

A Direct Atomic-Orbital Based Relativistic Two-Component Linear Response Method for Calculating Excited State Fine Structures

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Abstract

In this work we present a linear-response formalism of the complex two-component Hartree-Fock Hamiltonian that includes relativistic effects within the the Douglas-Kroll-Hess and the Exact-Two-Component frameworks. The method includes both scalar and spin relativistic effects in the variational description of electronic ground and excited states, though it neglects the picture-change and explicit spin-orbit contributions arising from the two-electron interaction. An efficient direct formalism of solving the complex two-component response function is also presented in this work. The presence of spin-orbit couplings in the Hamiltonian and the two-component nature of the wave function and Fock operator allows the computation of excited-state zero-field splittings of systems for which relativistic effects are dominated by the one-electron term. Calculated results are compared to experimental reference values to assess the quality of the underlying approximations. The results show that the relativistic two-component linear response methods are able to capture the excited state zero-field splittings with good agreement with experiments for the systems considered here, with all approximations exhibiting a similar performance. However, the error increases for heavy elements and for states of high orbital angular momentum, suggesting the importance of two-electron relativistic effect in such situations.

1 Introduction

The relativistic treatment of electronic structure yields important quantum mechanical effects, arising from the resulting spin-orbit and spin-spin interactions.¹⁻³ These interactions are responsible for a variety of physical phenomena. Zero-field-splitting in magnetic systems, L-edge splitting in metal core-electron spectroscopy, and intersystem crossing rely on these interactions and cannot be explained in a strictly non-relativistic framework. Moreover, these effects govern the fundamental underpinnings of magnetic materials and spintronic devices.⁴⁻⁷

Relativistic effects are important when electrons are close to the nucleus and this effect increases with atomic number.⁸ Among the different relativistic effects, spin-orbit couplings play a crucial role in valence electronic structures of magnetic systems, such as transition metal complexes. For example, high-spin *d*-metal complexes can experience energy level splittings of the partially filled *d*-orbitals even in the absence of an external magnetic field (zero-field splittings, also known as fine structure splittings). While zero-field splittings are observed in the ground state of symmetric molecules, the presence of spin-orbit couplings also gives rise to the splitting of energy levels in the excited states. This phenomenon leads to the spectroscopic zero-field splittings. Zero-field splittings highlight the multiple-component nature of the wave function and the fact that the electronic wave function is no longer an eigenfunction of the spin operators. Non-relativistic and scalar relativistic calculations are unable to capture such effects, at times yielding qualitatively incorrect results.⁹

Spin-orbit couplings are generally neglected or treated perturbatively in routine calculations. This is because such interactions in light elements are often weak and represent small corrections to molecular properties. Furthermore, approximate treatments reduce the computational cost and complexity of electronic structure methods, by allowing the use of non-relativistic methods with minimal modifications. Perturbative methods, however, are not always indicated and variational alternatives may be preferable; this requires new developments to include relativistic effects beyond the perturbative regime within computational schemes that can be applied to both ground and excited states.

Recently, much work has extended the computational protocols developed for non-relativistic calculations so that they can treat relativistic and spin-dependent systems. These methods can be classified according to the number of components in the wave function description. The most accurate methods are based on the Dirac equation and employ a four-component wave function ansatz.^{10,11} Such methods are computationally expensive except for systems with few electrons. For most chemically relevant studies, approximate two-component methods are usually sufficient. Among the methods that have been developed there are the Nor-

malized Elimination of the Small Component (NESC),^{12–16} the Zero-Order Regular Approximation (ZORA),^{17–20} the Douglas-Kroll-Hess transformation (DKH),^{21–24} and the Exact Two Component method (X2C).^{25–30} These methods differ in the approximation they use to decouple the large and small components of the relativistic wave function. Each method has its own advantages and disadvantages. However, once an approximate decoupling is achieved, the quasi-relativistic Hamiltonian can be used with most electronic structure methods, provided a non-collinear formalism is employed.^{25,31–33} Regardless of the choice of approximate decoupling method, in practice, however, the two-electron operator is left untransformed. Therefore two-electron effects such as spin-own-orbit and spin-other-orbit interactions are either neglected or approximated.

Even in the absence of spin-orbit interactions, a non-collinear two-component description of the wave function may be required in the case of spin-frustrated systems that exhibit instabilities with respect to the relaxation of the collinearity constraint commonly employed in non-relativistic calculations.^{34,35} In such cases, electronic excited states should also be computed by using a two-component formalism in the response equations.

There were a number of developments that extended the ground state two-component methods to address excited state relativistic effects. The DKH method has been used for the study of excited states in both Self-Consistent-Field (SCF) methods^{36,37} and multi-configurational methods,³⁸ and the linear-response formalism was also employed by Yoshizawa and Hada for the calculation of frequency-dependent molecular magnetizabilities.³⁹ A relativistic two-component response formalism for the study of excited states has also been described for ZORA,^{40–43} X2C,^{44–47} and in the case of Effective Core Potentials (ECP).⁴⁸ In this work, we present a direct atomic-orbital based implementation of linear response two-component methods in the forms of X2C and DKH for the purpose of studying relativistic effects on excited states, with an emphasis of spin-orbit interactions. Note however that this formalism can be applied in other fields as well, such as in modeling spin-frustrated systems or in the modeling of phenomena such as phosphorescence and intersystem crossing, where transition between states of different spin multiplicities are involved.

2 Theory

Here we briefly review the ground state two-component theory and outline its application in the first-order response of the Hartree-Fock (HF) wave function to model zero-field splittings in the excited states. We adopt the notation that indices i, j, k, l (a, b, c, d) refer to occupied (unoccupied) complex two-component MOs, and p, q, r, s for general MOs. $\mu, \nu, \lambda, \delta$ will be used to label atomic orbital (AO), and σ, σ' to label different spin projections. MOs are

expanded in terms of real atomic spin-orbitals.

2.1 Four-component to Two-component Transformation

The relativistic time-independent Dirac Hamiltonian can be written in the four-component block form as:

$$\mathcal{H} = \begin{pmatrix} (V + mc^2) \cdot \mathbf{I}_2 & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & (V - mc^2) \cdot \mathbf{I}_2 \end{pmatrix} \quad (1)$$

where $\boldsymbol{\sigma}$ is a vector whose components are the Pauli matrices. V is the potential term that collects the nucleus-electron attraction and electron-electron repulsion terms. The wave function is usually expressed in a four-component form,

$$\psi = \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} \quad (2)$$

where the large (L) and small (S) components of the wave function each is in a two-component form, $\psi_L = (\psi_L^\alpha, \psi_L^\beta)^\top$, $\psi_S = (\psi_S^\alpha, \psi_S^\beta)^\top$.

A two-component method seeks to eliminate the need to evaluate the small component by “folding” it into the large by means of a unitary transformation \mathcal{U} applied to both the Dirac Hamiltonian and the wave function:

$$\mathcal{U} \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} = \begin{pmatrix} \tilde{\psi}_L \\ 0 \end{pmatrix} \quad (3)$$

$$\mathcal{U}\mathcal{H}\mathcal{U}^\dagger = \begin{pmatrix} H_+ & \mathbf{0}_2 \\ \mathbf{0}_2 & H_- \end{pmatrix} \quad (4)$$

The Hamiltonian is reduced to a block-diagonal form while the lower two components of the wave function have been zeroed out. Note that like ψ_L and ψ_S , $\tilde{\psi}_L$ is also a two-component wave function. For problems associated with electrons, only those solutions that correspond to the positive energy states (eigenfunctions of H_+) need be computed.

Two-component methods differ in the way they form the unitary transformation details of which have been described elsewhere.^{20,49,50} The leading error in two-component approaches arises from the neglect of the transformation of the two-electron Coulomb repulsion operator. The two-electron integrals used to form the Fock matrix are thus not subject to a picture change, greatly simplifying the development of relativistic electronic structure theory. Within this scheme, only one-electron terms (kinetic energy and electron-nuclear interaction) need to be transformed in the DKH, while the X2C transformation is obtained from the one-step diagonalization of the one-electron Dirac Hamiltonian represented in a

kinetically balanced basis. Note that in a more general formulation of the method, X2C can also be obtained from a mean-field four-component Hamiltonian^{20,49,51,52} which, while more expensive, affords a more accurate description of relativistic effects. If two-electron spin-orbit effects are neglected, the leading error comes from the spin-own-orbit term, which is opposite sign compared to the one-electron spin-orbit term. In order to partially correct for these approximations, the one-electron spin-orbit integrals are often scaled using fudge factors based on the angular momenta.^{53,54} Other correction schemes have been proposed,^{26,30,55,56} however the following discussion is independent of the particular choice of spin-orbit correction so long as the two-electron spin-orbit contribution does not explicitly depend on the density.

2.2 Variational Ground State Complex Two-Component Methods in the Atomic Orbital Basis

In the following discussion, we assume that the wave function and Hamiltonian operators are already in the transformed basis, and we removed the tilde notation for simplicity. In the two-component Hartree Fock method, the ground state reference is represented as a variationally optimized single Slater determinant of complex two-component molecular orbitals,

$$\psi_L = |\varphi_p \varphi_q \varphi_r \dots| \quad (5)$$

$$\varphi_p(\mathbf{r}, \sigma) = \sum_{\mu} \chi_{\mu}(\mathbf{r}) \begin{pmatrix} C_{\mu p}^{\alpha} \\ C_{\mu p}^{\beta} \end{pmatrix} \quad (6)$$

where the α and β components are expanded in the same set of basis $\{\chi_{\mu}\}$, and the expansion coefficients are complex. This form of the wave function is similar to the one in the generalized Hartree-Fock scheme,^{34,35,57-62} but with distinct differences in its association with the two-component transformations.

The transformed Fock operator differs from its non-relativistic counterpart in the one-electron term only because the two-electron operator r_{ij}^{-1} is not transformed. We can write the two-component Fock operator as

$$F^{2c} = h^{2c} + G^{2c}(\rho^{2c}) \quad (7)$$

where ρ^{2c} is the two-component density, and h^{2c} contains both the transformed kinetic energy and electron-nucleus potential terms. Relativistic effects appear in the two-electron term indirectly through the two-component electron density ρ .

The Fock operator contains terms that couple the α and β electron densities, therefore the SCF problem must be solved within the complex two-component framework. The SCF

equations for two-component wave function can be written in a spin-blocked form:³⁵

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^\alpha \\ \mathbf{C}^\beta \end{pmatrix} = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} \mathbf{C}^\alpha \\ \mathbf{C}^\beta \end{pmatrix} \boldsymbol{\varepsilon} \quad (8)$$

$$\mathbf{F}^{\sigma\sigma'} = \mathbf{h}_{\text{DKH}}^{\sigma\sigma'} + \delta_{\sigma\sigma'} \mathbf{J}(\mathbf{P}^{\alpha\alpha} + \mathbf{P}^{\beta\beta}) - \mathbf{K}(\mathbf{P}^{\sigma\sigma'}) \quad (9)$$

$$F_{\mu\nu}^{\sigma\sigma'} = \sum_i C_{\mu i}^\sigma C_{\nu i}^{*\sigma'} \quad (10)$$

where \mathbf{S} is the AO overlap matrix, $\boldsymbol{\varepsilon}$ is the diagonal matrix of the MO energies, \mathbf{P} is the density matrix in AO basis, \mathbf{J} and \mathbf{K} are the Coulomb and exchange integrals contracted with spin-blocked density matrices. Equation (8) can be solved with standard SCF techniques and followed by a stability test,³⁵ yielding a set of ground state complex two-component MOs.

2.3 Time-dependent Perturbation and Linear Response Formalism

To model excited states in a linear response formalism we start from the equation governing the time-dependence of the two-component Hartree-Fock density matrix of the system subject to a time-dependent perturbation:

$$i\hbar \frac{\partial}{\partial t} \rho^{2c} = [F^{2c}, \rho^{2c}] \quad (11)$$

Where the two-component Fock operator (Eq. (7)) is given by:

$$h_{2c} = \mathcal{U}(h^{4c} + V_{\text{ext}}^{4c}(t))\mathcal{U}^\dagger \quad (12)$$

$$h^{4c} + V_{\text{ext}}^{4c}(t) = \begin{pmatrix} (V_{\text{eN}} + V_{\text{ext}}(t)) \cdot \mathbf{I}_2 & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & (V_{\text{eN}} + V_{\text{ext}}(t) - 2mc^2) \cdot \mathbf{I}_2 \end{pmatrix} \quad (13)$$

Where the one-electron Hamiltonian includes the kinetic energy and the electron-nuclei attraction terms and V_{ext} is the external potential. It can be seen from Eq. (7) that in the Hess approximation that we employ, the two-component transformation is only applied to the one-electron part of the Hamiltonian.

The time-dependent perturbation V_{ext}^{4c} can be written as:

$$V_{\text{ext}}^{4c} = \frac{\lambda}{2} (v^{4c} e^{-i\omega t} + v^{4c\dagger}(-\omega) e^{i\omega t}) \quad (14)$$

where λ is a perturbation strength parameter. If we consider an electric-field perturbation the

interaction operator is simply the dipole moment of the system which, in the four component framework is diagonal.

$$v^{4c}(\omega) = -\vec{\mu} \cdot \vec{E}(\omega) \mathbf{I}_4 \quad (15)$$

The perturbation strength parameter λ can be alternatively viewed as the intensity of the external electric field \vec{E} .

Equation (11) may be solved by propagating the two-component density directly in real time,⁶² or by response theory. In the latter case, it is customary to separate the solution into orders of perturbation. The density and Fock operator are then expanded to different orders in the perturbation.

$$\rho(t) = \rho^0 + \lambda\rho^\lambda + \dots \quad (16)$$

$$F(t) = F^0 + \lambda F^\lambda + \dots \quad (17)$$

The first-order terms have components in both ω and $-\omega$, higher orders follow the same pattern. These expansions can be plugged into Eq. (11), which is separated into the different orders, and similar terms are collected:

$$0 = [F, \rho] \quad (18)$$

$$\hbar\omega\rho^\lambda(\omega) = [F, \rho^\lambda(\omega)] + [F^\lambda(\omega), \rho] \quad (19)$$

Analogous expressions are obtained for the $-\omega$ terms. To solve for the excited states of the system we need to solve this equation for the resonant frequencies ω as well as the transition densities ρ^λ , and in order to do so the Fock derivative with respect to the perturbation must be evaluated, taking into account the nature of the one-electron term, which has been transformed from a four-component to a two-component operator.

In practical calculations the density is expanded in terms of orbital pair transition contributions, therefore the previous equation is rewritten as:

$$\langle \varphi_p | \hbar\omega\rho^\lambda(\omega) | \varphi_q \rangle = \langle \varphi_p | [F, \rho^\lambda(\omega)] + [F^\lambda(\omega), \rho] | \varphi_q \rangle \quad (20)$$

It can be shown that the first-order density can only have occupied-virtual and virtual-occupied contributions:⁶³⁻⁶⁵

$$\rho^\lambda(x, x'; \omega) = \sum_{ai} (X_{ai}\varphi_a(x)\varphi_i^*(x') + Y_{ai}\varphi_i(x)\varphi_a^*(x')) \implies \mathbf{P}^\lambda = \begin{pmatrix} 0 & \mathbf{Y}^t \\ \mathbf{X} & 0 \end{pmatrix} \quad (21)$$

The Fock operator derivative must be performed with care because in the two-component

framework it contains DKH or X2C transformed terms:

$$\mathbf{F}^{2c,\lambda} = \frac{\partial \mathbf{h}^{2c}}{\partial \lambda} + \frac{\partial \mathbf{G}^{2c}}{\partial \mathbf{P}^{2c}} \cdot \mathbf{P}^{2c,\lambda} + \mathbf{G}^{2c,\lambda}(\mathbf{P}^{2c}) \quad (22)$$

The derivative of the two-electron operator with respect to the density (the second term) gives rise to the \mathbf{A} and \mathbf{B} in matrices Eq. (25), similar to those in the conventional TDHF equation. The electron-electron repulsion term does not directly depend on the perturbation, and is independent of the two-component transformation \mathcal{U} in the bare Coulomb operator approximation. As a result, $\mathbf{G}^\lambda = \mathbf{0}$. In a complete two-component formalism where the two-electron repulsion operator is also transformed, \mathbf{G}^λ is non-vanishing because the two-component transformation \mathcal{U} depends on the perturbation strength λ .

In the non-relativistic regime the derivative of the one-electron operator with respect to the field strength is the perturbation $v(\omega)$. In the two-component formalism, the effect of the perturbation on the transformation $\mathcal{U}(\lambda)$ must be taken into consideration:

$$\begin{aligned} \left(\frac{\partial h^{2c}}{\partial \lambda} \right) &= \left(\frac{\partial \mathcal{U}}{\partial \lambda} \right) h^{4c} \mathcal{U}^\dagger + \mathcal{U} h^{4c} \left(\frac{\partial \mathcal{U}^\dagger}{\partial \lambda} \right) + \mathcal{U} v^{4c} \mathcal{U}^\dagger \\ &= \left(\frac{\partial \mathcal{U}}{\partial \lambda} \right) \mathcal{U}^\dagger h^{2c} + h^{2c} \mathcal{U} \left(\frac{\partial \mathcal{U}^\dagger}{\partial \lambda} \right) + v^{2c} \end{aligned} \quad (23)$$

The first two terms describe the change in the two-component decoupling transformation \mathcal{U} , which is necessary in order to maintain the decoupling of the large and small components as the perturbation is applied to the system, whereas the third term is the perturbation itself subject to the picture-change effect.

Collecting all three terms in Eq. (23) into a one-electron perturbation term \mathbf{w} gives:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = - \begin{pmatrix} \mathbf{w}_{\text{vo}} \\ \mathbf{w}_{\text{ov}}^t \end{pmatrix} \quad (24)$$

where $A_{ai,bj} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + \langle aj || ib \rangle$ and $B_{ai,bj} = \langle ab || ij \rangle$, following the usual Mulliken notation for the double-bar integrals. X and Y represent the excitation and de-excitation amplitudes in the DKH or X2C transformed picture frame. As long as the excitation energies and transition density are concerned we need only extract the poles and residuals of this equation:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (25)$$

This is a non-Hermitian eigenvalue equation that can be solved iteratively using the Davidson algorithm,⁶⁶ provided an efficient algorithm for computing the complex matrix-vector

product in the 2c-spinor framework is available. Note that the resulting transition amplitude (X and Y) are still in the transformed picture frame.

Equation (25) suggests that the explicit response of the two-component transformation \mathcal{U} is not used for the calculation of excitation energies. The reason can be traced back to the fact that the two-electron operator is not transformed and the perturbation is also a one-electron operator. However, although the excitation energies are independent of picture change, the resulting excited state properties, such as oscillator strengths, need to be evaluated in the original non-transformed basis, therefore they call for the inclusion of picture change effects. In addition, when response properties such as frequency-dependent polarizabilities are evaluated, the response of the transformation matrix has to be evaluated on the right-hand-side of Eq. (24) as well.

2.4 Atomic-Orbital Based Direct Implementation of the 2c-TDHF Equation

Equation (25) is usually written in the basis of ground-state MOs. The spin-blocked representation is absorbed in the two-electron integrals in the MO basis,

$$(ai|bj) = \sum_{\substack{\sigma_1, \sigma_2, \sigma_3, \sigma_4 = \alpha, \beta \\ \mu\nu\lambda\delta}} C_{\mu a}^{r*\sigma_1} C_{\nu i}^{r*\sigma_2} C_{\lambda b}^{l\sigma_3} C_{\delta j}^{l\sigma_4} (\mu\nu|\lambda\delta) \quad (26)$$

The practicality of the 2c-TDHF equation for studying many-electron systems relies on an efficient implementation, both in terms of computational time and memory requirement. The AO to MO transformation (Eq. (26)) represents a bottleneck for the calculation because of its unfavorable scaling with the basis set size. In addition, the transformed two-electron integrals have a large memory requirement (O^2V^2) which could limit the applicability of the method.

The $\mathcal{O}(O^6V^6)$ scaling of full diagonalization of the RPA matrix (Eq. (25)) can be avoided by means of iterative eigensolvers, such as the Davidson algorithm,⁶⁶ or its energy-specific extension.^{67,68} The bottleneck of the algorithm is usually the multiplication of the RPA matrix with the trial vectors which can also be performed via a direct or on-the-fly contraction of four-index AO integrals with trial vectors. The algorithm starts by transforming the (trial) transition density $T = (X, Y)$ into the AO basis, and separating it into sixteen components according to its spin, real/imaginary, and symmetric/antisymmetric components:

$$\begin{aligned} \mathbf{T}^{\text{AO}} \rightarrow & \mathbf{T}^{\alpha\alpha\text{RS}}, \mathbf{T}^{\alpha\alpha\text{IS}}, \mathbf{T}^{\alpha\beta\text{RS}}, \mathbf{T}^{\alpha\beta\text{IS}}, \mathbf{T}^{\alpha\alpha\text{RA}}, \mathbf{T}^{\alpha\alpha\text{IA}}, \mathbf{T}^{\alpha\beta\text{RA}}, \mathbf{T}^{\alpha\beta\text{IA}}, \\ & \mathbf{T}^{\beta\beta\text{RS}}, \mathbf{T}^{\beta\beta\text{IS}}, \mathbf{T}^{\beta\alpha\text{RS}}, \mathbf{T}^{\beta\alpha\text{IS}}, \mathbf{T}^{\beta\beta\text{RA}}, \mathbf{T}^{\beta\beta\text{IA}}, \mathbf{T}^{\beta\alpha\text{RA}}, \mathbf{T}^{\beta\alpha\text{IA}} \end{aligned} \quad (27)$$

where R, I, S, and A stand for real, imaginary, symmetric, and antisymmetric, respectively.

Since we are using a real atom-centered AO basis, the symmetric same-spin, symmetric different-spin, and antisymmetric components of the transition density are then contracted in a direct fashion with the corresponding Raffennetti two-electron integrals⁶⁹ generated on-the-fly. The direct formalism of the 2c-TDHF method allows one to take advantage of the sparsity in AO integrals and in the transition density to reduce the computational cost. At the end of this step, the contracted matrices are reassembled into one, and transformed back into the MO basis to form the reduced matrix that is then diagonalized in the Davidson algorithm.

However, there is another characteristic of the 2c-TDHF method that leads to a significant increase in the dimensionality of the problem with respect to collinear methods such as Unrestricted Hartree-Fock (UHF). Since spins are not constrained, solutions of a 2c-TDHF calculation also include spin-flip states in addition to the states normally recovered in TDUHF,⁷⁰ whereas in the latter same-spin and spin-flip states can be converged separately if needed. This can be very beneficial and is in fact necessary in the context of relativistic calculations, where some of the degeneracy is lifted by the spin-orbit interaction and, as will be shown below, it allows the calculation of zero-field splittings for excited states. However, this increased flexibility takes its computational toll, as the number of states that need to be converged in the calculation is significantly higher (for instance, there are 118 excitations associated with the 5p→5d transition in La³⁺). To facilitate solving the 2c-TDHF equation for the state of interest, we use the energy-specific extension^{67,68} of the Davidson algorithm without solving for other low-lying states.

3 Benchmark and Applications to Excited-State Fine Structures

All calculations were performed with a locally modified version of the Gaussian⁷¹ quantum chemistry package. Dunning’s correlation-consistent basis sets were used for light-atoms calculations, and the Sapporo DKH basis sets were employed in the case of heavier atoms.^{72,73} All reported relativistic results were obtained using the DKH and X2C methods. For the uranyl ion we employed the cc-pVTZ basis on oxygen, and the SARC-DKH basis⁷⁴ for the uranium. In order to partially account for transformation of the two-electron interaction in the calculation of the spin-orbit terms, we employed the Boettger scaling.⁵³ The atomic nuclei, rather than being point-like, were described using *s*-type functions to address the problem of numerical instabilities that arise in relativistic calculations employing point-nuclei.^{75,76} The stability of the ground state wave function was fully tested.³⁵ Calculated results are compared with reference values obtained from the NIST website.⁷⁷

3.1 Light atoms

In this section we look at the excited-state zero-field splittings (ZFS) arising from the spin-orbit terms described in the two-component DKH4 and X2C frameworks. Table 1 summarizes the results for some Ne-like and Mg-like systems. Both two-component methods are able to correctly predict excited states energetic orderings: in the case of more than half-filled shells, in a same term, levels with a higher \mathbf{J} value are lower in energy than those with a lower \mathbf{J} value. The computed ZFS are in very good agreement with the reference values, even though the method lacks electron correlation in the description of the many-body wave function. In addition, the transformation of the Coulomb term in the Hamiltonian and the spin-spin interaction terms, which are known to contribute to zero-field splittings in many cases,^{53,54} are ignored in this formalism. X2C and DKH4 give essentially the same results with a difference of $\sim 1\%$. The mean absolute error in the computed values is 11 meV for Ne, 3 meV for Na^+ , 7 meV for Mg^{2+} , 4 meV for Mg, 4 meV for Al^+ , and 6 meV for Si^{2+} . Second and third row elements are expected to experience small relativistic corrections. The approximate decoupling methods employed here can give very accurate results, although the quality of these methods for molecular calculations remains to be validated. In the following section we descend the periodic table in order to establish a point at which the underlying approximations break down, calling for the inclusion of the leading effects neglected in this work.

3.2 Heavier atoms

Table 2 shows the excited-state zero-field splittings of a series of second-row (the fifth-row of the periodic table) transition metals computed at the DKH1, DKH4, and X2C levels. In addition, the sensitivity with respect to the basis set size is analyzed by comparing the DKH4 results computed with a triple-zeta and quadruple-zeta quality basis set.

It can be seen from the results that there is only a very small difference in the results obtained with the different levels of approximations considered here, or with a larger basis set. The DKH1 ZFSs only see a difference of 1-2 meV with respect to the DKH4 values, and the average difference in ZFS between X2C and DKH1 is 5 meV, with the largest observed difference of 13 meV or 2.8% of the computed ZFS for Nb^{5+} (${}^3\text{F}_3^o$ - ${}^3\text{F}_4^o$).

The table also presents a comparison with reference values. For ZFSs of small orbital angular momentum P , although the absolute errors increase compared to those for lighter elements in Tab. 1, the computed results are still in good agreement with experiments, showing a mean error of 72 meV or 22 % deviation from the reference values. However, the mean error of calculated results increases with the orbital angular momentum for all

Table 1. ZFS energies (in meV) of Ne-like systems, and Mg-like systems. Calculations employed a taug-cc-pVTZ-DK⁷⁸ basis set with the diffuse f functions removed. The presence of a superscript “o” in the term symbol denotes an odd state with respect to inversion.

Level	Type	Ne	Na ⁺	Mg ²⁺
$^3P_1^o - ^3P_2^o$	DKH4	71.95	100.46	164.98
	X2C	72.02	100.61	165.27
	Ref	51.76	94.88	152.23
$^3P_0^o - ^3P_1^o$	DKH4	50.44	70.97	118.42
	X2C	50.51	71.12	118.71
	Ref	44.55	73.40	122.00
$^3D_2 - ^3D_3$	DKH4	42.46	53.13	90.22
	X2C	42.50	53.18	90.33
	Ref	20.73	47.96	74.62
$^3D_1 - ^3D_2$	DKH4	44.96	66.35	107.31
	X2C	45.01	66.46	107.53
	Ref	36.87	65.69	105.12
$^3P_0 - ^3P_2$	DKH4	13.96	37.10	58.54
	X2C	13.93	37.07	58.50
	Ref	7.31	35.20	51.97
$^3P_1 - ^3P_0$	DKH4	11.91	13.42	22.34
	X2C	11.93	13.47	22.42
	Ref	15.00	14.79	23.65
Level	Type	Mg	Al ⁺	Si ²⁺
$^3P_1^o - ^3P_0^o$	DKH4	4.88	10.46	19.80
	X2C	4.89	10.49	19.85
	Ref	2.49	7.55	15.94
$^3P_2^o - ^3P_1^o$	DKH4	9.73	20.97	39.84
	X2C	9.75	21.02	39.96
	Ref	5.05	15.36	32.45

methods considered here. This observation suggests that the scaled one-electron spin-orbit term becomes insufficient to account for the majority of relativistic spin-coupling effect for states with high angular momentum. Overall the three decoupling methods perform similarly in reproducing reference values.

Table 2. ZFS energies (in meV) of some transition metal metals and ions. Calculations employed DKH Sapporo TZ and QZ basis set.^{72,73}

Level	Type	Y ³⁺	Zr ⁴⁺	Nb ⁵⁺	Mo ⁶⁺	Level	Pd	Ag ⁺	Cd ²⁺
DKH1/TZP		225	286	351	423		248	268	309
DKH4/TZP		224	285	350	421		244	266	307
DKH4/QZP	³ P ₁ ^o - ³ P ₀ ^o	226	286	352	423	³ D ₂ - ³ D ₃	248	269	309
X2C/TZP		228	289	355	427		244	267	307
Ref		213	270	332	399		148	196	236
DKH1/TZP		459	583	715	859		315	374	478
DKH4/TZP		457	581	713	857		316	377	481
DKH4/QZP	³ P ₂ ^o - ³ P ₁ ^o	460	584	718	860	³ D ₁ - ³ D ₂	324	386	493
X2C/TZP		464	589	722	868		317	378	482
Ref		430	546	670	805		290	372	479
DKH1/TZP		375	415	449	477		429	529	667
DKH4/TZP		374	412	447	474		427	527	664
DKH4/QZP	³ F ₃ ^o - ³ F ₄ ^o	376	418	451	477	³ P ₁ ^o - ³ P ₂ ^o	437	536	671
X2C/TZP		381	421	462	485		432	534	674
Ref		281	306	320	324		262	428	613
DKH1/TZP		460	557	663	778		254	327	426
DKH4/TZP		458	554	670	775		254	326	425
DKH4/QZP	³ F ₂ ^o - ³ F ₃ ^o	462	561	669	783	³ P ₀ ^o - ³ P ₁ ^o	260	333	433
X2C/TZP		468	566	673	790		266	330	430
Ref		376	447	520	594		237	312	416

We continue our discussion with investigations of sixth-row metals. As seen in Tab. 3, while the order of magnitude of the computed splittings is still correct, the deviation between calculation and experiment is much more significant. In particular, the higher angular momentum transitions yield splittings that in the case of La³⁺ are almost twice the reference value. The difference between calculated and reference data is to be ascribed to the lack of two-electron relativistic effects caused by the fact that the electron-electron repulsion term is left. The table also shows the comparison between different levels of two-component decoupling, from the lowest-order DKH to X2C. All methods considered here produce values of a similar quality, suggesting that higher-order contributions to the DKH expansion are small, certainly smaller than the other approximations made within the model.

Table 3. ZFS energies (in meV) computed using the Sapporo-DKH-2012-TZP basis set.^{72,73} The presence of a superscript “o” in the term symbol denotes an odd state with respect to inversion.

Level	Type	Cs ⁺	Ba ²⁺	La ³⁺
${}^3P_1^{\circ}-{}^3P_0^{\circ}$	DKH1	58	233	323
	DKH2	79	235	322
	DKH4	78	235	322
	X2C	81	239	328
	Ref	42	223	287
${}^3P_2^{\circ}-{}^3P_1^{\circ}$	DKH1	789	454	642
	DKH2	784	460	641
	DKH4	785	459	641
	X2C	786	467	651
	Ref	606	423	552
${}^3F_3^{\circ}-{}^3F_4^{\circ}$	DKH1	316	342	363
	DKH2	314	340	360
	DKH4	314	340	360
	X2C	323	350	372
	Ref	184	191	171
${}^3F_2^{\circ}-{}^3F_3^{\circ}$	DKH1	386	484	631
	DKH2	385	482	628
	DKH4	385	482	629
	X2C	392	492	642
	Ref	242	305	353

3.3 Uranyl

After testing the accuracy of various two-component methods on excited state atomic fine structures we proceed to study a larger molecular system. The uranyl ion, UO_2^{2+} is a system that has been the subject of computational research previously.^{47,79–82} As a system with 106 electrons it is sufficiently large to test the efficiency of the method. In the following calculations the U=O bond distance is set to be 1.708 Å and the the molecular structure is linear. With the choice basis set (cc-pVTZ for oxygen and SARC-DKH basis⁷⁴ for the uranium) this system has 219 real basis functions for each spin component. In the direct linear response 2c-TDHF calculation, the bottleneck is the product of the response matrix and guess vectors in AO basis in the Davidson algorithm (Eq. (25)). Table 4 presents the computational performance of the method developed in this work. When only two vectors are being contracted, the computational overhead limits the savings at four processors. As a direct AO based method, the linear response 2c-TDHF exhibit excellent parallel scaling when a large number of vectors are considered.

Table 4. Computational cost for performing a matrix-vector product with different number of cores employed using LR-X2C. Relative timings are computed as $\frac{T_{N,M}}{T_{1,2}}$ where $T_{N,M}$ is the wall-clock time from a computation for N vectors with M cores employed.

Vectors	1 core	2 cores	4 cores	8 cores
2	1.0	0.8	0.4	0.4
20	4.4	2.4	1.4	0.7
200	29.4	17.9	9.1	4.9

In Tab. 5 the lowest excitation energies computed using the linear response X2C are compared with CASPT2⁸² and LR-CCSD⁸⁰ results. Differences in the results can be ascribed to the intrinsic differences, such as the ground state reference and the level of correlation, between the methods, in the choice of basis set, geometry (the bond distance was 1.683 Å for the LR-CCSD values), as well as in the treatment of the spin-orbit couplings. These differences notwithstanding, the values are in fairly good agreement.

4 Conclusions and Perspectives

In this work, we have presented an efficient implementation of the linear response formalism of the complex two-component relativistic Hartree-Fock method for the modeling of excited states. The four-component approximate decoupling was achieved using the DKH and X2C methods. In addition to the scalar relativistic effect, the one-electron spin-orbit coupling is included in the description. The two-electron Coulomb operator is retained untransformed

Table 5. Calculated lowest excited state energies (in eV) of the uranyl(IV) cation.

State	LR-X2C	CASPT2 ⁸²	LR-CCSD ⁸⁰
2_g	2.15	2.38	2.83
1_g	2.31	2.49	2.85
3_g	2.56	2.51	2.96
2_g	2.73	2.77	3.13
4_g	3.11	3.15	3.45
3_g	3.38	3.26	3.60
2_g	3.96	3.61	4.01
1_g	4.21	3.88	4.30

with the leading order of error being corrected by a scaling factor applied to the one-electron spin-orbit term.

A direct formalism in the AO basis integral contraction scheme is presented that greatly reduces the computational cost of linear response two-component methods. The presented method is cost-effective since it requires a computational effort that is not significantly higher than a corresponding non-relativistic calculation, provided the set of excited-states of interest is partitioned and the energy window algorithm is applied in order to reduce the number of states that are converged in a single calculation.

It has been shown that, even though the chosen decoupling method neglects the transformation of the two-electron terms, it is still able to accurately model spin-orbit excited-state splittings in many test cases. Benchmark tests show that the different approximate decoupling mechanisms employed here perform similarly. All methods considered here can accurately predict excited state ZFS of small orbital angular momentum of most elements. However, the error increases as the atomic number and orbital angular momentum of state increase.

Much work remains to be done: extension to a TDDFT framework with a proper non-collinear DFT kernel^{25,31–33,60,61,83,84} to partially account for electron correlation would increase the accuracy of the computed energies and splittings, and once that is done, a full benchmark of excited-state properties in the case of molecular systems will be necessary to assess the full extent of the method’s applicability to molecular systems possessing interesting magnetic properties whose modeling can greatly benefit from the use of a method that can treat the leading spin-orbit interactions consistently in both the ground and excited states without a prohibitive increase in computational cost. This methodology could also be extended to the real-time framework, allowing one to follow the dynamics of the molecular magnetization under the influence of spin-orbit couplings in real time.⁶² Finally, in order to increase the accuracy and broad applicability of the method, a necessary development is

the inclusion of two-electron spin-orbit terms in both the ground-state and response calculations. In the TD calculation the method presented here would still apply, but it would include explicit two-electron spin-orbit terms in the expression of the response function.

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