The *Ab Initio* Calculation of Molecular Properties

Lecture Notes
for the 3. MERCOSUR School
on Molecular Physics

Stephan P. A. Sauer
Chemistry Laboratory IV, Department of Chemistry
University of Copenhagen
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark
sauer@kiku.dk
http://fyskem.ki.ku.dk/sauer

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Contents

The interaction of a molecule with a weak external electromagnetic field, or the interactions within a molecule involving internal electromagnetic moments such as a nuclear magnetic dipole moment or a nuclear electric quadrupole moment, are all described in terms of so-called "molecular properties". These are intrinsic properties of an electronic state of a molecule and are independent of the strength of the external field or internal moments.

Molecular properties include the electric dipole moment, the electric field gradient tensor, the frequency dependent polarizability tensor, the nuclear magnetic shielding tensor, the indirect nuclear spin-spin coupling tensor among many others. They play an important role in the interpretation of numerous phenomena including the refractive index, the Stark effect, the Kerr effect, nuclear magnetic resonance spectra. Long-range interactions between molecules can also be understood in terms of molecular electric moments.

In the following the properties will be defined in a classical context in chapter 1. These definitions will then be used in chapter 2 to derive quantum mechanical expressions for the properties. The approach used is semi-classical since only the electrons are treated quantum mechanically (and non-relativistically), whereas fields and nuclei are treated classically. Approximate methods which can be used to calculate molecular electromagnetic properties are described in chapter 3. The exposition is restricted to a discussion of *ab initio* methods and the Born-Oppenheimer approximation is assumed throughout.

These notes grew out of lecture notes which I have prepared for the *First Mercosur Summerschool on Molecular Physics* held in Corrientes, Argentina, 14. - 23. February 1999. A shortened version of the notes, to which Martin J. Packer, University of Sheffield, also contributed, is published as chapter 7 entitled *The Ab Initio Calculation of Molecular Properties other than the Potential Energy Surface* in the book *Computational Molecular Spectroscopy* edited by P. R. Bunker and P. Jensen, John Wiley and Sons, London (2000). During the fall of 1999 the original notes were largely extended and consequently used as textbook for the course *Ab Initio Calculation of Electromagnetic Properties* at the University of Copenhagen and during the *Second Mercosur Summerschool on Molecular Physics* held in Corrientes, Argentina, 7. - 22. February 2000.

Chapter 1

Definition of Molecular Properties

The classical definition of the molecular properties is discussed in this chapter. For that purpose a molecule is represented by a continuous static or dynamic distribution of positive and negative charges with charge density $\rho(\vec{r})$ and current density $\vec{j}(\vec{r})$. Although in the classical context it is unnecessary to assume a continuous distribution of charges, this is convenient in the light of the quantum mechanical treatment which follows.

1.1 Electric Multipole Expansion

Electric charges in a molecule give rise to an electric field and an electrostatic potential. Other molecules in the neighbourhood experience this field. Knowledge of the electrostatic potential around a molecule is, therefore, important for the study of long-range intermolecular interactions.

For a distribution of charges with charge density $\rho(\vec{r})$ the electrostatic potential $\phi^\rho(\vec{R})$ is given as superposition of the potentials due to the individual charges [1, 2]

$$\phi^\rho(\vec{R}) = \frac{1}{4\pi\epsilon_0} \int_{\tau'} \frac{\rho(\vec{r}\,')}{\mid \vec{R} - \vec{r}\,' \mid} \, d\tau', \tag{1.1}$$

where $d\tau'$ stands for $dx'dy'dz'$ throughout chapter 1 and $\int_{\tau'}$ denotes a triple integral $\int\int\int$ over the appropriate volume. This expression is exact but often it is not particularly useful because an integration has to be performed for each observation point $\vec{R}$ and because complete knowledge of the charge distribution $\rho(\vec{r})$ is required.

For an observation point $\vec{R}$ far from the charge distribution it is possible to expand $\frac{1}{|\vec{R}-\vec{r}\,'|}$ in a Taylor series around an origin $\vec{r}_o$ within the charge distribution

[3, 4, 5, 6]

$$\frac{1}{|\vec{R} - \vec{r}\,'|} = \frac{1}{|\vec{R} - \vec{r}_o|} + \sum_\alpha \left(\frac{\partial}{\partial r'_\alpha} \frac{1}{|\vec{R} - \vec{r}\,'|} \right) (r'_\alpha - r_{o,\alpha}) \tag{1.2}$$

$$+ \frac{1}{2} \sum_{\alpha\beta} \left(\frac{\partial^2}{\partial r'_\alpha \partial r'_\beta} \frac{1}{|\vec{R} - \vec{r}\,'|} \right) (r'_\alpha - r_{o,\alpha})(r'_\beta - r_{o,\beta}) + \dots \,,$$

where the derivatives have to be evaluated at the point $\vec{r}\,' = \vec{r}_o$. The Greek subscripts α, β, etc. denote vector or tensor components in the molecule fixed cartesian coordinate system. A summation over a Greek subscript will here and in the following denote summation over all three Cartesian components. Insertion in the expression for the electrostatic potential, equation (1.1), yields

$$\phi^\rho(\vec{R}) = \frac{1}{4\pi\epsilon_0} \left[\frac{1}{|\vec{R} - \vec{r}_o|} \int_{\tau'} \rho(\vec{r}\,') \, d\tau' \right.$$

$$+ \sum_\alpha \left(\frac{\partial}{\partial r'_\alpha} \frac{1}{|\vec{R} - \vec{r}\,'|} \right) \int_{\tau'} \rho(\vec{r}\,') \, (r'_\alpha - r_{o,\alpha}) \, d\tau'$$

$$+ \frac{1}{2} \sum_{\alpha\beta} \left(\frac{\partial^2}{\partial r'_\alpha \partial r'_\beta} \frac{1}{|\vec{R} - \vec{r}\,'|} \right) \int_{\tau'} \rho(\vec{r}\,') \, (r'_\alpha - r_{o,\alpha})(r'_\beta - r_{o,\beta}) \, d\tau'$$

$$\left. + \dots \right] . \tag{1.3}$$

By evaluating the derivatives and defining the electric moments of the charge distribution as

$$q = \int_{\tau'} \rho(\vec{r}\,') \, d\tau', \tag{1.4}$$

$$\mu_\alpha(\vec{r}_o) = \int_{\tau'} (r'_\alpha - r_{o,\alpha}) \, \rho(\vec{r}\,') \, d\tau', \tag{1.5}$$

$$Q_{\alpha\beta}(\vec{r}_o) = \int_{\tau'} (r'_\alpha - r_{o,\alpha}) \, (r'_\beta - r_{o,\beta}) \, \rho(\vec{r}\,') \, d\tau', \tag{1.6}$$

we obtain a multipole expansion of the electrostatic potential

$$\phi^\rho(\vec{R}) = \frac{1}{4\pi\epsilon_0} \left[q \frac{1}{|\vec{R} - \vec{r}_o|} + \sum_\alpha \mu_\alpha(\vec{r}_o) \frac{R_\alpha - r_{o,\alpha}}{|\vec{R} - \vec{r}_o|^3} \right. \tag{1.7}$$

$$\left. + \frac{1}{2} \sum_{\alpha\beta} Q_{\alpha\beta}(\vec{r}_o) \frac{(R_\alpha - r_{o,\alpha}) \, (R_\beta - r_{o,\beta}) - \delta_{\alpha\beta}(\vec{R} - \vec{r}_o)^2}{|\vec{R} - \vec{r}_o|^5} + \dots \right] .$$

The zeroth order electric moment q is the total charge, μ_α are components of the first order electric moment, called the electric dipole moment, and $Q_{\alpha\beta}$ are components of

the second order electric moment tensor. The contribution from the higher moments in the series will become negligible as the distance from the origin increases and the potential will then be accurately described by only the charge and dipole moment terms. Convergence of the multipole series for a particular value of $\vec{R}$ depends on the precise form of the charge distribution.

An important feature of the electric multipole moments is that the first nonvanishing moment of a charge distribution is independent of the choice of origin $\vec{r}_o$. However, all the higher moments depend on the origin. Thus the charge of an ion and the dipole moment of a neutral molecule are both independent of the origin $\vec{r}_o$, whereas the dipole molecule of an ion or the quadrupole moment of a neutral molecule with nonvanishing dipole moment is not.

Frequently a traceless quadrupole moment tensor $\Theta_{\alpha\beta}$ with only five independent elements is defined as

$$\Theta_{\alpha\beta}(\vec{r}_o) = \frac{1}{2} \int_{\tau'} \left[3(r'_\alpha - r_{o,\alpha}) \ (r'_\beta - r_{o,\beta}) - \delta_{\alpha\beta} \ (\vec{r}\,' - \vec{r}_o)^2 \right] \ \rho(\vec{r}\,') \ d\tau'. \qquad (1.8)$$

It essentially measures the deviation from spherical symmetry. To avoid confusion it is customary to take equation (1.6) as defining the second electric moment and equation (1.8) as defining the electric quadrupole moment.

Having obtained the electric multipole moments of a distribution of charges, we can calculate the electrostatic potential for any point $\vec{R}$ from the simple formula in equation (1.8) instead of evaluating the more complicated expression in equation (1.1) for each $\vec{R}$. This explains the importance of the electric multipole moments for the description of intermolecular forces [7].

1.2   Potential Energy in an Electric Field

Electric multipole moments also play an important role in the description of interactions between molecules and external electric fields. The potential energy W of a distribution of charges immersed in an external static electric field $\vec{E}$ is given as [8]

$$W = \int_{\tau'} \rho(\vec{r}\,') \ \phi^E(\vec{r}\,') \ d\tau', \qquad (1.9)$$

where $\phi^E(\vec{r}\,')$ is the scalar potential associated with the electric field. This is an exact expression for the potential energy, but evaluation of equation (1.9) requires that the charge density $\rho(\vec{r}\,')$ and the electric potential $\phi^E(\vec{r}\,')$ are known for all values of $\vec{r}\,'$. A more useful expression can be obtained, if we expand the scalar potential in a Taylor series around $\vec{r}_o$ [3, 9, 6]

$$\begin{aligned}
\phi^E(\vec{r}\,') &= \phi^E(\vec{r}_o) + \sum_\alpha (r'_\alpha - r_{o,\alpha}) \frac{\partial \phi^E(\vec{r}\,')}{\partial r'_\alpha} \\
&+ \frac{1}{2} \sum_{\alpha\beta} (r'_\alpha - r_{o,\alpha})(r'_\beta - r_{o,\beta}) \frac{\partial^2 \phi^E(\vec{r}\,')}{\partial r'_\alpha \partial r'_\beta} + \ \ldots, \qquad (1.10)
\end{aligned}$$

where the derivatives have to evaluated again at $\vec{r}\,' = \vec{r}_o$. The derivatives of the scalar potential ϕ^E define the electric field E_α

$$E_\alpha(\vec{r}_o) = \left. -\frac{\partial \phi^E(\vec{r}\,')}{\partial r'_\alpha} \right|_{\vec{r}\,'=\vec{r}_o} , \tag{1.11}$$

the electric field gradient tensor $E_{\alpha\beta}$

$$E_{\alpha\beta}(\vec{r}_o) = \left. -\frac{\partial^2 \phi^E(\vec{r}\,')}{\partial r'_\alpha \partial r'_\beta} \right|_{\vec{r}\,'=\vec{r}_o} , \tag{1.12}$$

etc. On insertion of equations (1.10) - (1.12) in equation (1.9) one obtains for the potential energy

$$W = \phi^E(\vec{r}_o) \int_{\tau'} \rho(\vec{r}\,') \, d\tau' - \sum_\alpha E_\alpha(\vec{r}_o) \int_{\tau'} (r'_\alpha - r_{o,\alpha}) \, \rho(\vec{r}\,') \, d\tau'$$

$$- \frac{1}{2} \sum_{\alpha\beta} E_{\alpha\beta}(\vec{r}_o) \int_{\tau'} (r'_\alpha - r_{o,\alpha}) (r'_\beta - r_{o,\beta}) \, \rho(\vec{r}\,') \, d\tau' + \ldots . \tag{1.13}$$

The integrals over $\rho(\vec{r}\,')$ are again the electric moments defined in equations (1.4) - (1.6). The energy W of the interaction between a charge distribution and a static but not homogeneous electric field can therefore be expressed in terms of the electric moments of the charge distribution

$$W = q \, \phi^E(\vec{r}_o) - \sum_\alpha \mu_\alpha(\vec{r}_o) E_\alpha(\vec{r}_o) - \frac{1}{2} \sum_{\alpha\beta} Q_{\alpha\beta}(\vec{r}_o) E_{\alpha\beta}(\vec{r}_o) + \ldots \tag{1.14}$$

similar to the multipole expansion of the electrostatic potential of a charge distribution in equation 1.8. Alternatively using the quadrupole moment tensor Θ we can write for the interaction energy

$$W = q \, \phi^E(\vec{r}_o) - \sum_\alpha \mu_\alpha(\vec{r}_o) E_\alpha(\vec{r}_o) - \frac{1}{3} \sum_{\alpha\beta} \Theta_{\alpha\beta}(\vec{r}_o) E_{\alpha\beta}(\vec{r}_o) + \ldots . \tag{1.15}$$

From this equation we can see that dipole moment and the quadrupole moment can also be defined as derivatives of the potential energy with respect to the field strength E_α or field gradient $E_{\alpha\beta}$

$$\mu_\alpha(\vec{r}_o) = -\frac{\partial W}{\partial E_\alpha(\vec{r}_o)} , \tag{1.16}$$

$$\Theta_{\alpha\beta}(\vec{r}_o) = -3\frac{\partial W}{\partial E_{\alpha\beta}(\vec{r}_o)} . \tag{1.17}$$

These definitions will be used in the derivation of quantum mechanical expressions for the moments in chapter 2.

1.3 Induced Electric Moments and Polarizabilities

So far it has been assumed that the distribution of charges is fixed and is not influenced by the external electric field apart from a change in its energy. However, if the charge distribution can be polarized in the presence of the electric field, it will redistribute itself such that the total energy is minimized. As a result, the moments of the charge distribution will change. The field dependent moments $\mu_\alpha^{ind}(\vec{E})$, $\Theta_{\alpha\beta}^{ind}(\vec{E})$ are induced by the external field in addition to the field independent, so called permanent, moments μ_α^{per}, $\Theta_{\alpha\beta}^{per}$. Traditionally [7] the moments of a charge distribution in the presence of an external field E_α and field gradient $E_{\alpha\beta}$ are expanded in the following way

$$
\begin{aligned}
\mu_\alpha(\vec{E}, \boldsymbol{E}) &= \mu_\alpha^{per} + \mu_\alpha^{ind}(\vec{E}, \boldsymbol{E}) \\
\mu_\alpha(\vec{E}, \boldsymbol{E}) &= \mu_\alpha^{per} + \sum_\beta \alpha_{\alpha\beta} E_\beta + \frac{1}{2} \sum_{\beta\gamma} \beta_{\alpha\beta\gamma} E_\beta E_\gamma + \frac{1}{6} \sum_{\beta\gamma\delta} \gamma_{\alpha\beta\gamma\delta} E_\beta E_\gamma E_\delta \\
&\quad + \frac{1}{3} \sum_{\beta\gamma} A_{\alpha,\beta\gamma} E_{\beta\gamma} + \frac{1}{3} \sum_{\beta\gamma\delta} B_{\alpha\beta,\gamma\delta} E_\beta E_{\gamma\delta} + \ \dots \ , \quad (1.18) \\
\Theta_{\alpha\beta}(\vec{E}, \boldsymbol{E}) &= \Theta_{\alpha\beta}^{per} + \Theta_{\alpha\beta}^{ind}(\vec{E}, \boldsymbol{E}) \\
\Theta_{\alpha\beta}(\vec{E}, \boldsymbol{E}) &= \Theta_{\alpha\beta}^{per} + \sum_\gamma A_{\gamma,\alpha\beta} E_\gamma + \frac{1}{2} \sum_{\gamma\delta} B_{\gamma\delta,\alpha\beta} E_\gamma E_\delta \\
&\quad + \sum_{\gamma\delta} C_{\alpha\beta,\gamma\delta} E_{\gamma\delta} + \ \dots \ . \quad (1.19)
\end{aligned}
$$

where here and in the rest of this section the origin dependence $"(\vec{r}_o)"$ of the moments is not written out explicitly, for the sake of readability, as well as E_α and $E_{\alpha\beta}$ are meant as abbreviations for $E_\alpha(\vec{r}_o)$ and $E_{\alpha\beta}(\vec{r}_o)$, respectively.

This equation defines the dipole polarizability tensor $\alpha_{\alpha\beta}$, the first $\beta_{\alpha\beta\gamma}$ and second $\gamma_{\alpha\beta\gamma\delta}$ dipole hyperpolarizability tensors, the dipole-quadrupole polarizability tensor $A_{\alpha,\beta\gamma}$, the quadrupole-quadrupole polarizability tensor $C_{\alpha\beta,\gamma\delta}$ and the dipole-quadrupole hyperpolarizability tensor $B_{\alpha\beta,\gamma\delta}$ as derivatives of the field dependent moments, as shown in Table 1.1.

Since we are concerned with a polarizable charge distribution, it is not possible to obtain an expression for the energy W of the charge distribution in the presence of the external field and field gradient by simply inserting the field and field gradient dependent moments, $\mu_\alpha(\vec{E}, \boldsymbol{E})$ and $\Theta_{\alpha\beta}^{ind}(\vec{E}, \boldsymbol{E})$ from equations (1.18) and (1.19), in the multipole expansion of the energy in equation (1.15). Instead, we first want to expand the field and field gradient dependent energy W in a Taylor series in the

field and field gradient

$$
\begin{aligned}
W(\vec{E}, \boldsymbol{E}) \;=\; & W^{(0)} + \sum_{\alpha} \left(\frac{\partial W}{\partial E_\alpha} \right) E_\alpha + \sum_{\alpha\beta} \left(\frac{\partial W}{\partial E_{\alpha\beta}} \right) E_{\alpha\beta} \\
& + \frac{1}{2} \sum_{\alpha\beta} \left(\frac{\partial^2 W}{\partial E_\alpha \partial E_\beta} \right) E_\alpha E_\beta + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \left(\frac{\partial^2 W}{\partial E_{\alpha\beta} \partial E_{\gamma\delta}} \right) E_{\alpha\beta} E_{\gamma\delta} \\
& \qquad\qquad + \sum_{\alpha\beta\gamma} \left(\frac{\partial^2 W}{\partial E_\alpha \partial E_{\beta\gamma}} \right) E_\alpha E_{\beta\gamma} \\
& + \frac{1}{6} \sum_{\alpha\beta\gamma} \left(\frac{\partial^3 W}{\partial E_\alpha \partial E_\beta \partial E_\gamma} \right) E_\alpha E_\beta E_\gamma + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \left(\frac{\partial^3 W}{\partial E_\alpha \partial E_\beta \partial E_{\gamma\delta}} \right) E_\alpha E_\beta E_{\gamma\delta} \\
& + \frac{1}{24} \sum_{\alpha\beta\gamma} \left(\frac{\partial^4 W}{\partial E_\alpha \partial E_\beta \partial E_\gamma \partial E_\delta} \right) E_\alpha E_\beta E_\gamma E_\delta \;+\; \dots \,,
\end{aligned}
\tag{1.20}
$$

where the derivatives are to be evaluated at zero electric field and field gradient. The first derivatives of the energy with respect to the field and field gradient are the electric dipole moment and electric quadrupole moment, as shown in equations (1.16) and (1.17). Evaluating them at at zero electric field and field gradient yields the permanent moments. The higher derivatives of the energy can then be obtained by taking the appropriate derivatives of the expansions of the field and field gradient dependent dipole and quadrupole moment in equations (1.18) and (1.19). As shown in the last column of Table 1.1, they turn out to be the various polarizabilities and hyperpolarizabilities. These alternative definitions of the (hyper)polarizabilities as derivatives of the energy will be employed in the latter chapters in order to obtain quantum mechanical expressions for these properties.

Substituting for the derivatives we finally obtain the well known expression [7] for the energy

$$
\begin{aligned}
W(\vec{E}) = \; & q \, \phi^E - \sum_{\alpha} \mu^{per}_\alpha E_\alpha - \frac{1}{3} \sum_{\alpha\beta} \Theta^{per}_{\alpha\beta} E_{\alpha\beta} \\
& - \frac{1}{2} \sum_{\alpha\beta} \alpha_{\alpha\beta} E_\alpha E_\beta - \frac{1}{6} \sum_{\alpha\beta\gamma\delta} C_{\alpha\beta,\gamma\delta} E_{\alpha\beta} E_{\gamma\delta} - \frac{1}{3} \sum_{\alpha\beta\gamma} A_{\alpha,\beta\gamma} E_\alpha E_{\beta\gamma} \\
& - \frac{1}{6} \sum_{\alpha\beta\gamma} \beta_{\alpha\beta\gamma} E_\alpha E_\beta E_\gamma - \frac{1}{6} \sum_{\alpha\beta\gamma\delta} B_{\alpha\beta,\gamma\delta} E_\alpha E_\beta E_{\gamma\delta} \\
& - \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \gamma_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta - \dots \,.
\end{aligned}
\tag{1.21}
$$

where again the origin dependence "$(\vec{r}_o)$" of the permanent moments and of the potential ϕ^E was dropped and E_α and $E_{\alpha\beta}$ are used as abbreviations for $E_\alpha(\vec{r}_o)$ and $E_{\alpha\beta}(\vec{r}_o)$, respectively. The importance of equation (1.21) is that knowing the various (hyper)polarizabilities one can calculate from this expression the change in energy

of a charge distribution due to an external electric field or field gradient of arbitrary strength.

Table 1.1 Definitions of tensor components of the electric polarizabilities and hyper-polarizabilities as derivatives[a] of components of the field dependent electric dipole $\mu_\alpha(\vec{E})$ and quadrupole $\Theta_{\gamma\delta}(\vec{E})$ moments or of the energy $W(\vec{E})$

	$\mu_\alpha(\vec{E})$	$\Theta_{\gamma\delta}(\vec{E})$	$W(\vec{E})$
μ_α^{per}			$-\dfrac{\partial}{\partial E_\alpha}$
$\Theta_{\gamma\delta}^{per}$			$-3\dfrac{\partial}{\partial E_{\gamma\delta}}$
$\alpha_{\alpha\beta}$	$\dfrac{\partial}{\partial E_\beta}$	—	$-\dfrac{\partial^2}{\partial E_\beta \partial E_\alpha}$
$\beta_{\alpha\beta\gamma}$	$\dfrac{\partial^2}{\partial E_\gamma \partial E_\beta}$	—	$-\dfrac{\partial^3}{\partial E_\gamma \partial E_\beta \partial E_\alpha}$
$\gamma_{\alpha\beta\gamma\delta}$	$\dfrac{\partial^3}{\partial E_\delta \partial E_\gamma \partial E_\beta}$	—	$-\dfrac{\partial^4}{\partial E_\delta \partial E_\gamma \partial E_\beta \partial E_\alpha}$
$A_{\alpha,\gamma\delta}$	$3\dfrac{\partial}{\partial E_{\gamma\delta}}$	$\dfrac{\partial}{\partial E_\alpha}$	$-3\dfrac{\partial^2}{\partial E_{\gamma\delta} \partial E_\alpha}$
$B_{\alpha\beta,\gamma\delta}$	$3\dfrac{\partial^2}{\partial E_{\gamma\delta} \partial E_\beta}$	$\dfrac{\partial^2}{\partial E_\beta \partial E_\alpha}$	$-3\dfrac{\partial^3}{\partial E_{\gamma\delta} \partial E_\beta \partial E_\alpha}$
$C_{\gamma\delta,\alpha\beta}$	—	$\dfrac{\partial}{\partial E_{\alpha\beta}}$	$-3\dfrac{\partial^2}{\partial E_{\gamma\delta} \partial E_{\alpha\beta}}$

[a] All derivatives have to be evaluated at zero field and field gradient.

In the same way as the charge distribution in a molecule is influenced by an external electric field it is also modified by the electric field due to other molecules in the neighbourhood. Permanent electric moments of the surrounding molecules induce moments in the molecule leading to a contribution to the intermolecular interaction energy. Since this so-called induction energy is determined by the polarizabilities of the molecules, detailed knowledge of the polarizabilities is also important for the description of intermolecular forces [7].

1.4 Magnetic Multipole Expansion

A dynamic system of charges with charge density $\rho(\vec{r})$ gives rise to a current density $\vec{j}(\vec{r})$ [3, 10]

$$\vec{j}(\vec{r}) = \rho(\vec{r}) \, \vec{v}(\vec{r}) \, , \tag{1.22}$$

where $\vec{v}(\vec{r})$ is the velocity distribution. The vector potential $\vec{A}^{j}(\vec{R})$ due to this current density is given as [11]

$$\vec{A}^{j}(\vec{R}) = \frac{\mu_0}{4\pi} \int_{\tau'} \frac{\vec{j}(\vec{r}\,')}{|\vec{R} - \vec{r}\,'|} \, d\tau' \, . \tag{1.23}$$

Using the Taylor expansion of $\frac{1}{|\vec{R}-\vec{r}\,'|}$ around an origin $\vec{r}_o$ within the charge distribution, equation (1.2), we can write a component of the vector potential [3, 11] as

$$
\begin{aligned}
A^{j}_{\alpha}(\vec{R}) \;=\;& \frac{\mu_0}{4\pi} \, \frac{1}{|\vec{R} - \vec{r}_o|} \int_{\tau'} j_{\alpha}(\vec{r}\,') \, d\tau' \\
&+ \frac{\mu_0}{4\pi} \sum_{\beta} \frac{R_\beta - r_{o,\beta}}{|\vec{R} - \vec{r}_o|^3} \int_{\tau'} j_{\alpha}(\vec{r}\,') \, (r'_\beta - r_{o,\beta}) \, d\tau' \;+\; \dots \, .
\end{aligned}
\tag{1.24}
$$

This can be simplified by using the following relation for an arbitrary function $f(\vec{r}\,')$

$$\int_{\tau'} \left(\vec{\nabla} f(\vec{r}\,') \right) \cdot \vec{j}(\vec{r}\,') \, d\tau' \;=\; 0 \tag{1.25}$$

valid [11] for a steady current distribution ($\vec{\nabla} \cdot \vec{j} = 0$). Chosing $f = r'_\alpha$ showes that the first (monopole) term in Eq. (1.24) vanishes and we will not consider higher terms than the second (dipole) term in accordance with the electric quadrupole approximation. The remaining (dipole) term

$$A^{j}_{\alpha}(\vec{R}) = \frac{\mu_0}{4\pi} \sum_{\beta} \frac{R_\beta - r_{o,\beta}}{|\vec{R} - \vec{r}_o|^3} \int_{\tau'} (r'_\beta - r_{o,\beta}) \, j_{\alpha}(\vec{r}\,') \, d\tau' + \dots \tag{1.26}$$

can also be written in terms of a symmetric and antisymmetric part

$$
\begin{aligned}
A^{j}_{\alpha}(\vec{R}) \;=\;& \frac{\mu_0}{4\pi} \sum_{\beta} \frac{R_\beta - r_{o,\beta}}{|\vec{R} - \vec{r}_o|^3} \frac{1}{2} \left[\int_{\tau'} \left((r'_\beta - r_{o,\beta}) \, j_{\alpha}(\vec{r}\,') + (r'_\alpha - r_{o,\alpha}) \, j_{\beta}(\vec{r}\,') \right) \, d\tau' \right. \\
&\left. + \int_{\tau'} \left((r'_\beta - r_{o,\beta}) \, j_{\alpha}(\vec{r}\,') - (r'_\alpha - r_{o,\alpha}) \, j_{\beta}(\vec{r}\,') \right) \, d\tau' \right] \\
&+ \; \dots \, .
\end{aligned}
\tag{1.27}
$$

Using Eq. (1.25) with $f = (r'_\alpha - r_{o,\alpha})(r'_\beta - r_{o,\beta})$ shows that the first term vanishes and one obtains

$$\vec{A}^j(\vec{R}) = \frac{\mu_0}{4\pi} \frac{1}{2} \int_{\tau'} \left[(\vec{r}\,' - \vec{r}_o) \times \vec{j}(\vec{r}\,') \right] \times \frac{(\vec{R} - \vec{r}_o)}{\mid \vec{R} - \vec{r}_o \mid^3} \, d\tau' + \ldots \tag{1.28}$$

or

$$\vec{A}^j(\vec{R}) = \frac{\mu_0}{4\pi} \, \vec{m}(\vec{r}_o) \times \frac{(\vec{R} - \vec{r}_o)}{\mid \vec{R} - \vec{r}_o \mid^3} + \ldots . \tag{1.29}$$

where the first order magnetic moment $\vec{m}(\vec{r}_o)$, the magnetic dipole moment, is defined as

$$\begin{aligned} \vec{m}(\vec{r}_o) &= \frac{1}{2} \int_{\tau'} d\tau' \, (\vec{r}\,' - \vec{r}_o) \times \vec{j}(\vec{r}\,') \\ &= \frac{1}{2} \int_{\tau'} d\tau' \, \rho(\vec{r}\,')(\vec{r}\,' - \vec{r}_o) \times \vec{v}(\vec{r}\,') . \end{aligned} \tag{1.30}$$

The absence of a zeroth order moment in equation (1.29) reflects that magnetic monopole moments do not exist. Higher magnetic moments are seldomly encountered [12] and are therefore not considered here. Neither do magnetic dipole moments play such an important role as their electric counterparts since most molecules do not posse a permanent magnetic moment. However, nuclei with non zero spin have a magnetic moment and equation (1.29) for their vector potential will be used in the following chapters.

1.5 Potential Energy in an Magnetic Induction

The potential energy of a distribution of charges immersed in an external magnetic induction $\vec{B}$ can be expressed in terms of the magnetic moments analogously to the electric field case in section 1.2. In general, the potential energy W of a current distribution in the presence of an external magnetic induction is given by [13]

$$W = - \int_{\tau'} \vec{j}(\vec{r}\,') \cdot \vec{A}^B(\vec{r}\,') \, d\tau' , \tag{1.31}$$

where $\vec{A}^B(\vec{r}\,')$ is the vector potential associated with the magnetic induction $\vec{B}$,

$$\vec{B}(\vec{r}) = \vec{\nabla} \times \vec{A}(\vec{r}) . \tag{1.32}$$

A simpler expression for the potential energy can be obtained by expanding a component of the vector potential $A_\alpha^B(\vec{r}\,')$ in a Taylor series around an origin $\vec{r}_o$ [14]

$$A_\alpha^B(\vec{r}\,') = A_\alpha^B(\vec{r}_o) + \sum_\beta (r'_\beta - r_{o,\beta}) \left(\frac{\partial A_\alpha^B(\vec{r}\,')}{\partial r'_\beta} \right)_{\vec{r}\,'=\vec{r}_o} + \ldots , \tag{1.33}$$

which leads to

$$
W = -\sum_\alpha A_\alpha^B(\vec{r}_o) \int_{\tau'} j_\alpha(\vec{r}\,') \, d\tau' - \sum_{\alpha\beta} \left(\frac{\partial A_\alpha^B(\vec{r}\,')}{\partial r_\beta'} \right)_{\vec{r}\,'=\vec{r}_o} \int_{\tau'} (r_\beta' - r_{o,\beta}) j_\alpha(\vec{r}\,') \, d\tau'
$$
$$
+ \ldots \tag{1.34}
$$

However, the integral in the first term was shown to vanish in section 1.4 and the second term can again be rewritten (Eq. (1.25)), such that

$$
W = -\sum_{\alpha\beta} \left(\frac{\partial A_\alpha^B(\vec{r}\,')}{\partial r_\beta'} \right)_{\vec{r}\,'=\vec{r}_o} \frac{1}{2} \int_{\tau'} \left[(r_\beta' - r_{o,\beta}) \, j_\alpha(\vec{r}\,') - (r_\alpha' - r_{o,\alpha}) \, j_\beta(\vec{r}\,') \right] \, d\tau'
$$
$$
+ \ldots \tag{1.35}
$$

or in vector notation

$$
W = -\frac{1}{2} \int_{\tau'} \left((\vec{r}\,' - \vec{r}_o) \times \vec{j}(\vec{r}\,') \right) \cdot \left(\vec{\nabla} \times \vec{A}^B(\vec{r}\,') \right)_{\vec{r}\,'=\vec{r}_o} d\tau' + \ldots \tag{1.36}
$$

Using the definition of the magnetic dipole moment given in equation (1.30) and the definition of the vector potential given in equation (1.32) the expansion of the energy can be written as

$$
W = -\sum_\alpha m_\alpha(\vec{r}_o) B_\alpha(\vec{r}_o) \tag{1.37}
$$

From this equation it can be seen that as an alternative to equation (1.30) the magnetic dipole moment can be defined as the derivative of the potential energy with respect to the field induction B_α,

$$
m_\alpha(\vec{r}_o) = -\frac{\partial W}{\partial B_\alpha(\vec{r}_o)} \ . \tag{1.38}
$$

1.6 Induced Magnetic Moments and Magnetizabilies

In the presence of a magnetic induction $\vec{B}$ the energy of the distribution of moving charges changes according to equation (1.37). A polarizable distribution of charges will adjust itself in order to minimize the energy. This leads to a change in the current density and in the moments of the current density, such that an additional current density $\vec{j}^{ind}(\vec{r})$ and magnetic moment $\vec{m}^{ind}$ are induced. An important source of magnetic induction, apart from an external magnetic field, is a neighbouring magnetic moment: in particular the magnetic dipole moment $\vec{m}^K$ of some nucleus K. The magnetic dipole moment $\vec{m}(\vec{B}, \vec{m}^K)$ in the presence of an external magnetic

induction and a nuclear magnetic moment can again be expanded in a Taylor series as [14]

$$
\begin{aligned}
m_\alpha(\vec{B}, \vec{m}^K) &= m_\alpha^{per} + m_\alpha^{ind}(\vec{B}, \vec{m}^K) \\
m_\alpha(\vec{B}, \vec{m}^K) &= m_\alpha^{per} + \sum_\beta \xi_{\alpha\beta} B_\beta - \sum_\beta \sigma_{\beta\alpha}^K m_\beta^K + \; \ldots \; ,
\end{aligned}
\tag{1.39}
$$

where $\xi_{\alpha\beta}$ and $\sigma_{\beta\alpha}^K$ are components of the dipole magnetizability and nuclear magnetic shielding tensor, respectively. The latter is closely related to the chemical shift measured in nuclear magnetic resonance spectroscopy and will be discussed in more detail in section 1.8.

Like in the electric case an expression for the energy can be obtained by first expanding it in a Taylor series

$$
\begin{aligned}
W(\vec{B}, \vec{m}^K) = W^{(0)} &+ \sum_\alpha \left(\frac{\partial W}{\partial B_\alpha} \right) B_\alpha + \frac{1}{2} \sum_{\alpha\beta} \left(\frac{\partial^2 W}{\partial B_\alpha \partial B_\beta} \right) B_\alpha B_\beta \\
&+ \sum_{\alpha\beta} \left(\frac{\partial^2 W}{\partial m_\beta^K \partial B_\alpha} \right) m_\beta^K B_\alpha + \; \ldots \; ,
\end{aligned}
\tag{1.40}
$$

where again the derivatives have to be evaluated at zero magnetic field and zero nuclear magnetic moment. The first derivative of the energy is the magnetic dipole moment, equation (1.38). The permanent magnetic dipole moment $\vec{m}^{per}$ is obtained, if the derivative is evaluated at zero magnetic field. The second derivatives, given in the last column of Table 1.2, can then be calculated as first derivatives of the magnetic dipole moment in the presence of an external magnetic induction or a nuclear magnetic moment, equation (1.39). The magnetizability as well as the nuclear magnetic shielding tensor can therefore also be defined as derivatives of the energy, as was the case for the polarizability and hyperpolarizability tensors.

Substituting for the derivatives in equation (1.40) yields then an expression for the energy of a polarizable charge and current distribution

$$
W(\vec{B}, \vec{m}^K) = W^{(0)} - \sum_\alpha m_\alpha B_\alpha - \frac{1}{2} \sum_{\alpha\beta} \xi_{\alpha\beta} B_\alpha B_\beta + \sum_{\alpha\beta} \sigma_{\beta\alpha}^K m_\beta^K B_\alpha + \; \ldots \; .
\tag{1.41}
$$

1.7 Molecular Electric and Magnetic Fields

In addition to the moments and polarizabilities which have been considered up to now, the electric and magnetic fields arising from a distribution of charges are important for describing various molecular properties.

Knowledge of the electrostatic potential $\phi^\rho(\vec{R})$ due to a distribution of charges, which was given in equation (1.1), is important for the study of intermolecular interactions and reactivity.

Table 1.2 Definitions of various magnetic properties as derivatives[a] of the perturbed energy $W(\vec{B}, \vec{m}^K, \vec{m}^L)$ or as derivatives[a] of components of the perturbed magnetic dipole moment $m_\alpha(\vec{B}, \vec{m}^K)$ and molecular magnetic induction $B_\beta^j(\vec{R}; \vec{B}, \vec{m}^L)$

	$m_\alpha(\vec{B}, \vec{m}^K)$	$B_\beta^j(\vec{R}; \vec{B}, \vec{m}^L)$	$B_\beta^j(\vec{R}_K; \vec{B}, \vec{m}^L)$	$W(\vec{B}, \vec{m}^K, \vec{m}^L)$
m_α^{per}				$-\dfrac{\partial}{\partial B_\alpha}$
$B_\alpha^{j,per}(\vec{R}_K)$				$-\dfrac{\partial}{\partial m_\alpha^K}$
$\xi_{\alpha\beta}$	$\dfrac{\partial}{\partial B_\beta}$	—	—	$-\dfrac{\partial^2}{\partial B_\beta \partial B_\alpha}$
$\sigma_{\beta\alpha}(\vec{R})$	—	$-\dfrac{\partial}{\partial B_\alpha}$	—	—
$\sigma_{\beta\alpha}^K$	$-\dfrac{\partial}{\partial m_\beta^K}$	—	$-\dfrac{\partial}{\partial B_\alpha}$	$\dfrac{\partial^2}{\partial m_\beta^K \partial B_\alpha}$
$K_{\beta\alpha}^L(\vec{R})$	—	$-\dfrac{\partial}{\partial m_\alpha^L}$	—	—
$K_{\beta\alpha}^{KL}$	—	—	$-\dfrac{\partial}{\partial m_\alpha^L}$	$\dfrac{\partial^2}{\partial m_\beta^K \partial m_\alpha^L}$

[a] All derivatives are evaluated at zero magnetic field and zero nuclear magnetic moment. $\xi_{\alpha\beta}$ - magnetizability; $\sigma_{\beta\alpha}(\vec{R})$ - magnetic shielding field; $\sigma_{\beta\alpha}^K$ - nuclear magnetic shielding; $K_{\beta\alpha}^L(\vec{R})$ - reduced spin-spin coupling field; $K_{\beta\alpha}^{KL}$ - reduced spin-spin coupling.

The derivatives of the molecular electrostatic potential are according to equations (1.11) and (1.12) the molecular electric field E_α^ρ and field gradient $E_{\alpha\beta}^\rho$

$$E_\alpha^\rho(\vec{R}) = \frac{1}{4\pi\epsilon_0} \int_{\tau'} \rho(\vec{r}\,')\frac{R_\alpha - r_\alpha'}{|\vec{R} - \vec{r}\,'|^3}\, d\tau' \, , \tag{1.42}$$

$$E_{\alpha\beta}^\rho(\vec{R}) = \frac{1}{4\pi\epsilon_0} \int_{\tau'} \rho(\vec{r}\,') \left[\frac{\delta_{\alpha\beta}}{|\vec{R} - \vec{r}\,'|^3} - 3\frac{(R_\alpha - r_\alpha')(R_\beta - r_\beta')}{|\vec{R} - \vec{r}\,'|^5} \right] \, d\tau' \, . \tag{1.43}$$

The molecular electric field gives rise to a force $\vec{F}$ acting on the charges in the charge distribution, where the contribution to the electric field from the charge in question has to be excluded, of course. For example the force acting on a nucleus K would then be

$$\vec{F}_K = Z_K e E^\rho(\vec{R}_K) \, . \tag{1.44}$$

For a charge distribution in equilibrium this force should obviously be zero. The implications of this is that actual calculations of the forces on the nuclei in molecules

will only give zero if the geometry of the molecule was optimized with the same method.

Although the fields and field gradients within a charge distribution are well defined, it is not possible to measure them at an arbitrary point. Only via an interaction with the nuclei in a molecule it is possible to get information about some of these field quantities. Fields can be probed by dipole moments. However, nuclei do not have electric dipole moments and the molecular electric field can thus not be investigated in this way. However, some nuclei possess an electric quadrupole moment Θ_K and via the interaction with the nuclear electric quadrupole moment one can study the molecular electric field gradient at the positions of the nuclei.

The molecular magnetic induction $\vec{B}^j(\vec{R})$ is obtained by application of equation (1.32) to the expression (1.23) for the vector potential $\vec{A}^j(\vec{R})$ of a current distribution

$$
\begin{aligned}
\vec{B}^j(\vec{R}) &= -\frac{\mu_0}{4\pi} \int_{\tau'} \frac{(\vec{R} - \vec{r}\,') \times \vec{j}(\vec{r}\,')}{|\vec{R} - \vec{r}\,'|^3}\, d\tau' \\
&= -\frac{\mu_0}{4\pi} \int_{\tau'} \rho(\vec{r}\,') \frac{(\vec{R} - \vec{r}\,') \times \vec{v}(\vec{r}\,')}{|\vec{R} - \vec{r}\,'|^3}\, d\tau' \ .
\end{aligned}
\tag{1.45}
$$

Like the molecular electric field it is of course defined everywhere, but only the value at the position of the nuclei can be probed experimentally. The interaction of a nuclear magnetic dipole moment $\vec{m}^K$ with the molecular magnetic induction gives rise to a change in the energy of the distribution of charges

$$
W = -\sum_\alpha m_\alpha^K B_\alpha^j(\vec{R}_K) \ .
\tag{1.46}
$$

Consequently the molecular magnetic induction at the position of some nucleus K can be defined as derivative of the energy of the distribution of charges,

$$
B_\alpha^j(\vec{R}_K) = -\frac{\partial W}{\partial m_\alpha^K} \ ,
\tag{1.47}
$$

with respect to its nuclear magnetic moment $\vec{m}^K$ (see Table 1.2).

1.8 Induced Magnetic Fields and NMR Parameters

In section 1.6 the interaction of a charge distribution with an external magnetic induction, $\vec{B}$, or with a nuclear magnetic moment, $\vec{m}^L$, was shown to lead to an induced current density $\vec{j}^{ind}(\vec{r})$. According to equation (1.45) this also gives rise to an induced molecular magnetic induction $\vec{B}^{j,ind}(\vec{R})$

$$
\begin{aligned}
B_\alpha^j(\vec{R}, \vec{B}, \vec{m}^L) &= B_\alpha^{j,per} + B_\alpha^{j,ind}(\vec{R}, \vec{B}, \vec{m}^L) \\
B_\alpha^j(\vec{R}, \vec{B}, \vec{m}^L) &= B_\alpha^{j,per} - \sum_\beta \sigma_{\alpha\beta}(\vec{R})\, B_\beta - \sum_\beta K_{\alpha\beta}^L(\vec{R})\, m_\beta^L + \ \ldots
\end{aligned}
\tag{1.48}
$$

where $\sigma_{\alpha\beta}(\vec{R})$ is the magnetic shielding tensor field [15] and $K_{\alpha\beta}^{L}(\vec{R})$ could be called a reduced spin-spin coupling tensor field. The precise definitions of both as derivatives of the molecular magnetic induction are also shown in table 1.2.

The value of the magnetic shielding tensor field $\sigma_{\alpha\beta}(\vec{R})$ at the position $\vec{R}_K$ of a nuclear magnetic dipole moment $\vec{m}^K$ is the well known nuclear magnetic shielding tensor $\sigma_{\alpha\beta}^{K} = \sigma_{\alpha\beta}(\vec{R}_K)$. The nuclear magnetic shielding constant $\sigma^K = \frac{1}{3}\sum_{\alpha\beta}\sigma_{\alpha\beta}^{K}$ is closely related to the chemical shift δ of nuclear magnetic resonance (NMR) spectroscopy via [16]

$$\delta = \frac{\sigma^{K,ref} - \sigma^K}{1 - \sigma^{K,ref}} \times 10^6 \approx \left(\sigma^{K,ref} - \sigma^K\right) \times 10^6 \; , \qquad (1.49)$$

where $\sigma^{K,ref}$ is the nuclear magnetic shielding of the same type of nucleus in a reference substance added to the experimental sample. In order to distinguish the nuclear magnetic shielding σ^K from the chemical shift δ it is often also called the absolute nuclear magnetic shielding.

The reduced indirect nuclear spin-spin coupling tensor, $K_{\alpha\beta}^{KL} = K_{\alpha\beta}^{L}(\vec{R}^K)$, is related to the indirect nuclear spin-spin coupling tensor $J_{\alpha\beta}^{KL}$ of NMR spectroscopy by [17]

$$J_{\alpha\beta}^{KL} = \frac{\gamma_K}{2\pi}\frac{\gamma_L}{2\pi}hK_{\alpha\beta}^{KL} \qquad (1.50)$$

where γ_K and γ_L are the gyromagnetic ratios of the two nuclei.

In the absence of permanent molecular magnetic fields, the local magnetic induction $\vec{B}^K = \vec{B}(\vec{R}^K)$ at the position of some nucleus K in an NMR experiment is then

$$B_\alpha^K = B_\alpha(\vec{R}^K, \vec{B}, \vec{m}^L) \;\; = \;\; B_\alpha + B_\alpha^{j,ind}(\vec{R}^K, \vec{B}, \vec{m}^L)$$

$$B_\alpha^K = B_\alpha(\vec{R}^K, \vec{B}, \vec{m}^L) \;\; = \;\; \sum_\beta \left(\delta_{\alpha\beta} - \sigma_{\alpha\beta}^{K}\right)B_\beta - \sum_\beta \frac{2\pi}{\gamma_K}\frac{2\pi}{\gamma_L}\frac{1}{h}J_{\alpha\beta}^{KL}m_\beta^L + \dots \; , \;\; (1.51)$$

where $\delta_{\alpha\beta}$ is the Kronecker δ.

The interaction of the permanent and induced molecular magnetic induction, equation (1.48), with the magnetic moment $\vec{m}^K$ of the nuclei gives according to equation (1.46) additional contributions to the potential energy of a charge distribution in equation (1.41). Following the same procedure as in sections 1.3 and 1.6 one obtains

$$W(\vec{B}, \vec{m}^K, \vec{m}^L) = W^{(0)} - \sum_\alpha m_\alpha^K B_\alpha^{j,per} + \sum_{\alpha\beta}\sigma_{\alpha\beta}^{K}m_\alpha^K B_\beta + \sum_{\alpha\beta}K_{\alpha\beta}^{KL}m_\alpha^K m_\beta^L + \; \dots \; .$$

$$(1.52)$$

The nuclear magnetic shielding $\sigma_{\alpha\beta}^{K}$ and reduced indirect nuclear spin-spin coupling tensors $K_{\alpha\beta}^{KL}$ can thus also be defined as the energy derivatives shown in table 1.2.

1.9 Molecular Rotation as Source for Magnetic Fields

In sections 1.6 and 1.8 it was discussed that an external magnetic induction $\vec{B}$ or the nuclear magnetic moment $\vec{m}^K$ of some nucleus K will lead to an induced current density $\vec{j}^{ind}(\vec{r})$ and thereby to an induced the magnetic moment $\vec{m}^{ind}$ and molecular magnetic induction $\vec{B}^{j,ind}$. Another source for the magnetic induction can be that the charge distribution rotates. A rigidly rotating charge distribution with angular velocity $\vec{\omega} = \boldsymbol{I}^{-1}\,\vec{J}$ will according to equations (1.30) and (1.45) produce a magnetic moment and a molecular magnetic induction

$$\vec{m}_J = \frac{1}{2}\int_{\tau'}\rho(\vec{r}\,')(\vec{r}\,' - \vec{r}_{CM})\times\left[(\vec{r}\,' - \vec{r}_{CM})\times(\boldsymbol{I}^{-1}\,\vec{J})\right]\,d\tau' \qquad (1.53)$$

$$\vec{B}_J^j(\vec{R}) = -\frac{\mu_0}{4\pi}\int_{\tau'}\rho(\vec{r}\,')\frac{(\vec{R}-\vec{r}\,')\times\left[(\vec{r}\,'-\vec{r}_{CM})\times(\boldsymbol{I}^{-1}\,\vec{J})\right]}{\mid\vec{R}-\vec{r}\,'\mid^3}\,d\tau' \qquad (1.54)$$

However, Lamor's theorem states that rotating charges give rise to an magnetic induction $\vec{B}^J$

$$\vec{B}^J = -\frac{2m_e}{e}\boldsymbol{I}^{-1}\,\vec{J} \qquad (1.55)$$

with the associated vector potential

$$\vec{A}^J = -\frac{m_e}{e}\boldsymbol{I}^{-1}\,\vec{J}\times(\vec{r}-\vec{R}_{CM}) \qquad (1.56)$$

This magnetic induction then leads to an induced magnetic moment $\vec{m}_J^{ind}$ and induced molecular magnetic field $\vec{B}_J^{j,ind}$ in addition to the magnetic moment $\vec{m}_J$ and molecular magnetic induction $\vec{B}_J$ of the rotating rigid charge distribution

$$
\begin{aligned}
m_{J,\alpha}(\vec{J}) &= m_{J,\alpha} + m_{J,\alpha}^{ind} \\
m_{J,\alpha}(\vec{J}) &= \frac{\mu_N}{\hbar}g_{J,\alpha\beta}J_\beta \\
B_{J,\alpha}^j(\vec{R},\vec{J}) &= B_{J,\alpha}^{j,per}(\vec{R}) + B_{J,\alpha}^{j,ind}(\vec{R},\vec{J}) \\
B_{J,\alpha}^j(\vec{R},\vec{J}) &= \frac{2\pi}{\mu_N g_K}M_{J,\alpha\beta}(\vec{R})J_\beta
\end{aligned}
\qquad
\begin{aligned}
\\
(1.57)\\
\\
(1.58)
\end{aligned}
$$

where $g_{J,\alpha\beta}$ and $M_{J,\alpha\beta}(\vec{R})$ are components of the rotational g tensor and the spin-rotation tensor field, respectively. The value of $M_{J,\alpha\beta}(\vec{R})$ at the position of a nuclear magnetic moment $\vec{m}^K$ is called the spin-rotation tensor $M_{J,\alpha\beta}^K$.

The energy of this rotational magnetic moment $\vec{m}_J(\vec{J})$ in an external magnetic induction or of a nuclear magnetic moment in the molecular magnetic induction

$\vec{B}_J^j(\vec{R}, \vec{J})$ is

$$W(\vec{B}, \vec{J}) = W^{(0)} - \frac{\mu_N}{\hbar} \sum_{\alpha\beta} g_{J,\alpha\beta} B_\alpha J_\beta \qquad (1.59)$$

$$W(\vec{m}^K, \vec{J}) = W^{(0)} - \frac{2\pi}{\mu_N g_K} \sum_{\alpha\beta} M_{J,\alpha\beta}^K m_\alpha^K J_\beta \qquad (1.60)$$

The components of the rotational g tensor and spin-rotation tensor can therefore be defined as derivatives of the rotational moment and the rotational magnetic induction or as derivatives of the corresponding interaction energies (Table 1.3).

Table 1.3 Definitions of the rotational g tensor $g_{J,\alpha\beta}$ and spin rotation tensor $M_{J,\alpha\beta}^K$ as derivatives[a] of the perturbed energy $W(\vec{B}, \vec{m}^K, \vec{J})$ or as derivatives[a] of components of the perturbed magnetic dipole moment $m_\alpha(\vec{J})$ and molecular magnetic induction $B_\beta^j(\vec{R}; \vec{J})$

	$m_\alpha(\vec{J})$	$B_\alpha^j(\vec{R}; \vec{J})$	$B_\alpha^j(\vec{R}_K; \vec{J})$	$W(\vec{B}, \vec{m}^K, \vec{J})$
$g_{J,\alpha\beta}$	$\dfrac{\hbar}{\mu_N} \dfrac{\partial}{\partial J_\beta}$	—	—	$-\dfrac{\hbar}{\mu_N} \dfrac{\partial^2}{\partial B_\alpha \partial J_\beta}$
$M_{J,\alpha\beta}(\vec{R})$	—	$\dfrac{\mu_N g_K}{2\pi} \dfrac{\partial}{\partial J_\beta}$	—	—
$M_{J,\alpha\beta}^K$	—	—	$\dfrac{\mu_N g_K}{2\pi} \dfrac{\partial}{\partial J_\beta}$	$-\dfrac{\mu_N g_K}{2\pi} \dfrac{\partial^2}{\partial m_\alpha^K \partial J_\beta}$

[a] All derivatives have to be evaluated for zero perturbation.

1.10 Time Dependent Fields

The discussion to this point has been limited to static electric and magnetic fields. However, molecules are often exposed to time-dependent fields, as for example in the interaction with electromagnetic radiation. The incluence of a time-dependent magnetic induction vector $\vec{B}(\vec{r}, t)$ and its associated molecular properties have little physical significance and are therefore usually ignored.

The electric field for a general polychromatic electromagnetic wave with wave vector $\vec{k}$ is given by

$$\vec{E}(\vec{r}, t) = \int_{-\infty}^{\infty} d\omega \vec{E}^\omega \cos(\vec{k} \cdot \vec{r} - \omega t) = \frac{1}{2} \int_{-\infty}^{\infty} d\omega \vec{E}^\omega \left(e^{\imath(\vec{k} \cdot \vec{r} - \omega t)} + e^{-\imath(\vec{k} \cdot \vec{r} - \omega t)} \right) \quad (1.61)$$

The expansion of the perturbation dependent electric dipole moment in equation

(1.18) generalizes then to [7]

$$
\begin{aligned}
\mu_\alpha(\vec{E}(t)) &= \mu_\alpha + \mu_\alpha^{ind}(\vec{E}(t)) \\
\mu_\alpha(\vec{E}(t)) &= \mu_\alpha + \sum_\beta \int_{-\infty}^{\infty} d\omega_1 \; \alpha_{\alpha\beta}(-\omega_1;\omega_1) E_\beta^{\omega_1} \cos(\vec{k}\cdot\vec{r}_o - \omega_1 t) \\
&\quad + \frac{1}{2}\sum_{\beta\gamma}\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \; \beta_{\alpha\beta\gamma}(-\omega_1-\omega_2;\omega_1,\omega_2) \\
&\qquad\qquad E_\beta^{\omega_1}\cos(\vec{k}\cdot\vec{r}_o - \omega_1 t) E_\gamma^{\omega_2}\cos(\vec{k}\cdot\vec{r}_o - \omega_2 t) \\
&\quad + \quad \ldots
\end{aligned}
\tag{1.62}
$$

where $\alpha_{\alpha\beta}(-\omega_1;\omega_1)$ and $\beta_{\alpha\beta\gamma}(-\omega_1-\omega_2;\omega_1,\omega_2)$ are components of the frequency dependent electric dipole polarizability and first hyperpolarizability tensors, respectively.

1.11 Exercises

1) Derive the two derivatives

$$\frac{\partial}{\partial r'_\alpha} \frac{1}{\mid \vec{R} - \vec{r}\,' \mid}$$

$$\frac{\partial^2}{\partial r'_\alpha \partial r'_\beta} \frac{1}{\mid \vec{R} - \vec{r}\,' \mid}$$

used in the derivation of equation (1.8).

2) Show that the dipole moment of an ion and the quadrupole moment of a neutral but polar molecule depend on the origin $\vec{r}_o$.

3) Show that the contribution of the second-order electric moment $\frac{1}{2}\sum_{\alpha\beta} Q_{\alpha\beta}(\vec{r}_o)E_{\alpha\beta}(\vec{r}_o)$ to the interaction energy in equation (1.14) is unchanged if an arbitrary constant C is added to the diagonal elements $Q_{\alpha\alpha}$ of the second-order electric moment.

4) Show that equations (1.14) and (1.15) are equivalent.

5) Derive equation (1.25) from the divergence theorem for a bounding surface S' that completely encloses the current distribution

$$\int_{\tau'} \vec{\nabla} \cdot \left(f(\vec{r}\,')\vec{j}(\vec{r}\,') \right) \; d\tau' \;=\; \oint f(\vec{r}\,')\vec{j}(\vec{r}\,') \cdot d\vec{S}' \;=\; 0$$

6) Prove that

$$\int_{\tau'} j_\alpha(\vec{r}\,') \; d\tau' = 0$$

and

$$\int_{\tau'} \left((r'_\beta - r_{o,\beta}) \, j_\alpha(\vec{r}\,') + (r'_\alpha - r_{o,\alpha}) \, j_\beta(\vec{r}\,') \right) \; d\tau' = 0$$

7) Derive the expression (1.43) for the electric field gradient.

8) Derive the expression (1.45) for the molecular magnetic induction.

Chapter 2

Exact Quantum Mechanical Expressions

Molecular properties were defined in the previous chapter as derivatives of the classical interaction energy of a system with respect to electric and magnetic fields and nuclear moments. Quantum mechanical expression for these properties will now be derived. Since the properties are defined as energy derivatives, it is necessary to find a quantum mechanical expression for the energy of the system in the presence of a perturbing field.

A complete quantum mechanical treatment would involve quantum electrodynamics and so a number of initial simplifications are required. First, only the molecular electronic structure is treated quantum mechanically. The perturbing fields and nuclear moments are considered to be unaffected by the molecular environment, the so-called minimal coupling approximation. Secondly, the exposition will be restricted to non-relativistic quantum mechanics, *i.e.* to the Schrödinger equation. However, electron spin perturbations, which can only be derived from a relativistic standpoint, can also be treated by including *ad hoc* spin operators, derived from the Dirac equation, in the Schrödinger Hamiltonian. Finally, the Born-Oppenheimer approximation is applied, yielding a field free electronic Schrödinger equation

$$\hat{H}^{(0)}\Psi_n^{(0)} = W_n^{(0)}\Psi_n^{(0)} \tag{2.1}$$

where $\Psi_n^{(0)}$ is the many-electron wavefunction for state n with electronic energy $W_n^{(0)}$ and the molecular field free electronic Hamiltonian is defined as

$$\hat{H}^{(0)} = \frac{1}{2m_e}\sum_i \hat{\vec{p}}_i^{\,2} - \frac{e^2}{4\pi\epsilon_0}\sum_{iK}\frac{Z_K}{|\vec{r}_i - \vec{R}_K|} + \frac{e^2}{4\pi\epsilon_0}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|} \tag{2.2}$$

Only the electronic contributions to the molecular properties will be obtained from this treatment. Contributions of the fixed nuclei have to be added afterwards according to the classical expressions given in the chapter 1.

2.1 Minimal Coupling - Non Relativistically

The usual way to treat the interaction between electromagnetic fields or nuclear electromagnetic moments and molecules is a semi-classical way, where the fields or nuclear moments are treated classically and the electrons are treated by quantum mechanics. The fields or nuclear moments are thus not part of the system, which is treated quantum mechanically, but they are merely considered to be perturbations which do not respond to the presence of the molecule. They enter therefore the molecular Hamiltonian in terms of external potentials similar to the coloumb potential due to the charges of the nuclei.

The common approach [18] to the derivation of the additional terms in the molecular Hamiltonian is to find the classical Lagrangian [19, 20] for the motion of a charged particle in the presence of electromagnetic fields. From this Lagrangian one can then define a classical Hamiltonian, which converted to operator form yields the desired Hamiltonian operator. We start therefore from the classical expression for the force $\vec{F}$ of an electromagnetic field on a particle with charge q and mass m, *i.e.* the Lorentz force [21]

$$\vec{F}(\vec{r}, t) = m \frac{d\vec{v}}{dt} = q \left(\vec{E}(\vec{r}, t) + \vec{v} \times \vec{B}(\vec{r}, t) \right) \ , \tag{2.3}$$

where $\vec{v} = \frac{d\vec{r}}{dt}$ is the velocity of the particle. Since we want to derive an Hamiltonian operator for the motion of an electron in external fields, we will in the following set $m = m_e$ and $q = -e$, where m_e is the mass of the electron and e is the elementary charge.

Generalizing the definitions of the scalar, $\phi^E(\vec{r}, t)$, and the vector potential, $\vec{A}^B(\vec{r}, t)$, in equations (1.11) and (1.32) to the time dependent case [22]

$$\vec{E}(\vec{r}, t) \ = \ -\vec{\nabla}\phi^E(\vec{r}, t) - \frac{\partial \vec{A}^B(\vec{r}, t)}{\partial t} \tag{2.4}$$

$$\vec{B}(\vec{r}, t) \ = \ \vec{\nabla} \times \vec{A}^B(\vec{r}, t) \ , \tag{2.5}$$

the Lorentz force can alternatively be expressed in terms of the potentials as

$$\vec{F} = -e \left(-\vec{\nabla}\phi^E(\vec{r}, t) - \frac{\partial \vec{A}^B(\vec{r}, t)}{\partial t} + \vec{v} \times \left(\vec{\nabla} \times \vec{A}^B(\vec{r}, t) \right) \right) \ . \tag{2.6}$$

We now have to find a Lagrangian L [19, 20]

$$L(\vec{r}, \vec{v}, t) = T - U \ , \tag{2.7}$$

where $T = \frac{1}{2m_e}(m_e\vec{v})^2$ is the kinetic energy and U is a generalized potential. The latter has to be chosen in such a way that on application of Langrange's equations of motion

$$\frac{d}{dt}\left[\frac{\partial L}{\partial v_\alpha} \right] - \frac{\partial L}{\partial r_\alpha} = 0 \tag{2.8}$$

the equation (2.6) for the Lorentz force is recovered. Chosing the generalized potential U as

$$U(\vec{r}, \vec{v}, t) = -e\ \phi^E(\vec{r}, t) + e\ \vec{v} \cdot \vec{A}^B(\vec{r}, t) \tag{2.9}$$

yields a Lagrangian L

$$L(\vec{r}, \vec{v}, t) = \frac{(m_e \vec{v})^2}{2} + e\ \phi^E(\vec{r}, t) - e\ \vec{v} \cdot \vec{A}^B(\vec{r}, t) \ , \tag{2.10}$$

which fulfills this condition.

The classical Hamiltonian [19, 20] is then defined as

$$H = \vec{p} \cdot \vec{v} - L \tag{2.11}$$

where the canonical momentum $\vec{p}$, the canonical conjugate to $\vec{r}$, is given as

$$p_\alpha = \frac{\partial L(\vec{r}, \vec{v}, t)}{\partial v_\alpha} \ . \tag{2.12}$$

For the Lagrangian in equation (2.10) this definition yields

$$\vec{p} = m_e\ \vec{v} - e\vec{A}^B \ , \tag{2.13}$$

and the classical Hamiltonian reads then

$$H = \frac{m_e\ \vec{v} \cdot \vec{v}}{2} - e\ \phi^E(\vec{r}, t) \ . \tag{2.14}$$

However, in order to use the usual substitution rule

$$\vec{p} \to \hat{\vec{p}} = -\imath\hbar\hat{\vec{\nabla}} \tag{2.15}$$

for the transition to quantum mechanics, the classical Hamiltonian has to be expressed in terms of the canonical momentum $\vec{p}$, equation (2.13), instead of in terms of the so-called kinematical or mechanical momentum $\vec{\pi}$

$$\vec{\pi} = m_e\ \vec{v}\ = \vec{p} + e\ \vec{A}^B \ , \tag{2.16}$$

leading to

$$H = \frac{1}{2m_e} \left(\vec{p} + e\vec{A}^B \right)^2 - e\ \phi^E \ . \tag{2.17}$$

Applying the substitution rule, equation (2.15), the classical Hamiltonian can now be translated to a quantum mechanical Hamiltonian operator $\hat{H}$ for a single particle

$$\hat{H} = \frac{1}{2m_e} \left(\hat{\vec{p}} + e\ \hat{\vec{A}}^B \right)^2 - e\ \hat{\phi}^E \ . \tag{2.18}$$

In Coulomb gauge, $\vec{\nabla} \cdot \vec{A}^B = 0$, this can then be written as

$$\hat{H} = \frac{1}{2m_e}\ \hat{\vec{p}}^{\ 2} + \frac{1}{m_e}\ e\ \hat{\vec{A}}^B \cdot \hat{\vec{p}} + \frac{1}{2m_e}\ q^2 (\hat{\vec{A}}^B)^2 - e\ \hat{\phi}^E \ . \tag{2.19}$$

This is a non-relativistic, Schrödinger, Hamiltonian for a single, spin-less particle. In section 2.4 it will be generalized to the case of many particles, electrons and nuclei.

2.2 Minimal Coupling - Relativistically

Electrons have spin and one should use a Hamiltonian operator fulfilling the requirements of special relativity. This so called Dirac Hamiltonian operator for a single particle in the presence of an electromagnetic field can be derived in the same ways as the non-relativistic analog in the previous section [18].

The Lorentz force in equation (2.6) is unchanged, but Newton's second law

$$\vec{F} = \frac{d}{dt}(m_e^r \vec{v}) \tag{2.20}$$

is changed due to the velocity dependence of the relativistic mass m_e^r

$$m_e^r = \frac{m_e}{\sqrt{1 - \frac{v^2}{c^2}}} \ , \tag{2.21}$$

where m_e is the rest mass.

The corresponding Lagrangian can be shown to be

$$L(\vec{r}, \vec{v}, t) = -m_e \ c^2 \sqrt{1 - \frac{v^2}{c^2}} + e \ \phi^E(\vec{r}, t) - e \ \vec{v} \cdot \vec{A}^B(\vec{r}, t) \ , \tag{2.22}$$

and we obtain

$$p_\alpha = \frac{\partial L(\vec{r}, \vec{v}, t)}{\partial v_\alpha} = \frac{m_e \ v_\alpha}{\sqrt{1 - \frac{v^2}{c^2}}} - e \ A_\alpha^B \tag{2.23}$$

for the canonical momentum. The classical Hamiltonian reads then

$$H = \frac{m_e \ c^2}{\sqrt{1 - \frac{v^2}{c^2}}} - e \ \phi^E(\vec{r}, t) \ , \tag{2.24}$$

or in terms of the canonical momentum

$$H = \sqrt{m_e^2 c^4 + (\vec{p} + e \ \vec{A}^B)^2 c^2} - e \ \phi^E(\vec{r}, t) \ . \tag{2.25}$$

Because of the square root, it is not possible to make the transition to quantum mechanics. Instead of, we can square and rearrange the equation

$$\frac{1}{c^2}(H + e \ \phi^E)^2 - m_e^2 c^2 - (\vec{p} + e \ \vec{A}^B)^2 = 0 \tag{2.26}$$

which can also be written as

$$\pi_0^2 - m_e^2 c^2 - \sum_{\mu=1}^{3} \pi_\mu^2 = 0 \ , \tag{2.27}$$

if we make use of the definition of the 4-vector analog of the mechanical momentum

$$\pi_0 = \frac{1}{c}(H + e\ \phi^E) \tag{2.28}$$

$$\pi_\mu = p_\mu + e\ A_\mu^B , \tag{2.29}$$

where μ can be $1(= x), 2(= y), 3(= z)$. The Dirac equation can now be obtained by "factorizing" equation (2.27)

$$\left(\pi_0 + \sum_{\mu=1}^{3} \boldsymbol{\alpha}_\mu \pi_\mu + \boldsymbol{\beta}\ m_e\ c\right)\left(\pi_0 - \sum_{\mu=1}^{3} \boldsymbol{\alpha}_\mu \pi_\mu - \boldsymbol{\beta}\ m_e\ c\right) = 0 , \tag{2.30}$$

applying the substitution rule

$$H \to \hat{H} = \imath\hbar\frac{\partial}{\partial t} \tag{2.31}$$

in addition to equation (2.15) and using the second term in an eigenvalue equation for the wavefunction

$$\left(\hat{\pi}_0 - \sum_{\mu=1}^{3} \boldsymbol{\alpha}_\mu \hat{\pi}_\mu - \boldsymbol{\beta}\ m_e\ c\right)\psi = 0 . \tag{2.32}$$

The Dirac equation can be rearranged in order to facilitate the comparison with the non-relativistic Schrödinger Hamiltonian operator in equation (2.19)

$$\left(c\sum_{\mu=1}^{3} \boldsymbol{\alpha}_\mu(\hat{p}_\mu + e\ \hat{A}_\mu^B) - e\ \hat{\phi}^E + \boldsymbol{\beta}\ m_e\ c^2\right)\psi = \imath\hbar\frac{\partial}{\partial t}\ \psi . \tag{2.33}$$

The $\boldsymbol{\alpha}'s$ have to fulfill the conditions

$$\boldsymbol{\alpha}_\mu^2 = 1 , \tag{2.34}$$

$$\boldsymbol{\alpha}_\mu \boldsymbol{\alpha}_\nu + \boldsymbol{\alpha}_\nu \boldsymbol{\alpha}_\mu = 0 \quad \text{for } \mu \neq \nu \tag{2.35}$$

(with $\boldsymbol{\alpha}_4 = \boldsymbol{\beta}$) in order for equations (2.27) and (2.30) to be identically. It turns out that the simplest solution to these equations are a set of 4×4 matrices defined as

$$\boldsymbol{\alpha}_4 = \boldsymbol{\beta} = \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{I} \end{pmatrix} , \qquad \boldsymbol{\alpha}_\mu = \begin{pmatrix} \boldsymbol{0} & \boldsymbol{\sigma}_\mu \\ \boldsymbol{\sigma}_\mu & \boldsymbol{0} \end{pmatrix} , \tag{2.36}$$

where $\boldsymbol{I}$ is a 2×2 unit matrix and the $\boldsymbol{\sigma}_\mu$ are the Pauli spin matrices

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \qquad \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix} , \qquad \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \tag{2.37}$$

The wavefunction ψ consists therefore of four components

$$\psi = \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} , \tag{2.38}$$

called a four-component spinor and the Dirac equation is actually a set of four coupled differential equations that couple the four components of the wavefunction. Substituting equation (2.36) for the $\boldsymbol{\alpha}$ matrices and (2.38) for four-component wavefunction, the Dirac equation can be written as two coupled two-component equations

$$c \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e \, \hat{A}_\mu^B) \right) \psi_S + \left(-e \, \hat{\phi}^E + m_e \, c^2 \right) \psi_L = \imath\hbar \frac{\partial}{\partial t} \, \psi_L \tag{2.39}$$

$$c \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e \, \hat{A}_\mu^B) \right) \psi_L + \left(-e \, \hat{\phi}^E - m_e \, c^2 \right) \psi_S = \imath\hbar \frac{\partial}{\partial t} \, \psi_S . \tag{2.40}$$

2.3 Elimination of the Small Component

We could continue now with the Dirac equation and derive expressions for the molecular properties using standard perturbation theory. However, as stated earlier, the exposition in these notes is restricted basically to a non-relativistic treatment with the exception that we want to include also interactions with the spin of the electrons. The appropriate operator can be found be a reduction of the Dirac equation to a non-relativistic two-component form, which can be achieved by several approaches [23]. Here we want to discuss only the simplest approach, the so-called elimination of the small component [24].

We assume that A_μ is time independent and collect the time dependence of the wavefunction in a phase factor

$$\psi = \bar{\psi}(\vec{r}) \, e^{-\imath E t/\hbar} , \tag{2.41}$$

which implies that ψ is an eigenfunction of $\imath\hbar \frac{\partial}{\partial t}$ with eigenvalue E. Inserting this wavefunction in equations (2.39) and (2.40) and rearranging we obtain

$$c \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e \, \hat{A}_\mu^B) \right) \bar{\psi}_S = \left(E + e \, \hat{\phi}^E - m_e \, c^2 \right) \bar{\psi}_L \tag{2.42}$$

$$c \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e \, \hat{A}_\mu^B) \right) \bar{\psi}_L = \left(E + e \, \hat{\phi}^E + m_e \, c^2 \right) \bar{\psi}_S . \tag{2.43}$$

From equation (2.43) we can see that the small component of the wavefunction $\bar{\psi}_S$ can be expressed in terms of the large component as

$$\bar{\psi}_S = \frac{c}{E + e \, \hat{\phi}^E + m_e \, c^2} \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e \, \hat{A}_\mu^B) \right) \bar{\psi}_L . \tag{2.44}$$

Inserting this expression in equation (2.42) we obtain a single two component equation for the large component

$$\left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e\,\hat{A}_\mu^B)\right) \frac{c^2}{E + e\,\hat{\phi}^E + m_e\,c^2} \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e\,\hat{A}_\mu^B)\right) \bar{\psi}_L$$
$$= \left(E + e\,\hat{\phi}^E - m_e\,c^2\right) \bar{\psi}_L \; . \qquad (2.45)$$

This equation together with the expression for the small component in (2.44) is still the Dirac equation. In order to reduce it to a non-relativistic expression we have to expand $\frac{c^2}{E + e\,\hat{\phi}^E + m_e\,c^2}$ as

$$\frac{c^2}{E + e\,\hat{\phi}^E + m_e\,c^2} = \frac{1}{2\,m_e} \left(\frac{1}{1 + \frac{E^{NR} + e\,\hat{\phi}^E}{2\,m_e\,c^2}} \right)$$
$$= \frac{1}{2\,m_e} \left(1 - \frac{E^{NR} + e\,\hat{\phi}^E}{2\,m_e\,c^2} + \dots \right) , \qquad (2.46)$$

where we have introduce $E^{NR} = E - m_e\,c^2$ and assumed that $E \approx m_e\,c^2$ as well as that $|-e\,\phi^E| \ll m_e\,c^2$. Using only the first term, the equation for the large component reads

$$\frac{1}{2\,m_e} \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e\,\hat{A}_\mu^B)\right) \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu (\hat{p}_\mu + e\,\hat{A}_\mu^B)\right) \bar{\psi}_L = \left(E^{NR} + e\,\hat{\phi}^E\right) \bar{\psi}_L \; . \quad (2.47)$$

Using a relation valid for the Pauli spin matrices and two general vector operators $\hat{\vec{O}}_1$ and $\hat{\vec{O}}_2$

$$\left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu \hat{A}_\mu\right) \left(\sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu \hat{B}_\mu\right) = \sum_{\mu=1}^{3} \hat{A}_\mu \hat{B}_\mu + \imath \sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu \left(\hat{\vec{A}} \times \hat{\vec{B}}\right)_\mu , \qquad (2.48)$$

we finally obtain the non-relativistic Schrödinger-Pauli equation

$$\left(\frac{1}{2\,m_e} (\hat{\vec{p}} + e\,\hat{\vec{A}}^B)^2 + \frac{e\,\hbar}{2\,m_e} \sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu \left(\hat{\vec{\nabla}} \times \hat{\vec{A}}^B\right)_\mu - e\,\hat{\phi}^E\right) \bar{\psi}_L = E^{NR} \bar{\psi}_L \; . \qquad (2.49)$$

On comparision with the Schrödinger Hamiltonian in equation (2.18) we can identify the additional term due to the interaction of the electron spin with a magnetic field, a so-called Zeeman term

$$\hat{H}^{Zeeman} = \frac{e\,\hbar}{2\,m_e} \sum_{\mu=1}^{3} \boldsymbol{\sigma}_\mu \left(\hat{\vec{\nabla}} \times \hat{\vec{A}}^B\right)_\mu \qquad (2.50)$$

The electron spin operator $\hat{\vec{s}}$ in units of Js is related to the Pauli spin matrices $\vec{\sigma}$ by

$$\hat{\vec{s}} = \frac{\hbar}{2}\,\vec{\sigma}\;,\tag{2.51}$$

and the electron spin Zeeman operator becomes therefore

$$\hat{H}^{Zeeman} = \frac{2\,e}{2\,m_e}\,\hat{\vec{s}}\cdot\left(\hat{\vec{\nabla}}\times\hat{\vec{A}}^{\vec{B}}\right)\;.\tag{2.52}$$

However, from quantum electrodynamics we know that this should be written as

$$\hat{H}^{Zeeman} = \frac{g_e\,e}{2\,m_e}\,\hat{\vec{s}}\cdot\left(\hat{\vec{\nabla}}\times\hat{\vec{A}}^{\vec{B}}\right)\;,\tag{2.53}$$

where $g_e \approx 2.002$ is the electron g-factor.

2.4 The Molecular Electronic Hamiltonian

In the last three sections it was shown that in the minimal coupling approximation the vector potential enters the mechanical momentum of electron i

$$m_e\hat{\vec{v}}_i = \hat{\vec{p}}_i + e\hat{\vec{A}}(\vec{r}_i)\tag{2.54}$$

and a scalar potential, $-e\phi(\vec{r}_i)$, is added to the electronic Hamiltonian, yielding

$$\hat{H} = \frac{1}{2m_e}\sum_i\left(\hat{\vec{p}}_i + e\hat{\vec{A}}(\vec{r}_i)\right)^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{iK}\frac{Z_K}{|\vec{r}_i - \vec{R}_K|} + \frac{e^2}{4\pi\epsilon_0}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_i e\hat{\phi}(\vec{r}_i)\;.\tag{2.55}$$

In addition, electron spin is introduced via the Zeeman term of the Pauli Hamiltonian, equation (2.53),

$$\hat{H} = \sum_i\frac{g_e e}{2m_e}\hat{\vec{s}}_i\cdot\left(\hat{\vec{\nabla}}\times\hat{\vec{A}}(\vec{r}_i)\right)\;.\tag{2.56}$$

In the Coulomb gauge, *i.e.* $\vec{\nabla}\cdot\vec{A} = 0$, the Hamiltonian operator can thus be written as

$$\begin{aligned}
\hat{H} &= \hat{H}^{(0)} + \hat{H}^{(1)} + \hat{H}^{(2)}\\
&= \sum_i\hat{h}^{(0)}(i) + \sum_{i<j}\hat{g}(i,j) + \sum_i\left(\hat{h}^{(1)}(i) + \hat{h}^{(2)}(i)\right)\\
&= \frac{1}{2m_e}\sum_i\hat{\vec{p}}_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{iK}\frac{Z_K}{|\vec{r}_i - \vec{R}_K|} + \frac{e^2}{4\pi\epsilon_0}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|}\\
&\quad + \frac{e}{m_e}\sum_i\hat{\vec{A}}(\vec{r}_i)\cdot\hat{\vec{p}}_i + \frac{g_e e}{2m_e}\sum_i\hat{\vec{s}}_i\cdot\left(\hat{\vec{\nabla}}\times\hat{\vec{A}}(\vec{r}_i)\right) - e\sum_i\hat{\phi}(\vec{r}_i)\\
&\quad + \frac{e^2}{2m_e}\sum_i\hat{\vec{A}}^2(\vec{r}_i)\;.
\end{aligned}\tag{2.57}$$

$\hat{H}$ is the full electronic Hamiltonian operator for a molecule in an electromagnetic field, subject to the approximations outlined earlier. $\hat{H}^{(0)}$ is the unperturbed Hamiltonian from equation (2.2), $\hat{H}^{(1)}$ includes all operators linear in the perturbing field (first order) and $\hat{H}^{(2)}$ all quadratic terms (second order).

In the following we will derive explicit forms for the perturbing operators by expressing the scalar and vector potentials in terms of the electric and magnetic fields. The scalar potential of a electric field with non-zero gradient is, Eq. (1.8),

$$\hat{\phi}^E(\vec{r}_i) = - (\vec{r}_i - \vec{R}_O) \cdot E(\vec{r}_i) \tag{2.58}$$
$$- \frac{1}{2} \sum_{\alpha\beta} \left((r_{i,\alpha} - R_{O,\alpha})(r_{i,\beta} - R_{O,\beta}) - \frac{1}{3}\delta_{\alpha\beta}(\vec{r}_i - \vec{R}_O)^2 \right) E_{\alpha\beta}(\vec{r}_i) \ ,$$

where the scalar potential at the origin of the coordinate system, $\phi^E(\vec{R}_O)$ is set to zero. For the vector potential we want to consider a uniform magnetic induction

$$\vec{\hat{A}}^B(\vec{r}_i) = \frac{1}{2}\vec{B} \times (\vec{r}_i - \vec{R}_{GO}) \ , \tag{2.59}$$

where $\vec{R}_{GO}$ is the arbitrary gauge origin; the magnetic induction due to the rotation of a molecule, Eq. (1.56),

$$\vec{\hat{A}}^J(\vec{r}_i) = -\frac{m_e}{e}\left(\boldsymbol{I}^{-1}\ \vec{J} \right) \times (\vec{r}_i - \vec{R}_{CM}) \ ; \tag{2.60}$$

and the magnetic dipole moment of nucleus K, equation (1.29),

$$\vec{\hat{A}}^K(\vec{r}_i) = \frac{\mu_0}{4\pi}\vec{m}^K \times \frac{\vec{r}_i - \vec{R}_K}{\mid \vec{r}_i - \vec{R}_K \mid^3} \ , \tag{2.61}$$

whose magnetic induction is

$$\vec{B}^K(\vec{r}_i) = \frac{\mu_0}{4\pi}\left(\frac{3\left(\vec{m}^K \cdot (\vec{r}_i - \vec{R}_K) \right)(\vec{r}_i - \vec{R}_K)}{\mid \vec{r}_i - \vec{R}_K \mid^5} - \frac{\vec{m}^K}{\mid \vec{r}_i - \vec{R}_K \mid^3} \right)$$
$$+ \frac{\mu_0}{4\pi}\frac{8\pi}{3}\delta(\vec{r}_i - \vec{R}_K)\vec{m}^K \ . \tag{2.62}$$

After some manipulation, we obtain the following expressions for the first and second-order Hamiltonians :

$$\hat{H}^{(1)} = - \sum_{\alpha}\left(\hat{O}^{lB}_{\alpha} + \hat{O}^{sB}_{\alpha} \right) B_{\alpha} \ + \ \sum_{\alpha}\left(\hat{O}^{lJ}_{\alpha} + \hat{O}^{sJ}_{\alpha} \right)(\boldsymbol{I}^{-1}\ \vec{J})_{\alpha} \tag{2.63}$$
$$- \sum_{K}\sum_{\alpha}\left(\hat{O}^{lm^K}_{\alpha} + \hat{O}^{sm^K}_{\alpha} \right) m^K_{\alpha} \ - \ \sum_{\alpha}\hat{O}^E_{\alpha}\ E_{\alpha} \ - \ \sum_{\alpha\beta}\hat{O}^{\nabla E}_{\alpha\beta}\ E_{\alpha\beta}$$

$$\hat{H}^{(2)} = \sum_{\alpha\beta} \hat{O}^{BB}_{\alpha\beta} \, B_\alpha B_\beta \; + \; \sum_{\alpha\beta} \hat{O}^{JJ}_{\alpha\beta} \, (\boldsymbol{I}^{-1}\vec{J})_\alpha (\boldsymbol{I}^{-1}\vec{J})_\beta \; + \; \sum_{KL}\sum_{\alpha\beta} \hat{O}^{m^K m^L}_{\alpha\beta} \, m^K_\alpha m^L_\beta \quad (2.64)$$

$$+ \; \sum_{\alpha\beta} \hat{O}^{BJ}_{\alpha\beta} \, B_\alpha (\boldsymbol{I}^{-1} \, \vec{J})_\beta \; + \; \sum_K \sum_{\alpha\beta} \hat{O}^{m^K B}_{\alpha\beta} \, m^K_\alpha B_\beta \; + \; \sum_K \sum_{\alpha\beta} \hat{O}^{m^K J}_{\alpha\beta} \, m^K_\alpha (\boldsymbol{I}^{-1} \, \vec{J})_\beta$$

The interaction operators $\hat{O}$ are thereby defined as

$$\hat{O}^{lB}_\alpha \; = \; \sum_i \hat{o}^{lB}_\alpha(i) = -\frac{e}{2m_e} \sum_i \left((\vec{r}_i - \vec{R}_{GO}) \times \hat{\vec{p}}_i \right)_\alpha \qquad (2.65)$$

$$\hat{O}^{sB}_\alpha \; = \; \sum_i \hat{o}^{sB}_\alpha(i) = -\frac{g_e e}{2m_e} \sum_i \hat{s}_{i,\alpha} \qquad (2.66)$$

$$\hat{O}^{lJ}_\alpha \; = \; \sum_i \hat{o}^{lJ}_\alpha(i) = \frac{2m_e}{e} \, \hat{O}^{lB}_\alpha \qquad (2.67)$$

$$\hat{O}^{sJ}_\alpha \; = \; \sum_i \hat{o}^{sJ}_\alpha(i) = \frac{2m_e}{e} \, \hat{O}^{sB}_\alpha \qquad (2.68)$$

$$\hat{O}^{lm^K}_\alpha \; = \; \sum_i \hat{o}^{lm^K}_\alpha(i) = -\frac{e}{m_e}\frac{\mu_0}{4\pi} \sum_i \left(\frac{\vec{r}_i - \vec{R}_K}{|\, \vec{r}_i - \vec{R}_K\,|^3} \times \hat{\vec{p}}_i \right)_\alpha \qquad (2.69)$$

$$\hat{O}^{sm^K}_\alpha \; = \; \sum_i \hat{o}^{sm^K}_\alpha(i) = -\frac{g_e e}{2m_e}\frac{\mu_0}{4\pi}\frac{8\pi}{3} \sum_i \delta(\vec{r}_i - \vec{R}_K)\hat{s}_{i,\alpha} \qquad (2.70)$$

$$-\frac{g_e e}{2m_e}\frac{\mu_0}{4\pi} \sum_i \left(\frac{\left(\hat{\vec{s}}_i \cdot (\vec{r}_i - \vec{R}_K)\right)(r_{i,\alpha} - R_{K,\alpha})}{|\, \vec{r}_i - \vec{R}_K\,|^5} - \frac{\hat{s}_{i,\alpha}}{|\, \vec{r}_i - \vec{R}_K\,|^3} \right)$$

$$\hat{O}^E_\alpha \; = \; \sum_i \hat{o}^E_\alpha(i) = -e \sum_i (r_{i,\alpha} - R_{O,\alpha}) \qquad (2.71)$$

$$\hat{O}^{\nabla E}_{\alpha\beta} = \sum_i \hat{o}^{\nabla E}_{\alpha\beta}(i)$$

$$= -\frac{e}{2} \sum_i \left((r_{i,\alpha} - R_{O,\alpha})(r_{i,\beta} - R_{O,\beta}) - \frac{1}{3}\delta_{\alpha\beta}(\vec{r}_i - \vec{R}_O)^2 \right) \qquad (2.72)$$

$$\hat{O}^{BB}_{\alpha\beta} = \sum_i \hat{o}^{BB}_{\alpha\beta}(i)$$

$$= \frac{e^2}{8m_e} \sum_i \left((\vec{r}_i - \vec{R}_{GO})^2 \delta_{\alpha\beta} - (r_{i,\alpha} - R_{GO,\alpha})(r_{i,\beta} - R_{GO,\beta}) \right) \qquad (2.73)$$

$$
\begin{aligned}
\hat{O}^{JJ}_{\alpha\beta} &= \sum_i \hat{o}^{JJ}_{\alpha\beta}(i) \\
&= \frac{m_e}{2} \sum_i \left((\vec{r}_i - \vec{R}_{CM})^2 \delta_{\alpha\beta} - (r_{i,\alpha} - R_{CM,\alpha})(r_{i,\beta} - R_{CM,\beta}) \right) \quad (2.74)
\end{aligned}
$$

$$
\begin{aligned}
\hat{O}^{m^K m^L}_{\alpha\beta} &= \sum_i \hat{o}^{m^K m^L}_{\alpha\beta}(i) = \frac{e^2}{2m_e} \left(\frac{\mu_0}{4\pi} \right)^2 \sum_i \left(\frac{(\vec{r}_i - \vec{R}_L)}{\mid \vec{r}_i - \vec{R}_L \mid^3} \cdot \frac{(\vec{r}_i - \vec{R}_K)}{\mid \vec{r}_i - \vec{R}_K \mid^3} \delta_{\alpha\beta} \right. \\
&\quad \left. - \frac{(r_{i,\alpha} - R_{L,\alpha})}{\mid \vec{r}_i - \vec{R}_L \mid^3} \frac{(r_{i,\beta} - R_{K,\beta})}{\mid \vec{r}_i - \vec{R}_K \mid^3} \right) \quad (2.75)
\end{aligned}
$$

$$
\begin{aligned}
\hat{O}^{BJ}_{\alpha\beta} &= \sum_i \hat{o}^{BJ}_{\alpha\beta}(i) = -\frac{e}{2} \sum_i \left((\vec{r}_i - \vec{R}_{CM}) \cdot (\vec{r}_i - \vec{R}_{GO}) \delta_{\alpha\beta} \right. \\
&\quad \left. -(r_{i,\alpha} - R_{CM,\alpha})(r_{i,\beta} - R_{GO,\beta}) \right) \quad (2.76)
\end{aligned}
$$

$$
\begin{aligned}
\hat{O}^{m^K B}_{\alpha\beta} &= \sum_i \hat{o}^{m^K B}_{\alpha\beta}(i) = \frac{e^2}{2m_e} \frac{\mu_0}{4\pi} \sum_i \left((\vec{r}_i - \vec{R}_{GO}) \cdot \frac{(\vec{r}_i - \vec{R}_K)}{\mid \vec{r}_i - \vec{R}_K \mid^3} \delta_{\alpha\beta} \right. \\
&\quad \left. - (r_{i,\alpha} - R_{GO,\alpha}) \frac{(r_{i,\beta} - R_{K,\beta})}{\mid \vec{r}_i - \vec{R}_K \mid^3} \right) \quad (2.77)
\end{aligned}
$$

$$
\begin{aligned}
\hat{O}^{m^K J}_{\alpha\beta} &= \sum_i \hat{o}^{m^K J}_{\alpha\beta}(i) = -e \frac{\mu_0}{4\pi} \sum_i \left((\vec{r}_i - \vec{R}_{CM}) \cdot \frac{(\vec{r}_i - \vec{R}_K)}{\mid \vec{r}_i - \vec{R}_K \mid^3} \delta_{\alpha\beta} \right. \\
&\quad \left. - (r_{i,\alpha} - R_{CM,\alpha}) \frac{(r_{i,\beta} - R_{K,\beta})}{\mid \vec{r}_i - \vec{R}_K \mid^3} \right) \quad (2.78)
\end{aligned}
$$

2.5 Rayleigh-Schrödinger Perturbation Theory

In chapter 1 we defined electronic contributions to molecular properties as derivatives of the electronic energy. In order to take derivatives we need to determine the energy of a system described by the Hamiltonian given in equation (2.57). In general, however, it is not possible to find exact solutions for this Hamiltonian, *i.e.* to solve the Schrödinger equation

$$
\hat{H} \Psi_0 = W_0 \Psi_0 \ . \quad (2.79)
$$

Instead, perturbation or variational methods must be applied to approximate wave-functions.

In non-degenerate Rayleigh-Schrödinger perturbation theory one assumes that exact energies and wavefunctions of the unperturbed Hamiltonian $\hat{H}^{(0)}$ are known,

i.e. that equation (2.1) has been solved exactly, and that the energies and wavefunctions of the total Hamiltonian, equation (2.57), can be expanded in a series using the exact solutions of the unperturbed Hamiltonian, $W_n^{(0)}$ and $\Psi_n^{(0)}$, as zeroth order energies and wavefunctions

$$W_0 = W_0^{(0)} + W_0^{(1)} + W_0^{(2)} + \cdots \tag{2.80}$$

$$\Psi_0 = \Psi_0^{(0)} + \Psi_0^{(1)} + \Psi_0^{(2)} + \cdots \ . \tag{2.81}$$

First and second-order corrections to the energy are then given as

$$W_0^{(1)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle \tag{2.82}$$

$$W_0^{(2)} = \langle \Psi_0^{(0)} | \hat{H}^{(2)} | \Psi_0^{(0)} \rangle + \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle \ . \tag{2.83}$$

Expanding the first-order wavefunction in the complete set of unperturbed wavefunctions $\{\Psi_n^{(0)}\}$

$$| \Psi_0^{(1)} \rangle = \sum_{n \neq 0} | \Psi_n^{(0)} \rangle \frac{\langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}} \ , \tag{2.84}$$

the second-order correction to the energy becomes

$$W_0^{(2)} = \langle \Psi_0^{(0)} | \hat{H}^{(2)} | \Psi_0^{(0)} \rangle + \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}} \ . \tag{2.85}$$

The second order energy correction consists thus of two terms : a ground state expectation value over the second order Hamiltonian $\hat{H}^{(2)}$ and a so-called sum-over-states term, which involves a summation over all excited states of the system and transition moments between the ground state and these excited states with the first order Hamiltonian $\hat{H}^{(1)}$.

Substituting for the first and second-order Hamiltonians, equations (2.63) and (2.64), in the first and second-order energy corrections, equations (2.82) and (2.85), we are ready to obtain expressions for the molecular properties. Either we take the derivatives of W_0 given in equations (1.16), (1.17), (1.38), (1.47) and tables 1.1 - 1.3, or we compare the expressions for the first and second-order energy corrections with the classical expressions for the interaction energies as given in equations (1.21), (1.41), (1.52), (1.59) and (1.60).

Using both approaches, the first-order molecular properties are then given as

$$\mu_\alpha^{el}(\vec{R}_O) = \langle \Psi_0^{(0)} | \hat{O}_\alpha^E | \Psi_0^{(0)} \rangle \tag{2.86}$$

$$\Theta_{\alpha\beta}^{el}(\vec{R}_O) = 3\langle \Psi_0^{(0)} | \hat{O}_{\alpha\beta}^{\nabla E} | \Psi_0^{(0)} \rangle \tag{2.87}$$

$$m_\alpha^{el}(\vec{R}_{GO}) = \langle \Psi_0^{(0)} | \hat{O}_\alpha^{lB} + \hat{O}_\alpha^{sB} | \Psi_0^{(0)} \rangle \tag{2.88}$$

$$B_\alpha^{j,el}(\vec{R}_K) = \langle \Psi_0^{(0)} | \hat{O}_\alpha^{lm^K} + \hat{O}_\alpha^{sm^K} | \Psi_0^{(0)} \rangle \tag{2.89}$$

and the second order molecular properties are given as

$$P^{(2)} = f_1 \langle \Psi_0^{(0)} | \hat{O}_1 | \Psi_0^{(0)} \rangle \; + \; f_2 \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{O}_2 | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}_3 | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}}$$

$$+ \; f_2 \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{O}_3 | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}_2 | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}} \; , \quad (2.90)$$

where the operators $\hat{O}_1$, $\hat{O}_2$ and $\hat{O}_3$ and the factors f_1 and f_2 are collected in table 2.1.

Table 2.1 Operators and factors for the exact second-order Rayleigh-Schrödinger perturbation theory expressions for molecular properties. See equation (2.90).

$P^{(2)}$	f_1	$\hat{O}_1$	f_2	$\hat{O}_2$	$\hat{O}_3$
$\alpha_{\alpha\beta}^{el}$			-1	$\hat{O}_\alpha^E$	$\hat{O}_\beta^E$
$\alpha_{\alpha\beta}^{el}$			-1	$\hat{O}_\alpha^E$	$\hat{O}_\beta^E$
$A_{\alpha,\beta\gamma}^{el}(\vec{R}_O)$			-3	$\hat{O}_\alpha^E$	$\hat{O}_{\beta\gamma}^{\nabla E}$
$C_{\alpha\beta,\gamma\delta}^{el}(\vec{R}_O)$			-3	$\hat{O}_{\alpha\beta}^{\nabla E}$	$\hat{O}_{\beta\gamma}^{\nabla E}$
$\xi_{\alpha\beta}^{el}(\vec{R}_{GO})$	-2	$\hat{O}_{\alpha\beta}^{BB}$	-1	$\hat{O}_\alpha^{lB}$	$\hat{O}_\beta^{lB}$
$\sigma_{\alpha\beta}^{K,el}(\vec{R}_{GO})$	1	$\hat{O}_{\alpha\beta}^{m^K B}$	1	$\hat{O}_\alpha^{lm^K} + \hat{O}_\alpha^{sm^K}$	$\hat{O}_\beta^{lB}$
$K_{\alpha\beta}^{KL,el}$	2	$\hat{O}_{\alpha\beta}^{m^K m^L}$	1	$\hat{O}_\alpha^{lm^K} + \hat{O}_\alpha^{sm^K}$	$\hat{O}_\beta^{lm^L} + \hat{O}_\beta^{sm^L}$
$g_{J,\alpha\beta}^{ind}(\vec{R}_{GO})$	$-\dfrac{\hbar}{\mu_N}$	$(\boldsymbol{\hat{O}}^{BJ}\boldsymbol{I}^{-1})_{\alpha\beta}$	$\dfrac{\hbar}{\mu_N}$	$\hat{O}_\alpha^{lB}$	$(\hat{\vec{O}}^{lJ}\boldsymbol{I}^{-1})_\beta$
$M_{J,\alpha\beta}^{K,ind}$	$-\dfrac{\mu_N g_K}{2\pi}$	$(\boldsymbol{\hat{O}}^{m^K J}\boldsymbol{I}^{-1})_{\alpha\beta}$	$\dfrac{\mu_N g_K}{2\pi}$	$\hat{O}_\alpha^{lm^K} + \hat{O}_\alpha^{sm^K}$	$(\hat{\vec{O}}^{lJ}\boldsymbol{I}^{-1})_\beta$

From Table 2.1 we can see that the second order magnetic properties, *i.e.* the magnetizability tensor $\boldsymbol{\xi}$, nuclear magnetic shielding tensor $\boldsymbol{\sigma}^K$, reduced nuclear spin-spin coupling tensor $\boldsymbol{K}^{KL}$, rotational g tensor $\boldsymbol{g}_J^{ind}$ and spin rotation tensor $\boldsymbol{M}_J^{K,ind}$, consist of a sum-over-states term and a contribution from the second order Hamiltonian operator $\hat{H}^{(2)}$ in equation (2.64). The latter is in general called the *diamagnetic* contribution to the properties, with the exception of the spin-spin coupling constants, where it is called the *orbital diamagnetic* or *diamagnetic spin-orbit* term. On the other hand, the sum-over-states terms are called the *paramagnetic* terms.

Since non-degenerate perturbation theory is used, the ground state $\Psi_0^{(0)}$ was assumed to be a singlet state and to have no orbital degeneracies. This implies that

$$\langle \Psi_0^{(0)} | \hat{O}_\alpha^{sB} | \Psi_0^{(0)} \rangle = \langle \Psi_0^{(0)} | \hat{O}_\alpha^{sm^K} | \Psi_0^{(0)} \rangle = \langle \Psi_0^{(0)} | \hat{O}_\alpha^{sB} | \Psi_n^{(0)} \rangle = 0 \qquad (2.91)$$

and

$$\langle \Psi_0^{(0)} | \hat{O}_\alpha^{lB} | \Psi_0^{(0)} \rangle = \langle \Psi_0^{(0)} | \hat{O}_\alpha^{lm^K} | \Psi_0^{(0)} \rangle = 0 \quad . \tag{2.92}$$

The corresponding terms are therefore not included in table 2.1 and the permanent magnetic dipole moment, equation (2.88), as well as the permanent molecular magnetic induction, equation (2.89), are zero. The expressions for the molecular magnetic properties are thus only valid for the case of closed shell molecules.

For all the operators $\hat{O}_2$ and $\hat{O}_3$, which do not contain the electron spin operator $\hat{\vec{s}}_i$, the exited states $\Psi_n^{(0)}$ in equation (2.90) have the same spin state as the ground state $\Psi_0^{(0)}$, *i.e.* they are singlet states, whereas for the operator $\hat{O}_\alpha^{sm^K}$ the exited states $\Psi_n^{(0)}$ have to be triplet states. This implies that the operator $\hat{O}_2 = \hat{O}_\alpha^{sm^K}$ does not contribute to the nuclear magnetic shielding tensor $\sigma_{\alpha\beta}^K$ and to the spin rotation tensor $M_{J,\alpha\beta}^{K,ind}$. Furthermore only two of the possible four sum-over-states contributions to the spin-spin coupling tensor $K_{\alpha\beta}^{KL}$ exist. The term with $\hat{O}_2 = \hat{O}_\alpha^{lm^K}$ and $\hat{O}_3 = \hat{O}_\beta^{lm^K}$ is called the *orbital paramagnetic* or *paramagnetic spin-orbit* term. As $\vec{O}_\alpha^{sm^K}$, equation (2.70), consists of two operators we obtain three more sum-over-states contributions to the spin-spin coupling tensor from $\hat{O}_2 = \hat{O}_\alpha^{sm^K}$ and $\hat{O}_3 = \hat{O}_\beta^{sm^K}$. The are called the *Fermi contact*, *spin-dipolar* and *Fermi contact - spin-dipolar cross* terms. However, the trace of the latter is zero and it will therefore not contribute to the spin-spin coupling constant.

2.6 Static Response Theory

It was shown in chapter 1 that molecular properties like the polarizability can also be defined as derivatives of the corresponding perturbation dependent multipole moments. One therefore needs to find quantum mechanical operators for the perturbation dependent electric and magnetic multipole moments and the molecular magnetic induction. These can be obtained by application of the Hellmann-Feynman theorem, which states, that for a hermitian operator $\hat{H}(\lambda)$ depending on a real parameter λ with normalized eigenfunctions $\Psi_n(\lambda)$,

$$\langle \Psi_n(\lambda) | \Psi_n(\lambda) \rangle = 1 \quad , \tag{2.93}$$

and eigenvalue $W_n(\lambda)$,

$$\hat{H}(\lambda) \Psi_n(\lambda) = W_n(\lambda) \Psi_n(\lambda) \quad , \tag{2.94}$$

the derivative of the eigenvalue $W_n(\lambda)$ with respect to λ is given as

$$\frac{\partial}{\partial \lambda} W_n(\lambda) = \langle \Psi_n(\lambda) | \frac{\partial}{\partial \lambda} \hat{H}(\lambda) | \Psi_n(\lambda) \rangle \quad . \tag{2.95}$$

In the derivation of the Hellmann-Feynman theorem it is used that

$$
\begin{aligned}
\langle \frac{\partial}{\partial \lambda} \Psi_n(\lambda) \,|\, \hat{H}(\lambda) \,|\, \Psi_n(\lambda) \rangle &+ \langle \Psi_n(\lambda) \,|\, \hat{H}(\lambda) \,|\, \frac{\partial}{\partial \lambda} \Psi_n(\lambda) \rangle \\
&= W_n(\lambda) \left\{ \langle \frac{\partial}{\partial \lambda} \Psi_n(\lambda) \,|\, \Psi_n(\lambda) \rangle + \langle \Psi_n(\lambda) \,|\, \frac{\partial}{\partial \lambda} \Psi_n(\lambda) \rangle \right\} \quad (2.96) \\
&= W_n(\lambda) \, \frac{\partial}{\partial \lambda} \langle \Psi_n(\lambda) \,|\, \Psi_n(\lambda) \rangle \;=\; 0 \;\; ,
\end{aligned}
$$

which is a consequence of the normalization of the eigenfunctions $\Psi_n(\lambda)$ for all values of λ.

Expressions for perturbation dependent operators [12, 14] of the electronic contribution to the electric dipole and quadrupole moment, the magnetic dipole moment and the molecular magnetic induction can therefore be obtained by taking the appropriate derivatives, as given in equations (1.16), (1.17), (1.38) and (1.47), of the Hamiltonian in equation (2.57). This leads to

$$
\hat{\mu}_\alpha^{el} \;=\; \hat{O}_\alpha^E \tag{2.97}
$$

$$
\hat{\Theta}_{\alpha\beta}^{el} \;=\; 3\hat{O}_{\alpha\beta}^{\nabla E} \tag{2.98}
$$

$$
\hat{m}_\alpha^{el} \;=\; \hat{O}_\alpha^{lB} + \hat{O}_\alpha^{sB} - 2\,\hat{O}_{\alpha\beta}^{BB} B_\beta - \hat{O}_{\alpha\beta}^{BJ}(\boldsymbol{I}^{-1}\,\vec{J})_\beta - \sum_K \hat{O}_{\beta\alpha}^{m^K B} m_\beta^K \tag{2.99}
$$

$$
\hat{B}_\alpha^j(\vec{R}_K) \;=\; \hat{O}_\alpha^{lm^K} + \hat{O}_\alpha^{sm^K} - \hat{O}_{\alpha\beta}^{m^K B} B_\beta - \hat{O}_{\alpha\beta}^{m^K J}(\boldsymbol{I}^{-1}\,\vec{J})_\beta - \sum_L \hat{O}_{\beta\alpha}^{m^K m^L} m_\beta^L \;\; . \tag{2.100}
$$

Having thus defined operators which are valid in the presence of external and internal perturbations, one can proceed by evaluating expectation values of these operators with the perturbed wavefunctions in equation (2.81)

$$
\langle \Psi_0 \,|\, \hat{O} \,|\, \Psi_0 \rangle = \langle \Psi_0^{(0)} \,|\, \hat{O} \,|\, \Psi_0^{(0)} \rangle + \langle \Psi_0^{(1)} \,|\, \hat{O} \,|\, \Psi_0^{(0)} \rangle + \langle \Psi_0^{(0)} \,|\, \hat{O} \,|\, \Psi_0^{(1)} \rangle + \cdots \quad . \tag{2.101}
$$

The molecular properties are obtained by taking derivatives of the expectation value, as given in tables 1.1, 1.2 and 1.3, or by comparison with the classical expression for the perturbation dependent moments and fields in equations (1.18), 1.19, (1.39) and (1.48). One should note that molecular properties like the polarizability, which were called second order properties in the context of the Rayleigh-Schrödinger perturbation theory described in section 2.5, are named linear response functions here and in the following section. For exact states the expressions obtained in the previous section for the molecular properties, equation (2.90) and table 2.1, can be recovered from equation (2.101) by insertion of the first order correction to the wavefunction, equation (2.84).

This so-called response theory approach can be generalized to the case of time and thus frequency dependent perturbations which will be discussed in the following section.

2.7 Time Dependent Response Theory

When dealing with time dependent fields one has to find solutions to the time dependent Schrödinger equation

$$\imath\hbar\frac{\partial}{\partial t}\Psi_0(t) = \left(\hat{H}^{(0)} + \hat{H}^{(1)}(t)\right)\Psi_0(t) \quad, \tag{2.102}$$

where the time dependent Hamiltonian $\hat{H}^{(1)}(t)$ can be written as

$$\hat{H}^{(1)}(t) = \hat{V}_{\alpha\ldots}F(t)_{\alpha\ldots} \quad, \tag{2.103}$$

or can be expressed in terms of its Fourier components

$$\hat{H}^{(1)}(t) = \int_{-\infty}^{\infty} d\omega \ \hat{H}^{(1)}(\omega) = \int_{-\infty}^{\infty} d\omega \ \hat{V}_{\alpha\ldots}^{\omega}F(\omega)_{\alpha\ldots} \ e^{-\imath\omega t} \quad. \tag{2.104}$$

The operator $\hat{V}_{\alpha\ldots}$ may depend on coordinates and moment of the electrons but is independent of time, whereas the time dependent field $F(t)_{\alpha\ldots}$ does not depend on the electrons. The subscript $\alpha\cdots$ denotes components of a tensor of appropriate rank.

In time dependent response theory, as described by Zubarev [25], properties are evaluated as expectation values. The time dependent expectation value of an operator $\hat{O}$ is thus formally expanded in a series

$$\langle\Psi_0(t)\,|\,\hat{O}\,|\,\Psi_0(t)\rangle = \langle\Psi_0^{(0)}\,|\,\hat{O}\,|\,\Psi_0^{(0)}\rangle + \int_{-\infty}^{\infty} dt' \ \langle\langle\hat{O}^t;\hat{V}_{\alpha\ldots}^{t'}\rangle\rangle F(t')_{\alpha\ldots} \tag{2.105}$$

$$+ \frac{1}{2}\int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' \ \langle\langle\hat{O}^t;\hat{V}_{\alpha\ldots}^{t'},\hat{V}_{\beta\ldots}^{t''}\rangle\rangle F(t')_{\alpha\ldots} \ F(t'')_{\beta\ldots} + \cdots \quad,$$

where $\hat{O}^t = e^{\imath\hat{H}^{(0)}t/\hbar}\hat{O}e^{-\imath\hat{H}^{(0)}t/\hbar}$ denotes the interaction representation [26] of operator $\hat{O}$. The kernels of the integrals are the linear $\langle\langle\hat{O}^t;\hat{V}_{\alpha\ldots}^{t'}\rangle\rangle$ and quadratic response function $\langle\langle\hat{O}^t;\hat{V}_{\alpha\ldots}^{t'},\hat{V}_{\beta\ldots}^{t''}\rangle\rangle$ in the time domain. The linear response function is also called the polarization propagator. Alternatively, by Fourier transforming the response functions to the frequency or energy domain, the expansion can be written as

$$\langle\Psi_0(t)\,|\,\hat{O}\,|\,\Psi_0(t)\rangle = \langle\Psi_0^{(0)}\,|\,\hat{O}\,|\,\Psi_0^{(0)}\rangle + \int_{-\infty}^{\infty} d\omega_1 \ e^{-\imath\omega_1 t}\langle\langle\hat{O};\hat{V}_{\alpha\ldots}^{\omega_1}\rangle\rangle_{\omega_1}F(\omega_1)_{\alpha\ldots} \tag{2.106}$$

$$+ \frac{1}{2}\int_{-\infty}^{\infty} d\omega_1 \ e^{-\imath\omega_1 t} \int_{-\infty}^{\infty} d\omega_2 \ e^{-\imath\omega_2 t}\langle\langle\hat{O};\hat{V}_{\alpha\ldots}^{\omega_1},\hat{V}_{\beta\ldots}^{\omega_2}\rangle\rangle_{\omega_1,\omega_2}F(\omega_1)_{\alpha\ldots}F(\omega_2)_{\beta\ldots} + \cdots \quad.$$

In order to obtain expressions for the response functions in equation (2.105) we have to insert an expansion of the time dependent wavefunction $\Psi_0(t)$ in terms of the eigenfunctions of the unperturbed Hamiltonian $\hat{H}^{(0)}$ in the time dependent

expectation value $\langle \Psi_0(t) \mid \hat{O} \mid \Psi_0(t) \rangle$. There exist many different but equivalent approaches [25, 27, 28, 29, 30] for the derivation of the time dependent wavefunction.

Here we want to make use of the interaction representation [26] of the time dependent wavefunction

$$\Psi_0^t(t) = e^{\imath \hat{H}^{(0)} t / \hbar} \Psi_0(t) \quad . \tag{2.107}$$

We begin by taking the time derivative $\imath \hbar \frac{\partial}{\partial t}$ of $\Psi_0^t(t)$

$$\imath \hbar \frac{\partial}{\partial t} \Psi_0^t(t) = -\hat{H}^{(0)} e^{\imath \hat{H}^{(0)} t / \hbar} \Psi_0(t) + e^{\imath \hat{H}^{(0)} t / \hbar} \imath \hbar \frac{\partial}{\partial t} \Psi_0(t) \tag{2.108}$$

and inserting the time dependent Schrödinger equation, (2.102), in the second term. This leads to an equation of motion for $\Psi_0^t(t)$

$$\imath \hbar \frac{\partial}{\partial t} \Psi_0^t(t) = \hat{H}^{(1),t}(t) \, \Psi_0^t(t) \quad . \tag{2.109}$$

The time dependent wavefunction $\Psi_0^t(t)$ in the interaction picture is then obtained by integration

$$\Psi_0^t(t) - \Psi_0^t(-\infty) = \frac{1}{\imath \hbar} \int_{-\infty}^{t} \hat{H}^{(1),t'}(t') \, \Psi_0^{t'}(t') \, dt' \quad , \tag{2.110}$$

where $\Psi_0^t(-\infty) = \Psi_0^{(0)}$ is the eigenfunction of the unperturbed Hamiltonian and the time dependent wavefunction $\Psi_0(t)$ in the normal Schrödinger picture is given as

$$\Psi_0(t) = e^{-\imath \hat{H}^{(0)} t / \hbar} \Psi_0^{(0)} + \frac{1}{\imath \hbar} \int_{-\infty}^{t} e^{-\imath \hat{H}^{(0)} (t-t') / \hbar} \hat{H}^{(1)}(t') \, \Psi_0(t') \, dt' \quad . \tag{2.111}$$

However, this equation has to be solved iteratively. In the first iteration, we set $\Psi_0(t')$ in the integral equal to the time dependent solution $e^{-\imath \hat{H}^{(0)} t' / \hbar} \Psi_0^{(0)}$ of the unperturbed Hamiltonian and obtain thereby an perturbation expansion of the time dependent wavefunction

$$\Psi_0(t) = \Psi_0^{(0)}(t) + \Psi_0^{(1)}(t) + \cdots \tag{2.112}$$

with

$$\Psi_0^{(0)}(t) = e^{-\imath \hat{H}^{(0)} t / \hbar} \Psi_0^{(0)} \tag{2.113}$$

$$\Psi_0^{(1)}(t) = e^{-\imath \hat{H}^{(0)} t / \hbar} \frac{1}{\imath \hbar} \int_{-\infty}^{t} \hat{H}^{(1),t'}(t') \, \Psi_0^{(0)} \, dt' \quad . \tag{2.114}$$

We can now insert the expansion of the time dependent wavefunction, equation

(2.112), in the time dependent expectation value

$$
\begin{aligned}
\langle \Psi_0(t) \,|\, \hat{O} \,|\, \Psi_0(t) \rangle & \\
&= \langle \Psi_0^{(0)} \,|\, \hat{O} \,|\, \Psi_0^{(0)} \rangle + \langle \Psi_0^{(0)}(t) \,|\, \hat{O} \,|\, \Psi_0^{(1)}(t) \rangle + \langle \Psi_0^{(1)}(t) \,|\, \hat{O} \,|\, \Psi_0^{(0)}(t) \rangle + \cdots \\
&= \langle \Psi_0^{(0)} \,|\, \hat{O} \,|\, \Psi_0^{(0)} \rangle + \frac{1}{\imath\hbar} \int_{-\infty}^{t} dt' \, \langle \Psi_0^{(0)}(t) \,|\, \hat{O} e^{-\imath \hat{H}^{(0)} t/\hbar} \hat{H}^{(1),t'}(t') \,|\, \Psi_0^{(0)} \rangle \\
&\qquad - \frac{1}{\imath\hbar} \int_{-\infty}^{t} dt' \, \langle \Psi_0^{(0)} \,|\, \hat{H}^{(1),t'}(t') \, e^{\imath \hat{H}^{(0)} t/\hbar} \hat{O} \,|\, \Psi_0^{(0)}(t) \rangle + \cdots \\
&= \langle \Psi_0^{(0)} \,|\, \hat{O} \,|\, \Psi_0^{(0)} \rangle + \frac{1}{\imath\hbar} \int_{-\infty}^{t} dt' \, \langle \Psi_0^{(0)} \,|\, \left[\hat{O}^t, \hat{H}^{(1),t'}(t') \right] \,|\, \Psi_0^{(0)} \rangle + \cdots \quad . \quad (2.115)
\end{aligned}
$$

The integration limit can be extended to ∞, if we introduce the Heaviside step function $\Theta(t)$, which is equal to 1 for $t > 0$ and zero for $t < 0$, yielding

$$
\begin{aligned}
\langle \Psi_0(t) \,|\, \hat{O} \,|\, \Psi_0(t) \rangle &= \langle \Psi_0^{(0)} \,|\, \hat{O} \,|\, \Psi_0^{(0)} \rangle & (2.116) \\
&+ \frac{1}{\imath\hbar} \int_{-\infty}^{\infty} dt' \, \Theta(t-t') \, \langle \Psi_0^{(0)} \,|\, \left[\hat{O}^t, \hat{H}^{(1),t'}(t') \right] \,|\, \Psi_0^{(0)} \rangle + \cdots \quad .
\end{aligned}
$$

Comparison of this equation with the formal expansion in equation (2.105) shows that the linear response function or polarization propagator in the time domain is given as

$$
\langle\langle \hat{O}^t ; \hat{V}_{\alpha\cdots}^{t'} \rangle\rangle = \Theta(t-t') \frac{1}{\imath\hbar} \langle \Psi_0^{(0)} \,|\, \left[\hat{O}^t, \hat{V}_{\alpha\cdots}^{t'} \right] \,|\, \Psi_0^{(0)} \rangle \quad . \quad (2.117)
$$

By Fourier transformation to the frequency domain (exercise 2.10) one obtains a spectral representation of the linear response function or polarization propagator

$$
\langle\langle \hat{O} ; \hat{V}_{\alpha\cdots}^{\omega_1} \rangle\rangle_{\omega_1} = \sum_{n \neq 0} \left\{ \frac{\langle \Psi_0^{(0)} \,|\, \hat{O} \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{V}_{\alpha\cdots}^{\omega_1} \,|\, \Psi_0^{(0)} \rangle}{\hbar\omega_1 + W_0^{(0)} - W_n^{(0)}} \right.
$$
$$
\left. + \frac{\langle \Psi_0^{(0)} \,|\, \hat{V}_{\alpha\cdots}^{\omega_1} \,|\, \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \,|\, \hat{O} \,|\, \Psi_0^{(0)} \rangle}{-\hbar\omega_1 + W_0^{(0)} - W_n^{(0)}} \right\} \quad . \quad (2.118)
$$

In order to derive expressions for the quadratic response function we have to iterate once more on equation (2.111). Setting $\Psi_0(t')$ in the integral in equation (2.111) equal to $\Psi_0^{(0)}(t') + \Psi_0^{(1)}(t')$ we obtain

$$
\Psi_0^{(2)}(t) = e^{-\imath \hat{H}^{(0)} t/\hbar} \left(\frac{1}{\imath\hbar} \right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \, \hat{H}^{(1),t'}(t') \, \hat{H}^{(1),t''}(t'') \, \Psi_0^{(0)} \quad . \quad (2.119)
$$

for the second order correction to the the time dependent wavefunction, equation (2.112). The next, *i.e.* quadratic, term in the expansion of the time dependent expectation value, equation (2.115), becomes then

$$
\left(\frac{1}{\imath\hbar} \right)^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \, \langle \Psi_0^{(0)} \,|\, \left[\left[\hat{O}^t, \hat{H}^{(1),t'}(t') \right], \hat{H}^{(1),t''}(t'') \right] \,|\, \Psi_0^{(0)} \rangle \quad (2.120)
$$

or

$$\left(\frac{1}{\imath\hbar}\right)^2 \int_{-\infty}^{\infty} dt' \, \Theta(t-t') \int_{-\infty}^{\infty} dt'' \, \Theta(t'-t'') \, \langle \Psi_0^{(0)} | \left[\left[\hat{O}^t, \hat{H}^{(1),t'}(t')\right], \hat{H}^{(1),t''}(t'')\right] | \Psi_0^{(0)} \rangle \tag{2.121}$$

using the Heaviside step function and extending the integration limits. Comparison with the formal expansion in equation (2.105) shows that the quadratic response function is thus given as

$$\langle\langle \hat{O}^t; \hat{V}_{\alpha\cdots}^{t'}, \hat{V}_{\beta\cdots}^{t''} \rangle\rangle = \Theta(t-t')\Theta(t'-t'') \left(\frac{1}{\imath\hbar}\right)^2 \langle \Psi_0^{(0)} | \left[\left[\hat{O}^t, \hat{V}_{\alpha\cdots}^{t'}\right], \hat{V}_{\beta\cdots}^{t''}\right] | \Psi_0^{(0)} \rangle \tag{2.122}$$

in the time domain and as

$$\langle\langle \hat{O}; V_{\alpha\cdots}^{\omega_1}, V_{\beta\cdots}^{\omega_2} \rangle\rangle_{\omega_1',\omega_2'}$$

$$= \sum_{n\neq 0, m\neq 0} \left\{ \frac{\langle \Psi_0^{(0)} | \hat{O} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \overline{\hat{V}_{\alpha\cdots}^{\omega_1}} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{V}_{\beta\cdots}^{\omega_2} | \Psi_0^{(0)} \rangle}{\left(W_n^{(0)} - W_0^{(0)} - \hbar(\omega_1'+\omega_2')\right)\left(W_m^{(0)} - W_0^{(0)} - \hbar\omega_2'\right)} \right.$$

$$+ \frac{\langle \Psi_0^{(0)} | \hat{O} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \overline{\hat{V}_{\alpha\cdots}^{\omega_2}} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{V}_{\beta\cdots}^{\omega_1} | \Psi_0^{(0)} \rangle}{\left(W_n^{(0)} - W_0^{(0)} - \hbar(\omega_1'+\omega_2')\right)\left(W_m^{(0)} - W_0^{(0)} - \hbar\omega_1'\right)}$$

$$+ \frac{\langle \Psi_0^{(0)} | \hat{V}_{\beta\cdots}^{\omega_1} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \overline{\hat{O}} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{V}_{\alpha\cdots}^{\omega_2} | \Psi_0^{(0)} \rangle}{\left(W_n^{(0)} - W_0^{(0)} + \hbar\omega_1'\right)\left(W_m^{(0)} - W_0^{(0)} - \hbar\omega_2'\right)}$$

$$+ \frac{\langle \Psi_0^{(0)} | \hat{V}_{\alpha\cdots}^{\omega_2} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \overline{\hat{O}} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{V}_{\beta\cdots}^{\omega_1} | \Psi_0^{(0)} \rangle}{\left(W_n^{(0)} - W_0^{(0)} + \hbar\omega_2'\right)\left(W_m^{(0)} - W_0^{(0)} - \hbar\omega_1'\right)}$$

$$+ \frac{\langle \Psi_0^{(0)} | \hat{V}_{\alpha\cdots}^{\omega_2} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \overline{\hat{V}_{\beta\cdots}^{\omega_1}} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{O} | \Psi_0^{(0)} \rangle}{\left(W_n^{(0)} - W_0^{(0)} + \hbar\omega_2'\right)\left(W_m^{(0)} - W_0^{(0)} + \hbar(\omega_1'+\omega_2')\right)}$$

$$+ \left. \frac{\langle \Psi_0^{(0)} | \hat{V}_{\alpha\cdots}^{\omega_1} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \overline{\hat{V}_{\beta\cdots}^{\omega_2}} | \Psi_m^{(0)} \rangle \langle \Psi_m^{(0)} | \hat{O} | \Psi_0^{(0)} \rangle}{\left(W_n^{(0)} - W_0^{(0)} + \hbar\omega_1'\right)\left(W_m^{(0)} - W_0^{(0)} + \hbar(\omega_1'+\omega_2')\right)} \right\} \tag{2.123}$$

in the frequency domain, where $\langle \Psi_n^{(0)} | \overline{\hat{O}} | \Psi_m^{(0)} \rangle$ denotes $\langle \Psi_n^{(0)} | \hat{O} - \langle \Psi_0^{(0)} | \hat{O} | \Psi_0^{(0)} \rangle | \Psi_m^{(0)} \rangle$, *i.e.* the matrix element of a fluctuation operator.

An alternative expression for the polarization propagator can be obtained by taking the time derivative of equation (2.117). Before doing so we should note that the linear response function only depends on the time difference $t - t'$, *i.e.*

$$\langle\langle \hat{O}^t; \hat{V}_{\alpha\cdots}^{t'} \rangle\rangle = \Theta(t-t') \frac{1}{\imath\hbar} \langle \Psi_0^{(0)} | \left[\hat{O}^t, \hat{V}_{\alpha\cdots}^{t'}\right] | \Psi_0^{(0)} \rangle$$

$$= \Theta(t-t') \frac{1}{\imath\hbar} \langle \Psi_0^{(0)} | \left[\hat{O}, \hat{V}_{\alpha\cdots}^{t'-t}\right] | \Psi_0^{(0)} \rangle = \langle\langle \hat{O}; \hat{V}_{\alpha\cdots}^{t'-t} \rangle\rangle \quad, \tag{2.124}$$

which follows from the fact that $\Psi_0^{(0)}$ is an eigenfunction of $\hat{H}^{(0)}$. We can therefore change the variable, *i.e.* and set $s = t' - t$. The derivative with respect to this new time variable s is thus given as

$$
\begin{aligned}
i\hbar\frac{d}{ds}&\langle\langle\hat{O};\hat{V}_{\alpha\cdots}^s\rangle\rangle \\
&= i\hbar\frac{d\Theta(-s)}{ds}\frac{1}{i\hbar}\langle\Psi_0^{(0)}\,|\left[\hat{O},\hat{V}_{\alpha\cdots}^s\right]|\,\Psi_0^{(0)}\rangle \\
&\quad + \Theta(-s)\frac{d}{ds}\langle\Psi_0^{(0)}\,|\left[\hat{O},\hat{V}_{\alpha\cdots}^s\right]|\,\Psi_0^{(0)}\rangle \\
&= -\delta(-s)\langle\Psi_0^{(0)}\,|\left[\hat{O},\hat{V}_{\alpha\cdots}^s\right]|\,\Psi_0^{(0)}\rangle - \Theta(-s)\frac{1}{i\hbar}\langle\Psi_0^{(0)}\,|\left[\hat{O},\left[\hat{H}^{(0)},\hat{V}_{\alpha\cdots}^s\right]\right]|\,\Psi_0^{(0)}\rangle \\
&= -\delta(s)\langle\Psi_0^{(0)}\,|\left[\hat{O},\hat{V}_{\alpha\cdots}\right]|\,\Psi_0^{(0)}\rangle - \langle\langle\hat{O};[\hat{H}^{(0)},\hat{V}_{\alpha\cdots}^s]\rangle\rangle \quad,
\end{aligned}
\tag{2.125}
$$

where it was used that

$$
\frac{d}{dt}\hat{V}_{\alpha\cdots}^t = \frac{1}{i\hbar}[\hat{V}_{\alpha\cdots}^t\,,\,\hat{H}^{(0)}]\quad,
\tag{2.126}
$$

that the Heaviside step function $\Theta(t)$ is the integral of the Dirac δ function

$$
\Theta(t) = \int_{-\infty}^{t}\delta(t')\,dt'
\tag{2.127}
$$

and that due to the Dirac delta function $\delta(s)$ the operator $\hat{V}_{\alpha\cdots}^s$ in the first term can be replaced by $\hat{V}_{\alpha\cdots}^{s=0} = \hat{V}_{\alpha\cdots}$.

The equation-of-motion transformed to the frequency domain (exercise 2.9) is

$$
\hbar\omega\langle\langle\hat{O};\hat{V}_{\alpha\cdots}^\omega\rangle\rangle_\omega = \langle\Psi_0^{(0)}\,|\,[\hat{O},\hat{V}_{\alpha\cdots}^\omega]\,|\,\Psi_0^{(0)}\rangle + \langle\langle\hat{O};[\hat{H}^{(0)},\hat{V}_{\alpha\cdots}^\omega]\rangle\rangle_\omega\quad.
\tag{2.128}
$$

Iterating on this equation leads to a so-called moment expansion of the polarization propagator

$$
\begin{aligned}
\langle\langle\hat{O};\hat{V}_{\alpha\cdots}^\omega\rangle\rangle_\omega &= \left(\frac{1}{\hbar\omega}\right)\langle\Psi_0^{(0)}\,|\,[\hat{O},\hat{V}_{\alpha\cdots}^\omega]\,|\,\Psi_0^{(0)}\rangle \\
&\quad + \left(\frac{1}{\hbar\omega}\right)^2\langle\Psi_0^{(0)}\,|\left[\hat{O},\left[\hat{H}^{(0)},\hat{V}_{\alpha\cdots}^\omega\right]\right]|\,\Psi_0^{(0)}\rangle \\
&\quad + \left(\frac{1}{\hbar\omega}\right)^3\langle\Psi_0^{(0)}\,|\left[\hat{O},\left[\hat{H}^{(0)},\left[\hat{H}^{(0)},\hat{V}_{\alpha\cdots}^\omega\right]\right]\right]|\,\Psi_0^{(0)}\rangle + \cdots
\end{aligned}
\tag{2.129}
$$

which can be expressed in a more compact form by using the so-called superoperator formalism [31]. The operators $\hat{O}$, $\hat{V}_{\alpha\cdots}^\omega$ belong then to an infinite dimensional vector space of operators with a binary product defined as

$$
(\hat{O}\,|\,\hat{V}_{\alpha\cdots}^\omega) = \langle\Psi_0^{(0)}\,|\,[\hat{O}^\dagger,\hat{V}_{\alpha\cdots}^\omega]\,|\,\Psi_0^{(0)}\rangle\quad.
\tag{2.130}
$$

Operators in this vector space of operators are called superoperators. Commonly only the superoperator Hamiltonian $\widehat{H}^{(0)}$ and the superoperator identity operator $\widehat{I}$ are used, which are defined as

$$\widehat{H}^{(0)}\hat{V}^{\omega}_{\alpha\cdots} = [\hat{H}^{(0)}, \hat{V}^{\omega}_{\alpha\cdots}] \tag{2.131}$$

and

$$\widehat{I}\ \hat{V}^{\omega}_{\alpha\cdots} = \hat{V}^{\omega}_{\alpha\cdots}\ . \tag{2.132}$$

The moment expansion of the polarization propagator becomes then

$$
\begin{aligned}
\langle\langle \hat{O}; \hat{V}^{\omega}_{\alpha\cdots}\rangle\rangle_{\omega} &= \left(\frac{1}{\hbar\omega}\right)\langle\Psi_0^{(0)}|\,[\hat{O}, \widehat{I}\ \hat{V}^{\omega}_{\alpha\cdots}]\,|\Psi_0^{(0)}\rangle \\
&+ \left(\frac{1}{\hbar\omega}\right)^2 \langle\Psi_0^{(0)}|\,\left[\hat{O}, \widehat{H}^{(0)}\hat{V}^{\omega}_{\alpha\cdots}\right]\,|\Psi_0^{(0)}\rangle \\
&+ \left(\frac{1}{\hbar\omega}\right)^3 \langle\Psi_0^{(0)}|\,\left[\hat{O}, (\widehat{H}^{(0)})^2\hat{V}^{\omega}_{\alpha\cdots}\right]\,|\Psi_0^{(0)}\rangle + \cdots
\end{aligned}
\tag{2.133}
$$

or

$$
\begin{aligned}
\langle\langle \hat{O}; \hat{V}^{\omega}_{\alpha\cdots}\rangle\rangle_{\omega} &= \left(\frac{1}{\hbar\omega}\right)(\hat{O}^{\dagger}\mid \widehat{I}\ \hat{V}^{\omega}_{\alpha\cdots}) + \left(\frac{1}{\hbar\omega}\right)^2 (\hat{O}^{\dagger}\mid \widehat{H}^{(0)}\hat{V}^{\omega}_{\alpha\cdots}) \\
&+ \left(\frac{1}{\hbar\omega}\right)^3 (\hat{O}^{\dagger}\mid (\widehat{H}^{(0)})^2\hat{V}^{\omega}_{\alpha\cdots}) + \cdots
\end{aligned}
\tag{2.134}
$$

Finally, defining the superoperator resolvent by the expansion

$$\left(\hbar\omega\widehat{I} - \widehat{H}^{(0)}\right)^{-1} = \left(\frac{1}{\hbar\omega}\right)\left\{\widehat{I} + \sum_{n=1}^{\infty}\left(\frac{\widehat{H}^{(0)}}{\hbar\omega}\right)^n\right\}\ , \tag{2.135}$$

the moment expansion of the polarization propagator can be written as

$$\langle\langle \hat{O}; \hat{V}^{\omega}_{\alpha\cdots}\rangle\rangle_{\omega} = \left(\hat{O}^{\dagger}\mid (\hbar\omega\widehat{I} - \widehat{H}^{(0)})^{-1}\hat{V}^{\omega}_{\alpha\cdots}\right)\ . \tag{2.136}$$

Instead of using the superoperator resolvent, which is an inverse operator, it is advantageous to work with a matrix representation. Using the inner projection with a complete set of excitation and de-excitation operators $\{h_n\}$, arranged as column vector $\boldsymbol{h}$ or as row vector $\tilde{\boldsymbol{h}}$, an exact matrix representation of the polarization propagator is obtained [32] (exercise 2.11)

$$
\begin{aligned}
&\langle\langle \hat{O}; V^{\omega}_{\alpha\cdots}\rangle\rangle_{\omega} \\
&= \left(\hat{O}^{\dagger}\mid \tilde{\boldsymbol{h}}\right)\left(\boldsymbol{h}\mid (\hbar\omega\widehat{I} - \widehat{H}^{(0)})\mid \tilde{\boldsymbol{h}}\right)^{-1}\left(\boldsymbol{h}\mid \hat{V}^{\omega}_{\alpha\cdots}\right) \\
&= \langle\Psi_0^{(0)}|[\hat{O}, \tilde{\boldsymbol{h}}]|\Psi_0^{(0)}\rangle\langle\Psi_0^{(0)}|[\boldsymbol{h}^{\dagger}, \hbar\omega\tilde{\boldsymbol{h}} - [\hat{H}^{(0)}, \tilde{\boldsymbol{h}}]]|\Psi_0^{(0)}\rangle^{-1}\langle\Psi_0^{(0)}|[\boldsymbol{h}^{\dagger}, \hat{V}^{\omega}_{\alpha\cdots}]|\Psi_0^{(0)}\rangle\ .
\end{aligned}
\tag{2.137}
$$

Completeness of the set of operators $\{h_n\}$ means that all possible excited states $\mid \Psi_n^{(0)} \rangle$ of the system must be generated by operating on $\mid \Psi_0^{(0)} \rangle$, *i.e.* $h_n \mid \Psi_0^{(0)} \rangle = \mid \Psi_n^{(0)} \rangle$. This more general expression for the polarization propagator reduces to equation (2.118) if one chooses the operators $\{h_n\}$ to be $\left\{ \mid \Psi_n^{(0)} \rangle \langle \Psi_0^{(0)} \mid, \mid \Psi_0^{(0)} \rangle \langle \Psi_n^{(0)} \mid \right\}$ (exercise 2.12).

The most important application of time dependent perturbation theory or response theory in the context of molecular properties is to evaluate the time dependent expectation value of the electric dipole operator $\langle \Psi_0(t) \mid \hat{\mu}_\alpha^{el} \mid \Psi_0(t) \rangle$ in the presence of a monochromatic electromagnetic wave of frequency ω_0. Employing the dipole approximation, which implies setting $\vec{k} \cdot \vec{r} = 0$ in equation (1.61), the perturbation Hamilton operator for the periodic and spatially uniform electric field of the electromagnetic wave is

$$\hat{H}^{(1)}(t) = -\sum_\alpha \hat{O}_\alpha^E E_\alpha(t) = -\sum_\alpha \hat{O}_\alpha^E \frac{E_\alpha^{\omega_0}}{2} \left(e^{-\iota\omega_0 t} + e^{\iota\omega_0 t} \right) \quad . \tag{2.138}$$

Comparison with equation (2.104) shows that the Fourier components of the operator and the field are

$$\hat{V}_{\alpha\cdots}^\omega = -\hat{O}_\alpha^E \tag{2.139}$$

$$F(\omega)_{\alpha\cdots} = \frac{E_\alpha^{\omega_0}}{2} \left(\delta(\omega - \omega_0) + \delta(\omega + \omega_0) \right) \quad . \tag{2.140}$$

Insertion of these operators in equation (2.106) yields

$$\langle \Psi_0(t) \mid \hat{\mu}_\alpha^{el} \mid \Psi_0(t) \rangle = \langle \Psi_0^{(0)} \mid \hat{O}_\alpha^E \mid \Psi_0^{(0)} \rangle \tag{2.141}$$
$$+ \sum_\beta \left(\langle\langle \hat{O}_\alpha^E; -\hat{O}_\beta^E \rangle\rangle_{\omega_0} e^{-\iota\omega_0 t} + \langle\langle \hat{O}_\alpha^E; -\hat{O}_\beta^E \rangle\rangle_{-\omega_0} e^{\iota\omega_0 t} \right) \frac{E_\beta^{\omega_0}}{2} + \cdots \quad .$$

From the definition of the linear response function in the frequency domain, equation (2.118), it can be seen that for the hermitian and real operators $\hat{O}_\alpha^E$ and $\hat{O}_\beta^E$ the two response functions $\langle\langle \hat{O}_\alpha^E; -\hat{O}_\beta^E \rangle\rangle_{\omega_0}$ and $\langle\langle \hat{O}_\alpha^E; -\hat{O}_\beta^E \rangle\rangle_{-\omega_0}$ become equal. Thus

$$\langle \Psi_0(t) \mid \hat{\mu}_\alpha^{el} \mid \Psi_0(t) \rangle = \langle \Psi_0^{(0)} \mid \hat{O}_\alpha^E \mid \Psi_0^{(0)} \rangle + \sum_\beta \langle\langle \hat{O}_\alpha^E; -\hat{O}_\beta^E \rangle\rangle_{\omega_0} E_\beta^{\omega_0} \cos(\omega_0 t) + \cdots \quad ,$$
$$\tag{2.142}$$

which can be compared with the classical expansion of a time dependent dipole moment in equation (1.62). The frequency dependent polarizability tensor is then identified as

$$\alpha_{\alpha\beta}(-\omega_0; \omega_0) = -\langle\langle \hat{O}_\alpha^E; \hat{O}_\beta^E \rangle\rangle_{\omega_0} \quad . \tag{2.143}$$

For $\omega_0 = 0$ this reduces to the expression obtained by static response theory or Rayleigh-Schrödinger perturbation theory.

2.8 Vibrational Averaging

The expressions for the molecular properties given in chapters 2.5 - 2.7 were derived for a fixed set of nuclear coordinates. However, this is not a realistic description of a molecule, since even at 0 K a molecule vibrates. In order to obtain agreement with experimental data it is therefore necessary to take account of the effects of nuclear motion. The contribution that these corrections make is not negligible especially for higher polarizabilities, to the extent that calculated first and second hyperpolarizabilities which do not include any vibrational correction [33] are of questionable relevance to experiment, even though they may be of value for benchmarking purposes. In addition, experimentally observable effects like temperature dependence and isotope shifts of *e.g.* NMR parameters are solely due to differences in these nuclear motion corrections.

The static polarizability will be used to illustrate how these vibrational corrections can be incorporated [34, 35]. A detailed description of vibrational corrections to hyperpolarizabilities can be found in the reviews by Bishop [33, 36].

In order to incorporate the effects of nuclear motion one requires a Hamiltonian, which includes kinetic energy operators for the nuclei. The corresponding eigenfunctions are the so-called vibronic wavefunctions Φ_{nv} with energy W_{nv} and are characterized by the electronic, n, and vibrational, v, quantum numbers, where v stands throughout the chapter collectively for the vibrational quantum numbers of all vibrational modes of the molecule. The proper approach for the treatment of the nuclear motion effects would be to use the unperturbed vibronic wavefunctions $\Phi_{nv}^{(0)}$ instead of the unperturbed electronic wavefunctions $\Psi_n^{(0)}$ in the derivation of expression for the molecular properties in sections 2.5 - 2.7. However, we still want to make use of the Born-Oppenheimer approximation and have therefore the choice of applying it before or after the effect of the external perturbation is introduced in Hamiltonian.

In the first approach, the so-called *sum-over-states* treatment of the corrections due to molecular vibration, the effects of the perturbation on the electronic and vibrational part of the wavefunction are treated simultaneously. The vibronic wavefunction for, *e.g.*, the electronic ground state $n = 0$ and an arbitrary vibrational state v is thus in the presence of a perturbation, E_β, given through first order as

$$\Phi_{0v} = \Phi_{0v}^{(0)} + \Phi_{0v}^{(1)} = \Phi_{0v}^{(0)} + \sum_{nv' \neq 0v} \mid \Phi_{nv'}^{(0)} \rangle \frac{\langle \Phi_{nv'}^{(0)} \mid -\sum_\beta \hat{O}_\beta^E \, E_\beta \mid \Phi_{0v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{nv'}^{(0)}} \quad . \tag{2.144}$$

Using perturbation theory, section 2.5, one obtains then for a static polarizability

$$\alpha_{\alpha\beta} = -2 \sum_{nv' \neq 0v} \frac{\langle \Phi_{0v}^{(0)} \mid \hat{O}_\alpha^E \mid \Phi_{nv'}^{(0)} \rangle \langle \Phi_{nv'}^{(0)} \mid \hat{O}_\beta^E \mid \Phi_{0v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{nv'}^{(0)}} \quad . \tag{2.145}$$

The summation can be broken in two parts

$$\alpha_{\alpha\beta}^{e} = -2 \sum_{n \neq 0, v'} \frac{\langle \Phi_{0v}^{(0)} | \hat{O}_{\alpha}^{E} | \Phi_{nv'}^{(0)} \rangle \langle \Phi_{nv'}^{(0)} | \hat{O}_{\beta}^{E} | \Phi_{0v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{nv'}^{(0)}} \tag{2.146}$$

$$\alpha_{\alpha\beta}^{v} = -2 \sum_{v' \neq v} \frac{\langle \Phi_{0v}^{(0)} | \hat{O}_{\alpha}^{E} | \Phi_{0v'}^{(0)} \rangle \langle \Phi_{0v'}^{(0)} | \hat{O}_{\beta}^{E} | \Phi_{0v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{0v'}^{(0)}} \quad, \tag{2.147}$$

where the first contribution is called the electronic polarizability and the second is the vibrational polarizability, sometimes also called atomic polarizability.

Applying now the Born-Oppenheimer approimation, *i.e.* making the following ansatz for the zeroth order vibronic wavefunctions

$$\Phi_{nv}^{(0)} = \Psi_{n}^{(0)} \Theta_{v}^{(0)} \quad, \tag{2.148}$$

one obtains for the two contributions

$$\alpha_{\alpha\beta}^{e} = -2 \sum_{v'} \sum_{n \neq 0} \frac{\langle \Theta_{v}^{(0)} | \langle \Psi_{0}^{(0)} | \hat{O}_{\alpha}^{E} | \Psi_{n}^{(0)} \rangle | \Theta_{v'}^{(0)} \rangle \langle \Theta_{v'}^{(0)} | \langle \Psi_{n}^{(0)} | \hat{O}_{\beta}^{E} | \Psi_{0}^{(0)} \rangle | \Theta_{v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{nv'}^{(0)}} \tag{2.149}$$

$$\alpha_{\alpha\beta}^{v} = -2 \sum_{v' \neq v} \frac{\langle \Theta_{v}^{(0)} | \langle \Psi_{0}^{(0)} | \hat{O}_{\alpha}^{E} | \Psi_{0}^{(0)} \rangle | \Theta_{v'}^{(0)} \rangle \langle \Theta_{v'}^{(0)} | \langle \Psi_{0}^{(0)} | \hat{O}_{\beta}^{E} | \Psi_{0}^{(0)} \rangle | \Theta_{v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{0v'}^{(0)}} \quad, \tag{2.150}$$

where, using equation (2.86), the vibrational polarizability can also be written as

$$\alpha_{\alpha\beta}^{v} = -2 \sum_{v' \neq v} \frac{\langle \Theta_{v}^{(0)} | \mu_{\alpha}^{el} | \Theta_{v'}^{(0)} \rangle \langle \Theta_{v'}^{(0)} | \mu_{\beta}^{el} | \Theta_{v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{0v'}^{(0)}} \tag{2.151}$$

In order to evaluate the electronic polarzability, equation (2.149), one needs to know not only all excited electronic states, $\Psi_{n}^{(0)}$ but also all the vibrational states, $\Theta_{v'}^{(0)}$, of these excited states. This makes this approach rather difficult to apply in actual calculations.

In the second approach, the so-called *clamped-nucleus* treatment, the effect of the perturbation on the electronic and nuclear motion is treated sequentially. Firstly, the Born-Oppenheimer approximation is applied to the vibronic wavefunction Φ_{0v}, which is therefore expressed a product of an electronic wavefunction Ψ_{0} and a vibrational wavefunction Θ_{v}. Secondly, in the presence of a perturbation, E_{β}, the perturbation enters the electronic Hamiltonian (see section 2.4) and the electronic wavefunction for the electronic ground state $n = 0$ is expanded in a perturbation series (see section 2.5). To first order the electronic wavefunction is then given as

$$\Psi_{0} = \Psi_{0}^{(0)} + \Psi_{0}^{(1)} = \Psi_{0}^{(0)} + \sum_{n \neq 0} | \Psi_{n}^{(0)} \rangle \frac{\langle \Psi_{n}^{(0)} | - \sum_{\beta} \hat{O}_{\beta}^{E} E_{\beta} | \Psi_{0}^{(0)} \rangle}{W_{0}^{(0)}(\{\vec{R}\}) - W_{n}^{(0)}(\{\vec{R}\})} \quad, \tag{2.152}$$

where $W_0^{(0)}(\{\vec{R}\})$ indicates that the electronic energies are for a given set of nuclear coordinates $\{\vec{R}\}$. The nuclear Schrödinger equation in the Born-Oppenheimer approximation reads then

$$\left\{ \sum_K \frac{1}{2M_K} \hat{\vec{p}}_K^2 + \frac{e^2}{4\pi\epsilon_0} \sum_{KL} \frac{Z_K Z_L}{|\vec{R}_K - \vec{R}_L|} + W_0(\{\vec{R}\}) \right\} \mid \Theta_v \rangle = W_v \mid \Theta_v \rangle \;, \qquad (2.153)$$

where $W_0(\{\vec{R}\})$ is the electronic energy in the presence of the perturbation, which to first order is given as

$$W_0(\{\vec{R}\}) = W_0^{(0)}(\{\vec{R}\}) + \langle \Psi_0^{(0)} \mid -\sum_\beta \hat{O}_\beta^E \, E_\beta \mid \Psi_0^{(0)} \rangle \;. \qquad (2.154)$$

The perturbation, E_β, enters the nuclear Hamiltonian thus as an expectation value with the electronic wavefunction. The vibrational wavefunction for an arbitrary vibrational state v of the given electronic state is then also expanded in a perturbation series and is to first order given as

$$\Theta_v = \Theta_v^{(0)} + \Theta_v^{(1)} = \Theta_v^{(0)} + \sum_{n \neq v'} \mid \Theta_{v'}^{(0)} \rangle \frac{\langle \Theta_{v'}^{(0)} \mid \langle \Psi_0^{(0)} \mid -\sum_\beta \hat{O}_\beta^E \, E_\beta \mid \Psi_0^{(0)} \rangle \mid \Theta_v^{(0)} \rangle}{W_{0v}^{(0)} - W_{0v'}^{(0)}} \;. $$

$$(2.155)$$

An expression for the polarizability can finally be obtained by static response theory as described in Section 2.6,

$$\alpha_{\alpha\beta} = \frac{\partial}{\partial E_\beta} \langle \Phi_{0v} \mid \hat{O}_\alpha^E \mid \Phi_{0v} \rangle^{(1)} \qquad (2.156)$$

$$= \frac{\partial}{\partial E_\beta} \left\{ \langle \Theta_v^{(0)} \Psi_0^{(1)} \mid \hat{O}_\alpha^E \mid \Psi_0^{(0)} \Theta_v^{(0)} \rangle + \langle \Theta_v^{(0)} \Psi_0^{(0)} \mid \hat{O}_\alpha^E \mid \Psi_0^{(1)} \Theta_v^{(0)} \rangle \right.$$

$$= \left. + \langle \Theta_v^{(1)} \Psi_0^{(0)} \mid \hat{O}_\alpha^E \mid \Psi_0^{(0)} \Theta_v^{(0)} \rangle + \langle \Theta_v^{(0)} \Psi_0^{(0)} \mid \hat{O}_\alpha^E \mid \Psi_0^{(0)} \Theta_v^{(1)} \rangle \right\} \;, (2.157)$$

yielding two contributions: the electronic polarizability

$$\alpha_{\alpha\beta}^{e,v} = -2 \, \langle \Theta_v^{(0)} \mid \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} \mid \hat{O}_\alpha^E \mid \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} \mid \hat{O}_\beta^E \mid \Psi_0^{(0)} \rangle}{W_0^{(0)}(\{\vec{R}\}) - W_n^{(0)}(\{\vec{R}\})} \mid \Theta_v^{(0)} \rangle = \langle \Theta_v^{(0)} \mid \alpha_{\alpha\beta}(\{\vec{R}\}) \mid \Theta_v^{(0)} \rangle$$

$$(2.158)$$

and the vibrational polarizability,, given in equation (2.150) or (2.151). Although the expression for the vibrational polarizability is thus the same as the one obtained with the *sum-over-states* treatment, the expression for the electronic contribution differs from equation (2.149). The electronic contribution in equation (2.158) is simply the polarizability as given in table 2.1 or equation (2.143) averaged with the vibrational wavefunction $\Theta_v^{(0)}$. However, making the approximations

1) that in equation (2.149) the differences between the vibrational energies are much smaller than the differences between the electronic energies, *i.e.*

$$W_{0v}^{(0)} - W_{nv'}^{(0)} \approx W_{00}^{(0)} - W_{n0}^{(0)} \quad , \tag{2.159}$$

2) that closure is carried out over the vibrational wavefunctions $\Theta_{v'}^{(0)}$ in equation (2.149), *i.e.*

$$1 = \sum_{v'} |\Theta_{v'}^{(0)}\rangle\langle\Theta_{v'}^{(0)}| \quad , \tag{2.160}$$

one obtains from equation (2.149) an expression

$$\alpha_{\alpha\beta}^e = -2 \sum_{n \neq 0} \frac{\langle\Theta_v^{(0)}|\langle\Psi_0^{(0)}|\hat{O}_\alpha^E|\Psi_n^{(0)}\rangle\langle\Psi_n^{(0)}|\hat{O}_\beta^E|\Psi_0^{(0)}\rangle|\Theta_v^{(0)}\rangle}{W_{00}^{(0)} - W_{n0}^{(0)}} \quad , \tag{2.161}$$

which is similar to equation (2.158).

For linear molecules the vibrational wavefunctions can be obtained numerically as solution of the one-dimensional Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} + \frac{J(J+1)}{R^2} \right) + V(R) \right\} |\Theta_{v,J}\rangle = W_{v,J} |\Theta_{v,J}\rangle \quad , \tag{2.162}$$

where J is the rotational quantum number and $V(R)$ is the sum of the electronic energy and the nuclear repulsion term. The vibrational averaging in the *clamped-nucleus* treatment in equation (2.158) can then be carried out numerically, if one calculates the polarizability as given in table 2.1 or equation (2.143) as a function of the internuclear distance R.

For polyatomic molecules the electronic polarizability in the *clamped-nucleus* treatment is frequently expressed as the polarizability evaluated at an equilibrium geometry $\{\vec{R}_e\}$ plus a so-called zero point vibrational correction (ZPVC)

$$\alpha_{\alpha\beta}^{e,v} = \langle\Theta_v^{(0)}|\alpha_{\alpha\beta}(\{\vec{R}\})|\Theta_v^{(0)}\rangle = \alpha_{\alpha\beta}(\{\vec{R}_e\}) + \Delta\alpha_{\alpha\beta}^{ZPVC} \quad . \tag{2.163}$$

The latter is usually obtained by perturbation theory. The polarizability is thereby expanded in a power series in the normal coordinates $\{Q_a\}$

$$\alpha_{\alpha\beta}(\{\vec{R}\}) = \alpha_{\alpha\beta}(\{\vec{R}_e\}) + \sum_a \left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_a} \right) Q_a + \frac{1}{2} \sum_{ab} \left(\frac{\partial^2\alpha_{\alpha\beta}}{\partial Q_a\partial Q_b} \right) Q_aQ_b + \cdots \tag{2.164}$$

and the vibrational wavefunctions $\Theta_v^{(0)}$ are found by solving the vibrational Schrödinger equation with the anharmonic potential

$$V(\{\vec{R}\}) = V(\{\vec{R}_e\}) + \frac{1}{2} \sum_a \omega_a^2 Q_a^2 + \frac{1}{6} \sum_{abc} K_{abc} Q_aQ_bQ_c + \cdots \quad , \tag{2.165}$$

where ω_a and K_{abc} are the harmonic vibrational frequencies and cubic force constants, respectively. The potential is normally terminated after the cubic term and the vibrational wavefunctions $\Theta_v^{(0)}$ are then expressed as perturbed harmonic oscillator functions, *i.e.* they are expanded in a basis set $\{\theta_v\}$, where each θ_v consists of a product of harmonic oscillator wavefunctions (one for each normal mode),

$$| \Theta_v^{(0)} \rangle \approx | \theta_v \rangle - \sum_{v' \neq v} | \theta_v \rangle \frac{\langle \theta_v' | \frac{1}{6} \sum_{abc} K_{abc} Q_a Q_b Q_c | \theta_v \rangle}{\hbar(\omega_{v'} - \omega_v)} \quad . \tag{2.166}$$

Inserting equations (2.166) and (2.164) into equation (2.163) and using the properties of the harmonic oscillator functions, one obtains for the zero-point-vibrational correction in first order (exercise 2.13)

$$\Delta\alpha_{\alpha\beta}^{ZPVC} = -\frac{\hbar}{4} \sum_a \frac{1}{\omega_a^2} \left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_a} \right) \left(\sum_b \frac{K_{abb}}{\omega_b} \right) + \frac{\hbar}{4} \sum_a \frac{1}{\omega_a} \left(\frac{\partial^2\alpha_{\alpha\beta}}{\partial Q_a^2} \right) \quad , \tag{2.167}$$

where the first term arises because of the anharmonic term in the potential, equation (2.165), and the second term comes from the non-linear term in the expansion of the polarizability, equation (2.164). Equivalent expressions for higher vibrational levels have also been derived [37].

For the evaluation of the vibrational polarizability, equation (2.151), one needs to calculate the vibrational energies, $W_{0v}^{(0)}$, as well as vibrational transition moments, $\langle \Theta_v^{(0)} | \mu_\alpha^{el} | \Theta_{v'}^{(0)} \rangle$, of the electronic contribution to the electric dipole moment. Both can be obtained by a perturbation theory treatment similar to the one used in the evaluation of the ZPVC [38].

The effect of temperature, T, can finally be included by Boltzmann averaging the polarizability over several vibrational states of energy E_v

$$\alpha_{\alpha\beta}(T) = \frac{\sum_v \alpha_{\alpha\beta}^{e,v} \, e^{\frac{-E_v}{kT}}}{\sum_v \, e^{\frac{-E_v}{kT}}}. \tag{2.168}$$

Table 2.2 Calculated zero-point-vibrational corrections (ZPVC) to the static dipole polarizability α (in units of $e^2 a_0^2 E_h^{-1}$) and static dipole second hyperpolarizability $\bar{\gamma}$ (in units of $e^4 a_0^4 E_h^{-3}$)

Molecule	Property	result at R$_e$	ZPVC	%	Ref.
HF	α	5.48	0.10	1.8	[39]
CO	α	13.86	0.05	0.4	[39]
N$_2$	α	11.73	0.05	0.4	[39]
CH$_4$	$\bar{\gamma}$	2152	285	13.2	[40]

In Tables 2.3 - 2.2 some illustrative examples for the zero point vibrational corrections to nuclear magnetic shielding constants, σ, indirect nuclear spin-spin coupling

Table 2.3 Calculated zero-point-vibrational corrections (ZPVC) to the nuclear magnetic shielding constant (in ppm)

Molecule	Property	result at R_e	ZPVC	%	Ref.
HF	$\sigma^{19}F$	419.68	-10.01	2.4	[41]
HF	$\sigma^{1}H$	29.01	-0.32	1.1	[41]
H_2O	$\sigma^{17}O$	343.94	-9.86	2.9	[42]
H_2O	$\sigma^{1}H$	30.97	-0.48	1.6	[42]
F_2	$\sigma^{19}F$	-187.84	30.90	16.5	[43]
C_2H_2	$\sigma^{13}C$	128.89	-3.78	2.9	[44]
C_2H_2	$\sigma^{1}H$	30.45	-0.80	2.6	[44]
CO	$\sigma^{13}C$	5.29	-1.82	34.5	[43]
CO	$\sigma^{17}O$	-53.5	-4.8	9.0	[43]
N_2	$\sigma^{15}N$	-58.7	-3.5	5.9	[43]

Table 2.4 Calculated zero point vibrational corrections (ZPVC) to the indirect nuclear spin-spin coupling constant (in Hz)

Molecule	Property	result at R_e	ZPVC	%	Ref.
HF	$^{1}J^{1H-19F}$	526.4	-26.9	5.1	[41]
H_2O	$^{1}J^{1H-17O}$	-81.555	3.963	4.9	[45]
H_2O	$^{2}J^{1H-1H}$	-8.581	0.653	7.6	[45]
CH_4	$^{1}J^{1H-13C}$	123.846	5.030	4.1	[46]
CH_4	$^{2}J^{1H-1H}$	-14.450	-0.686	4.7	[46]
C_2H_2	$^{1}J^{13C-13C}$	189.995	4.861	1.9	[47]
C_2H_2	$^{1}J^{1H-13C}$	254.906	-9.212	4.9	[47]
C_2H_2	$^{2}J^{1H-13C}$	51.727	-3.237	6.3	[47]
C_2H_2	$^{3}J^{1H-1H}$	11.311	-1.184	10.5	[47]

constants, J, dipole polarizabilities, α and dipole second hyperpolarizabilities, $\bar{\gamma}$ are collected (See also exercise 2.14). The results are taken from the recent literature and were all obtained using correlated *ab initio* methods as described in Section 3.

A few general conclusions can be drawn from these examples. Zero point vibrational corrections are usually larger for properties which describe an interaction with nuclear magnetic moments, like the nuclear magnetic shielding constant and the spin-spin coupling constant, than for other properties like dipole polarizabilities. Higher order properties, like hyperpolarizabilities, also have larger zero point vibrational corrections than linear response properties. The large zero point vibrational corrections to the nuclear magnetic shielding constants of F_2 and CO are two extreme cases, well known in the literature.

2.9 The Gauge Origin Problem

In section 2.1 the relations [22]

$$\vec{E}(\vec{r}_i, t) = -\vec{\nabla}\phi^E(\vec{r}_i, t) - \frac{\partial \vec{A}^B(\vec{r}_i, t)}{\partial t} \qquad (2.169)$$

$$\vec{B}(\vec{r}_i, t) = \vec{\nabla} \times \vec{A}^B(\vec{r}_i, t) \qquad (2.170)$$

between the time dependent electric field, $\vec{E}(\vec{r}_i, t)$, and the time dependent magnetic induction $\vec{B}(\vec{r}_i, t)$ on one side and the scalar, $\phi^E(\vec{r}_i, t)$, and vector potential, $\vec{A}^B(\vec{r}_i, t)$, on the other side were used in the derivation of the molecular Hamiltonian. However, the potentials are not uniquely defined by these equations. Given an arbitrary scalar function $\chi(\vec{r}_i, t)$, the transformations of the vector potential

$$\vec{A}^B(\vec{r}_i, t) \rightarrow \vec{A}^{B'}(\vec{r}_i, t) = \vec{A}^B(\vec{r}_i, t) + \vec{\nabla}\chi(\vec{r}_i, t) \qquad (2.171)$$

and simultaneously of the scalar potential

$$\phi^E(\vec{r}_i, t) \rightarrow \phi^{E'}(\vec{r}_i, t) = \phi^E(\vec{r}_i, t) - \frac{\partial \chi(\vec{r}_i, t)}{\partial t} \ , \qquad (2.172)$$

will leave the fields, $\vec{E}(\vec{r}_i, t)$ and $\vec{B}(\vec{r}_i, t)$, unchanged [22] (exercise 2.15). The transformations in equations (2.171) and (2.172) are so-called gauge transformation and $\chi(\vec{r}_i, t)$ is a gauge function.

The fact that the observable fields ($\vec{E}(\vec{r}_i, t)$ and $\vec{B}(\vec{r}_i, t)$) do not change under a gauge transformation implies that all equations describing the physics of a system must be form invariant under a gauge transformation. This applies in particular to the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = \hat{H}\Psi(t) \ , \qquad (2.173)$$

with the Hamiltonian $\hat{H}$ given in equation (2.55). Replacing the potentials $\phi^E(\vec{r}_i, t)$ and $\vec{A}^B(\vec{r}_i, t)$ in the Hamiltonian $\hat{H}$ by $\phi^{E'}(\vec{r}_i, t)$ and $\vec{A}^{B'}(\vec{r}_i, t)$, according to equations (2.171) and (2.172), yields a new Hamiltonian $\hat{H}'$. This gauge transformed Hamiltonian can also be obtained (see exercises 2.16) by the following transformation

$$\hat{H}' - i\hbar \frac{\partial}{\partial t} = e^{-i\sum_i \frac{e}{\hbar}\chi(\vec{r}_i, t)} \left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) e^{i\sum_i \frac{e}{\hbar}\chi(\vec{r}_i, t)} \ , \qquad (2.174)$$

where the summation is over all electrons i. Form invariance of the time dependent Schrödinger equation under the gauge transformations in equations (2.171) and (2.172) or in equation (2.174) is therefore obtained if also the wavefunction $\Psi(t)$ is simultaneously transformed according to

$$\Psi(t) \rightarrow \Psi'(t) = e^{-i\sum_i \frac{e}{\hbar}\chi(\vec{r}_i, t)} \Psi(t) \ . \qquad (2.175)$$

Form invariance of the time independent Schrödinger equation under a gauge transformation is guaranteed by the simultaneous transformation of the total Hamiltonian

$$\hat{H}' = e^{-\imath \sum_i \frac{e}{\hbar} \chi(\vec{r}_i)} \, \hat{H} \, e^{\imath \sum_i \frac{e}{\hbar} \chi(\vec{r}_i)} \quad , \tag{2.176}$$

or the vector potential in the Hamiltonian

$$\vec{A}^B(\vec{r}_i) \to \vec{A}^{B'}(\vec{r}_i) = \vec{A}^B(\vec{r}_i) + \vec{\nabla}\chi(\vec{r}_i) \tag{2.177}$$

together with the transformation of the time independent wavefunction

$$\Psi \to \Psi' = e^{-\imath \sum_i \frac{e}{\hbar} \chi(\vec{r}_i)} \, \Psi \quad . \tag{2.178}$$

The form invariance of the Schrödinger equation will then lead to gauge invariant expectation values. However, it turns out that expectation values of the canonical momentum operator, given in equation (2.15), are not gauge invariant, whereas expectation values of the mechanical or kinematical momentum operator, given in equation (2.54), are gauge invariant (exercise 2.17)

$$\langle \Psi' | \sum_i \hat{\vec{\pi}}'_i | \Psi' \rangle = \langle \Psi | \sum_i \hat{\vec{\pi}}_i | \Psi \rangle \quad . \tag{2.179}$$

The latter operator is therefore sometimes also called the gauge invariant momentum operator.

An important gauge transformation in the context of the calculation of molecular properties is given by the following gauge function

$$\chi(\vec{r}_i) = -\frac{1}{2} \, \vec{B} \times \vec{R}_o \cdot \vec{r}_i \quad , \tag{2.180}$$

where $\vec{R}_o$ is the arbitrary gauge origin. This gauge function implies that

$$\vec{\nabla}\chi(\vec{r}_i) = -\frac{1}{2} \, \vec{B} \times \vec{R}_o \tag{2.181}$$

and that the vector potential for a uniform magnetic induction

$$\vec{A}^{B'}(\vec{r}_i) = \frac{1}{2} \, \vec{B} \times (\vec{r}_i - \vec{R}_o) \quad , \tag{2.182}$$

previously given in equation (2.59), becomes a linear function of the arbitrary gauge origin $\vec{R}_o$ under this gauge transformation.

As a consequence the diamagnetic and paramagnetic contribution to the magnetizability tensor $\boldsymbol{\xi}$ and to the nuclear magnetic shielding tensor $\boldsymbol{\sigma}^K$ in table 2.1 depend on the gauge origin $\vec{R}_{GO}$. However, the sum of the dia- and paramagnetic contribution is for exact states independent of the gauge origin (exercise 2.18).

2.10 Exercises

1. Show that the vector potential $\vec{A}^B$ can be chosen to be divergence free, *i.e.* $\vec{\nabla} \cdot \vec{A}^B = 0$.

2. Show that the Lagrangians in equation (2.10) and (2.22) fulfill the Lagrange equations (2.8).

3. Derive the expressions for the classical relativistic Hamiltonian in equations (2.24) and (2.25).

4. Show that the α matrices in equation (2.36) fulfill the conditions (2.34) and (2.35).

5. Prove relation (2.48).

6. Derive equation (2.49) from equation (2.47).

7. Derive the expression for the third order energy correction in Rayleigh-Schrö dinger perturbation theory.

8. Show that the diamagnetic contributions to the magnetizability $\xi_{\alpha\beta}^{el}(\vec{R}_{GO})$, nuclear magnetic shielding $\sigma_{\alpha\beta}^{K,el}(\vec{R}_{GO})$ and reduced indirect nuclear spin-spin coupling tensors $K_{\alpha\beta}^{KL,el}$ can also be written in the following way as a sum-over-states [48, 49, 50, 51]

$$P^{dia} = f_2 \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{O}_2 | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}_3 | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}}$$
$$+ f_2 \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{O}_3 | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}_2 | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}}$$

where

P	f_2	$\hat{O}_2$	$\hat{O}_3$
$\xi_{\alpha\beta}^{el}(\vec{R}_{GO})$	$-\dfrac{e^2}{4m_e^2}$	$\sum_i \left((\vec{r}_i - \vec{R}_{GO}) \times \left((\vec{r}_i - \vec{R}_{GO}) \times \hat{\vec{p}}_i \right) \right)_\alpha$	$\sum_i \hat{p}_{i,\beta}$
$\sigma_{\alpha\beta}^{K,el}(\vec{R}_{GO})$	$\dfrac{e^2}{2m_e^2}\dfrac{\mu_0}{4\pi}$	$\sum_i \left(\dfrac{\vec{r}_i - \vec{R}_K}{\mid \vec{r}_i - \vec{R}_K \mid^3} \times \left((\vec{r}_i - \vec{R}_{GO}) \times \hat{\vec{p}}_i \right) \right)_\alpha$	$\sum_i \hat{p}_{i,\beta}$
$K_{\alpha\beta}^{KL,el}$	$\dfrac{e^2}{m_e^2}\left(\dfrac{\mu_0}{4\pi}\right)^2$	$\sum_i \left(\dfrac{\vec{r}_i - \vec{R}_K}{\mid \vec{r}_i - \vec{R}_K \mid^3} \times \left(\dfrac{\vec{r}_i - \vec{R}_L}{\mid \vec{r}_i - \vec{R}_L \mid^3} \times \hat{\vec{p}}_i \right) \right)_\alpha$	$\sum_i \hat{p}_{i,\beta}$

Hint :

- Try to derive the usual ground state average value expression from the sum-over-states expression above.
- Recall the commutator relation

$$[\vec{r}, \hat{H}^{(0)}] = \frac{\imath\hbar}{m_e}\hat{\vec{p}}$$

- Recall that the set of excited states $\Psi_n^{(0)}$ is complete, *i.e.*

$$\sum_n \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid = 1$$

9. Derive the expression for the polarization propagator in the frequency domain, equation (2.118), from the expression in the time domain, equation (2.117). Hint :

- The Fourier transform is defined as

$$\langle\langle A; B\rangle\rangle_\omega = \int_{-\infty}^{\infty} \langle\langle A; B^t\rangle\rangle e^{-\imath\omega t}dt$$

- Insert the resolution of the identity $\sum_n \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid = 1$ between $\hat{O}^t$ and $\hat{V}_{\alpha\cdots}^{t'}$.
- Use that

$$\frac{1}{\imath}\int_{-\infty}^{\infty} e^{\imath at}\Theta(t)dt = \lim_{\eta\to 0^+}\int_{-\infty}^{\infty}\frac{\delta(a-x)}{x+\imath\eta}dx = \lim_{\eta\to 0^+}\frac{1}{a+\imath\eta} = \frac{1}{a}$$

10. Derive the equation of motion for the polarization propagator, equation (2.128), from equation (2.125).

- The Fourier transform of polarization propagator is defined as

$$\langle\langle A; B^t\rangle\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle A; B\rangle\rangle_\omega e^{-\imath\omega t}d\omega$$

- The Dirac delta function can be represented as

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-\imath\omega t}d\omega$$

11. Derive the inner projection of the superoperator resolvent

$$\left(\hbar\omega\widehat{I} - \widehat{H}^{(0)}\right)^{-1} = \mid \tilde{\boldsymbol{h}})(\boldsymbol{h} \mid (\hbar\omega\widehat{I} - \widehat{H}^{(0)}) \mid \tilde{\boldsymbol{h}})^{-1}(\boldsymbol{h} \mid$$

Hint :

- The set of operators $\boldsymbol{h}$ is complete *i.e.*

$$\widehat{I} = \ \mid \tilde{\boldsymbol{h}})(\boldsymbol{h} \mid \tilde{\boldsymbol{h}})^{-1}(\boldsymbol{h} \mid$$

12. Derive equation (2.118) from equation (2.137) using that the operators $\{h_n\}$ are $\left\{\mid \Psi_n^{(0)}\rangle\langle\Psi_0^{(0)} \mid, \mid \Psi_0^{(0)}\rangle\langle\Psi_n^{(0)} \mid\right\}$.

13. Derive the expression for the zero point vibrational correction (ZPVC) in equation (2.167). Hint :

   - Use that the multiple harmonic oscillator wavefunctions $\mid \theta_v\rangle$ are products of single harmonic oscillator wavefunctions $\mid v_i\rangle$ for each mode i and the following expectation values of the normal coordinates

$$\begin{aligned} \langle v \mid Q_a \mid v'\rangle &= \ 0 \ \text{if} \ \ v' \neq v \pm 1 \\ \langle v \mid Q_a \mid v+1\rangle &= \ \sqrt{(\frac{\hbar}{2\omega_a}(v+1)} \\ \langle v \mid Q_a Q_a \mid v\rangle &= \ \frac{\hbar}{\omega_a}(v+\frac{1}{2}) \end{aligned}$$

14. In this exercise we want to investigate the effect of nuclear motion on the results for the static polarizability, nuclear magnetic shielding constant and indirect nuclear spin-spin coupling constants of H_2O at the SCF level.

   The effect of nuclear motion is approximated by only considering the contribution of the symmetric stretch mode S_1.

$$S_1 = \frac{1}{\sqrt{2}}(\Delta R_{OH_1} + \Delta R_{OH_2})$$

   In this approximation the zero point vibrational correction (ZPVC) to a property P of H_2O is obtained as

$$\Delta P^{ZPVC} = 0.023842\left(\frac{\partial P}{\partial S_1}\right) + 0.002305\left(\frac{\partial^2 P}{\partial S_1^2}\right)$$

   where S_1 is assumed to be in Ångstrøm.

   The first $\left(\frac{\partial P}{\partial S_1}\right)$ and second derivative $\left(\frac{\partial^2 P}{\partial S_1^2}\right)$ of the property with respect to the symmetric stretch mode is calculated numerically with a simple three point formula

$$\begin{aligned} \left(\frac{\partial P}{\partial S_1}\right) &= \ \frac{P(+S_1) - P(-S_1)}{2S_1} \\ \left(\frac{\partial^2 P}{\partial S_1^2}\right) &= \ \frac{P(+S_1) + P(-S_1) - 2P(eq)}{S_1^2} \end{aligned}$$

The equilibrium geometry of H_2O is $R_{OH} = 0.95843$ Å, $\angle_{HOH} = 104.45°$. For the symmetric stretch mode S_1 we use one pair of values from $\{\pm\ 0.025$ Å, $\pm\ 0.05$ Å, $\pm\ 0.075$ Å, $\pm\ 0.1$ Å$\}$.

As basis set we use the aug-cc-pVDZ basis set from the basis set library of Dalton. The DALTON manual can be found on
http://www.kjemi.uio.no/software/dalton/Master/Master.html

15. Show that the electric field and the magnetic induction in equations (2.169) and (2.170) are invariant to the gauge transformations in equations (2.172) and (2.171). Hint :

   - Recall that $\vec{\nabla} \times \vec{\nabla}\chi(\vec{r}, t) = 0$

16. Prove equation (2.174).

17. Prove equation (2.179).

18. The expressions for the diamagnetic and paramagnetic contributions to the magnetizability and nuclear magnetic shielding tensor in table 2.1 depend on the gauge origin $\vec{R}_{GO}$ of the vector potential $\vec{A}(\vec{r}_i)$, equation (2.59), for the magnetic induction.

   Show that the sum of the diamagnetic and paramagnetic contributions, however, is independent of $\vec{R}_{GO}$.

   Hint :

   - Move the gauge origin from $\vec{R}_{GO}$ to $\vec{R}_{GO} + \vec{D}$ and show that the terms depending on $\vec{D}$ cancel.

   - Recall the commutator relation

   $$[\vec{r}, \hat{H}^{(0)}] = \frac{i\hbar}{m_e}\hat{\vec{p}}$$

   - Recall that the set of excited states $\Psi_n^{(0)}$ is complete, i.e.

   $$\sum_n \mid \Psi_n^{(0)}\rangle\langle\Psi_n^{(0)} \mid = 1$$

Chapter 3

Ab Initio Methods for the Calculation of Molecular Properties

Ab initio methods for the calculation of molecular electromagnetic properties can be categorized according to several criteria.

- Expressions for the molecular properties can be derived either as derivatives of the electronic energy or as derivatives of molecular electromagnetic moments and fields. This distinction is important for some approximate wavefunctions which do not obey the Hellmann-Feynman theorem, equation (2.95). This means that first-order properties obtained as a derivative of the energy for truncated CI or perturbation theory wavefunctions, do not agree with the expectation value of the corresponding operator. It also follows that second and higher order properties will also depend on the use of either energy derivatives or derivatives of the expectation value.

  In general, for an approximate wavefunction $\Phi(\{C_i(\lambda)\})$, which typically depends on a set of parameters $\{C_i(\lambda)\}$ consisting of molecular orbital and configuration coefficients, the derivative of the electronic energy $W(\{C_i(\lambda)\}, \lambda)$ with respect to a real parameter λ in the Hamiltonian $\hat{H}(\lambda)$ is

$$\frac{dW(\{C_i(\lambda)\}, \lambda)}{d\lambda} = \frac{\partial W(\{C_i(\lambda)\}, \lambda)}{\partial \lambda} + \sum_i \left(\frac{\partial (W(\{C_i(\lambda)\}, \lambda))}{\partial C_i(\lambda)} \right) \left(\frac{\partial C_i(\lambda)}{\partial \lambda} \right).$$

(3.1)

  If the wavefunction is variationally optimized with respect to all parameters, *i.e.* $\partial W(\{C_i(\lambda)\}, \lambda)/\partial C_i(\lambda) = 0$, as is the case for a self-consistent field (SCF) and multiconfigurational self-consistent field (MCSCF) wavefunction, the Hellmann-Feynman theorem is satisfied. Truncated configuration interaction (CI) wavefunctions, by contrast, are not variationally optimized with respect to the molecular orbital coefficients. The Hellmann-Feynman theorem is therefore satisfied only in the limit of a full CI wavefunction, when

the molecular orbital coefficients are redundant. Similar problems arise for non-variational approaches such as Møller-Plesset perturbation theory (MP) and coupled-cluster (CC). It is however possible to redefine the expectation value for coupled-cluster wavefunctions to remove this discrepancy. Arponen [52] defined an energy functional which consists of a transition expectation value between the coupled-cluster state and a dual bra state, equations (3.76) - (3.80), which is stationary with respect to the wavefunction parameters and which therefore satisfies the Hellmann-Feynman theorem.

- A distinction can be made between methods which evaluate properties based on perturbation theory, with a partitioning of the Hamiltonian and a series expansion of the wavefunction (Sections 3.1-3.2) and those which use derivatives of the energy or first-order expectation values (see Section 3.3). The former methods can be further classified according to whether approximate wavefunctions are substituted for the exact wavefunction in the expressions obtained in Sections 2.5 – 2.7 or whether perturbation theory is applied directly to approximate wavefunctions. In the case of a variational wavefunction these two alternatives yield identical results - for example, RPA and coupled Hartree-Fock are formally equivalent [53]. Non-variational wavefunctions, on the other hand, give entirely different formulations and results.

- Finally, not all methods are capable of treating time-dependent perturbations to yield frequency-dependent properties. Even though most *ab initio* approaches have now been generalized to the time-dependent case, the pole structure (i.e. values of the perturbing frequency, ω, for which the denominator in Eq. (2.118) goes to zero) of MP-based properties can differ (Section 3.3.2), giving very different behaviour in the region of resonances.

The following notational conventions will be adopted. The one-electron spatial functions which are solutions to the closed shell Hartree-Fock (HF) equations

$$\hat{f}(i)\phi_p(i) = \epsilon_p \phi_p(i) \tag{3.2}$$

are denoted $\{\phi_p\}$ with Latin indices and are called molecular orbitals. Occupied and unoccupied spatial molecular orbitals are denoted with the indices $i, j, k, \ldots$ and $a, b, c, \ldots$, respectively, while the indices of general spatial molecular orbitals are denoted by $p, q, r, \ldots$ The Fock operator is defined as

$$\hat{F} = \sum_i \hat{f}(i) = \sum_i \left(\hat{h}^{(0)}(i) + \hat{v}^{HF}(i) \right) \quad , \tag{3.3}$$

where $\hat{v}^{HF}(i)$ is an effective one-electron potential, called the Hartree-Fock potential. ϵ_p is the molecular orbital energy. In the Roothaan-Hartree-Fock approach [54] the molecular orbitals are expanded in a basis of one-electron functions, $\{\chi_\mu\}$, denoted

by Greek indices, called atomic orbitals (although there is no restriction on their position within the molecule)

$$\phi_p = \sum_\mu \chi_\mu c_{\mu p}, \tag{3.4}$$

where $\{c_{\mu p}\}$ are the molecular orbital coefficients. One of the most widely-used methods for treating the electron correlation missing in the Hartree-Fock wavefunction is Møller-Plesset (MP) perturbation theory [55, 56]. The field free Hamiltonian $\hat{H}^{(0)}$ is partitioned to give the Fock operator $\hat{F}$ and the so-called fluctuation potential $\hat{V}$

$$\hat{H}^{(0)} = \hat{F} + \hat{V} \tag{3.5}$$

and the wavefunction is expanded in a perturbation series in $\hat{V}$

$$\mid \Psi_0^{(0)} \rangle = N \left(\mid \Phi_{\mathrm{SCF}} \rangle + \mid \Phi^{(1)} \rangle + \mid \Phi^{(2)} \rangle \ldots \right), \tag{3.6}$$

where N is a normalization constant and the zeroth-order wavefunction is the single determinant SCF wavefunction, $\mid \Phi_{\mathrm{SCF}} \rangle$, *i.e.* the antisymmetrized product of the occupied molecular orbitals $\{\phi_i\}$. The first order MP correction to the wavefunction $\mid \Phi^{(1)} \rangle$,

$$\mid \Phi_0^{(1)} \rangle = \sum_{n \neq 0} \mid \Phi_n^{(0)} \rangle \frac{\langle \Phi_n^{(0)} \mid \hat{V} \mid \Phi_{SCF} \rangle}{\langle \Phi_{SCF} \mid \hat{F} \mid \Phi_{SCF} \rangle - \langle \Phi_n^{(0)} \mid \hat{F} \mid \Phi_n^{(0)} \rangle}, \tag{3.7}$$

consists of determinants which are double excited with respect to $\mid \Phi_{SCF} \rangle$

$$\mid \Phi_0^{(1)} \rangle = \mid DE^{(1)} \rangle = \frac{1}{4} \sum_{\substack{ai \\ bj}} \kappa_{ij}^{ab} \mid \Phi_{ij}^{ab} \rangle, \tag{3.8}$$

where the first order doubles correlation coefficients are given as

$$\kappa_{ij}^{ab} = \frac{(ai \mid bj)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \tag{3.9}$$

The second order MP correction to the energy is then

$$W^{(2)} = \frac{1}{2} \sum_{\substack{ab \\ ij}} (ia \mid jb) \left\{ 4\kappa_{ij}^{ab} - 2\kappa_{ji}^{ab} \right\}. \tag{3.10}$$

The second order MP correction to the wavefunction

$$\mid \Phi_0^{(2)} \rangle = \sum_{n \neq 0} \mid \Phi_n^{(0)} \rangle \left\{ \frac{\langle \Phi_n^{(0)} \mid \hat{V} \mid \Phi_0^{(1)} \rangle}{\langle \Phi_{SCF} \mid \hat{F} \mid \Phi_{SCF} \rangle - \langle \Phi_n^{(0)} \mid \hat{F} \mid \Phi_n^{(0)} \rangle} \right.$$
$$\left. - \langle \Phi_{SCF} \mid \hat{V} \mid \Phi_{SCF} \rangle \frac{\langle \Phi_n^{(0)} \mid \Phi_0^{(1)} \rangle}{\langle \Phi_{SCF} \mid \hat{F} \mid \Phi_{SCF} \rangle - \langle \Phi_n^{(0)} \mid \hat{F} \mid \Phi_n^{(0)} \rangle} \right\} \tag{3.11}$$

contains single, double, triple and quadruple excited determinants

$$| \Phi_0^{(2)} \rangle = | SE^{(2)} \rangle + | DE^{(2)} \rangle + | TE^{(2)} \rangle + | QE^{(2)} \rangle \tag{3.12}$$

with *e.g.*

$$| SE^{(2)} \rangle = \sum_{ai} \kappa_i^a | \Phi_i^a \rangle \quad , \tag{3.13}$$

where the second order singles correlation coefficients are given as

$$\kappa_i^a = \frac{1}{\sqrt{2}} \frac{1}{\epsilon_i - \epsilon_a} \left(\sum_{jbc} (ab \mid jc) \left\{ 4\kappa_{ij}^{bc} - 2\kappa_{ji}^{bc} \right\} - \sum_{jkb} (ki \mid jb) \left\{ 4\kappa_{jk}^{ba} - 2\kappa_{kj}^{ba} \right\} \right) \quad . \tag{3.14}$$

3.1 Approximations to exact Perturbation Theory Expressions

In the current context, exact refers to the ground state wavefunction used in Rayleigh-Schrödinger perturbation theory in Section 2.5 or response theory in Sections 2.6 - 2.7. Computational development from these theories requires approximate wavefunctions to be substituted for the exact wavefunctions.

3.1.1 Ground State Expectation Values

According to equations (2.82) or (2.101) first-order properties can be evaluated as ground state expectation values. An alternative expression can be obtained by introducing the reduced one electron density matrix [57]

$$\gamma(\vec{x}_1, \vec{x}_1') = N \int d\vec{x}_2 \cdots d\vec{x}_N \; \Psi_0^{(0)}(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) \; \Psi_0^{(0)*}(\vec{x}_1', \vec{x}_2, \cdots, \vec{x}_N) \quad , \tag{3.15}$$

where $\vec{x}_i = \vec{r}_i s_i$ with the spin variable s_i and N is the total number of electrons. By integration over the spin of electron 1 the spinless reduced one electron density matrix is obtained

$$\rho(\vec{r}_1, \vec{r}_1') = \int_{s_1' = s_1} ds_1 \; \gamma(\vec{x}_1, \vec{x}_1') \quad . \tag{3.16}$$

The latter can be expanded in the basis of the molecular $\{\phi_p\}$ or atomic orbitals $\{\chi_\mu\}$

$$\rho(\vec{r}_1, \vec{r}_1') = \sum_{pq} \phi_p(\vec{r}_1) \; D_{pq} \; \phi_q^*(\vec{r}_1') \tag{3.17}$$

$$= \sum_{\mu\nu} \chi_\nu(\vec{r}_1) \; D_{\mu\nu} \; \chi_\nu^*(\vec{r}_1') \quad . \tag{3.18}$$

The coefficients in this expansion, which are also called density matrices, are given as

$$D_{pq} = \int d\vec{r}_1 \, d\vec{r}\,'_1 \, \phi_p^*(\vec{r}_1) \, \rho(\vec{r}_1, \vec{r}\,'_1) \, \phi_q(\vec{r}\,'_1) \tag{3.19}$$

$$D_{\mu\nu} = \int d\vec{r}_1 \, d\vec{r}'_1 \, \chi_\mu^*(\vec{r}_1) \, \rho(\vec{r}_1, \vec{r}\,'_1) \, \chi_\nu(\vec{r}\,'_1) \ . \tag{3.20}$$

The expectation value of an operator $\hat{O} = \sum_i \hat{o}(i)$ can thus be written as

$$\langle \Psi_0^{(0)} | \hat{O} | \Psi_0^{(0)} \rangle = \int d\vec{x}_1 \cdots d\vec{x}_N \, \Psi_0^{(0)*} \sum_i \hat{o}(i) \, \Psi_0^{(0)}$$

$$= N \int_{\vec{x}'_1 = \vec{x}_1} d\vec{x}_1 \cdots d\vec{x}_N \, \hat{o}(1) \, \Psi_0^{(0)}(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) \, \Psi_0^{(0)*}(\vec{x}'_1, \vec{x}_2, \cdots, \vec{x}_N)$$

$$= \int_{\vec{x}'_1 = \vec{x}_1} d\vec{x}_1 \, \hat{o}(1) \, \gamma(\vec{x}_1, \vec{x}'_1) = \int_{\vec{r}'_1 = \vec{r}_1} d\vec{r}_1 \, \hat{o}(1) \, \rho(\vec{r}_1, \vec{r}\,'_1)$$

$$= \sum_{pq} D_{pq} \, \langle \phi_q | \hat{o} | \phi_p \rangle = \sum_{\mu\nu} D_{\mu\nu} \, \langle \chi_\nu | \hat{o} | \chi_\mu \rangle \ , \tag{3.21}$$

where the distinction between $\vec{r}_1$ and $\vec{r}'_1$ becomes important for a differential operator $\hat{o}(i)$, which otherwise would act on both wavefunctions.

For a closed-shell self-consistent wavefunction $| \Phi_{SCF} \rangle$, for example, the density matrix in the atomic orbital and molecular orbital basis are given as

$$D_{\mu\nu}^{SCF} = 2 \sum_i c_{\mu i}^* c_{\nu i} \tag{3.22}$$

$$D_{ij}^{SCF} = 2\delta_{ij} \ . \tag{3.23}$$

Using the MP wavefunction, equation (3.6), in equation (3.15) and keeping all terms which are second order in the fluctuation potential a so-called *unrelaxed* second order

---

Table 3.1 Electric dipole moment (in a.u. $\approx 8.478358 \times 10^{-30}$ C m) of the hydrogenhalides, HX, and methylhalides, CH_3X, calculated with an SCF as well as an unrelaxed and relaxed MP2 density matrix [a]

Molecule	SCF	unrelaxed MP2	relaxed MP2	Exp.
HF	0.7570	0.6994	0.7100	0.7094
HCl	0.4725	0.4455	0.4419	0.4305
HBr	0.3777	0.3375	0.3417	0.3219
CH_3F	0.8443	0.7521	0.7380	0.7312
CH_3Cl	0.8095	0.7271	0.7589	0.7461
CH_3Br	0.8456	0.7524	0.7462	0.7162

[a] *Ab initio* results taken from Ref. [58], experimental equilibrium geometry data for HX from Ref. [59] and for CH_3X from Ref. [60].

(MP2) correction $\boldsymbol{D}^{(2)}$ to the density matrix in the molecular orbital basis is obtained [61]

$$D_{ij}^{(2)} = -\sum_{abk} \kappa_{ik}^{ab} \left(4\kappa_{jk}^{ab} - 2\kappa_{kj}^{ab} \right) \tag{3.24}$$

$$D_{ab}^{(2)} = \sum_{cij} \kappa_{ij}^{ac} \left(4\kappa_{ij}^{bc} - 2\kappa_{ji}^{bc} \right) \tag{3.25}$$

$$D_{ia}^{(2)} = D_{ai}^{(2)} = \sqrt{2}\, \kappa_i^a \quad . \tag{3.26}$$

Table 3.2 The orbital diamagnetic contribution to the indirect nuclear spin-spin coupling constants (in Hz) calculated with an SCF and an unrelaxed second order (MP2) density matrix ^{a}

		SCF	unrelaxed MP2
HF	$^1J^{^1H-^{19}F}$	-0.03	0.04
H_2O	$^1J^{^1H-^{17}O}$	-0.04	-0.05
	$^2J^{^1H-^1H}$	-7.23	-7.13
CH_4	$^1J^{^1H-^{13}C}$	0.24	0.25
	$^2J^{^1H-^1H}$	-3.54	-3.55
N_2	$^1J^{^{15}N-^{14}N}$	0.10	0.10
CO	$^1J^{^{13}C-^{17}O}$	0.03	0.03
C_2H_2	$^1J^{^{13}C-^{13}C}$	0.01	0.01
	$^1J^{^1H-^{13}C}$	0.27	0.26
	$^2J^{^1H-^{13}C}$	-1.35	-1.35
	$^3J^{^1H-^1H}$	-3.60	-3.60

^{a} Results taken from Ref. [62].

In Tables 3.1 and 3.2 some results for the electric dipole moment [58] of the hydrogenhalides, HX, and methylhalides, CH_3X, and for the the orbital diamagnetic contribution to the indirect nuclear spin-spin coupling constants of some small molecules [62] are shown. They are calculated with the SCF density matrix, equation (3.23) and with the unrelaxed second order (MP2) density matrix in equations (3.24) - (3.26). The results for the dipole moments, in Table 3.1, are clearly improved by the unrelaxed MP2 correction to the density matrix. Correlation at this level reduces the dipole moments on average by 9 %. The root-mean-square percentage deviation of the unrelaxed MP2 results from the experimental equilibrium geometry values is 3.6 % with a maximum and minimum deviation of 5.0 % and -1.4 %, respectively. Experimental values for the orbital diamagnetic term are not available since the orbital diamagnetic term is only one of four contributions to the indirect nuclear spin-spin coupling constants. Nevertheless one can see that in most cases the correlations corrections to the orbital diamagnetic term are unimportant.

3.1.2 Sum-over-States Methods

The Sum-over-States method for the calculation of second or higher order properties is based on equations (2.90) and (2.118). The main task is thus to obtain a set of excitation energies $W_n^{(0)} - W_0^{(0)}$ and transition moments $\langle \Psi_0^{(0)} \mid \hat{O} \mid \Psi_n^{(0)} \rangle$ with the appropriate operator $\hat{O}$ or alternatively a ground state wavefunction $\mid \Psi_0^{(0)} \rangle$ and a set of excited state wavefunctions $\mid \Psi_n^{(0)} \rangle$ from which the excitation energies and transition moments can be calculated.

Approximating the excitation energies $W_n^{(0)} - W_0^{(0)}$ by molecular orbital energy differences $\epsilon_a - \epsilon_i$ and the transition moments $\langle \Psi_0^{(0)} \mid \hat{O} \mid \Psi_n^{(0)} \rangle$ by matrix elements of $\hat{O}$ in the molecular orbital basis $\langle \phi_i \mid \hat{o} \mid \phi_a \rangle$ gives the uncoupled Hartree-Fock approximation [63], which played an important role in the early days of calculations of molecular properties.

Nowadays the Sum-over-States method is mostly used in three cases. The first is benchmark studies of two electron systems using explicitly correlated wavefunctions (see *e.g.* [64]). The second is the study of hyperpolarizabilities of larger systems using semi-empirical methods. Finally it is used in the analysis of contributions to a molecular property from excitations between individual, typically localized, molecular orbitals (see *e.g.* [65, 66]). The latter is normally done at the level of the random phase approximation (RPA), for which excitation energies and transition moments can easily be obtained.

3.1.3 Polarization Propagator Methods

Under polarization propagator methods one can understand methods in which approximations are made to the exact matrix representation of the linear response function or polarization propagator given in equation (2.137). This equation is exact as long as a complete set of excitation and de-excitation operators $\{h_n\}$ is used and the reference state $\mid \Psi_0^{(0)} \rangle$ is an eigenfunction of the unperturbed Hamiltonian. Approximate polarization propagator methods are obtained by truncating the set of operators and by using an approximate reference state $\mid \Psi_0^{(0)} \rangle$. Multiconfigurational self-consistent field (MCSCF) and Møller-Plesset (MP) perturbation theory wavefunctions are commonly employed as approximate reference states in polarization propagator approximations.

Møller-Plesset Perturbation Theory Polarization Propagator Methods

In polarization propagator approximations based on MP perturbation theory the reference state is approximated by the wavefunction in equation (3.6) and the complete set of operators $\boldsymbol{h}$ was shown [67] to consist of all possible single excitation and de-excitation operators, $\boldsymbol{h}_2 = \{\boldsymbol{q}^\dagger, \boldsymbol{q}\}$, all possible double excitation and de-excitation operators, $\boldsymbol{h}_4 = \{\boldsymbol{q}^\dagger \boldsymbol{q}^\dagger, \boldsymbol{q}\boldsymbol{q}\}$, up to all possible N-tuple excitation and de-excitation operators with respect to the N-electron Hartree-Fock state $\mid \Phi_{SCF} \rangle$. The matrix

form of the polarization propagator, (2.137), can thus be written as

$$
\langle\langle \hat{O}; \hat{V}_{\alpha\cdots}^{\omega}\rangle\rangle_{\omega} = \Big(\ \langle\Psi_0^{(0)}|[\hat{O},\tilde{\boldsymbol{h}}_2]|\Psi_0^{(0)}\rangle \ \ \langle\Psi_0^{(0)}|[\hat{O},\tilde{\boldsymbol{h}}_4]|\Psi_0^{(0)}\rangle \ \cdots \ \Big)
$$

$$
\times \left[\hbar\omega \begin{pmatrix} \boldsymbol{S}_{22}^{[2]} & \boldsymbol{S}_{24}^{[2]} & \cdots \\ \boldsymbol{S}_{42}^{[2]} & \boldsymbol{S}_{44}^{[2]} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} - \begin{pmatrix} \boldsymbol{E}_{22}^{[2]} & \boldsymbol{E}_{24}^{[2]} & \cdots \\ \boldsymbol{E}_{42}^{[2]} & \boldsymbol{E}_{44}^{[2]} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \right]^{-1} \quad (3.27)
$$

$$
\times \begin{pmatrix} \langle\Psi_0^{(0)}|[\boldsymbol{h}_2^{\dagger},\hat{V}_{\alpha\cdots}^{\omega}]|\Psi_0^{(0)}\rangle \\ \langle\Psi_0^{(0)}|[\boldsymbol{h}_4^{\dagger},\hat{V}_{\alpha\cdots}^{\omega}]|\Psi_0^{(0)}\rangle \\ \vdots \end{pmatrix} \ ,
$$

where

$$
\boldsymbol{S}_{ij}^{[2]} = \langle\Psi_0^{(0)}|[\boldsymbol{h}_i^{\dagger},\tilde{\boldsymbol{h}}_j]|\Psi_0^{(0)}\rangle \qquad (3.28)
$$

$$
\boldsymbol{E}_{ij}^{[2]} = \langle\Psi_0^{(0)}|[\boldsymbol{h}_i^{\dagger},[\hat{F}+\hat{V},\tilde{\boldsymbol{h}}_j]]|\Psi_0^{(0)}\rangle \ . \qquad (3.29)
$$

A series of approximations of increasing order n is obtained by requiring that all the matrix elements $\boldsymbol{S}_{ij}^{[2]}$, $\boldsymbol{E}_{ij}^{[2]}$ as well as $\langle\Psi_0^{(0)}|[\hat{O},\tilde{\boldsymbol{h}}_i]|\Psi_0^{(0)}\rangle$ are evaluated through order n in the fluctuation potential.

For a first order polarization propagator approximation (FOPPA) it is only necessary to keep $\boldsymbol{h}_2$ in the set of operators and the reference state is the Hartree-Fock state $|\ \Phi_{SCF}\rangle$. This approximation is better known as time dependent Hartree-Fock approximation (TDHF) [68], see section 3.2.1, or random phase approximation (RPA) [69] and can also be derived as linear response of an SCF wavefunction, as described in section 3.2.2. The polarization propagator in the RPA is then given as

$$
\langle\langle \hat{O}; \hat{V}_{\alpha\cdots}^{\omega}\rangle\rangle_{\omega} = \Big(\ \langle\Phi_{SCF}|[\hat{O},\tilde{\boldsymbol{q}}^{\dagger}]|\Phi_{SCF}\rangle \ \ \langle\Phi_{SCF}|[\hat{O},\tilde{\boldsymbol{q}}]|\Phi_{SCF}\rangle \ \Big) \begin{pmatrix} \boldsymbol{X}(\omega) \\ \boldsymbol{Y}(\omega) \end{pmatrix} \qquad (3.30)
$$

$$
\begin{pmatrix} \boldsymbol{X}(\omega) \\ \boldsymbol{Y}(\omega) \end{pmatrix} = \left[\hbar\omega \begin{pmatrix} \boldsymbol{1} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{1} \end{pmatrix} - \begin{pmatrix} \boldsymbol{A}^{(0,1)} & \boldsymbol{B}^{(1)} \\ \boldsymbol{B}^{(1)} & \boldsymbol{A}^{(0,1)} \end{pmatrix} \right]^{-1} \begin{pmatrix} \langle\Phi_{SCF}|[\boldsymbol{q},\hat{V}_{\alpha\cdots}^{\omega}]|\Phi_{SCF}\rangle \\ \langle\Phi_{SCF}|[\boldsymbol{q}^{\dagger},\hat{V}_{\alpha\cdots}^{\omega}]|\Phi_{SCF}\rangle \end{pmatrix} \ , \ (3.31)
$$

where the $\boldsymbol{A}^{(0,1)}$ and $\boldsymbol{B}^{(1)}$ matrices are defined as

$$
\boldsymbol{A}^{(0,1)} = \langle\Phi_{SCF}|[\boldsymbol{q},[\hat{F}+\hat{V},\tilde{\boldsymbol{q}}^{\dagger}]]|\Phi_{SCF}\rangle \qquad (3.32)
$$

$$
\boldsymbol{B}^{(1)} = \langle\Phi_{SCF}|[\boldsymbol{q},[\hat{F}+\hat{V},\tilde{\boldsymbol{q}}]]|\Phi_{SCF}\rangle \ . \qquad (3.33)
$$

Based on a partitioned form of the propagator

$$
\langle\langle \hat{O}; \hat{V}_{\alpha\cdots}^{\omega}\rangle\rangle_{\omega} =
$$

$$
\Big(\langle\Psi_0^{(0)}|[\hat{O},\tilde{\boldsymbol{h}}_2]|\Psi_0^{(0)}\rangle - \langle\Psi_0^{(0)}|[\hat{O},\tilde{\boldsymbol{h}}_4]|\Psi_0^{(0)}\rangle(\hbar\omega\boldsymbol{S}_{44}^{[2]}-\boldsymbol{E}_{44}^{[2]})^{-1}(\hbar\omega\boldsymbol{S}_{42}^{[2]}-\boldsymbol{E}_{42}^{[2]}) \Big)
$$

$$
\times \left[(\hbar\omega\boldsymbol{S}_{22}^{[2]}-\boldsymbol{E}_{22}^{[2]}) - (\hbar\omega\boldsymbol{S}_{24}^{[2]}-\boldsymbol{E}_{24}^{[2]})(\hbar\omega\boldsymbol{S}_{44}^{[2]}-\boldsymbol{E}_{44}^{[2]})^{-1}(\hbar\omega\boldsymbol{S}_{42}^{[2]}-\boldsymbol{E}_{42}^{[2]}) \right]^{-1} \quad (3.34)
$$

$$
\times \Big(\langle\Psi_0^{(0)}|[\boldsymbol{h}_2^{\dagger},\hat{V}_{\alpha\cdots}^{\omega}]|\Psi_0^{(0)}\rangle - (\hbar\omega\boldsymbol{S}_{24}^{[2]}-\boldsymbol{E}_{24}^{[2]})(\hbar\omega\boldsymbol{S}_{44}^{[2]}-\boldsymbol{E}_{44}^{[2]})^{-1}\langle\Psi_0^{(0)}|[\boldsymbol{h}_4^{\dagger},\hat{V}_{\alpha\cdots}^{\omega}]|\Psi_0^{(0)}\rangle \Big)
$$

the second order polarization propagator approximation (SOPPA) [70] was histor-
ically defined to be second order in the single excitation dominated part, *i.e* in
matrix elements which contain only $\boldsymbol{h}_2$ operators. This implies that $\boldsymbol{E}_{22}^{[2]}$, $\boldsymbol{S}_{22}^{[2]}$,
$\langle \Psi_0^{(0)} | [\hat{O}, \tilde{\boldsymbol{h}}_2] | \Psi_0^{(0)} \rangle$ and $\langle \Psi_0^{(0)} | [\boldsymbol{h}_2^\dagger, \hat{V}_{\alpha\cdots}^\omega] | \Psi_0^{(0)} \rangle$ are evaluated through second order,
$\boldsymbol{E}_{24}^{[2]}$, $\boldsymbol{S}_{24}^{[2]}$, $\boldsymbol{E}_{42}^{[2]}$, $\boldsymbol{S}_{42}^{[2]}$, $\langle \Psi_0^{(0)} | [\hat{O}, \tilde{\boldsymbol{h}}_4] | \Psi_0^{(0)} \rangle$ and $\langle \Psi_0^{(0)} | [\boldsymbol{h}_4^\dagger, \hat{V}_{\alpha\cdots}^\omega] | \Psi_0^{(0)} \rangle$ are evaluated
through first order and $\boldsymbol{E}_{44}^{[2]}$ and $\boldsymbol{S}_{44}^{[2]}$ only through zeroth order [71]. An analy-
sis of the matrix elements shows that besides the first order MP wavefunction $| \Phi^{(1)} \rangle$
only $| SE^{(2)} \rangle$ is required from the second order MP wavefunction, equation (3.13).

A complete third order polarization propagator approximation has been derived
but only parts have been implemented [72]. However, two other SOPPA-like methods
have been used widely. Both methods are based on the assumption that replace-
ment of the first order MP doubles correlation coefficients in equation (3.8) and of
the second order MP singles correlation coefficient in equation (3.13) by coupled
cluster singles and doubles amplitudes will give improved results. In the second
order polarization propagator with coupled cluster singles and doubles amplitudes
- SOPPA(CCSD) - method [73] this is done in all matrix elements, whereas in its
precursor, the coupled cluster singles and doubles polarization propagator approxi-
mation (CCSDPPA) [72], this was not the case.

Multiconfigurational Polarization Propagator Methods

In the multiconfigurational polarization propagator approximation [74], normally
called multiconfigurational random phase approximation (MCRPA), the set of op-
erators contains state transfer operators $\{\boldsymbol{R}^\dagger, \boldsymbol{R}\}$ in addition to the non-redundant
single excitation $\boldsymbol{q}^\dagger$ and de-excitation $\boldsymbol{q}$ operators. The state transfer operators are
defined as

$$R_n^\dagger = | \Psi_n \rangle \langle \Psi_{MCSCF} | \qquad (3.35)$$

where $| \Psi_n \rangle = \sum_i | \Phi_i \rangle C_{in}$ are the orthogonal complement states of the MCSCF
state $| \Psi_{MCSCF} \rangle = \sum_i | \Phi_i \rangle C_{i0}$ and $\{| \Phi_i \rangle\}$ is the set of configuration state functions.
The expression for the polarization propagator in MCRPA can be obtained from
equation (3.27) if one identifies $\boldsymbol{h}_4$ with $\{\boldsymbol{R}^\dagger, \boldsymbol{R}\}$ and $| \Psi_0^{(0)} \rangle$ with $| \Psi_{MCSCF} \rangle$. Since
this is a variational wavefunction, MCRPA can also be obtained by application of
linear response theory, section 3.2.2, or of the quasienergy derivative method, section
3.3.3, for an MCSCF state.

Illustrative Polarization Propagator Calculations

In the following we want to compare the performance of the four polarization prop-
agator methods : RPA, SOPPA, SOPPA(CCSD) and MCRPA. In Tables 3.3 - 3.6
results from the recent literature [45, 62, 75, 76, 77, 41, 78] for static dipole polar-
izabilties α (Table 3.3) and indirect nuclear spin-spin coupling constants J (Tables
3.4, 3.5 and 3.6) are shown.

Table 3.3 Comparison of different polarization propagator methods for the calculation of static dipole polarizabilities α (in units of $e^2 a_0^2 E_h^{-1}$)[a] using the daug-cc-pVTZ basis sets[b]

	RPA	SOPPA	SOPPA (CCSD)	Exp.[c]
HF	4.913	5.952	5.731	5.60
HCl	16.728	17.651	17.368	17.39
H_2O	8.538	10.089	9.782	9.64
H_2S	23.681	24.756	24.243	24.71
NH_3	12.960	14.441	14.161	14.56
PH_3	29.829	30.881	30.076	30.93
CH_4	16.217	16.754	16.510	17.27
SiH_4	29.776	31.153	30.606	31.90
F_2	8.597	8.760	8.456	8.38
Cl_2	29.939	31.411	30.651	30.417
C_2H_4	28.493	28.145	27.537	27.70
CO_2	15.920	19.238	18.611	17.51
SO_2	23.698	28.235	27.116	25.61

[a] Results taken from [75]. [b] [79, 80]. [c] References for the experimental values are given in [75].

Table 3.4 Comparison of different polarization propagator methods for the calculation of indirect nuclear spin-spin coupling constants J (in Hz)[a]

		RPA	MCRPA	SOPPA	SOPPA (CCSD)	Exp.[b]
N_2	$^1J^{^{15}N-^{14}N}$	-14.9	0.8	2.7	2.1	1.4 ± 0.6 [c]
CO	$^1J^{^{13}C-^{17}O}$	-5.7	16.1	20.4	18.6	15.6 ± 0.1 [c]
C_2H_2	$^1J^{^{13}C-^{13}C}$	409.5	181.2	189.3	188.7	184.52 [c]
HF	$^1J^{^1H-^{19}F}$	666.9	543.7	539.5	529.4	540 [c]
H_2O	$^1J^{^1H-^{17}O}$	-103.4	-83.9	-82.4	-80.6	-83.04 ± 0.02 [c]
CH_4	$^1J^{^1H-^{13}C}$	156.9	135.7	126.9	122.3	120.87 ± 0.05 [c]
C_2H_2	$^1J^{^1H-^{13}C}$	411.1	232.1	262.9	253.6	242.40 [c]
H_2O	$^2J^{^1H-^1H}$	-22.4	-9.6	-9.1	-8.8	-7.8 ± 0.7 [c]
CH_4	$^2J^{^1H-^1H}$	-27.0	-20.8	-15.3	-14.0	-11.878 ± 0.00 4[c]
C_2H_2	$^2J^{^1H-^{13}C}$	-49.9	50.1	52.6	51.7	53.76 [c]
C_2H_2	$^3J^{^1H-^1H}$	84.9	10.8	12.2	11.3	10.11 [c]

[a] RPA, SOPPA, SOPPA(CCSD) results taken from [62], MCRPA results with CAS wavefunctions are taken from [76, 77, 41, 45, 78]. [b] References for the experimental values are given in [62, 47]. [c] Experimental data for the equilibrium geometry, *i.e.* corrected with calculated ro-vibrational corrections.

Table 3.5 Comparison of different polarization propagator methods for the calculation of the orbital paramagnetic contribution J^{OP} to the indirect nuclear spin-spin coupling constants (in Hz)[a]

	J^{OP}	RPA	MCRPA	SOPPA (CCSD)
N_2	$^1J^{15N-14N}$	0.43	2.69	3.00
CO	$^1J^{13C-17O}$	11.81	12.89	14.11
C_2H_2	$^1J^{13C-13C}$	15.05	—	6.34
HF	$^1J^{1H-19F}$	195.05	182.0	189.82
H_2O	$^1J^{1H-17O}$	-12.27	-11.45	-11.51
CH_4	$^1J^{1H-13C}$	1.47	1.48	1.50
C_2H_2	$^1J^{1H-13C}$	-3.60	—	-0.85
H_2O	$^2J^{1H-1H}$	9.09	9.23	9.31
CH_4	$^2J^{1H-1H}$	3.73	3.59	3.72
C_2H_2	$^2J^{1H-13C}$	8.28	—	5.60
C_2H_2	$^3J^{1H-1H}$	5.54	—	4.81

[a] RPA, SOPPA(CCSD) results taken from [62], MCRPA results with CAS wavefunctions are taken from [76, 41, 45, 78].

Table 3.6 Comparison of different polarization propagator methods for the calculation of the spin-dipolar, J^{SD}, and Fermi contact J^{FC} contributions to the indirect nuclear spin-spin coupling constants (in Hz)[a]

		J^{SD}			J^{FC}		
		RPA	MCRPA	SOPPA (CCSD)	RPA	MCRPA	SOPPA (CCSD)
N_2	$^1J^{15N-14N}$	-7.84	-1.95	-1.76	-7.49	-0.53	0.79
CO	$^1J^{13C-17O}$	-9.07	-4.77	-4.37	-8.53	3.90	8.76
C_2H_2	$^1J^{13C-13C}$	29.06	—	8.46	365.35	—	173.92
HF	$^1J^{1H-19F}$	-11.73	-1.41	-0.94	483.62	363.2	340.50
H_2O	$^1J^{1H-17O}$	-0.01	-0.41	-0.47	-91.12	-72.08	-68.56
CH_4	$^1J^{1H-13C}$	-0.21	0.02	0.03	155.42	123.53	120.58
C_2H_2	$^1J^{1H-13C}$	3.04	—	0.43	411.41	—	253.73
H_2O	$^2J^{1H-1H}$	1.25	1.03	0.89	-25.50	-12.70	-11.87
CH_4	$^2J^{1H-1H}$	0.46	0.35	0.36	-27.68	-15.73	-14.53
C_2H_2	$^2J^{1H-13C}$	-1.52	—	0.98	-55.25	—	46.47
C_2H_2	$^3J^{1H-1H}$	3.02	—	0.59	79.93	—	9.49

[a] RPA, SOPPA(CCSD) results taken from [62], MCRPA results with CAS wavefunctions are taken from [76, 41, 45, 78].

The root-mean-square (rms) of the deviation of the SOPPA(CCSD) results for the static dipole polarizability (Table 3.3) from the experimental values is 0.73 a.u. with a maximum deviation of 1.5 a.u. for SO_2. In terms of percentage deviations the rms value is 3.3 %. At the RPA level the rms deviation is 1.23 a.u. (7.3%) with maximum deviation of -2.12 a.u. for SiH_4, which shows that inclusion of electron correlation at the SOPPA(CCSD) level clearly improves the agreement with experiment. The correlation corrections are for most molecules smaller than 4 % with the exception of NH_3 (9 %), H_2O (15 %), HF (17 %), CO_2 (17 %) and SO_2 (14 %).

The agreement of the SOPPA(CCSD) results for some indirect nuclear spin-spin coupling constants with the experimental values is also very good. For most molecules in Table 3.4 the deviations are less than 4 Hz with a rms value of 2.3 Hz, apart from HF and $^1J^{^1H-^{13}C}$ in C_2H_2, where the deviations are about 10 Hz. Including also those couplings increase the rms to 5.1 Hz. The rms value of the percentage deviations is for all molecules 18% (10 % without HF and $^1J^{^1H-^{13}C}$ in C_2H_2). Based on these statistical data one can conclude that spin-spin coupling constants are more difficult to calculate than dipole polarizabilities. This can also be seen if one compares the correlation corrections to both properties as calculated at the SOPPA(CCSD) level. The correlation corrections for the molecules in Table 3.4 vary between 20 % for HF and 426 % for CO. The calculation of a spin-spin coupling constants is also complicated because it consists of four terms (see section 2.5), of which the three linear response function contributions are shown in Tables 3.5 and 3.6. In section 2.5, it was discussed that two of them, the spin-dipolar and the Fermi contact contribution, consist of excited triplet states, which uncorrelated methods like RPA are often not able to describe properly. The large correlation effects in the spin-spin coupling constants are thus normally due to the Fermi contact term.

Reduced Linear Equations

A feature common to all propagator methods is that the response is given as the product of a "property gradient" vector $\tilde{\boldsymbol{T}}(\hat{O})$ with an inverse "Hessian" or principal propagator matrix $(\hbar\omega\boldsymbol{S} - \boldsymbol{E})$ and another "property gradient" vector $\boldsymbol{T}(\hat{V}^\omega_{\alpha\dots})$

$$\langle\langle\hat{O}; \hat{V}^\omega_{\alpha\dots}\rangle\rangle_\omega = \tilde{\boldsymbol{T}}(\hat{O})(\hbar\omega\boldsymbol{S} - \boldsymbol{E})^{-1}\boldsymbol{T}(\hat{V}^\omega_{\alpha\dots}) \tag{3.36}$$

$$= \tilde{\boldsymbol{T}}(\hat{O})\boldsymbol{N}(\hat{V}^\omega_{\alpha\dots}) \ . \tag{3.37}$$

In actual calculations, however the inverse of the principal propagator is never evaluated. A set of coupled linear equations for the response vector $\boldsymbol{N}(\hat{V}^\omega_{\alpha\dots})$

$$(\hbar\omega\boldsymbol{S} - \boldsymbol{E}) \ \boldsymbol{N}(\hat{V}^\omega_{\alpha\dots}) = \boldsymbol{T}(\hat{V}^\omega_{\alpha\dots}) \tag{3.38}$$

is instead solved iteratively by expanding the response vector in a basis of orthogonal trial vectors $\{\boldsymbol{b}_i\}$ [81]

$$\boldsymbol{N} = \sum_i \boldsymbol{b}_i c_i \ . \tag{3.39}$$

In a given iteration n the linear equations transformed to the basis of the trialvectors $\{\boldsymbol{b}_1 \cdots \boldsymbol{b}_n\}$, to the so-called reduced space,

$$(\hbar\omega \boldsymbol{S}^R - \boldsymbol{E}^R) \ \boldsymbol{N}^R(\hat{V}_{\alpha\cdots}^\omega) = \boldsymbol{T}^R(\hat{V}_{\alpha\cdots}^\omega) \tag{3.40}$$

are solved by standard techniques. The elements of the solution vector, $\boldsymbol{N}^R(\hat{V}_{\alpha\cdots}^\omega$ in the reduced space are the optimal coefficients $\{c_i\}$ in equation (3.39) for the trial vector $\boldsymbol{N}(\hat{V}_{\alpha\cdots}^\omega)$ in iteration n. The elements of the other matrices in the reduced space are defined as

$$S_{ij}^R \ = \ \tilde{\boldsymbol{b}}_i \ \boldsymbol{S} \ \boldsymbol{b}_j \tag{3.41}$$

$$E_{ij}^R \ = \ \tilde{\boldsymbol{b}}_i \ \boldsymbol{E} \ \boldsymbol{b}_j \tag{3.42}$$

$$T_i^R(\hat{V}_{\alpha\cdots}^\omega) \ = \ \tilde{\boldsymbol{b}}_i \ \boldsymbol{T}(\hat{V}_{\alpha\cdots}^\omega) \ . \tag{3.43}$$

The iterations are converged if the residual vector, defined as,

$$\boldsymbol{R}_n = (\hbar\omega \boldsymbol{S} - \boldsymbol{E}) \ \boldsymbol{N}_n(\hat{V}_{\alpha\cdots}^\omega) - \boldsymbol{T}(\hat{V}_{\alpha\cdots}^\omega) \tag{3.44}$$

is smaller than a given threshold. A new trial vector for the next iteration, $n + 1$, can be generated by a generalization of the conjugate gradient method

$$\boldsymbol{b}_{n+1} = (\hbar\omega \boldsymbol{S}^{diag} - \boldsymbol{E}^{diag})^{-1} \ \boldsymbol{R}_n \ , \tag{3.45}$$

where $\boldsymbol{S}^{diag}$ and $\boldsymbol{E}^{diag}$ are diagonal matrices consisting of the diagonal elements of $\boldsymbol{S}$ and $\boldsymbol{E}$.

In each iteration one has then to calculate the linear transformation of the new trial vector $(\hbar\omega \boldsymbol{S} - \boldsymbol{E})\boldsymbol{b}_i$ which can be done directly without ever calculating the $(\hbar\omega \boldsymbol{S} - \boldsymbol{E})$ matrix explicit [29, 82]. For the RPA and SOPPA polarization propagators this can also be done directly from the two electron integrals in the basis of the atomic orbitals [83, 84, 85].

3.1.4   Perturbed Electron Propagator Method

The definition of a propagator in equation (2.117) can also be generalized to other types of operators [86]. The electron propagator matrix $\mathbf{G}(\omega)$ in the frequency domain, *e.g.*, is defined as

$$G_{pq}(\omega) = \langle\langle a_p^\dagger; a_q \rangle\rangle_\omega \ , \tag{3.46}$$

where $a_p^\dagger$, a_q are second quantization creation and annihilation operators. An important property of the electron propagator is that the ground state one electron density matrix can be obtained from it by complex integration over the Coulson contour $\mathcal{C}$

$$D_{pq} = \frac{1}{2\pi\imath} \oint_{\mathcal{C}} d\omega \ G_{pq}(\omega) \ . \tag{3.47}$$

First order properties can then be calculated with this one density matrix *via* equation (3.21).

In addition it is also possible to calculate second and higher order properties using the perturbed electron propagator approach by Pickup [87]. In the presence of a perturbation the electron propagator matrix is changed and can be expanded in powers of the perturbation

$$\mathbf{G}(\omega) = \mathbf{G}^{(0)}(\omega) + \mathbf{G}^{(1)}(\omega) + \cdots \quad . \tag{3.48}$$

Contour integration of this higher order electron propagators yields corresponding higher order density matrices.

$$D_{pq}^{(1)} = \frac{1}{2\pi\imath} \oint_C d\omega \; G_{pq}^{(1)}(\omega) \quad , \tag{3.49}$$

and second order properties, like a static polarizability, can then be calculated as

$$\alpha_{\alpha\beta} = \sum_{pq} \langle \phi_q \,|\, \hat{o}_\alpha^E \,|\, \phi_p \rangle \; D_{\beta,pq}^{(1)} \quad . \tag{3.50}$$

The exact electron propagator matrix can be written as [88]

$$\boldsymbol{G}(\omega) = \left(\omega\mathbf{1} - \boldsymbol{F}(D^{HF}) - \boldsymbol{\Sigma}(\omega)\right)^{-1} = \left(\omega\mathbf{1} - \boldsymbol{F}(D^{corr}) - \boldsymbol{M}(\omega)\right)^{-1} \quad , \tag{3.51}$$

where $\boldsymbol{F}$ and $\boldsymbol{\Sigma}(\omega)$ are the Fock and self-energy matrices, respectively. Expressions for $\mathbf{G}^{(0)}(\omega)$, $\mathbf{G}^{(1)}(\omega)$, $\cdots$ can be obtained *via* an expansion of the inverse

$$\mathbf{G}^{(0)}(\omega) = \left(\omega\mathbf{1} - \boldsymbol{F}^{(0)}(D^{corr}) - \boldsymbol{M}^{(0)}(\omega)\right)^{-1} \tag{3.52}$$

$$\mathbf{G}^{(1)}(\omega) = \mathbf{G}^{(0)}(\omega) \left(\boldsymbol{F}^{(1)}(D^{(1),corr}) - \boldsymbol{M}^{(1)}(\omega)\right) \mathbf{G}^{(0)}(\omega) \quad . \tag{3.53}$$

However, the Fock matrix depends on the one electron density matrix and one has to iterate on equations (3.49) and (3.53).

Approximations to the electron propagator can obtained using several methods, see *e.g.* [89]. Setting $\boldsymbol{M}^{(0)}(\omega) = \boldsymbol{M}^{(1)}(\omega) = 0$ and approximating $\boldsymbol{F}^{(0)}(D^{corr})$ by orbital energies yields the coupled Hartree-Fock approximation, described in the following section 3.2.1. Correlation corrections can be obtained using a MP perturbation theory expansion of the self-energy [87, 90].

3.2 Perturbation Theory with Approximate Wavefunctions

3.2.1 Coupled Hartree-Fock and Time Dependent Coupled Hartree-Fock Theory

In the coupled Hartree-Fock method (CHF), probably derived the first time by Peng [91], second and higher order static properties are obtained by solving the Hartree-Fock equations self-consistently in the presence of the perturbation. The molecular

orbitals $\{\phi_{\beta,p}\}$ in the presence of the perturbation, *e.g.* an electric field E_β, can be expanded in the set of unperturbed molecular orbitals $\{\phi_p^{(0)}\}$

$$\phi_{\beta,p} = \sum_q \phi_q^{(0)} \, U_{\beta,qp} \quad . \tag{3.54}$$

Inserting these in the Hartree-Fock equations, (3.2), gives

$$\hat{f}_\beta(i) \sum_q \phi_q^{(0)} \, U_{\beta,qp} = \epsilon_{\beta,p} \sum_q \phi_q^{(0)} \, U_{\beta,qp} \quad , \tag{3.55}$$

or in matrix form

$$\sum_q F_{\beta,rq} \, U_{\beta,qp} = \epsilon_{\beta,p} \sum_q \delta_{rq} \, U_{\beta,qp} \quad . \tag{3.56}$$

The perturbed Fock matrix in the basis of the molecular orbitals $F_{\beta,pq}$, the perturbed orbital energies $\epsilon_{\beta,p}$ and the coefficients $U_{\beta,qp}$ are then expanded in orders of the perturbation

$$F_{\beta,pq} = F_{pq}^{(0)} + F_{\beta,pq}^{(1)} \, E_\beta + \cdots \quad , \tag{3.57}$$

$$\epsilon_{\beta,p} = \epsilon_p^{(0)} + \epsilon_{\beta,p}^{(1)} \, E_\beta + \cdots \quad , \tag{3.58}$$

$$U_{\beta,qp} = U_{qp}^{(0)} + U_{\beta,qp}^{(1)} \, E_\beta + \cdots \quad , \tag{3.59}$$

where $U_{qp}^{(0)} = \delta_{qp}$ and $F_{pq}^{(0)} = \epsilon_p^{(0)} \, \delta_{pq}$. Inserting these expansion in the perturbed Hartree-Fock equations, (3.56), and separating orders, one obtains the first order Hartree-Fock equations

$$\sum_q (F_{rq}^{(0)} \, U_{\beta,qp}^{(1)} + F_{\beta,rq}^{(1)} \, U_{qp}^{(0)}) = (\epsilon_p^{(0)} \sum_q \delta_{rq} \, U_{\beta,qp}^{(1)} + \epsilon_{\beta,p}^{(1)} \sum_q \delta_{rq} \, U_{qp}^{(0)}) \quad , \tag{3.60}$$

which after evaluation of the zeroth order terms are given as

$$(\epsilon_r^{(0)} - \epsilon_p^{(0)}) \, U_{\beta,rp}^{(1)} = \epsilon_{\beta,p}^{(1)} \, \delta_{rp} - F_{\beta,rp}^{(1)} \quad . \tag{3.61}$$

For $p \neq r$ one finally obtains

$$U_{\beta,rp}^{(1)} = -\frac{F_{\beta,rp}^{(1)}}{\epsilon_r^{(0)} - \epsilon_p^{(0)}} \quad , \tag{3.62}$$

an equation which must be solved iteratively since the first order Fock matrix, $F_{\beta,rp}^{(1)}$, depends on $U_{\beta,rp}^{(1)}$.

For the calculation of molecular properties only the virtual-occupied block $U_{\beta,ai}^{(1)}$ of the coefficient matrix is necessary, since the total wavefunction is not changed by mixing of the occupied orbitals among themselves. Evaluation of $F_{\beta,ai}^{(1)}$ leads to

$$\sum_{bj} \left(A_{ai,bj}^{(0,1)} \mp B_{ai,bj}^{(1)} \right) U_{\beta,bj}^{(1)} = -\langle \phi_a | \hat{h}_\beta^{(1)} | \phi_i \rangle \quad , \tag{3.63}$$

for real $(-)$ and purely imaginary $(+)$ perturbation operators with matrices $\boldsymbol{A}^{(0,1)}$ and $\boldsymbol{B}^{(1)}$ given in equations (3.32) and (3.33). Comparison with equation (3.31) shows that

$$\boldsymbol{U}_{\beta}^{(1)} = (\boldsymbol{X}(0) \mp \boldsymbol{Y}(0)) \quad . \tag{3.64}$$

The first order correction to the density matrix is then

$$D_{\beta,\mu\nu}^{(1),SCF} = 2 \sum_i \left(c_{\beta,\mu i}^{(1)*} c_{\nu i} + c_{\mu i}^* c_{\beta,\nu i}^{(1)} \right) = 2 \left(U_{\beta,\mu\nu}^{(1)*} + U_{\beta,\nu\mu}^{(1)} \right) \quad , \tag{3.65}$$

and a static polarizability can be calculated from equation (3.50).

Time-dependent Hartree-Fock theory (TDHF) [28] introduces time dependent molecular orbitals which are also expanded in the unperturbed orbitals

$$\phi_{\beta,i} = \phi_i^{(0)} + \frac{1}{2} \sum_p E_\beta^\omega \left(U_{\beta,pi}^{(1)}(\omega) e^{\iota\omega t} + U_{\beta,pi}^{(1)}(-\omega) e^{-\iota\omega t} \right) \phi_p^{(0)} + \cdots \quad . \tag{3.66}$$

From the time dependent version of the Hartree-Fock equation,

$$\left(f(i) - \iota \frac{\partial}{\partial t} \right) \phi_p(i) = \epsilon_p \phi_p(i) \quad , \tag{3.67}$$

which can be derived from Frenkel's variational principle [92], equations for the coefficients $U_{\beta,pi}^{(1)}(\omega)$ and $U_{\beta,pi}^{(1)}(-\omega)$ can be obtained

$$\begin{pmatrix} \boldsymbol{U}_{\beta}^{(1)}(-\omega) \\ -\boldsymbol{U}_{\beta}^{(1)}(\omega) \end{pmatrix} = \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y} \end{pmatrix} \quad , \tag{3.68}$$

where $\boldsymbol{X}$ and $\boldsymbol{Y}$ are defined in equation (3.31).

As has already been mentioned, the variational nature of the Hartree-Fock wavefunction means that the CHF/TDHF equations are equivalent to the RPA equations. Unlike RPA and its correlated coevals, however, an atomic-orbital based solution of the iterative CHF equations cannot give excitation energies and transition moments. Historically, CHF, was favoured over RPA since it could be solved in the atomic orbital basis [93], rather than requiring a transformation to the molecular orbital basis. The need for an inverse Hessian in RPA/SOPPA also restricted the size of system which could be studied. However, the use of direct atomic orbital driven methods for RPA response properties [83] and for SOPPA [84, 85], coupled with iterative methods for solving the inverse Hessian, mean that they can now be applied as widely as CHF/TDHF and provide far more information about excited states and properties.

3.2.2 Response Theory

Multiconfigurational Response Functions

In the application of response theory to an SCF wavefuntion $| \Psi \rangle = | \Phi_{SCF} \rangle$, or to an MCSCF wavefunction $| \Psi \rangle = | \Psi_{MCSCF} \rangle$, first described by Olsen and Jørgensen

[29], the time dependent state $|\Psi_0(t)\rangle$ is usually expressed as

$$|\Psi_0(t)\rangle = e^{\imath\kappa(t)}e^{\imath S(t)}|\Psi\rangle \quad, \tag{3.69}$$

where

$$\kappa(t) = \sum_\mu(\kappa_\mu(t)q_\mu^\dagger + \kappa_\mu^*(t)q_\mu) \tag{3.70}$$

$$S(t) = \sum_n(S_n(t)R_n^\dagger + S_n^*(t)R_n) \quad, \tag{3.71}$$

and $S_n(t) = S_n^*(t) = 0$ for the SCF case. The time dependent parameters, collected in a vector $\boldsymbol{\gamma}(t) = (\kappa_\mu(t), \kappa_\mu^*(t), S_n(t), S_n^*(t))^T$, are then expanded in orders of the perturbation $\hat{H}^{(1)}(t)$

$$\boldsymbol{\gamma}_\mu(t) = \sum_i \boldsymbol{\gamma}_\mu^{(i)}(t) \quad. \tag{3.72}$$

Equations for the coefficients in each order are obtained from a particular form of the time dependent Schrödinger equation, called the generalized Ehrenfest theorem,

$$\frac{d}{dt}\langle\Psi_0(t)|\hat{O}|\Psi_0(t)\rangle + \imath\langle\Psi_0(t)|[\hat{O}, \hat{H}^{(0)} + \hat{H}^{(1)}(t)]|\Psi_0(t)\rangle = 0 \quad. \tag{3.73}$$

Inserting equation (3.69) for $|\Psi_0(t)\rangle$ and seperating orders one finds for the the first order equation

$$\imath\langle\Psi|[\hat{O}, \frac{d}{dt}\kappa(t)^{(1)} + \frac{d}{dt}S(t)^{(1)}]|\Psi_0\rangle - \langle\Psi_0|[[\hat{O}, \hat{H}^{(0)}], \kappa(t)^{(1)} + S(t)^{(1)}]|\Psi_0\rangle$$
$$= -\imath\langle\Psi_0|[\hat{O}, \hat{H}^{(1)}(t)]|\Psi_0\rangle \quad. \tag{3.74}$$

Using the set of operators $\{q_\mu^\dagger, q_\mu, R_n^\dagger, R_n\}$ for $\hat{O}$ one obtains a linear system of ordinary differential equations

$$\imath\boldsymbol{S}\frac{d}{dt}\boldsymbol{\gamma}^{(1)}(t) - \boldsymbol{E}\boldsymbol{\gamma}^{(1)}(t) = \boldsymbol{T}(\hat{H}^{(1)}(t)) \quad. \tag{3.75}$$

which Fourier transformed to the frequency domain yields again the set of coupled linear equations given in equation (3.38) [94].

Coupled Cluster Response Functions

Coupled Cluster response functions were derived by Koch and Jørgensen [95] starting from the time dependent transition expectation value of Arponen [52]

$$\langle\Phi_\Lambda(t)|\hat{O}|\Phi_{CC}(t)\rangle \quad, \tag{3.76}$$

where the time dependent coupled cluster state $|\Phi_{CC}(t)\rangle$ and dual or "lambda" state $\langle\Phi_\Lambda(t)|$ are defined as

$$|\Phi_{CC}(t)\rangle = e^{T(t)}|\Phi_{SCF}\rangle \tag{3.77}$$

$$\langle\Phi_\Lambda(t)| = \langle\Phi_{SCF}|(1 + \Lambda(t))e^{-T(t)} \quad. \tag{3.78}$$

The time dependent cluster operator and Λ operator consist of n-tuple excitation, $\tau_\mu^\dagger$, and de-excitation operators, τ_μ, respectively

$$T(t) \;=\; \sum_\mu t_\mu(t)\,\tau_\mu^\dagger \tag{3.79}$$

$$\Lambda(t) \;=\; \sum_\mu \lambda_\mu(t)\,\tau_\mu \;\;, \tag{3.80}$$

where $\{\tau_\mu^\dagger, \tau_\mu\}$ is a shorthand notation for single $\{q_\mu^\dagger, q_\mu\}$, double $\{q_\mu^\dagger q_\mu^\dagger, q_\mu q_\mu\}$, etc. excitation and de-excitation operators. $t_\mu(t)$ and $\lambda_\mu(t)$ are the corresponding time dependent amplitudes.

The time-dependent amplitudes, $t_\mu(t)$ and $\lambda_\mu(t)$, are then determined from the coupled-cluster time-dependent Schrödinger equations

$$e^{-T(t)}\imath\frac{d}{dt}\,|\,\Phi_{CC}(t)\rangle \;=\; e^{-T(t)}\hat{H}\,|\,\Phi_{CC}(t)\rangle \tag{3.81}$$

$$\left(\frac{d}{dt}\langle\Phi_\Lambda(t)\,|\right)e^{T(t)} \;=\; \imath\langle\Phi_\Lambda(t)\,|\,\hat{H}e^{T(t)} \tag{3.82}$$

by projecting them on $\langle\Phi_{SCF}\,|\,\tau_\mu$ and $\tau_\mu^\dagger\,|\,\Phi_{SCF}\rangle$, respectively, yielding systems of ordinary linear differential equations

$$\frac{dt_\mu(t)}{dt} \;=\; -\imath\,\langle\Phi_{SCF}\,|\,\tau_\mu e^{-T(t)}\hat{H}\,|\,\Phi_{CC}(t)\rangle \tag{3.83}$$

$$\frac{d\lambda_\mu(t)}{dt} \;=\; \imath\,\langle\Phi_\Lambda(t)\,|\,[\hat{H},\tau_\mu^\dagger]\,|\,\Phi_{CC}(t)\rangle \;\;. \tag{3.84}$$

In the presence of an time-dependent perturbation $\hat{H}^{(1)}(t)$, equation (2.103), the amplitudes $t_\mu(t)$ and $\lambda_\mu(t)$ are expanded in a perturbation series $t_\mu(t) = t_\mu^{(0)}(t) + t_\mu^{(1)}(t) + \cdots$ and $\lambda_\mu(t) = \lambda_\mu^{(0)}(t) + \lambda_\mu^{(1)}(t) + \cdots$ yielding a series of equations. In first order they read

$$\frac{dt_\mu^{(1)}(t)}{dt} = -\imath\,\langle\Phi_{SCF}\,|\,\tau_\mu e^{-T}\hat{H}^{(1)}(t)\,|\,\Phi_{CC}\rangle\imath\,\langle\Phi_{SCF}\,|\,\tau_\mu e^{-T}[\hat{H}^{(0)},T^{(1)}(t)]\,|\,\Phi_{CC}\rangle \tag{3.85}$$

$$\frac{d\lambda_\mu^{(1)}(t)}{dt} = \imath\,\langle\Phi_\Lambda\,|\,\Big([[\hat{H}^{(0)},\tau_\mu^\dagger],T^{(1)}(t)] + [\hat{H}^{(1)}(t),\tau_\mu^\dagger]\Big)\,|\,\Phi_{CC}\rangle + \imath\sum_\nu \lambda_\nu^{(1)}(t)A_{\nu\mu} \tag{3.86}$$

where $|\,\Phi_{CC}\rangle$ and $\langle\Phi_\Lambda\,|$ are the time independent, unperturbed coupled cluster and "lambda" state, respectively, T is the time independent, unperturbed cluster operator and the $\boldsymbol{A}$ matrix is here defined as

$$\boldsymbol{A} = \langle\Phi_{SCF}\,|\,\boldsymbol{\tau}e^{-T}[\hat{H}^{(0)},\tilde{\boldsymbol{\tau}}^\dagger]\,|\,\Phi_{CC}\rangle \;\;, \tag{3.87}$$

with $\{\tau_\mu^\dagger\}$ arranged as row vector $\tilde{\boldsymbol{\tau}}^\dagger$ and $\{\tau_\nu\}$ arranged as column vector $\boldsymbol{\tau}$.

Equations (3.85) and (3.86) are solved by Fourier transformation of $t_\mu^{(1)}(t)$ and $\lambda_\mu^{(1)}(t)$ to the frequency domain, $X_\mu^{(1)}(\omega)$ and $Y_\mu^{(1)}(\omega)$, which gives two sets of coupled linear equations

$$\boldsymbol{X}^{(1)}(\omega) = \left(-\boldsymbol{A} + \hbar\omega\,\boldsymbol{1}\right)^{-1} \left(\langle \Phi_{SCF} | \tilde{\boldsymbol{\tau}} e^{-T} \hat{V}_{\alpha\ldots}^\omega | \Phi_{CC}\rangle\right) \tag{3.88}$$

$$\boldsymbol{Y}^{(1)}(\omega) = -\left(\langle \Phi_\Lambda | [\hat{V}_{\alpha\ldots}^\omega, \tilde{\boldsymbol{\tau}}^\dagger] | \Phi_{CC}\rangle + \boldsymbol{F}\boldsymbol{X}^{(1)}(\omega)\right)\left(-\boldsymbol{A} + \hbar\omega\,\boldsymbol{1}\right)^{-1} \quad , \tag{3.89}$$

where the $\boldsymbol{F}$ matrix is here defined as

$$\boldsymbol{F} = \langle \Phi_\Lambda | [[\hat{H}^{(0)}, \boldsymbol{\tau}^\dagger], \tilde{\boldsymbol{\tau}}^\dagger] | \Phi_{CC}\rangle \quad . \tag{3.90}$$

After insertion of these results for the amplitudes in a perturbation expansion of the time dependent transition expectation value, $\langle \Phi_\Lambda(t) | \hat{O} | \Phi_{CC}(t)\rangle$, the response functions can be identified by comparison with equation (2.106). The coupled cluster linear response functions is thus given as

$$\langle\langle \hat{O}; \hat{V}_{\alpha\ldots}^\omega \rangle\rangle_\omega = \boldsymbol{Y}^{(1)}(\omega)\left(\langle \Phi_{SCF} | \boldsymbol{\tau}\hat{O} | \Phi_{CC}\rangle\right) + \left(\langle \Phi_\Lambda | [\hat{O}, \tilde{\boldsymbol{\tau}}^\dagger] | \Phi_{CC}\rangle\right)\boldsymbol{X}^{(1)}(\omega) \quad . \tag{3.91}$$

3.3 Derivative Methods

3.3.1 The Finite Field Method

The finite field method of Cohen and Roothaan [96] and Pople, McIver and Ostlund [97] involves numerical evaluation of derivatives of the electronic energy, of first or higher order properties, in general of a property, P, in the presence of a perturbation operator, $\hat{O}_\alpha^F\, F_\alpha$. Calculations of P are performed for various values of field strength F_α. The desired derivative, at zero field strength, can then be obtained either by finite differences or by fitting the calculated values of P to a Taylor expansion in the field strength F_α.

In a finite field calculation of the static dipole polarizability α, for example, the perturbation operator, $-\hat{O}_\alpha^E\, E_\alpha$, is added to the Hamiltonian, $H^{(0)}$, and the electronic energy or the electronic contribution to the dipole moment is calculated for various finite values of the electric field strength E_α. The dipole polarizability is then obtained as the numerical first derivative of the electric field dependent dipole moment or as the numerical second derivative of the electric field dependent electronic energy.

The property P for which derivatives are taken need not to be a static property, but could also be a frequency dependent polarizability $\alpha(-\omega; \omega)$, as done by Jaszuński [98]. Finite field calculations on $\alpha(-\omega; \omega)$ facilitate calculation of $\beta(-\omega; \omega, 0)$, $\gamma(-\omega; \omega, 0, 0)$.

The finite field method is by far the easiest method to implement as long as the perturbations are real. Any program for the calculation of the property P can be used, as long as it allows for the inclusion of additional one-electron operators in the

Hamiltonian can be used. The finite field method can thus be applied at any level of approximation or correlation and even to approximations for which a wavefunction or a ground state energy is not defined.

Imaginary perturbation operators, like $\hat{O}_\alpha^{lB}$, $\hat{O}_\alpha^{sB}$, $\hat{O}_\alpha^{lm^K}$ and $\hat{O}_\alpha^{sm^K}$, require the use of complex arithmetic, which prevented a routine usage of the finite field method for the calculation of magnetic properties. Nevertheless finite field approaches to the calculation of nuclear magnetic shielding constants [99] and nuclear spin-spin coupling constants [100] have been presented. In this method the sum-over-states contribution to $\sigma_{\alpha\beta}^K$, for example, is evaluated as numerical derivative of the expectation value of $\hat{O}_\alpha^{lm^K}$ with respect to B_β, the expectation value having been calculated to second order in electron correlation and in the presence of the magnetic induction B_β. The sum-over-states contributions to the coupling constants $J_{\alpha\beta}^{KL}$ are obtained as numerical derivatives with respect to m_α^K of an expression for the energy, which is second order in electron correlation and first order in $-\left(\hat{O}_\beta^{lm^L} + \hat{O}_\beta^{sm^L}\right)$ and is calculated in the presence of the perturbation $-\left(\hat{O}_\alpha^{lm^K} + \hat{O}_\alpha^{sm^K}\right) m_\alpha^K$. Mixed electric magnetic properties, on the other hand, like nuclear magnetic shielding polarizabilities can be evaluated as numerical derivatives of electric field dependent nuclear magnetic shielding tensors without complex arithmetic.

A disadvantage of the finite field method lies in the nature of numerical differentiation. Care is required in setting the field strength, in our example E_α, which must not be too high and in the number of evaluations of property P which are used. For higher order properties or multiple perturbations the method becomes cumbersome since the number of calculations to be performed increases rapidly. Finally the method can obviously not be used for time dependent perturbations and therefore for frequency dependent properties.

A variation of this method is the finite point charge method, used by Maroulis and Thakkar [101], in which the external electric field or field gradient is simulated by an appropriate arrangement of point charges. This method is even more simple to implement, since it only requires the option to include centres with a charge but no basis functions, rather than a modified one-electron Hamiltonian.

The finite field method has been widely used but is becoming increasingly obsolete because of the advances in the analytical derivative methods: most properties of interest can now be calculated analytically, obviating the need for a finite field calculation.

3.3.2 The Analytical Derivative Method

In the analytic derivative method for the calculation of molecular properties, approximate expressions for P within a given method are differentiated analytically with respect to the perturbation. It is equally general as the finite field method and does not suffer from the numerical problems of the latter method. However, it is much more difficult to apply to a new type of wavefunction, since expressions

for the analytical derivatives have to be derived and implemented. Nevertheless, expressions for first and second order properties have been implemented for most *ab initio* methods following the derivation of analytical derivatives with respect to changes in the nuclear coordinates. Explicit expressions can be found in several reviews [102, 103, 104].

The first derivative of the energy of a system described by the Hamiltonian $\hat{H}^{(0)} + \hat{H}^{(1)} + \hat{H}^{(2)}$, given in equations (2.57), (2.63) and (2.64) with respect to one of the perturbations E_α, B_α and m_α^K or in general F_α can be written for most methods as

$$\left.\frac{dW(F_\alpha)}{dF_\alpha}\right|_{F_\alpha=0} = \sum_{pq} D_{pq}\langle\phi_p|\frac{\partial\hat{h}^{(1)}(i)}{\partial F_\alpha}|\phi_q\rangle = \sum_{\mu\nu} D_{\mu,\nu}\langle\chi_\mu|\frac{\partial\hat{h}^{(1)}(i)}{\partial F_\alpha}|\chi_\nu\rangle \quad . \quad (3.92)$$

The atomic orbitals χ_μ are here assumed to be independent of the perturbation. For variational wavefunctions, *i.e.* methods which fulfill the Hellmann-Feynman theorem, this is equivalent to equation (3.21). However, for non-variational wavefunctions, as for example in the case of MP perturbation theory and the CC methods, the density matrix is not consistent with the definition in equation (3.19) and was therefore also called relaxed or response density matrix [105]. The Hellmann-Feynman theorem can be fulfilled in coupled cluster theory, however, when the energy and first order properties are evaluated as transition expectation values, defined in section 3.2.2 (see *e.g.* [106])

$$\left.\frac{d\langle\widetilde{CC}|\hat{H}^{(0)} + \hat{H}^{(1)}|CC\rangle}{dF_\alpha}\right|_{F_\alpha=0} = \langle\widetilde{CC}|\frac{\partial\hat{H}^{(1)}}{\partial F_\alpha}|CC\rangle \quad . \quad (3.93)$$

The relaxed density matrix can be decomposed in an SCF and correlation part

$$\boldsymbol{D} = \boldsymbol{D}^{SCF} + \boldsymbol{D}^{corr} \quad . \quad (3.94)$$

The SCF density is given in equation (3.23) and the correlation part consists of two parts

$$\boldsymbol{D}^{corr} = \boldsymbol{D}^{amp} + \boldsymbol{D}^{orb} \quad , \quad (3.95)$$

where $\boldsymbol{D}^{amp}$ contains amplitudes or correlation coefficients and $\boldsymbol{D}^{orb}$, obtained as a solution of the so-called Z-vector equations [107], arises because of the relaxation of the orbitals for non-variational wavefunctions. Only the occupied-virtual and virtual-occupied blocks are non-zero in $\boldsymbol{D}^{orb}$, which is again a result of the Brillouin condition for the SCF ground state.

At the level of second order MP perturbation theory (MP2), *e.g.*, straigthforward differentiation of the MP2 energy, equation (3.10), would give

$$\left.\frac{dW^{(2)}(F_\alpha)}{dF_\alpha}\right|_{F_\alpha=0} = \sum_{ab} D_{ab}^{(2)}\langle\phi_a|\frac{\partial\hat{h}^{(1)}(i)}{\partial F_\alpha}|\phi_b\rangle + \sum_{ij} D_{ij}^{(2)}\langle\phi_i|\frac{\partial\hat{h}^{(1)}(i)}{\partial F_\alpha}|\phi_j\rangle + \sum_{ai} L_{ai}^{(2)}U_{\alpha,ai}^{(1)}$$

$$(3.96)$$

where $L_{ai}^{(2)}$ is the so-called Lagrangian and $U_{ai}^{(1)}$ are the solutions of the coupled Hartree-Fock in equation (3.63). Instead of solving the coupled Hartree-Fock equations for all components of the perturbation, one can solve one set of coupled Hartree-Fock equations for the so-called Z-vector [107], with the Lagrangian as right hand side

$$\sum_{bj} \left(A_{ai,bj}^{(0,1)} - B_{ai,bj}^{(1)} \right) Z_{bj} = L_{ai}^{(2)} \quad . \tag{3.97}$$

The last term in equation (3.96) can then be written as

$$\sum_{ai} L_{ai}^{(2)} U_{\alpha,ai}^{(1)} = \sum_{ai} Z_{ai} \langle \phi_a | \frac{\partial \hat{h}^{(1)}(i)}{\partial F_\alpha} | \phi_i \rangle = \sum_{ai} D_{ai}^{(2)} \langle \phi_a | \frac{\partial \hat{h}^{(1)}(i)}{\partial F_\alpha} | \phi_i \rangle \quad , \tag{3.98}$$

identifying the occupied-virtual and virtual-orbital blocks D_{ia} and D_{ai} of the relaxed density matrix as the Z vector. It is also these occupied-virtual and virtual-orbital blocks which differ between a density matrix consistent through second order [61], equations (3.24) - (3.26), and the MP2 relaxed density matrix [104, 108].

The second derivative of the energy can be written as

$$\frac{d^2 W(F_\beta, F_\alpha)}{dF_\alpha dF_\beta}\bigg|_{F_\alpha = F_\beta = 0} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 \langle \chi_\mu | \hat{h}_1(i) | \chi_\nu \rangle}{\partial F_\beta \partial F_\alpha} + \sum_{\mu\nu} D_{\beta,\mu\nu}^{(1)} \frac{\partial \langle \chi_\mu | \hat{h}_1(i) | \chi_\nu \rangle}{\partial F_\alpha} \quad , \tag{3.99}$$

where $\hat{h}_1(i)$ stands for $\hat{h}^{(0)}(i) + \hat{h}^{(1)}(i) + \hat{h}^{(2)}(i)$ and the atomic orbitals could depend on the perturbation. The derivative of the relaxed density matrix, so called first order relaxed density matrix, in the atomic orbital basis is given as

$$D_{\beta,\mu\nu}^{(1)} = \frac{\partial D_{\mu\nu}}{\partial F_\beta} = \sum_{pq} c_{\mu p}^* \frac{\partial D_{pq}}{\partial F_\beta} c_{\nu q} + \sum_{pq} D_{pq} \left(\frac{\partial c_{\mu p}^*}{\partial F_\beta} c_{\nu q} + c_{\mu p}^* \frac{\partial c_{\nu q}}{\partial F_\beta} \right) \quad . \tag{3.100}$$

The derivatives of the molecular orbital coefficients $\{c_{\nu q}\}$ are obtained by solving the coupled-perturbed Hartree-Fock equations, which are described in section 3.2.2. The first order density matrix at the SCF level was given in equation (3.65). The occupied-occupied and virtual-virtual blocks of the correlated first order density matrix contain derivatives of the amplitudes or correlation coefficients, which can be obtained by straightforward differentiation of the equations defining the amplitudes. The occupied-virtual and virtual-occupied part requires the solution of the first order Z-vector equations, *i.e.* the derivative of the Z-vector equations. Explicit expressions for the relaxed density matrices and first order relaxed density matrices for many methods can also be found in *e.g.* [102, 103, 104, 109].

Illustrative Calculations

In the following we want to illustrate the performance of different analytical derivative methods with results from the recent literature [75, 110, 111, 112, 113, 109, 114] for the static dipole polarizabilties α (Table 3.7) and the nuclear magnetic shielding

constants σ (Table 3.8). The results are obtained using second, third and fourth order Møller-Plesset perturbation theory as well as Coupled Cluster methods.

It is interesting to note that the differences between the MP3, CCSD and CCSD(T) results for the nuclear magnetic shielding constants, Table 3.8, of the XH_n molecules are rather small, whereas large changes are observed for XY molecules. It is therefore not clear whether in the case of the XY molecules the results at the CCSD(T) level are converged.

In case of the polarizabilities, Table 3.7, it is more difficult to draw general conclusion, which is probably due to the missing ro-vibrational corrections.

Table 3.7 Comparison of different analytical derivative methods for the calculation of static dipole polarizabilities α (in units of $e^2 a_0^2 E_{\mathrm{h}}^{-1}$)[a] using the medium size polarized basis sets [b]

	SCF	MP2	MP4	CCSD	Exp.[c]
HF	4.874	5.674	5.770	5.724	5.60
HCl	16.664	17.368	17.433	17.499	17.39
H_2O	8.492	9.792	9.866	9.824	9.64
H_2S	23.614	24.570	24.542	24.604	24.71
NH_3	12.926	14.432	14.411	14.411	14.56
PH_3	29.915	30.689	30.510	30.674	30.93
CH_4	16.120	16.754	16.704	16.709	17.27
SiH_4	29.960	31.035	31.216	31.467	31.90
F_2	8.593	8.219	8.662	8.550	8.38
Cl_2	29.886	30.556	30.707	30.905	30.417
C_2H_4	28.303	27.793	27.635	27.534	27.70
CO_2	15.841	17.884	17.846	18.013	17.51
SO_2	23.653	26.174	26.343	26.444	25.61

[a] Results taken from [75, 110]. [b] [115, 116, 117]. [c] References for the experimental values are given in [75].

Table 3.8 Comparison of different analytical derivative methods for the calculation of nuclear magnetic shielding constants σ (in ppm)[a]

		SCF	MP2	MP3	CCSD	CCSD(T)	Exp.[b]
HF	σ^{19F}	413.6	424.2	417.8	418.1	418.6	419.7 ± 6 [c]
H_2O	σ^{17O}	328.1	346.1	336.7	336.9	337.9	337 ± 2 [c]
NH_3	σ^{15N}	262.3	276.5	270.1	269.7	270.7	273.3 ± 0.1 [c]
CH_4	σ^{13C}	194.8	201.0	198.8	198.7	198.9	198.4 ± 0.9 [c]
F_2	σ^{19F}	-167.9	-170.0	-176.9	-171.1	-186.5	-192.8 [c]
N_2	σ^{15N}	-112.4	-41.6	-72.2	-63.9	-58.1	-59.6 ± 1.5 [c]
CO	σ^{13C}	-25.5	20.6	-4.2	0.8	5.6	2.8 ± 0.9 [c]
	σ^{17O}	-87.7	-46.5	-68.3	-56.0	-52.9	-36.7 ± 17.2 [c]

[a] Results taken from [111, 112, 113, 109, 114]. [b] References for the experimental values can be found in the articles given in footnote a. [c] Experimental data for the equilibrium geometry, *i.e.* corrected with calculated ro-vibrational corrections.

3.3.3 Time Dependent Analytical Derivatives

The analytical energy derivative method has be extended to the case of time-dependent perturbations using the pseudo-energy derivative method of Rice and Handy [118] and the quasi-energy derivative method of Sasagane, Aiga and Itoh [119]. Both methods define the frequency-dependent properties as derivatives of the quasi-energy, as defined by Löwdin and Mukherjee [120] or Kutzelnigg [121]

$$\tilde{W}(t) = \langle \Psi(t) | \hat{H}^{(0)} + \hat{H}^{(1)}(t) - i\frac{\partial}{\partial t} | \Psi(t) \rangle \quad , \tag{3.101}$$

but in the pseudo-energy derivative method (PED) the frequency dependent polarizability is defined as

$$\alpha_{\alpha\beta}(-\omega;\omega) = -\left.\frac{\partial^2 \tilde{W}(t)}{\partial E_\beta^\omega \partial E_\alpha^0}\right|_{E=0} = -\left.\frac{\partial^2 \tilde{W}(t)}{\partial E_\alpha^0 \partial E_\beta^\omega}\right|_{E=0} \quad , \tag{3.102}$$

where as in the quasi-energy derivative method (QED) it is defined as

$$\alpha_{\alpha\beta}(-\omega;\omega) = -\frac{\partial^2 \tilde{W}(t)}{\partial E^{-\omega}\,sba\partial E_\beta^\omega}\,|_{E=0} \quad . \tag{3.103}$$

PED [118, 122] and QED [123] expressions for the frequency dependent polarizability and first hyperpolarizability at the SCF and MP2 level have been derived, whereas QED expressions have also been presented at the coupled cluster level [124] and for second and third hyperpolarizabilities in SCF, MCSCF, full and truncated CI wavefunctions [119]. At the SCF level both methods lead to the time dependent Hartree-Fock approximation (TDHF). The quasienergy derivative method for an

MCSCF energy was also shown to yield the same expressions as obtained from response theory . However, at the MP2 level the PED and QED methods differ despite the fact that they give the correct static perturbation limit. In both methods the Hamiltonian is partitioned in the following way

$$\hat{H}^{(0)} + \hat{H}^{(1)}(t) - i\frac{\partial}{\partial t} = \hat{F} - i\frac{\partial}{\partial t} + \hat{V} \quad . \tag{3.104}$$

The PED method starts then from the usual expression for the MP2 closed shell energy, in which the expansion, equation (3.66), of the molecular orbitals in the time dependent fields is inserted. In addition the condition

$$\langle \Psi(t) \mid \frac{\partial \Psi(t)}{\partial E_\alpha^0} \rangle \tag{3.105}$$

has to be fulfilled for the first order MP wavefunction

$$\mid \Psi(t) \rangle = \mid \Phi_{SCF}(t) \rangle + \mid \Phi^{(1)}(t) \rangle \quad . \tag{3.106}$$

In the QED method, by contrast, the derivatives of an MP2 quasienergy Lagrangian are taken, which is variational in the TDHF coefficients, equation (3.68), first order MP2 amplitudes as well as in Lagrangian multipliers for the TDHF coefficients and first order MP2 amplitudes. A constraint like equation (3.105) is not necessary in the QED method as a result of the fact that the second derivative is with respect to $E_\alpha^{-\omega}$. The TDHF coefficients have to be obtained by solving the TDHF equations, equation (3.68), as in the PED method, the first order MP2 amplitudes as well as the Lagrangian multipliers for the TDHF coefficients and first order MP2 amplitudes are obtained by solving appropriate response equations. Two further differences between the PED and QED method at the MP2 level are that the PED polarizability tensor is not symmetric and that the PED expression contains Hartree-Fock orbital energy differences as poles (excitation energies) whereas the QED method has the TDHF poles and in the latest version, called QED-MP2 [125] also MP2 poles. This difference is potentially very important for low-lying excitation energies, where the error in the Hartree-Fock values is likely to be appreciable.

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