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**Molecular Quadratic Response Properties  
with  
Inclusion of Relativity**

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Platinum acetylide compound used in optical power  
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## Abstract

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This thesis concerns quadratic response properties and their application to properties in Jablonski diagrams such as resonant two-photon absorption and excited state absorption. Our main interest lies in optical power limiting applications, and in this context, molecules containing heavy metal atoms prove superior. Therefore, we are interested in how relativity affects these properties, and in order to address this, a four-component relativistic framework is adopted.

To properly address the molecular properties of interest, both relativistic effects and electron correlation need to be accounted for. These two properties are not additive, and, therefore, correlation needs to be incorporated into the four-component framework. We present the implementation of quadratic response properties at the four-component density functional level of theory. For second-harmonic generation, we have, with numerical examples, demonstrated that correlation and relativity are indeed not additive and that the inclusion of noncollinear magnetization is of little importance. We report that both electron correlation as well as relativity strongly affect results for second-harmonic generation. For example, relativity alone reduces the  $\mu\beta$ -response signal by 62% and 75% for *meta*- and *ortho*-bromobenzene, respectively, and enhances the same response by 17% and 21% for *meta*- and *ortho*-iodobenzene, respectively.

In the four-component framework, we present the implementations of single and double residues of the quadratic response function, which allows for the evaluation of resonant two-photon absorption cross sections and excited state properties. Using these tools, we discuss different levels of approximation to the relativistic Hamiltonian and we demonstrate that for two-photon absorption, a proper treatment of relativistic effects qualitatively alters the spectrum. For example, already for an element as light as neon, significant differences are seen between the relativistic and nonrelativistic spectra as triplet transitions acquire substantial absorption cross sections in the former case.

Finally, quantum mechanics in conjunction with electrodynamics is applied to determine clamping levels in macroscopic samples. The microscopic properties of

the optically active chromophores are determined by response theory, and then, electrodynamics is used to describe the interactions between the chromophores and incident laser pulses. Using this approach a series of molecules have been investigated and their performances have been compared and ranked in order to find novel materials for optical power limiting applications.

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## Populärvetenskaplig sammanfattning

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Då ljus färdas genom ett material kommer ljuset och materialet att ömsesidigt påverka varandra. Ett materials färg är t.ex. relaterad till dess absorption. Vid låga ljusintensiteter kommer denna växelverkan att vara linjär, men då intensiteten ökar alltmer kommer ickeinjära effekter att bli märkbara. Ett exempel på detta är tvåfotonsabsorption, där ett material kan vara genomskinligt i normalt ljus men mörkt eller färgat då det träffas av laserljus.

Denna avhandling behandlar hur kvantmekaniska beräkningar kan användas för att bestämma ickeinjära optiska effekter i olika molekyler. Fokus ligger på hur dessa molekyler kan användas för att skydda optiska sensorer från att bli skadade av laserljus. Många av de molekyler som visat sig framgångsrika i dessa applikationer innehåller tunga metallatomer och för tyngre grundämnen har relativistiska effekter en stor inverkan på egenskaperna. Om man bortser från relativistiska effekter skulle beräkningar visa att guld är silverfärgat, medan den korrekta färgen erhålls då dessa effekter tas i beaktande. Mot denna bakgrund har vi utvecklat metoder för att se hur relativistiska effekter påverkar ickeinjära optiska egenskaper. Vidare illustreras en metod där kvantmekanik tillsammans med elektrodynamik används för att visa hur molekyler ingjutna i glasmaterial växelverkar med en ljuspuls som färdas genom materialet. Detta arbete visar hur man i ett kombinerat ramverk av dessa båda teorier kan simulera egenskaper för ett makroskopiskt objekt genom att man känner till egenskaperna för dess mikroskopiska beståndsdelar.



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## Preface

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This thesis is a compilation of work carried out in the Computational Physics group at the Department of Physics, Chemistry and Biology at Linköping University since May 2003. The first three chapters serve as introduction to the papers included thereafter. Chapter 1 puts the thesis into its context and describes the applications that motivate this work. In the second chapter, the theoretical background is described, and finally, in the third chapter, an example is presented that puts the different pieces of this thesis together.

I would like to take this opportunity to thank some persons without whom these years would not have passed by as fast as they did. First, and foremost, I want to thank my advisor Patrick Norman for providing me with this great opportunity, which has not only introduced me to challenging tasks to work with, but also to many interesting persons and friends. He also deserves many thanks for his guidance, help, and patience during the work leading up to this thesis. I would also like to direct my gratitude to my collaborators, especially Dr. Hans Jørgen Aa. Jensen and Dr. Trond Saue for the projects initiated by them and my secondments in their groups. To Hans Jørgen, a special thanks for arranging my three month stay as research assistant at the Department of Chemistry at University of Southern Denmark within the EU Marie Curie network NANOQUANT.

Beyond the purely scientific, I would like to thank Ingegård Andersson for taking care of most administrative matters and making paper work flow smoothly. Then, last but not least, my friends, both inside and outside academia. Hopefully no one will feel left out, but there are some who deserve a special mentioning: Ulf Ekström for our collaboration and discussions concerning our work on DALTON and DIRAC, Auayporn Jiemchoroj and Magnus Hultell for helpful comments on this thesis, Peter Jaksch and Michael Öster for all our discussions on various topics (not only the ones concerning physics and mathematics), and, of course, to those PhD and Master students, past and present, in the Computational and Theoretical Physics groups who have participated in discussions and joined in on social activities both at work as well as outside.

Finally, I would like to thank the National Graduate School in Scientific Computing (Grant No. 200-02-084), the EU Marie Curie network NANOQUANT, and the Swedish Defence Research Agency (FOI) for funding.

Johan Henriksson  
Linköping, February 2008

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## Contents

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<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Optical Power Limiting . . . . .	2
1.2	Passive Protection and Jablonski Diagrams . . . . .	3
1.3	Active Protection and Spin-transitions . . . . .	4
<b>2</b>	<b>Molecular Electronic-structure Theory</b>	<b>7</b>
2.1	Self-consistent Field Theory . . . . .	7
2.1.1	Wave Function Methods . . . . .	8
2.1.2	Density Functional Theory . . . . .	9
2.1.3	Relativistic Considerations . . . . .	11
2.2	Basis Sets . . . . .	13
2.2.1	Effective Core Potentials . . . . .	15
2.3	Response Theory . . . . .	17
2.3.1	Electric Field Induced Response Functions . . . . .	18
<b>3</b>	<b>Clamping Levels in Optical Power Limiting</b>	<b>23</b>
	<b>Bibliography</b>	<b>29</b>
	<b>List of Publications</b>	<b>35</b>



# CHAPTER 1

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## Introduction

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“Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science.”

AUGUSTE COMTE, *Cours de Philosophie Positive*, 1830

In light of the above quote by Auguste Comte, this thesis seems to make little sense; however, within a hundred years this statement would prove utterly wrong. The late 19<sup>th</sup> and early 20<sup>th</sup> century introduced radical changes in the views on physics and chemistry — on the macroscopic scale, the theory of relativity was introduced and, on the microscopic scale, quantum mechanics made its entry. In the light of these developments, Paul Dirac stated:<sup>14</sup>

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”

The “approximate practical methods” called for are what this thesis is concerned with, more precisely in a context where relativity needs to be incorporated with quantum mechanics.

The definition of a “practical method” is, of course, intimately connected to the accuracy wanted and the computational resources at hand. In the early days of quantum mechanics, crude approximations were needed, but as computers were introduced and grew more complex and capable, so did the applicability of quantum

mechanical calculations. Worth noticing is that this development was predicted as early as 1838 when Charles Babbage, an English mathematician, philosopher, and mechanical engineer who originated the idea of a programmable computer, stated that with such a machine at hand

”All of chemistry, and with it crystallography, would become a branch of mathematical analysis which, like astronomy, taking its constants from observation, would enable us to predict the character of any new compound and possibly the source from which its formation might be anticipated.”

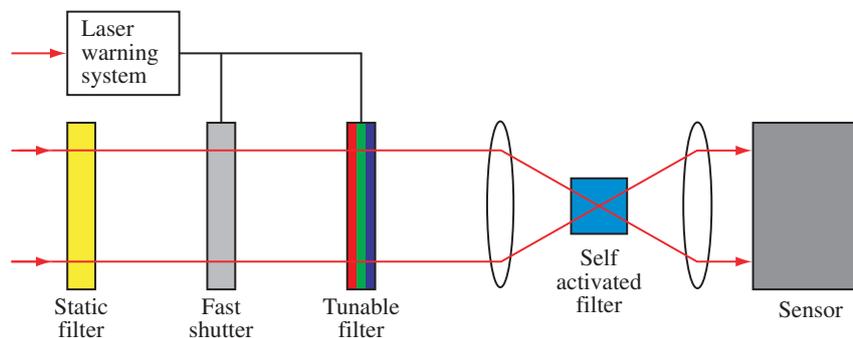
Over the last decades, the advances in computational methods and computer hardware have made Babbage’s vision, to predict properties of novel materials, a reality. For example, today, computations are routinely used to aid interpretation of experimental data as well as predicting properties of new, functionalized, materials before they are even synthesized. In a world where smaller and smaller building blocks are considered when manufacturing devices, accurate computational predictions form valuable and cost effective tools. Some of these tools are treated in this thesis, and the common denominator of the different topics is the strive for a device protecting optical sensors from laser radiation.

## 1.1 Optical Power Limiting

In 1960, the first laser was constructed by Theodore Maiman at Hughes Research Laboratories.<sup>35</sup> Since then, lasers have developed considerably — the intensity has been largely increased, lasers have been made tunable so that they are not locked at a specific wavelength, devices get smaller, etc.<sup>12</sup> All these developments have made lasers powerful tools useful in many applications ranging from high quality spectroscopy through medicine to cutting tools. The intensity and focus of the laser beam, which makes lasers such a useful tool in many applications, poses a potential problem when it comes to optical sensors which might be dazzled, blinded, or even destroyed if subjected to laser radiation. In light of this, a need and demand for optical power limiting devices to protect optical sensors have emerged, and over recent years, the Swedish Defence Research Agency, FOI, has coordinated a collaboration with the goal to develop such a product. Within this collaboration, theoretical modeling of molecular materials has been employed as guidance for which materials to focus on.

The apparent issue when it comes to protecting optical sensors from laser damage is that light in this case is both the origin of information and the cause of damage. For apparent reasons, the source of harm cannot be screened permanently, since then, the optical information one strives to retrieve will also be lost. The key difference between useful and harmful light is the intensity, i.e., laser light is high-intensive, and, thus, it can damage sensors. The task at hand is to create a device (see Figure 1.1<sup>34</sup>) that will allow useful light to enter the system at intensities below the damage threshold, whereas it blocks high-intensive light beyond this threshold.

Since high-intensive lasers might damage a sensor in a single pulse, a self-activated part filter is called for since there is no time to activate a filter upon

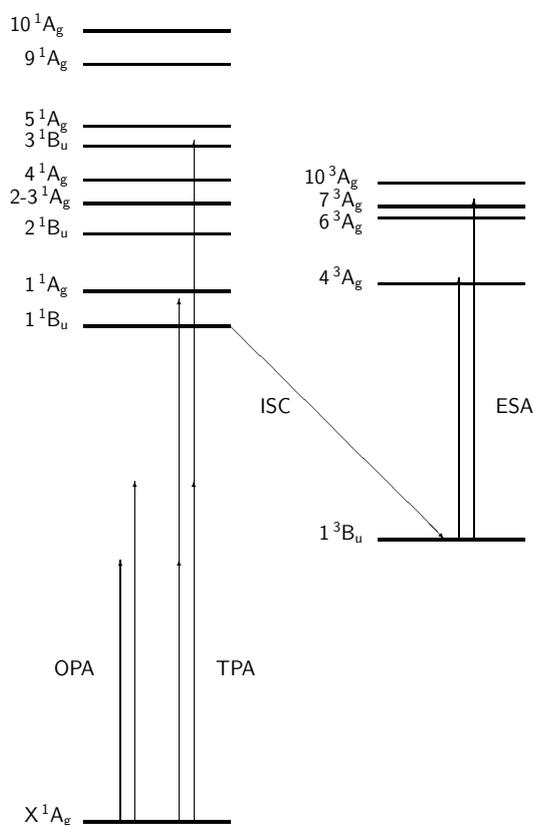


**Figure 1.1.** Schematic layout of a laser protection device under development by the Swedish Defence Research Agency.<sup>34</sup>

detection of an incident laser pulse. This has been successfully achieved using two-photon absorption and processes following,<sup>10,37,42,45,51,52,53</sup> which is further discussed in Section 1.2. Due to saturation, this self-activated part of the device will only be able to block a first pulse, or maybe the first few pulses, but it will not work against continuous lasers or consecutive pulses. Despite saturation, the self-activating part plays a crucial role as it enables for a second, controlled part of the device to be activated. For apparent reasons, the controlled filter has to have a response time shorter than the saturation of the self-activating one, which is why FOI has turned their attention to so-called spin-transition materials. These materials and their functions are outlined in Section 1.3.

## 1.2 Passive Protection and Jablonski Diagrams

Upon light irradiation, a molecule may absorb photons, resulting in an excited molecular state. Figure 1.2, a so-called Jablonski diagram, illustrates different optical properties of the platinum compound studied in Paper VI. As can be seen, one photon is not sufficient to bring this molecule into an excited singlet state, which means that the material will be transparent at low intensities, i.e., when one-photon absorption (OPA) is the dominating process. However, as the intensity increases, the probability of absorbing two or more photons simultaneously becomes significant. Thus, at high intensities, two-photon absorption (TPA) can bring the molecule into an excited state, which is the onset of the filter. Once in an excited state, a rapid relaxation to the lowest excited singlet state follows ( $\tau \sim 1$  ps).<sup>53</sup> From this state, relaxation brings the molecule either back into its ground state ( $\tau \sim 10$  ns) or via an intersystem crossing (ISC) into the triplet state manifold ( $\tau \sim 100$  ns).<sup>53</sup> The triplet state has a significant lifetime ( $\tau \sim 1$   $\mu$ s),<sup>38</sup> and, thus, from here, it is possible to achieve significant OPA within the triplet manifold. This is known as excited state absorption (ESA). Utilizing materials with large TPA cross section and high yield in the ISC open the possibilities to create materials suitable for self-activating protections.



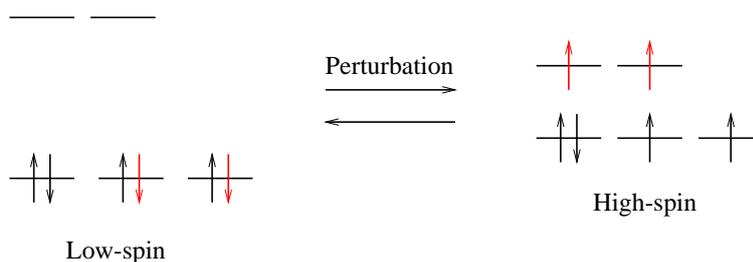
**Figure 1.2.** Jablonski diagram illustrating the absorption processes in a Pt(II) compound. For further details, see Paper VI.

Computational evaluation of properties related to the Jablonski diagram form the main part of this thesis, as will also be further illustrated in Chapter 3. The main focus lies on how relativity affects these properties and how it is included into the calculations. The need to account for this springs from the fact that materials containing heavy metal atoms provide superior ISC yields.<sup>37</sup>

### 1.3 Active Protection and Spin-transitions

The active part of the device sketched in Figure 1.1 is used to provide protection when the self-activated part saturates. The requirement that the controlled part is activated before saturation is reached, eliminates any mechanical solutions or solutions based on liquid crystals since their response times are orders of magnitude too slow. Instead of relying on reconfiguration of entire molecules, like liquid crystals, in order to change the optical properties of a material, the Swedish Defence Research Agency considers the possibility to use the much faster process

of electronic reconfiguration. If the electronic configuration of a molecule can be controlled by external perturbations, and if one configuration is colored whereas the other one is colorless, it will be possible to realize a fast controlled filter. The approach investigated by FOI is to use so-called spin-transition (ST) materials. The concept of such a spin-transition is illustrated in Figure 1.3, where it is shown how reversible transitions between two different electronic configurations can be brought about, all depending on external perturbations such as changes in temperature, pressure, light irradiation, etc. Below follows a brief introduction to the materials investigated by FOI and treated by us in Ref. 23.



**Figure 1.3.** Schematic illustration of the electron configurations of the low-spin and high-spin states.

In atomic iron, the  $3d$ -orbitals are all degenerate, however, if ligands are attached in octahedral coordination, this degeneracy is lifted, and, in the  $O_h$  point group, the three  $3d$ -orbitals of symmetry  $t_{2g}$  will be lower in energy than the two of symmetry  $e_g$ .<sup>6</sup> These orbitals are illustrated in Figure 1.3. If six valence electrons are distributed among these  $3d$ -orbitals, in a weak ligand field, the splitting of the  $t_{2g}$ - and  $e_g$ -orbitals is small, and, thus, Hund's rules apply forming a quintet configuration with four open shells, a high-spin (HS) state. If, on the other hand, the ligand field is strong, the orbital splitting is large and all six electrons are found in the  $t_{2g}$ -orbitals forming a closed-shell, or low-spin (LS), state.<sup>21</sup> In the intermediate case, the state of the system depends on external perturbations. The different electronic structures of the two states are associated with different molecular properties, the most obvious being the change in magnetic properties.

From a practical point of view, the challenge lies in finding materials with suitable optical properties in the two states as well as a switching criterion that enables practical devices. Experiment can be largely aided by computational investigations since the synthesis of the considered spin-transition compounds is tedious. For example, if the absorption spectra of the different states can be calculated, only the most promising systems need to be synthesized, or, if one can assess the relative stability of the high- and low-spin states, candidates not capable of spin-transitions can be ruled out. These topics have been touched upon in Ref. 23, but will not be treated further in this thesis.



## CHAPTER 2

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### Molecular Electronic-structure Theory

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“I think that I can safely say that nobody understands quantum mechanics.”

RICHARD FEYNMAN, *The Character of Physical Law*, 1965

The cornerstone, and starting point, when describing a quantum mechanical system is the quantum mechanical wave equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle. \quad (2.1)$$

This equation gives the possibility to describe matter by wave functions, but analytical solutions exist only for a very limited number of systems. The necessity for approximative solutions were, as quoted in the Introduction, pointed out by Dirac and further emphasized by Gilbert Lewis<sup>32</sup>

”...in the Schrödinger equation we very nearly have the mathematical foundation for the solution of the whole problem of atomic and molecular structure...”

[but]

“...the problem of the many bodies contained in the atom and the molecule cannot be completely solved without a great further development in mathematical technique.”

The tools needed to attack these problems are introduced in this chapter.

### 2.1 Self-consistent Field Theory

The wave equation (2.1) provides the tool for describing quantum mechanical systems, however, as pointed out, approximate methods are necessary and the key issue is to find good approximations. In the following, two different approaches

to tackle this problem are outlined; wave function and density functional theory (DFT) methods. The discussion will only focus on solving the electronic structure problem for fixed nuclear positions, i.e., the Born–Oppenheimer approximation is employed. This approximation states that the quantum mechanical wave equation, to good approximation, can be separated into an electronic part solved for fixed nuclear positions and a nuclear part where the electronic solution is utilized as potential energy surface. The justification for this lies in the fact that the much heavier nuclei move much slower than the electrons.

### 2.1.1 Wave Function Methods

In a fixed nuclear framework, the electronic Hamiltonian of a molecule is

$$\hat{H} = \sum_i \hat{h}_i + \sum_{i>j} \hat{g}_{ij}, \quad (2.2)$$

where  $\hat{h}_i$  is the one-electron part of the Hamiltonian,  $\hat{g}_{ij}$  is the two-electron part, and  $i$  and  $j$  are indices referring to electrons. Given a wave function,  $\psi$ , the energy of a system can be evaluated according to

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (2.3)$$

and if the wave function is constructed such that it contains variational parameters, it is possible to adjust these parameters until the minimum energy is found. Together with the variational principle,<sup>20</sup> which states that for any given wave function,  $\psi$ , the energy functional yields an upper bound of the true ground state energy  $E_0$ , i.e.,

$$E_0 \leq E[\psi], \quad (2.4)$$

where the equality holds if and only if  $\psi$  is the exact ground state wave function.<sup>62</sup> This maps a route toward finding approximate solutions in an iterative fashion.

Turning the attention to the wave function, in a quantum mechanical system containing  $N$  electrons, let these electrons be distributed among  $N$  orthogonal spin-orbitals,  $\phi_i$ . The total wave function can now be constructed from these spin-orbitals under the restriction that a physical wave function is retrieved. One way to achieve this is by forming a Slater determinant<sup>62</sup>

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}, \quad (2.5)$$

where  $\mathbf{r}$  denotes electron coordinates. If, for simplicity, the wave function is constructed from a single Slater determinant, i.e., neglecting electron correlation, we arrive at the Hartree–Fock equations<sup>62</sup>

$$\hat{F}\phi_i = \sum_j \lambda_{ij}\phi_j, \quad (2.6)$$

where  $\lambda_{ij}$  are Lagrangian multipliers and  $\hat{F}$  is the Fock operator

$$\hat{F} = \hat{h} + \sum_j^{\text{occ}} (\hat{J}_j - \hat{K}_j), \quad (2.7)$$

where  $\hat{J}$  and  $\hat{K}$  are the Coulomb and exchange operators, respectively.<sup>62</sup> Equation (2.6) can be diagonalized yielding the canonical Hartree–Fock equations,

$$\hat{F}\phi'_i = \varepsilon_i\phi'_i, \quad (2.8)$$

where  $\varepsilon_i$  are the orbital energies.

So far, the spin-orbitals have only been treated as abstract entities, but in order to be useful in numerical calculations, a concrete form is required. In a molecule, the spin-orbitals will be molecular orbitals, extended over the whole or parts of the molecule. Introducing a basis set (see Section 2.2 for further details) of atomic orbitals,  $\chi_j$ , the molecular orbitals can be expressed as linear combinations thereof,

$$\phi_i = \sum_j c_{ji}\chi_j, \quad (2.9)$$

which finally turns the Hartree–Fock equations into a matrix equation known as the Roothaan–Hall equation,

$$FC = SCE, \quad (2.10)$$

where the Fock matrix elements are given by

$$F_{ij} = \langle \chi_i | \hat{F} | \chi_j \rangle, \quad (2.11)$$

the overlap matrix elements by

$$S_{ij} = \langle \chi_i | \chi_j \rangle, \quad (2.12)$$

all the expansion coefficients  $c_{ij}$  have been collected in  $C$ , and  $E$  is a diagonal matrix with the orbital energies,  $\varepsilon_i$ , as diagonal elements. Given a wave function, the Fock matrix can be constructed, and the generalized eigenvalue problem (2.10) yields a new  $C$ -matrix. This in turn updates the wave function according to Eq. (2.9), and the procedure is repeated until convergence is reached — the so-called self-consistent field method.

### 2.1.2 Density Functional Theory

Above, the wave function formalism was outlined, and as could be seen, every single electron is explicitly accounted for, i.e.,  $N$  sets of electron coordinates have to be dealt with. If instead considering the electron density,

$$\rho(\mathbf{r}) = N \cdot \int \cdots \int |\psi|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N, \quad (2.13)$$

a quantity which is always described by three spatial coordinates, the complexity remains the same regardless of system size. Hence, a tempting thought is to base

a theory on the electron density instead of the wave function. This idea was raised in the very early days of quantum mechanics by both Thomas and Fermi, the so-called Thomas–Fermi theory (see for example Ref. 49 for a detailed discussion). However, this theory, and modifications thereof, proved inadequate and unable to compete with wave function methods. For over thirty years, density based methods were fighting an uphill battle, but this drastically changed in 1964 with the groundbreaking paper by Hohenberg and Kohn.<sup>26</sup> In this paper it is proven that the ground state electron density uniquely determines both the potential defining the system,  $v(\mathbf{r})$ , within an additive constant, as well as the number of electrons,  $N$ , and, thus, all ground state properties. Following this, the ground state energy can be written in terms of density functionals according to

$$\begin{aligned} E[\rho] &= T[\rho] + V_{ee}[\rho] + V_{ne}[\rho] \\ &= T[\rho] + V_{ee}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \\ &= F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \end{aligned} \quad (2.14)$$

where the terms in the first line correspond to the kinetic energy of the electrons and the potential energy terms due to electron-electron and electron-nuclear interactions. Treating the electron-nuclear interaction separately leaves a universal functional,  $F[\rho]$ , valid for any potential and any number of electrons. Furthermore, Hohenberg and Kohn proved that for electronic ground states, the variational principle holds. Any given density  $\rho \geq 0$  will, inserted into the energy functional, provide an upper bound of the ground state energy,  $E_0$ , i.e.,

$$E_0 \leq E[\rho]. \quad (2.15)$$

The paper by Hohenberg and Kohn provided a theoretical foundation for density functional methods, but practical problems still remained since knowledge of the functional form of  $F[\rho]$  was required, or rather of the kinetic energy functional and the functional describing electron-electron interactions. This problem was addressed a year later, in 1965, by Kohn and Sham.<sup>31</sup> As a starting point, they reintroduced the concept of orbitals and considered a system of  $N$  noninteracting electrons in  $N$  orbitals  $\phi_i$ . For such a system, it is possible to find the exact solution to the wave equation

$$\left[ \hat{T} + v_s(\mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i, \quad (2.16)$$

where  $\hat{T}$  is the kinetic energy operator and  $v_s(\mathbf{r})$  is a potential chosen such that

$$\rho(\mathbf{r}) = \sum_i \langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle \quad (2.17)$$

yields the exact electron density of the corresponding interacting system. Using the orbitals introduced, the kinetic energy of the noninteracting system is given by

$$T_s[\rho] = \sum_i \left\langle \phi_i \left| \hat{T} \right| \phi_i \right\rangle. \quad (2.18)$$

Now, returning to Eq. (2.14), using the kinetic energy of the noninteracting system,  $T_s$ , and explicitly accounting for the Coulomb part of the electron-electron interaction,  $J$ , it is possible to rewrite the energy functional (2.14) as

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad (2.19)$$

where the exchange-correlation functional

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) \quad (2.20)$$

has been introduced. An exchange-correlation potential is now defined through

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}, \quad (2.21)$$

which leads to the the Kohn–Sham equations

$$\left[ \hat{h} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (2.22)$$

It is easy to see the resemblance between these equations and the Hartree–Fock ones. The difference is that the exchange term in the Hartree–Fock equations has been replaced by the exchange-correlation term. Thus, it is realized that the machinery established for solving the Hartree–Fock equations, the self-consistent field method, is equally well applicable for solving the Kohn–Sham ones. It should finally be noted that knowledge of the exact exchange-correlation functional will yield the exact density, and, hence, the exact ground state properties of the system under consideration.

### 2.1.3 Relativistic Considerations

Up until now, no reference has been made to whether the quantum mechanical wave equation is nonrelativistic or relativistic. The theory as such has only been presented in terms of the Hamiltonian and its constituent operators. It is first when these operators are investigated, the differences, and, thus, the effects of a relativistic theory, show.

For a free particle, the Schrödinger equation, i.e., the nonrelativistic wave equation, takes the form

$$i\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi, \quad (2.23)$$

which is a first-order differential equation in time but second-order in space. The different orders of derivatives with respect to space and time prevent this equation from being Lorentz covariant, and, hence, it is not consistent with special relativity.<sup>58</sup>

Introducing the concept of the correspondence principle,<sup>59</sup> quantum mechanical operators are to correspond to observables in classical physics. From the action

of operators on plane waves, the quantum mechanical energy and momentum operators are assigned as

$$\hat{E} = i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad \hat{p} = \frac{\hbar}{i} \nabla, \quad (2.24)$$

respectively, and it is seen that the Schrödinger equation for a free particle is in accordance with the energy expression,  $E = p^2/2m$ , from classical mechanics. Along these lines, attempts were made to reach a relativistic wave equation from the relativistic energy expression  $E^2 = (cp)^2 + (mc^2)^2$ . Such an approach was considered already by Schrödinger and later also by several others, leading to what today is known as the Klein–Gordon equation.<sup>60</sup> However, due to the second-order derivative in time, the probability density is not positive definite, and, therefore, the equation was discarded as unphysical.<sup>a</sup>

The negative probability density of the Klein–Gordon equation led Dirac toward an equation linear in both space and time, the equation known as the Dirac equation.<sup>13</sup> For a free electron, the Dirac equation is written as

$$i\hbar \frac{\partial}{\partial t} \psi = \{c\alpha^k \hat{p}_k + \beta mc^2\} \psi, \quad (2.25)$$

where Einstein summation is applied over the index  $k$ . A closer examination shows that the coefficients  $\alpha$  and  $\beta$  are Hermitian matrices and that rank 4 is the smallest dimension satisfying the demands put upon them.<sup>58</sup> The matrices are given by

$$\alpha^i = \begin{pmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathbb{I}_2 & 0 \\ 0 & -\mathbb{I}_2 \end{pmatrix}, \quad (2.26)$$

where  $\sigma^i$  are the Pauli spin matrices. As compared to the Schrödinger equation where the wave functions are scalar functions, the solutions of the Dirac equation have four components, so-called four-spinors. The solutions spanning the four components fall into two categories, two with positive-energy solutions and two with negative ones. The interpretation of the different terms will be outlined below, following the discussion by Schwabl.<sup>58</sup>

Considering an electron at rest, it is seen that the components of the spinor give rise to two positive-energy solutions and two negative ones. (It should be noted that the occurrence of both positive- and negative-energy solutions requires that special attention is paid to the self-consistent field procedure.<sup>57</sup>) In order to continue the interpretation, an electromagnetic field is applied. Due to the vector potential,  $\mathbf{A}$ , this modifies the momentum operator according to

$$\hat{\mathbf{p}} \rightarrow \hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} - \frac{e}{c} \mathbf{A} \quad (2.27)$$

and, furthermore, a term,  $e\Phi$ , related to the scalar potential is added. Hence, in an electromagnetic field, the Dirac equation is<sup>58</sup>

$$i\hbar \frac{\partial}{\partial t} \psi = \{c\alpha^k \pi_k + \beta mc^2 + e\Phi\} \psi. \quad (2.28)$$

---

<sup>a</sup>N.b., it was later discovered by Pauli and Weisskopf<sup>50</sup> that the Klein–Gordon equation properly describes massive particles with spin 0.

Going to the nonrelativistic limit, it is found that the negative-energy solutions are roughly a factor  $v/c$  smaller than the positive-energy solutions, and they are therefore referred to as small- and large-component solutions, respectively.<sup>58</sup> Focusing on the positive-energy solutions, it is seen that the Dirac equation reduces to the so-called Pauli equation,<sup>59</sup> which describes spin added *ad hoc* to nonrelativistic theory. Thus, the Dirac equation intrinsically describes spin, and the components of the four-spinor are

$$\psi = \begin{pmatrix} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{pmatrix}, \quad (2.29)$$

where  $\alpha$  and  $\beta$  refer to spin and  $L$  and  $S$  refer to the large- and small-components.

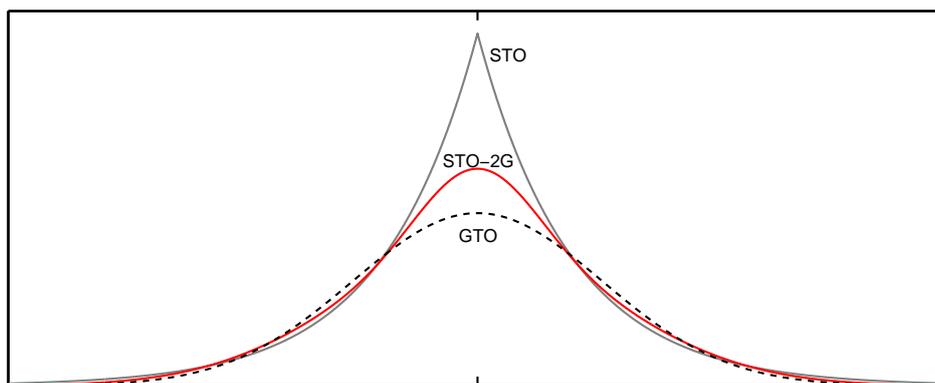
### Reductions of Relativistic Hamiltonians

Computationally, the four-component Dirac equation will, for technical reasons, be about two orders of magnitude more demanding than its nonrelativistic counterpart.<sup>27</sup> Considerable efforts have been put into reducing these costs at the four-component level,<sup>7,33,41,54,56,63,64</sup> but still, these methods are computationally demanding. One of the key issues is the coupling between the large- and small-component bispinors of the four-spinor. Considering the Dirac equation, two types of operators can be identified — even ones that do not couple the large- and small-components, and odd ones that do. In chemical applications in general, the contributions from the small-component bispinor are small.<sup>54</sup> Therefore, methods have been sought that decouple the large- and small-component bispinors of the Dirac equation in order to achieve two two-component equations, where the interest lie in the large-component equation. In the literature, two approaches to decouple the positive energy solutions from the negative ones exist; elimination of the small-component and decoupling by a unitary transformation. Recently, it has been shown that these two methods are equivalent.<sup>27</sup> As for decoupling through a unitary transformation, the idea was introduced by Foldy and Wouthuysen,<sup>18</sup> and detailed accounts of this transformation is, for example, given in the books by Schabl<sup>58</sup> and Strange.<sup>61</sup> The basic idea is that successive application of a unitary transformation will form weaker and weaker couplings between the two components, i.e., reducing the influence of odd operators, at the same time as relativistic correction terms are added. The scalar relativistic correction terms are easily incorporated into nonrelativistic codes, whereas dedicated programs are needed in order to account for couplings between the two spin-components, e.g., spin-orbit coupling. Numerous modifications of the Foldy–Wouthuysen scheme have been proposed, e.g., the Douglas–Kroll–Heß,<sup>15,24,25</sup> Barysz–Sadlej–Snijders,<sup>4,5</sup> and infinite-order two-component<sup>27</sup> Hamiltonians.

## 2.2 Basis Sets

Above, the quantum chemical methods and the underlying equations have been dealt with. However, apart from Eq. (2.9), nothing has been said about the ba-

sis functions,  $\chi$ , and basis sets thereof spanning the matrix equations. From a physical point of view, so-called Slater-type functions,  $e^{-\alpha r}$ , have the same radial dependence as hydrogen orbitals, but, from a computational point of view, they call for numerical integration. If, on the other hand, Gaussian-type functions,  $e^{-\alpha r^2}$ , are used, analytical evaluation of integrals is gained to the cost of the loss of the physical shape of the orbitals. The computational gain in using Gaussian-type orbitals (GTOs) is so high, that in practice, linear combinations of GTOs are used to describe the atomic orbitals. Figure 2.1 illustrates the radial distribution function for a hydrogen 1s-orbital. The true wave function, i.e., the Slater-type orbital (STO), the optimized Gaussian-type orbital (GTO), and an optimized orbital formed by a linear combination of two GTOs (the so-called STO-2G basis set) are plotted for comparison. The plot is only to show the concept, STO-2G is the very simplest Gaussian-type basis set there is, and the more complex and advanced the basis sets, the closer the resemblance to the true orbital. A detailed account of different basis sets is given in Ref. 22.



**Figure 2.1.** Illustration of hydrogenic wave functions for fixed angles and varying  $r$ .

In the nonrelativistic realm, the use of basis sets is straightforward since the wave functions are scalar functions. However, in the relativistic theory, special attention is called for due to the different components in the solutions. Consider two basis sets — one for the large-component and one for small-component spinors. From the Dirac equation for a free particle, Eq. (2.25), it is seen that the two basis sets are connected through the operator  $\sigma^k p_k$ . For basis sets where this connection is fulfilled, the kinetic energy has a maximum,<sup>17</sup> and, in the nonrelativistic limit, any other connection will underestimate the kinetic energy.<sup>16</sup> This gives rise to so-called kinetically balanced basis sets where the small-component basis sets are derived from the large-component ones. It should be noted that kinetic balance makes the use of contracted basis sets nontrivial in relativistic calculations, which is why uncontracted basis sets are widely used.<sup>16</sup>

### 2.2.1 Effective Core Potentials

The cost of an electronic structure calculation using the self-consistent field method outlined depends on the number of electrons treated and the size of the basis sets used. As the number of basis functions increases, so does the computational cost. However, for heavy elements, most of the electrons are situated in the core region and do not contribute significantly to most chemical and spectroscopic properties. Thus, when dealing with such elements, vast savings would be achieved if the effect of the core electrons could be emulated by a potential leaving only the valence electrons to be explicitly accounted for. Effective core potentials (ECPs) provide such an approach.

The concept of effective core potentials was introduced by Kahn and Goddard in 1972.<sup>30</sup> They suggested to replace core electrons with an effective potential

$$U(\mathbf{r}) = \sum_{l,m} U_l(r) |lm\rangle\langle lm|, \quad (2.30)$$

where  $U_l(r)$  is a potential depending on the angular momentum quantum number  $l$  and  $|lm\rangle\langle lm|$  is the angular momentum projection operator (projector). In principle, the summation over  $l$  is infinite, however, in practice  $U_l(r) \approx U_L(r)$  for  $l > L$ , where  $L$  is taken to be the largest  $l$  quantum number in the core.<sup>39</sup> Using the closure relation, this results in the potential

$$U(\mathbf{r}) = U_L(r) + \sum_{l=0}^L \sum_{m=-l}^l [U_l(r) - U_L(r)] |lm\rangle\langle lm|, \quad (2.31)$$

where the first part is referred to as the local part and the second one as the nonlocal part. In accordance with Kahn *et al.*<sup>29</sup> the potential fitting is applied to  $U_L(r)$  and  $[U_l(r) - U_L(r)]$  separately, resulting in different sets of parameters for the local part and each  $l$  of the nonlocal part according to

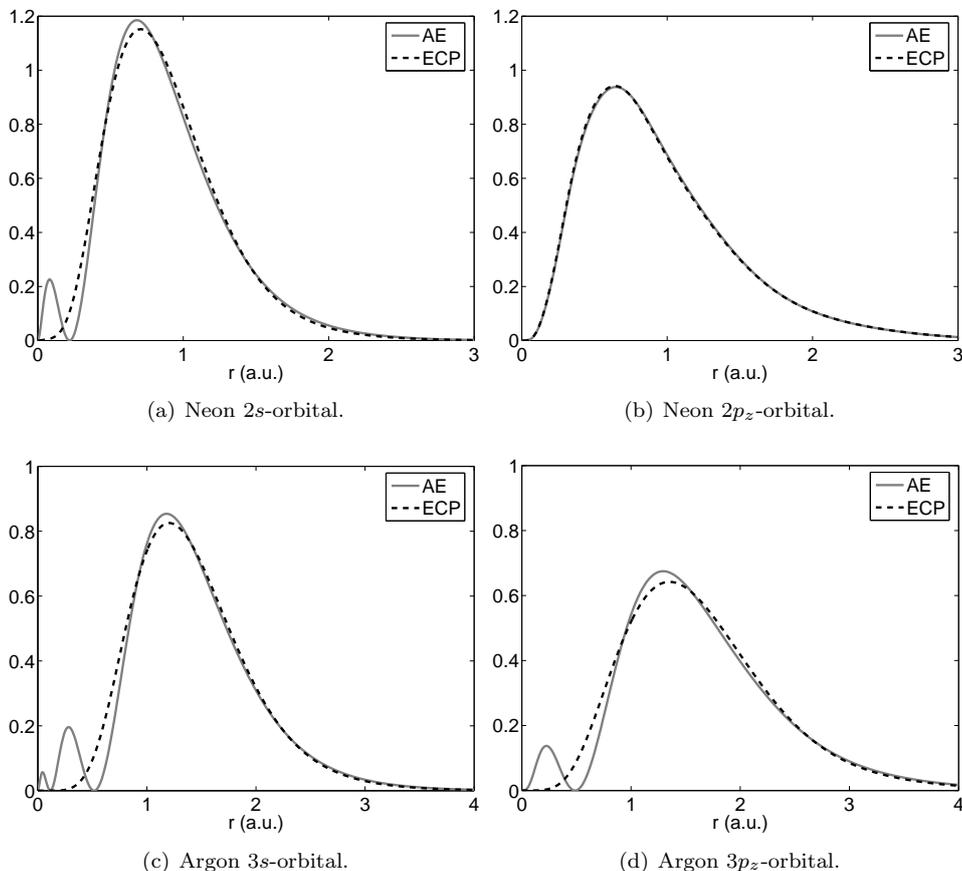
$$r^2 \left[ U_L(r) - \frac{N_c}{r} \right] = \sum_i d_{iL} r^{n_i} \exp(-\xi_i r^2), \quad (2.32)$$

where  $N_c$  is the number of core electrons, and

$$r^2 [U_l(r) - U_L(r)] = \sum_i d_{il} r^{n_i} \exp(-\xi_i r^2), \quad (2.33)$$

respectively.

To show ECPs at work, calculations on neon and argon have been performed at the Hartree–Fock level, and the radial distribution function is illustrated in Figure 2.2. In order to make comparisons between ECP and all-electron calculations, the all-electron basis set is also used as valence basis set for the ECP. It is clearly seen that the valence region is properly described by the ECP. Now, the question arises what happens if an electric field is applied. To show this, a static electric field,  $\mathbf{E} = E\mathbf{e}_z$ , is applied to argon, inducing a dipole moment in the  $z$ -direction,  $\mu_z$ . At a field strength  $E = 0.1$  a.u., the all-electron calculation

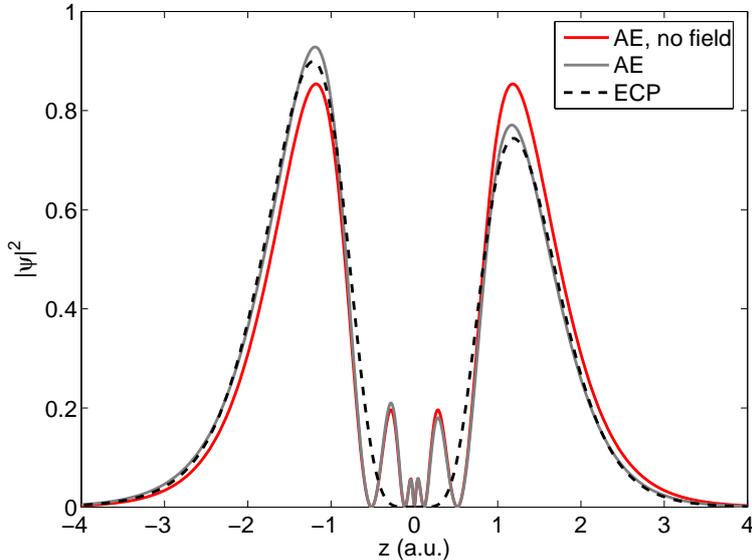


**Figure 2.2.** Comparison between the radial distribution functions for the valence orbitals in neon and argon obtained with all-electron and ECP Hartree–Fock calculations.

yields  $\mu_z = 0.656$  a.u., whereas the ECP calculation yields  $\mu_z = 0.653$  a.u. Thus, it is seen that the ECP manages to describe polarization well. The corresponding  $3s$ -orbital is depicted in Figure 2.3, where  $|\psi|^2$  has been plotted along the  $z$ -axis.

Effective core potentials are of prime interest for heavy elements since these have large numbers of electrons. It is also in heavy elements that relativistic effects are prominent — the heavier the atom, the larger the relativistic effect. This opens for a second important role of ECPs, namely to include indirect relativistic effects. If the potentials are optimized based on relativistic calculations, relativistic effects will be built into the potential, and, thus, also be included when applied in nonrelativistic calculations.

In Paper V we have compared nonrelativistic calculations using ECPs to nonrelativistic and relativistic all-electron calculations. We come to the conclusion that ECPs outperform nonrelativistic calculations also for sensitive properties such as the hyperpolarizability. E.g., the errors in hyperpolarizability of *meta*-di-



**Figure 2.3.**  $|\psi|^2$  of the 3s-orbital in argon plotted along the  $z$ -axis when an electric field  $\mathbf{E} = E\mathbf{e}_z$  with  $E = 0.1$  a.u. has been applied.

iodobenzene compared to full relativistic calculations are reduced from 18% to 7% when an ECP is used to describe iodine in the nonrelativistic calculation. However, when it comes to for example two-photon absorption, the relativistic effects introduced by the ECPs are no longer sufficient to provide good agreement with relativistic calculations. Typically, we see comparable integrated cross sections, but the nonrelativistic calculations are more narrowbanded. In nonrelativistic calculations, triplet excitations are strictly spin-forbidden, whereas at the relativistic level they attain significant cross sections. This drastically broadens the spectra, an effect we have attributed to spin-orbit coupling.

## 2.3 Response Theory

In Section 2.1, the route to solving the wave equation has been outlined for a molecular system described by a time-independent Hamiltonian; now, attention is turned to systems subjected to time-dependent perturbations. Due to the perturbations, the solutions are no longer stationary, and, hence, the molecular properties are affected. The changes in molecular properties, the responses, due to perturbations can, given a variational wave function, be treated using so-called response theory, for which the work by Olsen and Jørgensen<sup>48</sup> is considered the starting point. A reformulation of response theory, including not only variational electronic structure methods but also nonvariational ones, was introduced by Christiansen *et al.*<sup>9</sup> Recently, response theory has also been extended to the near-resonant and resonant regimes by Norman *et al.*<sup>43,44</sup> In the following, only the basic ideas of

response theory will be treated and for further detail the reader is referred to the references listed above.

Consider a time-dependent perturbation of the form

$$\hat{V}^t = \int_{-\infty}^{\infty} \hat{V}^\omega e^{-i\omega t} d\omega, \quad (2.34)$$

which is adiabatically switched on at  $t = -\infty$ . Under the influence of this perturbation, the time-evolution of the electronic reference state can be parameterized using a unitary exponential operator according to<sup>48,55</sup>

$$|\tilde{0}(t)\rangle = e^{i\hat{\kappa}(t)}|0\rangle, \quad \hat{\kappa}(t) = \sum_{a,i} \left( \kappa_{ai} \hat{a}_a^\dagger \hat{a}_i + \kappa_{ai}^* \hat{a}_i^\dagger \hat{a}_a \right), \quad (2.35)$$

where a nonredundant parameterization includes electron transfer from occupied orbitals ( $i$ ) to unoccupied orbitals ( $a$ ). In the relativistic case  $a$  also includes negative energy orbitals (sometimes referred to as positronic orbitals), and the corresponding transfer amplitudes are denoted  $\kappa^{e-e}$  and  $\kappa^{e-p}$ , respectively. In order to solve the time dependence of the state transfer parameters, following the work by Olsen and Jørgensen,<sup>48</sup> the parameters are expanded in a power series over the perturbation and the Ehrenfest theorem is then applied for each order in the perturbation. Since the time evolution of the molecular state is now known, the expectation value of any operator  $\hat{\Omega}$  can be expanded in powers of the perturbation, and the different response functions are identified as the Fourier coefficients in this expansion,<sup>48</sup> i.e.,

$$\begin{aligned} \langle \tilde{0} | \hat{\Omega} | \tilde{0} \rangle &= \langle 0 | \hat{\Omega} | 0 \rangle \\ &+ \int \langle \langle \hat{\Omega}; \hat{V}^{\omega_1} \rangle \rangle e^{-i\omega_1 t} d\omega_1 \\ &+ \frac{1}{2} \int \langle \langle \hat{\Omega}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle \rangle e^{-i(\omega_1 + \omega_2)t} d\omega_1 d\omega_2 \\ &+ \frac{1}{3!} \int \langle \langle \hat{\Omega}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2}, \hat{V}^{\omega_3} \rangle \rangle e^{-i(\omega_1 + \omega_2 + \omega_3)t} d\omega_1 d\omega_2 d\omega_3 \\ &+ \dots \end{aligned} \quad (2.36)$$

### 2.3.1 Electric Field Induced Response Functions

In the applications we focus on, molecules interact with visible or near-visible light, or electromagnetic radiation. The wavelengths of interest are much more extended than the molecules considered, and, hence, to good approximation, the electric vector potential can be assumed to be constant over the entire molecule. This assumption has two implications for the coupling of the electromagnetic field to the molecular properties. First, the electric field is constant over the entire molecule which implies that in an expansion over electric multipole moments, only the molecular dipole moment will couple to the field. Second, no magnetic interactions will be included. Therefore, this is called the electric dipole approximation.<sup>11</sup>

Having established the electric dipole approximation, to second order, the expectation value of the dipole moment becomes

$$\begin{aligned} \langle \tilde{0} | \hat{\mu} | \tilde{0} \rangle &= \langle 0 | \hat{\mu}_\alpha | 0 \rangle \\ &- \int \langle \langle \hat{\mu}_\alpha; F^{\omega_1} \hat{\mu}_\beta^{\omega_1} \rangle \rangle e^{-i\omega_1 t} d\omega_1 \\ &+ \frac{1}{2} \int \langle \langle \hat{\mu}_\alpha; F^{\omega_1} \hat{\mu}_\beta^{\omega_1}, F^{\omega_2} \hat{\mu}_\gamma^{\omega_2} \rangle \rangle e^{-i(\omega_1 + \omega_2)t} d\omega_1 d\omega_2 \\ &+ \dots, \end{aligned} \quad (2.37)$$

which can be compared to the expression<sup>47</sup>

$$\mu(t) = \mu_0 + F^{\omega_1} \alpha_{\alpha\beta}(-\omega_1; \omega_1) + \frac{1}{2} F^{\omega_1} F^{\omega_2} \beta_{\alpha\beta\gamma}(\omega_\sigma; \omega_1, \omega_2) + \dots, \quad (2.38)$$

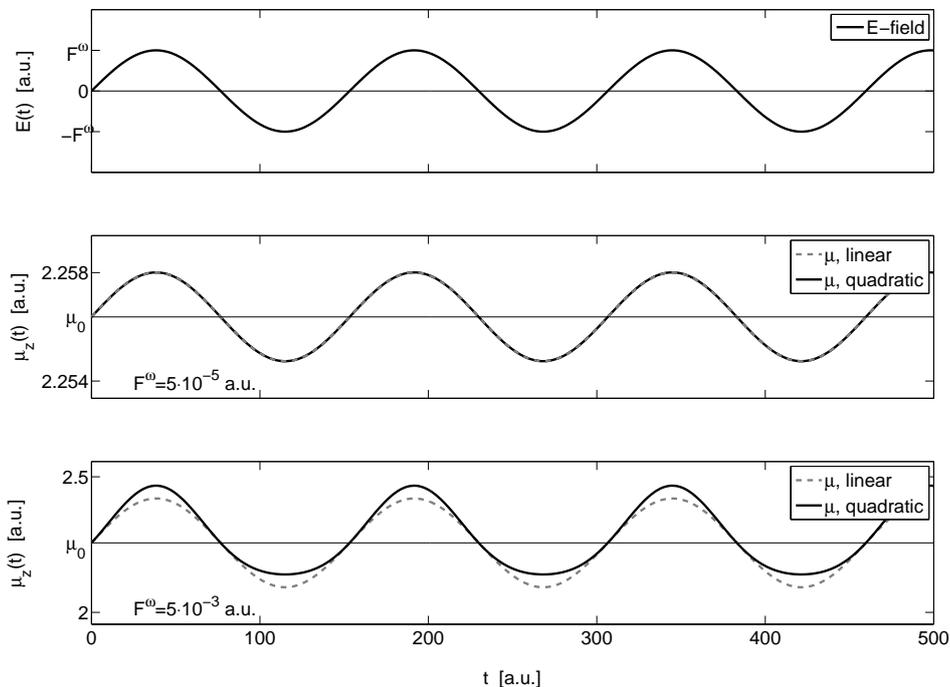
where  $\omega_\sigma = -(\omega_1 + \omega_2)$ . It is seen that the first term in the expansion (2.37) is the permanent dipole moment of the molecule, the second term, the linear response function,  $\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta \rangle \rangle$ , is associated with the polarizability of the system,<sup>47</sup>

$$\alpha_{\alpha\beta}(-\omega; \omega) = -\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta \rangle \rangle_\omega, \quad (2.39)$$

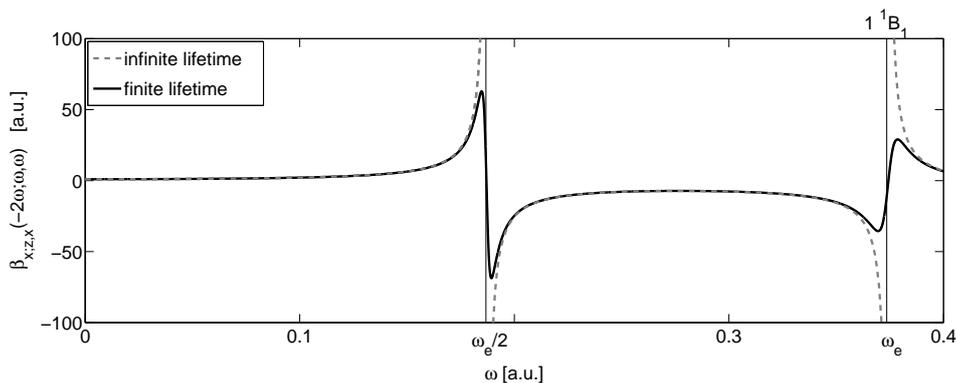
and the third term, the quadratic response function, represents the first-order hyperpolarizability, or for short hyperpolarizability,<sup>47</sup>

$$\beta_{\alpha\beta\gamma}(\omega_\sigma; \omega_1, \omega_2) = \langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{\mu}_\gamma \rangle \rangle_{\omega_1, \omega_2}. \quad (2.40)$$

As an illustrative example, consider a lithium hydride (LiH) molecule and assume an electric field of the form  $\mathbf{E} = F_z^\omega \sin(\omega t)$ . At a weak electric field strength ( $F_z^\omega = 5 \cdot 10^{-5}$  a.u.), the dipole moment follows the oscillations of the electric field, as seen in the mid panel of Figure 2.4. In this plot, the time-dependent dipole moment is plotted both to linear and quadratic order, but the nonlinear contributions are too small to be noticeable. If, on the other hand, the electric field strength is increased by two orders of magnitude, as shown in the lower panel, the nonlinear effects are clearly visible. The dipole moment variations still follow the variations in the electric field, however, in an unsymmetric way. All the above calculations were carried out in the nonrelativistic realm and far away from resonances (the frequency of the electric field is 35% of the lowest singlet state transition frequency). Figure 2.5 shows  $\beta_{x;z,x}(-2\omega; \omega, \omega)$  for water. It is seen that in resonant regions, the response theory formulations by Olsen and Jørgensen<sup>48</sup> and Christiansen *et al.*<sup>9</sup> diverges due to the infinite lifetime approximation.<sup>47</sup> The thin vertical lines indicate the singlet excited state energy at  $\omega_e$  and the corresponding two-photon resonance at  $\omega_e/2$ . To treat resonant regions, the finite lifetime formulation by Norman *et al.*<sup>43,44</sup> has to be adopted, as is illustrated by the solid line in Figure 2.5. It should be noted that in relativistic calculations, triplet state transitions are allowed, and, thus, the response functions diverge in these regions as well.



**Figure 2.4.** LiH molecule in a time-dependent electric field  $\mathbf{E} = F_z^\omega \sin(\omega t)$ . The uppermost plot shows the time-dependence of the electric field. In the middle, the time-dependent dipole moment is shown in a weak electric field, and it is seen that the nonlinear influence is negligible. In the lower plot, the field strength has been increased such that the nonlinear effects can be clearly seen. The solid line represents the dipole moment up to second order contributions in the electric field strength, whereas the dashed line shows only the linear contribution.



**Figure 2.5.** The dispersion of  $\beta_{x;zx}(-2\omega; \omega, \omega)$  for water. The dashed line adopts the infinite lifetime approximation, and, thus, breaks down at resonance, whereas the solid line shows the effect when finite lifetimes are accounted for.

Through the polarizability, the refraction index and absorption are given by the real and imaginary parts, respectively, and at resonance, the transition moments for one-photon absorption,  $M_{\alpha}^{0 \rightarrow f}$ , are given by<sup>47</sup>

$$\lim_{\omega \rightarrow \omega_f} (\omega_f - \omega) \{-\langle\langle \hat{\mu}_{\alpha}; \hat{\mu}_{\beta} \rangle\rangle_{\omega}\} = M_{\alpha}^{0 \rightarrow f} \langle f | \hat{\mu}_{\beta} | 0 \rangle. \quad (2.41)$$

Going to the nonlinear regime, analogously, evaluating the residue of the quadratic response function yields the two-photon transition matrix elements<sup>47</sup>

$$\lim_{\omega_2 \rightarrow \omega_f} (\omega_f - \omega_2) \langle\langle \hat{\mu}_{\alpha}; \hat{\mu}_{\beta}, \hat{\mu}_{\gamma} \rangle\rangle_{\omega_1, \omega_2} = S_{\alpha\beta}^{0 \rightarrow f}(\omega_{\sigma}) \langle f | \hat{\mu}_{\gamma} | 0 \rangle \quad (2.42)$$

whereas from the double residue,

$$\begin{aligned} & \lim_{\substack{\omega_1 \rightarrow \omega_{f_1} \\ \omega_2 \rightarrow \omega_{f_2}}} (\omega_{f_1} - \omega_1)(\omega_{f_2} - \omega_2) \langle\langle \hat{\mu}_{\alpha}; \hat{\mu}_{\beta}, \hat{\mu}_{\gamma} \rangle\rangle_{\omega_1, \omega_2} \\ &= \langle 0 | \hat{\mu}_{\beta} | f_1 \rangle \langle f_1 | \bar{\hat{\mu}}_{\alpha} | f_2 \rangle \langle f_2 | \hat{\mu}_{\gamma} | 0 \rangle, \end{aligned} \quad (2.43)$$

the entity  $\langle f_1 | \bar{\hat{\mu}}_{\alpha} | f_2 \rangle$  is identified as the excited state dipole moment if  $|f_1\rangle = |f_2\rangle$  and the excited state transition moment if  $|f_1\rangle \neq |f_2\rangle$ .

Using the transition moments and transition matrix elements above, the cross section for a transition, i.e., its probability, can be evaluated. For the one-photon case this is given by the oscillator strength, and, in order to compare with gas phase results an orientationally averaged value is given by

$$\delta_{\text{OPA}} = \frac{2}{3} \omega_{0f} \sum_{\alpha} M_{\alpha}^{0 \rightarrow f} [M_{\alpha}^{0 \rightarrow f}]^*. \quad (2.44)$$

In the two-photon case the situation is more complex. For a randomly oriented sample, the two-photon absorption cross section is<sup>36,40</sup>

$$\begin{aligned} \delta_{\text{TPA}} = \frac{1}{30} \sum_{\alpha, \beta} \left\{ & F S_{\alpha\alpha}^{0 \rightarrow f} \left( \frac{\omega_f}{2} \right) \left[ S_{\beta\beta}^{0 \rightarrow f} \left( \frac{\omega_f}{2} \right) \right]^* \\ & + G S_{\alpha\beta}^{0 \rightarrow f} \left( \frac{\omega_f}{2} \right) \left[ S_{\alpha\beta}^{0 \rightarrow f} \left( \frac{\omega_f}{2} \right) \right]^* \\ & + H S_{\alpha\beta}^{0 \rightarrow f} \left( \frac{\omega_f}{2} \right) \left[ S_{\beta\alpha}^{0 \rightarrow f} \left( \frac{\omega_f}{2} \right) \right]^* \right\}, \end{aligned} \quad (2.45)$$

where  $F$ ,  $G$ , and  $H$  are factors depending on the polarization of the two photons. If both photons come from the same monochromatic source, in the linearly polarized case  $F = G = H = 2$ , whereas in the circularly polarized one  $F = -2$  and  $G = H = -3$ . With these properties defined, it is now possible to address the absorption spectra, and, thus, the properties in the Jablonski diagram as discussed in Section 1.2.

The quadratic response function and its residues form the foundation for all papers included in this thesis. Papers I and II are the most fundamental ones, dealing with the implementation of the quadratic response functions at the four-component relativistic density functional level of theory. In previous work by

Norman and Jensen<sup>46</sup> the quadratic response function has been implemented at the four-component relativistic Hartree–Fock level. With this as a starting point, the extension to DFT, i.e., the contribution from the exchange-correlation functional, is dealt with. In Paper I, spin-polarization is neglected whereas in Paper II, noncollinear magnetization is included.

Papers III and IV report the implementations of the single and double residues of the quadratic response function, which allows for the evaluation of resonant two-photon absorption cross sections and excited state properties. The implementations described are based on the quadratic response function for a Kramers-restricted Hartree–Fock wave function.<sup>46</sup> However, the implementations as such are open-ended and require no modifications in order to be compatible with DFT, and, thus, the recent implementations described in Papers I and II.

In Paper V, a detailed investigation of the influence of relativity on quadratic response functions and two-photon absorption is carried out. The quadratic response functions are evaluated at different levels of approximation ranging from nonrelativistic calculations through effective core potentials to a full four-component treatment using the Dirac–Coulomb Hamiltonian. The effects, benefits, and shortcomings of core potentials has already been discussed in Section 2.2.1.

Finally, in Paper VI, quantum mechanical absorption calculations are used together with electromagnetic pulse propagation in order to describe the macroscopic behavior of optically active materials. This will be discussed in greater detail in Chapter 3, where the essence of this thesis is put into an illustrative example.

## CHAPTER 3

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### Clamping Levels in Optical Power Limiting

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“Erwin kann mit seinem Psi  
kalkulieren wie noch nie.  
Doch wird jeder gleich einsehn:  
Psi lässt sich nicht recht verstehn.”

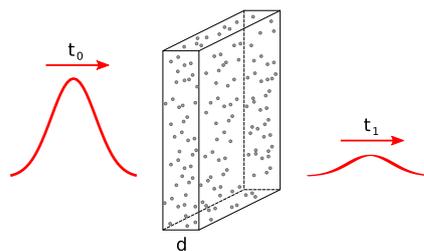
ERICH HÜCKEL

“Erwin with his psi can do  
calculations quite a few.  
But one thing has not been seen:  
Just what does psi really mean?”

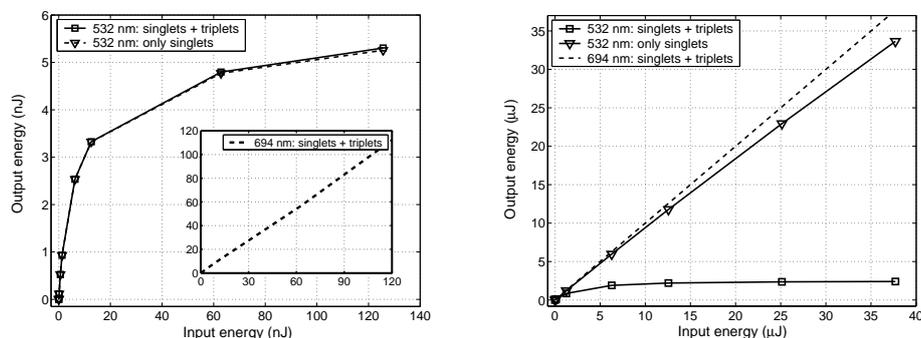
English translation by FELIX BLOCH

Our quantum mechanical calculations treat isolated molecules at zero temperature. Solvation effects and finite temperatures can be accounted for in different ways, but have not been included in our investigations. The coupling to phenomena on the macroscopic scale, e.g., the interaction between an optically active material and an electromagnetic field, has attracted less attention in the literature. However, a framework for the latter situation has been laid down in the work by Gel'mukhanov and co-workers.<sup>1,2,19</sup> This work introduces pulse propagation through a medium containing optically active molecules. A proof of principle is presented in Paper VI and the following chapter is an illustrative example of this concept based on this paper as well as the continuation thereof.<sup>3</sup>

At time  $t_0$ , a laser pulse approaches an optically active material and at time  $t_1$  it has passed through the material, see Figure 3.1. If the properties of the incident laser pulse and the material are known, the question arises: What are the properties of the pulse at  $t_1$ ? As the laser pulse propagates through the material, which consists of randomly oriented optically active



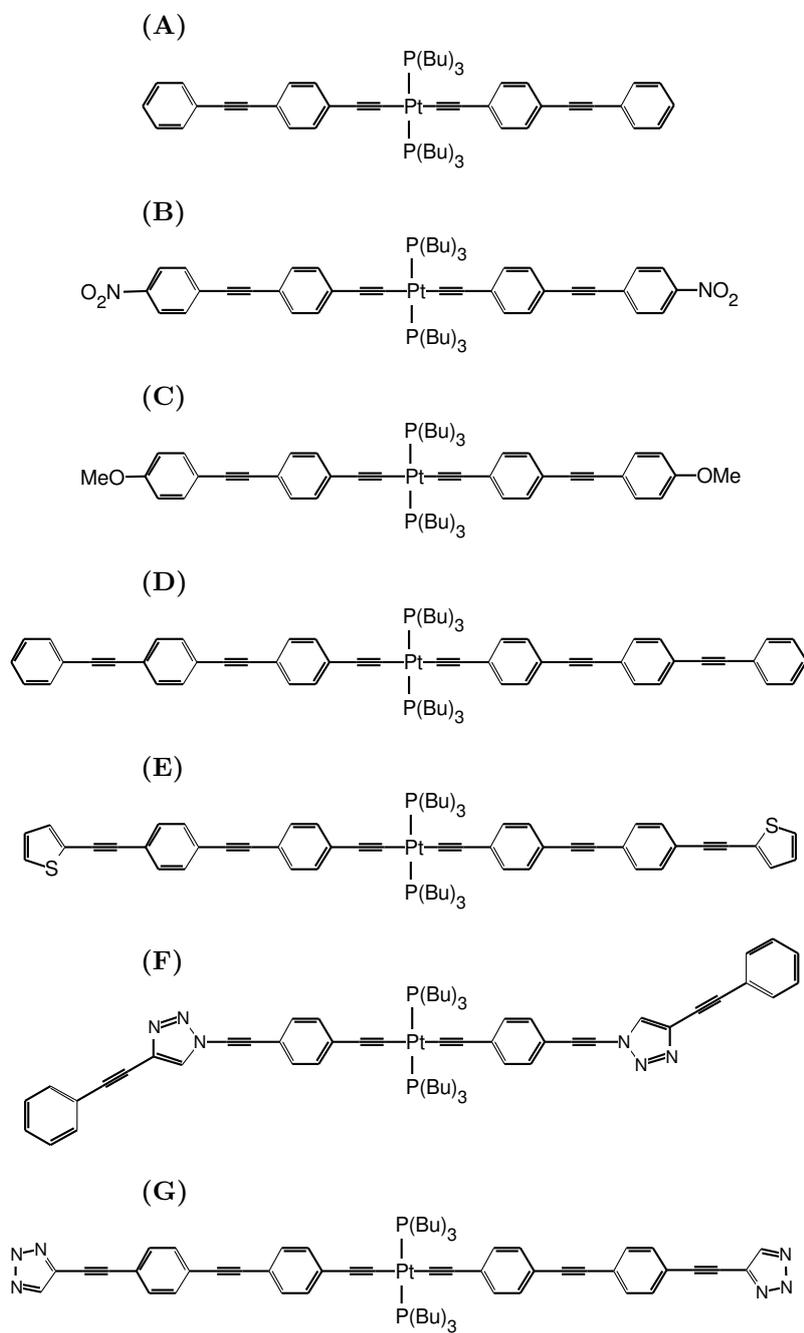
**Figure 3.1.** At time  $t_0$ , a laser pulse approaches an optically active material. As it passes through the material, the pulse interacts with the materials, and as it has passed through the material at time  $t_1$ , its properties have been altered.



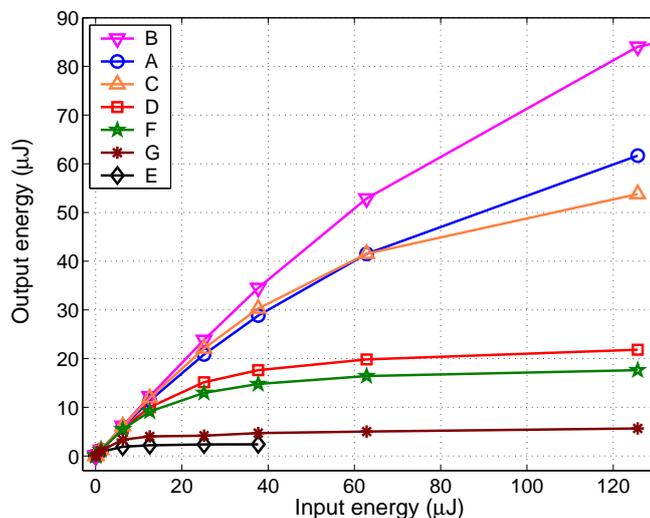
**Figure 3.2.** Simulated clamping levels for the Pt(II) compound seen in Figure 3.3(E). The simulations are performed for a 1 mm thick sample with a chromophore concentration of 0.02 M. Two wavelengths, 532 and 694 nm, are considered. On the left, the pulse duration is 100 fs, whereas on the right it is 10 ns. The need to include excited state absorption in the triplet state manifold is clearly seen.

molecules, chromophores, embedded in a host material, its properties are altered. Assuming that the pulse is a plane wave, this interaction is described by the paraxial wave equation<sup>28</sup> which couples the amplitude function,  $\mathcal{E}(\mathbf{r}, t)$ , of the electric field to the polarization of the material,  $\mathcal{P}(\mathbf{r}, t)$ . The polarization of the material has one contribution from the host material and one from the chromophores, where the former is assumed to have no influence on the nonlinear characteristics of the material. The part associated with the chromophores depends on the molecular properties, and it is here the link to quantum chemistry enters. The parameters of the Jablonski diagram determined by calculations enter as input to the Liouville equation,<sup>8</sup> and through the density matrix formulation of quantum mechanics, the polarization due to the chromophores is determined, as described in Paper VI. Thus, the interplay between the macroscopic laser field and the microscopic properties of the chromophores is now defined.

In, for example, the work by McKay *et al.*,<sup>37</sup> it is shown experimentally that  $\pi$ -conjugated platinum(II) compounds work as broadband power limiters. Therefore, the Swedish Defence Research Agency has considered materials in this family of molecules for power limiting applications. One such chromophore that has proved promising in experiments is the one seen in Figure 3.3(E). Therefore, this molecule was used as test case in the proof of principle presented in Paper VI. The properties of the Jablonski diagram, see Figure 1.2, have been evaluated by first principles quantum chemical calculations, and the simulated clamping levels for different pulses are shown in Figure 3.2. Two different wavelengths, 532 and 694 nm, are considered for two different pulse durations, and it is obvious that this particular chromophore is only suitable for the shorter of the two wavelengths. However, of greater interest and importance is the results for the longer pulse, see the right panel. At 532 nm, two utterly different results are achieved depending on whether or not excited state absorption in the triplet state manifold is included. On the one hand, as triplets are excluded, linear transmittance is seen, whereas on the other



**Figure 3.3.** Molecular structure of Pt(II)-compounds used in clamping level simulations.



**Figure 3.4.** Simulated clamping levels for the Pt(II) compounds in Figure 3.3. The simulations consider 1 mm thick samples with a chromophore concentrations of 0.02 M subjected to 10 ns long laser pulses at 532 nm.

hand, when included, a rapid clamping is achieved. This behavior is attributed to excited state triplet absorption close to 532 nm. The calculated clamping level is in good agreement with experiments carried out by FOI. Unfortunately, these results are classified and a direct comparison cannot be presented.

The above results show the significance of the combined theoretical framework based on quantum mechanics in conjunction with pulse propagation based on electrodynamics. Molecular quantum mechanics alone is not able to predict the clamping levels, e.g., the extent of the importance of the triplet state excitations cannot be foreseen. Now, a direct connection can be made between macroscopic clamping levels and microscopic properties of the chromophores, which enables the possibility to design molecular materials suitable for a particular purpose. Not only does this provide the means to address clamping levels from molecular properties, but it also enables the ability to find which molecular properties to look for in order to achieve a certain clamping level in a given frequency range.

The molecule investigated in Paper VI show excellent clamping levels, but experimentally it is difficult to solvate in order to manufacture doped sol-gel glass materials. Therefore, an extended survey<sup>3</sup> was pursued where a number of similar chromophores were investigated, see Figure 3.3. Yet again, a sample thickness of 1 mm and a chromophore concentration of 0.02 M was used. The simulated clamping levels for a 10 ns laser pulse are depicted in Figure 3.4. The seven investigated materials split up in two distinct groups, where molecules with longer ligand chains attached to the platinum have lower clamping levels. All four compounds (D, E, F, and G) have triplet excited states close to 532 nm, whereas such features are missing in the other three compounds.

This chapter, compiled from our work in Paper VI and Ref. 3, point out the capabilities of computational chemistry of today. A large number of properties can be accurately addressed on a computational basis, in many cases at a much reduced cost and a large gain in time. In light of this, the developments presented in this thesis form a natural step toward more accurate assessments of properties, enabling even greater detail to be treated. Still, large areas need to be charted out and understood in order properly account for certain effects, but I think it is safe to say that we are at a point where we approach the visions of Charles Babbage (see p. 2). The development we see in computational sciences is rather a useful complement to experiments than, as stated by Comte (see p. 1), a “degradation of that science”.



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- [I] Johan Henriksson, Trond Saue, and Patrick Norman. Quadratic response functions in the relativistic four-component Kohn–Sham approximation. *The Journal of Chemical Physics*, **128**, 024105 (2008).
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**Papers not included in this thesis**

- [VII] Alexander Baev, Pontus Welinder, Robert Erlandsson, Johan Henriksson, Patrick Norman, and Hans Ågren. A quantum mechanical-electrodynamical approach to nonlinear properties: Application to optical power limiting with platinum-organic compounds. *Journal of Nonlinear Optical Physics and Materials*, **16**, 157 (2007).
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