The ab initio calculation of molecular properties
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The *ab initio* calculation of molecular properties

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The interaction of a molecule with weak external electromagnetic fields or internal electromagnetic moments, like nuclear magnetic dipole or nuclear electric quadrupole moments, is commonly described in terms of so-called molecular electromagnetic properties. They are intrinsic properties of a given molecule and are therefore independent of the strength of the perturbations, i.e. the external fields or internal nuclear moments. These properties, like the electric dipole moment, the frequency dependent polarizability tensor, the nuclear magnetic shielding tensor, the indirect nuclear spin-spin coupling tensor etc. play an important role in the interpretation of many phenomena including the refractive index, the Stark effect, the Kerr effect, nuclear magnetic resonance spectroscopy and many more. Also the long-range interactions between molecules can be expressed 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. However, the approach will be semi-classical since only the electrons are treated by non-relativistic quantum mechanics, whereas the fields and nuclei are treated classically. Finally in chapter 3 approximate methods, which can be used in actual computations of the molecular electromagnetic properties, are described. The exposition will be restricted to so-called ab initio methods.
Chapter 1

Definition of Molecular Properties

In this chapter the classical definitions of the molecular properties will be discussed. For that purpose a continuous static or dynamic distribution of charges with charge density \( \rho(\vec{r}) \) and current density \( \vec{j}(\vec{r}) \) will be considered. 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 in the following chapter.

1.1 Electric Multipole Expansion

Electric charges give rise to an electric field and an electrostatic potential. 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

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

For an observation point \( \vec{R} \) far from the charge distribution it is possible to expand \( \frac{1}{|\vec{R} - \vec{r}'|} \) and thus the potential in a Taylor series around a point \( \vec{r}_o \) within the charge distribution.

\[
\phi^\rho(\vec{R}) = \frac{1}{4\pi\epsilon_0} \left[ \frac{1}{|\vec{R} - \vec{r}_o|} \int_{\tau'} \rho(\vec{r}') \, d\tau' \right. \\
\left. + \frac{1}{2} \frac{\partial^2}{\partial r_{\alpha}\partial r_{\beta}} \frac{1}{|\vec{R} - \vec{r}'|} \int_{\tau'} \rho(\vec{r}') (r_{\alpha}' - r_{\alpha,0})(r_{\beta}' - r_{\beta,0}) \, d\tau' \right] + \ldots
\]

where the derivatives have to be evaluated at the point \( \vec{r}' = \vec{r}_o \). The Greek subscripts \( \alpha, \beta \) denote vector or tensor components and can be equal to \( x, y, z \). A
CHAPTER 1. DEFINITION OF MOLECULAR PROPERTIES

repeated Greek subscript will here and in the following denote summation over all three Cartesian components. By evaluating the derivatives and defining the electric moments of the charge distribution as

\[ q = \int \rho(\vec{r}') \, d\tau' \quad (1.3) \]

\[ \mu_\alpha(\vec{r}_o) = \int (r_\alpha' - r_{o,\alpha}) \rho(\vec{r}') \, d\tau' \quad (1.4) \]

\[ Q_{\alpha\beta}(\vec{r}_o) = \int (r_\alpha' - r_{o,\alpha}) (r_\beta' - r_{o,\beta}) \rho(\vec{r}') \, d\tau' \quad (1.5) \]

the multipole expansion of the electrostatic potential is obtained

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

\[ \left. + \frac{1}{2} Q_{\alpha\beta}(\vec{r}_o) \frac{(R_\alpha - r_{o,\alpha})(R_\beta - r_{o,\beta})}{|\vec{R} - \vec{r}_o|} \right] + \ldots \quad (1.6) \]

The zeroth order electric moment \( q \) is the total charge, \( \mu_\alpha \) are components of the vector of the first order electric moment, called the electric dipole moment, and \( Q_{\alpha\beta} \) are components of the second order electric moment tensor.

An important feature of these electric multipole moments is that the first nonvanishing moment of a charge distribution is independent of the choice of origin \( \vec{r}_o \). All the higher moments, however, will depend on the origin. Thus the dipole moment of a neutral molecule is 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

\[ \Theta_{\alpha\beta}(\vec{r}_o) = \frac{1}{2} \int \left[ 3(r_\alpha' - r_{o,\alpha})(r_\beta' - r_{o,\beta}) - \delta_{\alpha\beta} (\vec{r}' - \vec{r}_o)^2 \right] \rho(\vec{r}') \, d\tau' \quad (1.7) \]

It essentially measures the deviation from spherical symmetry. To avoid confusion it is customary to take equation (1.5) as defining the second electric moment and equation (1.7) as defining the electric quadrupole moment.

Having once obtained the electric multipole moments of a distribution of charges, one can calculate the electrostatic potential for any distant observation point \( \vec{R} \) from the simple formula in equation (1.6) 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 [1].

1.2 Potential Energy in an Electric Field

The electric multipole moments also play an important role in the interaction of a molecule with an external electric field. The potential energy \( W \) of a distribution of
1.2. POTENTIAL ENERGY IN AN ELECTRIC FIELD

charges immersed in an external static electric field \( \vec{E} \) is given as

\[
W = \int \rho(\vec{r}') \, \phi^E(\vec{r}') \, d\tau'
\]  
(1.8)

where \( \phi^E(\vec{r}') \) is the scalar potential associated with the electric field. A more useful expression can be obtained, if one expands the scalar potential in a Taylor series around \( \vec{r}_o \)

\[
\phi^E(\vec{r}') = \phi^E(\vec{r}_o) + (\vec{r}' - \vec{r}_o) \cdot \frac{\partial \phi^E(\vec{r}')}{\partial \vec{r}_o} + \frac{1}{2} (\vec{r}' - \vec{r}_o)(\vec{r}' - \vec{r}_o) \cdot \frac{\partial^2 \phi^E(\vec{r}')}{\partial \vec{r}_o \, \partial \vec{r}_o} + \ldots
\]  
(1.9)

where the derivatives have to evaluated again at \( \vec{r}' = \vec{r}_o \). The derivatives of the scalar potential \( \phi^E \) define the electric field \( E_\alpha \), the electric field gradient tensor \( E_{\alpha\beta} \), etc

\[
E_\alpha(\vec{r}_o) = -\frac{\partial \phi^E(\vec{r}')}{\partial \vec{r}_\alpha}
\]  
(1.10)

\[
E_{\alpha\beta}(\vec{r}_o) = -\frac{\partial^2 \phi^E(\vec{r}')}{\partial \vec{r}_\alpha \partial \vec{r}_\beta}
\]  
(1.11)

On insertion of equations (1.9) - (1.11) in equation (1.8) and usage of equations (1.3) - (1.5) the energy \( W \) of the interaction between a charge distribution and a static but not homogeneous electric field can be expressed in terms of the electric moments of the charge distribution

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

or alternatively with the quadrupole moment \( \Theta \)

\[
W = q \, \phi^E(\vec{r}_o) - \mu_\alpha(\vec{r}_o) E_\alpha(\vec{r}_o) - \frac{1}{3} \Theta_{\alpha\beta}(\vec{r}_o) E_{\alpha\beta}(\vec{r}_o) + \ldots
\]  
(1.12)

From this equation it can be seen that dipole moment and the quadrupole moment can alternatively be defined as derivatives of the potential energy with respect to the field strength \( E_\alpha \) or field gradient \( E_{\alpha\beta} \)

\[
\mu_\alpha(\vec{r}_o) = -\frac{\partial W}{\partial E_\alpha}
\]  
(1.13)

\[
\Theta_{\alpha\beta}(\vec{r}_o) = -\frac{3}{2} \frac{\partial W}{\partial E_{\alpha\beta}}
\]  
(1.14)

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1.3 Induced Electric Moments and Polarizabilities

In the previous chapter it was assumed that the distribution of charges was fixed and will not be influenced by the external electric field apart from a change in energy. However, if the charge distribution is not fixed, it gets polarized in the presence of the electric field and it will redistribute itself such that the energy is minimized. The moments of the charge distribution will therefore change and field dependent moments \( \mu^{\text{ind}} \), \( \Theta^{\text{ind}} \) are induced by the external field in addition to the field independent, so called permanent, moments \( \mu_\alpha \), \( \Theta_{\alpha\beta} \). Traditionally [1] the moments depending on the field \( E_\alpha \) and field gradient \( E_{\alpha\beta} \) are expanded in the following way

\[
\begin{align*}
\mu_\alpha(\vec{E}) & = \mu_\alpha + \mu^{\text{ind}}_\alpha(\vec{E}) \\
\mu_\alpha(\vec{E}) & = \mu_\alpha + \alpha_\alpha E_\beta + \frac{1}{2} \beta_{\alpha\beta\gamma} E_\beta E_\gamma + \frac{1}{6} \gamma_{\alpha\beta\gamma\delta} E_\beta E_\gamma E_\delta \\
& \quad + \frac{1}{3} A_{\alpha\beta\gamma\delta} E_\beta E_\gamma E_\delta + \ldots \\
\Theta_{\alpha\beta}(\vec{E}) & = \Theta_{\alpha\beta} + \Theta^{\text{ind}}_{\alpha\beta}(\vec{E}) \\
\Theta_{\alpha\beta}(\vec{E}) & = \Theta_{\alpha\beta} + A_{\gamma\alpha\beta\gamma} E_\gamma + \frac{1}{2} B_{\gamma\delta\alpha\beta} E_\gamma E_\delta \\
& \quad + C_{\alpha\beta\gamma\delta} E_\gamma E_\delta + \ldots
\end{align*}
\] (1.15)

thereby defining 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 permanent moments.

The energy of this polarizable distribution of charges is obtained by insertion of equations (1.15) and (1.16) in equations (1.13) and (1.14) and integration

\[
W(\vec{E}) = W(0) - \mu_\alpha E_\alpha - \frac{1}{2} \alpha_\alpha E_\alpha E_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} E_\alpha E_\beta E_\gamma - \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta \\
- \frac{1}{3} A_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta - \frac{1}{6} B_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta \\
- \frac{1}{6} C_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta
\] (1.17)

Thus, the polarizabilities and hyperpolarizabilities can also be defined as derivatives of the energy. The two ways of defining the the polarizabilities and hyperpolarizabilities are summarized in table 1.1. By evaluating the derivatives in equations (1.13) and (1.14) at zero field strength the permanent, i.e. field independent, moments are obtained.
Table 1.1 Definitions of tensor components of the electric polarizabilities and hyperpolarizabilities 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 \(W(\vec{E})\)

<table>
<thead>
<tr>
<th>(\mu_\alpha)</th>
<th>(\Theta_{\gamma\delta})</th>
<th>(W(\vec{E}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{\partial}{\partial E_\alpha})</td>
<td>(-3\frac{\partial}{\partial E_{\gamma\delta}})</td>
<td>(-\frac{\partial}{\partial E_\alpha})</td>
</tr>
<tr>
<td>(\alpha_{\alpha\beta})</td>
<td>(\frac{\partial^2}{\partial E_\beta\partial E_\alpha})</td>
<td>(-\frac{\partial^2}{\partial E_\beta\partial E_\alpha})</td>
</tr>
<tr>
<td>(\beta_{\alpha\beta\gamma})</td>
<td>(\frac{\partial^3}{\partial E_\gamma\partial E_\beta\partial E_\alpha})</td>
<td>(-\frac{\partial^3}{\partial E_\gamma\partial E_\beta\partial E_\alpha})</td>
</tr>
<tr>
<td>(\gamma_{\alpha\beta\gamma\delta})</td>
<td>(\frac{\partial^4}{\partial E_\delta\partial E_\gamma\partial E_\beta\partial E_\alpha})</td>
<td>(-\frac{\partial^4}{\partial E_\delta\partial E_\gamma\partial E_\beta\partial E_\alpha})</td>
</tr>
<tr>
<td>(A_{\alpha,\gamma\delta})</td>
<td>(3\frac{\partial}{\partial E_{\gamma\delta}})</td>
<td>(-3\frac{\partial^2}{\partial E_{\gamma\delta}\partial E_\alpha})</td>
</tr>
<tr>
<td>(B_{\alpha\beta,\gamma\delta})</td>
<td>(3\frac{\partial^2}{\partial E_{\gamma\delta}\partial E_\beta\partial E_\alpha})</td>
<td>(-3\frac{\partial^3}{\partial E_{\gamma\delta}\partial E_\beta\partial E_\alpha})</td>
</tr>
<tr>
<td>(C_{\gamma\delta,\alpha\beta})</td>
<td>(-\frac{\partial}{\partial E_{\alpha\beta}})</td>
<td>(-3\frac{\partial^2}{\partial E_{\gamma\delta}\partial E_{\alpha\beta}})</td>
</tr>
</tbody>
</table>

\(^a\) All derivatives have to be evaluated for zero field and field gradient.

1.4 Magnetic Multipole Expansion

A dynamic system of charges with charge density \(\rho(\vec{r})\) gives rise to a current density \(\vec{j}(\vec{r})\)

\[
\vec{j}(\vec{r}) = \rho(\vec{r}) \; \vec{v}(\vec{r}) \tag{1.18}
\]

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

\[
\vec{A}(\vec{R}) = \frac{\mu_0}{4\pi} \int_{\tau'} \frac{\vec{j}(\vec{r}')}{|\vec{R} - \vec{r}'|} \; d\tau' \tag{1.19}
\]

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CHAPTER 1. DEFINITION OF MOLECULAR PROPERTIES

Using the same Taylor expansion as in chapter 1.1 for a component of the vector potential one obtains

\[
A_j^\alpha(\vec{R}) = \frac{\mu_0}{4\pi} \frac{1}{| \vec{R} - \vec{r}_o |} \int_{\tau'} j_\alpha(\vec{r}') \, d\tau' \\
+ \frac{\mu_0}{4\pi} \left( \frac{\partial}{\partial r_\beta} \frac{1}{| \vec{R} - \vec{r}' |} \right) \int_{\tau'} j_\alpha(\vec{r}') \, (r'_\beta - r_{o,\beta}) \, d\tau' \\
+ \ldots
\]  

(1.20)

where the derivatives have to be evaluated again at \( \vec{r}' = \vec{r}_o \). This can be simplified by using the following relation for an arbitrary function \( f(\vec{r}') \)

\[
\int_{\tau'} \left( \vec{\nabla} f(\vec{r}') \right) \cdot \vec{j}(\vec{r}') \, d\tau' = 0
\]  

(1.21)

valid [2] for a steady current distribution (\( \vec{\nabla} \cdot \vec{j} = 0 \)). Chosing \( f = r'_\alpha \) proves that the first (monopole) term in Eq. (1.20) vanishes and we will not consider higher terms than the second (dipole) term in accordance with the electric quadrupole approximation. The remaining (dipole) term

\[
A_j^\alpha(\vec{R}) = \frac{\mu_0}{4\pi} \frac{R_\beta - r_{o,\beta}}{| \vec{R} - \vec{r}_o |^3} \int_{\tau'} (r'_\beta - r_{o,\beta}) \, j_\alpha(\vec{r}') \, d\tau'
\]  

(1.22)

can also be written as

\[
A_j^\alpha(\vec{R}) = \frac{\mu_0}{4\pi} \frac{R_\beta - r_{o,\beta}}{| \vec{R} - \vec{r}_o |^3} \left\{ \frac{1}{2} \int_{\tau'} \left[ ((r'_\beta - r_{o,\beta}) \, j_\alpha(\vec{r}') + (r'_\alpha - r_{o,\alpha}) \, j_\beta(\vec{r}')) \right] \, d\tau' \\
+ \int_{\tau'} ((r'_\beta - r_{o,\beta}) \, j_\alpha(\vec{r}') - (r'_\alpha - r_{o,\alpha}) \, j_\beta(\vec{r}')) \, d\tau'
\} 
\]  

(1.23)

Using Eq. (1.21) with \( f = (r'_\alpha - r_{o,\alpha})(r'_\beta - r_{o,\beta}) \) shows that the first term vanishes and one obtains

\[
\vec{A}_j(\vec{R}) = \frac{\mu_0}{4\pi} \frac{1}{2} \int_{\tau'} \left[ (\vec{r}' - \vec{r}_o) \times \hat{j}(\vec{r}') \right] \times \frac{(\vec{R} - \vec{r}_o)}{| \vec{R} - \vec{r}_o |^3} \, d\tau'
\]  

(1.24)

or

\[
\vec{A}_j(\vec{R}) = \frac{\mu_0}{4\pi} \vec{m}(\vec{r}_o) \times \frac{(\vec{R} - \vec{r}_o)}{| \vec{R} - \vec{r}_o |^3} + \ldots
\]  

(1.25)

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

\[
\vec{m}(\vec{r}_o) = \frac{1}{2} \int_{\vec{r}'} d\tau' (\vec{r}' - \vec{r}_o) \times \vec{j}(\vec{r}')
\]

\[
= \frac{1}{2} \int_{\vec{r}'} d\tau' \rho(\vec{r}') (\vec{r}' - \vec{r}_o) \times \vec{v}(\vec{r}')
\]  

(1.26)

The absence of a zeroth order moment in equation (1.25) reflects that magnetic monopole moments do not exist. Higher magnetic moments are seldomly encountered 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 possess a permanent magnetic moment. However, nuclei with non zero spin have a magnetic moment and equation (1.25) for their vector potential will be used in the following chapters.

### 1.5 Potential Energy in an Magnetic Induction

Similar to the electric case in chapter 1.2 also 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. In general the potential energy \( W \) of a current distribution in the presence of an external magnetic induction is given as

\[
W = -\int_{\vec{r}'} \vec{j}(\vec{r}') \cdot \vec{A}^B(\vec{r}') \ d\tau'
\]  

(1.27)

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

\[
\vec{B}(\vec{r}) = \nabla \times \vec{A}(\vec{r})
\]  

(1.28)

A simpler expression for the potential energy can be obtained by expanding a component of the vector potential \( A^B_\alpha(\vec{r}') \) in a Taylor series around \( \vec{r}_o \).

\[
A^B_\alpha(\vec{r}') = A^B_\alpha(\vec{r}_o) + (\vec{r}'_\beta - \vec{r}_o,\beta) \left( \frac{\partial A^B_\alpha(\vec{r}')}{\partial \vec{r}_\beta} \right)_{\vec{r}' = \vec{r}_o} + \ldots
\]  

(1.29)

which leads to

\[
W = -A^B_\alpha(\vec{r}_o) \int_{\vec{r}'} j_\alpha(\vec{r}') \ d\tau' - \left( \frac{\partial A^B_\alpha(\vec{r}')}{\partial \vec{r}_\beta} \right)_{\vec{r}' = \vec{r}_o} \int_{\vec{r}'} (\vec{r}'_\beta - \vec{r}_o,\beta) j_\alpha(\vec{r}') \ d\tau' + \ldots
\]  

(1.30)

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CHAPTER 1. DEFINITION OF MOLECULAR PROPERTIES

However, the integral in the first term was shown to vanish in section 1.4 and the second term can again be rewritten (Eq. (1.21)), such that

\[
W = -\left( \frac{\partial \mathcal{A}_B^B(\vec{r}')}{\partial \tau_\beta} \right)_{\vec{r}'=\vec{r}_o} \frac{1}{2} \int_{\vec{r}'} ((\vec{r}'_\beta - \vec{r}_{o,\beta}) j_\alpha(\vec{r}')
\]

\[-(\vec{r}'_\alpha - \vec{r}_{o,\alpha}) j_\beta(\vec{r}')) d\tau' + \ldots \tag{1.31}
\]

or in vector notation

\[
W = -\frac{1}{2} \int_{\vec{r}'} \left( (\vec{r}' - \vec{r}_o) \times \vec{j}(\vec{r}') \right) \cdot \left( \vec{\nabla} \times \vec{A}_B(\vec{r}') \right)_{\vec{r}'=\vec{r}_o} \, d\tau' + \ldots \tag{1.32}
\]

Using the definition of the magnetic dipole moment given in equation (1.26) and of the vector potential given in equation (1.28) the expansion of the energy can be written as

\[
W = -\vec{m}(\vec{r}_o) \cdot \vec{B}(\vec{r}_o) \tag{1.33}
\]

From this equation it can be seen that also the magnetic dipole moment can alternatively to equation (1.26) be defined as derivative of the potential energy with respect to the field induction \( B_\alpha \)

\[
m_\alpha(\vec{r}_o) = -\frac{\partial W}{\partial B_\alpha} \tag{1.34}
\]

1.6 Induced Magnetic Moments and Magnetizabilities

In the presence of a magnetic induction \( \vec{B} \) the energy of the distribution of moving charges changes according to equation (1.33). 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 for the magnetic induction \( \vec{B} \) apart from an external magnetic field are other magnetic moments and in particular the magnetic dipole moment \( \vec{m}_K \) of a nucleus \( K \) in the molecule. 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 be expanded in a Taylor series

\[
m_\alpha(\vec{B}, \vec{m}_K) = m_\alpha + m_\alpha^{ind}(\vec{B}, \vec{m}_K)
\]

\[
m_\alpha(\vec{B}, \vec{m}_K) = m_\alpha + \xi_{\alpha\beta} B_\beta - \sigma^{K}_{\beta\alpha} m^{K}_\beta + \ldots \tag{1.35}
\]

where \( \xi_{\alpha\beta} \) and \( \sigma^{K}_{\beta\alpha} \) are components of the magnetizability and nuclear magnetic shielding tensor, respectively. The latter is closely related to the chemical shift
1.6. INDUCED MAGNETIC MOMENTS AND MAGNETIZABILITIES

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 \(B_\beta^j(\vec{R}; \vec{B}, \vec{m}^L)\)

<table>
<thead>
<tr>
<th></th>
<th>(m_\alpha(\vec{B}, \vec{m}^K))</th>
<th>(B_\alpha^j(\vec{R}_K; \vec{B}, \vec{m}^L))</th>
<th>(B_\beta^j(\vec{R}_K; \vec{B}, \vec{m}^L))</th>
<th>(W(\vec{B}, \vec{m}^K, \vec{m}^L))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_\alpha)</td>
<td>(\frac{\partial}{\partial B_\alpha})</td>
<td>(-\frac{\partial}{\partial m_\alpha^K})</td>
<td>(-\frac{\partial}{\partial m_\alpha^L})</td>
<td>(-\frac{\partial}{\partial B_\alpha})</td>
</tr>
<tr>
<td>(B_\alpha^j(\vec{R}_K))</td>
<td>(-\frac{\partial}{\partial B_\alpha})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^L})</td>
<td>(-\frac{\partial}{\partial m_\alpha^K})</td>
</tr>
<tr>
<td>(\xi_{\alpha\beta})</td>
<td>(-\frac{\partial}{\partial B_\beta})</td>
<td>(-\frac{\partial}{\partial B_\alpha})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\beta^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\beta^L})</td>
</tr>
<tr>
<td>(\sigma_{\beta\alpha}(\vec{R}))</td>
<td>(-\frac{\partial}{\partial B_\alpha})</td>
<td>(-\frac{\partial}{\partial B_\alpha})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^L})</td>
</tr>
<tr>
<td>(\sigma^K_{\beta\alpha})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\beta^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\beta^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
</tr>
<tr>
<td>(K^K_{\beta\alpha}(\vec{R}))</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
</tr>
<tr>
<td>(K^{KL}_{\beta\alpha})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
<td>(-\frac{\partial}{\partial \vec{m}_\alpha^K})</td>
</tr>
</tbody>
</table>

\(^a\) All derivatives have to be evaluated for zero magnetic induction and zero nuclear magnetic moment.

measured in nuclear magnetic resonance spectroscopy and will be discussed in more detail in chapter 1.8.

By insertion of this expansion in equation (1.34) and integration, the energy of this polarizable charge distribution and current distribution is obtained as

\[
W(\vec{B}, \vec{m}^K) = W(0) - m_\alpha B_\alpha - \frac{1}{2} \xi_{\alpha\beta} B_\alpha B_\beta + \sigma^K_{\beta\alpha} m^K_\beta B_\alpha + \ldots \quad (1.36)
\]

The magnetizability as well as the nuclear magnetic shielding tensor can thus also be defined as the derivatives of the energy as was the case for the polarizability and hyperpolarizability tensors. This is summarized in Table 1.2. In order to obtain the permanent, \(i.e.\) field independent, magnetic moment \(\vec{m}\) the derivative in equation (1.34) has to be evaluated for zero magnetic field strength.
CHAPTER 1. DEFINITION OF MOLECULAR PROPERTIES

1.7 Molecular Electric and Magnetic Fields

In the previous chapters only moments of the charge and current densities were considered. But also several field quantities like the electric and magnetic fields arising from a distribution of charges are important molecular properties.

Knowledge of the electrostatic potential \( \phi(\vec{R}) \) due to the distribution of charges, as given in equation (1.1), is important for the study of intermolecular interactions and reactivity. The derivatives of the electrostatic potential are according to equations (1.10) and (1.11) the electric field \( E_\alpha^p \) and field gradient \( E_{\alpha\beta}^p \)

\[
E_\alpha^p(\vec{R}) = \frac{1}{4\pi\epsilon_0} \int \rho(\vec{r}') \frac{R_\alpha - r'_\alpha}{|\vec{R} - \vec{r}'|^3} d\tau'
\]

\[
E_{\alpha\beta}^p(\vec{R}) = \frac{1}{4\pi\epsilon_0} \int \rho(\vec{r}') \left[ \frac{\delta_{\alpha\beta}}{|\vec{R} - \vec{r}'|^3} - 3 \frac{(R_\alpha - r'_\alpha)(R_\beta - r'_\beta)}{|\vec{R} - \vec{r}'|^5} \right] d\tau'
\]

The electric field gives rise to a force \( \vec{F} \) acting on the nuclei, for nucleus \( K \)

\[
\vec{F}_K = Z_K e E^p(\vec{R}_K)
\]

where the contribution of nucleus \( K \) to the electric field has to be excluded, of course. This force should be zero for any nucleus in a molecule, but it will be only so, if the geometry has been optimised.

Fields can be probed by dipole moments. As nuclei do not have electric dipole moments the molecular electric field cannot be investigated in this way. However, some nuclei possess an electric quadrupole moment \( \Theta_K \) and the interaction between those and the molecular electric field gradient can be used to 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 (1.28) to the expression 1.19) for the vector potential \( \vec{A}^j(\vec{R}) \) of a current distribution

\[
\vec{B}^j(\vec{R}) = \frac{\mu_0}{4\pi} \int \rho(\vec{r}') \frac{(\vec{R} - \vec{r}') \times \vec{j}(\vec{r}')}{|\vec{R} - \vec{r}'|^3} d\tau'
\]

\[
= -\frac{\mu_0}{4\pi} \int \rho(\vec{r}') \frac{(\vec{R} - \vec{r}') \times \vec{v}(\vec{r}')}{|\vec{R} - \vec{r}'|^3} d\tau'
\]

Although defined everywhere, 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

\[
W = -\vec{m}^K \cdot \vec{B}^j(\vec{R}_K)
\]

Consequently the molecular magnetic induction can be defined as derivative of the energy of the distribution of charges

\[
B_{\alpha}^j(\vec{R}_K) = -\frac{\partial W}{\partial m^K_{\alpha}}
\]

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1.8 Induced Magnetic Fields and NMR Parameters

In chapter 1.6 it was discussed that the interaction of a distribution of charges with an external magnetic induction $\vec{B}$ or with nuclear magnetic moments $\vec{m}^L$ leads to an induced current density $\vec{j}^{\text{ind}}(\vec{r})$. According to equation (1.40) this gives also rise to an induced molecular magnetic induction $\vec{B}^{\text{ind}}(\vec{R})$

$$
\begin{align*}
B^i_\alpha(\vec{R}, \vec{B}, \vec{m}^L) &= B^{(0)}_\alpha + B^{\text{ind}}_\alpha(\vec{R}, \vec{B}, \vec{m}^L) \\
B^j_\alpha(\vec{R}, \vec{B}, \vec{m}^L) &= B^{(0)}_\alpha - \sigma_{\alpha\beta}(\vec{R})B_\beta - K^L(\vec{R})_\alpha\beta m^L_\beta + \ldots
\end{align*}
$$

(1.43)

where $\sigma_{\alpha\beta}(\vec{R})$ is the magnetic shielding tensor field and $K^L_{\alpha\beta}(\vec{R})$ 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 at the position $\vec{R}_K$ of nuclear magnetic dipole moment $\vec{m}^K$ is the well known nuclear magnetic shielding tensor $\sigma^K_{\alpha\beta} = \sigma_{\alpha\beta}(\vec{R}_K)$ of nuclear magnetic resonance (NMR) spectroscopy. $K^K_{\alpha\beta} = K^L_{\alpha\beta}(\vec{R}_K)$ is the reduced indirect nuclear spin-spin coupling tensor, which is related to the indirect nuclear spin-spin coupling tensor $J^K_{\alpha\beta}$ of NMR spectroscopy by

$$
J^K_{\alpha\beta} = \frac{\gamma_K \gamma_L}{2\pi} \hbar K^K_{\alpha\beta}
$$

(1.44)

where $\gamma_K$ and $\gamma_L$ are the gyromagnetic ratios of the two nuclei.

The energy of the distribution of charges is obtained as usually by inserting equation (1.43) in equation (1.42) and integration

$$
W(\vec{B}, \vec{m}^K, \vec{m}^L) = W^{(0)} - m^K_\alpha B^{(0)}_\alpha + \sigma^K_{\alpha\beta} m^K_\alpha B_\beta + K^K_{\alpha\beta} m^K_\alpha m^L_\beta + \ldots
$$

(1.45)

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

1.9 Molecular Rotation as Source for Magnetic Fields

In chapter 1.6 and 1.8 the magnetic moments $\vec{m}^{\text{ind}}$ and molecular magnetic inductions $\vec{B}^{\text{ind}}$ induced by an external magnetic induction $\vec{B}$ or a nuclear magnetic moment $\vec{m}^K$ were defined. Another reason for the induction of magnetic moments or fields can be that a molecule rotates. A rigidly rotating charge distribution with angular velocity $\vec{\omega} = I^{-1} \hat{J}$ will according to equations (1.26) and (1.40) produce a
magnetic moment and a molecular magnetic induction

\[ \vec{m}_J = \frac{1}{2} \int \rho\vec{r}'(\vec{r}' - \vec{r}_{CM}) \times \left[ (\vec{r}' - \vec{r}_{CM}) \times (I^{-1} \vec{J}) \right] \]  

(1.46)

\[ \vec{B}_J(\vec{R}) = -\frac{\mu_0}{4\pi} \int \rho(\vec{r}') \frac{(\vec{R} - \vec{r}')}{|\vec{R} - \vec{r}'|^3} \left[ (\vec{r}' - \vec{r}_{CM}) \times (I^{-1} \vec{J}) \right] \, d\tau' \]  

(1.47)

However, Lamor’s theorem states that rotating charges give rise to an magnetic induction \( \vec{B}_J \)

\[ \vec{B}_J = -\frac{2m_e}{e} I^{-1} \vec{J} \]  

(1.48)

with the associated vector potential

\[ \vec{A}_J = -\frac{m_e}{e} I^{-1} \vec{J} \times (\vec{r} - \vec{r}_{CM}) \]  

(1.49)

This magnetic induction then leads to an induced magnetic moment \( \vec{m}_{J,\text{ind}} \) and induced molecular magnetic field \( \vec{B}_{J,\text{ind}} \) in addition to the magnetic moment \( \vec{m}_J \) and molecular magnetic induction \( \vec{B}_J \) of the rotating rigid charge distribution

\[ m_{J,\alpha}(\vec{J}) = m_{J,\alpha} + m_{J,\alpha}^{\text{ind}} \]

\[ m_{J,\alpha}(\vec{J}) = \frac{\mu_N}{\hbar} \, g_{J,\alpha\beta} J_\beta \]  

(1.50)

\[ B_{J,\alpha}(\vec{R}, \vec{J}) = B_{J,\alpha}^{(0)}(\vec{R}) + B_{J,\alpha}^{\text{ind}}(\vec{R}, \vec{J}) \]

\[ B_{J,\alpha}(\vec{R}, \vec{J}) = \frac{2\pi}{\mu_N g_K} M_{J,\alpha\beta}(\vec{R}) J_\beta \]  

(1.51)

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

\[ W(\vec{B}, \vec{J}) = W^{(0)} - \frac{\mu_N}{\hbar} g_{J,\alpha\beta} B_\alpha J_\beta \]  

(1.52)

\[ W(\vec{m}_K, \vec{J}) = W^{(0)} - \frac{2\pi}{\mu_N g_K} M_{J,\alpha\beta}^K m_\alpha J_\beta \]  

(1.53)

The rotational \( g \) tensor and spin-rotation tensor can therefore either be defined as derivatives of the rotational moment and the rotational magnetic induction or of the corresponding interaction energies (table 1.3).
1.10 Time Dependent Fields

So far the effects of static electric or magnetic fields on the molecular electric and magnetic moments or fields were considered. However, molecules are often exposed to time varying fields, as for example in the interaction with electromagnetic radiation. Then also the molecular properties become time dependent.

In this chapter only the generalization of the electric properties described in chapter 1.3 and the effects of the time dependent electric field vector \( \vec{E}(\vec{r}, t) \) of the electromagnetic radiation will be described. The influence of the corresponding time dependent magnetic induction vector \( \vec{B}(\vec{r}, t) \) and the associated molecular properties have little physical significance and are therefore usually ignored.

For a general polychromatic electromagnetic wave with wave vector \( \vec{k} \) the electric field vector is given as

\[
\vec{E}(\vec{r}, t) = \int_{-\infty}^{\infty} d\omega \vec{E}_\omega \cos(\vec{k} \cdot \vec{r} - \omega t) = \frac{1}{2} \int_{-\infty}^{\infty} d\omega \vec{E}_\omega \left( e^{i(\vec{k} \cdot \vec{r} - \omega t)} + e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right)
\]

(1.54)

The expansion of the perturbation dependent electric dipole moment in equation (1.15) generalizes then to

\[
\mu_\alpha(\vec{E}(t)) = \mu_\alpha + \mu_\alpha^{\text{ind}}(\vec{E}(t))
\]

\[
\mu_\alpha(\vec{E}(t)) = \mu_\alpha + \int_{-\infty}^{\infty} d\omega_1 \alpha_\alpha\beta(-\omega_1; \omega_1)E_\beta^{\omega_1} \cos(\vec{k} \cdot \vec{r}_o - \omega_1 t)
\]

\[
+ \frac{1}{2} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \beta_\alpha\beta\gamma(-\omega_1 - \omega_2; \omega_1, \omega_2)
\]

\[
E_\beta^{\omega_1} \cos(\vec{k} \cdot \vec{r}_o - \omega_1 t)E_\gamma^{\omega_2} \cos(\vec{k} \cdot \vec{r}_o - \omega_2 t)
\]

\[
+ \ldots
\]

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Table 1.3 Definitions of the rotational \( g \) tensor \( g_{J,\alpha\beta} \) and spin rotation tensor \( M^K_{J,\alpha\beta} \) 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 \( B^J_\alpha(\vec{R}; \vec{J}) \)

<table>
<thead>
<tr>
<th>( g_{J,\alpha\beta} )</th>
<th>( m_\alpha(\vec{J}) )</th>
<th>( B^J_\alpha(\vec{R}; \vec{J}) )</th>
<th>( B^J_\alpha(\vec{R}_K; \vec{J}) )</th>
<th>( W(\vec{B}, \vec{m}^K, \vec{J}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\hbar}{\mu_N} \frac{\partial}{\partial J_\beta} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( - \frac{\hbar}{\mu_N} \frac{\partial^2}{\partial B_\alpha \partial J_\beta} )</td>
</tr>
<tr>
<td>( M_{J,\alpha\beta}(\vec{R}) )</td>
<td>-</td>
<td>( \frac{\mu_N g_K}{2\pi} \frac{\partial}{\partial J_\beta} )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( M^K_{J,\alpha\beta} )</td>
<td>-</td>
<td>-</td>
<td>( \frac{\mu_N g_K}{2\pi} \frac{\partial}{\partial J_\beta} )</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) All derivatives have to be evaluated for zero perturbation.
where all the terms were neglected which involve the electric field gradient, the time derivatives of the electric field and field gradient as well as all the terms related to the time dependent magnetic induction vector $\vec{B}(\vec{r}, t)$. $\alpha_{\alpha\beta}(-\omega_1; \omega_1)$ 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.
Chapter 2

Exact Quantum Mechanical Expressions

2.1 The Molecular Electronic Hamiltonian

In the previous chapter several molecular properties were defined as derivatives of the classical interaction energy of a system with electric and magnetic fields and nuclear moments. In this chapter quantum mechanical expression for these properties will be derived. Due to the definition of the properties as energy derivatives one needs to find a quantum mechanical expression for the energy of the system in the presence of electric and magnetic fields and nuclear moments.

In order to do so some approximations are made to a full quantum mechanical treatment, which would involve quantum electrodynamics. Firstly the fields and nuclear moments are treated classically and only the electrons are treated by quantum mechanics. The fields and nuclear moments are thus not part of the system, which is treated quantum mechanically, but rather they are treated as mere perturbations which do not react to the presence of the molecule, the so-called minimal coupling. Secondly, the exposition will be restricted to non-relativistic quantum mechanics, i.e. to the Schrödinger equation. However, it will not be ignored that electrons have spin, which can interact with magnetic fields and magnetic moments of nuclei, and the corresponding interaction operators, derivable from the relativistic Dirac equation, will be added to the Schrödinger Hamiltonian in an ad hoc fashion. Finally the Born-Oppenheimer approximation for the separation of electronic and nuclear motion is applied. This implies that the electronic wavefunction and energy and therefore also the molecular properties are obtained for a given set of nuclear coordinates, i.e. they depend parametrically on the positions of the nuclei. The effect of nuclear motion can be included approximately by the so-called vibrational averaging as described in chapter 2.5.

This yields the field free electronic Schrödinger equation

\[ \hat{H}^{(0)}\Psi^{(0)}_n = W^{(0)}_n\Psi^{(0)}_n \]  \hspace{1cm} (2.1)
where $\Psi_n^{(0)}$ is the many-electron wavefunction for state $n$ with electronic energy $W_n^{(0)}$ and the molecular electronic Hamiltonian is defined as

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

Since only the electronic energy is considered in the following, only the pure electronic contributions to the molecular properties will be obtained. The contributions of the fixed nuclei have to be added afterwards according to the classical expressions given in the chapter 1.

Using minimal coupling, the vector potential enters the mechanical momentum of electron $i$, $m_e\hat{v}_i$

$$m_e\hat{v}_i = \hat{p}_i + e\hat{A}(\vec{r}_i)$$  \hspace{1cm} (2.3)

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

$$\hat{H} = \frac{1}{2m_e} \sum_i \left(\hat{p}_i + e\hat{A}(\vec{r}_i)\right)^2 - \frac{1}{4\pi\epsilon_0} \sum_{iK} \frac{Z_K}{|\vec{r}_i - \vec{R}_K|} + \frac{1}{4\pi\epsilon_0} \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} - e\sum_i \phi(\vec{r}_i)$$  \hspace{1cm} (2.4)

In addition the Zeeman term of the Breit-Pauli Hamiltonian

$$\hat{H} = \sum_i \frac{g_e e}{2m_e} \hat{s}_i \cdot \left(\vec{\nabla} \times \hat{A}(\vec{r}_i)\right)$$  \hspace{1cm} (2.5)

is often included. Here $\hat{s}_i$ is the operator of the spin of electron $i$.

From equation (1.28) it can be seen that the vector potential can be chosen to be divergences free, i.e. $\vec{\nabla} \cdot \hat{A} = 0$, which is called the Coulomb gauge. The Hamiltonian can thus be written as

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} + \hat{H}^{(2)} = \sum_i \hat{h}_i^{(0)}(i) + \sum_{i<j} \hat{g}(i, j) + \sum_i \left(\hat{h}_i^{(1)}(i) + \hat{h}_i^{(2)}(i)\right)$$  \hspace{1cm} (2.6)

Inserting in this general expression the vector potential of a uniform magnetic induction

$$\hat{A}(\vec{r}_i) = \frac{1}{2} \vec{B} \times (\vec{r}_i - \vec{R}_{GO})$$  \hspace{1cm} (2.7)

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2.1. THE MOLECULAR ELECTRONIC HAMILTONIAN

where $\hat{R}_{GO}$ is the arbitrary gauge origin; the vector potential of the magnetic induction arising because of the rotation of the molecule, Eq. (1.49),

$$\vec{A}^J(\vec{r}_i) = -\frac{m_e}{e} \left( \vec{I}^{-1} \vec{J} \right) \times (\vec{r}_i - \vec{R}_{CM})$$  (2.8)

the vector potential of the magnetic dipole moment of nucleus $K$, equation (1.25),

$$\vec{A}^K(\vec{r}_i) = \frac{\mu_0}{4\pi} \vec{m}^K \times \frac{\vec{r}_i - \vec{R}_K}{|\vec{r}_i - \vec{R}_K|^3}$$  (2.9)

whose magnetic induction is

$$\vec{B}^K(\vec{r}_i) = \frac{\mu_0}{4\pi} \left( \left( \vec{m}^K \cdot (\vec{r}_i - \vec{R}_K) \right) \left( \vec{r}_i - \vec{R}_K \right) \frac{1}{|\vec{r}_i - \vec{R}_K|^5} - \frac{\vec{m}^K}{|\vec{r}_i - \vec{R}_K|^3} \right)$$

$$+ \frac{\mu_0}{4\pi} \frac{8\pi}{3} \delta(\vec{r}_i - \vec{R}_K) \vec{m}^K$$  (2.10)

and the scalar potential of a electric field with non-zero gradient, Eq. (1.6),

$$\phi^E(\vec{r}_i) = -\frac{1}{2} \left( \vec{r}_{i,\alpha} - R_{O,\alpha} \right) \left( \vec{r}_{i,\beta} - R_{O,\beta} \right) - \frac{1}{3} \delta_{\alpha\beta}(\vec{r}_i - \vec{R}_O)^2 \right) E_{\alpha\beta}(\vec{r}_i)$$  (2.11)

where the scalar potential at the origin of the coordinate system, $\phi^E(\vec{R}_O)$ was set zero, yields after some manipulations

$$\hat{H}^{(1)} = - \left( \hat{O}_{\alpha}^{IB} \right) B_{\alpha} + \left( \hat{O}_{\alpha}^{JJ} \right) \left( \vec{I}^{-1} \vec{J} \right) $$

$$- \sum_{K} \left( \hat{O}_{\alpha}^{mK} + \hat{O}_{\alpha}^{smK} \right) m_{\alpha}^K - \hat{O}_{\alpha}^{E} E_{\alpha} - \hat{O}_{\alpha}^{\nabla E} E_{\alpha\beta}$$  (2.12)

$$\hat{H}^{(2)} = \hat{O}_{\alpha\beta}^{BB} B_{\alpha} B_{\beta} + \hat{O}_{\alpha\beta}^{JJ} \left( \vec{I}^{-1} \vec{J} \right)_{\alpha} \left( \vec{I}^{-1} \vec{J} \right)_{\beta} + \sum_{KL} \hat{O}_{\alpha\beta}^{mK,mL} m_{\alpha}^K m_{\beta}^L$$

$$+ \hat{O}_{\alpha\beta}^{BJ} B_{\alpha} \left( \vec{I}^{-1} \vec{J} \right)_{\beta} + \sum_{K} \hat{O}_{\alpha\beta}^{mK,B} m_{\alpha}^K B_{\beta} + \sum_{K} \hat{O}_{\alpha\beta}^{mK,J} m_{\alpha}^K \left( \vec{I}^{-1} \vec{J} \right)_{\beta}$$  (2.13)

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

$$\hat{O}_{\alpha}^{IB} = \sum_{i} \hat{O}_{\alpha}^{IB}(i) = -\frac{e}{2m_e} \sum_{i} \left( \left( \vec{r}_i - \vec{R}_{GO} \right) \times \hat{p}_i \right)_{\alpha}$$  (2.14)

$$\hat{O}_{\alpha}^{BB} = \sum_{i} \hat{O}_{\alpha}^{BB}(i) = -\frac{g_e}{2m_e} \sum_{i} \hat{s}_{i,\alpha}$$  (2.15)

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\[ \hat{O}_\alpha^{ij} = \sum_i \hat{o}_\alpha^{ij}(i) = \frac{2me}{e} \hat{O}_\alpha^{jB} \] (2.16)

\[ \hat{O}_\alpha^{kJ} = \sum_i \hat{o}_\alpha^{kJ}(i) = \frac{2me}{e} \hat{O}_\alpha^{sB} \] (2.17)

\[ \hat{O}_\alpha^{lmK} = \sum_i \hat{o}_\alpha^{lmK}(i) = -\frac{e}{m_e} \mu_0 \frac{8\pi}{4\pi} \sum_i \left( \frac{\hat{r}_i - \hat{R}_K}{|\hat{r}_i - \hat{R}_K|^3} \times \hat{p}_i \right) \hat{s}_{i,\alpha} \] (2.18)

\[ \hat{O}_\alpha^{smK} = \sum_i \hat{o}_\alpha^{smK}(i) = -\frac{e}{m_e} \frac{\mu_0}{4\pi} \sum_i \left( \frac{\hat{r}_i - \hat{R}_K}{|\hat{r}_i - \hat{R}_K|^3} \hat{s}_{i,\alpha} \right) \] (2.18)

\[ \hat{O}_\alpha^{E} = \sum_i \hat{o}_\alpha^{E}(i) = -e \sum_i (\hat{r}_{i,\alpha} - R_{O,\alpha}) \] (2.20)

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

\[ = -\frac{e}{2} \sum_i \left( (\hat{r}_{i,\alpha} - R_{O,\alpha})(\hat{r}_{i,\beta} - R_{O,\beta}) - \frac{1}{3} \delta_{\alpha\beta}(\hat{r}_i - \hat{R}_O)^2 \right) \] (2.21)

\[ \hat{O}_\alpha^{BB} = \sum_i \hat{o}_\alpha^{BB}(i) \]

\[ = \frac{e^2}{8m_e} \sum_i \left( (\hat{r}_i - \hat{R}_{GO})^2 \delta_{\alpha\beta} - (\hat{r}_{i,\alpha} - R_{GO,\alpha})(\hat{r}_{i,\beta} - R_{GO,\beta}) \right) \] (2.22)

\[ \hat{O}_\alpha^{JJ} = \sum_i \hat{o}_\alpha^{JJ}(i) \]

\[ = \frac{me}{2} \sum_i \left( (\hat{r}_i - \hat{R}_{CM})^2 \delta_{\alpha\beta} - (\hat{r}_{i,\alpha} - R_{CM,\alpha})(\hat{r}_{i,\beta} - R_{CM,\beta}) \right) \] (2.23)

\[ \hat{O}_\alpha^{mKmL} = \sum_i \hat{o}_\alpha^{mKmL}(i) = \frac{e^2}{2m_e} \frac{(\mu_0)^2}{4\pi} \sum_i \left( \frac{\hat{r}_i - \hat{R}_L}{|\hat{r}_i - \hat{R}_L|^3} \cdot \frac{\hat{r}_i - \hat{R}_K}{|\hat{r}_i - \hat{R}_K|^3} \delta_{\alpha\beta} - \frac{(\hat{r}_{i,\alpha} - R_{L,\alpha})(\hat{r}_{i,\beta} - R_{K,\beta})}{|\hat{r}_i - \hat{R}_L|^3 |\hat{r}_i - \hat{R}_K|^3} \right) \] (2.24)
\[ \hat{O}_{\alpha\beta}^{BJ} = \sum_i \hat{o}_{\alpha\beta}^{BJ}(i) = -\frac{e}{2} \sum_i \left( (\hat{r}_i - \hat{R}_{CM}) \cdot (\hat{r}_i - \hat{R}_{GO}) \delta_{\alpha\beta} \\
- (\hat{r}_{i,\alpha} - R_{CM,\alpha})(\hat{r}_{i,\beta} - R_{GO,\beta}) \right) \tag{2.25} \]

\[ \hat{O}_{\alpha\beta}^{KB} = \sum_i \hat{o}_{\alpha\beta}^{KB}(i) = e^2 \frac{\mu_0}{2m_e 4\pi} \sum_i \left( \frac{\hat{r}_i - \hat{R}_{GO}}{\|\hat{r}_i - \hat{R}_{K}\|^3} \delta_{\alpha\beta} \\
- (\hat{r}_{i,\alpha} - R_{GO,\alpha})(\hat{r}_{i,\beta} - R_{K,\beta}) \right) \tag{2.26} \]

\[ \hat{O}_{\alpha\beta}^{KJ} = \sum_i \hat{o}_{\alpha\beta}^{KJ}(i) = -e \frac{\mu_0}{4\pi} \sum_i \left( \frac{\hat{r}_i - \hat{R}_{CM}}{\|\hat{r}_i - \hat{R}_{K}\|^3} \delta_{\alpha\beta} \\
- (\hat{r}_{i,\alpha} - R_{CM,\alpha})(\hat{r}_{i,\beta} - R_{K,\beta}) \right) \tag{2.27} \]

2.2 Rayleigh-Schrödinger Perturbation Theory

In chapter 1 it was shown that molecular electromagnetic properties can be defined as derivatives of the energy. The electronic contributions to the molecular properties can therefore be obtained as derivatives of the electronic energy. In order to take the derivatives one needs to find the electronic energy of a system described by the Hamiltonian given in equation (2.6). However in general it is not possible to find exact solutions of this Hamiltonian, i.e. to solve the Schrödinger equation

\[ \hat{H}\Psi_0 = W_0 \Psi_0 \tag{2.28} \]

In non-degenerate Rayleigh-Schrödinger perturbation theory one assumes therefore a) 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 b) that the energies and wavefunctions of the total Hamiltonian, equation (2.6), 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

\[ W_0 = W_0^{(0)} + W_0^{(1)} + W_0^{(2)} + \cdots \tag{2.29} \]

\[ \Psi_0 = \Psi_0^{(0)} + \Psi_0^{(1)} + \Psi_0^{(2)} + \cdots \tag{2.30} \]

The first and second order corrections to the energy are then given as

\[ W_0^{(1)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle \tag{2.31} \]

\[ W_0^{(2)} = \langle \Psi_0^{(0)} | \hat{H}^{(2)} | \Psi_0^{(0)} \rangle + \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle \tag{2.32} \]

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CHAPTER 2. EXACT QUANTUM MECHANICAL EXPRESSIONS

Expanding the first order wavefunction in the complete set of unperturbed wavefunctions \( \{ \Psi^{(0)}_n \} \)

\[
| \Psi^{(1)}_0 \rangle = \sum_{n \neq 0} | \Psi^{(0)}_n \rangle \langle \Psi^{(0)}_n | \hat{H}^{(1)} | \Psi^{(0)}_0 \rangle W^{(0)} - W^{(0)}_n
\]  

(2.33)

the second order correction to the energy becomes

\[
W^{(2)}_0 = \langle \Psi^{(0)}_0 | \hat{H}^{(2)} | \Psi^{(0)}_0 \rangle + \sum_{n \neq 0} \frac{\langle \Psi^{(0)}_0 | \hat{H}^{(1)} | \Psi^{(0)}_n \rangle \langle \Psi^{(0)}_n | \hat{H}^{(1)} | \Psi^{(0)}_0 \rangle}{W^{(0)} - W^{(0)}_n}
\]  

(2.34)

After insertion of the first and second order Hamiltonians, equations (2.12) and (2.13), in equations (2.31) and (2.34), expressions for the molecular properties defined in equations (1.13), (1.34), (1.42) and tables 1.1 and 1.2 are obtained by taking the appropriate derivatives of \( W_0 \) or equivalently by comparison with the classical expressions for the interaction energies (1.17), (1.36) and (1.45). The first order molecular properties are then given as

\[
\mu^{el}_{\alpha}(\vec{R}_O) = \langle \Psi^{(0)}_0 | \hat{O}_E^\alpha | \Psi^{(0)}_0 \rangle
\]  

(2.35)

\[
\Theta^{el}_{\alpha\beta}(\vec{R}_O) = 3 \langle \Psi^{(0)}_0 | \hat{O}_{E\alpha\beta}^\alpha | \Psi^{(0)}_0 \rangle
\]  

(2.36)

\[
m^{el}_{\alpha}(\vec{R}_GO) = \langle \Psi^{(0)}_0 | \hat{O}_{B}^\alpha | \Psi^{(0)}_0 \rangle
\]  

(2.37)

\[
B^{el}_{\alpha}(\vec{R}_K) = \langle \Psi^{(0)}_0 | \hat{O}_{lm}^{\alpha\alpha} | \Psi^{(0)}_0 \rangle
\]  

(2.38)

and the second order molecular properties are given as

<table>
<thead>
<tr>
<th>( P^{(2)} )</th>
<th>( f_1 )</th>
<th>( \hat{O}_1 )</th>
<th>( f_2 )</th>
<th>( \hat{O}_2 )</th>
<th>( \hat{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{\alpha\beta}^{el} (\vec{R}_O) )</td>
<td>-2</td>
<td>( \hat{O}_{\alpha\beta}^{BB} )</td>
<td>-1</td>
<td>( \hat{O}_\alpha^E )</td>
<td>( \hat{O}_\beta^E )</td>
</tr>
<tr>
<td>( \zeta_{\alpha\beta}^{el} (\vec{R}_GO) )</td>
<td>1</td>
<td>( \hat{O}_{\alpha\beta}^{mK} )</td>
<td>1</td>
<td>( \hat{O}_\alpha^{lm} )</td>
<td>( \hat{O}_\beta^{lm} )</td>
</tr>
<tr>
<td>( \sigma_{\alpha\beta}^{K,KL,el} (\vec{R}_GO) )</td>
<td>2</td>
<td>( \hat{O}_{\alpha\beta}^{mK} )</td>
<td>1</td>
<td>( \hat{O}<em>\alpha^{lm} ) + ( \hat{O}</em>\alpha^{sm} )</td>
<td>( \hat{O}<em>\beta^{lm} ) + ( \hat{O}</em>\beta^{sm} )</td>
</tr>
</tbody>
</table>

\[
P^{(2)} = f_1 \langle \Psi^{(0)}_0 | \hat{O}_1 | \Psi^{(0)}_0 \rangle + f_2 \sum_{n \neq 0} \frac{\langle \Psi^{(0)}_0 | \hat{O}_2 | \Psi^{(0)}_n \rangle \langle \Psi^{(0)}_n | \hat{O}_3 | \Psi^{(0)}_0 \rangle}{W^{(0)} - W^{(0)}_n}
\]

\[
+ f_2 \sum_{n \neq 0} \frac{\langle \Psi^{(0)}_0 | \hat{O}_3 | \Psi^{(0)}_n \rangle \langle \Psi^{(0)}_n | \hat{O}_2 | \Psi^{(0)}_0 \rangle}{W^{(0)} - W^{(0)}_n}
\]  

(2.39)

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2.3. STATIC RESPONSE THEORY

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. 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

$$
\langle \Psi_0^{(0)} | \hat{O}_s B^{(0)} | \Psi_0^{(0)} \rangle = \langle \Psi_0^{(0)} | \hat{O}_s m^K | \Psi_0^{(0)} \rangle = \langle \Psi_0^{(0)} | \hat{O}_s B | \Psi_0^{(0)} \rangle = 0 \quad (2.40)
$$

and the corresponding terms are not included in table 2.1. The expressions for the molecular magnetic properties are thus only valid for the case of closed shell molecules.

2.3 Static Response Theory

In chapter 1 it was shown that molecular properties like the polarizability can also be defined as derivatives of the corresponding perturbation dependent moments. One therefore needs to find quantum mechanical operators for the perturbation dependent electric and magnetic 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 $\lambda$ with normalized eigenfunction $\Psi(\lambda)$ and eigenvalue $W(\lambda)$ the derivative of the eigenvalue $W(\lambda)$ with respect to $\lambda$ is given as

$$
\frac{d}{d\lambda} W(\lambda) = \langle \Psi(\lambda) | \frac{\partial}{\partial \lambda} \hat{H}(\lambda) | \Psi(\lambda) \rangle \quad (2.41)
$$

Taking the appropriate derivatives, equations (1.13), (1.34) and (1.42), of the Hamiltonian in equation (2.6) leads to the following expressions for perturbation dependent operators of the electronic contribution to the electric dipole and quadrupole moment, the magnetic dipole moment and the molecular magnetic induction

$$
\hat{\mu}_e^{\alpha} = \hat{O}_e^{\alpha} \quad (2.42)
$$
$$
\hat{\Theta}_{\alpha\beta}^{el} = 3 \hat{O}_{\alpha \beta}^{\nabla E} \quad (2.43)
$$
$$
\hat{m}_e^{\alpha} = \hat{O}_e^{B} + \hat{O}_e^{n} - 2 \hat{O}_e^{B B} B_{\beta} - \hat{O}_e^{B J} (I - 1) \vec{J}_{\beta} - \sum K \hat{O}_{\mu K}^{m K} B_{\beta} - \sum L \hat{O}_{\mu L}^{m K} \hat{O}_{\mu L}^{m K} \quad (2.44)
$$
$$
\hat{B}_{\alpha}^{L}(\vec{R}_K) = \hat{O}_{\alpha}^{l K} + \hat{O}_{\alpha}^{m K} - \hat{O}_{\alpha}^{m K} B_{\beta} - \hat{O}_{\alpha}^{m K} (I - 1) \vec{J}_{\beta} - \sum L \hat{O}_{\mu L}^{m K} \hat{O}_{\mu L}^{m K} \quad (2.45)
$$

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 (2.30)

$$
\langle \Psi_0 | \hat{O} | \Psi_0 \rangle = \langle \Psi_0^{(0)} | \hat{O} | \Psi_0^{(0)} \rangle + \langle \Psi_1^{(1)} | \hat{O} | \Psi_0^{(0)} \rangle + \langle \Psi_0^{(0)} | \hat{O} | \Psi_1^{(1)} \rangle + \cdots \quad (2.46)
$$

The molecular properties are obtained by taking derivatives of the expectation value, as given in tables 1.1 and 1.2, or by comparison with the classical expression for the
perturbation dependent moments and fields in equations (1.15), (1.35) and (1.43). 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 2.2, 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 (2.39) and table 2.1, can be recovered from equation (2.46) by insertion of the first order correction to the wavefunction, equation (2.33).

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.

2.4 Time Dependent Response Theory

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

\[ \frac{i}{\hbar} \frac{\partial}{\partial t} \Psi_0(t) = \left( \hat{H}^{(0)} + \hat{H}^{(1)}(t) \right) \Psi_0(t) \]  

(2.47)

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

\[ \hat{H}^{(1)}(t) = \hat{V}_{\alpha \cdots} F(t)_{\alpha \cdots} \]  

(2.48)
or can be expressed in terms of its Fourier components

\[ \hat{H}^{(1)}(t) = \int_{-\infty}^{\infty} d\omega \hat{H}^{(1)}(\omega) = \int_{-\infty}^{\infty} d\omega \hat{V}_{\alpha \cdots}^\omega F(\omega)_{\alpha \cdots} e^{-i\omega t} \]  

(2.49)

The operator \( \hat{V}_{\alpha \cdots} \) may depend on coordinates and moment of the electrons but is independent of time, whereas the time dependent field \( F(t)_{\alpha \cdots} \) 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 [3], properties are evaluated as expectation values. The time dependent expectation value of an operator \( \hat{O} \) is thus formally expanded in a series

\[ \langle \Psi_0(t) | \hat{O} | \Psi_0(t) \rangle = \langle \Psi_0^{(0)} | \hat{O} | \Psi_0^{(0)} \rangle + \int_{-\infty}^{\infty} dt' \langle \hat{O}^{t'}; \hat{V}_{\alpha \cdots}^{t'} \rangle F(t')_{\alpha \cdots} + \frac{1}{2} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' \langle \hat{O}^{t'}; \hat{V}_{\alpha \cdots}^{t'}; \hat{V}_{\beta \cdots}^{t''} \rangle F(t')_{\alpha \cdots} F(t'')_{\beta \cdots} + \cdots \]  

(2.50)

where \( \hat{O}^t = e^{i\hat{H}^{(0)}t/\hbar} \hat{O} e^{-i\hat{H}^{(0)}t/\hbar} \) denotes the Heisenberg representation of operator \( \hat{O} \). The kernels of the integrals are the linear \( \langle \hat{O}^{t'}; \hat{V}_{\alpha \cdots}^{t'} \rangle \) and quadratic response
2.4. TIME DEPENDENT RESPONSE THEORY

function \( \langle \langle \hat{O}^t; \hat{V}^t_{\alpha_1^*}, \hat{V}^t_{\beta_2^*} \rangle \rangle \) in the time domain. The linear response function is also called the polarization propagator. Alternatively, using the Fourier transforms of the response functions to the frequency or energy domain, the expansion can be written as

\[
\langle \hat{\Psi}_0(t) | \hat{O} | \hat{\Psi}_0(t) \rangle = \langle \hat{\Psi}_0^0 | \hat{O} | \hat{\Psi}_0^0 \rangle + \int_{-\infty}^{\infty} d\omega_1 \ e^{-i\omega_1 t} \langle \langle \hat{O} ; \hat{V}_{\alpha_1^*}^\omega \rangle \rangle \omega_1 F(\omega_1)_{\alpha_1 \cdots} \quad (2.51)
\]

\[
+ \frac{1}{2} \int_{-\infty}^{\infty} d\omega_1 \ e^{-i\omega_1 t} \int_{-\infty}^{\infty} d\omega_2 \ e^{-i\omega_2 t} \langle \langle \hat{O} ; \hat{V}_{\alpha_1^*}^\omega , \hat{V}_{\beta_2^*}^\omega \rangle \rangle \omega_1 \omega_2 F(\omega_1)_{\alpha_1 \cdots}F(\omega_2)_{\beta_2 \cdots} + \cdots
\]

Expressions for the response functions are obtained by standard time dependent perturbation theory in which the set of exact eigenfunctions \( \{\hat{\Psi}_n^{(0)}\} \) of the unperturbed Hamiltonian \( \hat{H}^{(0)} \) are used as basis

\[
| \Psi_0(t) \rangle = \frac{| \Psi_0^{(0)} \rangle + \sum_{n \neq 0} | \Psi_n^{(0)} \rangle C_n(t)}{\sqrt{1 + \sum_{n \neq 0} C_n^*(t)C_n(t)}} \quad (2.52)
\]

and the time dependent coefficients are expanded in a perturbation series

\[
\langle \Psi_n^{(0)} | \Psi_0(t) \rangle = C_n(t) = C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots \quad (2.53)
\]

The individual terms in the expansion of the coefficients are then determined from the time dependent Schrödinger equation or a time dependent variation principle. Evaluating the time dependent expectation value \( \langle \Psi_0(t) | \hat{O} | \Psi_0(t) \rangle \) of an operator \( \hat{O} \) with the wavefunction given in equation (2.52) and collecting terms of the same order allows one to identify the response functions in equation (2.50). The linear response function or polarization propagator is thus given in the time domain as

\[
\langle \langle \hat{O}^t; \hat{V}^t_{\alpha_1^*} \rangle \rangle = \Theta(t - t') \frac{1}{i\hbar} \langle \hat{\Psi}_0^0 | \hat{O} | \hat{\Psi}_0^0 \rangle \left[ \hat{O}_1^t, \hat{V}^t_{\alpha_1^*} \right] \langle \hat{\Psi}_0^0 \rangle \quad (2.54)
\]

and its Fourier transform to the frequency domain is

\[
\langle \langle \hat{O}; \hat{V}_{\alpha_1^*}^\omega \rangle \rangle_{\omega_1} = \sum_{n \neq 0} \left\{ \frac{\langle \hat{\Psi}_0^0 | \hat{O} | \hat{\Psi}_n^{(0)} \rangle \langle \hat{\Psi}_n^{(0)} | \hat{V}_{\alpha_1^*}^\omega | \hat{\Psi}_0^{(0)} \rangle}{\hbar \omega_1 + W_n^{(0)} - W_n^{(0)}} + \frac{\langle \hat{\Psi}_0^0 | \hat{V}_{\alpha_1^*}^\omega | \hat{\Psi}_n^{(0)} \rangle \langle \hat{\Psi}_n^{(0)} | \hat{O} | \hat{\Psi}_0^{(0)} \rangle}{-\hbar \omega_1 + W_n^{(0)} - W_n^{(0)}} \right\} \quad (2.55)
\]

Correspondingly for the quadratic response function

\[
\langle \langle \hat{O}^t; \hat{V}^t_{\alpha_1^*}, \hat{V}^t_{\beta_2^*} \rangle \rangle = \Theta(t - t') \frac{1}{i\hbar} \langle \hat{\Psi}_0^0 | \left[ \hat{O}_1^t, \hat{V}^t_{\alpha_1^*} \right] \langle \hat{\Psi}_0^0 \rangle \quad (2.56)
\]

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\[ \langle \langle \hat{O}; V^{\omega_{1}}_{\alpha_{1}}, V^{\omega_{2}}_{\beta_{2}} \rangle \rangle_{\omega_{1}, \omega_{2}} \]

\[ = \sum_{n \neq 0, m \neq 0} \left\{ \begin{array}{l}
\langle \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta}^{(0)} | \hat{\Psi}^{(0)}_{n} | \overline{V^{\omega_{1}}_{\alpha_{1}}} | \hat{\Psi}^{(0)}_{m} | \hat{V}^{\omega_{2}}_{\beta_{2}} | \hat{\Psi}^{(0)}_{0} \rangle \\
\left( W^{(0)}_{n} - W^{(0)}_{0} - \hbar(\omega'_{1} + \omega'_{2}) \right) \left( W^{(0)}_{m} - W^{(0)}_{0} - \hbar\omega'_{2} \right)
\end{array} \right. \\
+ \langle \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta}^{(0)} | \hat{\Psi}^{(0)}_{n} | \overline{V^{\omega_{1}}_{\alpha_{1}}} | \hat{\Psi}^{(0)}_{m} | \hat{V}^{\omega_{2}}_{\beta_{2}} | \hat{\Psi}^{(0)}_{0} \rangle \\
\left( W^{(0)}_{n} - W^{(0)}_{0} - \hbar(\omega'_{1} + \omega'_{2}) \right) \left( W^{(0)}_{m} - W^{(0)}_{0} - \hbar\omega'_{2} \right)
\end{array} \right. \\
+ \langle \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta}^{(0)} | \hat{\Psi}^{(0)}_{n} | \overline{V^{\omega_{1}}_{\alpha_{1}}} | \hat{\Psi}^{(0)}_{m} | \hat{V}^{\omega_{2}}_{\beta_{2}} | \hat{\Psi}^{(0)}_{0} \rangle \\
\left( W^{(0)}_{n} - W^{(0)}_{0} + \hbar\omega'_{1} \right) \left( W^{(0)}_{m} - W^{(0)}_{0} - \hbar\omega'_{2} \right)
\end{array} \right. \\
+ \langle \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta}^{(0)} | \hat{\Psi}^{(0)}_{n} | \overline{V^{\omega_{1}}_{\alpha_{1}}} | \hat{\Psi}^{(0)}_{m} | \hat{V}^{\omega_{2}}_{\beta_{2}} | \hat{\Psi}^{(0)}_{0} \rangle \\
\left( W^{(0)}_{n} - W^{(0)}_{0} + \hbar\omega'_{1} \right) \left( W^{(0)}_{m} - W^{(0)}_{0} + \hbar(\omega'_{1} + \omega'_{2}) \right)
\right\} \] 

(2.57)

where \( \langle \langle \hat{\Psi}^{(0)}_{m} | \overline{\hat{O}} | \hat{\Psi}^{(0)}_{m} \rangle \rangle \) denotes \( \langle \hat{\Psi}^{(0)}_{m} | \hat{\Theta} - \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta} | \hat{\Psi}^{(0)}_{m} \rangle \rangle \), \textit{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 (2.54). This equation-of-motion transformed to the frequency domain is

\[ \hbar \omega \langle \langle \hat{\Theta}; \hat{V}^{\omega}_{\alpha_{1}} \rangle \rangle_{\omega} = \langle \langle \hat{\Psi}^{(0)}_{0} | [\hat{\Theta}, \hat{V}^{\omega}_{\alpha_{1}}] | \hat{\Psi}^{(0)}_{0} \rangle + \langle \langle \hat{\Theta}; [\hat{H}^{(0)}, \hat{V}^{\omega}_{\alpha_{1}}] \rangle \rangle_{\omega} \] 

(2.58)

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

\[ \langle \langle \hat{\Theta}; \hat{V}^{\omega}_{\alpha_{1}} \rangle \rangle_{\omega} = \left( \frac{1}{\hbar \omega} \right)^{0} \langle \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta}^{(0)} | \hat{V}^{\omega}_{\alpha_{1}} \rangle \hat{\Psi}^{(0)}_{0} \rangle \\
+ \left( \frac{1}{\hbar \omega} \right)^{2} \langle \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta}^{(0)} | \hat{\Theta}^{(0)} \hat{V}^{\omega}_{\alpha_{1}} \rangle \hat{\Psi}^{(0)}_{0} \rangle \\
+ \left( \frac{1}{\hbar \omega} \right)^{3} \langle \langle \hat{\Psi}^{(0)}_{0} | \hat{\Theta}^{(0)} | \hat{\Theta}^{(0)} \hat{\Theta}^{(0)} \hat{V}^{\omega}_{\alpha_{1}} \rangle \hat{\Psi}^{(0)}_{0} \rangle + \cdots \] 

(2.59)

This expansion can be expressed in a more compact by using the so-called superoperator formalism [4]. The operators \( \hat{\Theta}, \hat{V}^{\omega}_{\alpha_{1}} \) belong then to an infinite dimensional vector space of operators with a binary product defined as

\[ \langle \langle \hat{\Theta}; \hat{V}^{\omega}_{\alpha_{1}} \rangle \rangle = \langle \langle \hat{\Psi}^{(0)}_{0} | [\hat{\Theta}^{(0)} \hat{V}^{\omega}_{\alpha_{1}}] \rangle \hat{\Psi}^{(0)}_{0} \rangle \] 

(2.60)
Operators in this vector space of operators are called superoperators. Commonly only the superoperator Hamiltonian $\hat{H}^{(0)}$ and the superoperator identity operator $\hat{I}$ are used, which are defined as

$$\hat{H}^{(0)} \hat{V}_\omega^{\alpha\ldots} = [\hat{H}^{(0)}, \hat{V}_\omega^{\alpha\ldots}]$$ (2.61)

and

$$\hat{I} \hat{V}_\omega^{\alpha\ldots} = \hat{V}_\omega^{\alpha\ldots}$$ (2.62)

The moment expansion of the polarization propagator becomes then

$$\langle\langle \hat{O}; \hat{V}_\omega^{\alpha\ldots} \rangle\rangle_\omega = \left( \frac{1}{\hbar \omega} \right) \langle \hat{O} | \hat{I} \hat{V}_\omega^{\alpha\ldots} | \Psi_0^{(0)} \rangle + \left( \frac{1}{\hbar \omega} \right)^2 \langle \hat{O} | \hat{H}^{(0)} \hat{V}_\omega^{\alpha\ldots} | \Psi_0^{(0)} \rangle + \left( \frac{1}{\hbar \omega} \right)^3 \langle \hat{O} | \hat{H}^{(0)}^2 \hat{V}_\omega^{\alpha\ldots} | \Psi_0^{(0)} \rangle + \ldots$$ (2.63)

or

$$\langle\langle \hat{O}; \hat{V}_\omega^{\alpha\ldots} \rangle\rangle_\omega = \left( \frac{1}{\hbar \omega} \right) \hat{O}^\dagger + \left( \frac{1}{\hbar \omega} \right)^2 \hat{O}^\dagger \hat{H}^{(0)} + \left( \frac{1}{\hbar \omega} \right)^3 \hat{O}^\dagger \hat{H}^{(0)}^2 + \ldots$$ (2.64)

Finally, defining the superoperator resolvent by the expansion

$$\left( \hbar \omega \hat{I} - \hat{H}^{(0)} \right)^{-1} = \left( \frac{1}{\hbar \omega} \right) \left\{ \hat{I} + \sum_{n=1}^\infty \left( \frac{\hat{H}^{(0)}}{\hbar \omega} \right)^n \right\}$$ (2.65)

the moment expansion of the polarization propagator can be written as

$$\langle\langle \hat{O}; \hat{V}_\omega^{\alpha\ldots} \rangle\rangle_\omega = \left( \hat{O}^\dagger \right) \langle \hat{V}_\omega^{\alpha\ldots} \rangle$$ (2.66)

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 $\hat{h}$ or as row vector $\hat{h}^\dagger$, an exact matrix representation of the polarization propagator is obtained [5]

$$\langle\langle \hat{O}; \hat{V}_\omega^{\alpha\ldots} \rangle\rangle_\omega = \langle \hat{O}^\dagger | (\hbar \omega \hat{I} - \hat{H}^{(0)})^{-1} \hat{V}_\omega^{\alpha\ldots} \rangle$$ (2.67)
Completeness of the set of operators \( \{ h_n \} \) means that operating on \( | \Psi_0^{(0)} \rangle \) all possible excited states \( | \Psi_n^{(0)} \rangle \) of the system must be generated, i.e. \( h_n | \Psi_0^{(0)} \rangle = | \Psi_n^{(0)} \rangle \). This more general expression for the polarization propagator reduces to equation (2.55) if one chooses the operators \( \{ h_n \} \) to be \( \{ | \Psi_n^{(0)} \rangle \langle \Psi_0^{(0)} |, | \Psi_0^{(0)} \rangle \langle \Psi_n^{(0)} | \} \).

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 \( \langle \Psi_0(t) | \hat{\mu}_\alpha \Psi_0(t) \rangle \) in the presence of a monochromatic electromagnetic wave of frequency \( \omega_0 \). Employing the dipole approximation, which implies setting \( \vec{k} \cdot \vec{r} = 0 \) in equation (1.54), the perturbation Hamilton operator for the periodic and spatially uniform electric field of the electromagnetic wave is

\[
\hat{H}^{(1)}(t) = -\hat{O}_E \alpha \dot{E}_\alpha(t) = -\hat{O}_E \alpha \frac{E_{\alpha \omega_0}}{2} (e^{-i\omega_0 t} + e^{i\omega_0 t})
\]  

(2.68)

Comparison with equation (2.49) shows that the Fourier components of the operator and the field are

\[
\hat{V}_{\alpha \omega} = -\hat{O}_E \alpha \\
F(\omega)_{\alpha \omega} = \frac{E_{\alpha \omega_0}}{2} (\delta(\omega - \omega_0) + \delta(\omega + \omega_0))
\]  

(2.69) (2.70)

Insertion of these operators in equation (2.51) yields

\[
\langle \Psi_0(t) | \hat{\mu}_\alpha \hat{\mu}_\beta \Psi_0(t) \rangle = \langle \Psi_0^{(0)} | \hat{O}_E \alpha \hat{O}_E \beta \Psi_0^{(0)} \rangle \\
+ \left( \langle \hat{O}_E \alpha ; \hat{O}_E \beta \rangle_{\omega_0} e^{-i\omega_0 t} + \langle \hat{O}_E \alpha ; -\hat{O}_E \beta \rangle_{-\omega_0} e^{i\omega_0 t} \right) \frac{E_{\alpha \omega_0}}{2} + \cdots
\]  

(2.71)

From the definition of the linear response function in the frequency domain, equation (2.55), it can be seen that for the hermitian and real operators \( \hat{O}_E \alpha \) and \( \hat{O}_E \beta \) the two response functions \( \langle \hat{O}_E \alpha ; \hat{O}_E \beta \rangle_{\omega_0} \) and \( \langle \hat{O}_E \alpha ; -\hat{O}_E \beta \rangle_{-\omega_0} \) become equal. Thus

\[
\langle \Psi_0(t) | \hat{\mu}_\alpha \hat{\mu}_\beta \Psi_0(t) \rangle = \langle \Psi_0^{(0)} | \hat{O}_E \alpha \hat{O}_E \beta \Psi_0^{(0)} \rangle + \langle \hat{O}_E \alpha ; -\hat{O}_E \beta \rangle_{-\omega_0} E_{\alpha \omega_0} \cos(\omega_0 t) + \cdots
\]  

(2.72)

which can be compared with the classical expansion of a time dependent dipole moment in equation (1.55). The frequency dependent polarizability tensor is then identified as

\[
\alpha_{\alpha \beta}(-\omega_0; \omega_0) = -\langle \hat{O}_E \alpha ; \hat{O}_E \beta \rangle_{\omega_0}
\]  

(2.73)

For \( \omega_0 = 0 \) this reduces to the expression obtained by static response theory or Rayleigh-Schrödinger perturbation theory.
2.5 Vibrational Averaging

The expressions for the molecular properties given in chapters 2.2 - 2.4 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. 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.

In the following the static polarizability is used as an example for the discussion of these corrections [6, 7]. A detailed description of the vibrational corrections to hyperpolarizability can be found in the reviews by Bishop [8, 9].

In order to incorporate the effects of nuclear motion one has to start with a Hamiltonian, which includes the terms due to the motion of the nuclei. The corresponding eigenfunctions are the so-called vibronic wavefunctions \( \Phi_{nv} \) and are characterized by the electronic, \( n \), and vibrational, \( v \), quantum numbers. In the presence of a perturbation, \( E_\beta \), the vibronic wavefunction for, e.g., the electronic ground state \( n = 0 \) and an arbitrary vibrational state \( v \) is in first order given as

\[
\Phi_{0v} = \Phi_{0v}^{(0)} + \Phi_{0v}^{(1)} = \Phi_{0v}^{(0)} + \sum_{n\neq 0,v'} | \Phi_{nv'}^{(0)} \rangle \langle \hat{O}^E_{\beta} E_\beta | \Phi_{0v}^{(0)} \rangle \frac{W_{0v} - W_{nv'}}{W_{0v} - W_{nv'}}
\]

Using perturbation theory one obtains then for a static polarizability

\[
\alpha_{\alpha\beta} = -2 \sum_{n\neq 0,v'} \frac{\langle \Phi_{0v}^{(0)} | \hat{O}^E_{\alpha} | \Phi_{nv'}^{(0)} \rangle \langle \Phi_{nv'}^{(0)} | \hat{O}^E_{\beta} | \Phi_{0v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{nv'}^{(0)}}
\]

The summation can be broken in two parts

\[
\alpha_{\alpha\beta}^e = -2 \sum_{n\neq 0,v'} \frac{\langle \Phi_{0v}^{(0)} | \hat{O}^E_{\alpha} | \Phi_{nv'}^{(0)} \rangle \langle \Phi_{nv'}^{(0)} | \hat{O}^E_{\beta} | \Phi_{0v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{nv'}^{(0)}}
\]

\[
\alpha_{\alpha\beta}^v = -2 \sum_{v' \neq v} \frac{\langle \Phi_{0v}^{(0)} | \hat{O}^E_{\alpha} | \Phi_{0v'}^{(0)} \rangle \langle \Phi_{0v'}^{(0)} | \hat{O}^E_{\beta} | \Phi_{0v}^{(0)} \rangle}{W_{0v}^{(0)} - W_{0v'}^{(0)}}
\]

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

Making the following ansatz for the zeroth order vibronic wavefunctions

\[
\Phi_{nv}^{(0)} = \Psi_n^{(0)} \Theta_v^{(0)}
\]
one obtains for the two contributions

\[
\alpha_{\alpha\beta}^e = -2 \sum_{\nu' \neq \nu} \frac{\langle \Psi_0^{(0)} | \hat{O}_\alpha^E | \Psi_n^{(0)} \rangle \langle \Theta_{\nu'}^{(0)} | \hat{O}_\beta^E | \Psi_0^{(0)} \rangle}{W_{0\nu}^{(0)} - W_{n\nu'}^{(0)}}
\]

\[
\alpha_{\alpha\beta}^v = -2 \sum_{\nu' \neq \nu} \frac{\langle \Theta_\nu^{(0)} | \hat{O}_\alpha^E | \Psi_0^{(0)} \rangle \langle \Theta_{\nu'}^{(0)} | \hat{O}_\beta^E | \Psi_0^{(0)} \rangle}{W_{\nu\nu'}^{(0)} - W_{0\nu'}^{(0)}}
\]

where, using equation (2.35), the vibrational polarizability can also be written as

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

In this so-called sum-over-states treatment of the effects of molecular vibration the effects of the perturbation on the electronic and vibrational part of the wavefunction are treated simultaneously, as can be seen from equation (2.74). However, this approach has not been used frequently.

A second approach, in which the effect of the perturbation on the electronic and nuclear motion is treated sequentially is the so-called clamped-nucleus approach has not been used frequently.

It can be derived [7] from an expression for the polarizability obtained by static response theory

\[
\alpha_{\alpha\beta} = \frac{\partial}{\partial E_\beta} \langle \Phi_{0e} | \hat{O}_\alpha^E | \Phi_{0e} \rangle^{(1)}
\]

Expressing the vibronic wavefunction \( \Phi_{0e} \) as a product of an electronic wavefunction

\[
\Psi_0 = \Psi_0^{(0)} + \Psi_0^{(1)} = \Psi_0^{(0)} + \sum_{n \neq 0} | \Psi_n^{(0)} \rangle \frac{\langle \Psi_n^{(0)} | \hat{O}_\beta^E E_\beta | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}}
\]

and a vibrational wavefunction

\[
\Theta_\nu = \Theta_\nu^{(0)} + \Theta_\nu^{(1)} = \Theta_\nu^{(0)} + \sum_{n \neq 0} | \Theta_{\nu'}^{(0)} \rangle \frac{\langle \Theta_{\nu'}^{(0)} | \hat{O}_\beta^E E_\beta | \Theta_\nu^{(0)} \rangle}{W_{\nu\nu'}^{(0)} - W_{\nu'}^{(0)}}
\]

the following expressions for the electronic and vibrational polarizabilities are obtained

\[
\alpha_{\alpha\beta}^e = -2 \langle \Theta_\nu^{(0)} | \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | \hat{O}_\alpha^E | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{O}_\beta^E | \Psi_0^{(0)} \rangle}{W_0^{(0)} - W_n^{(0)}} | \Theta_{\nu'}^{(0)} \rangle
\]

\[
\alpha_{\alpha\beta}^v = -2 \sum_{\nu' \neq \nu} \frac{\langle \Theta_{\nu'}^{(0)} | \langle \Psi_0^{(0)} | \hat{O}_\alpha^E | \Psi_0^{(0)} \rangle | \Theta_{\nu'}^{(0)} \rangle \langle \Theta_{\nu'}^{(0)} | \hat{O}_\beta^E | \Psi_0^{(0)} \rangle | \Theta_{\nu'}^{(0)} \rangle}{W_{\nu\nu'}^{(0)} - W_{\nu\nu'}^{(0)}}
\]
2.5. VIBRATIONAL AVERAGING

where \( W^{(0)}_{0} (\{ \vec{R} \}) \) indicates that the electronic energies are for a given set of nuclear coordinates \( \{ \vec{R} \} \). Although the expression for the vibrational polarizability is the same as the one obtained with the sum-over-states treatment in equation (2.80), the expression for the electronic contribution differs from equation (2.79). The electronic contribution in equation (2.85) is simply the polarizability as given in table 2.1 or equation (2.73) averaged with the vibrational wavefunction \( \Theta^{(0)}_{v} \). However, making the approximations 1) that in equation (2.79) the differences between the vibrational energies are much smaller than the differences between the electronic energies, i.e.

\[
W^{(0)}_{v 0} - W^{(0)}_{n 0} \approx W^{(0)}_{0 0} - W^{(0)}_{n 0} \tag{2.87}
\]

2) that closure is carried out over the vibrational wavefunctions \( \Theta^{(0)}_{v'} \) in equation (2.79), i.e.

\[
1 = \sum_{v'} | \langle \Theta^{(0)}_{v'} | \rangle | \tag{2.88}
\]

one obtains from equation (2.79) an expression

\[
\alpha^{e}_{\alpha \beta} = -2 \sum_{n \neq 0} \frac{\langle \Theta^{(0)}_{v} | \langle \hat{O}^{E} | \Psi^{(0)}_{n} \rangle \langle \Psi^{(0)}_{n} | \hat{O}^{E} | \Psi^{(0)}_{v} \rangle | \Theta^{(0)}_{v} \rangle}{W^{(0)}_{v 0} - W^{(0)}_{n 0}} \tag{2.89}
\]

which is similar to equation (2.85).

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

\[
\left\{ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dR^2} + \frac{J(J+1)}{R^2} \right) + V(R) \right\} | \Theta_{v,J} \rangle = W_{v,J} | \Theta_{v,J} \rangle \tag{2.90}
\]

where \( J \) is the rotational quantum number and \( V(R) \) is the nuclear repulsion term. The vibrational averaging in the clamped-nucleus treatment in equation (2.85) can then be carried out numerically, if one calculates the polarizability as given in table 2.1 or equation (2.73) 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)

\[
\alpha^{e}_{\alpha \beta} = \langle \Theta^{(0)}_{v} | \alpha^{e}_{\alpha \beta}(\{ \vec{R}_e \}) | \Theta^{(0)}_{v} \rangle = \alpha^{e}_{\alpha \beta}(\{ \vec{R}_e \}) + \Delta \alpha^{ZPVC}_{\alpha \beta} \tag{2.91}
\]

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

\[
\alpha^{e}_{\alpha \beta}(\{ \vec{R} \}) = \alpha^{e}_{\alpha \beta}(\{ \vec{R}_e \}) + \sum_a \left( \frac{\partial \alpha^{e}_{\alpha \beta}}{\partial Q_a} \right) Q_a + \frac{1}{2} \sum_{a b} \left( \frac{\partial^2 \alpha^{e}_{\alpha \beta}}{\partial Q_a \partial Q_b} \right) Q_a Q_b + \cdots \tag{2.92}
\]
and the vibrational wavefunctions $\Theta_v^{(0)}$ are found by solving the vibrational Schrödinger equation with the anharmonic potential

$$V(\{\vec{R}\}) = V(\{\vec{R}_e\}) + \frac{1}{2} \sum_a \omega_a^2 Q_a^2 + \frac{1}{6} \sum_{abc} K_{abc} Q_a Q_b Q_c + \cdots \quad (2.93)$$

where $\omega_a$ 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 the basis of the harmonic oscillator wavefunctions $\{\theta_v\}$

$$| \Theta_v^{(0)} \rangle \approx | \theta_v \rangle - \sum_{v' \neq v} | \theta_{v'} \rangle \frac{\langle \theta_{v'} | \frac{1}{6} \sum_{abc} K_{abc} Q_a Q_b Q_c | \theta_v \rangle}{\hbar (\omega_{v'} - \omega_v)} \quad (2.94)$$

Inserting equations (2.94) and (2.92) into equation (2.91) and using the properties of the harmonic oscillator functions, one obtains for the zero-point-vibrational correction in first order

$$\Delta \alpha^{ZPVC}_{\alpha\beta} = -\frac{\hbar}{4} \sum_a \frac{1}{\omega_a^2} \left( \frac{\partial \alpha_{\alpha\beta}}{\partial Q_a} \right) \left( \sum_b \frac{K_{abb}}{\omega_b} \right) + \frac{\hbar}{4} \sum_a \frac{1}{\omega_a} \left( \frac{\partial^2 \alpha_{\alpha\beta}}{\partial Q_a^2} \right) \quad (2.95)$$

where the first term arises because of the anharmonic term in the potential, equation (2.93), and the second term comes from the non-linear term in the expansion of the polarizability, equation (2.92). Equivalent expressions for higher vibrational levels have also been derived [10].
Chapter 3

Ab Initio Methods for the Calculation of Molecular Properties

The \textit{ab initio} methods for the calculation of molecular electromagnetic properties can be categorized according to several criteria. A first being whether the method uses the definition of molecular properties as derivatives of the electronic energy or the definition as derivatives of molecular electromagnetic moments or fields. This is important for some approximate wavefunctions, which do not obey the Hellman-Feynman theorem. 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 $\lambda$ in the Hamiltonian $\hat{H}(\lambda)$ is

$$
\frac{dW(\{C_i(\lambda)\}, \lambda)}{d\lambda} = \frac{\partial W(\{C_i(\lambda)\}, \lambda)}{\partial \lambda} + \sum_i \left( \frac{\partial (W(\{C_i(\lambda)\}, \lambda))}{\partial C_i(\lambda)} \right) \left( \frac{\partial C_i(\lambda)}{\partial \lambda} \right) \quad (3.1)
$$

If the wavefunction is variationally optimized with respect to all wavefunction parameters, \textit{i.e.} $\partial W(\{C_i(\lambda)\}, \lambda)/\partial C_i(\lambda) = 0$, as it is the case for a selfconsistent field (SCF) and multiconfigurational selfconsistent field (MCSCF) wavefunction, the Hellmann-Feynman theorem is obeyed. Configuration interaction (CI) wavefunctions, on the other hand are not variationally optimized with respect to the molecular orbital coefficients. Therefore only in the limit of a full CI wavefunction, where the molecular orbital coefficients are redundant, the Hellmann-Feynman theorem is fulfilled. For non-variational wavefunctions like in Møller-Plesset perturbation theory (MP) and the Coupled-Cluster method (CC) the Hellmann-Feynman theorem does not hold either. In that case the results for a first order property obtained either as derivative of the energy or as expectation value of the corresponding operator do not agree. Consequently also the definition of second and higher order properties as energy derivatives or derivatives of a first order property will not lead to identical results. However, in the normal CC method of Arponen [11] the Hellmann-Feynman
CHAPTER 3. 

AB INITIO METHODS

Theorem is also fulfilled since the energy is defined as an energy functional, which consists of a transition expectation value between the coupled cluster state and a dual bra state and is stationary with respect to the wavefunction parameters.

Secondly one can distinguish between methods described in chapter 3.3, which evaluate properties directly as derivatives of the energy or first order properties in the presence of the perturbation, and those discussed in chapters 3.1 and 3.2, which are based on perturbation theory with a partitioning of the Hamiltonian and a series expansion of the wavefunction. The latter methods can further be classified according to whether the approximations are made to the exact expressions for the molecular properties, which were obtained in chapters 2.2 – 2.4 using the properties of exact solutions of the unperturbed Schrödinger equation, or whether expressions for the molecular properties are derived directly using approximate solutions of the Schrödinger equation. This are described in chapters 3.1 and 3.2, respectively.

Finally not all methods are capable of treating time dependent perturbations and frequency dependent properties can therefore not be calculated by all methods.

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

\[ f(i)\phi_p(i) = \epsilon_p \phi_p(i) \]  

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, whereas the indices of general spatial molecular orbital are \(p, q, r, \ldots\). The Fock operator is defined as

\[ \hat{F} = \sum_i f(i) = \sum_i \left( \hat{h}^{(0)}(i) + \hat{v}^{HF}(i) \right) \]  

were \(\hat{v}^{HF}(i)\) is an effective one-electron potential, called the Hartree-Fock potential. \(\epsilon_p\) is the molecular orbital energy. In the Hartree-Fock-Roothaan method the molecular orbitals are expanded in a basis of one-electron functions, \{\chi_\mu\} with greek indices, called atomic orbitals

\[ \phi_p = \sum_\mu \chi_\mu c_{\mu p} \]  

where \{c_{\mu p}\} are the molecular orbital coefficients. One of the methods for treating the electron correlation missing in the Hartree-Fock approximation is Möller-Plesset perturbation theory. In this method the field-free Hamiltonian \(\hat{H}^{(0)}\) is partitioned in the Fock operator \(\hat{F}\) and the so-called fluctuation potential \(\hat{V}\)

\[ \hat{H}^{(0)} = \hat{F} + \hat{V} \]  

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

\[ | \Psi_0^{(0)} \rangle = N \left( | \Phi_{SCF} \rangle + | \Phi_0^{(1)} \rangle + | \Phi_0^{(2)} \rangle \cdots \right) \]  

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

\[
|\Phi^{(1)}_0\rangle = \sum_{n \neq 0} |\Phi^{(0)}_n\rangle \frac{\langle \Phi^{(0)}_n | \hat{V} | \Phi_{SCF}\rangle}{\langle \Phi_{SCF} | \hat{F} | \Phi_{SCF}\rangle - \langle \Phi^{(0)}_n | \hat{F} | \Phi^{(0)}_n\rangle} (3.7)
\]

consists of determinants which are double excited with respect to \(|\Phi_{SCF}\rangle\)

\[
|\Phi^{(1)}_0\rangle = |DE^{(1)}\rangle = \frac{1}{4} \sum_{ij} \kappa^{ab}_{ij} |\Phi^{ab}_{ij}\rangle (3.8)
\]

where the first order doubles correlation coefficients are given as

\[
\kappa^{ab}_{ij} = \frac{(ai | bj)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} (3.9)
\]

The second order MP correction to the energy is then

\[
W^{(2)} = \frac{1}{2} \sum_{ij} (ia | jb) \left\{4\kappa^{ab}_{ij} - 2\kappa^{ba}_{ji}\right\} (3.10)
\]

The second order MP correction to the wavefunction

\[
|\Phi^{(2)}_0\rangle = \sum_{n \neq 0} |\Phi^{(0)}_n\rangle \left\{\frac{\langle \Phi^{(0)}_n | \hat{V} | \Phi^{(1)}_0\rangle}{\langle \Phi_{SCF} | \hat{F} | \Phi_{SCF}\rangle - \langle \Phi^{(0)}_n | \hat{F} | \Phi^{(0)}_n\rangle} - \langle \Phi^{(0)}_n | \hat{V} | \Phi_{SCF}\rangle \frac{\langle \Phi^{(0)}_n | \Phi^{(1)}_0\rangle}{\langle \Phi_{SCF} | \hat{F} | \Phi_{SCF}\rangle - \langle \Phi^{(0)}_n | \hat{F} | \Phi^{(0)}_n\rangle} \right\} (3.11)
\]

contains single, double, triple and quadruple excited determinants

\[
|\Phi^{(2)}_0\rangle = |SE^{(2)}\rangle + |DE^{(2)}\rangle + |TE^{(2)}\rangle + |QE^{(2)}\rangle (3.12)
\]

with \textit{e.g.}

\[
|SE^{(2)}\rangle = \sum_{ai} \kappa^a_i |\Phi^a_i\rangle (3.13)
\]

where the second order singles correlation coefficients are given as

\[
\kappa^a_i = \frac{1}{\sqrt{2}} \frac{1}{\epsilon_i - \epsilon_a} \left(\sum_{jbc} (ab | jc) \left\{4\kappa^{bc}_{ij} - 2\kappa^{bc}_{ji}\right\} - \sum_{jkb} (ki | jb) \left\{4\kappa^{ba}_{jk} - 2\kappa^{ba}_{kj}\right\}\right) (3.14)
\]

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3.1 Approximations to exact Perturbation Theory Expressions

3.1.1 Ground State Expectation Values

According to equations (2.31) or (2.46) first order properties can be evaluated as ground state expectation values. An alternative expression can be obtained by introducing the one electron density matrix in the basis of the molecular \( \{ \phi_p \} \) or atomic orbitals \( \{ \chi_\mu \} \)

\[
D_{pq} = \int d\vec{r}_1 \, dr'_1 \, d\vec{s}_1 \, ds'_1 \, \phi^*_p(\vec{r}_1) \, \phi_q(\vec{r}'_1) \quad (3.15)
\]

\[
D_{\mu\nu} = \int d\vec{r}_1 \, dr'_1 \, d\vec{s}_1 \, ds'_1 \, \chi^*_\mu(\vec{r}_1) \, \chi_\nu(\vec{r}'_1) \quad (3.16)
\]

where

\[
\gamma(\vec{x}_1, \vec{x}'_1) = N \int d\vec{x}_2 \cdots d\vec{x}_N \psi_0(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) \psi_0^*(\vec{x}'_1, \vec{x}_2, \cdots, \vec{x}_N) \quad (3.17)
\]

and \( \vec{x}_i = \vec{r}_i \vec{s}_i \). The expectation value of an operator \( \hat{O} = \sum_i \hat{o}(i) \) can thus be written as

\[
\langle \psi_0^0 \mid \hat{O} \mid \psi_0^0 \rangle = \sum_{pq} D_{pq} \langle \phi_p \mid \hat{o} \mid \phi_q \rangle = \sum_{\mu\nu} D_{\mu\nu} \langle \chi_\mu \mid \hat{o} \mid \chi_\nu \rangle \quad (3.18)
\]

For a closed shell selfconsistent wavefunction \( | \Phi_{SCF} \rangle \), e.g., the density matrix in the atomic orbital basis and molecular orbital basis are given as

\[
D_{\mu\nu}^{SCF} = 2 \sum_i c^*_\mu c_\nu \quad (3.19)
\]

\[
D_{ij}^{SCF} = 2 \delta_{ij} \quad (3.20)
\]

Using the MP wavefunction, equation (3.6), in equation (3.17) and keeping all terms which are second order in the fluctuation potential a so-called unrelaxed second order correction \( D^{(2)} \) to the density matrix in the molecular orbital basis is obtained

\[
D_{ij}^{(2)} = - \sum_{abk} \kappa^a_{ik} (4 \kappa^b_{jk} - 2 \kappa^b_{kj}) \quad (3.21)
\]

\[
D_{ab}^{(2)} = \sum_{cij} \kappa^a_{ij} (4 \kappa^b_{ij} - 2 \kappa^b_{ji}) \quad (3.22)
\]

\[
D_{ia}^{(2)} = D_{ai}^{(2)} = \sqrt{2} \kappa^a_i \quad (3.23)
\]

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3.1. APPROXIMATIONS TO EXACT PERTURBATION THEORY

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 (2.39) and (2.55). The main task is thus to obtain a set of excitation energies \( W_n^{(0)} - W_0^{(0)} \) and transition moments \( \langle \Psi_0^{(0)} | \hat{O} | \Psi_n^{(0)} \rangle \) with the appropriate operator \( \hat{O} \) or alternatively a ground state wavefunction \( | \Psi_0^{(0)} \rangle \) and a set of excited state wavefunctions \( | \Psi_n^{(0)} \rangle \) 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 \( \langle \Psi_0^{(0)} | \hat{O} | \Psi_n^{(0)} \rangle \) by matrix elements of \( \hat{O} \) in the molecular orbital basis \( \langle \phi_i | \hat{o} | \phi_a \rangle \) gives the uncoupled Hartree-Fock approximation [12], 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. [13]). 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. [14]). 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 (2.67). This equation is exact as long as a complete set of excitation and de-excitation operators \( \{ h_n \} \) is used and the reference state \( | \Psi_0^{(0)} \rangle \) 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 \( | \Psi_0^{(0)} \rangle \). MCSCF and MP perturbation theory wavefunctions are commonly employed as approximate reference states in polarization propagator approximations.

Møller-Plesset Perturbation Theory Polarization Propagator Methods

In the polarization propagator approximations based on Møller-Plesset perturbation theory the reference state is approximated by the MP wavefunction in equation (3.6) and the complete set of operators \( h \) was shown [15] to consist of all possible single excitation and de-excitation \( h_2 = \{ q^\dagger, q \} \), double excitation and de-excitation \( h_4 = \{ q^\dagger q^\dagger, qq \} \) etc. operators with respect to the Hartree-Fock state \( | \Phi_{SCF} \rangle \).
polarization propagator, (2.67), can thus be written as
\[
\langle \langle \hat{O}; \hat{V}^\omega_{\alpha\cdots\alpha} \rangle \rangle^\omega = \left( \begin{array}{c} \langle \Psi_0^{(0)} \mid [\hat{O}, \hat{h}_2] \mid \Psi_0^{(0)} \rangle \\ \langle \Psi_0^{(0)} \mid [\hat{O}, \hat{h}_4] \mid \Psi_0^{(0)} \rangle \\ \vdots \end{array} \right) \times \begin{pmatrix} S_{22}^{[2]} & S_{24}^{[2]} & \cdots \\
 S_{42}^{[2]} & S_{44}^{[2]} & \cdots \\
 \vdots & \vdots & \ddots \end{pmatrix}^{-1} \begin{pmatrix} E_{22}^{[2]} \\ E_{24}^{[2]} \\ \vdots \end{pmatrix} \left( \begin{array}{c} \langle \Psi_0^{(0)} \mid [\hat{h}_1, \hat{V}^\omega_{\alpha\cdots\alpha}] \mid \Psi_0^{(0)} \rangle \\ \langle \Psi_0^{(0)} \mid [\hat{h}_1, \hat{V}^\omega_{\alpha\cdots\alpha}] \mid \Psi_0^{(0)} \rangle \\ \vdots \end{array} \right)
\]
(3.24)

where
\[
S_{ij}^{[2]} = \langle \Psi_0^{(0)} \mid [\hat{h}_i, \hat{h}_j] \mid \Psi_0^{(0)} \rangle
\]
(3.25)
\[
E_{ij}^{[2]} = \langle \Psi_0^{(0)} \mid [\hat{h}_i, [\hat{F} + \hat{V}, \hat{h}_j]] \mid \Psi_0^{(0)} \rangle
\]
(3.26)

A series of approximations of increasing order \( n \) is obtained by requiring that all the matrix elements \( S_{ij}^{[2]} \), \( E_{ij}^{[2]} \) as well as \( \langle \Psi_0^{(0)} \mid [\hat{O}, \hat{h}_1] \mid \Psi_0^{(0)} \rangle \) are evaluated through order \( n \) in the fluctuation potential.

For a first order polarization propagator approximation (FOPPA) it is only necessary to keep \( h_2 \) in the set of operators and the reference state is the Hartree-Fock state. This approximation is better known as time dependent Hartree-Fock approximation (TDHF) [16], see section 3.2.1, or random phase approximation (RPA) [17] 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
\[
\langle \langle \hat{O}; \hat{V}^\omega_{\alpha\cdots\alpha} \rangle \rangle^\omega = \left( \begin{array}{c} \langle \Phi_{SCF} \mid [\hat{O}, \hat{q}] \mid \Phi_{SCF} \rangle \\ \langle \Phi_{SCF} \mid [\hat{O}, \hat{q}] \mid \Phi_{SCF} \rangle \end{array} \right) \begin{pmatrix} X(\omega) \\ Y(\omega) \end{pmatrix}
\]
(3.27)
\[
\begin{pmatrix} X(\omega) \\ Y(\omega) \end{pmatrix} = \begin{pmatrix} \hbar \omega & 1 \\ 1 & -\hbar \omega \end{pmatrix} - \begin{pmatrix} A^{(0,1)} & B^{(1)} \\ B^{(1)} & A^{(0,1)} \end{pmatrix}^{-1} \begin{pmatrix} \langle \Phi_{SCF} \mid q, \hat{V}^\omega_{\alpha\cdots\alpha} \mid \Phi_{SCF} \rangle \\ \langle \Phi_{SCF} \mid q, \hat{V}^\omega_{\alpha\cdots\alpha} \mid \Phi_{SCF} \rangle \end{pmatrix}
\]
(3.28)

where the \( A^{(0,1)} \) and \( B^{(1)} \) matrices are defined as
\[
A^{(0,1)} = \langle \Phi_{SCF} \mid [q, [\hat{F} + \hat{V}, \hat{q}]] \mid \Phi_{SCF} \rangle
\]
(3.29)
\[
B^{(1)} = \langle \Phi_{SCF} \mid [q, [\hat{F} + \hat{V}, \hat{q}]] \mid \Phi_{SCF} \rangle
\]
(3.30)

Based on a partitioned form of the propagator
\[
\langle \langle \hat{O}; \hat{V}^\omega_{\alpha\cdots\alpha} \rangle \rangle^\omega = 
\left( \langle \Psi_0^{(0)} \mid [\hat{O}, \hat{h}_2] \mid \Psi_0^{(0)} \rangle - \langle \Psi_0^{(0)} \mid [\hat{O}, \hat{h}_4] \mid \Psi_0^{(0)} \rangle (h_\omega S_{44}^{[2]} - E_{44}^{[2]})^{-1} (h_\omega S_{44}^{[2]} - E_{44}^{[2]}) \right)
\times \left[ (h_\omega S_{22}^{[2]} - E_{22}^{[2]}) - (h_\omega S_{24}^{[2]} - E_{24}^{[2]}) (h_\omega S_{44}^{[2]} - E_{44}^{[2]})^{-1} (h_\omega S_{44}^{[2]} - E_{44}^{[2]}) \right]^{-1}
\times \left( \langle \Psi_0^{(0)} \mid [\hat{h}_1, \hat{V}^\omega_{\alpha\cdots\alpha}] \mid \Psi_0^{(0)} \rangle - (h_\omega S_{24}^{[2]} - E_{24}^{[2]}) (h_\omega S_{44}^{[2]} - E_{44}^{[2]})^{-1} \langle \Psi_0^{(0)} \mid [\hat{h}_1, \hat{V}^\omega_{\alpha\cdots\alpha}] \mid \Psi_0^{(0)} \rangle \right)
\]
(3.31)
the second order polarization propagator approximation (SOPPA) [18] is historically defined to be second order in the single excitation dominated part. This implies that $E^{[2]}_{22}, S^{[2]}_{22}, \langle \Psi_0^{(0)} | [\hat{h}, \hat{V}_\omega^{\alpha_\cdots}] | \Psi_0^{(0)} \rangle$ and $\langle \Psi_0^{(0)} | \hat{h}_4 | \Psi_0^{(0)} \rangle$ are evaluated through second order, $E^{[2]}_{42}, S^{[2]}_{42}, \langle \Psi_0^{(0)} | [\hat{O}, \hat{h}_4] | \Psi_0^{(0)} \rangle$ and $\langle \Psi_0^{(0)} | \hat{h}_4, \hat{V}_\omega^{\alpha_\cdots} | \Psi_0^{(0)} \rangle$ are evaluated through first order and $E^{[2]}_{44}, S^{[2]}_{44}$ only through zeroth order [19]. An analysis of the matrix elements shows that besides the first order MP wavefunction $| \Phi^{(1)} \rangle$ only the part of the second order MP wavefunction consisting of single excited determinants $| SE^{(2)} \rangle$ is needed.

A complete third order polarization propagator approximation has been derived but only parts have been implemented [20]. However, two other SOPPA like methods have been used widely. Both methods are based on the assumption that replacement 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(CCSSD) - method of Sauer [21] this is done in all matrix elements, whereas in its precursor, the coupled cluster singles and doubles polarization propagator approximation (CCSDPPA) [20], this was not the case.

**Multiconfigurational Polarization Propagator Methods**

In the multiconfigurational polarization propagator approximation of Yeager and Jørgensen [22], normally called multiconfigurational random phase approximation (MCRPA), the set of operators contains state transfer operators $R^\dagger, R$ in addition to the non-redundant single excitation $q^\dagger$ and de-excitation $q$ operators. The state transfer operators are defined as

$$R^\dagger_n = | \Psi_n \rangle \langle \Psi_{MCSCF} |$$

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 (3.24) if one identifies $h_4$ with $\{R^\dagger, R\}$ and $| \Psi_0^{(0)} \rangle$ with $| \Psi_{MCSCF} \rangle$. The MCRPA can also be obtained by application of linear response theory, in section 3.2.2, or of the quasienergy derivative method, in section 3.3.3, to an MCSCF state.

**Reduced Linear Equations**

Common for all propagator methods is the form of the propagator as row “property gradient” vector $\hat{T}(\hat{O})$ times the inverse of a “Hessian” or principal propagator matrix ($\hbar \omega S - E$) times a column “property gradient” vector $\hat{T}(\hat{V}_\omega^{\alpha_\cdots})$.

$$\langle \hat{O}; \hat{V}_\omega^{\alpha_\cdots} \rangle_\omega = \hat{T}(\hat{O})(\hbar \omega S - E)^{-1}\hat{T}(\hat{V}_\omega^{\alpha_\cdots})$$

$$= \hat{T}(\hat{O}) N(\hat{V}_\omega^{\alpha_\cdots})$$

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In actual calculations, however, the inverse of the principal propagator is never evaluated, but a set of coupled linear equations for the response vector \( \mathbf{N}(\hat{V}_\alpha^{\omega\omega}) \)

\[
(\hbar \omega \mathbf{S} - \mathbf{E}) \mathbf{N}(\hat{V}_\alpha^{\omega\omega}) = \mathbf{T}(\hat{V}_\alpha^{\omega\omega})
\]

(3.35)
is solved iteratively. The response vector is thereby expanded in a basis of trial vectors \( \{b_i\} \) [23]

\[
\mathbf{N} = \sum_i b_i c_i
\]

(3.36)

In a given iteration \( n \) the linear equations transformed to the basis of the trial vectors \( \{b_1 \cdots b_n\} \), to the so-called reduced space,

\[
(\hbar \omega \mathbf{S}^R - \mathbf{E}^R) \mathbf{N}^R(\hat{V}_\alpha^{\omega\omega}) = \mathbf{T}^R(\hat{V}_\alpha^{\omega\omega})
\]

(3.37)

are solved by standard techniques. The elements of the solution vector, \( \mathbf{N}^R(\hat{V}_\alpha^{\omega\omega}) \) in the reduced space are the optimal coefficients \( \{c_i\} \) in equation (3.36) for the trial vector \( \mathbf{N}(\hat{V}_\alpha^{i\omega}) \) in iteration \( n \). The elements of the other matrices in the reduced space are defined as

\[
S^R_{ij} = \tilde{b}_i \mathbf{S} \tilde{b}_j
\]

(3.38)

\[
E^R_{ij} = \tilde{b}_i \mathbf{E} \tilde{b}_j
\]

(3.39)

\[
T^R_i(\hat{V}_\alpha^{\omega\omega}) = \tilde{b}_i \mathbf{T}(\hat{V}_\alpha^{\omega\omega})
\]

(3.40)
The iterations are converged if the residual vector, defined as,

\[
\mathbf{R}_n = (\hbar \omega \mathbf{S} - \mathbf{E}) \mathbf{N}_n(\hat{V}_\alpha^{\omega\omega}) - \mathbf{T}(\hat{V}_\alpha^{\omega\omega})
\]

(3.41)
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

\[
b_{n+1} = (\hbar \omega \mathbf{S}^{\text{diag}} - \mathbf{E}^{\text{diag}})^{-1} \mathbf{R}_n
\]

(3.42)

where \( \mathbf{S}^{\text{diag}} \) and \( \mathbf{E}^{\text{diag}} \) are diagonal matrices consisting of the diagonal elements of \( \mathbf{S} \) and \( \mathbf{E} \).

In each iteration one has then to calculate the linear transformation of the new trial vector \( (\hbar \omega \mathbf{S} - \mathbf{E})b_i \) which can be done directly without ever calculating the \( (\hbar \omega \mathbf{S} - \mathbf{E}) \) matrix explicit [24, 25]. 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 [26].

### 3.1.4 Perturbed Electron Propagator Method

The definition of a propagator in equation (2.54) can also be generalized to other types of operators [27]. The electron propagator matrix \( \mathbf{G}(\omega) \) in the frequency domain, \( \text{e.g.,} \), is defined as

\[
\mathbf{G}_{pq}(\omega) = \langle \langle a_p^\dagger; a_q \rangle \rangle_\omega
\]

(3.43)
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 $C$

$$D_{pq} = \frac{1}{2\pi i} \oint_C d\omega \, G_{pq}(\omega) \quad (3.44)$$

First order properties can then be calculated with this one density matrix via equation (3.18).

In addition it is also possible to calculate second and higher order properties using the perturbed electron propagator approach by Pickup [28]. In the presence of a perturbation the electron propagator matrix is changed and can be expanded in powers of the perturbation

$$G(\omega) = G^{(0)}(\omega) + G^{(1)}(\omega) + \cdots \quad (3.45)$$

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

$$D^{(1)}_{pq} = \frac{1}{2\pi i} \oint_C d\omega \, G^{(1)}_{pq}(\omega) \quad (3.46)$$

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

$$\alpha_{\alpha\beta} = \sum_{pq} \langle \phi_p | \hat{E}_\alpha | \phi_q \rangle \, D^{(1)}_{\beta,pq} \quad (3.47)$$

The exact electron propagator matrix can be written as

$$G(\omega) = (\omega 1 - F(D^{HF}) - \Sigma(\omega))^{-1} = (\omega 1 - F(D^{corr}) - M(\omega))^{-1} \quad (3.48)$$

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

$$G^{(0)}(\omega) = \left( \omega 1 - F^{(0)}(D^{corr}) - M^{(0)}(\omega) \right)^{-1} \quad (3.49)$$

$$G^{(1)}(\omega) = G^{(0)}(\omega) \left( F^{(1)}(D^{corr}) - M^{(1)}(\omega) \right) G^{(0)}(\omega) \quad (3.50)$$

However, the Fock matrix depends on the one electron density matrix and one has to iterate on equations (3.46) and (3.50).

Approximations to the electron propagator can obtained using several methods, see e.g. [29]. Setting $M^{(0)}(\omega) = M^{(1)}(\omega) = 0$ and approximating $F^{(0)}(D^{corr})$ 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 [28, 30].

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CHAPTER 3. AB INITIO METHODS

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 [31], second and higher order static properties are obtained by solving the Hartree-Fock equations selfconsistently in the presence of the perturbation. The molecular orbitals \( \{ \phi_i \} \) in the presence of the perturbation, \( e.g. \) an electric field \( E_\beta \), can be expanded in the set of unperturbed molecular orbitals \( \{ \phi^{(0)}_p \} \)

\[
\phi_{\beta,i} = \sum_p \phi^{(0)}_p U_{\beta,pi}
\]  (3.51)

The Fock matrices \( F_{ij} \), orbital energies \( \epsilon_i \) and the coefficients \( U_{pi} \) are then expanded in orders of the perturbation

\[
U_{\beta,pi} = U^{(0)}_{pi} + U^{(1)}_{\beta,pi} E_\beta + \cdots
\]  (3.52)

where \( U^{(0)}_{pi} = \delta_{pi} \). From the first order HF equation an equation for the first order coefficients can be derived

\[
U^{(1)}_{\beta,ai} = - \frac{F^{(1)}_{\beta,ai}}{\epsilon^{(0)}_a - \epsilon^{(0)}_i}
\]  (3.53)

however this equation has to be solved iteratively as the first order Fock matrix depends on \( U^{(1)}_{\beta,ai} \). Evaluation of \( F^{(1)}_{\beta,ai} \) leads to

\[
\sum_{bj} \left( A^{(0,1)}_{ai,bj} \mp B^{(1)}_{ai,bj} \right) U^{(1)}_{\beta,bj} = - \langle \phi_a | \hat{h}^{(1)}_{\beta} | \phi_i \rangle
\]  (3.54)

for real (\( - \)) and purely imaginary (\( + \)) perturbations with the \( A^{(0,1)} \) and \( B^{(1)} \) matrices given in equations (3.29) and (3.30). Comparison with equation (3.28) shows that

\[
U^{(1)}_{\beta} = (X(0) \mp Y(0))
\]  (3.55)

The first order correction to the density matrix is then

\[
D^{(1),SCF}_{\beta,\mu\nu} = 2 \sum_i \left( c^{(1)*}_{\beta,\mu i} c^{(1)*}_{\nu i} + c^{(1)*}_{\mu i} c^{(1)*}_{\beta,\nu i} \right) = 2 \left( U^{(1)*}_{\beta,\mu\nu} + U^{(1)}_{\beta,\nu\mu} \right)
\]  (3.56)

and a static polarizability can be calculated from equation (3.47).

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3.2. PERTURBATION THEORY WITH APPROXIMATE WAVEFUNCTIONS

In the time dependent version of coupled Hartree-Fock theory \[32\] the time dependent molecular orbitals are also expanded in the unperturbed orbitals

\[
\phi_{\beta,i} = \phi_i^{(0)} + \frac{1}{2} \sum_p E_p^\omega \left( U_{\beta,pi}^{(1)}(\omega)e^{i\omega t} + U_{\beta,pi}^{(1)}(-\omega)e^{-i\omega t} \right) \phi_p^{(0)} + \cdots \tag{3.57}
\]

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

\[
\left(f(i) - i\frac{\partial}{\partial t}\right) \phi_p(i) = \epsilon_p \phi_p(i) \tag{3.58}
\]

which can be derived from Frenkel’s variational principle \[33\], equations for the coefficients \( U_{\beta,pi}^{(1)}(\omega) \) and \( U_{\beta,pi}^{(1)}(-\omega) \) can be obtained

\[
\begin{pmatrix}
U_{\beta}^{(1)}(-\omega) \\
U_{\beta}^{(1)}(\omega)
\end{pmatrix} = \begin{pmatrix}
X \\
Y
\end{pmatrix} \tag{3.59}
\]

where \( X \) and \( Y \) are defined in equation (3.28).

3.2.2 Response Theory

Multiconfigurational Response Functions

In the application of response theory to an SCF, \(| \Psi \rangle = | \Phi_{SCF} \rangle\), or MCSCF, \(| \Psi \rangle = | \Psi_{MCSCF} \rangle\), wavefunction, first described by Olsen and Jørgensen \[24\], the time dependent state \(| \Psi_0(t) \rangle\) is usually expressed as

\[
| \Psi_0(t) \rangle = e^{i\kappa(t)}e^{iS(t)} | \Psi \rangle \tag{3.60}
\]

where

\[
\kappa(t) = \sum_\mu \left( \kappa_\mu(t) q_\mu^\dagger + \kappa_\mu^*(t) q_\mu \right) \tag{3.61}
\]

\[
S(t) = \sum_n \left( S_n(t) R_n^\dagger + S_n^*(t) R_n \right) \tag{3.62}
\]

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

\[
\gamma_\mu(t) = \sum_i \gamma_\mu^{(i)}(t) \tag{3.63}
\]

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

\[
\frac{d}{dt} (|\Psi_0(t) \rangle |\hat{O} |\Psi_0(t) \rangle) + i(|\Psi_0(t) \rangle [\hat{O}, \hat{H}^{(0)} + \hat{H}^{(1)}(t)] |\Psi_0(t) \rangle) = 0 \tag{3.64}
\]
Inserting equation (3.60) for $|\Psi_0(t)\rangle$ and separating orders one finds for the first order equation
\[
 i\langle \Psi | [\hat{O}, \kappa(t)]^\dagger | \Psi_0\rangle - \langle \Psi_0 | [[\hat{O}, \hat{H}(0)], \kappa(t) + S(t)] | \Psi_0\rangle = -i\langle \Psi_0 | (\hat{O}, \hat{H}(1)(t)) | \Psi_0\rangle
\] (3.65)

Using the set of operators \{\hat{O}\} for \hat{O} one obtains a linear system of ordinary differential equations
\[
 iS \frac{d}{dt} \gamma^{(1)}(t) - E \gamma^{(1)}(t) = T(\hat{H}(1)(t))
\] (3.66)

which Fourier transformed to the frequency domain yields again the set of coupled linear equations given in equation (3.35) [34].

**Coupled Cluster Response Functions**

Coupled Cluster response functions were derived by Koch and Jørgensen [35] starting from the time dependent transition expectation value of Arponen [11]
\[
\langle \Phi_A(t) | \hat{O} | \Phi_{CC}(t) \rangle
\] (3.67)

where the time dependent coupled cluster state $| \Phi_{CC}(t) \rangle$ and dual or “lambda” state $\langle \Phi_A(t) |$ are defined as
\[
| \Phi_{CC}(t) \rangle = e^{T(t)} | \Phi_{SCF} \rangle
\] (3.68)

\[
\langle \Phi_A(t) | = \langle \Phi_{SCF} | (1 + \Lambda(t))e^{-T(t)}
\] (3.69)

The time dependent cluster operator and \Lambda operator consist of n-tuple excitation, \tau^\dagger_\mu, and de-excitation operators, \tau_\mu, respectively
\[
T(t) = \sum_\mu t_\mu(t) \tau^\dagger_\mu
\] (3.70)

\[
\Lambda(t) = \sum_\mu \lambda_\mu(t) \tau_\mu
\] (3.71)

where \{\tau^\dagger_\mu, \tau_\mu\} is a shorthand notation for single \{q^\dagger_\mu, q_\mu\}, double \{q^\dagger_\mu q^\dagger_\nu, q_\mu q_\nu\}, ... 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
\[
e^{-T(t)}i\frac{d}{dt} | \Phi_{CC}(t) \rangle = e^{-T(t)}\hat{H} | \Phi_{CC}(t) \rangle
\] (3.72)

\[
\left( \frac{d}{dt} \langle \Phi_A(t) | \right) e^{T(t)} = i\langle \Phi_A(t) | \hat{H} e^{T(t)}
\] (3.73)
by projecting them on $\langle \Phi_{SCF} | \tau_\mu \rangle$ and $\tau_\mu | \Phi_{SCF} \rangle$, respectively, yielding systems of ordinary linear differential equations

$$\frac{dt_\mu(t)}{dt} = -i \langle \Phi_{SCF} | \tau_\mu e^{-T(t)} \hat{H} | \Phi_{CC}(t) \rangle \tag{3.74}$$

$$\frac{d\lambda_\mu(t)}{dt} = i \langle \Phi_{A}(t) | [\hat{H}, \tau_\mu] | \Phi_{CC}(t) \rangle \tag{3.75}$$

In the presence of an time dependent perturbation $\hat{H}^{(1)}(t)$, equation (2.48), 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

$$\frac{dt_\mu^{(1)}(t)}{dt} = -i \langle \Phi_{SCF} | \tau_\mu e^{-T} \hat{H}^{(1)}(t) | \Phi_{CC}(t) \rangle + i \langle \Phi_{A}(t) | [\hat{H}^{(0)}, T^{(1)}(t)] | \Phi_{CC}(t) \rangle \tag{3.76}$$

$$\frac{d\lambda_\mu^{(1)}(t)}{dt} = i \langle \Phi_{A}(t) | [[\hat{H}^{(0)}, \tau_\mu], T^{(1)}(t)] + [\hat{H}^{(1)}(t), \tau_\mu] \rangle | \Phi_{CC}(t) \rangle + i \sum_\nu \lambda_\nu^{(1)}(t) A_{\nu\mu} \tag{3.77}$$

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

$$A = \langle \Phi_{SCF} | \tau e^{-T} [\hat{H}^{(0)}, \tau] | \Phi_{CC} \rangle \tag{3.78}$$

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

Equations (3.76) and (3.77) are solved by Fourier transformation of $t_\mu^{(1)}(t)$ and $\lambda_\mu^{(1)}(t)$ to the frequency domain, $X^{(1)}(\omega)$ and $Y^{(1)}(\omega)$, which gives two sets of coupled linear equations

$$X^{(1)}(\omega) = (-A + i\omega \text{ } 1)^{-1} \langle \Phi_{SCF} | \tau e^{-T} \hat{V}_\omega^{\dagger} | \Phi_{CC} \rangle \tag{3.79}$$

$$Y^{(1)}(\omega) = -\langle \Phi_{A} | [\hat{V}_\omega^{\dagger}, \tau^\dagger] | \Phi_{CC} \rangle + F X^{(1)}(\omega) (-A + i\omega \text{ } 1)^{-1} \tag{3.80}$$

where the $F$ matrix is here defined as

$$F = \langle \Phi_{A} | [[\hat{H}^{(0)}, \tau^\dagger], \tau^\dagger] | \Phi_{CC} \rangle \tag{3.81}$$

After insertion of these results for the amplitudes in a perturbation expansion of the time dependent transition expectation value, $\langle \Phi_{A}(t) | \hat{O} | \Phi_{CC}(t) \rangle$, the response functions can be identified by comparison with equation (2.51). The coupled cluster linear response functions is thus given as

$$\langle \langle \hat{O} \rangle \rangle_\omega = Y^{(1)}(\omega) \left( \langle \Phi_{SCF} | \tau \hat{O} | \Phi_{CC} \rangle \right) + \left( \langle \Phi_{A} | [\hat{O}, \tau^\dagger] | \Phi_{CC} \rangle \right) X^{(1)}(\omega) \tag{3.82}$$
3.3 Derivative Methods

3.3.1 The Finite Field Method

The finite field method of Cohen and Rotheaan [36] and Pople, McIver and Ostlund [37] is the numerical evaluation of derivatives of the perturbation dependent electronic energy, of perturbation dependent first or higher order properties, or in general of a perturbed property, $P$. It implies that calculations of $P$ are performed in the presence of the perturbation of varying strength. The desired derivative can then be obtained either by finite differences or by fitting the calculated values of $P$ to a Taylor expansion in the strength of the perturbation.

In a finite field calculation of the static dipole polarizability $\alpha$, e.g., the perturbation operator, $-\hat{O}_E E$, is added to the Hamiltonian, $H^{(0)}$, and the electronic energy or the electronic contribution to the dipole moment is calculated with this Hamilton operator for various finite values of the strength of the electric field $E$. 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 $P$ of 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 [38]. Finite field calculations on $\alpha(-\omega; \omega)$ allow thus the evaluation of $\beta(-\omega; \omega; 0), \gamma(-\omega; \omega, 0, 0)$ and so forth.

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 $P$ which allows for the inclusion of additional one-electron operators in the Hamiltonian, can be used. In addition a program to generate the appropriate one-electron perturbation integrals is needed. The finite field method can thus be applied to whatever level of approximation or correlation treatment one wants and even to approximations, for which a wavefunction or a ground state energy is not defined.

Imaginary perturbation operators, like $\hat{O}^{LI}_\alpha$, $\hat{O}^{LI}_\alpha$, $\hat{O}^{LM}_\alpha K$ and $\hat{O}^{SM}_\alpha K$, 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 [39] and nuclear spin-spin coupling constants [40] have been presented. In this method the sum-over-states contribution to $\sigma^K_{\alpha\beta}$ is evaluated as numerical derivative with respect to $B_\beta$ of the expectation value of $\hat{O}^{lm}_\alpha K$, which is calculated to second order in electron correlation and in the presence of the magnetic induction $B_\beta$. The sum-over-states contributions to the coupling constants $J^{KL}_{\alpha\beta}$ are obtained as numerical derivatives with respect to $m^K_\alpha$ of an expression for the energy, which is second order in electron correlation and first order in $-\left(\hat{O}^{lm\ell}_\alpha + \hat{O}^{sm\ell}_\alpha\right)$ and is calculated in the presence of the perturbation $-\left(\hat{O}^{lm}_\alpha + \hat{O}^{sm}_\alpha\right) m^K_\alpha$. Mixed electric magnetic properties, on the other hand, like nuclear magnetic shielding polarizabilities can be evaluated as numerical...
3.3. DERIVATIVE METHODS

derivatives of electric field dependent nuclear magnetic shielding tensors without complex arithmetic.

Another disadvantage of the method lies in the nature of numerical differentiation. It requires a certain amount of experience, to choose the strength of the perturbation, in our example $E_\alpha$, and for how many values of $E_\alpha$ the property $P$ should be calculated. Also the choice of the finite difference formula or the number of fitting parameters in the expansion of $P$ is not a trivial matter. For higher order properties or multiple perturbations the method becomes cumbersome as 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 [41], 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 in the calculation.

The finite field method has been widely used but nowadays becomes more and more obsolete because of the advances in the analytical derivative methods.

3.3.2 The Analytical Derivative Method

In the analytic derivative method for the calculation of molecular properties the approximate expressions for $P$ in the 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 approximate method, since the expressions for the analytical derivatives have to be derived and implemented first. 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 [42, 43, 44].

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 (2.6), (2.12) and (2.13) with respect to one of the perturbations $E_\alpha$, $B_\alpha$ and $m^K_\alpha$ or in general $F_\alpha$ can be written for most methods as

$$\frac{dW(F_\alpha)}{dF_\alpha} \bigg|_{F_\alpha=0} = \sum_{pq} D_{pq} \langle \phi_p | \frac{\partial \hat{h}^{(1)}(i)}{\partial F_\alpha} | \phi_q \rangle = \sum_{\mu\nu} D_{\mu,\nu} \langle \chi_\mu | \frac{\partial \hat{h}^{(1)}(i)}{\partial F_\alpha} | \chi_\nu \rangle$$ (3.83)

The atomic orbitals $\chi_\mu$ 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 (3.18). However, for non-variational wavefunctions as, e.g. in the case of MP perturbation theory and the CC methods, the
density matrix is not consistent with the definition in equation (3.15) and was therefore also called relaxed or response density matrix [45]. Nevertheless also in coupled cluster theory the Hellmann-Feynman theorem can be fulfilled, when the energy and first order properties are evaluated as the transition expectation values, defined in section 3.2.2 (see e.g. [46])

\[
\left. \frac{d\langle CC | \hat{H}^{(0)} + \hat{H}^{(1)} | CC \rangle}{dF_a} \right|_{F_a=0} = \langle CC | \frac{\partial \hat{H}^{(1)}}{\partial F_a} | CC \rangle
\]

(3.84)

The relaxed density matrix can be decomposed in an SCF and correlation part

\[
D = D^{\text{SCF}} + D^{\text{corr}}
\]

(3.85)

The SCF density is given in equation (3.20) and the correlation part consists of two parts

\[
D^{\text{corr}} = D^{\text{amp.}} + D^{\text{orb.}}
\]

(3.86)

where \( D^{\text{amp.}} \) contains amplitudes or correlation coefficients. \( D^{\text{orb.}} \) arises because of the relaxation of the orbitals for non-variational wavefunctions and is obtained as solution of the so-called Z-vector equations [47]. It has therefore in the molecular orbital basis only non-zero elements in the occupied-virtual and virtual-occupied block.

At the level of second order MP perturbation theory (MP2), e.g., straightforward differentiation of the MP2 energy, equation (3.10), would give

\[
\left. \frac{dW^{(2)}(F_a)}{dF_a} \right|_{F_a=0} = \sum_{ab} D_{ab}^{(2)} \langle \phi_a | \frac{\partial \hat{h}^{(1)}}{\partial F_a} | \phi_b \rangle + \sum_{ij} D_{ij}^{(2)} \langle \phi_i | \frac{\partial \hat{h}^{(1)}}{\partial F_a} | \phi_j \rangle + \sum_{ai} L_{ai}^{(2)} U_{\alpha,ai}^{(1)}
\]

(3.87)

where \( L_{ai}^{(2)} \) is the so-called Lagrangian and \( U_{ai}^{(1)} \) are the solutions of the coupled Hartree-Fock in equation (3.54). 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 [47], with the Lagrangian as right hand side

\[
\sum_{bj} \left( A_{ai,bj}^{(0,1)} - B_{ai,bj}^{(1)} \right) Z_{bj} = L_{ai}^{(2)}
\]

(3.88)

The last term in equation (3.87) can then be written as

\[
\sum_{ai} L_{ai}^{(2)} U_{\alpha,ai}^{(1)} = \sum_{ai} Z_{ai} \langle \phi_a | \frac{\partial \hat{h}^{(1)}}{\partial F_a} | \phi_i \rangle = \sum_{ai} D_{ai}^{(2)} \langle \phi_a | \frac{\partial \hat{h}^{(1)}}{\partial F_a} | \phi_i \rangle
\]

identifying the occupied-virtual and virtual-orbital blocks \( D_{ai} \) and \( D_{ia} \) of the relaxed density matrix as the Z vector. It is thus these occupied-virtual and virtual-orbital
blocks which differ between a density matrix consistent through second order, equations (3.21) - (3.23), and the MP2 relaxed density matrix.

The second derivative of the energy can be written as

$$\frac{d^2 W(F_{\beta}, F_{\alpha})}{dF_{\alpha}dF_{\beta}} \bigg|_{F_{\alpha}=F_{\beta}=0} = \sum_{\mu \nu} D_{\mu\nu} \frac{\partial^2 \langle \chi_\mu | \hat{h}_1(i) | \chi_\nu \rangle}{\partial F_{\beta} \partial F_{\alpha}} + \sum_{\mu \nu} D^{(1)}_{\beta,\mu\nu} \frac{\partial \langle \chi_\mu | \hat{h}_1(i) | \chi_\nu \rangle}{\partial F_{\alpha}}$$

(3.90)

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

$$D^{(1)}_{\beta,\mu\nu} = \frac{\partial D_{\mu\nu}}{\partial F_{\beta}} = \sum_{pq} c^*_{\mu p} \frac{\partial D_{pq}}{\partial F_{\beta}} c_{\nu q} + \sum_{pq} D_{pq} \left( \frac{\partial c^*_{\mu p}}{\partial F_{\beta}} c_{\nu q} + c^*_{\mu p} \frac{\partial c_{\nu q}}{\partial F_{\beta}} \right)$$

(3.91)

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. At the SCF level the first order density matrix was given in equation (3.56). 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. [42, 43, 44, 50].

### 3.3.3 Time Dependent Analytical Derivatives

The analytical energy derivative method has recently be extended to the case of time-dependent perturbations in the pseudo-energy derivative method of Rice and Handy [51] and in the quasienergy derivative method of Sasagane, Aiga and Itoh [52]. Both methods define the frequency dependent properties as derivatives of the quasienergy, as defined by Löwdin and Mukherjee [53] or Kutzelnigg [54]

$$\tilde{W}(t) = \langle \Psi(t) | \hat{H}^{(0)} + \hat{H}^{(1)}(t) - i \frac{\partial}{\partial t} | \Psi(t) \rangle$$

(3.92)

but in the pseudo-energy derivative method (PED) the frequency dependent polarizability, e.g., is defined as

$$\alpha_{\alpha\beta}(-\omega; \omega) = -\frac{\partial^2 \tilde{W}(t)}{\partial E_\beta^0 \partial E_\alpha^0} \bigg|_{E=0} = -\frac{\partial^2 \tilde{W}(t)}{\partial E_\alpha^0 \partial E_\beta^0} \bigg|_{E=0}$$

(3.93)
where as in the quasienergy derivative method (QED) it is defined as
\[
\alpha_{\alpha\beta}(-\omega;\omega) = -\left. \frac{\partial^2 \tilde{W}(t)}{\partial E^{-\omega}_\alpha \partial E^\omega_\beta} \right|_{E=0} \tag{3.94}
\]
PED \[51, 55\] and QED \[56\] expressions for the frequency dependent polarizability and first hyperpolarizability at the SCF and MP2 level have been derived, whereas QED expressions were also presented at the coupled cluster level \[57\] and QED expressions for even second or third hyperpolarizabilities were derived for SCF, MCSCF, full and truncated CI wavefunctions \[52\]. 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
\[
\hat{H}^{(0)} + \hat{H}^{(1)}(t) - i \frac{\partial}{\partial t} = \hat{F} - i \frac{\partial}{\partial t} + \hat{V} \tag{3.95}
\]
The PED method starts then from the usual expression for the MP2 closed shell energy, in which the expansion, equation (3.57), of the molecular orbitals in the time dependent fields is inserted. In addition the condition
\[
\langle \Psi(t) | \frac{\partial \Psi(t)}{\partial E^\alpha_\alpha} \rangle \tag{3.96}
\]
has to be fulfilled for the first order MP wavefunction
\[
| \Psi(t) \rangle = | \Phi_{SCF}(t) \rangle + | \Phi^{(1)}(t) \rangle \tag{3.97}
\]
In the QED method, on the other hand, the derivatives are taken of a MP2 quasienergy Lagrangian, which is variational in the TDHF coefficients, equation (3.59), first order MP2 amplitudes as well as in Lagrangian multipliers for the TDHF coefficients and first order MP2 amplitudes. A constraint like equation (3.96) is not necessary in the PED method as a result of the fact that the second derivative is with respect to $E^{-\omega}_\alpha$. The TDHF coefficients have to be obtained by solving the TDHF equations, equation (3.59), 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 other differences between the PED and QED method at the MP2 level are that in the PED method the polarizability tensor is not symmetric and that the PED expression contains Hartree-Fock orbital energy differences as poles whereas the QED method has the TDHF poles.
Chapter 4

Exercises

4.1 Exercises to Chapter 2.2

1) Derive the expression for the third order energy correction in Rayleigh-Schrödinger perturbation theory (2.2).

2) The diamagnetic contributions to the magnetizability, nuclear magnetic shielding and indirect nuclear spin-spin coupling tensors can also be written in the following way as a sum-over-states

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

(4.1)

where

<table>
<thead>
<tr>
<th>Table 4.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P )</td>
</tr>
<tr>
<td>( \xi_{\alpha\beta} (\hat{R}_{GO}) )</td>
</tr>
<tr>
<td>( \sigma_{\alpha\beta}^{K,el} (\hat{R}_{GO}) )</td>
</tr>
<tr>
<td>( K_{\alpha\beta}^{K,L,el} )</td>
</tr>
</tbody>
</table>

51
Hint:

- Try to derive the usual ground state average value expression from the sum-over-states expression above.
- Recall the commutator relation 
  \[ [\hat{r}, \hat{H}^{(0)}] = \frac{i\hbar}{m_e} \hat{p} \]  
  (4.2)
- Recall that the set of excited states \( \Psi_n^{(0)} \) is complete, i.e.
  \[ \sum_n |\Psi_n^{(0)}\rangle \langle \Psi_n^{(0)}| = 1 \]  
  (4.3)

3) 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 \( \hat{R}_{GO} \) of the vector potential \( \hat{A}(\hat{r}_i) \), equation (2.7), for the magnetic induction.

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

Hint:

- Move the gauge origin from \( \hat{R}_{GO} \) to \( \hat{R}_{GO} + \hat{D} \) and show that the terms depending on \( \hat{D} \) cancel.
- Recall the commutator relation 
  \[ [\hat{r}, \hat{H}^{(0)}] = \frac{i\hbar}{m_e} \hat{p} \]  
  (4.4)
- Recall that the set of excited states \( \Psi_n^{(0)} \) is complete, i.e.
  \[ \sum_n |\Psi_n^{(0)}\rangle \langle \Psi_n^{(0)}| = 1 \]  
  (4.5)
4.2 Exercises to Chapter 2.4

1) Derive the expression for the polarization propagator in the frequency domain, equation (2.55), from the expression in the time domain, equation (2.54).

2) Derive the equation of motion for the polarization propagator, equation (2.58), from equation (2.54).

3) Derive the inner projection of the superoperator resolvent

\[
\left(\frac{\hbar \omega \hat{T} - \hat{H}^{(0)}}{\hat{H}^{(0)}}\right)^{-1} = |\hat{h}(h)| |(\hbar \omega \hat{T} - \hat{H}^{(0)}) | \hat{h})^{-1}(h)|
\]  

(4.6)

Hint:
- The set of operators $\hat{h}$ is complete i.e.

\[
\hat{T} = |\hat{h}(h)| \hat{h})^{-1}(h)|
\]  

(4.7)

4) Derive equation (2.55) from equation (2.67) using that the operators $\{h_n\}$ are $\left\{ |\Psi_n^{(0)}\rangle \langle \Psi_n^{(0)}|, |\Psi_n^{(0)}\rangle \langle \Psi_n^{(0)}| \right\}$.

4.3 Exercises to Chapter 2.5

1) Derive the expression for the zero point vibrational correction (ZPVC) in equation (2.95). Hint:
- Use that the multiple harmonic oscillator wavefunctions $|\theta_v\rangle$ are products of single harmonic oscillator wavefunctions $|v_i\rangle$ for each mode $i$ and the following expectation values of the normal coordinates

\[
\langle v | Q_a | v' \rangle = 0 \text{ if } v' \neq v \pm 1 
\]  

(4.8)

\[
\langle v | Q_a | v + 1 \rangle = \sqrt{\frac{\hbar}{2\omega_a}}(v + 1) 
\]  

(4.9)

\[
\langle v | Q_a Q_a | v \rangle = \frac{\hbar}{\omega_a}(v + \frac{1}{2}) 
\]  

(4.10)

4.4 Exercises to Chapter 3

1) Derive the coupled Hartree-Fock equation (3.53).
4.5 Computational Exercises using the DALTON Program Package

In this exercise we want to investigate the effect of electron correlation and nuclear motion on the results for the static polarizability, nuclear magnetic shielding constant and indirect nuclear spin-spin coupling constants of H$_2$O.

The effect of static correlation is investigated by performing uncorrelated calculations with the random phase approximation (RPA) and correlated calculations with its multiconfigurational generalization (MCRPA). In the language of response theory this would be linear response calculations with an SCF and a MCSCF wavefunction.

As MCSCF wavefunction we want to use a so-called complete active space (CASSCF) wavefunction, where we keep the core 1s orbital of oxygen inactive/frozen and include all occupied valence orbitals in the active space. In addition we include an unoccupied orbital of the same symmetry for each occupied valence orbital in the active space.

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

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

(4.11)

In this approximation the zero point vibrational correction (ZPVC) to a property $P$ of H$_2$O is obtained as

\[
\Delta P^{ZPV C} = 0.023842 \left( \frac{\partial P}{\partial S_1} \right) + 0.002295 \left( \frac{\partial^2 P}{\partial S_1^2} \right)
\]  

(4.12)

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

\[
\left( \frac{\partial P}{\partial S_1} \right) = \frac{P(+S_1) - P(-S_1)}{2S_1}
\]  

(4.13)

\[
\left( \frac{\partial^2 P}{\partial S_1^2} \right) = \frac{P(+S_1) + P(-S_1) - 2P(eq)}{S_1^2}
\]  

(4.14)

The equilibrium geometry of H$_2$O is $R_{OH} = 0.95843 \text Å$, $\angle_{HOH} = 104.45^\circ$. For the symmetric stretch mode $S_1$ we use one pair of values from $\{ \pm 0.025 \text Å, \pm 0.05 \text Å, \pm 0.075 \text Å, \pm 0.1 \text Å \}$.

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

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