Higher-order SCF response functions in a quasi-energy formulation

Andreas J. Thorvaldsen

A dissertation for the degree of Philosophiae Doctor

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Author:
Andreas Johan Thorvaldsen

Address:
Centre for Theoretical and Computational Chemistry
Department of Chemistry
University of Tromsø
NO-9037 TROMSØ
NORWAY

E-mail address:
Andreas.Thorvaldsen@chem.uit.no

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Andreas J. Thorvaldsen
Abstract

This thesis is concerned with computer modelling of molecules interacting with electromagnetic radiation, for applications in spectroscopy. *Response theory* is used, in which time-dependent perturbation theory applied to the ground state permits the study of both ground and excited states. For the class of *self-consistent field* (SCF) electronic structure models, which includes Hartree-Fock- and all Kohn-Sham DFT models, a full hierarchy of new formulas for *response functions* have been derived. Although there are several equivalent formulas for a given response function, typically a specific one is preferable due to computational considerations.

The derived formulas are expressed in terms of the atomic orbital (AO) *density matrix*, and valid also with time- and perturbation dependent AOs, such as the magnetic field-dependent *London* or *gauge-including* AOs, which are employed to obtain improved basis set convergence and gauge-origin independent results. The density matrix has an advantage over the more common molecular orbital coefficient matrix (MO) parameterization in that it decays rapidly with the distance between atoms (except in directions of conduction). For large molecules one may therefore *truncate* the density matrix and treat it as *sparse*. Although this is not presently utilized in our implementation, it is expected to lead to great computational savings.

To resolve any ambiguity in the definition of response theory, we formulate it by applying perturbation theory to Floquet theory, which is a quantum-mechanical theory that includes so-called semi-classical radiation, by which both stimulated and spontaneous emission and absorption can be predicted. The central quantity in Floquet theory is the *quasi-energy*, and this is therefore the 'quasi-energy formalism' of response theory.

The DALTON quantum chemistry program has since long been the leading software for computing molecular properties. Using the program structures already present in the code, such as integrals and integral derivatives, in addition to recently implemented SCF and SCF-response program modules (the 'linsca' development branch), we have implemented several new response
functions, relevant to spectroscopies such as Cotton-Mouton, coherent anti-Stokes Raman scattering (CARS), and electric-field-gradient induced birefringence (EFGB).
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Chapter 1

Introduction

It was unexplained observations in spectroscopy that led to the advent of quantum mechanics in the mid 1920s\(^1\). The radiation emitted by hot gases showed sharp peaks at certain wavelengths, which could not be predicted with existing theories. The two equivalent theories of quantum mechanics proposed by Heisenberg and Schrödinger\(^2\) explained the peaks as arising when the molecule jumps between two of its eigenstates, with the wavelength of the peak determined by the difference between the two eigenenergies, and the intensity of the peaks by the populations of the eigenstates together with the transition dipole moment.

However, both the spectra themselves and the Schrödinger equation, which must be solved in order to predict spectra, are vastly complex, as expressed by another pioneer, Dirac\(^3\):

\[
\text{The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely unknown, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.}
\]

In the early days of computational (theoretical) chemistry, calculations were

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carried out by hand (pencil and paper)\textsuperscript{4,5} or by mechanical calculators. With the invention of the digital computer, computational chemistry soon became one of its main tasks, and has continued to be so. But still today, after 80 years of knowing the theoretical foundation and many billion-fold increases in computing power, there is still a considerable gap between the accuracy delivered by computation, and that of the experiments conducted in chemical laboratories\textsuperscript{6}. Thus, at present it seems Dirac was right.

Although computation has yet to replicate experiment, it already serves well to complement, estimate or preview experiment, as, for instance, in the pharmaceutical industry. Most of the efforts of computational (and theoretical) chemists, and their computers, are put into solving the \textit{time-independent} Schrödinger equation (SE): Molecular geometries, reaction energies, reaction barriers, electron affinities, ionization energies, dissociation energies, \textit{etc}. All these tasks consist of finding either just one, or a few solutions of the SE. The prediction of electromagnetic spectra, however, requires the solution of the \textit{time-dependent} Schrödinger equation (TDSE). Fortunately, only a slight adaptation of the methods used to solve the SE are needed in order for their application to the TDSE. Moreover, the error inherited from the underlying SE method will typically dominate those introduced by the approximations to the TDSE. Therefore, computational spectroscopy, the topic of this thesis, is mainly concerned with finding the right adaptations for a specific class of SE models, and interpreting the computed results in relation to experimental observations.

The rest of this thesis is organized as follows: Chapter 2 presents the fundamental equation which governs molecular quantum mechanics, namely the Schrödinger equation, together with the Born-Oppenheimer and self-consistent-field approximations applied to it. In Chapter 3, molecular properties and spectroscopy are presented in a quasi-classical formulation known as Floquet theory, where the electrons and nuclei obey quantum mechanics, whereas the external electromagnetic field obeys the classical Maxwell equations. Response theory is then formulated by applying (Rayleigh-Schrödinger) perturbation theory to Floquet theory. Finally, Chapter 4 summarizes the results in this thesis, as well as gives some remarks on future developments and applications.


\textsuperscript{6}That is, by equally ‘affordable’ computers and laboratory equipment.
Chapter 2

Quantum mechanics

2.1 Schrödinger equation

In quantum mechanics, a system (molecule) consisting of $N$ particles (electrons and nuclei) is described by a \textit{wavefunction} $\psi(r_1, r_2 \ldots r_N)$, a complex-valued function of the set of particle coordinates\footnote{Particles have an additional \textit{spin} coordinate which is 'hidden' in $r_2$ here.} $r_1, r_2 \ldots r_N$

$$\psi(r_1, r_2 \ldots r_N) \in \mathbb{C}. \quad (2.1)$$

In the so-called 'Copenhagen interpretation' of the wavefunction, the \textit{probability} $P$ of 'finding' all particles within the range $\delta$ of the positions $t_1, t_2 \ldots t_N$ is the integral of the square absolute value of the wavefunction over the corresponding $3N$-dimensional volume

$$P = \int \limits_{\|r_1 - t_1\| < \delta} \int \limits_{\|r_2 - t_2\| < \delta} \ldots \int \limits_{\|r_N - t_N\| < \delta} |\psi|^2 \, d\mathbf{r}_1 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N. \quad (2.2)$$

Thus $|\psi|^2 = \psi^* \psi$ is the probability density of the positions of the particles. Since all the particles must be somewhere in space, the corresponding probability $P$ for $\delta = \infty$ must be 1 (which means 100%)

$$1 = \int \int \ldots \int \psi^* \psi \, d\mathbf{r}_1 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N = \langle \psi | \psi \rangle, \quad (2.3)$$

which is called \textit{normalization} of the wavefunction $\psi$. The 'bra-ket' $\langle \ldots | \ldots \rangle$ is a short-hand notation for such integrals over all coordinates\footnote{More precisely, rather than an integral, it is an \textit{average} over the 'center-of-mass coordinate'}. Additionally, the wavefunction should fulfill so-called spin-statistics: When identical
fermions (nuclei with an odd number of nucleons and electrons) are interchanged (swap coordinates), the wavefunction should change sign. This is the Pauli exclusion principle. Moreover, when identical bosons (nuclei with an even number of nucleons) are interchanged, the wavefunction should not change.

The time evolution of the molecule (its wavefunction) is determined by the time-dependent Schrödinger equation, which is a linear differential equation

$$\hat{H}\psi = i\frac{d}{dt}\psi, \quad (2.4)$$

where the differential operator $\hat{H}$ is the molecule’s Hamiltonian. The Hamiltonian consists of a kinetic energy operator $\hat{T}_p$ for each particle, and a potential energy operator $\hat{V}_{pq}$ for each (distinct) pair of particles. Ignoring interactions due to particle spin, the kinetic- and potential-energy operators are given by the Laplace operator and Coulomb potential

$$\hat{H} = \sum_p \hat{T}_p + \sum_{p>q} \hat{V}_{pq}, \quad (2.5)$$

$$\hat{T}_p = -\frac{1}{2m_p} \nabla^2_p = -\frac{1}{2m_p} \left( \frac{\partial^2}{\partial x_p^2} + \frac{\partial^2}{\partial y_p^2} + \frac{\partial^2}{\partial z_p^2} \right), \quad (2.6)$$

$$\hat{V}_{pq} = \frac{q_p q_q}{r_{pq}} = \frac{q_p q_q}{\|\mathbf{r}_p - \mathbf{r}_q\|} = \frac{q_p q_q}{\sqrt{(x_p - x_q)^2 + (y_p - y_q)^2 + (z_p - z_q)^2}}, \quad (2.7)$$

where atomic units have been used, and $m_p$ are the particles’ masses and $q_p$ the charges. Note that the Coulomb potential between particles of opposite charge is attractive ($q_p q_q$ negative), while it is repulsive ($q_p q_q$ positive) between those of same charge. The kinetic energy is always positive.

If the wavefunction $\psi$ is an eigenfunction (eigenstate) of the Hamiltonian with eigenvalue $E$ (the eigenenergy), it is a stationary state, as $e^{-iE_t}\psi$ solves the time-dependent Schrödinger equation

$$\hat{H}\psi = E\psi \Rightarrow \hat{H}(e^{-iE_t}\psi) = i\frac{d}{dt}(e^{-iE_t}\psi), \quad (2.8)$$

and the phase factor $e^{-iE_t}$ cancels when computing the square absolute value $|e^{-iE_t}\psi|^2$, leaving the interpretation (probabilities $P$ above) of the wavefunction constant in time (stationary). The eigenstates $\psi$ fulfill the variation principle, which states that expectation value of the Hamiltonian $\langle \psi|\hat{H}|\psi \rangle$ is stationary with respect to variations in $\psi$. One may therefore search for the ground state, the eigenstate with lowest $E$, by minimizing this expectation value.
2.2 Born-Oppenheimer approximation

The nuclei are the heaviest particles in a molecule; the lightest nucleus, the proton $^1\text{H}$ is $\approx 1836$ times as heavy as an electron, while the most abundant carbon nucleus $^{12}\text{C}$ is $\approx 21863$ times as heavy. Since these large masses appear in the denominator in the kinetic energy operator in Eq. 2.6, nuclei will have little kinetic energy relative to electrons. In the Born-Oppenheimer approximation$^3$, the nuclear kinetic energy operators $\hat{T}_n$ are at first separated from the electronic Hamiltonian $\hat{H}^{\text{el}}$, which then consists of zero-electron, 1-electron and 2-electron parts ($n, m$ denoting nuclei, $e, f$ electrons)

$$\hat{H}^{\text{tot}} = \sum_n \hat{T}_n + \hat{H}^{\text{el}}$$

(2.9)

$$\hat{H}^{\text{el}} = \sum_{n>m} \hat{V}_{nm} = \hbar_{\text{nuc}},$$

(2.10)

$$+ \sum_e \left( \hat{T}_e + \sum_n \hat{V}_{en} \right) = \hat{h}_e,$$

(2.11)

$$+ \sum_{e>f} \hat{V}_{ef} = \hat{g}_e,$$

(2.12)

where the nuclear coordinates $\mathbf{r}_n$ enter $\hbar_{\text{nuc}}$ and $\hat{h}_e$ as parameters. The electronic Schrödinger equation is then solved for all electronic states ($k$)

$$\hat{H}^{\text{el}} \psi^{\text{el}}_k(\mathbf{r}_e; \mathbf{r}_n) = E^{\text{el}}_k(\mathbf{r}_n) \psi^{\text{el}}_k(\mathbf{r}_e; \mathbf{r}_n), \quad k = 0, 1 \ldots \infty, \quad \text{(2.13)}$$

each depending parametrically$^4$ on $\mathbf{r}_n$. The solutions $E^{\text{el}}_k(\mathbf{r}_n)$ are called ‘potential energy surfaces’ (PES), and the ‘equilibrium geometry’ is defined as the configuration of $\mathbf{r}_n$ that gives the lowest electronic energy on the ground-state PES.

In a second step, the complete Schrödinger equation is solved with an expansion over the electronic solutions $\psi^{\text{el}}_k$

$$\psi^{\text{tot}}(\mathbf{r}_n, \mathbf{r}_e) = \sum_k \psi^{\text{nuc}}_k(\mathbf{r}_n) \psi^{\text{el}}_k(\mathbf{r}_e; \mathbf{r}_n), \quad \hat{H}^{\text{tot}} \psi^{\text{tot}} = E^{\text{tot}} \psi^{\text{tot}}, \quad \text{(2.14)}$$

where the $\psi^{\text{nuc}}_k$ are the coefficients and the $\psi^{\text{el}}_k$ the basis of the expansion. Since the $\psi^{\text{el}}_k$ are eigenstates of $\hat{H}^{\text{el}}$ and orthogonal (for all $\mathbf{r}_n$), Eq. 2.14 leads


$^4$This is a differential equation in $\mathbf{r}_e$, but an ordinary (parametric) equation in $\mathbf{r}_n$. 
to an infinite set of coupled Schrödinger equations

\[
\sum_n \hat{T}_n + E_k^{\text{cl}}(\mathbf{r}_n) \psi_k^{\text{mc}}(\mathbf{r}_n) = E_k^{\text{tot}} \psi_k^{\text{mc}}(\mathbf{r}_n)
\]  \hspace{1cm} (2.15)

where the potential energy surfaces \( E_k^{\text{cl}}(\mathbf{r}_n) \) have the role of potential operators (hence the name).

Although the equation set Eq. 2.15 is no less complicated than the original Schrödinger equation Eq. 2.4, it can be truncated to a good approximation, both in the number of PESs included, and in the range and precision of each PES. The approximations range from the simplest, which is to 'clamp' the nuclei in the equilibrium geometry (one PES, one \( \mathbf{r}_n \)); to the harmonic, in which the ground state PES is approximated to second order about a point \( \mathbf{r}_n \); to more complicated approximations of several PESs etc.

### 2.3 Self-consistent field approximation

Even in the crudest Born-Oppenheimer approximation, the so-called clamped nucleus approximation, in which only one geometry \( \mathbf{r}_n \) on one PES is sought, an \( N \)-electron Schrödinger equation is still too difficult to solve. In the self-consistent field (SCF) approximation, this is tackled by writing the wave function as a Slater determinant, an anti-symmetrized product of \( N \) orthonormal orbitals \( \phi_1, \phi_2 \ldots \phi_N \) (1-electron wavefunctions)

\[
\psi(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\
\phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N)
\end{vmatrix}.
\]  \hspace{1cm} (2.16)

A matrix determinant is the sum of all possible products of one term from each row and column, with sign + or − depending on whether it is an even or odd permutation. This ensures that the wavefunction switches sign when two electrons are interchanged, as required by the Pauli principle. Moreover, since the orbitals are orthonormal, all the \( N! \) terms in the determinant are also orthonormal, and the factor \( 1/\sqrt{N!} \) gives a normalized \( \psi \). The SCF class of models have in common that they attempt to solve an \( N \)-electron Schrödinger equation (Eq. 2.8) by solving coupled 1-electron Schrödinger equations. The term 'self-consistent' is derived from the coupling between the 1-electron Hamiltonian, called the Fock operator, and the solutions (orbitals).
2.3 Self-consistent field approximation

Applying the variation principle to the Slater determinant, one obtains the Hartree-Fock model\textsuperscript{5}, which is the most basic SCF model. Although derived on a different basis, Kohn-Sham density functional theory\textsuperscript{6} models are a broad class of SCF models, and thus share the main characteristics with Hartree-Fock.

2.3.1 Hartree-Fock

Inserting the Slater determinant Eq. 2.16 into the expression for the energy expectation value \( E = \langle \psi | H | \psi \rangle \), it is reduced to

\[
E = \frac{h_{\text{nuc}}}{\mu} + \sum_k \left< \phi_k \right| \frac{-\frac{1}{2} \nabla^2 - \sum_n \frac{q_n}{|r - r_n|}}{\phi_k} \right>
\]

\[
+ \sum_{j > k} \int \int \phi_j^*(r_1) \phi_k^*(r_2) \frac{1}{r_{12}} \left[ \phi_j(r_1) \phi_k(r_2) - \phi_k(r_1) \phi_j(r_2) \right] dr_1 dr_2,
\]

where the nuclear repulsion \( h_{\text{nuc}} \) is given by Eq. 2.10. Since the diagonal terms \( j = k \) in the second summation will cancel, it can be rewritten as

\[
\frac{1}{2} \sum_{j < k} \int \int \phi_j^*(r_1) \phi_k^*(r_2) \frac{1}{r_{12}} \left[ \phi_j(r_1) \phi_k(r_2) - \phi_k(r_1) \phi_j(r_2) \right] dr_1 dr_2,
\]

where the contributions from the first term in the bracket are called the Coulomb repulsion, and those from the second term the exchange interaction. Expanding the orbitals in a basis of atomic orbitals\textsuperscript{7} (AOs) \( \chi_\mu(r) \)

\[
\phi_\mu(r) = \sum_\mu \chi_\mu(r) C_{\mu k},
\]

the energy can be written in matrix form in terms of the orbital coefficient matrix \( C \) as

\[
E = h_{\text{nuc}} + \operatorname{Tr} C^\dagger HC + \frac{1}{2} \operatorname{Tr} C^\dagger G(CC^\dagger) C \]

\[
= h_{\text{nuc}} + \operatorname{Tr} HD + \frac{1}{2} \operatorname{Tr} G(D)D,
\]

where \( \operatorname{Tr} \) denotes matrix trace, and \( \ldots ^\dagger \) the complex-conjugated matrix transpose. Using the invariance of the trace under cyclic permutations of a matrix


\textsuperscript{7}Commonly nucleus-centered Gaussian-type functions: \( x^k y^l z^m e^{-\xi r^2} \)
product, the density matrix $D = CC^\dagger$ has been introduced. The 1- and 2-electron integral matrices $H$ and $G(D)$ contains the integrals of the operators $\hat{h}$ and $\hat{g}$, respectively, over the AO basis $\chi_\mu$

$$H_{\mu\nu} = \langle \chi_\mu | \hat{h} | \chi_\nu \rangle = \langle \chi_\mu | -\frac{1}{2}\nabla^2 - \sum_n \frac{q_n}{|r_n - r_n|} | \chi_\nu \rangle, \quad (2.21)$$

$$G_{\mu\nu,\rho\sigma} = \int \int \chi_\mu^*(r_1)\chi_\rho^*(r_2)\frac{1}{r_{12}}\left[\chi_\nu(r_1)\chi_\sigma(r_2) - \chi_\sigma(r_1)\chi_\nu(r_2)\right]dr_1dr_2,$$

$$G(D)_{\mu\nu} = \sum_{\rho\sigma} G_{\mu\nu,\rho\sigma}D_{\rho\sigma}. \quad (2.22)$$

The orbitals $\phi_k$ are required to be orthonormal, which translates into the following matrix equations to be satisfied by $C$ and $D$

$$\langle \phi_j | \phi_k \rangle = \delta_{jk} \Rightarrow \ C^\dagger SC = 1 \Rightarrow DSD = D, \quad (2.23)$$

where $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ is the overlap matrix for the AO basis $\chi_\mu$. The latter equation is commonly referred to as the idempotency condition for the density matrix.

Since $C$ must satisfy the orthonormality relation, it is constrained, and the Lagrange multiplier method$^8$ can be used to derive the variational condition

$$E(C, \Lambda) = h_{\text{nuc}} + \text{Tr} C^\dagger HC + \frac{1}{2}\text{Tr} C^\dagger G(CC^\dagger)C \quad (2.24)$$

$$- \text{Tr} \Lambda (C^\dagger SC - 1),$$

$$\frac{\partial}{\partial C}E(C, \Lambda) = (H + G(CC^\dagger))C - SCA = 0, \quad (2.25)$$

where $\Lambda$ is the Lagrange multiplier matrix for the orthonormality condition. Introducing the Fock matrix $F = H + G(D)$, the variational condition can be expressed in terms of $D$ as$^9$

$$FDS = SDF, \quad (2.26)$$

which is the SCF equation in terms of the density matrix.

### 2.3.2 Kohn-Sham DFT

Hohenberg and Kohn$^{10}$ showed that there is a one-to-one relation between the potential functions $v(r)$ in the electronic Schrödinger equation, and the

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$^8$J.-L. Lagrange: “Théorie des fonctions analytiques”, (1797, p. 198)


2.3 Self-consistent field approximation

electron density $\rho(r)$ of the ground state (solution)

$$\rho(r) = N \int \ldots \int |\psi(r, r_2 \ldots r_N)|^2 \, dr_2 \ldots dr_N. \quad (2.27)$$

For a molecule, $v(r)$ is the sum of Coulomb attractions to each nucleus

$$v(r) = -\sum_n \frac{q_n}{||r-r_n||}, \quad (2.28)$$

and it enters the electronic Hamiltonian together with the nuclear repulsion $h_{\text{nuc}}$, the electronic kinetic energy, and electron repulsion. Basically this means that two different electronic Hamiltonians (different $v(r)$) cannot have the same ground state density $\rho(r)$. For molecules this is perhaps not surprising—the peaks in the ground state density, and their heights, indicate the positions and charges of the nuclei, from which $v(r)$ can be determined.

Under the additional assumption that the ground state is non-degenerate (has multiplicity 1), Hohenberg and Kohn also proved the existence of a variational density functional $E_v[\rho]^{11}$ for the energy, which minimum $\rho(r)$ is the ground state density corresponding to $v(r)$, hence the name ‘density functional theory’ (DFT). The nuclear repulsion and nuclear attraction are known contributions to $E_v[\rho]$, while the kinetic energy $T$ and electron repulsion $V$ are unknowns

$$E_v[\rho] = h_{\text{nuc}} + \int v(r) \rho(r) \, dr + (T+V)[\rho]. \quad (2.29)$$

The formulation of a density functional for the kinetic energy is a difficult task, as the ground state kinetic energy can change abruptly with small changes in the density. To account for this, Kohn and Sham$^{12}$ proposed to expand the density in terms of orthonormal orbitals, and use the Hartree-Fock (or non-interacting) kinetic energy $T_s$ as the main contribution, with the remaining kinetic energy expected to vary more slowly. Analogously, the Coulomb contribution $J[\rho]$ (see Eq. 2.18) is separated from the electron repulsion, leaving the ‘exchange-correlation functional’ $E_{xc}[\rho]$ as the unknown

$$E_v[\rho] = h_{\text{nuc}} + \int v(r) \rho(r) \, dr + T_s[\rho] + J[\rho] + E_{xc}[\rho], \quad (2.30)$$

$$J[\rho] = \frac{1}{2} \int \rho(r_1) \frac{1}{|r_1-r_2|} \rho(r_2) \, dr_1 dr_2, \quad (2.31)$$

$$E_{xc}[\rho] = (T - T_s + V - J)[\rho]. \quad (2.32)$$

---

$^{11}$It is customary to write a density functional with square brackets [...] around its argument instead of (...)  

This is the form of the basic Kohn-Sham density functional theory. If $E_{xc}[\rho]$ is an integral over a function $F(\rho(r))$, it is said to be a local density approximation (LDA), whereas an integral over $F(\rho(r), \|\nabla \rho(r)\|)$ is a generalized gradient approximation (GGA). If an additional 'exact exchange' contribution (meaning Hartree-Fock exchange, see Eq. 2.18) is separated from $V$, it is a 'hybrid' functional.

As was the case with Hartree-Fock in the previous section, expanding the orbitals in terms of AOs results in a matrix expression for the Kohn-Sham energy, and a variational condition of the same form as the SCF equation Eq. 2.26.
Chapter 3
Properties and spectra

The basic interpretation of spectroscopy is that it measures differences between the stationary states of (atoms and) molecules, the eigenstates of the Hamiltonian and solutions of the time-independent Schrödinger equation. The molecule absorbs radiation at frequencies $\omega_{yx} = E_x - E_y$, which correspond to differences between two eigenenergies, at a rate $A$ proportional to the intensity of incoming radiation $I(\omega_{yx})$, the transition dipole moment, and the population $|c_y|^2$ of the lower state $\psi_y$

$$A(\omega_{yx}) \propto I(\omega_{yx})|\langle \psi_x | \hat{\mu} | \psi_y \rangle|^2 |c_y|^2. \quad (3.1)$$

The molecule also emits radiation at the same set of frequencies, at a rate $S$ proportional to the same transition moment and the population of the higher state $\psi_x$

$$S(\omega_{yx}) \propto |\langle \psi_y | \hat{\mu} | \psi_x \rangle|^2 |c_x|^2. \quad (3.2)$$

These two processes are linear absorption and spontaneous emission, respectively. Thus, in the absence of any incoming radiation to be absorbed, a molecule in a mixture of states will eventually decay to the ground state by spontaneous emission of radiation. Moreover, a system of molecules in thermodynamic equilibrium (constant populations) will emit radiation with frequencies and intensities reflecting the populations and transition moments.

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1. This section is based on Robert C. Hilborn: “Einstein coefficients, cross sections, f values, dipole moments, and all that”, 2002 revision of Am. J. Phys. 50, 982–986 (1982)
3.1 Propagation and Floquet theory

In order to predict absorption and emission spectra, we need a way to determine the expansion coefficients $c_g(t)$ and $c_x(t)$ of the wavefunction\(^2\) $\tilde{\psi}(t)$, for a given experimental environment

\[
\tilde{\psi}(t) = c_g\psi_g + \sum_x c_x\psi_x.
\]  

(3.3)

In general, this amounts to solving the time-dependent Schrödinger equation, in which the incoming radiation gives rise to a time-dependent external potential $\tilde{V}_t$ (which will be presented in the next section)

\[
(\hat{H} + \theta(t)\hat{V}_t)\tilde{\psi} = i\frac{d}{dt}\tilde{\psi},
\]

where $\theta(t)$ is some function 'switching' the radiation on; either instantaneously, such as with the step function $\theta(t=0)=0$, $\theta(t>0)=1$; or gradually, as with the error function $\theta(t)=\text{erf}(\varepsilon t)$; or exponentially, $\theta(t)=\exp(\varepsilon t)$. As initial condition of the linear differential equation Eq. 3.4, one may specify the wave function at some time, for instance $\tilde{\psi}(-\infty)=\psi_g$ or $\tilde{\psi}(0)=\psi_g$. This procedure of setting an initial condition followed by solving the time-dependent Schrödinger equation is called *propagation*, and treated in propagator theories.\(^3\)

In this work we make the simplest possible choice of switching function, namely $\theta(t)=1$. Rather than specifying an initial condition, we require that the wave function is the product of a phase factor $e^{-iQt}$ and a quasi-periodic\(^4\) wave function $\psi(t)$

\[
\tilde{\psi}(t) = e^{-iQt}\psi(t) = e^{-iQt}\sum_{\omega\in\Omega} e^{i\omega t}\psi_{\omega},
\]

(3.5)

where the frequency set $\Omega(V^t)$ characterizing quasi-periodicity consists of “all combinations of integer multiples of frequencies in the external potential $V^t$”. This means that $\psi$ is a Fourier series in all frequencies appearing in $V^t$. That is, if $V^t$ is monochromatic, as when the molecule is irradiated by

\(^2\)The tilde is put on this wavefunction, to reserve $\psi(t)$ for the phase isolated Floquet state in Eq. 3.5.


3.1 Propagation and Floquet theory

A single laser, \( \psi \) is a Fourier series in the laser frequency, and thus periodic. Analogously, in the case of two lasers, \( \psi \) is a bi-variate Fourier series, which is periodic only when the two frequencies have a common divisor, but generally quasi-periodic. Unless the frequencies in \( V^t \) have a common divisor (are commensurate), the set \( \Omega(V^t) \) is dense in the real numbers.

Inserting the quasi-periodic wave function Eq. 3.5 into the time-dependent Schrödinger equation Eq. 3.4 with \( \theta(t)=1 \), expanding the time derivative and cancelling the phase factor, the time-dependent Schrödinger equation takes the form of an eigenvalue equation

\[
(\hat{H} + \hat{V}^t)e^{-iQ\psi} = i\frac{d}{dt}e^{-iQ\psi}, \tag{3.6}
\]

\[
e^{-iQ\psi}(\hat{H} + \hat{V}^t)\psi = e^{-iQ\psi}(Q + i\frac{d}{dt})\psi, \tag{3.7}
\]

\[
(\hat{H} + \hat{V}^t - i\frac{d}{dt})\psi = Q\psi. \tag{3.8}
\]

This will be referred to as the Floquet-Schrödinger equation. The operator \( \hat{H} + \hat{V}^t - i\frac{d}{dt} \) is the Floquet operator, and its eigenvalue \( Q \) the quasi-energy. The eigenfunctions \( \psi \) will in the following be referred to as Floquet states. The operator \( i\frac{d}{dt} \) is Hermitian in the time-averaged scalar product

\[
\{\langle \psi | \phi \rangle \}_t = \{\frac{d}{dt}\langle \psi | \phi \rangle \}_t - i\{\langle \psi | \phi \rangle \}_t = 0 + \{\langle i\dot{\psi} | \phi \rangle \}_t, \tag{3.9}
\]

where the time-average is well defined for quasi-periodic functions and leads to the time average of a time derivative being zero

\[
\{\ldots\}_t = \lim_{r,s \to \infty} \frac{1}{r+s}\int_{-r}^{s}\ldots dt, \quad \{\frac{d}{dt}\ldots\}_t = 0. \tag{3.10}
\]

The Floquet operator is therefore Hermitian and the quasi-energies \( Q \) real-valued. For each Floquet state \( \psi \) with quasi-energy \( Q \), there is an infinite set of Floquet states \( e^{i\omega t}\psi \) with quasi-energies \( Q - \omega \) for all frequencies \( \omega \) taken from the set \( \Omega(V^t) \), as can be seen by inserting \( e^{i\omega t}\psi \) in Eq. 3.5. Floquet states that in this way only differ by a phase factor \( e^{i\omega t} \) are said to be degenerate.

The non-degenerate Floquet states are orthogonal (at each time \( t \)). This is seen by expanding the matrix element of the Floquet operator in two different ways

\[
0 = \langle \psi_a | \hat{H} + \hat{V}^t - i\frac{d}{dt} | \psi_b \rangle - \langle \psi_a | \hat{H} + \hat{V}^t - i\frac{d}{dt} | \psi_b \rangle
\]

\[
= \langle \psi_a | Q_b \psi_b \rangle - \langle (\hat{H} + \hat{V}^t - i\frac{d}{dt})\psi_a | \psi_b \rangle + i\frac{d}{dt}\langle \psi_a | \psi_b \rangle
\]

\[
= (Q_b - Q_a)\langle \psi_a | \psi_b \rangle + i\frac{d}{dt}\langle \psi_a | \psi_b \rangle. \tag{3.11}
\]

As taught in introductory mathematics courses, the general solution of this first-order linear differential equation is

\[
\langle \psi_a | \psi_b \rangle = c e^{i(Q_b - Q_a)t}, \tag{3.12}
\]
where $c$ is a complex constant. Since $\psi_a$ and $\psi_b$ are quasi-periodic, $\langle \psi_a | \psi_b \rangle$ must also be quasi-periodic, but the frequency $Q_b - Q_a$ does not in general belong to the quasi-periodic set $\Omega(V^t)$ (unless $\psi_a$ and $\psi_b$ happen to be degenerate), hence $c$ must be zero and the states are orthogonal.

### 3.2 Radiation potential

The potential\(^5\) $V^t$ arising from a static external (first order-) inhomogeneous electric field and a static external homogeneous magnetic field is given by the expression

$$V^t = - F \cdot \hat{\mu} - G \cdot \hat{\Theta} - B \cdot \hat{m} - \frac{1}{2} B \cdot \hat{\xi} B,$$

(3.13)

where $F$, $G$ and $B$ are the electric field (at the origin of the coordinate system), the electric field gradient and the magnetic field, respectively, which multiply the (negative) electric dipole operator

$$\hat{\mu} = \sum_p q_p r_p,$$

(3.14)

electric quadrupole operator (symmetric $3 \times 3$ matrix)\(^6\)

$$\hat{\Theta} = \sum_p \frac{q_p}{2} r_p r_p^T,$$

(3.15)
magnetic dipole operator

$$\hat{m} = \sum_p \frac{m_p}{2m_p} \hat{I}_p = \sum_p \frac{m_p}{2m_p} r_p \times \nabla_p,$$

(3.16)

and magnetic susceptibility operator (symmetric $3 \times 3$ matrix)

$$\hat{\xi} = \sum_p \frac{\mu_p}{4m_p} (r_p r_p^T - (r_p \cdot r_p) 1),$$

(3.17)

respectively. The external potential is in this case time-independent (static), and the notation $V^t$ perhaps misleading, but as will be shown below, the presence of radiation leads to time-dependent $F$, $G$ and $B$ (and hence $V^t$). An electromagnetic wave, radiation with a single frequency and direction, is a simple solution of Maxwell’s equations\(^7\)

$$\nabla \cdot F = 4\pi \rho, \quad \frac{d}{dt} F = c^2 \nabla \times B - 4\pi j,$$

$$\nabla \cdot B = 0, \quad \frac{d}{dt} B = - \nabla \times F,$$

(3.18)

(3.19)

\(^5\)This section is based on L. D. Barron and C. G. Gray: “Multipole interaction Hamiltonian for time-dependent fields”, J. Phys. A 6(1), 59-61 (1973)

\(^6\)There are several ways to define $\Theta$. In this definition, $\Theta$ is not traceless and scaled so that it multiplies the electric field gradient.

\(^7\)These are Maxwell’s equations in the ‘Lorentz force’ convention, where the electric and magnetic fields differ in magnitude by a factor $\frac{1}{c}$, as opposed to the ‘Gaussian’ convention.
which for empty space (charge $\rho$ and current density $j$ zero) state that the fields are divergence-free (have no sources), and time-evolution is determined by the opposite field’s curl (rotation). The speed of light $c$ is $\approx 137$ in atomic units.

An electromagnetic wave with frequency $\omega$, propagating in the (normalized) direction $k$ is on the form

$$\begin{align*}
F(r) &= f e^{-i\omega t} \exp\left(\frac{ik}{c} \cdot r\right) + \text{c.c.}, \\
B(r) &= b e^{-i\omega t} \exp\left(\frac{ik}{c} \cdot r\right) + \text{c.c.},
\end{align*}$$

(3.20) (3.21)

where $f$ is the wave’s Jones vector, a complex vector which determines the wave’s intensity, phase, and (electric) polarization, and is perpendicular to $k$. The corresponding magnetic vector is given by $b=\frac{1}{2} k \times f$, and is perpendicular to both $k$ and $f$, and differs from $f$ in magnitude by a factor $\frac{1}{2}$. The terms ‘c.c.’ in Eqs. 3.20 and 3.21 denote the complex conjugate of the preceding expression, thus the fields are real-valued.

The polarization of the wave is linear if the real and imaginary parts of $f$ are parallel (or either is zero), circular (right or left) if perpendicular, and elliptic in other cases.

The electromagnetic field $F(r), B(r)$ is ‘translated’ to an external potential operator $\hat{V}^t$ through the scalar- and vector potentials $\phi(r)$ and $A(r)$, by the relation

$$\begin{align*}
\hat{V}^t &= \sum_p \frac{iq_p}{2m_p} (\nabla_p \cdot A(r_p) + A(r_p) \cdot \nabla_p) \\
&\quad + \sum_k \frac{q_k^2}{2m_k} A(r_p) \cdot A(r_p) + \sum_p q_p \phi(r_p),
\end{align*}$$

(3.22)

where the potentials $\phi(r)$ and $A(r)$ are related to the fields by

$$\begin{align*}
F(r) &= -\frac{\partial}{\partial t} A(r) - \nabla \phi(r), \\
B(r) &= \nabla \times A(r).
\end{align*}$$

(3.23)

However, these relations leave a great deal of freedom in the choice of $\phi(r)$ and $A(r)$, called gauge. By requiring $\mathbf{r} \cdot \mathbf{A}(r) = 0$, which is to adopt the multipolar gauge (about the origin), the potentials are given as simple integrals over the fields

$$\begin{align*}
\phi(r) &= -r \cdot \int_0^1 F(\mathbf{u}r) du, \\
A(r) &= -r \times \int_0^1 B(\mathbf{u}r) du,
\end{align*}$$

(3.24)

---


which for the fields given by Eqs. 3.20 and 3.21 can be calculated explicitly

$$\phi(\mathbf{r}) = -\mathbf{r} \cdot \left( f e^{-i\omega t} \exp\left( \frac{i\mathbf{k} \cdot \mathbf{r}}{c} \right) - 1 + \text{c.c.} \right), \quad (3.25)$$

$$\mathbf{A}(\mathbf{r}) = -\mathbf{r} \times \left( b e^{-i\omega t} \left( 1 - \frac{i\mathbf{k} \cdot \mathbf{r}}{c} \right) \exp\left( \frac{i\mathbf{k} \cdot \mathbf{r}}{c} \right) - 1 + \text{c.c.} \right) / \left( \frac{c}{\varepsilon k} \right)^2 \quad (3.26)$$

The wavelengths $\lambda = 2\pi c/\omega$ used in spectroscopy are in general several times the size of the molecules studied. Therefore, it is convenient to truncate the scalar and vector potentials to second and first order in $\mathbf{r}$, respectively, so that $V_t$ in Eq. 3.22 becomes accurate to first order in $11^{-1} \frac{1}{c}$ (due to the difference in magnitude between $f$ and $b$)

$$\phi(\mathbf{r}) = -\mathbf{r} \cdot \left( f e^{-i\omega t} \left( 1 + \frac{i\mathbf{k} \cdot \mathbf{r}}{2c} \right) \right) + \text{c.c.} \quad (3.27)$$

$$\mathbf{A}(\mathbf{r}) = -\mathbf{r} \times \left( b e^{-i\omega t} \left( \frac{1}{2} \right) + \text{c.c.} \right) \quad (3.28)$$

where the electric field at the origin, the electric field gradient and the magnetic field have been introduced retrievable

$$\mathbf{F} = f e^{-i\omega t} + \text{c.c.}, \quad (3.29)$$

$$\mathbf{G} = \frac{\omega}{c} (\mathbf{k} f^T + f \mathbf{k}^T) e^{-i\omega t} + \text{c.c.}, \quad (3.30)$$

$$\mathbf{B} = b e^{-i\omega t} + \text{c.c.} = \frac{c}{\varepsilon} (\mathbf{k} \times f) e^{-i\omega t} + \text{c.c.} \quad (3.31)$$

Inserting these expressions into Eq. 3.22, the external potential operator becomes

$$\hat{V}_t = \sum_p \frac{q_p}{2m_p} \left( i \nabla_p \cdot \left( -\frac{1}{2} \mathbf{r}_p \times \mathbf{B} \right) + \left( -\frac{1}{2} \mathbf{r}_p \times \mathbf{B} \right) \cdot i \nabla_p \right) \quad (3.32)$$

$$+ \sum_p \frac{q_p}{2m_p} \left( -\frac{1}{2} \mathbf{r}_p \times \mathbf{B} \right) \cdot \left( -\frac{1}{2} \mathbf{r}_p \times \mathbf{B} \right) - \sum_p q_p \mathbf{F} \cdot \mathbf{r}_p - \sum_p \frac{q_p}{2} \mathbf{G} \cdot \mathbf{r}_p \mathbf{r}_p^T,$$

which can be rearranged into

$$\hat{V}_t = -\mathbf{B} \cdot \left( \sum_p \frac{q_p}{2m_p} (\mathbf{r}_p \times i \nabla_p) \right) + \frac{1}{2} \mathbf{B} \cdot \left( \sum_p \frac{q_p}{4m_p} (\mathbf{r}_p \mathbf{r}_p^T - (\mathbf{r}_p \cdot \mathbf{r}_p) 1) \right) \mathbf{B}$$

$$- \mathbf{F} \cdot \left( \sum_p q_p \mathbf{r}_p \mathbf{r}_p \right) \mathbf{B} - \mathbf{G} \cdot \left( \sum_p \frac{q_p}{2} \mathbf{r}_p \mathbf{r}_p^T \right)$$

$$= -\mathbf{F} \cdot \hat{\mu} - \mathbf{G} \cdot \hat{\Theta} - \mathbf{B} \cdot \hat{m} - \frac{1}{2} \mathbf{B} \cdot \hat{\xi} \mathbf{B}, \quad (3.33)$$

\(^{11}\) Called the fine-structure constant, and commonly denoted by $\alpha$
which is on the same form as Eq. 3.13, except the fields are time-dependent. This is the electric quadrupole–magnetic dipole approximation to the radiation potential. For a field consisting of several waves of different frequencies and directions, there will be several time-dependent contributions to $F, G$ and $B$.

### 3.3 Response theory

When exposed to radiation, the molecule starts fluctuating, rotating and vibrating in various ways. This means the molecular wavefunction is distributed over a number of eigenstates of the Hamiltonian

$$\psi(t) = c_k(t)\psi_k + \sum_x c_x(t)\psi_x,$$

which makes the explicit solution of the Floquet-Schrödinger equation Eq. 3.8 very demanding, and only applicable to small atoms. For molecules, the only option is therefore to resort to approximate solutions by means of perturbation theory.

Having solved the time-independent Schrödinger equation (with $\hat{V} = 0$), and thus found a time-independent eigenstate $\psi_k$ with eigenenergy $E_k$, the quasi-energy $Q$ and Floquet state $\psi$ can be written as a perturbation expansion (Taylor series) in the field parameters $f, b, g$ etc., that enter $\hat{V}^t$

$$Q|_{f,b,g} = E_k + f Q^f + f^* Q^{f^*} + b Q^b + b^* Q^{b^*} + g Q^g + g^* Q^{g^*}$$

$$+ \frac{1}{2} f f Q^{ff} + f f^* Q^{f^* f^*} + f f^* Q^{f^* f^*} + f b Q^{fb} + f b^* Q^{fb^*}$$

$$+ \frac{1}{2} b b Q^{bb} + b^* b^* Q^{bb^*} + b^* b^* Q^{bb^*} + b b^* Q^{bb^*} + \frac{1}{2} b b^* Q^{bb^*}$$

$$+ f g Q^{fg} + f^* g Q^{f^* g^*} + b g Q^{bg} + b g^* Q^{bg^*} + \frac{1}{2} g g Q^{gg}$$

$$+ f^* g Q^{fg^*} + f^* g^* Q^{f^* g^*} + b^* g Q^{bg^*} + b^* g Q^{bg^*} + \frac{1}{2} g g Q^{gg}$$

$$+ b^* g Q^{bg^*} + g g^* Q^{gg^*} + \frac{1}{2} f f Q^{ff} + \ldots$$

$$\psi|_{f,b,g} = \psi_k + f \psi^f + f^* \psi^{f^*} + b \psi^b + b^* \psi^{b^*} + \ldots$$

where superscripts are used as short-hand notation for derivatives, i.e. $Q^{fg} = \frac{d}{df^*} \frac{d}{dg} Q$, and the vector-tensor products are contracted. Note that also derivatives with respect to the complex-conjugate fields $f^*, b^*, g^*$ appear in the series. We will refer to the derivatives of the quasi-energy $Q^{fb^*}$ etc., as responses, and derivatives of the wave function $\psi^b$ etc., as perturbed wavefunctions. They
are determined by the corresponding derivatives of the Floquet-Schrödinger equation, Eq. 3.8 and the normalization condition Eq. 2.3
\[ \frac{d}{df} (\hat{H} + \hat{V}^t - i \frac{d}{df} - Q) \psi = 0, \quad \frac{d}{df} (\langle \psi | \psi \rangle - 1) = 0, \tag{3.37} \]
Expanding the derivatives and inserting Eq. 3.33, we get
\[ (\hat{H} + \hat{V}^t - i \frac{d}{df} - Q) \psi_f = (e^{-i\omega t} \hat{\mu} + Q^b) \psi, \tag{3.38} \]
\[ \langle \psi_f | \psi \rangle + \langle \psi | \psi_f \rangle = 0. \tag{3.39} \]
Applying \( \langle \psi | \ldots \rangle \) to the first equation and rearranging
\[ \langle \psi | \hat{H} + \hat{V}^t - i \frac{d}{df} - Q | \psi_f \rangle = \langle \psi | e^{-i\omega t} \hat{\mu} + Q^f | \psi \rangle, \tag{3.40} \]
\[ \langle \hat{H} + \hat{V}^t - i \frac{d}{df} - Q | \psi_f \rangle - i \frac{d}{df} \langle \psi | \psi_f \rangle = e^{-i\omega t} \langle \psi | \hat{\mu} | \psi \rangle + Q^f \langle \psi | \psi \rangle. \tag{3.41} \]
The first term vanishes and the last term is 1 due to normalization. Taking the time average, the second term also vanishes (the average of a time derivative is zero, see Eq. 3.10)
\[ \{ -i \frac{d}{df} \langle \psi | \psi_f \rangle \}_t = \{ e^{-i\omega t} \langle \psi | \hat{\mu} | \psi \rangle \}_t + Q^f \Rightarrow Q^f = -\mu_\omega, \tag{3.42} \]
and the derivative \( Q^f \) of the quasi-energy with respect to an oscillating electric field, is found to be minus the \( \omega \)-frequency component of the electric dipole moment. This property is known as the (time-dependent) Hellmann-Feynman theorem\(^{12,13}\): “The first derivative is given by the expectation value of the perturbing operator”. Thus, no knowledge of \( \psi_f \) is required to obtain \( Q^f \).

Differentiating \( Q^b \), which according to the previous discussion is given by \( -\{ e^{i\omega t} \langle \psi | \hat{m} | \psi \rangle \}_t \), with respect to \( f \), the linear response \( Q^{bf} \) is obtained
\[ Q^{bf} = -\frac{d}{df} \{ e^{i\omega t} \langle \psi | \hat{m} | \psi \rangle \}_t = -\{ e^{i\omega t} (\langle \psi_f | \hat{m} | \psi \rangle + \langle \psi | \hat{m} | \psi_f \rangle) \}_t. \tag{3.43} \]
In this case, however, \( \psi_f \) cannot be eliminated from the formula. Going back to Eq. 3.38, and using that the unperturbed wavefunction \( \psi = \psi_g \) is time-independent, and thus \( Q^f = -\mu_\omega \) is zero (unless \( \omega = 0 \))
\[ (\hat{H} - i \frac{d}{df} - E_g) \psi_f = e^{-i\omega t} \hat{\mu} \psi_g. \tag{3.44} \]
Since only the phase factor \( e^{-i\omega t} \) is time-dependent on the right-hand side, and \( \psi_f \) is the only time-dependent factor on the right-hand side, \( \psi_f \) must

\(^{12}\)H. Hellmann: Einführung in die Quantenchemie (Leipzig: Deuticke) (1937)

carry the same phase factor: \( \psi_f(t) = e^{-i\omega t}\psi_f(0) \). This means that \( \frac{d}{dt}\psi_f = -i\omega \psi_f \), and the equation becomes

\[
(\hat{H} - \omega - E_g)\psi_f = e^{-i\omega t}\hat{\mu}\psi_g. \tag{3.45}
\]

If \( \psi_g \) together with all the other eigenstates \( \psi_x \) of \( \hat{H} \) form a complete orthonormal set, we can write \( \hat{H} \) as

\[
\hat{H} = E_g|\psi_g\rangle\langle\psi_g| + \sum_x E_x|\psi_x\rangle\langle\psi_x|, \tag{3.46}
\]

and the inverse of the operator on the left-hand side of Eq. 3.45 can be written as

\[
(\hat{H} - \omega - E_g)^{-1} = \frac{1}{E_g-\omega-E_g}|\psi_g\rangle\langle\psi_g| + \frac{1}{E_x-\omega-E_g}|\psi_x\rangle\langle\psi_x|. \tag{3.47}
\]

The solution \( \psi_f \) is therefore given by

\[
\psi_f = e^{-i\omega t} \left( -\frac{\langle \psi_g | \hat{\mu} | \psi_g \rangle}{\omega} \psi_g + \sum_x \frac{\langle \psi_x | \hat{\mu} | \psi_g \rangle}{E_x - \omega - E_g} \psi_x \right), \tag{3.48}
\]

from which \( \psi_f^* \) is obtained by changing \( \omega \) to \( -\omega \). Inserting for \( \psi_f^* \) and \( \psi_f \) in the linear response in Eq. 3.43, the so-called sum-over-states expression for the linear response is obtained

\[
\frac{d}{dt}Q^{bf} = -\left\{ e^{i\omega t} \left( -\frac{\langle \psi_g | \hat{\mu} | \psi_g \rangle}{\omega} \psi_g + \sum_x \frac{\langle \psi_x | \hat{\mu} | \psi_g \rangle}{E_x + \omega - E_g} \psi_x \right) |\bar{m}| \psi_g \right\} \\
+ e^{i\omega t} \langle \psi_g | \bar{m} | e^{-i\omega t} \left( -\frac{\langle \psi_g | \hat{\mu} | \psi_g \rangle}{\omega} \psi_g + \sum_x \frac{\langle \psi_x | \hat{\mu} | \psi_g \rangle}{E_x - \omega - E_g} \psi_x \right) \rangle \} t \\
= -\sum_x \frac{\langle \psi_g | \hat{\mu} | \psi_x \rangle \langle \psi_x | \bar{m} | \psi_g \rangle}{E_x + \omega - E_g} - \sum_x \frac{\langle \psi_g | \bar{m} | \psi_x \rangle \langle \psi_x | \hat{\mu} | \psi_g \rangle}{E_x - \omega - E_g}. \tag{3.49}
\]

Observe that the contributions from the first terms in \( \psi_f \) and \( \psi_f^* \) have canceled. This is also the case for the time-dependent phase factors, making the time average redundant.

As there in general will be infinitely many excited states \( \psi_x \), using Eq. 3.47 is not a practical way to solve the response equation Eq. 3.45. Rather, it is preferrables to solve Eq. 3.45 iteratively, using a preconditioner (approximation to Eq. 3.45) to improve convergence. An iterative technique is also preferrable for finding \( \psi_g \) in the first place, and the two techniques are related.
Due to the time-independence of the reference state $\psi_g$, and the frequency dependence of the applied fields, quasi-energy derivatives (responses) are non-zero only when the frequencies of the fields sum to zero. Thus, the following second derivatives are zero, for instance

$$Q^{ff} = Q^{bb} = Q^{ff'} = Q^{bf'} = 0,$$

(3.50)

since the frequencies of the fields sum to $2\omega, 2\omega, -2\omega$ and $-2\omega$, respectively.

For higher-order responses, involving several different frequencies, it is more convenient to use a notation which specifies both the fields and their frequencies, such as

$$Q^{FF}_{\omega_1 \omega_2 \omega_3} = Q^{FB}_{\omega_1 \omega_2 \omega_3} = Q^{FG}_{\omega_1 \omega_2 \omega_3} = Q^{FFBB}_{\omega_1 \omega_2 \omega_3 \omega_4},$$

(3.51)

where $F$ is understood as the electric field, $B$ the magnetic field, and $G$ the electric field gradient, respectively. A well-established notation is the double bracket$^{14}$

$$\langle \langle \mu; \mu, m \rangle \rangle_{\omega, \nu} = (-1)^3 Q^{FFBB}_{-\omega - \nu, \omega, \nu, \nu}, \quad \langle \langle \mu; \Theta, m, \mu \rangle \rangle_{\omega, \nu, \gamma} = (-1)^4 Q^{FFBB}_{-\omega - \nu - \gamma, \omega, \nu, \gamma},$$

which lists the perturbing operators, the first designated as the 'outgoing' field and the others as 'incoming' fields, along with the incoming frequencies.

### 3.4 Resonance

Even if the singularity in $\psi^f$ Eq. 3.48 at $\omega=0$ is absent from the linear response function Eq. 3.49, singularities remain at all excitation energies $\omega=E_x-E_g$. At first glance this may seem as a problem with response theory.

But as will be explained in this section$^{15}$, these are resonances — discontinuous 'jumps' in $\psi$ and $Q$ as the field is switched on.

For simplicity, we will consider a two-state system, so that the Floquet state $\psi$ can be written as a linear combination of the two unperturbed eigenstates $\psi_g$ and $\psi_x$

$$\psi = c_g(t)\psi_g + c_x(t)\psi_x, \quad \hat{H} = E_g|\psi_g\rangle\langle\psi_g| + E_x|\psi_x\rangle\langle\psi_x|,$$

(3.52)


$^{15}$This section is based on S. H. Autler and C. H. Townes: “Stark Effect in Rapidly Varying Fields”, Phys. Rev. 100(2), 703 (1955)
where the two coefficients are complex $\frac{2\pi}{\omega}$-periodic functions of time, expressed as Fourier series

$$c_g(t) = \sum_{-\infty}^{\infty} c_{gk} e^{i k \omega t}, \quad c_x(t) = \sum_{-\infty}^{\infty} c_{xk} e^{i k \omega t}.$$  \hspace{1cm} (3.53)

Furthermore, we write the external potential as coupling these two states, and consider only one field direction (say $\hat{\mu}_z$). In addition, assume without loss of generality that the field strength $f$ is real-valued, so that the time-dependent factor becomes $2 \cos \omega t$

$$\hat{V}_t = -f(e^{-i \omega t} + e^{i \omega t}) (\mu | \psi_x^t \rangle \langle \psi_x^t | + \mu | \psi_g^t \rangle \langle \psi_g^t |),$$  \hspace{1cm} (3.54)

where the transition moment $\mu = \langle \psi_g^t | \hat{\mu}_z | \psi_x^t \rangle$ is assumed real-valued, as any phase could be absorbed into $\psi_g$ or $\psi_x$. Inserting Eqs. 3.52, 3.53 and 3.54 into the Floquet-Schrödinger equation Eq. 3.8, we get

$$0 = (\hat{H} + \hat{V}_t - i \frac{d}{dt} - Q) \left( \sum_{-\infty}^{\infty} c_{gk} e^{i k \omega t} \psi_g^t + \sum_{-\infty}^{\infty} c_{xk} e^{i k \omega t} \psi_x^t \right) \hspace{1cm} (3.55)$$

$$= \sum_{-\infty}^{\infty} (E_g c_{gk} - f \mu c_{xk} (e^{-i \omega t} + e^{i \omega t}) + k \omega c_{gk} - Q c_{gk}) e^{i k \omega t} \psi_g^t$$
$$+ \sum_{-\infty}^{\infty} (E_x c_{xk} - f \mu c_{gk} (e^{-i \omega t} + e^{i \omega t}) + k \omega c_{xk} - Q c_{xk}) e^{i k \omega t} \psi_x^t.$$

To move the time-dependent factors $e^{-i \omega t}$ and $e^{i \omega t}$ outside the parenthesis, we rename $k$ to $k+1$ and $k-1$ (shift the summations) in those terms

$$0 = \sum_{-\infty}^{\infty} (E_g c_{gk} - f \mu (c_{k+1} + c_{k-1}) + k \omega c_{gk} - Q c_{gk}) e^{i k \omega t} \psi_g^t \hspace{1cm} (3.56)$$
$$+ \sum_{-\infty}^{\infty} (E_x c_{xk} - f \mu (c_{gk+1} + c_{gk-1}) + k \omega c_{xk} - Q c_{xk}) e^{i k \omega t} \psi_x^t.$$

Since the time- and space-dependent factors $e^{i k \omega t} \psi_g^t$ and $e^{i k \omega t} \psi_x^t$ are linearly independent, this leads to the set of equations

$$- f \mu c_{k-1} + (E_g + k \omega) c_{gk} - f \mu c_{k+1} = Q c_{gk}, \hspace{1cm} (3.57)$$
$$- f \mu c_{gk-1} + (E_x + k \omega) c_{xk} - f \mu c_{gk+1} = Q c_{xk}.$$  \hspace{1cm} (3.58)
which may be organized in the form of the eigenvalue equation for the infinite tri-diagonal Floquet matrix

\[
\begin{bmatrix}
\vdots & \vdots & \vdots \\
\cdots & E_x-2\omega -f_\mu & \cdots \\
\cdots & -f_\mu E_x+1\omega +f_\mu & \cdots \\
\vdots & \vdots & \vdots \\
\end{bmatrix}
\begin{bmatrix}
\cdots \\
C_{x-2} \\
C_{g-1} \\
C_{x-1} \\
C_{g0} \\
C_{x0} \\
C_{g1} \\
C_{x1} \\
C_{g2} \\
\vdots \\
\end{bmatrix}
= Q
\begin{bmatrix}
\cdots \\
\cdots \\
\cdots \\
\end{bmatrix}
\]

Written more compactly, this equation is of the form

\[
(H - fM - \omega S) c = Qc,
\]

where \( H \) contains the matrix elements of the Hamiltonian, \( E_g \) and \( E_x \) alternating along the diagonal; \( M \) contains the transition moment integral \( \mu \) on the first off-diagonals; \( S \) contains the integers \( k \) along the diagonal which multiply \( \omega \) (called Floquet indices); and \( c \) the Fourier series \( c_g(t) \) and \( c_x(t) \) of the wavefunction.

Figure 3.1: Floquet states corresponding to the (left) ground state \( \psi_g=\pi^{-1/4}e^{-x^2/2}, E_g = \frac{1}{2} \) and (right) first excited state \( \psi_x=(\pi/4)^{-1/4}e^{-x^2/2}, E_x=\frac{3}{2} \) of the one-dimensional Harmonic oscillator, in the potential Eq. 3.54 with \( \mu=(\psi_g|x|\psi_x)= -\frac{1}{\sqrt{2}}, f=0.03, \omega=0.99 \). The curves are \( |\psi|^2 \) for \(-3 \leq x \leq 3\) in 20 steps through one full period. Observe that the state on the left plot moves where \( \hat{V}t \) is negative (as \( \cos \omega t \)), whereas the right plot is on the opposite side (\( -\cos \omega t \)). The corresponding quasi-energies and polarizations are marked with dots in Fig. 3.2.
The eigenvalues $Q$ form two sets $Q_a + j\omega$ and $Q_b + j\omega$, where $j$ runs over all integers, as explained after Eq. 3.10. Fortunately, the middle eigenvalues of a truncated Floquet matrix converge rather quickly to representatives from each set. In the examples Figs. 3.1 and 3.2, the Floquet matrix was truncated to the range $c_{x-6} \ldots c_{g5}$.

![Figure 3.2: (left) Curves of the Harmonic oscillator quasi-energy for $0.8 \leq \omega \leq 1.2$, showing the avoided crossing occurring at $\omega = E_x - E_g = 1$. The curves are for $f = 0.003, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08$. The diagonal asymptote is $Q = E_x - \omega$. (right) For each curve on the left, the $\omega$-frequency component of the polarization $\{e^{i\omega t}\langle \psi | x | \psi \rangle \}$ of the corresponding state. Superimposed on the curves tending to the ground state as $f \to 0$ are the approximate quasi-energies $Q$ and polarizations $P(\omega)$ given by Eqs. 3.61 and 3.63. The lowest curve on the left corresponds to the highest curve on the right, and vice versa. The dots mark the two states illustrated in Fig. 3.1. As $f \to 0$, the polarization tends to zero everywhere, except at $\omega = 1$, where it remains at $\pm \frac{1}{2\lambda f}$. Analogous avoided crossings occur at $\omega = \frac{1}{2}, \frac{1}{3}, \frac{1}{4} \ldots$ between $\psi_g$ and $e^{-2i\omega t}\psi_x, e^{-3i\omega t}\psi_x, e^{-4i\omega t}\psi_x \ldots$ etc.]

Inspecting Eq. 3.59, it is apparent that, although multiplying different matrices, $f$ and $\omega$ have analogous roles. This means that we may generalize response theory to, not only field derivatives, such as $Q_{fg}$, but also frequency-of-field derivatives: $Q_{f^\omega}$. As we will see below, with this generalization can be derived a non-singular polarization spectrum from the singular linear response in Eq. 3.49.

As depicted in Fig. 3.2, the ground state $\psi_g$ and the excited state with Floquet index 1, $e^{-i\omega t}\psi_x$ exhibit an avoided crossing near the excitation energy $\omega = E_x - E_g$ (or resonance frequency). This poses a problem in perturbation theory, as the Taylor series in Eq. 3.35 cannot converge to a quasi-energy $Q$ with a discontinuity, and will therefore diverge. More crucially, the $\omega$-
frequency polarization
\[ p = P(\omega) = \{ e^{i\omega t} \langle \psi | \hat{\mu} | \psi \rangle \}_t = -\frac{d}{df} Q, \]  
(3.60)

which, unlike the quasi-energy, is an observable, changes sign at the resonance.

To tackle this, we will analyse the following approximation, valid for small \( f \) near resonance
\[ Q \approx \frac{1}{2}(E_g + E_x - \omega \pm \mu |\delta/\mu - 2if|), \]  
(3.61)
\[ \psi \approx \sqrt{\frac{1}{2} \pm \frac{1}{2|1-2if\mu/\delta|}} \psi_g \]  
(3.62)
\[ + \sqrt{\frac{1}{2} \pm \frac{1}{2|1-2if\mu/\delta|}} e^{-i\omega t} \psi_x, \]

\[ p = P(\omega) \approx \pm \frac{f \mu}{|\delta/\mu - 2if|}, \]  
(3.63)

where the detuning \( \delta = \omega - (E_x - E_g) \) has been introduced, and all the \( \pm \) are negative before the resonance and positive after. The validity of these approximations is demonstrated by Fig. 3.2. The derivatives of the polarization \( p \) with respect to the frequency \( \omega \) (or \( \delta \)), the field \( f \), and the mixed second derivative, are given by
\[ p^\omega = \frac{d}{d\omega} P(\omega) = \mp \frac{f \delta/\mu}{|\delta/\mu - 2if|^3}; \quad \lim_{f \to 0} p^\omega = 0, \]  
(3.64)
\[ p^f = \frac{d}{df} P(\omega) = \pm \frac{\delta^2/\mu}{|\delta/\mu - 2if|^3}; \quad \lim_{f \to 0} p^f = \pm \frac{\mu^2}{\delta}, \]  
(3.65)
\[ p^{\omega f} = \frac{d^2}{d\omega df} P(\omega) = \pm \frac{8f^2\delta/\mu - \delta^3/\mu^3}{|\delta/\mu - 2if|^5}; \quad \lim_{f \to 0} p^{\omega f} = \pm \frac{\mu^2}{\delta^2}, \]  
(3.66)

where also the limits \( f \to 0 \) have been calculated. The limit of \( p^f \) has a singularity at resonance \( \delta=0 \), as already seen in the formula for the linear response Eq. 3.49. By inspection of the formulas for \( p \) and \( p^\omega \), two combinations with non-singular, non-zero limits can be found: \( f/p^\omega \) and \( p^f/(fp^\omega) \)
\[ \lim_{f \to 0} \frac{f}{p^\omega} \left( \frac{\delta}{\mu} \right) = \lim_{f \to 0} \frac{d}{df} \left( \frac{\delta}{\mu} \right) = \lim_{f \to 0} \frac{1}{p^{\omega f}} = \pm \frac{\delta^2}{\mu^2}, \]  
(3.67)
\[ \lim_{f \to 0} \frac{p^2}{fp^\omega} \left( \frac{\delta}{\mu} \right) = \lim_{f \to 0} \frac{2pp^f}{fp^\omega + fp^{\omega f}} = \lim_{f \to 0} \frac{2p^2 + 2pp^f}{p^{\omega f} + fp^f} \]  
\[ = \lim_{f \to 0} \frac{p^{f 2}}{fp^\omega} \left( \frac{\delta}{\mu} \right) = \frac{2\left( \pm \frac{\mu^2}{\delta} \right)^2}{\mu^2/\delta^2} = \pm \mu^2, \]  
(3.68)
3.4 Resonance

where application of l'Hospital's rule to the zero-over-zero limits is indicated. Knowing these limits we may now approximate \( P(\omega) \) in Eq. 3.63 by substituting \( \pm \mu \) with \( \pm |p|^{1/2} / |p^{i\omega}|^{1/2} = p |p^{i\omega}|^{-1/2} \) and \( \delta / \mu \) with \( \pm |p^{i\omega}|^{-1/2} \)

\[
P(\omega)\bigg|_f \approx \frac{f_p |p^{i\omega}|^{-1/2}}{|\pm |p^{i\omega}|^{-1/2} - 2 \omega|^2}.
\]

which may be viewed as the first order Taylor expansion for the linear polarization \( f_p \), multiplied by the renormalization factor

\[
\frac{1}{\sqrt{1 + 4f^2 |p^{i\omega}|}}.
\]

Since the renormalized linear polarization given by Eq. 3.69 is expressed in terms of responses, it is also applicable to many-state systems such as atoms and molecules. Examples of this are shown in Fig. 3.3.

Note that although \( p^{i\omega} \) is a quadratic response, or third-order quasi-energy derivative, due to a property known as the the 2\( n \)+1 rule (see paper I), the second-order perturbed wavefunction \( \psi^{i\omega} \) is not required.

Although this analysis has provided a way to avoid the singularities (resonances) in the response functions, it has also revealed a problem with Floquet theory. The quasi-energy and polarization has branch-cut discontinuities at each resonance frequency (the branches that tend to \( \psi_g \) as \( f \to 0 \)), which may seem 'unphysical'. Other approaches to the resonance problem exist, for instance 'complex response theory'\(^{16} \), in which the polarization becomes purely imaginary at the resonance (goes as \( a \sin \omega t \), which is out-of-phase with the \( 2f \cos \omega t \) field), which is the expected behavior of an absorption.

Resonances are encountered in Paper II, which deals with CARS spectroscopy, where it is the difference of two field frequencies which coincides with the molecule's vibrational excitation energies (which appear in the lowest-order Born-Oppenheimer correction).

Figure 3.3: (top left) Renormalized $f=0.001$ isotropic linear polarization of furan $\text{C}_4\text{H}_4\text{O}$, and (top right) triazine $\text{C}_3\text{H}_3\text{N}_3$, and electric-field-gradient induced birefringence (explained in paper V) (bottom left) of formaldehyde $\text{CH}_2\text{O}$ and (bottom right) triazine, calculated from linear, respectively, quadratic Hartree-Fock response function. Although perhaps not evident at the resolution of these plots, there is a sign change at each resonance. The frequency derivative $p^\omega$ of the response was calculated by 3-point finite differences, rather than analytically. The plots were prepared with the assistance of Lara Ferrighi and Manuel Sparta.
Chapter 4

Summary and outlook

The first paper included in this thesis presents a new hierarchy of formulas for response functions for the SCF class of models, which is expressed in terms of the AO density matrix at all stages of computation. During recent years, the performance and scaling of SCF models have been considerably improved by changing from the molecular orbital to the density matrix parameterization\textsuperscript{1,2}. This has enabled calculations on molecules consisting of more than 1000 atoms. However, it has not been clear whether one could conveniently formulate the corresponding response theory in terms of the density matrix, or perhaps another equally well-scaling parameterization would be preferable\textsuperscript{3}. The formulas presented also take field-dependent (or perturbation-dependent) AOs correctly into account more straightforwardly than existing techniques\textsuperscript{4}. Moreover, the presented formula hierarchy is exhaustive, in that it covers responses of arbitrary order, and offers flexibility in the choice of which response equations (analogous to Eq. 3.45, but in terms of the density matrix) to solve, and of which orders. These 'rules' range from the simplest, but highest-order $n+1$ rule to the more complicated, lower-order $2n+1$ rule (due to Wigner), through intermediate rules of the form $(k+n)+1$.


where $k$ is here the the highest-order equation to be solved involving the first field, and $n$ the highest-order equation to be solved involving the remaining fields. Since response equations are solved iteratively, typically over 10–20 iterations, whereas the subsequent contraction of response functions is non-iterative, the ’rule’ with the lowest number of equations will in most cases be preferred.

In paper II we present results obtained using the $(0+2)+1$ rule for a quadratic response, the geometrical polarizability gradient, which is a third-order quasi-energy derivative

$$\frac{d}{dR} \alpha(-\omega, \omega) = -\frac{d}{dR} \langle \mu; \mu \rangle \omega = -\frac{d}{dR} \frac{d}{dF_0} \frac{d}{dF_0} Q = -Q^{RF}_{0,0,0}, \quad (4.1)$$

where $R$ collectively denotes the nuclear coordinates, $F_\omega$ is the $\omega$-frequency component of the electric field, and $\alpha(-\omega, \omega)$ the polarizability. By using the $(0+2)+1$ rule — that is, zero order $R$, second order in $F_\omega^*, F_\omega$, rather than the $(1+1)+1$ rule, we avoid the very numerous equations for the nuclear coordinates, and are left with solving 9 electric field equations (3 first-, 6 second-order). Within the so-called double-harmonic Born-Oppenheimer approximation, where only the linear term in the quadratic potential energy surface responds to the fields, the polarizability gradient Eq. 4.1 can be used to calculate the intensities of the stimulated vibrational transitions occurring in coherent anti-Stokes Raman scattering spectroscopy.

In paper III, also within the double-harmonic approximation, we have calculated the so-called pure-vibrational corrections to the static second hyperpolarizability (cubic response) $\gamma(0, 0, 0, 0)$, which is a fourth-order quasi-energy derivative

$$\gamma(0, 0, 0, 0) = -\langle \langle \mu; \mu, \mu \rangle \rangle_{0,0,0} = -\frac{d}{dF_0} \frac{d}{dF_0} \frac{d}{dF_0} Q = -Q^{FFFF}_{0,0,0,0}. \quad (4.2)$$

The corrections are determined by the geometry derivatives of the dipole moment $\mu$, static polarizability $\alpha(0, 0)$ and static first hyperpolarizability $\beta(0, 0, 0)$

$$\frac{d}{dR} \mu = -\frac{d}{dR} \frac{d}{dF_0} Q = -Q^{RF}_{0,0}, \quad (4.3)$$

$$\frac{d}{dR} \alpha(0, 0) = -\frac{d}{dR} \langle \langle \mu; \mu \rangle \rangle_{0,0} = -\frac{d}{dR} \frac{d}{dF_0} \frac{d}{dF_0} Q = -Q^{RFF}_{0,0}, \quad (4.4)$$

$$\frac{d}{dR} \beta(0, 0, 0) = \frac{d}{dR} \langle \langle \mu; \mu, \mu \rangle \rangle_{0,0,0} = -\frac{d}{dR} \frac{d}{dF_0} \frac{d}{dF_0} \frac{d}{dF_0} Q = -Q^{FFFF}_{0,0,0,0}, \quad (4.5)$$

which we, as in paper II, have calculated using the $(0+1)+1$, $(0+2)+1$ and $(0+3)+1$ rules, respectively, solving a total of 19 equations (3 first-, 6 second- and 10 third-order).
In paper IV, we present calculations of the Cotton-Mouton effect, which occurs when light passes through a sample of molecules in a static magnetic field. A beam entering with linear polarization will, depending on the field strength and the angle between the field and the beam’s polarization, become elliptic (see Sec. 3.2) as it passes through the medium. This is called linear birefringence, which means that the index of refraction is different for beams polarized parallel and perpendicular to the magnetic field. The effect is described by the Cotton-Mouton constant $mC$, which has two contributions: a temperature-dependent orientation term $\Delta[\alpha \xi]$, and a temperature-independent term $\Delta \eta$

$$mC = \frac{2\pi N_A}{27} \left( \Delta \eta + \frac{2}{15kT} \Delta[\alpha \xi] \right), \quad (4.6)$$

where $\Delta[\alpha \xi]$ is the anisotropy of the product of the polarizability $\alpha(-\omega, \omega)$ and the static magnetizability $\xi(0, 0)$, both of which are linear responses, and $\Delta \eta$ is the anisotropy of the hyper-magnetizability $\eta(-\omega, \omega, 0, 0)$, which is a cubic response

$$\alpha(-\omega, \omega) = -\langle \langle \mu; \mu \rangle \rangle_o = -\frac{d}{dF} \frac{d}{dF} Q = -Q^{FF}, \quad (4.7)$$

$$\xi(0, 0) = -\langle \langle m; m \rangle \rangle_0 + \xi = -\frac{d}{db} \frac{d}{db} Q = -Q^{BB}; \quad (4.8)$$

$$\eta(-\omega, \omega, 0, 0) = -\langle \langle \mu; m, m \rangle \rangle_{0,0} + \langle \langle \mu; \mu, \xi \rangle \rangle_{0,0}$$

$$\Delta[\alpha \xi] = \sum_{ij} (\alpha_{ij} \xi_{ij} - \frac{1}{3} \alpha_{ii} \xi_{jj}); \quad (4.10)$$

$$\Delta \eta = \frac{1}{5} \sum_{ij} (\eta_{ij} - \frac{1}{3} \eta_{ii} \xi_{jj}). \quad (4.11)$$

In the calculation of $\eta$, we have used the (1+2)+1 rule, solving a total of 21 response equations (6 first- and 15 second-order). Our calculations are the first on this effect employing magnetic-field-dependent so-called London AOs (or gauge-including AOs), which provide improved basis set convergence, and gauge-origin independent results, as explained in paper IV.

Paper V, the last paper included in this thesis, presents calculations on another linear birefringence, the electric-field-gradient induced birefringence, or Buckingham effect, which is a change in the ellipticity of a beam passing through a sample in the presence of an electric field gradient. It is described by the quantity $s$, which has temperature-independent and -dependent con-
tributions
\[ s = b(\omega) + \frac{1}{kT} \left\{ \sum_{ij} \Theta_{ij} \alpha_{ij} - \sum_{ijk} \mu_i \left[ A_{j,ij} + \frac{5}{\omega} \epsilon_{ijk} G_{jk}' \right] \right\}, \]

where \( \epsilon_{ijk} \) is the Levi-Civita tensor, and the temperature-independent term \( b(\omega) \) is a combination of three quadratic responses
\[ b(\omega) = \sum_{ij} (B_{ij,ij} - B_{i,ij,j}) - \frac{5}{\omega} \sum_{ijk} \epsilon_{ijk} J'_{ijk}, \tag{4.12} \]
\[ B(-\omega, \omega, 0) = \langle \langle \mu; \mu, \Theta \rangle \rangle_{\omega,0} = -\frac{d}{d\omega} - \frac{d}{d\omega} - \frac{d}{d\omega} Q = -Q^{GFF}_{\omega, -\omega}, \tag{4.13} \]
\[ B(-\omega, \omega, 0) = \langle \langle \mu; \Theta, \mu \rangle \rangle_{\omega,0} = -\frac{d}{d\omega} - \frac{d}{d\omega} - \frac{d}{d\omega} Q = -Q^{GFF}_0, \tag{4.14} \]
\[ J'(-\omega, \omega, 0) = -i \langle \langle \mu; m, \mu \rangle \rangle_{\omega,0} = -\frac{d}{d\omega} - \frac{d}{d\omega} - \frac{d}{d\omega} Q = -Q^{BFF}_{\omega, -\omega}, \tag{4.15} \]

and the temperature-dependent contributions are combinations of the dipole and quadrupole moments, \( \mu \) and \( \Theta \), with the polarizability \( \alpha(-\omega, \omega) \) and two other linear responses
\[ A(-\omega, \omega) = \langle \langle \mu; \Theta \rangle \rangle_{\omega} = Q^{GF}_{\omega, -\omega}, \tag{4.16} \]
\[ G'(-\omega, \omega) = i \langle \langle \mu; m \rangle \rangle_{\omega} = -iQ^{BF}_{\omega, -\omega}. \tag{4.17} \]

For the quadratic responses, we have used the \((0+2)+1\) rule, which means solving 21 electric field equations (6 first-, 15 second-order). Results obtained with London- and conventional AOs are compared, showing a greatly improved basis-set convergence.

The basis for our software implementation is the DALTON program. This code is being developed by a large group of European scientists, and is presently being extended to allow for large-scale SCF calculations in a future release. The techniques developed in this thesis are well-suited for this purpose. The implementation consists of four main components:

Matrix routines
In the Fortran 90 programming language one can define 'derived data types', and arithmetic operations in terms of these. For our type(matrix) we have also implemented aliasing (with reference counting), automatic (de-)allocation, and non-allocated zero matrices. Possible future optimizations could be 1) To hide transpose and scale operations in the derived type (A=3+trps(B) would make A an alias of B, without actually transposing or scaling any matrix elements); 2) Define a so-called
'proxy type' for binary operations, so that for instance C=C+A+B is
executed in one operation (DGEMM) rather than three, without allo-
cating any intermediate matrices; 3) Utilize transpose and point group
symmetry; 4) Distribute matrices in parallel calculations. At present all
(perturbed) matrices are stored and manipulated by the master node.
Only Coulomb-exchange and Kohn-Sham matrices are computed in
parallel. This leads to a significant load imbalance between the master
and slave nodes, which could be avoided.

**Property integrals interface**
DALTON's integral sub-program HERMIT provides an extensive cat-
alog of one-electron integrals, indexed by labels ('XDIPLEN', 'ZMAG-
MOM', etc.), while the various two-electron and Kohn-Sham contrac-
tions are separate calls. Two interface routines combine a list of field
labels ('EL', 'MAG', 'GEO', etc.) with a list of density matrices (a
perturbation expansion of some order) to produce an array of response
function contributions, or an array of Fock matrix contributions. A
third interface routine delivers perturbed overlap matrices.

**Response equation contractor and solver**
Given a list of field labels and associated frequencies, together with
the corresponding density and Fock matrix perturbation expansions,
this routine evaluates the perturbed TDSCF equation and idempotency
condition (see Paper I), then passes the residuals to the response solver,
which returns the solutions. The response solver was implemented by
Sonia Coriani and coworkers\(^5\).

**Response function contractor**
From a list of field labels and associated frequencies, together with the
corresponding density and Fock matrix perturbation expansions, with
vacancies (zeros) for each equation that has not been solved (according
to the \((k+n)+1\) rules), calculate the corresponding response function
(array). From a programming point of view, this is the most com-
licated component, and we have thus far only implemented certain
special cases.

The work on the implementation continues. Here, in the group of Kenneth
Ruud at the University of Tromsø, Radovan Bast is generalizing the inter-

Pawlowski, T. Helgaker, and P. Salek: “Linear-scaling implementation of molecular re-
sponse theory in self-consistent field electronic-structure theory”, J. Chem. Phys. 126,
154108 (2007).
face to the DIRAC program for 2- and 4-component relativistic calculations. Meanwhile, in the group of Poul Jørgensen at the University of Århus, Kasper Kristensen aims to generalize the code to calculate the residues (resonances) of the response functions.