

**Toward Calculating Excitation
Energies and Transition Moments
of Yb in Y₂O₃ and CaF₂ via
Response Functions using the
All-Electron Two-Component
Relativistic ZORA Hamiltonian**

Master Thesis

Debye Institute
Utrecht University

Sven Kähler

Utrecht, August 2014

1 Introduction

Large classes of molecular systems that are highly relevant for future technological developments contain heavy atoms, as for example Lanthanide atoms, that give rise to significant relativistic contributions to the systems' energy[1]. In these cases electronic structure calculations can no longer be based on a non-relativistic relation like the Schrödinger equation. Instead it is required to use methods based on the relativistic Dirac equation. Since the Dirac equation is considerably more complicated than the Schrödinger equation, it leads to an increase in the required computational resources, both for memory and computing time. As a consequence the range of systems for which calculations are computationally feasible is severely limited.

For that reason, different approaches to approximate the Dirac equation via a simpler relation have been pursued. One of these, the zeroth order regular approximation (ZORA)[2], has proven to be computationally efficient and adequately accurate for many tasks. The ZORA method, like other approximations to the Dirac equation, exists in two variants, the scalar and the spin-orbit ZORA method, also known as one- and two-component ZORA. Both variants provide a one-electron correction to the relativistic kinetic energy, but differ in how they represent the spin states of the electrons. The scalar variant assigns one of the two possible spin states, alpha or beta, to each molecular orbital, while in the spin-orbit variant the spin state of each molecular orbital is a linear combination of both alpha and beta states.

In non-relativistic calculations, the one-component representation is more compact and thereby more efficient than the two-component representation, while producing the same results for both (as long as magnetic interactions are disregarded). This is no longer necessarily the case for relativistic calculations, because spin states now generally differ in their contributions to the energy, because of an interaction between the spin and the angular momentum of orbitals, called spin-orbit coupling, that is not present in the non-relativistic case. For many systems, the spin-orbit interaction can be neglected and scalar ZORA provides an adequate model for relativistic calculations and has been very commonly applied for such cases. In other systems, specifically those with high angular momentum orbitals and open shell configurations, spin-orbit interaction is essential even for qualitatively correct models.

For a quantitative description and in certain cases already for qualitative investigations, models for calculations need to provide an accurate description of the electron-electron interaction. The Hartree-Fock method, the most basic of the standard models, accounts for interactions between electrons only in an average fashion. The part of the electron-electron interaction disregarded

by the Hartree-Fock method is known as electron correlation. Other methods that yield improvements to the Hartree-Fock results have long been known and are widely used. Currently the spin-orbit ZORA method is implemented in the GAMESS-UK program [3] only on the Hartree-Fock level. While an implementation of electron correlation corrections for the spin-orbit ZORA method is desirable, further preliminary investigations of the current Hartree-Fock implementation are required before, to ensure that the spin-orbit ZORA method leads to a correct representation of the spin states, in particular for the case of open shell systems.

Oftentimes spin-orbit coupling results in properties that are highly attractive for applications in future materials and therefore attract considerable research attention. An example for such properties is the existence of excited states, where the transition of an electron between states for which the overlap of spin states is different from zero or one. Without different energy contributions for the spin states, this overlap could only take the value zero or one. Since the rate of an optical transition depends on the overlap of the involved states, in such systems, it provides an additional variable to engineer the lifetime of the excitation to fit the needs of the application, by choosing an electronic environment that results in the right overlap.

One example of such a system that has been studied extensively is Ytterbium embedded in various crystal systems. Here we will focus on the Yttrium oxide and the Calcium fluoride crystal system. Both systems have been studied in the context of laser gain materials and fluorophores in optoelectric devices. Since the spectra of these systems are therefore readily available and a theoretical investigation of the mechanisms of their radiative transitions would be of interest, they constitute a good model system for an investigation of the spin state representation's accuracy for the spin-orbit ZORA implementation in GAMESS-UK. To do so, excitation energies and transition moments would have to be calculated based on spin-orbit ZORA results to then be compared to the experimental data. How this can be achieved will be discussed in the following. Alternatively, the GAMESS-UK ZORA results can be compared to those obtained from other relativistic calculations, in particular those that are computationally more involved and thereby more accurate.

2 Theory

2.1 Special Relativity in Quantum Mechanics

2.1.1 The Dirac Equation

A relativistic quantum mechanical system can be described by the Dirac equation [4]

$$(c\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta mc^2 + V)\Psi = i\frac{\partial\Psi}{\partial t}, \quad (1)$$

where c is the speed of light, m the mass of the particle, \boldsymbol{p} the momentum vector of the particle, Ψ the 4-component wave function vector and $\boldsymbol{\alpha}$ and β matrices, whose specific form depends on the basis chosen for the wave function. The $c\boldsymbol{\alpha} \cdot \boldsymbol{p}$ term corresponds to the kinetic energy of the particle, while the βmc^2 term corresponds to the energy of the particle at rest and V describes an external potential.

2.1.2 Separating Electronic and Positronic States

In order to explain the relations imposed by the $\boldsymbol{\alpha}$ and β matrix, it is first required to introduce a particular basis that states these relations in the most transparent manner. Here it is helpful to bear in mind that the Dirac equation has solutions with energy eigenvalues that can be either positive with values greater than or equal to the rest energy of a particle mc^2 or negative with values less than or equal to $-mc^2$. This means that the positive energy eigenvalues correspond to matter while the negative eigenvalues correspond to antimatter. Since often the main interest is in finding the ground state for a system that does not contain antimatter, i.e. the lowest possible positive energy eigenvalue, it is helpful to separate positive and negative eigenstates and to then derive an equation that only contains the positive eigenstates. As the first step, the separation of positive and negative energy eigenstates can be achieved by choosing a convenient basis via a unitary transformation[5]. This can be visualized as rotating the coordinate axes such that positive and negative energy states become approximately orthogonal. The 4-component wavefunction will then consist of two 2-component vectors ψ_+ and ψ_- , of which ψ_+ represents positive energy states and ψ_- negative energy states.

$$\Psi = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} \text{ with } \psi_+ = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \text{ and } \psi_- = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix} \quad (2)$$

While this separation is not complete and positive energy states will still have a small ψ_- component, the ψ_+ component will dominate (and vice versa for

negative energy states). Therefore the two components of ψ_+ are called the large components and the components of ψ_- are called the small components. Within ψ_+ , ψ_1 and ψ_2 represent the two possible spin states of positive energy eigenstates, while the two components of ψ_- , ψ_3 and ψ_4 , represent the two possible spin states of negative energy eigenstates. Stated for ψ as a 2-component vector of ψ_+ and ψ_- α and β are given by:

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (3)$$

This means that every matrix entry stands for a two-by-two matrix or, in case of σ , as a two-by-two-by-three tensor of the Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (4)$$

When dealing only with positive energy eigenstates, it is usually useful to shift the energy scale so that the zero point energy coincides with the lowest possible energy eigenstate. This shift is achieved by disregarding the rest energy contribution of the positive energy eigenstates while counting the rest energy contribution of the negative eigenstates twice. In the equation this is expressed by replacing β by β' :

$$\beta \rightarrow \beta' = \begin{pmatrix} 0 & 0 \\ 0 & -2 \end{pmatrix} \quad (5)$$

Writing now time-independent Dirac equation $H_D\Psi = E\Psi$, where H_D is the Dirac Hamiltonian, as a matrix equation using β' instead of β leads to:

$$H_D\Psi = \begin{pmatrix} V & c\sigma \cdot p \\ c\sigma \cdot p & V - 2mc^2 \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = E\Psi \quad (6)$$

2.1.3 The Zeroth Order Regular Approximation

While the positive and negative energy solutions are separated to a large extent, the large and small component are still coupled. Therefore any attempt to formulate an approximation of the Dirac equation that only contains the large component needs to resolve the dependency on the small component. Over the years various strategies to achieve this have been devised. Among the most relevant are the Douglas-Kroll method[6, 7], the Pauli expansion, Direct Perturbation Theory[8, 9], the normalized elimination of the small component of Dyall[10, 11] and the Zeroth Order Regular Approximation (ZORA)[2].

In the following the ZORA method will be discussed in detail. The ZORA method is the first and most simple out of the group of the so called Regular Approximation methods, which resolve the problem of the irregular behavior of the Pauli expansion in the core region[12]. The method is based on the initial contributions of Chang, Pelissier, and Durand[13]. Within ZORA the decoupling of the large and small component is achieved via a Foldy-Wouthuysen transformation[14], which replaces the large component vector ψ_+ by the eigenvector ψ_+^{FW} of a transformed Hamiltonian. Here ψ_+^{FW} is then no longer coupled to the small component vector:

$$\begin{pmatrix} \psi_+^{FW} \\ 0 \end{pmatrix} = U \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} \text{ with } U = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}} X^\dagger \\ -\frac{1}{\sqrt{1+X X^\dagger}} X & \frac{1}{\sqrt{1+X X^\dagger}} \end{pmatrix}. \quad (7)$$

From equation 7 then follows:

$$\psi_+^{FW} = \frac{1}{\sqrt{1+X^\dagger X}} \psi_+ + \frac{1}{\sqrt{1+X^\dagger X}} X^\dagger \psi_- \quad (8)$$

and

$$0 = \frac{1}{-\sqrt{1+X X^\dagger}} X \psi_+ + \frac{1}{\sqrt{1+X X^\dagger}} \psi_- \quad (9)$$

From equation 9 now can be deduced that $\psi_- = \bar{X} \psi_+ = c\sigma \cdot p(2mc^2 + E - V)^{-1} \psi_+$. This gives an energy dependent expression for \bar{X} that can be used in equation 8. Up to this point, the ZORA method is identical to the Pauli expansion. The Pauli expansion then proceeds to expand $(1/\sqrt{1+X^\dagger X})$ in powers of c^{-2} , which, for truncated expansions, leads to the divergence of the Coulomb potential[12]. Instead the ZORA method expands $(1/\sqrt{1+X^\dagger X})$ in $(2mc^2 - V)^{-1} E$, which results in a regular behavior[13, 15]. Applying this to equation 6 and limiting oneself to zeroth order, this leads to the ZORA Hamiltonian for the one electron case:

$$H^{\text{ZORA}} = V + \sigma \cdot p \frac{c^2}{2c^2 - V} \sigma \cdot p \quad (10)$$

One problem introduced by the ZORA Hamiltonian is that, due to the energy dependence of the operator, it is no longer gauge invariant because the expansion is not continued to infinity. This means that the energy for potentials that only differ by an additive constant is no longer the same. Thereby the total energy of the system becomes inaccurate and in particular the contribution of the core electrons is no longer reliable, because these are less shielded from the core potentials and thereby give rise to larger errors.

One solution to this problem is to include certain higher order contributions that lead to the so called scaled ZORA Hamiltonian $H_{\text{sc}}^{\text{ZORA}}$ [15]. For zeroth order scaled ZORA the inclusion of higher order contribution is achieved by replacing $(1/\sqrt{1+X^\dagger X})\Phi_i$ with $(1/\sqrt{1+\langle\Phi_i|X^\dagger X|\Phi_i\rangle})\Phi_i$. With this new approximation the transformed kinetic energy expression then becomes:

$$\frac{\sigma \cdot p \frac{c^2}{2c^2-V} \sigma \cdot p}{1 + \langle\Phi_i|\sigma \cdot p \frac{c^2}{2c^2-V} \sigma \cdot p|\Phi_i\rangle} \Phi_i = S^{-1} \sigma \cdot p \frac{c^2}{2c^2-V} \sigma \cdot p = E_i^{\text{scaled}} \Phi_i. \quad (11)$$

Further developments of the ZORA implementation in GAMESS-UK have made it unnecessary to recalculate the scaling factor in every scf cycle. Instead the scaling factor is only calculated once for each geometry. The difference between the unscaled and the scaled Fock matrix is then transformed to the atomic orbital basis and added as corrections to the one electron matrix in each scf cycle [16].

2.1.4 Wave Function Based ZORA in GAMESS-UK

Up to this point, the discussion has been focused on the one-electron Hamiltonian, now we proceed to the many electron case. While many of the developments in the ZORA method have been based on density functional theory, this work focuses on a wave function-based formulation[17, 18]. For the practical applicability in wave function-based calculations, a few additional considerations are required on how to efficiently implement the Hamiltonian that resulted from the previous derivation. For two-component calculations it is no longer sufficient to only optimize the weights of each atomic orbital in each molecular orbital. Since the spin states of the atomic orbitals contribute to the overall energy they too need to be optimized. Within the two-component ZORA calculation this requirement fulfilled by using two separate coefficients for each atomic orbital, one corresponding to α and one corresponding to β spin, so that each molecular orbital is given by an expression of the form

$$\psi_\nu = \sum_\mu (c_{\mu\nu}^\alpha \phi_\mu^\alpha + c_{\mu\nu}^\beta \phi_\mu^\beta). \quad (12)$$

Here in general the coefficients $c_{\mu\nu}^\alpha$ and $c_{\mu\nu}^\beta$ are complex valued. These coefficients can now be combined to form the density matrix, where each matrix element $p_{\mu\nu}^{\zeta\eta}$ is given by

$$p_{\mu\nu}^{\zeta\eta} = \sum_i c_{\mu,i}^{\zeta*} c_{\nu,i}^\eta, \quad (13)$$

which leads to the symmetry properties

$$p^{\alpha\alpha} = (p^{\alpha\alpha})^\dagger, p^{\beta\beta} = (p^{\beta\beta})^\dagger \text{ and } p^{\beta\alpha} = (p^{\alpha\beta})^\dagger. \quad (14)$$

While the non-relativistic electron-electron interaction is given by the operator $\frac{1}{r_{ij}}$, this is no longer accurate for the relativistic case. The effect of changes in position of one electron on the repulsive forces on all other electrons is no longer instantly present at the other electrons' positions but instead requires a finite time to be transmitted. In the framework of quantum electrodynamics, this is included as the exchange of photons. For a completely accurate description of the relativistic electron-electron interaction an expansion of the interaction in terms of photon frequency is required. As a first order approximation the Breit-Coulomb interaction[19] J_{ij}^{BC} is given by:

$$J_{ij}^{BC} = \frac{1}{r_{ij}} - \left(\frac{\alpha_i \alpha_j}{2r_{ij}} + \frac{(\alpha_i \cdot r_{ij})(\alpha_j \cdot r_{ij})}{2r_{ij}^3} \right) \quad (15)$$

For the low-order limited accuracy calculations used in this study it has been demonstrated that going even further and approximating J_{ij} as $\frac{1}{r_{ij}}$ has proven to provide satisfactory accuracy. Therefore $J_{ij} = \frac{1}{r_{ij}}$ is used in all calculations presented. Nevertheless it remains to be determined whether this approximation of J_{ij} is still sufficiently accurate when applied in the context of spin-orbit interactions, since it leads to a formally incorrect treatment of the interaction between the spin and orbit of different atoms.

Now the many-electron Fock operator in the ZORA formalism $F^{zora} = T^{zora} + V_{nuc} + J + K$ can be stated as:

$$F^{zora} = \vec{\sigma} \cdot \vec{p} \frac{c^2}{2c^2 - V_c^\psi} \vec{\sigma} \cdot \vec{p} + V_c^\psi - K_{\psi\psi} \quad (16)$$

with

$$V_c^\psi = V_{nuc} + J_{\psi\psi} \quad (17)$$

where the subscripts in $J_{\psi\psi}$ and $K_{\psi\psi}$ are included to emphasize that these operators do not depend on the positronic χ components, but can be evaluated completely within the two-component approach, where the matrix elements are then given by:

$$J_{\mu\nu}^{\alpha\alpha} = J_{\mu\nu}^{\beta\beta} = \sum_{\kappa\lambda} (p_{\kappa\lambda}^{\alpha\alpha} + p_{\kappa\lambda}^{\beta\beta}) (\phi_\mu \phi_\nu | \phi_\lambda \phi_\kappa) \quad (18)$$

and

$$K_{\mu\nu}^{\zeta\eta} = \sum_{\kappa\lambda} p_{\kappa\lambda}^{\zeta\eta} (\phi_\mu \phi_\kappa | \phi_\lambda \phi_\nu) \quad (19)$$

The last remaining set of matrix elements are now the elements of the one-electron Fock matrix T^{zora} that are given by

$$T_{\mu\nu}^{zora} = \frac{1}{2} \langle \phi_\mu \zeta_\mu | \vec{\sigma} \cdot \vec{p} \frac{1}{1 - \frac{V_c}{2c^2}} \vec{\sigma} \cdot \vec{p} | \phi_\nu \zeta_\nu \rangle. \quad (20)$$

Instead of the expression given in equation 20, in practise the operator $1/(1 - \frac{V_c}{2c^2})$ is replaced with its inverse $(1 - \frac{V_c}{2c^2})$, the resolution of identity $\hat{1} = \sum_\lambda |\phi_\lambda \zeta_\lambda\rangle S_\phi^{-1} \langle \phi_\lambda \zeta_\lambda|$ is applied on both sides and the inverse of the resulting matrix element taken. Here the factor S_ϕ^{-1} that is equal to the inverse of the metric of the basis, has to be included if the particular basis used is not orthogonal.

$$T_{\mu\nu}^{zora} = \frac{1}{2} \sum_{\lambda\kappa} \langle \phi_\mu \zeta_\mu | \vec{\sigma} \cdot \vec{p} | \phi_\lambda \zeta_\lambda \rangle \langle \phi_\lambda \zeta_\lambda | 1 - \frac{V_c}{2c^2} | \phi_\kappa \zeta_\kappa \rangle^{-1} \langle \phi_\kappa \zeta_\kappa | \vec{\sigma} \cdot \vec{p} | \phi_\nu \zeta_\nu \rangle \quad (21)$$

Since the inverse of the matrix elements of an inverse operator are only exactly equal to the matrix elements of the original operator in the case of a complete basis set, this approach introduces a source of inaccuracy. To ensure that the impact of the basis set error remains limited, a computational trick is employed. The term $\frac{1}{2} \langle \phi_\mu \zeta_\mu | \vec{\sigma} \cdot \vec{p} | \phi_\nu \zeta_\nu \rangle$ is first added once and subtracted once to the expression. Afterwards in the additive term, $\vec{\sigma} \cdot \vec{p}$ is evaluated to p^2 and in the subtractive term another resolution of identity is carried out. In the resulting expression

$$\begin{aligned} T_{\mu\nu}^{zora} &= \langle \phi_\mu \zeta_\mu | \frac{p^2}{2} | \phi_\nu \zeta_\nu \rangle - \frac{1}{2} \sum_\lambda \langle \phi_\mu \zeta_\mu | \vec{\sigma} \cdot \vec{p} | \phi_\lambda \zeta_\lambda \rangle \langle \phi_\lambda | \vec{\sigma} \cdot \vec{p} | \phi_\nu \zeta_\nu \rangle \\ &+ \frac{1}{2} \sum_{\lambda\kappa} \langle \phi_\mu \zeta_\mu | \vec{\sigma} \cdot \vec{p} | \phi_\lambda \zeta_\lambda \rangle \langle \phi_\lambda \zeta_\lambda | 1 - \frac{V_c}{2c^2} | \phi_\kappa \zeta_\kappa \rangle^{-1} \langle \phi_\kappa \zeta_\kappa | \vec{\sigma} \cdot \vec{p} | \phi_\nu \zeta_\nu \rangle \end{aligned} \quad (22)$$

the first term is equal to the non-relativistic kinetic energy and thereby recovers the correct result for the limit $c \rightarrow \infty$ for which the other two terms approach zero. For a complete basis set, the first and second term cancel. In practice the use of an incomplete basis leads to reasonable results, because the basis set error in the second and third term cancel partially.

To provide a computationally cheaper alternative for the many cases where one is only interested in including scalar relativistic effects, but not spin-orbit

coupling, one can derive another expression from equation 20 in which the scalar effects can be separated out[20]. As the first step, the $\vec{\sigma} \cdot \vec{p}$ and $\frac{c^2}{2c^2 - V_c}$ are commuted using the commutator relation $[(\vec{\sigma} \cdot \vec{p}, \frac{c^2}{2c^2 - V_c})] = -\frac{i}{c^2} (\frac{c^2}{2c^2 - V_c})^2 \vec{\sigma} \cdot \vec{\nabla} V_c$ and then $(\vec{\sigma} \cdot \vec{p})^2 = \vec{p} \cdot \vec{p}$. For the $\frac{c^2}{2c^2 - V_c} \vec{p} \cdot \vec{p}$ term, the commutator relation $[\vec{p}, b] = -\frac{i}{c^2} (\frac{c^2}{2c^2 - V_c})^2 \vec{\nabla} V_c$ is then applied. Afterwards the expression is simplified using $(\vec{\sigma} \cdot \vec{\nabla} V_c)(\vec{\sigma} \cdot \vec{p}) = \vec{\nabla} V_c \cdot \vec{p} + i\vec{\sigma} \cdot (\vec{\nabla} V_c \times \vec{p})$ leading to

$$\begin{aligned}
T^{zora} &= (\vec{\sigma} \cdot \vec{p}) \frac{c^2}{2c^2 - V_c} (\vec{\sigma} \cdot \vec{p}) = \frac{c^2}{2c^2 - V_c} (\vec{\sigma} \cdot \vec{p})(\vec{\sigma} \cdot \vec{p}) - \frac{i}{c^2} (\frac{c^2}{2c^2 - V_c})^2 \vec{\sigma} \cdot \vec{\nabla} V_c \\
&= \frac{c^2}{2c^2 - V_c} \vec{p} \cdot \vec{p} - \frac{i}{c^2} (\frac{c^2}{2c^2 - V_c})^2 \vec{\sigma} \cdot \vec{\nabla} V_c \\
&\quad \vec{p} \frac{c^2}{2c^2 - V_c} \vec{p} + \frac{1}{c^2} (\frac{c^2}{2c^2 - V_c})^2 \vec{\sigma} \cdot (\vec{\nabla} V_c \times \vec{p}).
\end{aligned} \tag{23}$$

In the resulting expression, the first term describes the one-component or scalar relativistic kinetic energy. For calculations where all non-scalar contributions can be neglected, T^{zora} can be substituted by $T^{zora,scalar} = \vec{p} \frac{c^2}{2c^2 - V_c} \vec{p}$. Following a derivation analogous to the one used for equation 22 the matrix elements of this operator can then be evaluated conveniently as

$$\begin{aligned}
T_{\mu\nu}^{zora,scalar} &= \langle \phi_\mu | \frac{p^2}{2} | \phi_\nu \rangle - \frac{1}{2} \sum_\lambda \langle \phi_\mu | \vec{p} | \phi_\lambda \rangle \langle \phi_\lambda | \vec{p} | \phi_\nu \rangle \\
&\quad + \frac{1}{2} \sum_{\lambda\kappa} \langle \phi_\mu | \vec{p} | \phi_\lambda \rangle \langle \phi_\lambda | 1 - \frac{V_c}{2c^2} | \phi_\kappa \rangle^{-1} \langle \phi_\kappa | \vec{p} | \phi_\nu \rangle
\end{aligned} \tag{24}$$

For the resolution of identity, it is advisable to use a different basis in the expansion, in the following referred to as internal basis[21], than the basis used in the other parts of the calculation, here for clarity called external basis.

The reason is that, while in most of the commonly used basis sets high exponent components are only present for the low angular momentum orbitals (because their contribution to the accuracy of the results does not justify the addition computational effort of including them), in this special case, including additional high exponent terms becomes necessary. This is because the resolution of identities leads to terms of the form $\langle \phi_\lambda \zeta_\lambda | \vec{\sigma} \cdot \vec{p} | \phi_\nu \zeta_\nu \rangle$, where the \vec{p} operator applied to any atomic orbital introduces terms with the same exponent but with an angular momentum that is increased by one order.

If this increased order angular momentum function is not available for this exponent the integral can not be evaluated correctly.

Ensuring that increased order angular angular momentum function are present for all atomic basis functions in the external basis set would lead to very large internal basis sets. It has however been demonstrated that it is sufficient to add increased order angular momentum functions only in those cases where the exponent is higher than the highest exponent of the resulting angular momentum in the external basis [21].

2.2 Electronic Excitations - Energies and Transition Probabilities

When a molecular system interacts with an electro-magnetic radiation field there is a certain probability that radiation will be absorbed by the system. The system will then undergo a transition from a lower energy initial state (usually its ground state), to higher energy state (the excited state). While there are multiple different mechanisms, based on different physical interactions, through which excitations can occur, here only the most simple type, the electric dipole transition due to a periodic electric field, will be discussed. In this case the Hamiltonian of the system is given by

$$H(t) = H_0 + V^t, \quad (25)$$

where the time-independent term H_0 is the Hamiltonian of the unperturbed system where the oscillating field is absent, and V^t is the periodic potential field.

For a specific system of electrons, the frequencies at which radiation will be absorbed and the probability of absorption at that frequency can be calculated by a variety of different methods [22]. These methods can be grouped into two different approaches: the stationary state approach and the time-dependent approach.

2.2.1 Stationary State Based Approach

The first approach is to calculate stationary states of a basis function expansion for the ground state and all excited states of interest. The excitation energies are then given by energy differences between the resulting states. As a measure for the probability of a transition between two states the oscillator strength can be calculated, which expressed the transition rate in units of the transition rate that would be obtained in the classical electric dipole oscillator model.

The methods that are based on the stationary state approach then differ from each other in the quality with which they model dynamic and static correlation and the computational effort required. In general an improvement in correlation treatment comes with an increase in computational cost, where the exact relation depends on various implementation details.

The most basic approach would be to optimize a Hartree-Fock wave function to higher energy stationary points instead of the minimum[23]. This kind of calculation requires a more sophisticated optimization procedure than the minimization of the energy performed in standard Hartree-Fock. Alternatively, excited states can be obtained via the configuration interaction singles (CIS) model[24], where the stationary states are given by the eigenfunctions of the Hamiltonian in the space of linear combinations of the Hartree-Fock determinant and those determinants that represent single excitations of the Hartree-Fock state. For both Hartree-Fock and CIS excited states only systems where both ground and excited states are well described by the Hartree-Fock ground state reference function can be expected to have reasonable results. Even then the results are more qualitative in nature because dynamic correlation is insufficiently represented. The accuracy of results can be improved by accounting for higher excitations in the CIS model, but the success has been limited [25].

For systems of multi-configurational character a multiconfigurational self-consistent field (MCSCF) or a complete active space (CAS) SCF calculation is required as reference function. For a CASSCF wave function dynamic correlation can be taken into account by performing a CASPT2 calculation.

2.2.2 Time-Dependent Approach

Over the years various approaches to describe an electronic system in the presence of a time-dependent radiation field have been developed[26, 27, 28], that instead of optimizing excited states obtain all information from the ground state and its time-derivatives. These methods are summarized under the term time-dependent response theory. In some of these methods the time-derivatives are then used to state conditions under which circumstances electronic transitions are possible. With these conditions in place, for a given combination of external perturbation and property of interest all required information can be obtained from the coefficient functions, the so called response functions. The response functions result from stating the time evolution of the expectation value of an operator, in the case discussed here the dipole moment operator, as a time dependent perturbation series. The excitation energies and respective transition moments can then be detected as resonances of the response functions with the external perturbation and can

be calculated as the poles and respective residues of the response function. Various other properties can be obtained in this way[29], for example two photon absorption cross sections, magnetic transition strengths, or frequency dependent hyperpolarizabilities. Response methods have been developed that are based on either the SCF, the MCSCF and the Coupled Cluster model for the reference wave function. Different formalisms have been developed to link properties and response functions that somewhat vary in their range of applications and the rigor of the derivation[27, 30, 31]. The formalism used in the following[30] is the same that was also used for the description of the implementation in GAMESS-UK of the time-dependent response method called random phase approximation (RPA)[32].

In the following the linear response of the electric dipole excitation, which yields the electronic dipole transition energies and transition strengths, will be discussed in detail with some hints provided on how the generalization to other scenarios would be accomplished. First the derivation will be carried out for exact states as an instructive special case. In a second part the discussion will be repeated for a Hartree-Fock state.

For the exact state the wave function of the system is given as a linear combination of a complete basis of eigenfunctions $|k\rangle$ of the time-independent Hamiltonian H_0 , where $H_0 |k\rangle = E_k |k\rangle$ and the coefficient then become time-dependent for the case of a time-dependent Hamiltonian. It can then be shown[28] that the time-dependent parametrization of the exact solution to the time-dependent Schrödinger equation can be given as:

$$|\tilde{0}\rangle = \exp(i \sum_{n>0} (P_n(t)\Lambda_n + P_n^*(t)\Lambda_{-n}) |0\rangle, \quad (26)$$

where $|0\rangle$ is the initial state of the transition (usually the ground state), $P_n(t)$ are time-dependent parameter function and the notation

$$\begin{pmatrix} \Lambda_m \\ \Lambda_{-m} \end{pmatrix} = \begin{pmatrix} |n\rangle \langle 0| \\ |0\rangle \langle n| \end{pmatrix} \quad (27)$$

is introduced for the excitation and deexcitation operators.

The time evolution of these parameters can then be determined by applying the Ehrenfest theorem [33], which here yields

$$\langle \tilde{0} | \Lambda | \dot{\tilde{0}} \rangle + \langle \dot{\tilde{0}} | \Lambda | \tilde{0} \rangle = \langle \tilde{0} | [\Lambda, H_0 + V^t] | \tilde{0} \rangle. \quad (28)$$

The derivatives of $|\tilde{0}\rangle$ can be determined by expanding equation 26 in a power series:

$$|\tilde{0}\rangle = |0^{(0)}\rangle + |0^{(1)}\rangle + |0^{(2)}\rangle + |0^{(3)}\rangle + \dots, \quad (29)$$

which leads to:

$$|0^{(0)}\rangle = |0\rangle \quad (30)$$

$$|0^{(1)}\rangle = i \sum_{n>0} |n\rangle P_n^{(1)}. \quad (31)$$

Inserting the time-derivative of $|\tilde{0}\rangle$ in the time evolution in equation 28 leads to

$$\begin{aligned} \sum_{n>0} (i \langle 0 | \Lambda | n \rangle \dot{P}_n^{(n)} - i \langle n | \Lambda | 0 \rangle \dot{P}_n^{*(n)} - \langle 0 | [\Lambda, H_0] | n \rangle P_n^{(n)} \\ + \langle n | [\Lambda, H_0] | 0 \rangle P_n^{*(n)}) = -i \langle 0 | [\Lambda, V^t] | 0 \rangle. \end{aligned} \quad (32)$$

Since these equations for positive and negative indices of Λ are complex conjugates of each other, they can be combined in a single equation

$$i \text{sgn}(k) \dot{P}_k^{(1)} - \omega_k P_k^{(1)} = -i V_k^t, \quad (33)$$

where

$$V_k^t = \begin{cases} \langle k | V^t | 0 \rangle, & k > 0 \\ -\langle 0 | V^t | k \rangle, & k < 0 \end{cases} \quad (34)$$

and

$$\omega_k = \omega_{-k} = E_k - E_0 \quad (35)$$

The solution for the set of differential equations given in equation 33 is then given by

$$\begin{aligned} P_k^{(1)} &= -i \text{sgn}(k) \exp(-i\omega_k \text{sgn}(k)t) \int_{-\infty}^t d\tau \\ &\times \exp[i\omega_k \text{sgn}(k)\tau] (-i) \int_{-\infty}^{\infty} d\omega V_k^\omega \times \exp(-i\omega + \epsilon)\tau \\ &= -i \int_{-\infty}^{\infty} d\omega_1 \exp[(-i\omega_1 + \epsilon)t] \times \frac{\text{sgn}(k) V_k^{\omega_1}}{\omega_1 - \text{sgn}(k)\omega_k + i\epsilon}, \end{aligned} \quad (36)$$

where ϵ is a positive infinitesimal and V_k^ω is defined analogue to equation 34 with the time dependent perturbation potential V^t replaced by its Fourier transform V^ω :

$$V^t = \int_{-\infty}^{\infty} d\omega V^\omega \exp(-i\omega + \epsilon)t \quad (37)$$

Now having determined a parametrization for the time evolution of the wave function, this approach can be also applied to the time evolution of the expectation value of an operator A :

$$A_{Av}(t) = \langle \tilde{0} | A | \tilde{0} \rangle, \quad (38)$$

for which $|\tilde{0}\rangle$ can be expanded as demonstrated above:

$$\begin{aligned} A_{Av}(t) &= \langle 0 | A | 0 \rangle + \langle 0^{(1)} | A | 0 \rangle + \langle 0 | A | 0^{(1)} \rangle \\ &+ \langle 0^{(2)} | A | 0 \rangle + \langle 0^{(1)} | A | 0^{(1)} \rangle + \langle 0 | A | 0^{(2)} \rangle + \dots \\ &= \langle 0 | A | 0 \rangle - i \sum_n A_{-n} P_n^{(1)} - i \sum_n A_{-n} P_n^{(2)} + \sum_{n,j>0} P_{-j}^{(1)} A_{j-n} P_n^{(1)} + \dots \end{aligned} \quad (39)$$

Here the solution obtained for the time evolution of the $P_n^{(k)}$ parameters demonstrated for the linear term in equation 36 can be used to yield the time evolution of the operator. For the linear terms needed for the linear response formulation this leads to

$$-i \sum_k A_{-k} P_k^{(1)} = - \int_{-\infty}^{\infty} d\omega_1 \exp[(-i\omega_1 + \epsilon)t] \frac{\text{sgn}(k) A_{-k} V_k^{\omega_1}}{\omega_1 - \text{sgn}(k)\omega_k + i\epsilon}. \quad (40)$$

Since only the coefficient function in the second term depends on the operator all information about the response of the operator to a perturbation can be extracted from it. This coefficient function is therefore called a response function. For the case of the linear response function we define the symbol $\langle\langle A; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon}$ for it as

$$\langle\langle A; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon} = \frac{\text{sgn}(k) A_{-k} V_k^{\omega_1}}{\omega_1 - \text{sgn}(k)\omega_k + i\epsilon}. \quad (41)$$

Analogue to the symbol for the linear response function defined in the previous equation similar double bracket symbols are defined for quadratic and higher order response functions. In all these symbols the first operator corresponds to the observable monitors and the following (in the case higher order response functions sequence of) operator(s) correspond(s) to the external field(s). In the case of an electric dipole interaction with a periodically

oscillating field both the observed and the perturbing operators are electric dipole operators μ and the perturbation potential V^t is then given by

$$V^t = -(E_0\mu)[\exp(-i\omega_b + \epsilon)t + \exp(i\omega_b + \epsilon)t] \quad (42)$$

and the response function becomes

$$\begin{aligned} \langle\langle\mu^a; \mu^b\rangle\rangle_{\omega_b+i\epsilon} &= -\sum_{k>0} \left(\frac{\mu_{-k}^a \mu_k^b}{\omega_b - \omega_k + i\epsilon} - \frac{\mu_{-k}^b \mu_k^a}{\omega_b + \omega_k + i\epsilon} \right) \\ &= -\sum_{k>0} \left(\frac{\langle 0 | \mu^a | m \rangle \langle m | \mu^b | 0 \rangle}{\omega_b - \omega_k} - \frac{\langle 0 | \mu^b | m \rangle \langle m | \mu^a | 0 \rangle}{\omega_b + \omega_k} \right). \end{aligned} \quad (43)$$

As mentioned in the beginning of this section, the frequencies of the excitation are then given by the poles of the response function given in equation 43. The poles of this expression occur when the condition

$$\omega_b = \pm\omega_k = \pm(E_k - E_0) \quad (44)$$

is met, which corresponds to the physical relation that the energy of the absorbed photon has to match the energy difference of the states between which the electron is transferred. More interestingly the corresponding residues are then given by

$$\lim_{\omega_b \rightarrow \omega_n} (\omega_b - \omega_n) \langle\langle\mu^a; \mu^b\rangle\rangle_{\omega_b} = -\mu_{-n}^a \mu_n^b = \langle 0 | \mu^a | n \rangle \langle n | \mu^b | 0 \rangle \quad (45)$$

$$\lim_{\omega_b \rightarrow -\omega_n} (\omega_b + \omega_n) \langle\langle\mu^a; \mu^b\rangle\rangle_{\omega_b} = \mu_{-n}^b \mu_n^a = -\langle 0 | \mu^b | n \rangle \langle n | \mu^a | 0 \rangle. \quad (46)$$

While these relations completely define the calculation of the desired properties for the case of an exact wave function, there appears to be no advantage over the stationary state approach that could have been applied directly without the need for lengthy derivations. The usefulness of the time-dependent approach only becomes apparent, when the same strategy is applied to approximate states. For the special case of a Hartree-Fock reference wave function, this requires to first state the time-dependent parametrization of the approximate wave-function and the respective time-evolution and then follow the steps carried out with the exact wavefunction before: rewriting the time-evolution in terms of time-dependent coefficient functions, expansion of the coefficients in strength of the time-dependent perturbation and truncation to desired order. The resulting expressions then define eigenvalue equations

that can be solved by diagonalizing the matrices involved, where the transition frequencies are obtained as the eigenvalues and the transition moments can be calculated from the eigenvectors.

Assuming now that $|0\rangle$ describes the Hartree-Fock ground state, in the second quantization formalism its time development is then given by

$$|\tilde{0}\rangle = \exp(i\Lambda(t)) |0\rangle \quad (47)$$

with

$$\Lambda(t) = \sum_{m>0} (\bar{\lambda}_m(t)\bar{Q}_m + \bar{\lambda}_m^*(t)\bar{Q}_m^\dagger) = \sum_m (\lambda_m(t)Q_m), \quad (48)$$

where

$$\lambda_m(t) = \begin{cases} \bar{\lambda}_m(t), & m > 0 \\ \bar{\lambda}_m^*(t), & m < 0 \end{cases} \quad (49)$$

and

$$Q_m(t) = \begin{cases} \bar{Q}_m(t), & m > 0 \\ \bar{Q}_m^\dagger(t), & m < 0 \end{cases} \quad (50)$$

Here the \bar{Q}_m and \bar{Q}_m^\dagger operators represent the set of all excitation and de-excitation operators between the molecular orbitals of the wavefunction. In non-relativistic systems the \bar{Q} and \bar{Q}^\dagger operators are usually restricted to only perform excitations that are consistent with the spin-symmetry of the system.

To be able to express the time evolution of the system in terms of matrix elements that can be evaluated as integrals over time-independent orbitals both the wavefunction and the excitation operator are written in time-dependent exponential parametrizations, where the time-dependent excitation operator, here used as its transposed \tilde{T}^\dagger , becomes:

$$\tilde{T}^\dagger = \begin{pmatrix} \tilde{Q} \\ \tilde{Q}^\dagger \end{pmatrix} = \begin{pmatrix} \exp(i\Lambda(t))Q \exp(-i\Lambda(t)) \\ \exp(i\Lambda(t))Q^\dagger \exp(-i\Lambda(t)) \end{pmatrix} = \exp(i\Lambda(t))T^\dagger \exp(-i\Lambda(t)) \quad (51)$$

Using this parametrization the Ehrenfest Theorem yields the following time-evolution of the system:

$$\frac{d}{dt} \langle \tilde{0} | \tilde{T}^\dagger | \tilde{0} \rangle = \langle \tilde{0} | \dot{\tilde{T}}^\dagger | \tilde{0} \rangle - i \langle \tilde{0} | [\tilde{T}^\dagger, H_0 + V^t] | \tilde{0} \rangle \quad (52)$$

The terms of this time evolution can now be rewritten by Baker-Cambbell-Hausdorff (BCH) expanding operators surrounded by exponentials in a convenient manner that allows to rewrite the equation in a form where an expansion in order of perturbation strength can then be easily carried out. Here the terms will be grouped as $\frac{d}{dt} \langle \tilde{0} | \tilde{T}^\dagger | \tilde{0} \rangle - \langle \tilde{0} | \dot{\tilde{T}}^\dagger | \tilde{0} \rangle$, $-i \langle \tilde{0} | [\tilde{T}^\dagger, H_0] | \tilde{0} \rangle$, and $-i \langle \tilde{0} | [\tilde{T}^\dagger, V^t] | \tilde{0} \rangle$, which will lead to the expansion terms $S^{[n+1]}$, $E^{[n+1]}$, and $V^{[n+1]}$ respectively.

For the BCH expansions the superoperator notation \hat{A} is used. Here in particular the option to write chained commutators as power of superoperators proves useful:

$$\hat{A}B = [A, B] \quad (53)$$

$$\hat{A}^2B = [A, [A, B]] \quad (54)$$

Using this notation the BCH expansion is given by:

$$\exp(-iA)B \exp(iA) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} (\hat{A}^n B). \quad (55)$$

The time-evolution of the BCH expanded terms then leads to expressions that contain various powers of superoperators of Λ operators. Subsequently Λ is resolved as a linear combination of generalized excitation operators Q using the definition in equation 48. To more easily carry out the perturbative expansion the resulting expressions that involve superoperators over linear combinations of operators are rewritten using the following notation:

$$\hat{\Lambda}^k = \left(\sum_m \hat{\lambda}_m(t) Q_m \right)^k = \sum_{j_1, \dots, j_k} \left(\prod_{\mu=1}^k \lambda_{j_\mu}(t) \prod_{\mu=1}^k Q_{j_\mu} \right) \quad (56)$$

Applied to the time-evolution this leads to:

$$\begin{aligned}
& \frac{d}{dt} \langle \tilde{0} | \tilde{T}^\dagger | \tilde{0} \rangle - \langle \tilde{0} | \dot{\tilde{T}}^\dagger | \tilde{0} \rangle \\
&= \langle 0 | \exp(-i\Lambda) (\exp(i\Lambda) [\sum_{n=0}^{\infty} \frac{(-1)^n (i)^{n+1}}{(n+1)!} (\hat{\Lambda}^n \dot{\Lambda}), T^\dagger] \exp(-i\Lambda)) \exp(i\Lambda) | 0 \rangle \\
&= \sum_{n=0}^{\infty} \frac{(-1)^n (i)^{n+1}}{(n+1)!} \langle 0 | [(\hat{\Lambda}^n \dot{\Lambda}), T^\dagger] | 0 \rangle \\
&= \sum_m \sum_{n=0}^{\infty} \sum_{l_1, \dots, l_n} \frac{(-1)^n (i)^{n+1}}{(n+1)!} \langle 0 | [\prod_{\mu=1}^n Q_{l_\mu} Q_m, T^\dagger] | 0 \rangle \dot{\lambda}_m \prod_{\mu=1}^n \lambda_{l_\mu} \\
&= \sum_m \sum_{n=1}^{\infty} \sum_{l_1, \dots, l_n} i^n S_{j_{l_1 \dots l_n}}^{[n+1]} \dot{\lambda}_m \prod_{\mu=2}^n \lambda_{l_\mu}
\end{aligned} \tag{57}$$

$$\begin{aligned}
& -i \langle \tilde{0} | [\tilde{T}^\dagger, H_0] | \tilde{0} \rangle = -i \langle 0 | \exp(-i\Lambda) [\tilde{T}^\dagger, H_0] \exp(i\Lambda) | 0 \rangle \\
&= -i \langle 0 | [T^\dagger, \exp(-i\Lambda) H_0 \exp(i\Lambda)] | 0 \rangle = -i \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \langle 0 | [T^\dagger, (\hat{\Lambda} H_0)] | 0 \rangle \\
&= \sum_{n=0}^{\infty} \sum_{l_1, \dots, l_n} \frac{(-i)^{n+1}}{n!} \langle 0 | [T^\dagger, \prod_{\mu=1}^n Q_{l_\mu}, H_0] | 0 \rangle \prod_{\mu=1}^n \lambda_{l_\mu} = \sum_{n=1}^{\infty} E^{[n+1]} \prod_{\mu=1}^n \lambda_{l_\mu}
\end{aligned} \tag{58}$$

$$\begin{aligned}
& -i \langle \tilde{0} | [\tilde{T}^\dagger, V^t] | \tilde{0} \rangle = -i \langle 0 | \exp(-i\Lambda) [\tilde{T}^\dagger, V^t] \exp(i\Lambda) | 0 \rangle \\
&= -i \langle 0 | [T^\dagger, \exp(-i\Lambda) V^t \exp(i\Lambda)] | 0 \rangle = -i \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \langle 0 | [T^\dagger, (\hat{\Lambda} V^t)] | 0 \rangle \\
&= \sum_{n=0}^{\infty} \sum_{l_1, \dots, l_n} \frac{(-i)^{n+1}}{n!} \langle 0 | [T^\dagger, \prod_{\mu=1}^n Q_{l_\mu}, V^t] | 0 \rangle \prod_{\mu=1}^n \lambda_{l_\mu} = \sum_{n=1}^{\infty} V^{[n+1]} \prod_{\mu=1}^n \lambda_{l_\mu}
\end{aligned} \tag{59}$$

In this notation the BCH expanded time-evolution is given by

$$\sum_{n=1}^{\infty} (i)^n S_{j_{l_1 \dots l_n}}^{[n+1]} \dot{\lambda}_{l_1} \prod_{\mu=2}^n \lambda_{l_\mu} = - \sum_{n=0}^{\infty} (i)^{n+1} E_{j_{l_1 \dots l_n}}^{[n+1]} \prod_{\mu=1}^n \lambda_{l_\mu} - \sum_{n=0}^{\infty} (i)^{n+1} V_{j_{l_1 \dots l_n}}^{t[n+1]} \prod_{\mu=1}^n \lambda_{l_\mu}. \tag{60}$$

If λ and $\dot{\lambda}$ are now expanded in orders of perturbation, the linear response equation results as a set of coupled linear differential equations

$$iS_{jl}^{[2]}\dot{\lambda}_l^{(1)} - E_{jl}^{[2]}\lambda_l^{(1)} = -iV_j^{t[1]} \quad (61)$$

and higher order response equations will have the form of

$$iS_{jl}^{[2]}\dot{\lambda}_l^{(k)} - E_{jl}^{[2]}\lambda_l^{(k)} = f_j^{(k)}(t), \quad (62)$$

where $f_j^{(k)}(t)$ will contain the dependence on parameters in lower orders of the perturbation, that will then also depend on higher order $S^{[n+1]}$, $E^{[n+1]}$ and $V^{t[n+1]}$ matrix elements. These equations can then be separated by simultaneously diagonalizing $S^{[2]}$ and $E^{[2]}$. The decoupled equations are then given by

$$i\sigma_j\dot{\lambda}_j^{(k)} - \omega_j\lambda_j^{(k)} = f_j^{(k)}(t), \quad (63)$$

with σ_j and ω_j representing the diagonal elements of $S_j^{[2]}$ and $E_j^{[2]}$ respectively. The simultaneous diagonalization of $S^{[2]}$ and $E^{[2]}$ can be viewed as equivalent to solving the eigenvalue problem

$$E^{[2]}X_j = \xi_j S^{[2]}X_j \quad (64)$$

with $\xi_j = \omega_j\sigma_j^{-1}$. Explicitly the matrices involved are given by:

$$E^{[2]} = \begin{pmatrix} \langle 0 | [Q_i, [H_0, Q_j^\dagger]] | 0 \rangle & \langle 0 | [Q_i, [H_0, Q_j]] | 0 \rangle \\ \langle 0 | [Q_i, [H_0, Q_j]] | 0 \rangle^* & \langle 0 | [Q_i, [H_0, Q_j^\dagger]] | 0 \rangle^* \end{pmatrix} \quad (65)$$

and

$$S^{[2]} = \begin{pmatrix} \langle 0 | [Q_i, Q_j^\dagger] | 0 \rangle & \langle 0 | [Q_i, Q_j] | 0 \rangle \\ \langle 0 | [Q_i, Q_j] | 0 \rangle^* & \langle 0 | [Q_i, Q_j^\dagger] | 0 \rangle^* \end{pmatrix}. \quad (66)$$

As previously discussed for the case of an exact state the parametrization of the time-evolution of the system can now used to describe the time-evolution of the expectation value of an operator A , where the time-dependent coefficient functions, the response functions, can then be written in terms of the λ parameters.

$$\begin{aligned} \langle \tilde{0} | A | \tilde{0} \rangle &= \langle 0 | \exp(-i\Lambda)A \exp(i\Lambda) | 0 \rangle = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \langle 0 | (\hat{\Lambda}^n A) | 0 \rangle \\ &= \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \langle 0 | \left(\prod_{\mu=1}^n Q_{l_\mu} \right) | 0 \rangle \prod_{\mu=1}^n \lambda_{l_\mu} = \sum_{n=0}^{\infty} (i)^n A_{l_1, \dots, l_n}^{[n]} \prod_{\mu=1}^n \lambda_{l_\mu} \end{aligned} \quad (67)$$

Thereby we arrive at the approximate wave function analogue for the exact linear response function found in equation 41, where we use the Einstein convention for repeating indices:

$$\langle\langle A; V^{\omega_1} \rangle\rangle_{\omega_1+i\epsilon}^{HF} = \text{sgn}(j) f_j^{(1)}(\omega_1) A_j^{[1]} = \frac{\text{sgn}(j) V_j^{\omega_1[1]} A_j^{[1]}}{\omega_1 - \text{sgn}(j)\omega_j + i\epsilon} \quad (68)$$

and for the case of dipole-dipole interaction this then leads to

$$\langle\langle \mu^a; \mu^b \rangle\rangle_{\omega_b+i\epsilon} = \frac{\langle 0 | [Q_j, \mu^a] | 0 \rangle \text{sgn}(j) \langle 0 | [\mu^b, Q_j] | 0 \rangle}{\omega_1 - \text{sgn}(j)\omega_j + i\epsilon} = \frac{\mu_j^{a[1]} \text{sgn}(j) \mu_j^{b[1]}}{\omega_1 - \text{sgn}(j)\omega_j + i\epsilon} \quad (69)$$

with the corresponding residues

$$\lim_{\omega_1 \rightarrow \omega_f} (\omega_1 - \omega_f) \langle\langle \mu^a; \mu^b \rangle\rangle_{\omega_1+i\epsilon} = \mu_f^{a[1]} \mu_f^{b[1]} \quad (70)$$

$$\lim_{\omega_1 \rightarrow -\omega_f} (\omega_1 + \omega_f) \langle\langle \mu^a; \mu^b \rangle\rangle_{\omega_1+i\epsilon} = -\mu_{-f}^{a[1]} \mu_{-f}^{b[1]}. \quad (71)$$

Instead of solving the full eigenvalue equation given in equation 64, alternative solution strategies have been developed that make it possible to selectively solve for only the lowest energy excitations[30, 34], which allows for the efficient use also for very large systems. Additionally response theory has been reformulated in atomic orbitals which in combination with integral screening leads to linear scaling of the computational effort[35]. Time-dependent response theory also forms the basis for time-dependent density functional theory.

Time-dependent response theory has been successfully applied to a range of relativistic systems for scalar, two- and four-component Hamiltonians[36] and the used approaches should also be applicable to two-component ZORA in GAMESS-UK. When calculating response functions for relativistic Hamiltonians that have been generated by unitary transformations as it is the case for the ZORA Hamiltonians the operators used in the formulation of the response function should also be subjected to the same transformation. If the operators are not transformed the resulting error is called the picture change error. Recently it has been argued that the picture change error can be neglected for all properties that do not primarily depend on the electronic structure very close to the nuclei[37].

3 Model System

In the model system used in the calculations ytterbium is embedded in two different crystal systems yttrium oxide (Y_2O_3) and calcium fluoride (CaF_2). Due to its comparatively high nuclear mass, ytterbium's electronic structure is clearly subject to relativistic effects. Since it is used as a fluorophor, the electronic transition spectrum has been studied quite extensively and experimental results for comparison are widely available. Here in particular the fact that, because of its filled 4f orbitals, excited states undergo efficient cross-system coupling from singlet to triplet states has attracted attention. For the studied model systems charge transfer luminescence has been reported to occur for the yttrium oxide but not for the calcium fluoride crystal system[38].

In the computational model, one challenge results from the requirement to accurately include the electrostatic potential of the crystal lattice atoms surrounding the ytterbium atom while keeping the computational effort low enough to be feasible. The approach taken here is a layered model: one ytterbium atom and its nearest neighbours, six oxygen atoms in Y_2O_3 or eight fluoride atoms in CaF_2 , are included with all their electrons. For Y_2O_3 it was necessary for the stability of the SCF calculation to include the next to nearest neighbors, twelve yttrium atoms, modelled with effective core potentials (ECPs) so that the three outer most electrons are included explicitly and all electrons on these atoms located further inwards are only represented by an electrostatic potential. For CaF_2 ECPs on the next to nearest neighbors hindered convergence of the SCF calculation and the next to nearest neighbors have therefore been included as charge points. The remaining crystal environment is then included via an array of charge points.

In the range of three crystal unit cells around the ytterbium atom each ion is represented as a charge point. The remaining electrostatic potential of the crystal system is represented by an expansion in electrostatic moments, which provides positions and charges for charge points so that the electrostatic moments of the resulting system are successively set to zero[39]. For CaF_2 the embedding charge points remove electrostatic moments up to third order while for Y_2O_3 due to memory restrictions not more than second moments were possible because of to the very large number of charge points that would have been required for the third moment.

As basis set on ytterbium, the SARC-ZORA basis set (SARC = segmented all-electron relativistically contracted) has been used. This basis set has been optimized to yield energies and properties of accuracies adequate for calculations carried out on the Hartree-Fock or DFT level. It thereby avoids the very large sizes of basis sets optimized for calculations that include high levels of

electron correlation, without resorting to the use of ECPs. The basis set has been specifically optimized in using DFT in combination with ZORA [40]. On the oxygen and fluorine atoms, double zeta basis sets are used. For the yttrium atoms, a combination of the CRENBs effective core potential and the associated basis set [41].

On these two systems both scalar and spin-orbit ZORA UHF calculations have been carried out. In both cases spherical harmonics have been used. For Y_2O_3 level shifting parameters had to be changed for the scalar calculation to 11.0 for 60 iterations and 0.1 for the remainder of the calculation, and for the spin-orbit calculation to 14.0 for the first 80 iterations and 0.1 for the remainder of the calculation. For CaF_2 the default level shifting setting of 1.0 for 5 iterations followed by 0.3 is sufficient for both scalar and spin-orbit calculation.

Calculations in a modified version of the DIRAC program[42] for two-component Hamiltonians with higher accuracy separation of electronic and positronic component or with the full four-component Hamiltonian have been prepared, but not pursued any further once it became apparent that the different treatment of open shell systems in DIRAC would not allow for a meaningful comparison.

For the calculation of excitation energies and transition moments molecular orbital optimizations of excited states have been attempted, but the calculations have always resulted in optimized ground state orbitals. Preliminary calculations with the RPA implementation in GAMESS-UK have revealed that it is not currently advisable to attempt an extension of RPA to allow for 2-component ZORA orbitals, because the memory management within the RPA routine does not work correctly for the systems as large as the model systems used in this project.

4 Results and Discussion

In adding the spin-orbit interaction the two-component ZORA calculation stabilizes the system further compared to the scalar ZORA result. The total energy of the Y_2O_3 system changes from -15191.3951 Eh for one-component ZORA to -15202.7801 Eh for 2-component ZORA and for CaF_2 from -16023.4476 Eh to -16242.0143 Eh. Convergence is slow for all calculations with 407 iterations for the scalar and 4004 iterations for the spin-orbit calculation on CaF_2 and 162 and 300 iterations respectively on Y_2O_3 . The slower convergence of the CaF_2 system can be explained by the relatively higher level shift for all but the first few iterations. The higher number of iterations for spin-orbit calculations results from the direct inversion of the iterative subspace (DIIS) convergence acceleration method[43] that is used for the scalar calculations but is not implemented yet for the spin-orbit ZORA Hamiltonian.

In table 1 the distributions of sizes atomic orbital spin state population coefficients for both scalar and spin-orbit ZORA are compared for Y_2O_3 and CaF_2 . While for the spin-orbit calculations the optimized coefficients of all molecular orbitals are aggregated, for the scalar calculations the spin states of the molecular orbitals are used as source for the spin information. In addition the distribution of the occurring differences between the scalar and spin-orbit values is tabulated for both systems. The atomic orbitals have been divided in categories depending on their spin state coefficients or differences of coefficients. The categories span intervals of adjacent powers of 0.1 as for example the interval between 0.1 and 0.01. Only the results for the alpha spin states are shown because the beta state results are very similar. Table 1 shows that for both scalar and spin-orbit ZORA as well as for the differences the typical values for Y_2O_3 fall in the range of 0.0001 whereas for CaF_2 the most common values are found around 0.00001.

In addition a comparison of the spin states of the atomic orbitals resulting from the scalar and the spin-orbit ZORA method is shown for Y_2O_3 in table 2 and for CaF_2 in table 3, where in both cases only the atomic orbitals that differ most between scalar and spin-orbit calculation are shown, in order to keep the size of the tables manageable. For Y_2O_3 only for those 41 out of 318 atomic orbitals are included for which either alpha or beta spin occupation (or both) change(s) by more than 0.1. For CaF_2 already a threshold of 0.000015 limits the number of atomic orbitals from 218 to 36.

One observation from tables 2 and 3 is that a majority of spin states coefficients move closer to zero for the spin-orbit ZORA results as compared to the

Table 1: Distribution of Absolute Sizes of Spin Population from Scalar and Spin-Orbit Calculations and of Differences between Scalar and Spin-Orbit Calculations Compared for Y_2O_3 and CaF_2

$[10^{x-1}; 10^x]$	scalar		spin-orbit		diffence	
	Y_2O_3	CaF_2	Y_2O_3	CaF_2	Y_2O_3	CaF_2
1	0	0	8	2	6	2
2	30	2	34	5	28	5
3	71	15	73	21	52	21
4	97	36	100	52	101	52
5	77	55	41	68	74	64
6	15	24	16	20	15	17

scalar ZORA. This observation also holds for the atomic states not shown here explicitly. The distribution of sizes of relative differences appear to be similar between Y_2O_3 and CaF_2 , which would be consistent with the observation from table 1 that the distribution of absolute values is very similar between scalar and spin-orbit results and the respective differences within each subsystem.

The data suggests that there is a clear difference between Y_2O_3 and CaF_2 in the degree to which spin populations of atomic orbitals average out to zero when the contributions of all occupied molecular orbitals are aggregated. This observation can be seen as a consequence of the different geometries and electronic structure of the surrounding ions. In this context the question arises to what extent the use of ECPs for Y_2O_3 but not for CaF_2 plays a role and should be investigated further by renewing efforts to complete a SCF calculation on CaF_2 . In a broader sense it would be useful to investigate how sensitive the system is to the choice of embedding model and whether the model described above is adequate for the intended qualitative study of spin-forbidden transition moments.

Table 2: Maximum Change Atomic Orbital Spin Populations for Y_2O_3

No.	AO label	alpha scalar	alpha so	% change	beta scalar	beta so	% change
17	1 yb s	0.01849	0.00025	-98.648	-0.12930	-0.01209	-90.650
18	1 yb s	-0.04774	0.00124	-102.597	0.08708	-0.00452	-105.191
53	1 yb y	-0.00183	0.00007	-103.825	0.13089	-0.00644	-104.920
104	xx-yy	-0.03400	0.00001	-100.029	0.09661	0.01439	-85.105
109	1 yb xxx	-0.35454	-0.29831	-15.860	0.37323	0.32435	-13.096
110	1 yb yyy	0.08738	0.07555	-13.539	-0.09027	-0.07865	-12.872
112	1 yb xxy	0.07833	0.07236	-7.622	-0.07988	-0.07473	-6.447
114	1 yb xyy	-0.17667	-0.19465	10.177	0.23378	0.24712	5.706
115	1 yb yyz	0.07323	0.07459	1.857	-0.06391	-0.06515	1.940
116	1 yb xzz	-0.32204	-0.34376	6.745	0.28098	0.29549	5.164
117	1 yb yzz	0.61991	0.62646	1.057	-0.64292	-0.64714	0.656
119	1 yb xxx	-0.05553	-0.05784	4.160	0.02882	0.05104	77.099
127	1 yb yzz	0.05786	0.06323	9.281	-0.05299	-0.05406	2.019
144	2 o y	0.00020	0.00022	10.000	0.11089	0.10496	-5.348
145	2 o z	-0.00174	-0.00165	-5.172	0.28197	0.26829	-4.852
154	3 o y	0.00020	0.00022	10.000	0.11089	0.10496	-5.348
155	3 o z	-0.00174	-0.00165	-5.172	0.28197	0.26829	-4.852
164	4 o y	-0.00448	-0.00406	-9.375	0.63334	0.59815	-5.556
167	4 o y	-0.00505	0.00005	-100.990	0.19570	0.17208	-12.069
174	5 o y	-0.00448	-0.00406	-9.375	0.63334	0.59815	-5.556
177	5 o y	-0.00505	0.00005	-100.990	0.19570	0.17208	-12.069
184	6 o y	0.00050	0.00047	-6.000	0.17548	0.16382	-6.645
185	6 o z	0.00282	0.00274	-2.837	0.50132	0.47040	-6.168
188	6 o z	0.00028	0.00013	-53.571	0.11536	0.11805	2.332
194	7 o y	0.00050	0.00047	-6.000	0.17548	0.16382	-6.645
195	7 o z	0.00282	0.00274	-2.837	0.50132	0.47040	-6.168
198	7 o z	0.00028	0.00013	-53.571	0.11536	0.11805	2.332
199	8 y s	0.17284	0.07336	-57.556	-0.35063	-0.15225	-56.578
201	8 y y	0.25707	0.18662	-27.405	-0.50300	-0.37245	-25.954
202	8 y z	0.04597	0.02795	-39.199	-0.08026	-0.05328	-33.616
204	xx-yy	0.04672	0.06401	37.008	-0.09087	-0.12098	33.135
209	9 y s	0.17284	0.07336	-57.556	-0.35063	-0.15225	-56.578
211	9 y y	0.25707	0.18662	-27.405	-0.50300	-0.37245	-25.954
212	9 y z	0.04597	0.02795	-39.199	-0.08026	-0.05328	-33.616
214	xx-yy	0.04672	0.06401	37.008	-0.09087	-0.12098	33.135
239	12 y s	0.00161	0.00090	-44.099	0.25225	0.13188	-47.719
242	12 y z	0.00338	0.00028	-91.716	0.18886	0.16321	-13.581
248	12 y yz	0.00077	0.00044	-42.857	0.31398	0.31187	-0.672
249	13 y s	0.00161	0.00090	-44.099	0.25225	0.13188	-47.719
252	13 y z	0.00338	0.00028	-91.716	0.18886	0.16321	-13.581
258	13 y yz	0.00077	0.00044	-42.857	0.31398	0.31187	-0.672

Table 3: Maximum Change Atomic Orbital Spin Populations for CaF_2

No.	AO label	alpha scalar	alpha so	% change	beta scalar	beta so	% change
15	1 yb s	-0.00561	-0.00094	-83.244	-0.00559	-0.00094	-83.184
31	1 yb x	0.00023	0.00052	126.087	0.00023	0.00054	134.783
34	1 yb x	0.00064	0.00131	104.687	0.00064	0.00135	110.938
36	1 yb z	0.00068	0.00275	304.412	0.00068	0.00269	295.588
37	1 yb x	0.00278	0.00134	-51.799	0.00284	0.00143	-49.648
38	1 yb y	0.00065	0.00022	-66.154	0.00067	0.00023	-65.672
39	1 yb z	0.00307	0.00340	10.749	0.00308	0.00335	8.766
40	1 yb x	0.00585	0.00336	-42.564	0.00576	0.00337	-41.493
41	1 yb y	0.00128	0.00067	-47.656	0.00126	0.00066	-47.619
42	1 yb z	0.00635	0.00486	-23.465	0.00616	0.00472	-23.377
43	1 yb x	-0.00891	-0.00159	-82.155	-0.00884	-0.00158	-82.127
44	1 yb y	-0.00223	-0.00041	-81.614	-0.00221	-0.00041	-81.448
45	1 yb z	-0.00956	-0.00143	-85.042	-0.00938	-0.00141	-84.968
46	1 yb x	0.00015	-0.00054	-460.000	0.00012	-0.00054	-550.000
109	1 yb xxx	0.02194	0.01930	-12.033	0.03071	0.02691	-12.374
111	1 yb zzz	0.27679	0.24084	-12.988	0.26902	0.23410	-12.980
112	1 yb xxy	0.00203	0.00202	-0.493	0.00205	0.00204	-0.488
113	1 yb xxz	0.62967	0.64347	2.192	0.61468	0.62811	2.185
114	1 yb xyy	0.01720	0.01801	4.709	0.01828	0.01931	5.635
115	1 yb yyz	0.01475	0.01808	22.576	0.01402	0.01720	22.682
116	1 yb xzz	0.01631	0.01717	5.273	0.02885	0.03013	4.437
117	1 yb yzz	0.00205	0.00204	-0.488	0.00203	0.00202	-0.493
118	1 yb xyz	0.00356	0.00343	-3.652	0.00368	0.00355	-3.533
119	1 yb xxx	0.00051	-0.00164	-421.569	0.00076	-0.00129	-269.737
121	1 yb zzz	0.00791	0.00802	1.391	0.00776	0.00783	0.902
122	1 yb xxy	-0.00161	-0.00187	16.149	-0.00163	-0.00188	15.337
123	1 yb xxz	0.01656	0.02624	58.454	0.01638	0.02580	57.509
124	1 yb xyy	-0.00222	-0.00208	-6.306	-0.00222	-0.00204	-8.108
126	1 yb xzz	-0.00049	-0.00108	120.408	-0.00018	-0.00054	200.000
127	1 yb yzz	-0.00176	-0.00195	10.795	-0.00177	-0.00197	11.299
128	1 yb xyz	-0.00343	-0.00319	-6.997	-0.00346	-0.00322	-6.936
133	1 yb xxz	0.00093	0.00038	-59.140	0.00089	0.00036	-59.551
135	1 yb yyz	0.00025	-0.00008	-132.000	0.00023	-0.00008	-134.783
136	1 yb xzz	0.00002	0.00003	50.000	0.00005	0.00005	0.000
145	2 f z	-0.00006	-0.00004	-33.333	-0.00008	-0.00007	-12.500
185	6 f z	-0.00006	-0.00004	-33.333	-0.00008	-0.00007	-12.500

5 Conclusion and Outlook

The SCF calculations discussed in the previous chapters constitute one approach to the calculation of the electronic structure of ytterbium in yttrium oxide and calcium fluoride crystal systems. The embedding approach and computational parameters chosen could potentially form the basis for calculations of excitation energies and transition moments. Trial calculations to this end have been performed that have provided insights into how the used methods might be improved to overcome their current deficiencies.

The embedding found for the crystal systems provides a compromise between the desired accuracy and stability of the calculations, the capabilities of GAMESS-UK and the available computational resources. As mentioned in the previous sections further investigations of alternatives and possible improvements are advisable, but a viable solution appears to have been reached with the current model. The combination of nearest neighbor atoms, ECPs and charge points and electrostatic moment expansion used might also serve as a good starting point for other embedding problems to be treated in GAMESS-UK.

For the calculation of excited states and also for faster spin-orbit ZORA ground state SCF optimizations the implementation of DIIS for two-component ZORA is one possible approach. The optimization of excited states might however require more sophisticated optimization methods that use second derivatives of the molecular orbital coefficients.

In conclusion, the results presented while falling short of providing excitation energies and transition moments signify substantial progress towards the calculation of all-electron spectra that include spin-orbit coupling.

References

- [1] Pekka Pyykkö. Relativistic effects in structural chemistry. *Chemical Reviews*, 88:563–594, 1988.
- [2] E. van Lenthe, E.J. Baerends, and J.G. Snijders. Relativistic regular two-component hamiltonians. *Journal of Chemical Physics*, 99(6):4597 – 4610, 1993.
- [3] Martyn F. Guest, Ian J. Bush, Huub J. J. van Dam, Paul Sherwood, Jens M. H. Thomas, Joop H. van Lenthe, Remco W. A. Havenith, and John Kendrick. The gamess-uk electronic structure package: algorithms, developments and applications. *Molecular Physics*, 103(6-8):719–747, 2005.
- [4] Paul A. M. Dirac. The quantum theory of the electron. *Proceedings of the Royal Society A*, 117:610 – 624, 1928.
- [5] R. E. Moss. *Advanced Molecular Quantum Mechanics*. Chapman and Hall Ltd, London, 1973.
- [6] Marvin Douglas and Norman M. Kroll. Quantum electrodynamical corrections to the fine structure of helium. *Annals of Physics*, 82:89–155, 1974.
- [7] Bernd A. Hess. Relativistic electronic-structure calculations employing a two-component no-pair formalism with external-field projection operators. *Physical Review A*, 33:3742–3748, 1986.
- [8] A. Rutkowski. Relativistic perturbation theory. i. a new perturbation approach to the dirac-equation. *Journal of Physics B: Atomic Molecular and Optical Physics*, 19:149–158, 1986.
- [9] W. Kutzelnigg. Perturbation theory of relativistic corrections. i. the non-relativistic limit of the dirac-equation and a direct perturbation expansion. *Zeitschrift für Physik D*, 11:15–28, 1989.
- [10] Kenneth G. Dyall. Interfacing relativistic and nonrelativistic methods. i. normalized elimination of the small component in the dirac equation. *Journal of Chemical Physics*, 106:9618–9626, 1997.
- [11] Kenneth G. Dyall. A systematic sequence of relativistic approximations. *Journal of Computational Chemistry*, 23:786–793, 2002.

- [12] W. Kutzelnigg. Perturbation theory of relativistic corrections. *Zeitschrift für Physik D*, 15:27–50, 1990.
- [13] Ch. Chang, M. Pelissier, and Ph. Durand. Regular two-component pauli-like effective hamiltonians in dirac theory. *Physica Scripta*, 4(5):394 – 404, 1986.
- [14] Leslie L. Foldy and Siegfried A. Wouthuysen. On the dirac theory of spin 1/2 particles and its non-relativistic limit. *Physical Review*, 78:29–36, 1950.
- [15] E. van Lenthe, E.J. Baerends, and J.G. Snijders. Relativistic total energy using regular approximations. *Journal of Chemical Physics*, 101(11):9783 – 9792, 1994.
- [16] S. Faas, J. H. van Lenthe, and J. G. Snijders. Regular approximated scalar relativistic correlated ab initio schemes: applications to rare gas dimers. *Molecular Physics*, 98:1467–1472, 2000.
- [17] E. van Lenthe, R. van Leeuwen, E.J. Baerends, and J.G. Snijders. Relativistic regular two-component hamiltonians. *International Journal of Quantum Chemistry*, 57:281–293, 1996.
- [18] S. Faas, J.G. Snijders, J.H. van Lenthe, E. van Lenthe, and E.J. Baerends. The zora formalism applied to the dirac-fock equation. *Chemical Physics Letters*, 246:632 – 640, 1995.
- [19] G. Breit. The effect of retardation on the interaction of two electrons. *Physical Review*, 34:553 – 573, 1929.
- [20] S. Faas, J.G. Snijders, and J.H. van Lenthe. Ab-initio zora calculations. In *Progress in Theoretical Chemistry and Physics*. Kluwer Academic Publishers, 2000.
- [21] S. Faas, J.H. van Lenthe, A.C. Hennen, and J.G. Snijders. An ab initio two-component relativistic method including spin-orbit coupling using the regular approximation. *Journal of Chemical Physics*, 113:4052–4059, 2000.
- [22] Leticia González, Daniel Escudero, and Luis Serrano-Andrés. Progress and challenges in the calculation of electronic excited states. *ChemPhysChem*, 13:28–51, 2012.
- [23] K. Morokuma and S. Iwata. Extended hartree-fock theory for excited states. *Chemical Physics Letters*, 16:192–197, 1972.

- [24] James B. Foresman, Martin Head-Gordon, John A. Pople, and Michael J. Frisch. Toward a systematic molecular orbital theory for excited states. *Journal of Physical Chemistry*, 96:135–149, 1992.
- [25] Martin Head-Gordon, Rudolph J. Rico, Manabu Oumi, and Timothy J. Lee. A doubles correction to electronic excited states from configuration interaction in the space of single substitutions. *Chemical Physics Letters*, 219:21–29, 1994.
- [26] A.D. McLachlan and M.A. Ball. Time-dependent hartree-fock theory for molecules. *Reviews of Modern Physics*, 36:844–855, 1964.
- [27] Jan Linderberg and Yngve Öhrn. *Propagators in Quantum Chemistry*. Academic Press, London and New York, 1973.
- [28] Poul Jørgensen and Jack Simons. *Second Quantization-Based Methods in Quantum Chemistry*. Academic Press, New York, 1981.
- [29] Trygve Helgaker, Sonia Coriani, Poul Jørgensen, Kasper Kristensen, Jeppe Olsen, and Kenneth Ruud. Recent advances in wave function-based methods of molecular-property calculations. *Chemical Reviews*, 112:543–631, 2012.
- [30] Jeppe Olsen and Poul Jørgensen. Linear and nonlinear response function for an exact state and for an mcscf state. *Journal of Chemical Physics*, 7:3235–3264, 1985.
- [31] Ove Christiansen, Poul Jørgensen, and Christof Hättig. Response functions from fourier component variational perturbation theory applied to a time-averaged quasienergy. *International Journal of Quantum Chemistry*, 68:1–52, 1998.
- [32] C. Fuchs, V. Bonačić-Koutecký, and J. Koutecký. Compact formulation of multiconfigurational response theory. applications to small alkali metal clusters. *The Journal of Chemical Physics*, 98(4):3121–2140, 1993.
- [33] Paul Ehrenfest. Bemerkung über die angenäherte gültigkeit der klassischen mechanik innerhalb der quantenmechanik. *Zeitschrift für Physik*, 45:455–457, 1927.
- [34] B.N. Parlett. *The Symmetric Eigenvalue Problem*. Prentice-Hall, Englewood Cliffs, NJ, 1980.

- [35] Sonia Coriani, Stinne Høst, Branislav Jansík, Lea Thøgersen, Jeppe Olsen, Poul Jørgensen, Simen Reine, Filip Pawłowski, Trygve Helgaker, and Paweł Sałek. Linear-scaling implementation of molecular response theory in self-consistent field electronic-structure theory. *The Journal of Chemical Physics*, 126:154108, 2007.
- [36] Radovan Bast, Andreas J. Thorvaldsen, Magnus Ringholm, and Kenneth Ruud. Atomic orbital-based cubic response theory for one-, two-, and four-component relativistic self-consistent field models. *Chemical Physics*, 356:177–186, 2009.
- [37] Trond Saue. Relativistic hamiltonians for chemistry: A primer. *ChemPhysChem*, 12:3077–3094, 2011.
- [38] L van Pieterson, M Heeroma, E de Heer, and A Meijerink. Charge transfer luminescence of yb^{3+} . *Journal of Luminescence*, 91(3-4):177 – 193, 2000.
- [39] Alain Gellé and Marie-Bernadette Lepetit. Fast calculation of the electrostatic potential in ionic crystals by direct summation method. *The Journal of Chemical Physics*, 128:244716, 2008.
- [40] Dimitrios A. Pantazis and Frank Neese. All-electron scalar relativistic basis sets for the lanthanides. *Journal of Chemical Theory and Computation*, 5:2229–2238, 2009.
- [41] L.A. LaJohn, P.A. Christiansen, R.B. Ross, T. Atashroo, and W.C. Ermler. Ab initio relativistic effective potentials with spin-orbit operators. iii. rb through xe. *The Journal of Chemical Physics*, 87:2812–2824, 1987.
- [42] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC13 (2013), written by L. Visscher, H. J. Aa. Jensen, R. Bast, and T. Saue, with contributions from V. Bakken, K. G. Dyall, S. Du-billard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. K. Lærdahl, Y. S. Lee, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kul-lie, C. V. Larsen, H. S. Nataraj, P. Norman, G. Olejniczak, J. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, K. Ruud, P. Sałek, B. Schimmelpfennig, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (see <http://www.diracprogram.org>).

- [43] Péter Pulay. Convergence acceleration of iterative sequences. the case of scf iteration. *Chemical Physics Letters*, 73:393–398, 1980.