yz} \]

etc.

One can build a combination table (also called multiplication table) which summarizes all possible combinations. The multiplication table of the $C_{2v}$ point group with four symmetry operations ($E, C^z_2, \sigma^{xz}, \sigma^{yz}$) is thus a $4 \times 4$ table.
In the $C_{2v}$ group, $A \cdot B$ is always equal to $B \cdot A$ (all operations commute), and one says that the group is Abelian. Not all groups are Abelian. An example of a non-Abelian group is the point group $C_{3v}$.

---

**Example 3: CH$_3$Cl:** $C_{3v}$ ($E, C_3, C_3^2, \sigma^a, \sigma^b, \sigma^c$), group of order 6.

With the help of Fig. 29, one can derive the multiplication table of the $C_{3v}$ point group. One sees that the group is not Abelian because not all operations commute (e.g., $C_3 \cdot \sigma^c = \sigma^b$ and $\sigma^a \cdot C_3 = \sigma^b$). Moreover, not all operations are their own inverse (e.g., $C_3 \cdot C_3 \neq E$).
Conjugated elements and classes

If $A$, $B$, $R$ are all group elements and if they obey the relation

$$RAR^{-1} = B,$$  \hspace{1cm} (284)

then $A$ and $B$ are called conjugated elements. All conjugated elements in a group form a class.

Example 4: Derivation of the elements of the point group $C_{3v}$ that belong to the same class as $C_3$.

Inserting $C_3 = A$ in Eq. (284), and taking for $R$ successively all group operations one obtains using the $C_{3v}$ multiplication table:

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$E$</th>
<th>$C_3$</th>
<th>$C_3^2$</th>
<th>$\sigma^a$</th>
<th>$\sigma^b$</th>
<th>$\sigma^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$\sigma^a$</td>
<td>$\sigma^b$</td>
<td>$\sigma^c$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$\sigma^c$</td>
<td>$\sigma^a$</td>
<td>$\sigma^b$</td>
</tr>
<tr>
<td>$C_3^2$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$\sigma^b$</td>
<td>$\sigma^c$</td>
<td>$\sigma^a$</td>
</tr>
<tr>
<td>$\sigma^a$</td>
<td>$\sigma^a$</td>
<td>$\sigma^b$</td>
<td>$\sigma^c$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
</tr>
<tr>
<td>$\sigma^b$</td>
<td>$\sigma^b$</td>
<td>$\sigma^c$</td>
<td>$\sigma^a$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$C_3$</td>
</tr>
<tr>
<td>$\sigma^c$</td>
<td>$\sigma^c$</td>
<td>$\sigma^a$</td>
<td>$\sigma^b$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$E$</td>
</tr>
</tbody>
</table>

Consequently, $C_3$ and $C_3^2$ are elements of the same class of order 2. Similarly, one can show that $\sigma^a$, $\sigma^b$ and $\sigma^c$ form a class of order 3.

Order of an element

The order $n$ of an element $A$ is the smallest integer with $A^n = E$.

$C_{3v}$: $C_3$ is of order 3, $\sigma^a$ of order 2.

All elements of a class have the same order.

6.3 Representations and character tables

Group operations can be represented by $n \times n$ matrices $B_i$ that fulfill the combination rule, whereby $n$ represents the dimension of the representation. These matrices represent transformations of vectors.
or functions of the form of Eq. (285)

\[ \vec{y} = R_i \vec{x}. \] (285)

The matrices depend on the coordinate system and can be transformed from one coordinate system to another using \( T_i = S R_i S^{-1} \) where the new, equivalent representation \( T_i \) is obtained from the original representation \( R_i \). The trace of a matrix remains unchanged upon an unitary coordinate transformation and the trace of the matrix is called its character. For the set of equivalent representations \( R_i \) and \( T_i \), one thus has

\[ \text{Tr}(T_i) = \text{Tr}(R_i) : \text{character of operation.} \] (286)

All elements of a class have the same character, as can be seen from Eq. (284). If the matrices of all elements of a representation of a group can be simultaneously brought into block-diagonal form by a given coordinate transformation, the representation is said to be reducible, if not, it is irreducible. The character table of a group lists all irreducible representations and gives for each representation the character of each class of elements.

A character table has the following structure:

| \( G \) | \( C_1 = E \) | \( C_2 \) | \( \ldots \) | \( C_n \) | \( x \) | \( y \) | \( z \) | \( R_x \) | \( R_y \) | \( R_z \) |
|---|---|---|---|---|---|---|---|---|---|
| \( \Gamma^{(1)} \) | \( \chi_1^{(1)} \) | \( \chi_2^{(1)} \) | \( \ldots \) | \( \chi_n^{(1)} \) | | | | | |
| \( \Gamma^{(2)} \) | \( \chi_1^{(2)} \) | \( \chi_2^{(2)} \) | | | | | | | |
| \( \vdots \) | \( \vdots \) | \( \vdots \) | | | | | | | |
| \( \Gamma^{(n)} \) | \( \chi_1^{(n)} \) | \( \chi_2^{(n)} \) | \( \ldots \) | \( \chi_n^{(n)} \) | | | | | |

In a character table, \( \Gamma^{(n)} \) designates the \( n \)-th representation, \( C_i \) the \( i \)-th class of elements and \( \chi_j^{(m)} \) the character of the elements of class \( j \) in the \( m \)-th representation. There are as many irreducible representations as classes. Character tables exist for all groups. Many groups have a finite number of representations, but groups with an infinite number of representations also exist such as the \( D_{\infty h} \) and \( C_{\infty v} \) point groups of diatomic molecules.

The character table of the \( C_{3v} \) point group has the following form:

<table>
<thead>
<tr>
<th>( C_{3v} )</th>
<th>( E )</th>
<th>( 2C_3 )</th>
<th>( 3\sigma_v )</th>
<th>( R_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( T_z )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>( R_z )</td>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>( T_x, T_y )</td>
</tr>
</tbody>
</table>

Next to the characters of the elements of the different classes, the character table also gives, in the last columns, how the translations \( T_x, T_y \) and \( T_z \) and the rotations \( R_x, R_y \) and \( R_z \) transform.
To construct an $n$-dimensional representation of a group, one takes $n$ linear independent functions or vectors $\Psi_i$, $i = 1, ..., n$ spanning a given $n$-dimensional space. Applying the group operations on $\Psi_i$ leads to a transformed function which is a linear combination of the original functions:

$$\hat{R}\Psi_i = \sum_{j=1}^{n} D_{ji}(R)\Psi_j.$$  \hfill (287)

**Example 5:** As possible one-dimensional representation ($n = 1$) of $C_{2v}$, one can take the functions $x$, $y$, or $z$.

$$\Psi_1 = x : \quad \hat{E} \cdot x = x \quad \Psi_2 = y : \quad \hat{E} \cdot y = y \quad \Psi_3 = z : \quad \hat{E} \cdot z = z$$

$\hat{C}_2^x \cdot x = -x$  
$\hat{C}_2^y \cdot y = -y$  
$\hat{C}_2^z \cdot z = z$

$\hat{\sigma}^{xz} \cdot x = x$  
$\hat{\sigma}^{xz} \cdot y = -y$  
$\hat{\sigma}^{xz} \cdot z = z$

$\hat{\sigma}^{yz} \cdot x = -x$  
$\hat{\sigma}^{yz} \cdot y = y$  
$\hat{\sigma}^{yz} \cdot z = z$

Therefore $x$, $y$, and $z$ correspond to the irreducible representations $B_1$, $B_2$, and $A_1$ of $C_{2v}$ in accord with the third column of the character table of the $C_{2v}$ point group.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$\hat{C}_2^x$</th>
<th>$\hat{\sigma}^{xz}$</th>
<th>$\hat{\sigma}^{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^{(x)} = A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^{(xy)} = A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma^{(x)} = B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma^{(y)} = B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

Instead of using $x$, $y$, or $z$, more complicated functions can be used to generate a one-dimensional representation, such as $x^2$, $xy$ or $\sin x$.

**Example 6**

$$\Psi_4 = x^2 : \quad (\hat{E}x^2) = (\hat{E}x)(\hat{E}x) = x^2$$

$$\hat{C}_2^x = (\hat{C}_2^x x)(\hat{C}_2^x x) = x^2$$

$$\hat{\sigma}^{xz} = (\hat{\sigma}^{xz} x)(\hat{\sigma}^{xz} x) = x^2$$

$$\hat{\sigma}^{yz} = (\hat{\sigma}^{yz} x)(\hat{\sigma}^{yz} x) = x^2$$

$$\Psi_5 = xy : \quad (\hat{E}(xy)) = (\hat{E}x)(\hat{E}y) = xy$$

$$\hat{C}_2^x = (\hat{C}_2^x x)(\hat{C}_2^y y) = xy$$

$$\hat{\sigma}^{xz} = (\hat{\sigma}^{xz} x)(\hat{\sigma}^{xz} y) = -xy$$

$$\hat{\sigma}^{yz} = (\hat{\sigma}^{yz} x)(\hat{\sigma}^{yz} y) = -xy$$

$$\Psi_6 = \sin x : \quad (\hat{E} \sin x) = \sin x$$

$$\hat{C}_2^x = \sin(-x) = - \sin x$$

$$\hat{\sigma}^{xz} = \sin x$$

$$\hat{\sigma}^{yz} = \sin(-x) = - \sin x$$

One sees that $x^2$, $xy$ and $\sin x$ transform as $A_1$, $A_2$ and $B_1$, respectively. It is easy to verify that $\chi^{xy} = \chi^x \cdot \chi^y$, a result that can be written as a direct product $\Gamma^x \otimes \Gamma^y = B_1 \otimes B_2 = (1 -1 1 -1) \otimes (1 -1 -1) = (1 1 -1 -1) = A_2$.

To evaluate a direct product such as $A_2 \otimes B_2 = B_1$ in $C_{2v}$, one multiplies the characters of each class of elements pairwise and obtains as direct product a representation of the group that can be either
irreducible or reducible. In the latter case, the reducible representation is usually reduced following the method described below in Subsection 6.4.

One can also look at the transformation properties of rotations, which in the case of the $R_z$ operation of the $C_{2v}$ group is illustrated in Fig. 30.

![Figure 30: Schematic representation of a rotation $R_z$ around the $z$ axis of the molecule-fixed coordinate system of H$_2$O](image)

$$E(R_z) = R_z$$
$$C_{2v}^z(R_z) = R_z$$
$$\sigma^{xz}(R_z) = -R_z \quad \text{Direction of rotation reversed.}$$
$$\sigma^{yz}(R_z) = -R_z \quad \text{Direction of rotation reversed.}$$

One can verify that $R_x$ and $R_y$ transform as $B_2$ and $B_1$, respectively.

Representations of higher dimensions can be obtained by looking at the transformation properties of two or more functions.

**Example 7: $C_{2v}$: Two dimensional representation ($\gamma$).**

$$E \cdot \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \quad \text{with } \chi_E^{(\gamma)} = 2$$

$$C_{2v}^z \cdot \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ -y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \quad \text{with } \chi_{C_{2v}^z}^{(\gamma)} = -2$$

$$\sigma^{xz} \cdot \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \quad \text{with } \chi_{\sigma^{xz}}^{(\gamma)} = 0$$

$$\sigma^{yz} \cdot \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ -y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \quad \text{with } \chi_{\sigma^{yz}}^{(\gamma)} = 0$$

The two-dimensional representation of ($\gamma$) is thus:

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_{2v}^z$</th>
<th>$\sigma^{xz}$</th>
<th>$\sigma^{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 × 2 Matrix</td>
<td>$\begin{pmatrix} 1 &amp; 0 \ 0 &amp; 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} -1 &amp; 0 \ 0 &amp; -1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 &amp; 0 \ 0 &amp; -1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} -1 &amp; 0 \ 0 &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>$\Gamma^{(\gamma)}$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

This representation is not an irreducible representation of $C_{2v}$. It is reducible, i.e., it corresponds to a linear com-
Combination of irreducible representations \( \Gamma^{(x)} = B_1 \oplus B_2 \).

\[
\begin{array}{cccc}
B_1 & 1 & -1 & 1 & -1 \\
B_2 & 1 & -1 & -1 & 1 \\
B_1 \oplus B_2 & 2 & -2 & 0 & 0
\end{array}
\]

Example 8: \( C_{2v} \): Two-dimensional representation spanned by 1s atomic orbitals \( \phi_{1s(H_1)} \) centered on the H atoms of a water molecule \( H_2O \), see Fig. 31.

\[
\begin{align*}
\phi_{1s(H_1)}: & \text{ 1s atom orbital on } H_1 \\
\phi_{1s(H_2)}: & \text{ 1s atom orbital on } H_2
\end{align*}
\]

Figure 31: 1s atomic orbitals on the H atoms of \( H_2O \)

\[
\begin{align*}
E \quad \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) &= \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) = \left( \begin{array}{cc} 1 & 0 \\
0 & 1 \end{array} \right) \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) ; \quad \chi_E = 2 \\
C_2^z \quad \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) &= \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) = \left( \begin{array}{cc} 0 & 1 \\
1 & 0 \end{array} \right) \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) ; \quad \chi_{C_2^z} = 0 \\
\sigma^{xz} \quad \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) &= \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) = \left( \begin{array}{cc} 0 & 1 \\
1 & 0 \end{array} \right) \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) ; \quad \chi_{\sigma^{xz}} = 0 \\
\sigma^{yz} \quad \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) &= \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) = \left( \begin{array}{cc} 1 & 0 \\
0 & 1 \end{array} \right) \left( \begin{array}{c} \phi_{1s(H_1)} \\
\phi_{1s(H_2)} \end{array} \right) ; \quad \chi_{\sigma^{yz}} = 2
\end{align*}
\]

The representation is two-dimensional and corresponds to \( A_1 \oplus B_2 \) as can be verified by inspection of the \( C_{2v} \) character table.

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( E )</th>
<th>( C_2^z )</th>
<th>( \sigma^{xz} )</th>
<th>( \sigma^{yz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 \times 2 ) Matrix</td>
<td>( \begin{pmatrix} 1 &amp; 0 \ 0 &amp; 1 \end{pmatrix} )</td>
<td>( \begin{pmatrix} 0 &amp; 1 \ 1 &amp; 0 \end{pmatrix} )</td>
<td>( \begin{pmatrix} 0 &amp; 0 \ 0 &amp; 1 \end{pmatrix} )</td>
<td>( \begin{pmatrix} 1 &amp; 0 \ 0 &amp; 1 \end{pmatrix} )</td>
</tr>
<tr>
<td>( A_1 \oplus B_2 )</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

6.4 Reducing reducible representations

All representations in a character table form a set of orthogonal vectors that span the complete space

\[
\sum_R \chi^i(R) \chi^j(R) = h \delta_{ij},
\]

(288)
where \( h \) represents the order of the group and \( R \) runs over all the elements of the group. (Note that some classes of non-Abelian groups contain more than one element!) Any reducible representation can thus be expressed as a linear combination of irreducible representations

\[
\Gamma^\text{red} = \sum_k c_k^\text{red} \Gamma^k,
\]

where \( \Gamma^k \) represents an irreducible representation. The expansion coefficients \( c_k^\text{red} \) can be determined using the reduction formula Eq. (290):

\[
c_k^\text{red} = \frac{1}{h} \sum_R \chi_k^\text{red}(R)^* \chi(R) \]

“Reduction formula”. (290)

---

**Example 8 (continuation): Reduction of \( \Gamma^{(2)} = (2 \, 0 \, 0 \, 2) \):**

\[
c_{A_1}^2 = \frac{1}{4}(2 \cdot 1 + 0 \cdot 1 + 0 \cdot 1 + 2 \cdot 1) = 1
\]

\[
c_{A_2}^2 = \frac{1}{4}(2 \cdot 1 + 0 \cdot 1 + 0 \cdot 1 + 2 \cdot (-1)) = 0
\]

\[
c_{B_1}^2 = \frac{1}{4}(2 \cdot 1 + 0 \cdot (-1) + 0 \cdot 1 + 2 \cdot (-1)) = 0
\]

\[
c_{B_2}^2 = \frac{1}{4}(2 \cdot 1 + 0 \cdot (-1) + 0 \cdot (-1) + 2 \cdot 1) = 1
\]

\[\Rightarrow \Gamma^2 = A_1 \oplus B_2.\]

One can therefore construct one linear combination of the two \( \phi_{1s(H)} \) orbitals of \( \text{H}_2\text{O} \) with \( A_1 \) symmetry (totally symmetric) and one with \( B_2 \) symmetry.

---

### 6.5 Determining symmetrized linear combinations

To find the symmetrized linear combination of atomic orbitals (LCAO), one uses so-called projectors \( P^\Gamma \) and applies them onto either of the two \( \phi_{1s(H)} \) orbitals. The projectors are defined as

\[
P^\Gamma = \frac{1}{h} \sum_R \chi^\Gamma(R)^* \cdot \hat{R}
\]

“Projection formula”. (291)

---

**Example 8 (continuation): Determining symmetrized LCAOs of the two 1s orbitals of the \( \text{H}_2\text{O} \) and the ground state electronic configuration of \( \text{H}_2\text{O} \).**

\[
P^{\Lambda_1}(\phi_{1s(H_1)}) = \frac{1}{2}(1 \cdot E \phi_{1s(H_1)} + 1C^2 \phi_{1s(H_1)} + 1\sigma_{zz} \phi_{1s(H_1)} + 1\sigma_{xy} \phi_{1s(H_1)})
\]

\[
= \frac{1}{2}(\phi_{1s(H_1)} + \phi_{1s(H_2)} + \phi_{1s(H_2)} + \phi_{1s(H_1)}) = \frac{1}{2}(\phi_{1s(H_1)} + \phi_{1s(H_2)})
\]

\[
P^{\Lambda_2}(\phi_{1s(H_1)}) = \frac{1}{2}(1 \cdot E \phi_{1s(H_1)} + 1C^2 \phi_{1s(H_1)} - 1\sigma_{zz} \phi_{1s(H_1)} - 1\sigma_{xy} \phi_{1s(H_1)})
\]

\[
= \frac{1}{2}(\phi_{1s(H_1)} + \phi_{1s(H_2)} - \phi_{1s(H_2)} - \phi_{1s(H_1)}) = 0
\]

As expected, no \( \Lambda_2 \) linear combination can be formed from the \( \phi_{1s(H)} \) functions. Similarly one finds \( P^{\Lambda_1}(\phi_{1s(H_2)}) = 0 \), and

\[
P^{\Lambda_2}(\phi_{1s(H_2)}) = \frac{1}{2}(\phi_{1s(H_2)} - \phi_{1s(H_2)}).
\]
6 INTRODUCTION TO GROUP THEORY AND APPLICATION TO MOLECULAR SPECTROSCOPY

These two orbital combinations of \( A_1 \) and \( B_2 \) symmetry can be represented schematically as in Fig. 32.

![Figure 32: Schematic representations of the two linear combinations of the 1s orbitals of the two H atoms of a water molecule which transform as the \( A_1 \) and \( B_2 \) irreducible representations of the \( C_{2v} \) point group](image)

The symmetrized LCAO can be used to determine the chemical bonds that can be formed with the p orbitals on the O atom. To this end, one must first determine the transformation properties of the p orbitals on the O atom depicted schematically in Fig. 33.

![Figure 33: Schematic representation of the three 2p orbitals of the O atom of a water molecule from which their symmetry properties in the \( C_{2v} \) point group can be derived](image)

\[
\begin{align*}
E_{p_z} & = p_z; C_2^z p_z = p_z; \sigma^{xz} p_z = p_z; \sigma^{yz} p_z = p_z \\
\Gamma^p_z & = A_1 \\
E_{p_y} & = -p_y; C_2^z p_y = -p_y; \sigma^{xz} p_y = -p_y; \sigma^{yz} p_y = p_y \\
\Gamma^p_y & = B_2 \\
E_{p_x} & = p_x; C_2^z p_x = -p_x; \sigma^{xz} p_x = p_x; \sigma^{yz} p_x = -p_x \\
\Gamma^p_x & = B_1
\end{align*}
\]

Only orbitals of the same symmetry can be combined to form bonding or antibonding molecular orbitals. The five symmetrized orbitals listed above can be used to form five molecular orbitals according to the following diagram (Fig. 34) which neglects the 1s and 2s orbitals on the oxygen atom by assuming that they are not involved in the formation of chemical bonds.

\[ \text{O} \ldots (2p)^4, \text{H} (1s)^1 : \text{6 valence electrons} \]

Placing the six valence electrons in these MOs following Pauli’s Aufbau-principle gives the ground state configuration: \( \ldots (b_2)^2(a_1)^2(b_1)^2 \) with an overall symmetry \( A_1 \). Because four of the six electrons are in bonding orbitals and two in a non bonding \( p_z \) orbital, one expects two chemical bonds in \( \text{H}_2\text{O} \). The energetical ordering of the two bonding MO of \( B_2 \) and \( A_1 \) symmetry depends on the bond angle \( \alpha \) defined in Fig. 35. Whereas the \( a_1 \) orbital becomes
nonbonding at $\alpha = 180^\circ$, the $b_2$ orbital remains bonding at $\alpha = 180^\circ$ but becomes antibonding at small angles. The angle dependence of the energies of the molecular orbitals in triatomic molecules can be exploited to predict whether the molecules are linear or bend in specific electronic states by means of correlation diagrams called Walsch diagrams, as discussed in Wörner and Merkt (2010).

Figure 35: Bond angle $\alpha$

6.6 Determining the symmetry of normal modes

We consider the $3N_k$-dimensional reducible representation spanned by the set of $3N_k$ Cartesian displacement coordinates of the nuclei in a molecule and reduce it into irreducible representations of the corresponding group. For $\text{H}_2\text{O}$, $3N_k = 9$ and the representation is nine-dimensional. The $3N_k = 9$ cartesian coordinates are depicted in Fig. 36. All irreducible representations of $C_{2v}$ are one-dimensional, but only three vibrational modes ($3N_k - 6$) exist in $\text{H}_2\text{O}$. The symmetry of these modes will be obtained by eliminating the six irreducible representations corresponding to the three translational and the three rotational degrees of freedom of the molecule. The procedure followed here can be extended to molecules consisting of more atoms in a straightforward way. A more complete treatment of the vibrational motion of polyatomic molecules and of symmetry-adapted normal modes can be found in Wilson et al. (1955) (see also Albert et al. (hrs 003 2010)).
The characters of the reducible representation only have contribution from atoms that are not symmetry operations are represented by $9 \times 9$ matrices:

$E$:

$$
E = \begin{pmatrix}
  x_1 & x_1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
y_1 & y_1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
z_1 & z_1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
x_2 & x_2 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
y_2 & y_2 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
z_2 & z_2 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
x_3 & x_3 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
y_3 & y_3 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
z_3 & z_3 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
$$  \hspace{1cm} (292)

$C_2^z$:

$$
C_2^z = \begin{pmatrix}
  x_1 & -x_2 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
y_1 & -y_2 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
z_1 & -z_2 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
x_2 & -x_1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
y_2 & -y_1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
z_2 & -z_1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
x_3 & -x_3 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
y_3 & -y_3 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
z_3 & -z_3 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
$$  \hspace{1cm} (293)

$\chi^E = 9; \chi^{C_2^z} = -1.$

The character of the unity operation is always equal to the dimension of the representation. Because the characters of the reducible representation only have contribution from atoms that are not exchanged by the symmetry operations, only these atoms must be considered to determine $\chi^R$.

$\sigma^{xz}$ exchanges the two H atoms and only the O atom needs to be considered:

$$
\sigma^{xz} x_3 = x_3; \quad \sigma^{xz} y_3 = -y_3; \quad \sigma^{xz} z_3 = z_3 \quad \Rightarrow \quad \chi^{\sigma^{xz}} = 1. \quad (294)
$$
\( \sigma^{yz} \) does not exchange any atom. For each atom, the \( x \) coordinate is inverted and the \( y \) and \( z \) coordinates are preserved:

\[
-1 + 1 - 1 + 1 - 1 + 1 + 1 = 3
\]

\[\Rightarrow \chi^{\sigma^{yz}} = 3.\]

The reducible 9-dimensional representation is therefore:

\[
\begin{array}{cccc}
C_2v & E & C_2^x & \sigma^{xz} & \sigma^{yz} \\
\Gamma^{9D} & 9 & -1 & 1 & 3 \\
\end{array}
\]

This representation can be reduced using the reduction formula (Eq. (290)):

\[
c_{A_1} = \frac{1}{4}(9 - 1 + 1 + 3) = 3 \quad (295)
\]

\[
c_{A_2} = \frac{1}{4}(9 - 1 - 1 - 3) = 1 \quad (296)
\]

\[
c_{B_1} = \frac{1}{4}(9 + 1 + 1 - 3) = 2 \quad (297)
\]

\[
c_{B_2} = \frac{1}{4}(9 + 1 - 1 + 3) = 3 \quad (298)
\]

\[
\Gamma^{9D} = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2. \quad (299)
\]

From these nine irreducible representations, three correspond to translations (\( \Gamma^x = B_1, \Gamma^y = B_2, \Gamma^z = A_1 \)) and three correspond to rotations (\( \Gamma^{R_x} = B_2, \Gamma^{R_y} = B_1, \Gamma^{R_z} = A_2 \)). The remaining three, namely \( 2A_1 \oplus B_2 \), correspond to the three vibrational modes of \( \text{H}_2\text{O} \) (\( 3N_k - 6 = 3 \), as \( \text{H}_2\text{O} \) is a non-linear molecule). To determine these modes, one can use the projection formula (Eq. (291)).

---

**Example 9:** normal mode of \( \text{H}_2\text{O} \) of \( B_2 \) symmetry. In practice, it is convenient to first treat the \( x, y \) and \( z \) displacements separately, and then to combine the \( x, y, \) and \( z \) motion.

**\( x \)-dimension:**

\[
P^{B_2x_1} = \frac{1}{4}(1Ex_1 - 1C_2x_1 - 1\sigma^{xz}x_1 + 1\sigma^{yz}x_1)
\]

\[= \frac{1}{4}(x_1 + x_2 - x_2 - x_1) = 0. \quad (300)\]

The \( B_2 \) mode does not involve \( x \)-coordinates.

**\( y \) - and \( z \)-dimensions:**

\[
P^{B_2y_1} = \frac{1}{4}(1Ey_1 - 1C_2^2y_1 - 1\sigma^{xz}y_1 + 1\sigma^{yz}y_1)
\]

\[= \frac{1}{4}(y_1 + y_2 + y_2 + y_1) = \frac{1}{2}(y_1 + y_2). \quad (301)\]

\[
P^{B_2z_1} = \frac{1}{4}(1Ez_1 - 1C_2^2z_1 - 1\sigma^{xz}z_1 + 1\sigma^{yz}z_1)
\]

\[= \frac{1}{4}(z_1 - z_2 - z_2 + z_1) = \frac{1}{2}(z_1 - z_2). \quad (302)\]
Figure 37: Determination of the nuclear motion corresponding to the B$_2$ vibrational mode of water

The B$_2$ mode involves both y and z coordinates. Drawing the displacement vectors one obtains a vectorial representation of the motion of the H atoms in the B$_2$ mode. The motion of the O atom can be reconstructed by ensuring that the center of mass of the molecule remains stationary.

The mode is easily seen to be the asymmetric stretching mode.

6.7 Determining the symmetry of vibrational levels

The nomenclature to label the vibrational states of a polyatomic molecule is

$$\nu_1^{v_1}, \nu_2^{v_2}, \ldots, \nu_{3N-6}^{v_{3N-6}}$$ (303)

where $\nu_i$ designate the mode and $v_i$ the corresponding vibrational quantum number. Usually only those modes $\nu_i$ are indicated for which $v_i \neq 0$. Alternatively the notation

$$(v_1, v_2, \ldots, v_{3N-6})$$ (304)

can be used, yet another convention writes $v_1 \nu_1 + v_2 \nu_2 + v_3 \nu_3 + \cdots$, retaining only $v_i \neq 0$. For the ordering of the modes, the totally symmetric modes come first in order of descending frequency, then the modes corresponding to the second irreducible representation in the character table in order of descending frequency, etc.

Example 10: H$_2$O: $v_1 = 2$, $v_2 = 1$, $v_3 = 3$.

Notation 1: $1^2 2^1 3^3$ (sometimes also lower indices are used: $1_2 2_1 3_3$).

Notation 2: $(2 1 3)$.

Notation 3: $2\nu_1 + \nu_2 + 3\nu_3$.

To find the overall symmetry of the vibrational wavefunction one must build the direct product

$$\Gamma_{\text{vib}} = (\Gamma_1)^{v_1} \otimes (\Gamma_2)^{v_2} \otimes \cdots \otimes (\Gamma_{3N-6})^{v_{3N-6}}.$$ (305)

Example 11:

$$\Gamma = (\text{H}_2\text{O}, 1^2 2^1 3^3) = A_1 \otimes A_1 \otimes A_1 \otimes B_2 \otimes B_2 \otimes B_2 = B_2.$$ (306)
Extensive tables of practical use for determining the symmetry of vibrational levels can be found in Wilson et al. (1955).

### 6.8 Determining the symmetry label of electronic states / configurations

Only partially filled subshells must be considered and the electronic symmetry labels of the configuration are obtained from a direct product of the symmetry of occupied orbitals. Moreover, one writes the symmetry of molecular orbitals with small letters and that of electronic states with capital letters.

**Example 12:** $\text{H}_2\text{O}$: $\ldots (b_2)^2(a_1)^2(b_1)^2 : \tilde{X}^1A_1$

$$\Gamma_{el} = b_2 \otimes b_2 \otimes a_1 \otimes a_1 \otimes b_1 \otimes b_1 = A_1 \quad (307)$$

$\text{H}_2\text{O}^+$: $\ldots (b_2)^2(a_1)^2(b_1)^1 : \tilde{X}^+^2B_1$

$$\Gamma_{el} = b_2 \otimes b_2 \otimes a_1 \otimes a_1 \otimes b_1 = B_1 \quad (308)$$

The letter $\tilde{X}$ / $\tilde{X}^+$ designates the ground electronic state. The first excited states of the same spin multiplicity as the ground state are labeled $\tilde{A}$ / $\tilde{A}^+$, $\tilde{B}$ / $\tilde{B}^+$. Electronically excited states of other spin multiplicity are labeled $\tilde{a}$, $\tilde{b}$, $\tilde{c}$,... In diatomic molecules, one does not write the “tilde” but only X, A, B, C,..., a, b, c,...

**Example 13:** Electronic ground state configuration of the methyl radical $\text{CH}_3$ ($D_{3h}$ point group).

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_v$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
<th>$R_z$, $R_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$x, y$</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>$z$</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>$R_z$, $R_x$</td>
</tr>
<tr>
<td>$A_1''$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$A_2''$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

We follow the same procedure as for $\text{H}_2\text{O}$ in section 6.5, retain the 2s and 2p orbitals on $\text{O}$ and the 1s orbitals on $\text{H}$. First, symmetrized “ligand” orbitals are constructed from the $\text{H}$ 1s orbitals; then these are combined with the $\text{O}$ orbitals to form bonding and antibonding orbitals. C: 2s 2p; H: 1s

For the ligand orbitals, a 3D-representation is spanned by the three 1s atomic orbitals on the $\text{H}$ atom.

---

\*One should note that there are many exceptions to this nomenclature because sometimes the lowest excited electronic state has only been found after the state labeled A.
Figure 38: CH$_3$ molecule with its coordinate system

\[
\begin{array}{c|cccccc}
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\Gamma^{3d} & 3 & 0 & 1 & 3 & 0 & 1 \\
\end{array}
\]

This representation can be reduced using the reduction formula (Eq. (290)):

\[
c_{A'_1} = \frac{1}{12}[3 \cdot 1 \cdot 1 + 0 \cdot 2 \cdot 1 + 1 \cdot 3 \cdot 1 + 3 \cdot 1 \cdot 1 + 0 \cdot 1 \cdot 1 + 1 \cdot 3 \cdot 1] = \frac{12}{12} = 1 
\]

(309)

\[
c_{A'_2} = \frac{1}{12}[3 \cdot 1 \cdot 1 + 0 + 1 \cdot 3 \cdot (-1) + 3 \cdot 1 \cdot 1 + 0 + 1 \cdot 3 \cdot (-1)] = 0 
\]

(310)

\[
c_{E'} = \frac{1}{12}[3 \cdot 1 \cdot 2 + 0 + 1 \cdot 3 \cdot 0 + 3 \cdot 1 \cdot 2 + 0 + 1 \cdot 3 \cdot 0] = 1 
\]

(311)

\[
\Gamma^{3d} = A'_1 \oplus E'.
\]

(312)

Figure 39 shows the ligand orbital of $A'_1$ symmetry found by intuition. The ligand orbitals of $E'$ symmetry are found

Figure 39: Schematic representation of the ligand orbitals of CH$_3$ which can be constructed with the three H 1s atom orbitals

by using the projection formula (Eq. (291)).

\[
P^{E'} = \frac{1}{12} \left[ 2 \cdot E 1s(1) - 1 \cdot C_3 1s(1) - 1 \cdot C_3^* 1s(1) + 2 \cdot \sigma_h 1s(1) - 1 \cdot S_3 1s(1) - 1 \cdot S_3^* 1s(1) \right] 
\]

\[
= \frac{1}{12} \left[ 2 \cdot 1s(1) - 1 \cdot 1s(2) - 1 \cdot 1s(3) + 2 \cdot 1s(1) - 1 \cdot 1s(2) - 1 \cdot 1s(3) \right] 
\]

\[
= \frac{1}{3} \left[ 1s(1) - \frac{1}{2} [1s(2) + 1s(3)] \right]. 
\]

(313)

To find the second orbital of $E'$ symmetry, one can repeat the procedure using the $1s(2)$ and $1s(3)$ orbitals to find two further molecular orbitals $\frac{1}{2}[1s(2) - \frac{1}{2}[1s(1) + 1s(3)]]$ and $\frac{1}{2}[1s(3) - \frac{1}{2}[1s(1) + 1s(2)]]$. These three orbitals are

\[^b^*\text{Note that the} \frac{1}{2}^*\text{factor in the projection formula is not really useful, because the orbital would need to be normalized anyway.}
linearly dependent. One can use linear algebra to eliminate one of these three orbitals and to find an orthogonal set of two orbitals of $E'$ symmetry (see Fig. 39) using the Graham-Schmidt orthogonalization procedure. The molecular orbitals are finally found by determining the symmetry of the 2s and 2p orbitals of the central C atom and combining the orbitals of the same symmetry into bonding and antibonding orbitals (see Fig. 40). One sees that the 2p$_z$ orbital of $a''_2$ symmetry must remain nonbonding because there are no ligand orbitals of $a''_2$ symmetry.

2s: $a'_1 \leftrightarrow a'_1$ ligand orbital
2p$_z$: $a''_2$

p$_x$, p$_y$: $e' \leftrightarrow e'$ ligand orbital

![Energy-level diagram of valence molecular orbitals of CH$_3$](image)

Figure 40: Energy-level diagram of valence molecular orbitals of CH$_3$

The electronic configuration of CH$_3$ (in total nine electrons) is therefore:

\[
\begin{align*}
(1a'_1)^2(2a'_1)^2(1e')^4(1a''_2)^1,
\end{align*}
\]

where the 1a$_1'$ orbital is the 1s orbital on C. Therefore, the ground state is $\tilde{X}^2E''_2$. The radical has three bonds and an unpaired electron in the p$_z$ orbital of 1a$_2''$ symmetry.

### 6.9 Determining selection rules with group theory

In the dipole approximation, the interaction between molecules and electromagnetic radiation is assumed to only come from the interaction

\[
\hat{V} = -\hat{M} \cdot \hat{E}.
\]

$\hat{M}$ is used here to distinguish the dipole moment of the molecule in the laboratory-fixed frame from $\hat{\mu}$, which is the dipole moment in the molecule-fixed frame. The polarization vector $\hat{E}$ of the radiation...
is defined in the laboratory-fixed frame \( (X,Y,Z) \), whereas the components of \( \vec{\mu} \) are defined in the molecule-fixed frame \( (x,y,z) \). For linearly polarized light \( \vec{E} = (0,0,E) \)

\[
\vec{V} = -M_z E.
\] (316)

The selection rule may be written:

\[
\langle f | M_z | i \rangle.
\] (317)

Figure 41: Relationship between the laboratory- and molecule-fixed frames with the example of the CH₃Cl molecule. The permanent dipole moment of CH₃Cl lies along the C-Cl bond, i.e. along the \( z \) axis is the molecule-fixed frame.

The space-fixed components \( M_x \), \( M_y \), and \( M_z \) of \( \vec{M} \) vary as the molecule rotates. The molecule-fixed components \( \mu_x \), \( \mu_y \), and \( \mu_z \) remain the same when the molecule rotates and the selection rules are expressed in terms of \( \mu_x \), \( \mu_y \), and \( \mu_z \).

\[
\mu_\xi = \sum_{i=1}^{N} e_i \xi_i
\] (318)

with \( \xi = x, y, z \) and \( e_i \) is the charge of particle \( i \).

The relative orientation of the space-fixed and molecule-fixed coordinate system is given by the three Euler angles \( (\phi, \theta, \chi) \) defined by three successive rotations depicted in Fig. 42 and defined as follows (see also Bauder (2010)):
6 INTRODUCTION TO GROUP THEORY AND APPLICATION TO MOLECULAR SPECTROSCOPY

Figure 42: Euler angles $\phi$, $\theta$, $\chi$ used to relate the molecule-fixed and the space-fixed reference frames.

Adapted from Zare (1988)

1. Rotation around $Z$ by $\phi$ ($\rightarrow x', y', z'$)

2. Rotation around $y'$ by $\theta$ ($\rightarrow x'', y'', z''$)

3. Rotation around $z''$ by $\chi$ ($\rightarrow x, y, z$).

\[
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix} = R_Z(\phi)
\begin{bmatrix}
  X \\
  Y \\
  Z
\end{bmatrix} =
\begin{bmatrix}
  \cos \phi & \sin \phi & 0 \\
  -\sin \phi & \cos \phi & 0 \\
  0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
  X \\
  Y \\
  Z
\end{bmatrix}
\]

\[
\begin{bmatrix}
  x'' \\
  y'' \\
  z''
\end{bmatrix} = R_y(\theta)
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix} =
\begin{bmatrix}
  \cos \theta & 0 & -\sin \theta \\
  0 & 1 & 0 \\
  \sin \theta & 0 & \cos \theta
\end{bmatrix}
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix}
\]

\[
\begin{bmatrix}
  x \\
  y \\
  z
\end{bmatrix} = R_z(\chi)
\begin{bmatrix}
  x'' \\
  y'' \\
  z''
\end{bmatrix} =
\begin{bmatrix}
  \cos \chi & \sin \chi & 0 \\
  -\sin \chi & \cos \chi & 0 \\
  0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
  x'' \\
  y'' \\
  z''
\end{bmatrix}
\]
Using Eq. (319), the laboratory- and molecule-fixed frames can be linked by the following transformation:

\[
\begin{bmatrix}
    x \\
    y \\
    z
\end{bmatrix} = R_z(\chi)R_y(\theta)R_Z(\phi) \begin{bmatrix}
    X \\
    Y \\
    Z
\end{bmatrix}
\]

\[
= \begin{bmatrix}
    \cos \phi \cos \theta \cos \chi - \sin \phi \sin \chi \\
    -\cos \phi \cos \theta \sin \chi - \sin \phi \cos \chi \\
    \cos \phi \sin \theta
\end{bmatrix}
\begin{bmatrix}
    \sin \phi \cos \theta \cos \chi + \cos \phi \sin \chi \\
    -\sin \phi \cos \theta \sin \chi + \cos \phi \cos \chi \\
    \sin \phi \sin \theta
\end{bmatrix}
\begin{bmatrix}
    X \\
    Y \\
    Z
\end{bmatrix}
\]

or its inverse

\[
\begin{bmatrix}
    X \\
    Y \\
    Z
\end{bmatrix} = \lambda \begin{bmatrix}
    x \\
    y \\
    z
\end{bmatrix},
\]

where \( \lambda \) is the direction cosine matrix. \( \lambda \) can thus be used to express the components of a vector in the laboratory-fixed frame as a function of the components of the same vector in the molecule-fixed frame. A rotation of the molecule in space leads to a change of the Euler angles, and the rotational wavefunctions \( \phi_{\text{rot}}(\phi, \theta, \chi) \) are expressed in the space-fixed frame as a function of these angles. Expressing \( M_Z \) as a function of \( \mu_x, \mu_y, \) and \( \mu_z \):

\[
M_Z = \lambda_{Zx} \mu_x + \lambda_{Zy} \mu_y + \lambda_{Zz} \mu_z
\]

and using the product forms

\[
\psi_\downarrow = \phi'_e \phi'_{\text{espin}} \phi'_{\text{vib}} \phi'_{\text{rot}} \phi'_{\text{nspin}}
\]

\[
\psi_\uparrow = \phi''_e \phi''_{\text{espin}} \phi''_{\text{vib}} \phi''_{\text{rot}} \phi''_{\text{nspin}}
\]

for the molecular wavefunctions, the transition moment \( \langle \psi_\downarrow | M_Z | \psi_\uparrow \rangle \) can be written as

\[
\langle \phi'_e \phi'_{\text{espin}} \phi'_{\text{vib}} \phi'_{\text{rot}} \phi'_{\text{nspin}} | \sum_\alpha \lambda_{Z\alpha} \mu_\alpha | \phi''_e \phi''_{\text{espin}} \phi''_{\text{vib}} \phi''_{\text{rot}} \phi''_{\text{nspin}} \rangle.
\]

Eq. (325) can be simplified if one makes several assumptions.

1) Only \( \phi_{\text{nspin}} \) depends on the nuclear spin variables, and only \( \phi_{\text{espin}} \) depends on the electron spin variables. The integration can thus be separated

\[
\langle \phi'_{\text{espin}} | \phi''_{\text{espin}} | \phi'_{\text{vib}} | \phi'_{\text{rot}} | \sum_\alpha \lambda_{Z\alpha} \mu_\alpha | \phi''_{\text{espin}} \phi''_{\text{vib}} \phi''_{\text{rot}} \phi''_{\text{nspin}} \rangle.
\]

Because electron- and nuclear-spin functions are orthogonal, Eq. (326) vanishes (transition forbidden) unless \( \phi'_{\text{espin}} = \phi''_{\text{espin}} \) and \( \phi'_{\text{nspin}} = \phi''_{\text{nspin}} \), from which the selection rules

\[
\Delta S = 0 \quad \text{intercombination “Verbot”}
\]

\[
\Delta I = 0 \quad \text{nuclear-spin conservation rule}
\]
follow.

2) The remaining rovibronic (rotational-vibrational-electronic) transition moment
\[ \langle \phi'_e \phi'_vib \phi'_rot | \sum_{\alpha} \lambda_{\alpha} \mu_{\alpha} | \phi''_e \phi''_vib \phi''_rot \rangle \]
can be further simplified. The functions \( \phi_e, \phi_{vib} \) and \( \mu_{\alpha} \)
do not depend on the Euler angles: \( \phi_e(q_i, Q), \phi_{vib}(Q), \mu_{\alpha}(q_i, Q) \). However, the direction cosine elements \( \lambda_{\alpha} \) and \( \phi_{rot} \) only depend on \( \phi, \theta, \chi \) and the integration can be further separated in an integral over angular variables and an integral over electronic coordinates and normal modes:
\[ \sum_{\alpha} \langle \phi'_rot | \lambda_{\alpha} | \phi''_rot \rangle \langle \phi'_e \phi'_vib | \mu_{\alpha} | \phi''_e \phi''_vib \rangle. \] (329)

The integral \( \langle \phi'_rot | \lambda_{\alpha} | \phi''_rot \rangle \) leads to angular momentum selection rules:

- \( \Delta J = 0, \pm 1; 0 \leftrightarrow 0 \) : angular momentum conservation (see also Chapter 2) (330)

- \( \alpha = z \) : \( \Delta K = 0 \) : symmetric top
  - \( \Delta \Lambda = 0 \) : diatomic molecule
  - \( \Delta K_{a,b,c} = z = 0 \) : asymmetric top

- \( \alpha = x, y \) : \( \Delta K = \pm 1 \) : symmetric top
  - \( \Delta \Lambda = \pm 1 \) : diatomic molecule
  - \( \Delta K_{a,b,c} = x, y = \pm 1 \) : asymmetric top

- \( M_Z \) : \( \Delta M = 0 \)
- \( M_X, M_Y \) : \( \Delta M = \pm 1 \). (338)

The integral
\[ \langle \phi'_e \phi'_vib | \mu_{\alpha} | \phi''_e \phi''_vib \rangle \] (339)
represents a selection rule for transitions between electronic and vibrational levels and its evaluation can be simplified if one considers several cases.

Case 1: \( \phi'_e = \phi''_e, \phi'_vib = \phi''_vib \): rotational spectroscopy. Eq. (339) represents the expectation value of \( \mu_{\alpha} \). Transitions are only allowed for molecules with a permanent dipole moment. The angular momentum selection rules are as above.

Case 2: \( \phi'_e = \phi''_e, \phi'_vib \neq \phi''_vib \): vibrational spectroscopy. Since, in the BO approximation, only \( \phi_e \) and \( \mu_{\alpha} \) depend on electron coordinates \( q_i \), the integration over \( q_i \) can be done first:
\[ \langle \phi'_vib(Q) | \langle \phi_e(q_i, Q) | \mu_{\alpha}(Q, q_i) | \phi'_e(Q, q_i) \rangle_{q_i} | \phi'_vib(Q) \rangle_Q = \langle \phi'_vib(Q) | \mu_{e,\alpha}(Q) | \phi''_vib(Q) \rangle. \] (340)

Whether Eq. (340) vanishes or not, can be determined by group theory. Indeed, an integral over a set of coordinates (here normal modes \( Q \)) is only non-vanishing if the integrand contains the totally
symmetric representation. Integration over non-totally symmetric functions vanish because for each positive value \( f(Q_i) \) of a function \( f \) there exists a negative value \( f(-Q_i) = -f(Q_i) \). Therefore, if
\[
\Gamma'_{\text{vib}} \otimes \Gamma_\alpha \otimes \Gamma''_{\text{vib}} \ni A_1,
\]
the transition is allowed and if
\[
\Gamma'_{\text{vib}} \otimes \Gamma_\alpha \otimes \Gamma''_{\text{vib}} \not\ni A_1,
\]
it is forbidden\(^c\). \( \Gamma_\alpha \) \((\alpha = x, y, z)\) transforms as the components of a vector and thus as \( \alpha \).

---

**Example 14: \( \text{H}_2\text{O} \)**

\( \phi''_{\text{vib}} = (0,0,0) \), \( \Gamma''_{\text{vib}} = A_1 \)

\( \Gamma_{\mu_z} = B_1 \), \( \Gamma_{\mu_y} = B_2 \), \( \Gamma_{\mu_z} = A_1 \)

a) \( \phi'_{\text{vib}} = (1,0,0) \), \( \Gamma'_{\text{vib}} = A_1 \)

\[
\Gamma' \otimes \Gamma_\alpha \otimes \Gamma'' = A_1 \otimes \left\{ \begin{array}{l} B_1 \\ B_2 \\ A_1 \end{array} \right\} \otimes A_1 = \left\{ \begin{array}{l} B_1 \\ B_2 \\ A_1 \end{array} \right\}
\]

The allowed transition originates from the \( z \) component of the transition dipole moment.

b) \( \phi'_{\text{vib}} = (0,0,1) \), \( \Gamma'_{\text{vib}} = B_2 \)

\[
B_2 \otimes \left\{ \begin{array}{l} B_1 \\ B_2 \\ A_1 \end{array} \right\} \otimes A_1 = \left\{ \begin{array}{l} A_2 \\ A_1 \\ B_2 \end{array} \right\}
\]

The allowed transition originates from the \( y \) component of the transition dipole moment. The component of the permanent dipole moment along the \( y \) axis is zero in \( \text{H}_2\text{O} \). Nevertheless a transition can be observed. The condition for a vibrational transition to be observable is that a change of the dipole moment must occur when exciting the vibration. This is obviously the case when the antisymmetric stretching mode is excited in \( \text{H}_2\text{O} \).

In \( \text{H}_2\text{O} \), transitions to all vibrational levels are allowed by symmetry. However, overtones are weaker than fundamental excitations, as explained in Albert et al. (hrs 003 2010).

---

**Case 3: \( \phi'_{\text{el}} \neq \phi''_{\text{el}} \): electronic spectroscopy.** The left hand side of Eq. (340) can be written as
\[
\langle \phi'_{\text{vib}}(Q) | \langle \phi'_{\text{el}}(Q, q_i) | \mu_{\alpha}(Q, q_i) | \phi''_{\text{el}}(Q, q_i) \rangle_q | \phi''_{\text{vib}}(Q) \rangle_Q,
\]
where the inner integral represents an electronic transition moment \( \mu_{\text{el},\alpha} \) obtained by integration over the electronic coordinates. An electronically allowed transition is one for which \( \mu_{\text{el},\alpha}^n \neq 0 \), which is

\(^c\) We use \( A_1 \) to designate the totally symmetric representation although, in some groups, the totally symmetric representation is labeled \( A'_1, A, \Sigma^+_g, \Sigma^+ \ldots \).
fulfilled if \( \Gamma'_{el} \otimes \Gamma_{\alpha} \otimes \Gamma''_{el} \ni A_1 \).

---

**Example 15:** \( \text{H}_2\text{O} \)

\( \tilde{X}^1A_1, \ldots (1b_2)^2(3a_1)^2(1b_1)^2 \) (orbital symmetry designations are in small letters)

\[
\Gamma'_{el} \otimes \Gamma_{\alpha} \otimes \Gamma''_{el} = \begin{cases} B_1 & \otimes \begin{cases} B_1 \\ B_2 \\ A_1 \end{cases} \\ A_1 \end{cases} \otimes \begin{cases} A_1 \\ A_1 \end{cases}
\]

Electric dipole transitions to electronic states of \( B_1, B_2 \) and \( A_1 \) symmetry are electronically allowed and transitions to electronic states of \( A_2 \) symmetry are electronically forbidden in \( \text{H}_2\text{O} \).

If one assumes that the transition moment function \( \mu_{el}^{\alpha}(Q) \) varies slowly with \( Q \), then \( \mu_{el}^{\alpha}(Q) \) can be described by a Taylor series and one can in good approximation neglect higher terms:

\[
\mu_{el}^{\alpha}(Q) = \mu_{el}^{\alpha}_{eq} + \sum_{j}^{3N-6} \frac{\partial \mu_{el}^{\alpha}}{\partial Q_j} \bigg|_{eq} Q_j + \ldots \tag{344}
\]

In electronically allowed transitions the first term in Eq. (344) is often the dominant one and the transition moment (Eq. (343)) becomes:

\[
\langle \phi'_{\text{vib}}(Q) | \phi''_{\text{vib}}(Q) \rangle \mu_{el}^{\alpha} \big|_{eq}.
\]

The intensity of a transition is proportional to the square of the transition moment and thus,

\[
I \propto |\langle \phi'_{\text{vib}}(Q) | \phi''_{\text{vib}}(Q) \rangle |^2. \tag{346}
\]

\( |\langle \phi'_{\text{vib}}(Q) | \phi''_{\text{vib}}(Q) \rangle |^2 \) is called a **Franck-Condon factor** and represents the square of the overlap of the vibrational wavefunctions. Equation (346) implies the vibrational selection rule for electronically allowed transitions

\[
\Gamma'_{\text{vib}} \otimes \Gamma''_{\text{vib}} \ni A_1. \tag{347}
\]

---

**Example 16:**

\( \text{H}_2\text{O} \tilde{X}^1A_1(0,0,0) \rightarrow \text{H}_2\text{O} \tilde{C}^1B_1 \):

\( \Gamma''_{vib} = A_1 \Rightarrow \Gamma'_{vib} = A_1 \)

Only the symmetric stretch (\( \nu_1 \)) and the bending \( \nu_2 \) modes can be excited. The asymmetric stretch \( \nu_3 \) of \( B_2 \) symmetry can only be excited if \( \nu_3 \) is even.

---

Electronically forbidden transitions can become weakly allowed if the electronic and vibrational degrees of freedom cannot be separated as in Eq. (343). The condition for them to be weakly observable is that

\[
\Gamma'_{vib} \otimes \Gamma'_{el} \otimes \Gamma_{\alpha} \otimes \Gamma''_{vib} \otimes \Gamma''_{el} \ni A_1. \tag{348}
\]
Example 17:

Transitions from H$_2$O $^\tilde{X} \; ^1A_1 (0,0,0)$ to electronically excited states of $A_2$ symmetry (electronically forbidden) may become weakly allowed (vibronically allowed) if a non totally symmetric mode is excited.

$^\tilde{X} \; ^1A_1 (0,0,0)$: $\Gamma'_{el} = A_1$, $\Gamma''_{vib} = A_1$, $\Gamma''_{ev} = A_1 \otimes A_1 = A_1$

$A_2 (0,0,1)$: $\Gamma'_{el} = A_2$, $\Gamma'_{vib} = B_2$, $\Gamma''_{ev} = A_2 \otimes B_2 = B_1$

$\Gamma''_{ev} \otimes \Gamma_a \otimes \Gamma''_{ev} = B_1 \otimes \begin{cases} B_1 \\ B_2 \\ A_1 \end{cases} \otimes A_1 = \begin{cases} A_1 \\ A_2 \\ B_1 \end{cases}$

The vibronically allowed transition originates from $\mu_x$.

Further examples of electronically allowed and electronically forbidden transitions are presented in Wörner and Merkt (2010).

7 Radiationless transitions and spectral lineshapes

7.1 General aspects

Radiative and radiationless transitions limit the lifetime of excited states and from this one can conclude by means of the fourth Heisenberg uncertainty relation $\Delta E \Delta t \geq \hbar/(4\pi)$ that the energy distribution in excited states cannot be a $\delta$-function, although it should be obvious that the inequality does not allow one to derive an equation to calculate $\Delta E$ from a known $\Delta t$.

Lifetimes of excited states determined only by their spontaneous emission lead to the so called “natural linewidth” of the spectral line. Sometimes the concept is extended to reactive decays of excited states, for instance by dissociation (then called “predissociation” in this context (see Herzberg (1950)) or ionization (then called preionization, autoionization or Auger effect). These phenomena were all observed in the early days of spectroscopy and quantum mechanics. Spectral line broadening by the Auger effect was discussed and photodissociation observed for NH$_3$ by Bonhoeffer and Farkas (1928) following an earlier observation of Henri (1923) and Henri and Teves (1924) in spectra of S$_2$, which become diffuse below about 260 nm. The quantum theory of radiationless transitions was given at about the same time by Wentzel (1927, 1928). The early history is well told in Herzberg (1950).

We shall in the present short section discuss the basic concepts for exponential decay as related to line broadening with a Lorentzian line shape. We shall also give a brief summary of other origins of spectral line broadening in high-resolution spectra: Doppler broadening with Gaussian line shape, Voigt line shapes, collisional broadening mechanisms, intensity or power broadening already discussed in section 3, and residence or interaction time broadening.
7.2 Lorentzian probability distribution of energies and exponential decay

If in a general expansion of the time-dependent wavefunctions in $\Psi(r,t)$ in a densely spaced or continuous spectrum the probability distribution $p(E)$ is Lorentzian with full width at half maximum (FWHM) equal to $\Gamma$

$$p(E) = \frac{1}{\pi} \frac{\Gamma/2}{(E - E_m)^2 + (\Gamma/2)^2}$$

(349)

then one can show that the survival probability of the initial state

$$p_{(A)}(t) = |\langle \Psi(r,t) \rangle \cdot \langle \Psi(r,0) \rangle|^2 = |\langle \Psi(r,0) \rangle \cdot \langle \Psi(r,t) \rangle|^2$$

(350)

with $p_{(A)}(0) = 1$, obviously follows an exponential decay law

$$p_{(A)}(t) = \exp(-kt)$$

(351)

with $k$ being given by

$$k = \frac{2\pi\Gamma}{\hbar}$$

(352)

This follows directly from the time-dependent Schrödinger equation by inserting the wavefunction in the eigenstate basis with the appropriate initial condition and noting the mathematical Fourier transformation relationship between the exponential function and the Lorentzian (Cauchy) function.

While this is well known, it is probably less widely appreciated that this provides no insight into the dynamical origin of the Lorentzian distribution. A priori one could choose as initial state of an arbitrary quantum system a Lorentzian energy distribution and will obtain the exponential decay of the survival probability $p_{(A)}(t)$. For instance, Marquardt and Quack (1994, 1996) have shown that a simple harmonic oscillator will show such an exponential decay if one chooses a Lorentzian energy distribution instead of the common Poisson distribution of the coherent state. In this case, one can derive the wavepacket associated with a decay, corresponding simply to a movement of the wavepacket away from the initial position. Strictly speaking, the distribution for the harmonic oscillator is discrete

$$p(E) = \sum_{n=0}^{\infty} p_n(E_n)\delta(E - E_n)$$

(353)

with the Dirac delta function and the energy level spacing $E_n - E_{n-1} = \Delta E = \hbar\nu$. However, if one has $\Gamma \gg \Delta E$ one finds the expected exponential decay initially, and oscillations with period

$$\tau = \frac{\hbar}{\Delta E}$$

(354)

are only observed at very long times. The “recurrence” time $\tau = \tau_r \gg \tau_{\text{decay}} = 1/k$ is much longer than the decay time and formally one could consider the limit $\Delta E \to 0$ with $\tau \to \infty$.

Another aspect which is not widely appreciated concerns the uncertainty relation $\Delta E \Delta t$ being satisfied by the pair Lorentzian/exponential quite perfectly (one has $\Delta E\Delta t = \infty \geq \hbar/4\pi$), but obviously, the uncertainty relation cannot be used then to derive Eq. (352) leading to a misunderstanding, which is one of the most common textbook flaws, indeed.
The key to understanding the physics of spectral line broadening and exponential decay are thus mechanisms providing either a Lorentzian energy distribution in the eigenstate spectrum or an exponential decay of some meaningful physical initial state.

7.3 Perturbation theory and the Bixon-Jortner model for exponential decay

Fig. 43 shows a scheme which is commonly used in the treatment of exponential decay. The Hamiltonian is decomposed into a zero-order Hamiltonian $\hat{H}_0$ and a coupling. For instance, $\hat{H}_0$ could be the Born-Oppenheimer Hamiltonian describing an excited electronic state which by means of non-Born-Oppenheimer coupling $\hat{V}$ can make a transition to dissociative continuum states of the electronic ground state. This would be the prototypical situation for predissociation. An early quantum mechanical theory of predissociation was presented by Wentzel (1927, 1928) who derived a rate constant expression from perturbation theory

$$k = \frac{4\pi^2 |V|^2}{\hbar \rho}$$

where $\rho$ is the density of quantum states in the continuum (or quasi-continuum). Various derivations of this expression can be found in the textbook literature (e.g. Messiah (1961); Cohen-Tannoudji et al. (1973)) and we shall not reproduce this here. We note, however, that the derivation of the expression by perturbation theory has a number of weak points, but provides a correct result. The expression (355) is also frequently called “Fermi’s Golden Rule” for no good historical reason.

a) $E_s; \psi_s \xrightarrow{\hat{V}} \psi_i; E_i = E_s - \alpha + k \cdot \varepsilon$

$\sum \varepsilon = 1/\rho$

b) $\begin{pmatrix}
E_s & V & V & V & V & V & V \\
V & 0 & 0 & 0 & 0 & 0 & 0 \\
V & 0 & 0 & 0 & 0 & 0 & 0 \\
V & 0 & 0 & 0 & 0 & 0 & 0 \\
V & 0 & 0 & 0 & E_i & 0 & 0 \\
V & 0 & 0 & 0 & 0 & 0 & 0 \\
V & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\alpha_s \\
\end{pmatrix}
= \begin{pmatrix}
E_i \\
E_i \\
E_i \\
E_i \\
E_i \\
E_i \\
E_i \\
\end{pmatrix}
\begin{pmatrix}
\beta_i \\
\beta_i \\
\beta_i \\
\beta_i \\
\beta_i \\
\beta_i \\
\beta_i \\
\end{pmatrix}$

Figure 43: a) The model of Bixon and Jortner (1968) describing the coupling between the state $\psi_s$ and an equidistant manifold of states $\psi_k$ (spacing $\varepsilon$) with constant coupling strength $V_{ks} = V$. b) Coupling scheme in the model of Bixon and Jortner expressed in the matrix representation of the Schrödinger equation.
In a very insightful paper Bixon and Jortner (1968) showed that a scheme with the quantitative properties shown in Fig. 43 (constant level spacing $\varepsilon = 1/\rho$ in the continuum and constant (real) coupling matrix elements $V$ between $\psi_s$ and $\psi_k$) can be solved exactly by diagonalization of the Hamiltonian giving eigenfunctions

$$\varphi_n = a_n \psi_s + \sum_k b_k^{(n)} \psi_k$$

(356)

with

$$|a_n|^2 = \frac{V^2}{(E_n - E_s)^2 + V^2 + (\pi V^2/\varepsilon)^2}$$

(357)

In the limit that $\pi^2 V^2/\varepsilon \gg 1$ or $|V| \gg \varepsilon$, this approaches a Lorentzian distribution with $\Gamma$(FWHM) being given by

$$\Gamma = 2\pi V^2 \rho$$

(358)

which provides an exact derivation of the Golden Rule expression for this particular model.

The physical motivation for this picture is shown in Fig. 44. The special “zero order” state $\psi_s$ might have the property of carrying a large transition moment from the ground state (a “bright state” or “chromophore state”), whereas the zero order background states would carry no oscillator strengths. It would thus be natural that light absorption generates initially $\psi_s$ which then decays by the coupling $V$. An important contribution of Bixon and Jortner (1968) is to show, that this result can be obtained exactly, not requiring the usual approximations of perturbation theory. Another important result was to show that essentially exponential decay for electronic relaxation by internal conversion or intersystem crossing can be obtained in discrete spectra (spacing $\varepsilon$) not only for continua. The initial decay can be exponential, while the recurrence time $\tau = h/\varepsilon$ can be exceedingly long for high densities of states applicable for polyatomic molecules (see Albert et al. (hrs 003 2010); Quack (2010)).

In the eigenstate picture of ultrahigh resolution one could, however, see individual spectral lines (Fig. 44 b), where the envelope of the intensities of the lines follows a Lorentzian, which provides the overall spectral lineshape. In this picture, a short pulse excitation with broadband light would generate a probability distribution with Lorentzian shape because of the transition line strengths, and a subsequent exponential decay of this time-dependent initial state because of the very general relations (350) - (352).

We might conclude here that particularly when the first-order contribution to decay vanishes (for symmetry reasons, for instance) one can include higher-order perturbations. The corresponding golden rule expression to second order (see Fig. 45 for the coupling scheme) will then be

$$k = \frac{4\pi^2}{h} \left( \left| V_{jn} + \sum_m \frac{V_{jm} V_{mn}}{E_n - E_m} \right|^2 \right) \rho(E)$$

(359)

where $\left< |X|^2 \right>$ indicates the average absolute square of the expression, which is the proper quantity to be introduced in general, provided that the distribution of matrix elements satisfies some mild conditions.
7 RADIATIONLESS TRANSITIONS AND SPECTRAL LINESHAPES

Figure 44: Description of the initial state after optical excitation. a) In the model of Bixon and Jortner (1968), the operator $H_0$ is chosen so that only state $\psi_s$ (chromophore) is optically accessible from the ground state with a large dipole transition moment $\langle \psi_s | \hat{\mu} | \psi_0 \rangle$. The coupling to the equidistant manifold of states $\psi_k$ leads to a Lorentzian distribution of line strengths $G_n$ in the eigenstate picture. b) In the eigenstate picture, the optical excitation from the ground state leads to an occupation distribution $p_n$ of the eigenstates $\phi_n$ with eigenvalues $E_n$ which corresponds to a Lorentzian distribution with width $\Gamma$.

7.4 More general coupling models, non-exponential decays and non-Lorentzian line shapes

Mies and Krauss (1966) have discussed a more general coupling model as described in Fig. 46. This model has been more extensively investigated by Mies (1968, 1969b,a) and discussed in relation to a statistical theory of unimolecular reactions by Quack and Troe (1974, 1981).

In the model by Mies and Krauss, a set of reactant states with density $\rho$ (or equal spacing $\delta = \rho^{-1}$) is coupled with a constant coupling $V$ to product states $\rho_p$, where one introduces a coupling parameter $\Gamma = 2\pi |V|^2 \rho$ as abbreviation into the model. It is easily seen that this model includes situations,
Figure 45: Schematic representation of first-order ($n \rightarrow j$) and second-order ($n \rightarrow m \rightarrow j$) transitions in a perturbation-theory treatment of the level coupling.

different from the Bixon-Jortner model, where one has a dense set of initial states, which all might decay. Physically such a situation might apply for the dissociation of larger polyatomic molecules, where one has a high density of vibrational (-rotational) states (see also Quack (2010)). This model leads to an expression for the initial decay rate constant (in general with a non-exponential decay).

$$k = \left( \frac{2 \pi \Gamma \rho}{1 + \frac{\pi}{2} \Gamma \rho} \right) \cdot \frac{1}{h \rho} = \gamma \cdot \frac{1}{h \rho}$$

One recognizes the limiting case with $\Gamma \ll \rho^{-1}$, $\Gamma \rho \ll 1$, $\gamma \ll 1$. This results in the Golden Rule expression (352), the reactant states lead to isolated, well separated Lorentzian lines and individual exponential decays of the corresponding states like in the Bixon-Jortner model. One also sees that the factor

$$0 \leq \gamma = \left( \frac{2 \pi \Gamma \rho}{1 + \frac{\pi}{2} \Gamma \rho} \right) \leq 1$$

plays the role of a transmission coefficient for a quasiperiodic motion with period $\tau = h \rho$ in the reactant spectrum. The maximum value $\gamma = 1$ is obtained, when $\pi \Gamma \rho = 1$ leading to a maximum (uncertainty limited) decay rate. As discussed by Quack and Troe (1974, 1975), inclusion of a total number of accessible continua (open adiabatic channels) $W(E, J, \ldots)$, taking also angular momentum conservation and other symmetries into account, one obtains a statistical expression for unimolecular decay

$$k(E, J, \ldots) = \langle \gamma \rangle \frac{W(E, J, \ldots)}{h \rho(E, J, \ldots)}$$

where $0 \leq \langle \gamma \rangle \leq 1$ is an average transmission coefficient and the rate constant has to be interpreted as a statistical average over a sufficiently large sample. This provides an independent route to statistical
rate constant expressions that are more commonly derived by microcanonical transition state theory (see Quack and Troe (1998) for further discussion).

\[
\delta = \rho^{-1} \quad V \quad \text{Product states } \rho_p \\
\text{Density of reactant states } \rho; \quad \text{Parameter } \Gamma = 2\pi|V|^2\rho_p
\]

Figure 46: Model of Mies and Krauss (1966) describing the coupling between manifolds of reactant and product states as described in detail in the text.

### 7.5 Other sources of line broadening

In interpreting spectral line shapes in terms of intramolecular processes, some caution is needed, as there are many other sources of line broadening. We have already mentioned intensity (power) broadening in section 3. Instrumental line broadening is a trivial source of broadening. The most common source of line broadening in high-resolution gas phase spectra is the inhomogeneous Doppler broadening with a width (FWHM) \( \Delta \nu_D \) and a Gaussian line shape resulting from the Doppler effect in combination with the thermal Maxwell-Boltzmann distribution of translational speeds. One finds thus for the absorption cross section of the ideal Doppler shape

\[
\sigma_G(\nu) = \sigma_0 \exp \left[-c^2(\nu - \nu_0)^2/(v_w^2\nu_0^2)\right]
\]

where \( v_w \) is the most probable speed of molecules of mass \( m \) at temperature \( T \)

\[
v_w = \left(\frac{2kT}{m}\right)^{1/2}
\]

The Doppler line shape can thus be used to evaluate the temperature of a sample by spectroscopy. When one has a true intramolecular process leading to a homogeneous Lorentzian line shape combined with inhomogeneous Doppler line shape one finds a shape from convolution of the two functions, a Voigt line shape (see Albert et al. (2010)). Sometimes, with very good data, the individual homogenous and inhomogeneous contributions can be separately evaluated (see for instance Hippler et al. (2007) for an example).

However, it is not always possible to simply convolute line shapes. If the Lorentzian line shape results from a bimolecular (pseudo first order) process by collisions with a heat bath (see Albert et al. (2010)), then the collisional broadening line shape cannot be simply convoluted with the Doppler shape, but one can have many complex effects such as Dicke narrowing, line mixing and shifting, etc. Such situations have to be dealt with by appropriate techniques (Albert et al. (2010); Hartmann et al.)
(2008)). It is nevertheless true that at higher pressures, when pressure broadening exceeds Doppler broadening, one may estimate the Lorentzian “pressure broadening width” from its behavior which is proportional to gas pressure (or collision rate or gas density). We refer to Hartmann et al. (2008) for a more detailed discussion.

Another broadening which has to be mentioned is residence-time and interaction-time broadening. At very high resolution, this becomes important, as the limited interaction time in the spectroscopic experiment can lead to a limitation on resolution by reason of the uncertainty principle.

### 7.6 Summary of intramolecular processes as related to molecular spectroscopy

The processes discussed here and in other parts of the handbook can be summarized briefly as follows.

1. Spontaneous radiative decay (natural line shape, usually Lorentzian).
   - Fluorescence: conserves electron spin.
   - Phosphorescence: changes electron spin.
2. Predissociation (frequently exponential, with Lorentzian line shape).
3. Internal conversion (IC) by change of electronic state with retaining spin (often exponential).
4. Intersystem crossing (ISC) by change of electronic state with change of spin (often exponential).
5. Intramolecular vibrational redistribution (IVR, frequently non-exponential, see Albert et al. (hrs 003 2010)).
6. Autoionization.

In the photochemistry and photophysics of polyatomic molecules, these processes are often summarized by the Jablonski diagram such as shown in Fig. 47. The original diagram by Jablonski contained fewer processes (Jablonski 1931, 1933), and, in particular, IVR has been added only during the last few decades (Albert et al. (hrs 003 2010)). The relative importance of the various processes occurring in competition is frequently characterized by the quantum yield $\Phi_i$ for a given process

$$\Phi_i = k_i / \sum_j k_j$$

(365)

where the $k_j$ are the rate constants for the individual processes, which we assumed to be exponential.

**References**

Figure 47: Generalized Jablonski scheme with various radiative and radiationless processes as discussed in the text.


REFERENCES


