Light Control using Organometallic Chromophores

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Abstract

The interaction between light and organometallic chromophores has been investigated theoretically in a strive for fast optical filters. The main emphasis is on two-photon absorption and excited state absorption as illustrated in the Jablonski diagram. We stress the need for relativistic calculations and have developed methods to address this issue. Furthermore, we present how quantum chemical calculations can be combined with Maxwell’s equations in order to simulate propagation of laser pulses through materials doped with chromophores with high two-photon absorption cross sections. Finally, we also discuss how fast agile filters using spin-transition materials can be modeled in order to accomplish theoretical material design.
Preface

The thesis following is a summary of my work in the Computational Physics group at the Department of Physics, Chemistry and Biology at Linköping University since May 2003. A brief introduction to the theoretical background of my work will serve as an introduction to the papers included thereafter.

I would like to take this opportunity to give some special thanks to 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 resulting in this thesis. Second, I would like to thank Ingegärd Andersson for taking care of most administrative matters and making paper work flow as smoothly as possible. Then, last but not least, my friends, both inside and outside the university. Hopefully no one will feel left out, but there are some who deserve a special mentioning; Ulf Ekström for helping out with various computer related issues as well as helpful discussions concerning our work on DALTON and DIRAC, Auayporn Jiemchooroj for giving helpful comments on this thesis, and, of course, all of the PhD and Master students, present and past ones, in the Computational and Theoretical Physics groups for discussions, company at coffee and lunch breaks, and other social activities.

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In 1960, the first laser was constructed by Theodore Maiman at Hughes Research Laboratories \cite{maiman1960}. 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, the devices get smaller, etc. \cite{marmo2010}. All these developments have made lasers powerful tools useful in many applications, all from high quality spectroscopy, through medicine to cutting tools. The intensity and focus of the laser beam, which makes lasers so useful in many applications, can of course also be used destructively, e.g., lasers can be used to dazzle, blind, or even destroy optical sensors. In the light of this development, a need and a demand for protection against such laser threats have emerged, and over recent years, the Swedish Defence Research Agency, FöI, have coordinated a collaboration ranging from theoretical modeling, through synthesis and experimental evaluation, to making a final product, a device to protect optical sensors from laser damage. Within this project, we have participated by theoretical modeling of molecular materials suitable for these applications.

One issue when it comes to protection against laser threats is that you deal with light that, for apparent reasons, cannot be screened permanently since then the optical information you strive to retrieve will also be blocked. The difference between these two sources of light is that lasers are high-intensive, and, thus, can damage sensors. Outside the wavelength range of interest, it is, of course, possible to block any incident radiation using a static filter, however, the issue is to create a device (see Figure \ref{fig:filter}) that will allow useful light to enter the system at intensities below the damage threshold, but that will block high intensities beyond this threshold. This requirement puts high demands on the device for several reasons. High-intensive lasers can create damage in a single pulse. Hence, there is no time to activate the filter upon detection of an incident laser pulse, which calls for a self-activating part. This has successfully been achieved using two-photon
absorption and processes following \cite{20}. The problem with this part of the device is that it will saturate, and, therefore, only be able to block a first, or a first few pulses, and not against continuous lasers or consecutive pulses. However, this initial, self-activating, part buys time necessary to activate a second, controlled part of the device triggered by a laser warning system, a part that preferably only filter away the harmful radiation and let other wavelengths through. When it comes to the controlled filter, it has to have a response time shorter than the saturation of the self-activating one, which puts a requirement below one microsecond. Thus, any kind of mechanical solutions or solutions involving liquid crystals are excluded due to their slow response times which are orders of magnitudes too large. Instead, so-called spin-transition (ST) materials have been considered as plausible candidates. Spin-transition materials can be found in either of two states depending on external perturbations, and if the two different states of an ST material have different optical properties, a fast agile filter can be achieved. Contrary to for example liquid crystals, ST materials have fast response times. The reason for this lies in the cause of the property changes. In liquid crystals, a reconfiguration of the nuclei is required, whereas in ST materials, an electronic reconfiguration takes place, and since nuclei are much heavier than electrons, their reconfiguration will be much slower due to their larger inertia.

In the following sections, the passive and active parts of the device mentioned above will be discussed in closer detail.

1.1 Passive Protection and Jablonski Diagrams

Upon light irradiation, a molecule may absorb photons, resulting in an excited molecular state. If the electromagnetic radiation (light) has a period time $T$, then
1.1 Passive Protection and Jablonski Diagrams

the average rate of energy absorbed per unit time is given by

$$\langle R_{\text{abs}} \rangle_T = \int_V \langle j \cdot E \rangle_T \, dr,$$

(1.1)

where \( j \) is the current density in the material, \( E \) is the applied electric field, and \( \langle \ldots \rangle_T \) is the integration over one period of the radiation \[1\]. At low intensities, one photon at the time is absorbed, however, as the intensity increases, nonlinear effects increase and the probability of absorbing two photons simultaneously becomes significant. This is illustrated in Figure 1.2. As the figure show, one-photon absorption (OPA) is insufficient to excite the molecule, however, if two or more photons are absorbed simultaneously, the energy gap can be overcome. This is the first step in the self-activating protection. Since at low intensities this material
does not absorb any photons, it is transparent, but at intensities caused by lasers, it will absorb due to nonlinear effects. Following this two-photon absorption (TPA), a rapid relaxation to the lowest excited singlet state will follow ($\tau \sim 1$ ps) [26]. From this state, the molecule can relax either back to the ground state ($\tau \sim 10$ ns) or via an intersystem crossing (ICS) to the triplet manifold ($\tau \sim 100$ ns) [26]. The triplet state have a significant lifetime ($\tau \sim 1$ $\mu$s) [17], and, thus, from here, it is possible to achieve significant OPA within the triplet manifold. This latter process is known as excited state absorption (ESA). Utilizing a high yield in the ICS opens the possibilities to create materials suitable for self-activating protections, and one way of improving this yield is to introduce metal atoms in the molecules.

1.2 Active Protection and Spin-transitions

In atomic iron, the 3d-orbitals are all degenerate, however, if ligands are attached at octahedric coordination, this degeneracy is lifted, and in the $O_h$ point group, the three 3d-orbitals of symmetry $t_{2g}$ are lower in energy than the two of symmetry $e_g$ [1]. The materials considered by FOI within this project are all based on Fe(II), and, hence, this will serve as example in all the following discussions. Fe(II) has six valence electrons distributed among the 3d-orbitals. In a weak ligand field, the splitting of the $t_{2g}$- and $e_g$-orbitals is small, and Hund’s rules are obeyed forming a quintet configuration with four open shells, a high-spin (HS) structure. 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), structure [8]. The interesting case is the intermediate situation, the situation where an external perturbation will be decisive for which state the system is found in, systems where a so-called spin-transition (ST), or spin-crossover (SC), occur, see Figure 1.3.

![Figure 1.3. Schematic illustration of the electron configurations of the low-spin and high-spin states.](image)

The perturbation can be changes in temperature, pressure, light irradiation, etc., or a combination of the above [2, 9, 25]. Transitions from one state to the other does not only bring about an electronic reconfiguration, but it also yields structural changes as well as changes in the molecular properties. As for structural changes, the bond lengths between the central iron and the ligands increase by about 0.2 Å at the transition from LS to HS [7]. Regarding molecular properties, the most
obvious change is that of the magnetic properties on going from a closed-shell to an open-shell structure, but also, of prime interest in optical filter applications, a change of the spectrum. If one of the states is transparent and the other one is opaque, or colored, at the same time as the ST occurs under reasonable conditions, it will be suitable in the device outlined above.

1.3 Motivation

As mentioned above, our part in this FOI coordinated project is to provide theoretical simulations of molecular properties. In order to contribute, high quality calculations are needed, but as heavy elements are often a part of the molecules considered, relativistic effects needs to be accounted for. However, we have found that relativistic effects play an important role also for lighter elements, e.g., big differences can be seen when comparing relativistic and nonrelativistic calculations of the one- and two-photon spectra of neon (see Paper I). Hence, new methods have been developed and implemented in order to gain a deeper insight into the key properties of the materials investigated. Considering the passive protection, this has resulted in code development in the DIRAC program [4] in order to evaluate TPA and ESA spectra at the relativistic level of theory. Furthermore, different integral approximations have been investigated in order to reduce the vast computing times needed at the relativistic level. This striving for fast, efficient, and accurate descriptions of TPA and ESA at the relativistic level of theory is also the reason for the extensive outline of the effective core potentials, ECPs, since these would provide great computational savings once implemented in the DIRAC program while still taking full account for the valence electron spin-orbit coupling. Furthermore, the outline of density functional theory is not only to describe the different methods used in the papers included, but is also included since another step toward fast and accurate descriptions of molecular properties is to develop methods to evaluate them within this formalism.
The cornerstone, and starting point, when trying to describe any quantum mechanical system is the quantum mechanical wave equation

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

This equation gives the possibility to describe matter by wave functions, however, analytical solutions exist only for a very limited number of systems, and, thus, the theory is of little use unless approximative methods can be applied.

### 2.1 Self-consistent Field Theory

The wave equation (2.1) provides the tool for describing quantum mechanical systems, however, as already have been pointed out, approximate methods are necessary, and the key issue is how to find good quality approximations. Following, two different approaches to tackle this problem are outlined; wave function methods and density functional theory (DFT).

#### 2.1.1 Wave Function Methods

Since nuclei are much heavier than electrons, their motion is much slower, and, thus, this provides justification for the Born–Oppenheimer approximation which states that a quantum mechanical wave equation, to good approximation, can be separated into one electronic part solved for fixed nuclear positions and one nuclear part where the electronic solution is utilized as potential energy surface. For a molecule this yields the electronic Hamiltonian

\[ \hat{H} = \sum_i \hat{h}_i + \sum_{i>j} \hat{g}_{ij}, \] (2.2)
where $\hat{h}_i$ is the one-electron part, $\hat{g}_{ij}$ is the two-electron part, and $i$ and $j$ refer to electrons.

Given a wave function, the energy of a system can be evaluated according to

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

(2.3)

and if the wave function is constructed such that it contains variational parameters, it is possible to adjust these parameters until the best approximation of the energy is found. It should be noted that special attention needs to be paid to this procedure in the relativistic case due to the positronic solutions [27]. Together with the variational principle, which states that for any given wave function, $\psi$, the energy functional yields an upper bound for the true ground state energy, $E_0$, i.e.,

$$E_0 \leq E[\psi],$$

(2.4)

where the equality holds if and only if the wave function is the exact one [29]. This maps a route toward finding approximate solutions in an iterative fashion.

So far, focus has been on the wave equation itself and it is time to turn the attention to the wave functions used. In a quantum mechanical system containing $N$ electrons, let the 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 convenient way to achieve this is by forming a so-called Slater determinant [29]

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_N(r_1) \\
\phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(r_N) & \phi_2(r_N) & \cdots & \phi_N(r_N)
\end{array} \right|,$$

(2.5)

where $r$ denote the 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 [29]

$$\hat{F}_i \phi_i = \sum_j \lambda_{ij} \phi_j,$$

(2.6)

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

$$\hat{F}_i = \hat{h}_i + \sum_j (\hat{J}_j - \hat{K}_j),$$

(2.7)

where $\hat{J}$ and $\hat{K}$ are the Coulomb and exchange operators, respectively [29]. Equation (2.6) can be diagonalized yielding the so-called canonical Hartree–Fock equations,

$$\hat{F}_i \phi_i' = \epsilon_i \phi_i',$$

(2.8)

where $\epsilon_i$ may be interpreted as orbital energies.
2.1 Self-consistent Field Theory

If a basis set of atomic orbitals, $\chi_i$, is introduced and the molecular orbitals are expressed as linear combinations thereof,

$$\phi_i = \sum \alpha c_{\alpha i} \chi_\alpha,$$

(2.9)

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

$$FC = SCE,$$

(2.10)

where the Fock matrix elements are given by

$$F_{ij} = \langle \chi_i | \hat{F} | \chi_j \rangle,$$

(2.11)

the overlap matrix elements by

$$S_{ij} = \langle \chi_i | \chi_j \rangle,$$

(2.12)

all the expansion coefficients have been collected in $C$, and $E$ is a diagonal matrix with $\epsilon_i$ as diagonal elements. Given a wave function, the Fock matrix can be constructed, and the generalized eigenvalue problem (2.10) can be solved yielding a new $C$-matrix. This in turn will update the wave function according to (2.9), and the procedure can be 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, explicit account is taken to every single electron, i.e., $N$ electron coordinates have to be dealt with. If instead considering the electron density,

$$\rho(r) = \int \cdots \int |\psi|^2 dr_2 \cdots dr_N,$$

(2.13)

a quantity which always is described by three spatial coordinates, and, thus, its complexity remains the same regardless of system size. Hence, a tempting idea would be 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. [23] for a detailed discussion), however, this theory, and modifications thereof, proved inadequate in order to compete with wave function methods. The scene drastically changed in 1964 with the groundbreaking paper by Hohenberg and Kohn [10]. In this paper they proved that the ground state electron density uniquely determines the potential defining the system, $v(r)$, 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

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{ne}[\rho]$$

$$= T[\rho] + V_{ee}[\rho] + \int v(r)\rho(r)dr$$

$$= F[\rho] + \int v(r)\rho(r)dr,$$

(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. Explicitly dealing with the electron-nuclear interaction 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.,

\[ E_0 \leq E[\rho]. \tag{2.15} \]

The paper by Hohenberg and Kohn cleared the road for density functional methods, but still big problems remained since knowledge of the functional form of \( F[\rho] \) was required, or rather of the kinetic energy functional and the functional describing the electron-electron interactions. This problem was addressed a year later, in 1965, by Kohn and Sham [14]. As a starting point, they considered a system of \( N \) noninteracting electrons in \( N \) orbitals \( \phi_i \). For such a system, it is possible to solve the wave equation exactly

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

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

\[ \rho(\mathbf{r}) = \sum_i \langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}) \rangle \tag{2.17} \]

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

\[ T_s[\rho] = \sum_i \left\langle \phi_i \left| \hat{T} \right| \phi_i \right\rangle. \tag{2.18} \]

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

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

where the exchange-correlation functional

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

has been introduced. Following, an exchange-correlation potential is defined through

\[ v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \tag{2.21} \]

which leads to the the Kohn–Sham equations

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

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

2.2 Response Theory

For a molecular system described by a time-independent Hamiltonian $\hat{H}_0$, the wave equation

$$\hat{H}_0 |n\rangle = \varepsilon_n |n\rangle$$  \hspace{1cm} (2.23)

can be solved using, for example, the self-consistent field methods outlined in the previous section. Through these solutions, the properties of the system may be computed, however, if the system is subject to a time-dependent perturbation, the solutions of the wave equation are no longer stationary and the properties will be affected accordingly. These changes in molecular properties, or their molecular response, due to the perturbation can, given a variational wave function, be treated using so-called response theory, for which the work by Olsen and Jørgensen [22] is considered the starting point.

Let the perturbation be of the form

$$V^t = \int_{-\infty}^{\infty} V^\omega e^{-i\omega t} d\omega,$$  \hspace{1cm} (2.24)

adiabatically switched on at $t = -\infty$. Under the influence of this perturbation, the time-evolution of the electronic state can be parameterized using a unitary exponential operator according to [22]

$$|\tilde{0}(t)\rangle = e^{i\hat{\kappa}(t)|0\rangle}, \quad \hat{\kappa}(t) = \sum_{i,s} \left( \kappa_{is} a^\dagger_s a_i + \kappa^*_i s a^\dagger_s a_i \right),$$ \hspace{1cm} (2.25)

where a nonredundant parameterization includes electron transfer from occupied electronic orbitals ($i$) to unoccupied electronic, and in the relativistic case also positronic, orbitals ($s$) – 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, they are expanded in a power series of the perturbation and the Ehrenfest theorem is then solved for each order in the perturbation. As the time evolution of the molecular state is known, the expectation value of any operator $\hat{\Omega}$ can now be expanded in powers of the perturbation and the different response
functions are identified as the Fourier coefficients in this expansion \[22\], i.e.,

\[
\langle \tilde{0} | \hat{\Omega} | \tilde{0} \rangle = \langle 0 | \hat{\Omega} | 0 \rangle + \int \langle \langle \hat{\Omega}; \hat{V}_1 \rangle \rangle e^{-i\omega_1 t} d\omega_1 + \frac{1}{2} \int \langle \langle \hat{\Omega}; \hat{V}_1, \hat{V}_2 \rangle \rangle e^{-i(\omega_1 + \omega_2) t} d\omega_1 d\omega_2 + \frac{1}{3!} \int \langle \langle \hat{\Omega}; \hat{V}_1, \hat{V}_2, \hat{V}_3 \rangle \rangle e^{-i(\omega_1 + \omega_2 + \omega_3) t} d\omega_1 d\omega_2 d\omega_3 + \ldots
\]  

(2.26)

In our case, the perturbation is caused by an electric field (light) and as it turns out, both the two-photon absorption as well as the excited state absorption can be calculated through residues of the quadratic response function \[21\]

\[
\langle \langle \hat{\mu}_\alpha; \hat{\mu}_\beta, \hat{\mu}_\gamma \rangle \rangle_{\omega_1, \omega_2}.
\]  

(2.27)

The two-photon transition matrix elements, \( S_{\alpha\beta}^{0-f} \), are calculated using a single residue

\[
\lim_{\omega_2 \to \omega_f} (\omega_f - \omega_2) \langle \langle \mu_\alpha; \mu_\beta, \mu_\gamma \rangle \rangle_{\omega_1, \omega_2} = S_{\alpha\beta}^{0-f} (f | \mu_\gamma | 0),
\]  

(2.28)

and the excited state transition moments \( \langle f_1 | \overline{\mu}_\alpha | f_2 \rangle, \langle f_1 \rangle \neq \langle f_2 \rangle \), is given by the double residue

\[
\lim_{\omega_1 \to \omega_{f_1}} \lim_{\omega_2 \to \omega_{f_2}} (\omega_{f_1} - \omega_1)(\omega_{f_2} - \omega_2) \langle \langle \mu_\alpha; \mu_\beta, \mu_\gamma \rangle \rangle_{\omega_1, \omega_2} = \langle 0 | \overline{\mu}_\beta | f_1 \rangle \langle f_1 | \overline{\mu}_\alpha | f_2 \rangle \langle f_2 | \mu_\gamma | 0 \rangle.
\]  

(2.29)

### 2.3 Effective Core Potentials

The cost of an electronic structure calculation using the self-consistent field methods outlined above depends on the number of electrons treated, and, hence, as the system size increases, so does the computational cost. For heavy elements, most of the electrons are situated in the core, and, hence, they will not contribute significantly to most chemical properties. Thus, when dealing with heavy elements, vast savings would be achieved if one could neglect the core electrons and only consider the valence ones. Effective core potentials (ECPs) is such an approach. ECPs are available in most nonrelativistic quantum chemistry codes, however this is not the case when it comes to relativistic codes. In nonrelativistic codes, ECPs play two important roles, first, as mentioned above, they reduce the number of electrons to treat, and, hence, they facilitate calculations where heavy elements otherwise would post a restriction. Second, they account for large portions of relativistic effects in molecules. It has been shown that in comparing nonrelativistic calculations using ECPs to nonrelativistic and relativistic all-electron calculations, the ECPs outperform the nonrelativistic calculations also when it comes to sensitive properties such as hyperpolarizability. This has been shown in Paper II,
where for example errors in hyperpolarizability of meta-di-iodobenzene compared to full relativistic calculations decrease from 18% to 7% when an ECP is used to describe iodine in the nonrelativistic calculations. 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 the relativistic calculations. Typically, we see comparable integrated cross sections when comparing relativistic and nonrelativistic calculations, however, the nonrelativistic ones are way more narrowbanded. In nonrelativistic calculations, triplet excitations are strictly spin-forbidden, however at the relativistic level they attain significant cross sections. This drastically broadens the spectra, an effect we have attributed to spin-orbit coupling. The above indicates that ECPs contain lots of physics in them concerning relativistic effects, but at the nonrelativistic level of theory accurate calculations are hampered by the lack of for example spin-orbit coupling, whereas, on the other hand, relativistic calculations intrinsically deals with spin-orbit effects but are limited by the number of electrons treated. Hence, we believe that introducing ECPs into a relativistic formalism will provide useful means for accurately treating larger systems containing heavy elements, and, thus, bring relativistic calculations from small test systems to systems of practical interest. Therefore, common ECP theory will be outlined below, mainly following the approach introduced by Kahn and Goddard [13] and the computational scheme by McMurchie and Davidson [18].

The idea introduced by Kahn and Goddard [13] is to replace core electrons with an effective potential

$$U(r) = \sum_{l,m} U_l(r)|lm\rangle\langle lm|,$$  \hspace{1cm} (2.30)

where $U_l(r)$ is a potential depending on the angular momentum quantum numbers $l$, and $|lm\rangle\langle lm|$ is the angular momentum projection operator (projector). In principle, the summation over $l$ is infinite, however, in practice there exists a value, say $l = L$, such that

$$U_l(r) \approx U_L(r), \quad l \geq L.$$  \hspace{1cm} (2.31)

Using the closure relation, this potential form

$$U(r) = U_L(r) + \sum_{l=0}^{L-1} \sum_{m=-l}^{l} [U_l(r) - U_L(r)] |lm\rangle\langle lm|,$$  \hspace{1cm} (2.32)

where the first part is referred to as the local part and the second one as the nonlocal part. The local part will affect all $l$-values equally much, whereas the nonlocal part will be $l$-dependent, and, thus, allow for different orbitals to be modified to a different extent.

Modifying the potential fit suggested by Kahn et al. [12] so that the fitting is applied to $U_L(r)$ and $[U_l(r) - U_L(r)]$ separately results in different, separate, sets of parameters for the local part and for each $l$ of the nonlocal part according to

$$r^2 \left[ U_L(r) - \frac{N_e}{r} \right] = \sum_i d_i L^m e^{-\xi_i r^2},$$  \hspace{1cm} (2.33)
where $N_c$ is the number of core electrons, and

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

(2.34)

respectively.

Before getting into the mathematical details on how to solve ECP-integrals, some illustrations showing their behavior might be helpful. To show ECPs at work, calculations of neon and argon have been performed at the Hartree–Fock level, and the radial distribution function is illustrated in Figure 2.1. The calculations have been carried out so that the all-electron basis set also has been 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, an electric field $\mathbf{E} = E\mathbf{e}_z$ is applied to argon. Using $E = 0.1$ a.u.,
2.3 Effective Core Potentials

A dipole moment is induced in the z-direction, for the all-electron calculation \( \mu_z = 0.656 \) 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 2.2 where \( |\psi|^2 \) has been plotted along the z-axis.

![Figure 2.2.](image)

Figure 2.2. \( |\psi|^2 \) of the 3s-orbital in argon plotted along the z-axis when an electric field \( E = E_\mathbf{e_z} \), \( E = 0.1 \) a.u. has been applied.

If we introduce unnormalized Cartesian Gaussian orbitals

\[
\phi_A(i_{x_A}, i_{y_A}, i_{z_A}, \alpha_A) = x_{i_{x_A}} y_{i_{y_A}} z_{i_{z_A}} \exp(-\alpha_A r_A^2),
\]

(2.35)

where

\[
r_A = r - R_A,
\]

(2.36)

and consider the integral \( \langle \phi_A | U(r_C) | \phi_B \rangle \), where the orbitals are positioned at atomic centers \( A \) and \( B \) and the ECP is situated at center \( C \), we arrive at two specific types of integrals given by McMurchie and Davidson [15, Eqs. (5) and (6)]

\[
\chi_{AB} = \int d\tau \phi_A r_{C}^{n'-2} \exp(-\xi r_{C}^2) \phi_B
\]

(2.37)

and

\[
\gamma_{AB} = \int dr_C \left[ \int d\Omega C \phi_A y_{lm}(\Omega_C) \right] r_C^{p'} \exp(-\xi r_C^2) \left[ \int d\Omega C y_{lm}(\Omega_C) \phi_B \right]
\]

(2.38)

respectively, where \( y_{lm} \) are real spherical harmonics. The local integrals are also called type 1 integrals whereas the nonlocal ones are referred to as type 2 integrals.
To proceed, the orbitals $\phi_A$ and $\phi_B$ are transformed to the ecp center $C$ using

$$\exp(-\alpha_A r_A^2) = \exp(-\alpha_A |r - R_A|^2) = \exp(-\alpha_A |r - R_C + R_C - R_A|^2) = \exp(-\alpha_A |r_C + R_{CA}|^2)$$ (2.39)

and

$$x_{iA}^a = (x - X_A)^{i_{xA}} = (x - X_C + X_C - X_A)^{i_{xA}} = (x_C + X_{CA})^{i_{xA}} = \sum_{a=0}^{i_{xA}} \binom{i_{xA}}{a} x_C^a x_{CA}^{i_{xA}-a}.$$ (2.40)

Together with the addition theorem (see for example [19, Eq. (12.36)] or [12, Eq. (64)])

$$\exp(k \cdot r_C) = 4\pi \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} i_\lambda(kr_C) y_{\lambda\mu}(\theta_k, \phi_k) y_{\lambda\mu}(\theta_C, \phi_C),$$ (2.41)

where $i_\lambda$ denote modified spherical Bessel functions of the first kind and $\theta_k$ and $\phi_k$ relate to $k$ whereas $\theta_C$ and $\phi_C$ relate to $r_C$, the definitions $D_{ABC} = 4\pi \exp(-\alpha_A |R_{CA}|^2 - \alpha_B |R_{CB}|^2)$, (2.42)

$$k_X = -2\alpha X R_{CX},$$ (2.43)

$$k = k_A + k_B,$$ (2.44)

and

$$\alpha = \alpha_A + \alpha_B + \xi,$$ (2.45)

leads to the final form of the integrals

$$\chi_{AB} = \sum_{a=0}^{i_{xA}} \sum_{b=0}^{i_{xB}} \sum_{c=0}^{i_{x_{CA}}} \sum_{a'=0}^{i_{x_{CA}}} \sum_{b'=0}^{i_{x_{CB}}} \sum_{c'=0}^{i_{x_{CB}}} i_{xA} \binom{i_{xA}}{a} i_{yA} \binom{i_{yA}}{b} i_{zA} \binom{i_{zA}}{c} i_{xA} \binom{i_{xA}}{a'} i_{yB} \binom{i_{yB}}{b'} i_{zB} \binom{i_{zB}}{c'}$$

$$\times x_{CA}^{i_{xA}-a} y_{CA}^{i_{xA}-b} Z_{CA}^{i_{xA}-c} x_{CB}^{i_{yA}-a'} y_{CB}^{i_{yB}-b'} Z_{CB}^{i_{zB}-c'}$$

$$\times D_{ABC} \sum_{\lambda=0}^{\infty} \int d\tau r_{C}^{n_{\lambda}-2} \exp(-\alpha r_C^2) i_\lambda(kr_C)$$

$$\times \sum_{\mu=-\lambda}^{\lambda} y_{\lambda\mu}(\theta_k, \phi_k) y_{\lambda\mu}(\theta_C, \phi_C) x_{C}^{i_{xA}+a'} y_{C}^{i_{yB}+b'} Z_{C}^{i_{zB}+c'}$$ (2.46)

and
2.3 Effective Core Potentials

\[ \gamma_{AB} = \sum_{a=0}^{i_{x_A}} \sum_{b=0}^{i_{y_A}} \sum_{c=0}^{i_{z_A}} \sum_{a'=0}^{i_{x_B}} \sum_{b'=0}^{i_{y_B}} \sum_{c'=0}^{i_{z_B}} \binom{i_{x_A}}{a} \binom{i_{y_A}}{b} \binom{i_{z_A}}{c} \binom{i_{x_B}}{a'} \binom{i_{y_B}}{b'} \binom{i_{z_B}}{c'} \times X_{CA}^{i_{x_A} - a} Y_{CA}^{i_{y_A} - b} Z_{CA}^{i_{z_A} - c} X_{CB}^{i_{x_B} - a'} Y_{CB}^{i_{y_B} - b'} Z_{CB}^{i_{z_B} - c'} \times 4\pi D_{ABC} \int dr_C \sum_{\lambda=0}^{\infty} \sum_{\lambda'=0}^{\infty} r_C^{\lambda'} \exp(-\alpha r_C^2) \lambda(k_{ARC} i_{x'}(k_{BRC})) \]

Finally, expressing the Cartesian monomials, \( x^A_C y^b_C z^c_C \), as linear combination of real spherical harmonics, \( y_{\lambda m} \), according to Appendix A, yields the ECP integrals

\[ \sum_{i=1}^{N_{\text{loc}}} d_i \gamma_{12} + \sum_{l=0}^{L_{\max}} \sum_{m=-l}^{l} \sum_{i=1}^{N_{\text{nonloc}}} d_i \gamma_{12} \]

\[ \times X_{CA}^{i_{x_A} - a} Y_{CA}^{i_{y_A} - b} Z_{CA}^{i_{z_A} - c} X_{CB}^{i_{x_B} - a'} Y_{CB}^{i_{y_B} - b'} Z_{CB}^{i_{z_B} - c'} D_{ABC} \]

\[ \times \left\{ \sum_{i=1}^{N_{\text{loc}}} d_i \sum_{\lambda=0}^{\lambda_{\max}} \int dr_C \sum_{\lambda'=0}^{\lambda_{\max} + \lambda_{\text{max}}} \exp(-\alpha r_C^2) \lambda(k_{ARC} i_{x'}(k_{BRC})) \right\} \]

\[ \times \left\{ \sum_{i=1}^{N_{\text{loc}}} d_i \sum_{\lambda=0}^{\lambda_{\max}} \sum_{l'=0}^{l_{\max}} \sum_{m'=0}^{l_{\max} + l_{\max}} a_{l'm'} \int d\Omega \ y_{\lambda m}(\theta_C, \phi_C) y_{l' m'}(\theta_C, \phi_C) \right\} \]

\[ + 4\pi \sum_{i=1}^{N_{\text{loc}}} d_i \sum_{\lambda=0}^{\lambda_{\max}} \sum_{l'=0}^{l_{\max}} \sum_{m'=0}^{l_{\max} + l_{\max}} a_{l'm'} \int d\Omega \ y_{\lambda m}(\theta_C, \phi_C) y_{l' m'}(\theta_C, \phi_C) \]

\[ \times \int dr_C \sum_{\lambda=0}^{\lambda_{\max}} \sum_{\lambda'=0}^{\lambda_{\max} + \lambda_{\text{max}}} \exp(-\alpha r_C^2) \lambda(k_{ARC} i_{x'}(k_{BRC})) \]

\[ \times \left\{ \sum_{\lambda=0}^{\lambda_{\max}} y_{\lambda m}(\Omega_{kA}) \sum_{\lambda'=0}^{\lambda_{\max}} \sum_{l'=0}^{l_{\max}} \sum_{m'=0}^{l_{\max} + l_{\max}} a_{l'm'} \int d\Omega \ y_{l' m'}(\Omega_{kC}) y_{\lambda m}(\Omega_{kC}) y_{\lambda m}(\Omega_{kC}) \right\} \]

\[ \times \left\{ \sum_{\lambda=0}^{\lambda_{\max}} y_{\lambda m}(\Omega_{kB}) \sum_{\lambda'=0}^{\lambda_{\max}} \sum_{l'=0}^{l_{\max}} \sum_{m'=0}^{l_{\max} + l_{\max}} a_{l'm'} \int d\Omega \ y_{l' m'}(\Omega_{kC}) y_{\lambda m}(\Omega_{kC}) y_{\lambda m}(\Omega_{kC}) \right\} \]
As for the type 1 integral, the angular part is trivial due to orthogonality between spherical harmonics, whereas the type 2 angular integrals can be evaluated using Wigner 3j-symbols, as is described in Appendix B. The approach to solving the angular integrals presented here differ from the one of McMurchie and Davidson [18], however, initial tests show a considerable speed-up when a restriction-free code dealing with t-quantum numbers of general order is considered.

The remaining concern is the radial integrals. Here, McMurchie and Davidson [18] adopt a semi-analytical approach where different methods are selected depending on the parameters of the integrand, where, for each method, they present settings in order to achieve a certain accuracy. A more appealing approach would be to use numerical quadrature for all given radial functions. Selecting a proper adaptive quadrature, it is possible to obtain a certain accuracy, and several such schemes have been proposed during recent years [6, 28]. The most appealing with this approach is that such a method is valid for any integrand, and an estimate of the error can be obtained.
CHAPTER 3

Comments on Papers

In the following, a short description of each paper is given and the papers are put into the context of this thesis.

3.1 Paper I

This first paper deals with the implementation of a code to calculate two-photon absorption cross sections within the relativistic four-component realm in the DIRAC program [4]. The theory and implementation is outlined and a set of calculations concerning the noble gases is presented. Furthermore, relativistic effects on TPA spectra are discussed.

3.2 Paper II

The relativistic effects on nonlinear optical properties are revisited. This time \(\pi\)-conjugated systems are investigated, namely dibromo- and di-iodobenzene in their meta- and ortho-conformations. Different integral approximations available for the four-component relativistic quantum chemical methods in DIRAC [4] are considered in order to find the best ratio of cost effective calculations versus accuracy. Furthermore, the discussion on how relativistic effects affect TPA spectra is continued.

3.3 Paper III

Continuing at the relativistic level of theory, we present the implementation of excited state properties in the DIRAC program [4]. In the long run, this can
be used to evaluate excited state absorption, but in this paper we use excited state electric dipole moments in CsAg and CsAu as test bed. Four-component Hartree–Fock calculations are compared to nonrelativistic all-electron as well as ECP ones. Furthermore, calculations disregarding spin are performed in order to see the extent of the scalar relativistic effects. These results are then compared to correlated nonrelativistic results at the DFT and CCSD levels of theory.

3.4 Paper IV

Nonrelativistic calculations of TPA and ESA spectra are combined with classical wave mechanics in order to model a light pulse propagating through a glass material doped with TPA chromophores. At this joint level of theory, multi-physics modeling, quantum mechanics meets Maxwell’s equations in order to estimate clamping levels in materials considered for use in self-activated laser filters.

3.5 Paper V

In this paper, we attempt to aid synthesis in finding plausible spin-transition materials suitable for agile filters. A method how to determine whether a material is an ST material or not is suggested, and based on these findings as well as calculated optical properties, a new category of ST materials is suggested.
In the present work the importance of relativistic effects in quantum chemical calculations has been addressed. We have shown that relativistic effects are of great importance when considering for example two-photon absorption, however, at present our efforts are limited to small test systems due to the substantial computing times required. Furthermore, introducing correlation into the quadratic response calculations is possible through post Hartree–Fock methods such as configuration interaction or coupled cluster, but yet again too expensive to be feasible for any systems of practical interest.

From this point of view, the prospects of achieving high quality calculations of quadratic response properties in the four-component realm seem distant, however, as has already been mentioned, two new directions of development could change this drastically; effective core potentials and density functional theory. If valence properties are wanted, the core electrons have little impact on the results, and as has been shown ECPs capture a large extent of this. The use of ECPs would drastically cut the number of electrons included in the calculations, and, thus, the computing time required. This would address the problem of making calculations on larger systems feasible, but in order to include correlation another direction is needed: DFT. An implementation of quadratic response in the DFT realm would enable relatively inexpensive means of including correlation, and in the nonrelativistic calculations this has proven very successful. Thus, the two trails we want to pursue are the inclusion of effective core potentials as well as quadratic response at the DFT level of theory in the four-component formalism.


Expansion of Cartesian Monomials in Spherical Harmonics

Spherical harmonics form a complete set of basis functions spanning angular space, and, thus, any angular function can be expanded in terms of such, see for example Varshalovich [30, p. 143]. Thus,

\[
f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} Y_{lm}, \tag{A.1}
\]

where

\[
a_{lm} = \int d\Omega \ Y_{lm}^* f(\theta, \phi), \tag{A.2}
\]

but since real spherical harmonics are only linear combinations of the complex ones, the above applies equally well to real spherical harmonics.

To represent the angular part of a Cartesian monomial as a linear combination of real spherical harmonics, first consider the Cartesian monomial written in spherical coordinates,

\[
x^a y^b z^c = r^{a+b+c} \sin^a \theta \cos^a \phi \sin^b \theta \sin^b \phi \cos^c \theta
\]

\[
= r^{a+b+c} \sin^{a+b} \theta \cos^a \phi \sin^b \phi. \tag{A.3}
\]

Thus, extracting the radial part, it is possible to find an expansion according to (A.1) for the angular part. In order to find the expansion in terms of the real spherical harmonics, consider the relationship to the complex ones defined through [30]

\[
y_{lm}(\theta, \phi) = \begin{cases} 
2^{-1/2}(Y_{lm}(\theta, \phi) + Y^*_{lm}(\theta, \phi)) = 2^{1/2}\text{Re}\{Y_{lm}(\theta, \phi)\} & m > 0 \\
Y_{l0}(\theta, \phi) & m = 0, \\
-i2^{-1/2}(Y_{l|m|}(\theta, \phi) - Y^*_{l|m|}(\theta, \phi)) = 2^{1/2}\text{Im}\{Y_{l|m|}(\theta, \phi)\} & m < 0 
\end{cases}
\tag{A.4}
\]
which by insertion of the definition of the complex spherical harmonics given by [30]

\[ Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta) e^{im\phi} \]  

(A.5)
yields

\[ y_{lm} = \sqrt{\frac{2l+1}{4\pi}} \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\cos \theta) \times \begin{cases} 
\frac{1}{2^{1/2} \cos(m\phi)} & m > 0 \\
1 & m = 0 \\
\frac{1}{2^{1/2} \sin(m\phi)} & m < 0
\end{cases} . \]  

(A.6)

Now, considering the \( \phi \)-part of the integration (A.2), it is immediately seen that due to symmetry properties, the integral will trivially equal to zero if \( b \) is odd when \( m \geq 0 \) or if \( b \) is even when \( m < 0 \). Using

\[ \int_0^{2\pi} d\phi e^{-im\phi} = \int_0^{2\pi} d\phi e^{i(n-m)\phi} = 2\pi \delta_{nm}, \]  

(A.7)
and rewriting the \( \phi \)-dependent part of (A.3) using Euler’s formulae and binomial expansion, for \( m \geq 0 \), we get

\[ \int d\phi \, \cos a \phi \sin b \phi \cos(m\phi) \]

\[ = \int d\phi \left\{ \frac{e^{i\phi} + e^{-i\phi}}{2} \right\}^a \left\{ \frac{e^{i\phi} - e^{-i\phi}}{2i} \right\}^b e^{im\phi} + e^{-im\phi} \]

\[ = \sum_{n=0}^a \sum_{n'=0}^b \binom{a}{n} \binom{b}{n'} \frac{(-1)^{n'-b}}{2^{a+b+1}} \frac{1}{(2i)^{a+b}} \int d\phi \left( e^{i(2(n+n')-(a+b))\phi} \right) \]

\[ \times \int d\phi \left( e^{i(2(n+n')-(a+b)+m)\phi} + e^{i(2(n+n')-(a+b)-m)\phi} \right) \]

\[ = \frac{\pi}{2^{a+b+1}} \sum_{n=0}^a \sum_{n'=0}^b \binom{a}{n} \binom{b}{n'} (-1)^{n'} \]

\[ \times \left\{ \delta_{2(n+n')-(a+b)+m} + \delta_{2(n+n')-(a+b)-m} \right\} \]  

(A.8)
and for \( m < 0 \) we analogously get

\[ -\frac{\pi}{2^{a+b+1}} \sum_{n=0}^a \sum_{n'=0}^b \binom{a}{n} \binom{b}{n'} (-1)^{n'} \]

\[ \times \left\{ \delta_{2(n+n')-(a+b)+m} - \delta_{2(n+n')-(a+b)-m} \right\} . \]  

(A.9)

From (A.8) and (A.9), we immediately see that \( a + b \) have to have the same parity as \( m \) in order for the expansion coefficient to be nonzero. It should be noted that
the imaginary factors left in the two equations above will vanish due to the parity of $b$.

The remaining issue is to solve the integral

$$
\int_0^{\pi} \sin^{a+b} \theta \cos^c \theta \ P_l^m(\cos \theta) \sin \theta \, d\theta. \tag{A.10}
$$

To do so, introduce the recursion relation [5]

$$(l - m + 1)P_{l+1}^m - (2l + 1) \cos \theta P_l^m + (l + m)P_{l-1}^m = 0 \tag{A.11}$$

for the associated Legendre functions together with

$$P_m^m(\cos \theta) = (-1)^m (2m - 1)!! \sin^m \theta. \tag{A.12}$$

This implies that the only integrals that need to be evaluated are powers in sine and cosine, for which

$$
\int_0^{\pi} \sin^p \theta \cos^q \theta \sin \theta \, d\theta = \frac{1}{2} \int_{-1}^{1} (1 - x^2)^{p/2} x^q \, dx = \frac{1 + (-1)^q \ \Gamma \left(\frac{2l+1}{2}\right) \ \Gamma \left(\frac{2l+2}{2}\right)}{\Gamma \left(\frac{2l+q+3}{2}\right)}.
$$

Yet again we see that a great number of integrals vanish, namely when $q$ is odd. Writing the $\Gamma$-functions as

$$\Gamma \left(\frac{m + 1}{2}\right) = \frac{(m - 1)!!}{2^{(m-1)/2}} \times \begin{cases} \left(\frac{\pi}{2}\right)^{1/2} & m \text{ even} \\ 1 & m \text{ odd} \end{cases}, \tag{A.14}$$

this yields that integral (A.13) equals to

$$2 \frac{p!!(q - 1)!!}{(p + q + 1)!!} \times \begin{cases} \pi & p \text{ is odd} \\ 1 & p \text{ is even} \end{cases} \tag{A.15}$$

when $q$ is even.

Using the recursion relation for the associated Legendre functions (A.11), we see that for any given $l \leq a + b + c$, it is possible to express (A.10) as a linear combination of simple integrals of the form (A.13) where the only thing needed is an increment of $q$ for each level of recursion. For a given $l$, we need to lower the order $l$ to $l_m$, i.e., using $l - m$ levels of recursion where in each step a new value of $q$ appears. Schematically, the recursion scheme will look like

<table>
<thead>
<tr>
<th>$l$</th>
<th>$q$</th>
<th>$q + 1$</th>
<th>$q + 2$</th>
<th>$q + 3$</th>
<th>$q + 4$</th>
<th>$q + 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l - 1$</td>
<td>1</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$l - 2$</td>
<td>$x$</td>
<td>2</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$l - 3$</td>
<td>3</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$l - 4$</td>
<td>$x$</td>
<td>4</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>$l - 5$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>
where the arrows show the dependence on previous elements and the number associated with each arrow tell at which level of recursion an element enters.

Example

Consider the monomial $x^2yz$, i.e., $a = 2$, $b = 1$, and $c = 1$. This means that spherical harmonics up to $l = a + b + c = 4$ has to be considered. As for the $\phi$-part, it will only depend on $m$, and, thus, it can be evaluated for all possible $m$-values needed, $m \in [-4, 4]$. However, taking the symmetry considerations stated above into account, all $m \geq 0$ are trivially equal to zero since $b$ is odd and the same goes for all even orders of $m$, since $m$ and $a + b$ has to have the same parity.

Hence, we only need to evaluate $m \in \{-3, -1\}$. Doing so results in

$$
\int d\phi \cos^2 \phi \sin \phi \sin(m\phi) = \begin{cases} 
-\frac{\pi}{4}, & m = -3 \\
-\frac{\pi}{4}, & m = -1 
\end{cases}.
$$

(A.16)

Now, as we know which $m$-values are nonzero, we see that the only associated Legendre functions in (A.10) that needs to be considered are those where $(l, m) \in \{(4, 3); (4, 1); (3, 3); (3, 1); (2, 1); (1, 1)\}$, i.e., six out of the original fifteen. However, this can be further reduced if the symmetry constraint that only even powers $q$ will survive in (A.13) is combined with knowledge of the structure of the recursion scheme used for the associated Legendre functions. Considering this recursion scheme in the case $P_{4}^{1}$, we now need to lower $l$ until $P_{1}^{1}$ is reached. The scheme above now turns into

\[
\begin{array}{cccc}
4 & 1 & 2 & 3 \\
3 & 1 & 7 & 7 \\
2 & 4 & 3 & 3 \\
1 & & & \\
\end{array}
\]

\[
\begin{array}{cccc}
4 & 1 & 2 & 3 \\
3 & 1 & 7 & 7 \\
2 & 4 & 3 & 3 \\
1 & & & \\
\end{array}
\]

\[
\begin{array}{cccc}
4 & 1 & 2 & 3 \\
3 & 1 & 7 & 7 \\
2 & 4 & 3 & 3 \\
1 & & & \\
\end{array}
\]

Since $p = a + b + m$, this yields that the $\theta$-integrals (A.13) that needs to be evaluated are the ones with $(p, q) \in \{(4, 2), (4, 4)\}$, and their corresponding prefactors can
be found immediately in the last table above. The integrals required are

\[
\int_{0}^{\pi} \sin^3 \theta \cos^q \theta \sin \theta \, d\theta = \begin{cases} 
\frac{16}{105}, & q = 2 \\
\frac{16}{315}, & q = 4 
\end{cases}, \quad (A.17)
\]

which, taking the prefactors of (A.12) into account, yields

\[
\int_{0}^{\pi} \sin^3 \theta \cos \theta P_4^1(\cos \theta) \sin \theta \, d\theta = \frac{15}{2} \frac{16}{105} - \frac{35}{2} \frac{16}{315} = \frac{16}{63}, \quad (A.18)
\]

Finally, using (A.16) and (A.18), remembering the prefactor of (A.6), this finally yields

\[
a_{41} = -\frac{1}{21} \sqrt{\frac{2\pi}{5}}, \quad (A.19)
\]

Following the same scheme for the other expansion coefficients yields

\[
\frac{1}{r^4} x^2 y z = \frac{1}{3} \sqrt{\frac{2\pi}{35}} y_{43} - \frac{1}{21} \sqrt{\frac{2\pi}{5}} y_{41} + \frac{2}{7} \sqrt{\frac{\pi}{15}} y_{21}. \quad (A.20)
\]
When evaluating angular integrals over products of spherical harmonics, the case involving a product of two is trivial due to orthogonality. In the case of three spherical harmonics it is not trivial any longer, but following Edmonds [5], utilizing the Wigner $3j$-symbols,

\[
\begin{pmatrix}
  l_1 & l_2 & l \\
  m_1 & m_2 & m
\end{pmatrix},
\]

\hspace{1cm} (B.1)

a product of two spherical harmonics can be expressed as a linear combination of single spherical harmonics according to

\[
Y_{l_1} Y_{l_2} Y_{l_3} = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)}{4\pi}} \ \left(\begin{array}{ccc}
  l_1 & l_2 & l \\
  m_1 & m_2 & m
\end{array}\right) \left(\begin{array}{ccc}
  l_1 & l_2 & l \\
  0 & 0 & 0
\end{array}\right) Y^*_{l m}.
\]

\hspace{1cm} (B.2)

Using this feature, the integral over three spherical harmonics becomes

\[
\int d\Omega \ Y_{l_1} Y_{l_2} Y_{l_3} = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)}{4\pi}} \ \left(\begin{array}{ccc}
  l_1 & l_2 & l_3 \\
  m_1 & m_2 & m_3
\end{array}\right) \left(\begin{array}{ccc}
  l_1 & l_2 & l_3 \\
  0 & 0 & 0
\end{array}\right).
\]

\hspace{1cm} (B.3)

If we instead are interested in real spherical harmonics, adapting the notation of Payne [24], start out by defining real spherical harmonics as

\[
y_{l m} = \sum_{m' = -l}^{l} U(m', m) Y_{l, m'},
\]

\hspace{1cm} (B.4)
where

\[ U(m', m) = \begin{cases} \frac{1}{\sqrt{2}} [\delta_{m', m} + (-1)^m \delta_{m', -m}] & m > 0 \\ \delta_{m', m} & m = 0 \\ -\frac{1}{\sqrt{2}} [\delta_{m', m} - (-1)^m \delta_{m', -m}] & m < 0 \end{cases} \]  \hspace{1cm} (B.5)

This is, using the relationship \[ [5] \]

\[ Y_{l, -m} = (-1)^m Y^*_l m, \]  \hspace{1cm} (B.6)

equivalent to the definition of the real spherical harmonics given in (A.6) in Appendix A. Then, following Payne [24], the above relations (B.2) and (B.3) can be transformed to deal with real spherical harmonics using

\[ \begin{bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{bmatrix} = \sum_{m_1', m_2', m'} (-1)^m U^*(m', m) U(m_1', m_1) U(m_2', m_2) \begin{bmatrix} l_1 & l_2 & l \\ m_1' & m_2' & m' \end{bmatrix}, \]  \hspace{1cm} (B.7)

which results in

\[ y_{l_1 m_1} y_{l_2 m_2} = \sum_{l, m} \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2l + 1)}{4\pi}} \begin{bmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{bmatrix} \begin{bmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{bmatrix} y_{l m}, \]  \hspace{1cm} (B.8)

and the angular integral of a product of three real spherical harmonics can hence be written

\[ \int d\Omega \ y_{l_1 m_1} y_{l_2 m_2} y_{l_3 m_3} = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)}{4\pi}} \begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{bmatrix} \begin{bmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{bmatrix}. \]  \hspace{1cm} (B.9)
List of Publications


[III] Erik Tellgren, Johan Henriksson, and Patrick Norman. First order excited state properties in the four-component Hartree–Fock approximation; the excited state electric dipole moments in CsAg and CsAu. *In manuscript*.


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Titel
Ljusreglering med organometalliska kromoforer

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Sammanfattning
The interaction between light and organometallic chromophores has been investigated theoretically in a strive for fast optical filters. The main emphasis is on two-photon absorption and excited state absorption as illustrated in the Jablonski diagram. We stress the need for relativistic calculations and have developed methods to address this issue. Furthermore, we present how quantum chemical calculations can be combined with Maxwell’s equations in order to simulate propagation of laser pulses through materials doped with chromophores with high two-photon absorption cross sections. Finally, we also discuss how fast agile filters using spin-transition materials can be modeled in order to accomplish theoretical material design.

Nyckelord
organometallic chromophores, two-photon absorption, excited state absorption, excited state dipole moment, four-component formalism, clamping levels, spin-transitions

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