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Four-Component Polarization Propagator Calculations of Electron Excitations: Spectroscopic Implications of Spin–Orbit Coupling Effects

Markus Pernpointner,^{*,†} Lucas Visscher,[‡] and Alexander B. Trofimov[§]

[†]Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

[‡]Theoretical Chemistry, Faculty of Science, Vrije Universiteit Amsterdam, De Boelelaan 1083, NL-1081HV Amsterdam, Netherlands

[§]Laboratory of Quantum Chemistry, Irkutsk State University, Karl Marx Street 1, 664003 Irkutsk, Russia

ABSTRACT: A complete implementation of the polarization propagator based on the Dirac–Coulomb Hamiltonian is presented and applied to excitation spectra of various systems. Hereby the effect of spin–orbit coupling on excitation energies and transition moments is investigated in detail. The individual perturbational contributions to the transition moments could now be separately analyzed for the first time and show the relevance of one- and two-particle terms. In some systems different contributions to the transition moments partially cancel each other and do not allow for simple predictions. For the outer valence spectrum of the $\text{H}_2\text{Os}(\text{CO})_4$ complex a detailed final state analysis is performed explaining the sensitivity of the excitation spectrum to spin–orbit effects. Finally, technical issues of handling double group symmetry in the relativistic framework and methodological aspects of our parallel implementation are discussed.

1. INTRODUCTION

Accurate theoretical predictions of absorption and emission spectra are of fundamental interest for the development of new optical devices and materials. A very important substance class possessing high quantum yields by triplet harvesting is based on metal–organic complexes with heavy transition metals as central ions. For a theoretical description of the absorption and emission properties not only the wavelengths but also the corresponding transition moments need to be accurately calculated. We note thereby that for symmetric molecules moments are mostly determined by the transformation properties of the participating electronic wave functions in the point group of the molecule. To obtain accurate predictions, a broad variety of ab initio methods can be used for small to medium sized systems such as the approximate coupled cluster singles and doubles approach (CC2)^{1,2} and its extension to triples (CC3)^{3–6} within the linear response approach,^{7–9} various models within the equation-of-motion approach,^{10–12} multireference configuration expansion (MRCI) methods,¹³ perturbational complete active space approaches,^{14,15} multiconfiguration self-consistent field (MCSCF) treatments,¹⁶ hybrid methods such as MRCI/density functional theory (DFT),¹⁷ multireference coupled cluster (MRCC) approaches,^{18–20} and polarization propagator methods using the algebraic-diagrammatic construction (ADC)^{21–31} or superoperator formalisms.^{32–34} The calculation of large systems is particularly prominent in current theoretical

research and requires computationally less demanding methods such as configuration interaction singles (CIS), time-dependent Hartree–Fock (TDHF), and time-dependent density functional theory (TDDFT) that are applied with great success (see ref 35 for these approaches).

For systems possessing a heavy central ion the accurate determination of excited states necessitates a balanced treatment of scalar relativistic, spin–orbit, and electron correlation effects. It has turned out that relativity and electron correlation are in general not additive and correlated methods directly based on the relativistic Dirac formalism are therefore valuable. Not all of the above-mentioned methodologies, however, are available in combination with the Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) Hamiltonians. Since in the presence of the DC or DCB Hamiltonians the orbitals are no longer separable into space and spin parts, excited state energy surfaces cannot be characterized in terms of singlet or triplet character. As a consequence, calculation of intersystem crossing (ISC) rates employing Fermi's golden rule in combination with transition matrix elements over a spin–orbit Hamiltonian will not be applicable straightforwardly anymore. Instead, methods that are preferably used in vibronic coupling theory together with a diabaticization of the accompanying states will play a major role. For a concise

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overview on the implications of spin–orbit coupling in photochemistry, we recommend the reviews by C. M. Marian.^{36,37}

One of the most important distinctions of the DC Hamiltonian based propagator approach to established methods including spin–orbit coupling such as multireference spin–orbit configuration interaction (MRSOCI),³⁸ MRCI/DFT,¹⁷ or multistate complete active space approaches in combination with perturbation theory (MS-CASPT2)³⁹ is that in the former one the correlation space is built from an orbital manifold fully relaxed with respect to scalar relativistic effects and spin–orbit coupling. In the latter approaches the correlation space is initially constructed from nonrelativistic or scalar relativistic configuration state functions and spin–orbit coupling is treated in a subsequent step. A relaxation of the one-particle functions upon sizable spin–orbit coupling is therefore not taking place. For light to medium atoms a perturbational calculation of these effects is justified because the orbital relaxation upon spin–orbit coupling is not very large. This situation will change, however, when it comes to excitations that involve orbitals that undergo major changes upon inclusion of spin–orbit (SO) coupling and substantially participate in the excited states.

In order to provide an efficient, size consistent method for the routine calculation of excitation spectra, the polarization propagator in a four-component framework has been recently realized,⁴⁰ and for its numerical solution the algebraic-diagrammatic construction (ADC)^{21–23} was employed. In ref 40 we outline the relativistic extensions to the polarization propagator formalism with respect to excitation energy calculations in a double group framework. At this time of development transition moments were not yet available. Comparison to experiment, however, is only possible under inclusion of the moments associated with each individual excited state. This gap is now closed in this work, and we will outline the effects of spin–orbit coupling on transition moments and outer valence absorption spectra for various systems. Larger systems can now be tackled by parallel implementations of the propagator and the Davidson diagonalizer.

2. THEORY

2.1. Polarization Propagator. Since the essential theory for the relativistic polarization propagator was already outlined in earlier work,⁴⁰ we can keep this section brief. The energy-dependent form of the polarization propagator reads as⁴¹

$$\Pi_{pq,rs}(\omega) = \underbrace{\sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{c}_q^\dagger \hat{c}_p | \Psi_n \rangle \langle \Psi_n | \hat{c}_r^\dagger \hat{c}_s | \Psi_0 \rangle}{\omega - (E_n - E_0) + i\eta}}_{\Pi^+(\omega)} + \underbrace{\sum_{n \neq 0} \frac{\langle \Psi_0 | \hat{c}_r^\dagger \hat{c}_s | \Psi_n \rangle \langle \Psi_n | \hat{c}_q^\dagger \hat{c}_p | \Psi_0 \rangle}{-\omega - (E_n - E_0) + i\eta}}_{\Pi^-(\omega)} \quad (1)$$

In this expression Ψ_0 and E_0 represent the *exact* ground state wave function and energy and the creation (annihilation) operators $\hat{c}_q^\dagger$ ($\hat{c}_p$) refer to the one-particle Hartree–Fock wave functions. Hereby, the positive infinitesimal $i\eta$ guarantees the convergence of the Fourier transformation between time and energy representations. The two parts of the polarization

propagator $\Pi^+(\omega)$ and $\Pi^-(\omega)$ are related to each other²¹ and contain the same physical information. By applying diagrammatic techniques, a matrix representation of eq 1 can be derived whose diagonalization yields the transition energies and final state eigenvectors.

An alternative and possibly more comprehensive way to the derivation of the ADC matrix is given by the intermediate state representation (ISR).^{42–44} In general, one is interested in a systematic classification of an (exact) excited state of the system in terms of electronic configurations. This is straightforwardly realized by the well-known configuration interaction (CI) approaches. However, truncated CI methods exhibit some undesirable properties such as lack of size consistency and slow convergence. In the propagator/ISR approach the shifted Hamilton operator $\hat{H} - E_0$ is now represented in a particular correlated and orthonormal basis $\tilde{\Psi}_I$ that is (formally) constructed by application of the physical excitation operators $\hat{C}_I$ to the exact ground state wave function $|\Psi_0\rangle$. In this intermediate state basis set $|\tilde{\Psi}_I\rangle$ the shifted Hamilton operator is represented as

$$M_{IJ} = \langle \tilde{\Psi}_I | \hat{H} - E_0 | \tilde{\Psi}_J \rangle \quad (2)$$

with M_{IJ} being identical to the diagrammatically derived ADC matrix and $\hat{H}$ is in our case the Dirac–Coulomb operator

$$\hat{H} = \hat{H}_{\text{DC}} = \sum_{i=1}^N (c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i m_e c^2 + V_{\text{ext}}(i) \mathbf{1}_4) + \sum_{i < j}^N \frac{1}{r_{ij}} \quad (3)$$

A diagonalization of M_{IJ} yields the excitation energies and corresponding eigenvectors representing the excited states. The procedure outlined so far is formal because initially one has no access to the exact ground state wave function of the system. For the actual realization of the algorithm, one expands all constituents of (2) in a perturbational series of a certain order n and groups all same-order terms together (ADC n schemes ($n = 1, 2, \dots$)). After diagonalization of M_{IJ} the eigenvectors X_n of M_{IJ} express a particular excited state $|\Psi_n\rangle$ according to

$$|\Psi_n\rangle = \sum_I X_{I,n} |\tilde{\Psi}_I\rangle \quad (4)$$

and the representation (4) is used to calculate transition moments and excited state properties.

The single-particle functions as elementary constituents for the ADC matrix transform according to an irreducible representation (irrep) of the corresponding molecular point double group C^* . Due to the fact that Kramers-restricted implementations of relativistic propagators always start from a single reference determinant possessing an even number of electrons, the transformation properties of the final states depend on the type of propagator used. For excitations the number of electrons remains unchanged leading to a bosonic transformation behavior of the corresponding final states, while for ionization the final states transform according to the fermionic representations of C^* .

For the excitation energy calculations all ADC matrix elements that belong to first and second order contributions contain antisymmetrized two-electron integrals of the form

$$\langle a j l l b i \rangle = \left[\int \phi_a^*(1) \phi_j^*(2) \frac{1}{r_{12}} \phi_b(1) \phi_i(2) d\tau_1 d\tau_2 - (b \leftrightarrow i) \right] \quad (5)$$

as an example. This necessitates the following symmetry relations to hold for this integral to be different from zero:

$$\gamma_a^* \otimes \gamma_j^* \otimes \gamma_b \otimes \gamma_i \stackrel{!}{=} \Gamma_0 \quad (6)$$

Hereby γ_p denotes the fermionic irrep of a particular molecular spinor $\phi_p(\mathbf{x})$ in the corresponding point double group and Γ_0 is the totally symmetric representation. This is in contrast to contributions involving property integrals (see section 2.2) where the fourfold direct product of spinor irreps does not necessarily evaluate to Γ_0 .

The relativistic Hamilton operator commutes with the symmetry operators of the molecular point group and leads to a set of decoupled ADC(2) equations for different irreps. The resulting Hermitian matrix therefore exhibits a block structure with respect to the boson irrep Γ_i (see Figure 1) and which considerably reduces the numerical effort for its diagonalization.

Figure 1. Illustration of the overall ADC matrix structure for the excited (bosonic) final state symmetries $\Gamma_1, \dots, \Gamma_4$ with decoupled Γ_i submatrices. A particular submatrix is hereby divided into the ph/ph main block, the $2p2h/ph$ coupling block, and the $2p2h/2p2h$ satellite block. Hereby, p stands for particle and h stands for hole, respectively.

2.2. Transition Moments. The derivation of transition moments (TMs) in the ADC scheme can be found in ref 21, and we therefore can restrict ourselves to the peculiarities occurring in the relativistic case. In ref 21 the expressions are derived in spin-orbital framework and can be directly used for a spinor-based implementation. In the nonrelativistic setup an additional spin integration is performed leading to distinct sets of equations for the singlet and triplet cases, a complication that can be avoided here.

The starting point of the TM calculation is the transition function

$$T(\omega) = \mathbf{D}^\dagger \mathbf{\Pi}^+(\omega) \mathbf{D} \quad (7)$$

where $\mathbf{D}$ is the matrix representation of the transition operator. We work in the dipole approximation so that it suffices to form matrix elements of the dipole moment operator in the molecular spinor basis. Following the ADC philosophy $T(\omega)$ can be expressed by a transformed nondiagonal matrix representation of (7) obtained in a basis of intermediate states:⁴²

$$T(\omega) = \mathbf{F}^\dagger \mathbf{\Gamma}(\omega) \mathbf{F} \quad (8)$$

where $\mathbf{F}$ are now modified transition moments that will be discussed in detail below, and $\mathbf{\Gamma}(\omega)$ is a nondiagonal representation of the polarization propagator according to

$$\mathbf{\Gamma}(\omega) = [\omega \mathbf{1} - (\mathbf{K} + \mathbf{C})]^{-1} \quad (9)$$

As already mentioned for the energies, the elements of $\mathbf{F}$, $\mathbf{K}$, and $\mathbf{C}$ can be derived algebraically following the usual formalism of perturbation theory where $\mathbf{F}$, $\mathbf{K}$, and $\mathbf{C}$ are expanded in increasingly high orders. Hereby $\mathbf{K}$ is a zero order diagonal matrix of the form $K_{ab,ij} = (\epsilon_a - \epsilon_i) \delta_{ab} \delta_{ij}$. Inserting these expansions into eq 8 and grouping according to different perturbational orders yield corresponding contributions to the transition moments, $T^{(0)}, T^{(1)}, \dots$

Diagonalizing $(\mathbf{K} + \mathbf{C})$ via

$$(\mathbf{K} + \mathbf{C})\mathbf{X} = \mathbf{X}\mathbf{\Omega} \quad (10)$$

yields the eigenvector matrix $\mathbf{X}$ necessary for the transition moment calculation. As mentioned before, it contains the state composition of a particular excited state in terms of the intermediate basis together with its excitation energy ω_n . The k th order vector $\mathbf{F}^{(k)}$ contains the modified transition moments that require the dipole moment integrals in molecular orbital (MO) basis for their calculation. The TMs are finally obtained by contracting this vector with the corresponding eigenvector $\mathbf{X}_n$. The state-specific information on an ADC calculation is thus contained in the eigenvector matrix $\mathbf{X}$, whereas the $\mathbf{F}$ -vector is the same for all states. The transition moment $T_n = \langle \Psi_n | \hat{D} | \Psi_0 \rangle$ from the ground state of the system to the excited state $|\Psi_n\rangle$ is obtained by the contraction

$$T_n = \mathbf{X}_n^\dagger \cdot \mathbf{F} \quad (11)$$

In our implementation we are able to separately evaluate the individual perturbational contributions to $T(\omega)$. This helps for a better characterization of relevant contributions to a particular excited state especially with respect to one-particle and two-particle parts.

For a proper processing of the TMs we need to extend the symmetry handling beyond the totally symmetric case. A typical first order ph contribution to the $\mathbf{F}$ -vector reads, for example, as

$$F_{\mu,ai}^{(1)} = \sum_{bj} \frac{\langle ab || ji \rangle}{\epsilon_a + \epsilon_b - \epsilon_j - \epsilon_i} D_{\mu,jb} \quad (12)$$

The μ subscript hereby indicates the spatial component (x, y , or z) of the dipole moment integral resulting in three components of the transition moment. For the dipole moment integral $D_{\mu,jb}$ being different from zero by symmetry, the following relations among the irreps need to be fulfilled:

$$\gamma_j^* \otimes \Gamma_\mu \otimes \gamma_b = \Gamma_{jb} \otimes \Gamma_\mu \stackrel{!}{=} \Gamma_0 \quad (13)$$

As the (bosonic) irrep of the property operator Γ_μ can be different from the totally symmetric irrep Γ_0 , the direct product $\Gamma_{jb} = \gamma_j^* \otimes \gamma_b$ is typically not totally symmetric if eq 13 shall be satisfied. Writing out the symmetry relations for the right-hand side of (12) explicitly leads to

$$\gamma_a^* \otimes \gamma_b^* \otimes \gamma_j \otimes \gamma_i \otimes \gamma_j^* \otimes \Gamma_\mu \otimes \gamma_b \stackrel{!}{=} \Gamma_0 \quad (14)$$

Taking into account that in Abelian double groups a multiplication with the complex conjugate of an irrep will always yield Γ_0 , we arrive at the relation

Figure 2. Implemented parallelization scheme for the partial matrix vector multiplication. The overall matrix $\mathbf{H}$ is partitioned on the nodes $N_1, \dots, N_n$ leading to the partial products $Y^{(i)}$. These are collected and added on the master node to the complete vectors $X^{(i+1)}$ for the next iteration.

$$\gamma_a^* \otimes \gamma_i \otimes \Gamma_\mu = \Gamma_0 \quad (15)$$

which implies $\gamma_a^* \otimes \gamma_i = \gamma_j^* \otimes \gamma_b = \Gamma_\mu^*$. This shows that the symmetry of the first order ph F-vector follows the symmetry of the dipole moment operator in the double group and so do all the higher order contributions to the F-vector.

Due to the structure of the ADC matrix an eigenvector $\mathbf{X}_n^\dagger$ has ph and $2p2h$ components and the contraction (11) can be expanded to

$$T_n = \sum_{ai} X_{n,ai}^* F_{ai} + \sum_{abij} X_{n,abij}^* F_{abij} \quad a > b, i > j \quad (16)$$

Here, $X_{n,ai}^*$ and $X_{n,abij}^*$ denote the ph and $2p2h$ components of the n th eigenvector $\mathbf{X}_n^\dagger$. In our implementation we are able to calculate individual contributions to T_n that are grouped according to the perturbational orders of the F-vector, and we observed a considerable difference in the various contributions (see section 4.2). In particular, we split the resulting T_n according to

$$T_n = \sum_{ai} X_{n,ai}^* \{F_{ai}^{(0)} + F_{ai}^{(1)} + F_{ai}^{(2),A,B,C} + F_{ai}^{(2),1} + \dots + F_{ai}^{(2),10}\} + \sum_{abij} X_{n,abij}^* F_{abij}^{(2)} \quad (17)$$

The $2p2h$ components of the F-vector only occur in second order. As mentioned above, an ADC eigenvector transforms according to a specific boson irrep Γ_μ (where the adjoint vector $\mathbf{X}_n^\dagger$ then transforms according to Γ_μ^*) of the underlying molecular point group. In the contraction (11) we only obtain nonvanishing contributions to T_n if the F-vector symmetry is identical to Γ_μ leading to $\Gamma_\mu^* \otimes \Gamma_\mu = \Gamma_0$ as required.

From a technical point of view the contractions necessary for the F-vector calculation are achieved by resorting the integral streams for contiguous contraction ranges in memory. As soon as contractions over D_{pq} elements are to be performed (see eq 12), nontotally symmetric extensions of the sorting routines have to be applied. This should briefly be demonstrated for the $F_{abij}^{(2)}$ vector components that read as

$$\begin{aligned}
 F_{abij}^{(2)} = & \sum_k \frac{\langle ab||ki \rangle}{\epsilon_a + \epsilon_b - \epsilon_k - \epsilon_i} D_{kj} \\
 & - \sum_k \frac{\langle ab||kj \rangle}{\epsilon_a + \epsilon_b - \epsilon_k - \epsilon_j} D_{ki} + \sum_c \frac{\langle cb||ij \rangle}{\epsilon_c + \epsilon_b - \epsilon_i - \epsilon_j} D_{ac} \\
 & - \sum_c \frac{\langle ca||ij \rangle}{\epsilon_c + \epsilon_a - \epsilon_i - \epsilon_j} D_{bc}
 \end{aligned} \quad (18)$$

For later use the first part incorporating the occupied–occupied dipole moment integrals D_{kj} and D_{ki} should be denoted as $2p2hA$ and the latter one involving the virtual–virtual dipole moment integrals D_{ac} and D_{bc} as $2p2hB$. Abbreviating the energy-containing fractions in the $2p2hA$ part as $v_{ab,ki}$ and $v_{ab,kj}$ and taking into account that $v_{ab,ki} = -v_{ab,ik}$ we arrive at the expression

$$F_{abij}^{(2)} = \sum_k v_{ab,ki} D_{kj} - \sum_k v_{ab,kj} D_{ki} + \dots \quad (19)$$

In order to contract over k , we resort $-v_{ab,ik}$ to an intermediate array $A_{abi,k}$ and contract with D_{kj} to another array B_{abij} . Additionally, it can be seen that the expression above also leads to an i, j antisymmetrized F-component which necessitates a backsorting algorithm from B_{abij} to $F_{abij}^{(2)}$. As a requirement for the contributing irreps we now have

$$\gamma_a^* \otimes \gamma_b^* \otimes \gamma_i \otimes \gamma_j = \Gamma_\mu$$

necessitating the extended logic in the sorters. Similar steps are to be performed for the $2p2hB$ part.

2.3. Parallelization. In iterative diagonalization schemes where only a small number of eigenvalues are needed, the total Hamiltonian can be projected onto a smaller subspace which is exactly diagonalized and whose eigenvalues form increasingly precise approximations to the true eigenenergies. For our purpose we implemented the Liu modification⁴⁵ of the original Davidson algorithm.⁴⁶ For this algorithm, the matrix times trial vector multiplication is the most time-consuming step and parallelization was achieved by slicing the large matrix into equal chunks for each individual compute node including the master node and forming partial matrix times vector products on each node. The sparsity of the Hamilton matrix is utilized in an index-driven storage scheme where the row and column index are stored together with a particular nonzero matrix element. This leads to a simple slicing of the matrix, and the final vector product can be constructed with the reduce/add operation of the message passing interface (MPI). After solving the subspace problem on the master node, new trial vectors are communicated to the compute nodes for the next iteration step. In Figure 2 the parallelization scheme is illustrated focusing on the matrix vector multiplication. Hereby one should note that horizontal slices on the nodes $N_1, \dots, N_n$ represent data chunks of equal size containing row and column indices together with the actual matrix entries. The resulting nonzero elements in the product vectors are therefore scattered over the whole vector length. We already work on more efficient storage schemes for this particular bottleneck of the algorithm.

3. COMPUTATIONAL DETAILS

For argon we employed an uncontracted (18s11p9d) primitive basis previously used by Trofimov and Schirmer.²² The nonrelativistic Hartree–Fock ground state energy obtained in ref 22 amounts to $-526.809\,304$ hartree, where our value of

$-526.808\,585$ hartree is slightly higher in energy due to the removal of totally symmetric contributions to the basis functions being equivalent to a transformation to spherical harmonics. Additionally, a point charge nucleus was applied for the nonrelativistic calculations whereas a Gaussian nuclear charge distribution is necessary for relativistic treatments in order to avoid singular behavior of the wave function in close vicinity to the core.

The use of uncontracted basis functions generally leads to very high lying virtuals not being included in the active correlation space. For the strict ADC(2) calculation of the argon excitations and transition moments where the off-diagonal elements in the satellite block are zero, we froze the 1s orbital and deleted virtuals above 500 au ($\approx 13\,600$ eV) resulting in 174 active spinors.

The geometry used for the hydrogen sulfide calculations was taken from ref 47. Hereby the H–S distance amounts to 1.3356 Å and the H–S–H bond angle is 92.11°. Due to the smallness of the system we could afford an aug-cc-pVTZ basis on each atom taken from refs 48 and 49 still leading to a moderately large active space of 142 spinors.

For the osmium complex $H_2Os(CO)_4$ cc-pVTZ basis sets on each atom were employed and the geometry was optimized within the density functional framework. We obtained a C_{2v} structure whose xyz coordinates can be found in the Appendix. This complex was chosen due to its compact ligand environment keeping the numerical effort at a minimum and, simultaneously, possessing a heavy metal center inferring sizable spin–orbit coupling. The small component basis increases the total number of functions in the uncontracted calculation up to 2468 already asking for a parallel computation. As always, the X2Cmmf (infinite-order two-component) transformation was applied prior to the atomic orbital (AO)/MO transformation step eliminating the necessity to generate half-transformed (SSlik) integrals.⁵⁰ Due to the requirement using uncontracted basis sets for a good description of kinetic balance a dense manifold of molecular orbitals arises, making the energy selection of the correlation space a nontrivial task. In order not to exceed the computational resources, we restricted the active space to -0.7 to $+1.25$ au (-19 to $+34$ eV) resulting in 194 spinors. Larger calculations approaching 300 active spinors are underway, but they are not necessary for what we want to demonstrate in this work.

Another important entity characterizing the type of transition is the pole strength (PS) formed as the sum of squares of the eigenvector components in the ph configuration space. In the case of excitations it reveals the amount of single excitation character of a particular final state with a maximum value of 1.0. This, of course, is never achieved due to the presence of $2p2h$ configurations accounting for electron correlation. In the case of single and double ionizations calculated with propagator methods, the pole strength is related to the observable peak height.

For time measurements with a various number of cores we chose the HOSF molecule in C_1 symmetry with a double- ζ basis on each atom. The absence of symmetry elements leads to complex two-electron integrals, and the real and imaginary contributions to the transition moments can freely mix depending on initial conditions and orientation of the molecule. However, the squared sum of all contributions yields identical oscillator strengths as it must be the case. The active correlation space for HOSF comprised 110 spinors, leading to long enough

integral batches for comparing run times on various numbers of cores.

4. RESULTS AND DISCUSSION

4.1. Atomic Excited States. In this section we will demonstrate the usefulness of the relativistic propagator for excited state calculations of the argon atom including spin-orbit coupling. According to the statements in section 2, the ADC matrix in nonrelativistic, spin-free (corresponds to scalar relativistic) or four-component representation is diagonalized per bosonic symmetry Γ_μ leading to a set of corresponding excitation energies and eigenstates in the ISR basis. In a spin-free calculation the excited states are classified by their angular and spin quantum numbers L and S , respectively, leading to an overall degeneracy of $g = (2L + 1)(2S + 1)$. This degeneracy is reflected by the occurrence of repeated eigenvalues in different Γ_μ 's that are automatically determined by the implementation. Then the total g can be determined by collecting all eigenvalues in the various Γ_μ 's which allows for a determination of L and S in the corresponding excited state. However, for some L, S combinations ambiguities can arise (see Table 1) that can be

Table 1. Computed Nonrelativistic Excitation Energies of Argon in Electronvolts Using the ADC(2) Method^a

state	conf	$E_{\text{exc}}^{\text{calc}}$ [eV]	g	L	S	term	PS	OS [au]
1	$3p^5 4s^1$	11.4078	9	1	1	3P	0.960	0.000
2	$3p^5 4s^1$	11.5756	3	1	0	1P	0.957	0.300
3	$3p^5 4p^1$	12.5994	3*	0	1	3S	0.961	0.000
4	$3p^5 4p^1$	12.8356	15	2	1	3D	0.957	0.000
5	$3p^5 4p^1$	12.8875	5	2	0	1D	0.955	0.000
6	$3p^5 4p^1$	12.9585	3*	1	0	1P	0.955	0.000
7	$3p^5 4p^1$	12.9588	9	1	1	3P	0.955	0.000
8	$3p^5 4p^1$	13.0894	1	0	0	1S	0.951	0.000

^aThe degeneracy g corresponds to the value $(2L + 1)(2S + 1)$, and the $3p^5 4p^1$ configuration exhibits two $g = 3$ degeneracies marked by an asterisk. All three Cartesian configurations $3p_{x,y,z}^5$ contribute to state 2. The abbreviations PS and OS stand for pole strength and oscillator strength, respectively.

resolved by application of Hund's rules. The angular and spin momenta are then further coupled to the total angular

momentum J with allowed values of $J = |L + S|, |L + S - 1|, \dots, |L - S|$ being of different energy only if spin-orbit coupling is taken into account. Therefore, states of different J 's are not further discerned in the spin-free case. In order to demonstrate the applicability of the method, we show nonrelativistic (Table 1) and four-component (Table 2) results for the lowest excitation manifold of argon. The type of excitation can be extracted from the corresponding eigenvector X_n in combination with a Mulliken population analysis.

From the energies in Table 1, one observes that the $3p^5 4s^1$ excitation manifold is clearly separated from the $3p^5 4p^1$ manifold where according to Hund's rules the 3S term is located below the 1P . Since excitation processes in atoms are calculated in lower symmetry than spherical, the transition moment for state 2 of 0.300 au was obtained as the sum of three individual moments emerging from the $3p_{x,y,z}^5 4s^1$ excitations. Each of these transitions appears in a different boson symmetry belonging to the same 1P term. Transition moments for $3p^5 4p^1$ excitations vanish identically. The nonrelativistic results cannot be directly compared to experiment where spin-orbit coupling is inherently present, but they serve as an important reference for verifying symmetry relations and degeneracies.

We now turn to the discussion of the four-component results given in Table 2. As before, the overall degeneracies are determined by collecting eigenvalues from all possible final states of symmetry Γ_μ and are now considerably reduced. For the $3p^5 4s^1$ type of excitation we have two $J = 3$ cases separated by a gap of 0.2 eV. Eigenvector analysis reveals that the source orbitals for the corresponding states are $3p_{3/2}$ and $3p_{1/2}$, respectively, where the $j = l - s$ orbital participates in the state of higher excitation energy due to a larger stabilization of the $3p_{1/2}$ in the atom. Despite some noticeable deviations in the onset of the excitation manifold, the energy differences between the states are in very good agreement with experiment for most of the states. There are states, however, that are not described to the same level of accuracy leading to larger deviations in the energy separations.

A good agreement with experimental high-resolution measurements of oscillator strengths done by Chan et al.^{52,53} could be achieved for the four-component calculations. Chan et al. obtained 0.0662 for the $3p_{3/2}^5 4s^1$ and 0.265 for the $3p_{1/2}^5 4s^1$

Table 2. Four-Component Excitation Energies and Oscillator Strengths of Argon Computed by Using the ADC(2) Method^a

state	conf	$E_{\text{exc}}^{\text{calc}}$ [eV]	$E_{\text{exc}}^{\text{calc}}$ [cm^{-1}]	ΔE^{calc}	$E_{\text{exc}}^{\text{exp}}$ [cm^{-1}]	ΔE^{exp}	g	J	PS	OS [au]
1	$3p_{3/2}^5 4s^1$	11.3156	91268.4		93143.800		5	2	0.960	0.0000
2	$3p_{3/2}^5 4s^1$	11.3897	91866.2	597.7	93750.639	606.839	3	1	0.959	0.0234
3	$3p_{1/2}^5 4s^1$	11.4965	92727.8	861.6	94553.707	803.068	1	0	0.959	0.0000
4	$3p_{1/2}^5 4s^1$	11.5916	93494.5	766.7	95399.870	846.163	3	1	0.957	0.0775
5	$3p_{3/2}^5 4p^1$	12.5637	101335.6		104102.144		3	1	0.961	0.0000
6	$3p_{3/2}^5 4p^1$	12.7576	102899.3	1563.7	105462.804	1360.660	7	3	0.957	0.0000
7	$3p_{3/2}^5 4p^1$	12.7773	103058.3	159.0	105617.315	154.511	5	2	0.957	0.0000
8	$3p_{3/2}^5 4p^1$	12.8389	103554.7	496.4	106087.305	469.990	3	1	0.956	0.0000
9	$3p_{3/2}^5 4p^1$	12.8558	103691.4	136.7	106237.597	150.292	5	2	0.956	0.0000
10	$3p_{1/2}^5 4p^1$	12.9448	104409.3	717.9	107054.319	816.722	1	0	0.954	0.0000
11	$3p_{1/2}^5 4p^1$	12.9727	104634.1	224.8	107131.755	77.436	3	1	0.956	0.0000
12	$3p_{1/2}^5 4p^1$	12.9904	104777.4	143.3	107289.747	157.992	5	2	0.956	0.0000
13	$3p_{1/2}^5 4p^1$	13.0172	104993.5	216.2	107496.463	206.716	3	1	0.955	0.0000
14	$3p_{1/2}^5 4p^1$	13.1234	105849.6	856.1	108722.668	1226.205	1	0	0.952	0.0000

^aFor comparison with experiment⁵¹ the values are also given in wavenumbers and the energy differences between states are listed for an estimation of the quality. The abbreviations PS and OS stand for pole strength and oscillator strength, respectively.

Figure 3. Individual contributions to the H_2S transition moment for the most intensive transition with the zero order contribution as a reference.

Figure 4. Individual contributions to the $\text{H}_2\text{Os}(\text{CO})_4$ transition moment for the most intensive transition with the zero order contribution as a reference.

transitions located at excitation energies of 11.624 and 11.828 eV, respectively. For a comparison one needs to multiply our values of states 2 and 4 from Table 2 by the degeneracy factors (3 in both cases) and one obtains 0.0701 and 0.2325, agreeing well with experiment. The sum of the latter two oscillator strengths yields the nonrelativistic value of state 2 in Table 1 as it should be.

Six substates contribute to the oscillator strengths of states 2 and 4, from which it becomes evident that some of the nonrelativistic ^3P components now participate in the spin-orbit coupled excitation manifold. Already for the lighter argon

atom SO coupling introduces new transitions and leads to intensity redistributions.

For the $3\text{p}^5 4\text{p}^1$ excited state configuration considerable structure is added in the four-component case. All states derivable from the application of the jj coupling scheme for two independent p electrons are covered in the calculation, albeit none of these states carries noticeable oscillator strength.

4.2. Transition Moments. As mentioned above, transition moments are necessary to connect the ADC eigenvectors to the experimentally observable spectra. In the following we will report and compare the individual contributions to the TMs for the weakly and strongly relativistic systems H_2S and H_2Os .

Figure 5. Four-component (upward) and spin-free (downward) excitation stick spectrum of $\text{H}_2\text{Os}(\text{CO})_4$ in the outer valence region. The peak height corresponds to the fraction of single excitations forming the state. It can be seen that inclusion of spin–orbit coupling leads to substantial energetic shifts and an increased number of peaks.

$(\text{CO})_4$, respectively. For transition metal complexes it is recommended to estimate the quality of a single reference description which is required for good propagator results (see ref 54 for a recent overview). A coupled cluster singles–doubles calculation of the osmium complex yielded a T_1 diagnostic value of 0.039, still in the range for a valid single reference ground state description.

In Figures 3 and 4 the individual TM contributions for both systems are shown where the zero order value serves as the reference due to its dominant contribution. For both systems the transition with the highest oscillator strength was chosen for the detailed analysis, which is the first singlet state in the case of H_2S and the fifth state for the osmium complex, respectively. For H_2S we compare nonrelativistic and four-component results, whereas for the heavy osmium system we intend to exclusively reveal the effect of spin–orbit coupling by comparing spin-free and four-component results.

At first it can be observed that in the weakly relativistic case of H_2S the nonrelativistic and four-component TM contributions to each perturbational order are nearly identical, which does not come as a surprise but needs to be verified. Additionally, the ph 2, 3 and ph 2, 4 parts nearly cancel each other, which will no longer occur in the osmium complex. Furthermore, the two-particle $2p2hB$ contributions should not be neglected even if a larger numerical effort is required for their calculation. The findings applicable to H_2S change substantially in the osmium complex where sizable deviations purely introduced by spin–orbit coupling are observed. As it was the case for H_2S , the $2p2hB$ part is still important in the osmium complex but now the $2p2hA$ elements start to gain relevance. Unlike for H_2S the ph 2, 3 and ph 2, 4 parts no longer cancel but still are of opposite sign, a fact that makes predictions nearly impossible for general cases. Therefore the cancellation in H_2S can be considered to be accidental. In both molecules the $2p2hB$ contributions outweigh the $2p2hA$ ones explicable by the large number of VV -type dipole moment

integrals and a correspondingly larger number of terms in the contractions.

The final oscillator strength of a particular transition calculates as

$$f_n(E) = \frac{2}{3}E(|T_n^{(x)}|^2 + |T_n^{(y)}|^2 + |T_n^{(z)}|^2) \quad (20)$$

where it is important to realize that in the low-symmetry cases the $T_n^{(x,y,z)}$ components take on complex values whose real and imaginary parts can freely mix under varying initial conditions. The resulting oscillator strengths (20), however, are always independent of initial conditions such as the reference orientation of the molecule.

In the following we analyze the effect of spin–orbit coupling on the outer valence excitation spectrum of $\text{H}_2\text{Os}(\text{CO})_4$ with its heavy central metal. In Figure 5 the stick spectra obtained by a spin-free and four-component ADC(2) calculation are shown where the spin-free spectrum is plotted downward. The peak heights reflect the amount of single excitation character of a particular transition calculated by squaring the coefficients of the ADC eigenvector within the ph manifold. In the case of a sizable double excitation contribution an extended ADC treatment including the off-diagonal terms in the satellite block may be in order for a better description of the corresponding final state. In our case, all peaks within the outer valence energy range have negligible $2p2h$ character and an extended treatment also being computationally more demanding is not required.

In the next step we take the computed transition moments into account and arrive at a more physical picture of the spectrum to be expected in experiment. Due to spin selection rules in nonrelativistic theory, all the triplet peaks in the spin-free spectrum disappear and the remaining singlet peak heights are now proportional to the corresponding oscillator strengths from eq 20. For taking experimental resolution into account, we convolute the resulting stick spectrum with a Lorentzian

Figure 6. Four-component (upward) and spin-free (downward) excitation spectrum of $\text{H}_2\text{Os}(\text{CO})_4$ convoluted with a Lorentzian envelope of 30 meV width at half-maximum. The individual peak heights correspond to the calculated transition moments. The underlying stick spectrum is shown in green.

envelope of 30 meV width at half-maximum and arrive at Figure 6, where the final spectrum is shown.

Inclusion of SO coupling induces additional structure in the low-energy range of the excitation spectrum in combination with a redistribution of intensity. Additionally, the two major features in the spectrum undergo a red shift by approximately 0.1 eV and the number of states is markedly increased. For the outer-valence spectrum one expects dominant transitions from the occupied CO π orbitals to the corresponding π^* orbitals. Therefore the question arises of how spin–orbit coupling can lead to the observed structural changes. This is only possible if metal orbitals contribute notably to the excited state configurations. To analyze this further, we performed the kind of state population analysis mentioned in the Introduction. In general, a characterization of an excited state configuration is obtained by looking at the occupied and virtual spinors in the leading determinant of the correlation expansion. As we saw before, all outer valence final states exhibit over 90% single excitation character and the corresponding expansion coefficient of the leading determinant is also above 0.9. It is therefore a valid approach to look at the atomic compositions of the molecular source and destination spinors forming the dominant hole/particle excitation in each state. If we pursue such a procedure, we arrive at Figure 7, where the atomic hole (particle) populations of each final state are shown in the upper (lower) half of the picture.

For the first group of excited states the hole space shows dominant carbon s/p, oxygen p, and hydrogen s composition with noticeable osmium contributions. This changes for the subsequent group of states where sizable metal–ligand charge transfer takes place (5.8–6 eV). The presence of large osmium contributions in each state rationalizes the considerable influence of spin–orbit coupling on the spectrum. Due to the relatively low symmetry of the molecule, considerable mixing of atomic spinors at different centers can occur as can be seen in Figure 7. The considerable hydrogen s portion in the hole space arises from a participation of the bonding orbital between

hydrogen and an occupied osmium d spinor serving as source orbitals for excitation.

In the particle space the accepting orbitals exhibit large carbon p and oxygen p contributions pointing to a π^* character. However, unoccupied osmium p orbitals are also mixed in and can act as acceptors for electron density in the excited state. Spin–orbit splitting in the osmium virtual p orbitals is considerably less pronounced than in the occupied d spinors, indicating that SO-induced shifts play a larger role in the hole space of the final state than in the particle space. In summary, both the hole space and particle space possess pronounced metal character and therefore react sensitively to changes in the osmium spinors that occur upon inclusion of spin–orbit coupling.

4.3. Parallelization. For large problems with ADC matrix ($\mathbf{H}$) dimensions exceeding 1 million or more, the $|c_j\rangle = \mathbf{H}|b_j\rangle$ multiplication becomes the most time-consuming step in the algorithm. The vectors $|c_j\rangle$ are needed for the projection of $\mathbf{H}$ on the trial vector subspace formed by the $|b_j\rangle$ according to $(\tilde{\mathbf{H}})_{ij} = \langle b_i|\mathbf{H}|b_j\rangle = \langle b_i|c_j\rangle$ and for the calculation of the residual vectors $|r_j\rangle$ for each one of the sought eigenstates. If memory resources allow for it, internal storage of the vectors $|c_j\rangle$, $j = 1, \dots, m$ is optimal, while otherwise we use external storage. We tested both alternatives and found that all of them are faster than recalculating the projection $(\tilde{\mathbf{H}})_{ij}$. Considering the construction of the projection $(\tilde{\mathbf{H}})_{ij}$, numerical effort is minimized by exclusively calculating the new blocks in the matrix $(\tilde{\mathbf{H}})_{ij}$ following the scheme depicted in Figure 8. Converged roots do not induce an extension of the trial vector space, which leads to considerably shorter computing times for the projection at the end of the Davidson run.

The example in Figure 8 is drawn for four microiterations where the subspace grows by n_r in each step. Should the desired convergence of the roots not have been reached, we reenter the algorithm with a new set of n_r trial start vectors $|b_j\rangle$ now constructed from the available space according to

Figure 7. Excited state compositions in terms of atomic contributions separated into occupied (hole) and virtual (particle) domains. Contributions from specific atomic s, p, d, ... functions are hereby combined and depicted in a single color. For each excited state the upper part hereby shows the composition of the source orbitals the electron is excited from and the lower part does the same for the target orbitals accepting the electron.

$$|\tilde{b}_j\rangle = \sum_{k=1}^N a_{kj} |b_k\rangle, \quad j = 1, \dots, n_r$$

where the a_{kj} are the eigenvector components of the (exactly) diagonalized projection $(\hat{\mathbf{H}})_{ij}$ possessing dimension N . Once this new set of start vectors is generated, we build up a new trial space corresponding to the upper left part in Figure 8. In actual implementations this procedure is often termed as *collapsing the subspace* and we follow this convention here.

In section 2.3 we outlined the parallelization strategy by distributing equally sized chunks of the matrix over the nodes. In Table 3 we list the corresponding timings for the calculation

of the HOSF excitation spectrum using one to eight cores. Hereby the distributed matrix multiplication was timed separately together with the overall time spent in the Davidson algorithm. It is observed that the crucial part forming $\mathbf{H}|\tilde{b}_j\rangle$ scales very well with increasing number of cores, although it is not perfectly linear. This is due to the fact that the completion of the partial vectors together with the forming of the scalar product $\langle b_i | c_j \rangle$ is done on the master only. The overall run times in Davidson do not show the same scaling efficiency because all computations where the complete vectors are required have to be done on the master node and therefore introduce some amount of sequential execution. In all parallel

Figure 8. Construction of the subspace projection $(\tilde{\mathbf{H}})_{ij} = \langle b_i | \mathbf{H} | b_j \rangle$ for the microiterations $m = 1, \dots, 4$. In each microiteration the dimension of the trial space grows by n_r at most. The new portions to be calculated are shown in full color; the reused parts are in shaded color. The resulting projected matrix is Hermitian.

Table 3. Measured Compute Times (in Seconds) for the Matrix Times Vector Part and the Complete Davidson Run^a

	number of cores			
	1	2	4	8
time for Krylov projection	290	150	90	50
total time in Davidson	12371	7980	7100	5200

^aFor larger systems the Krylov projection will be the most time-consuming step and that is the place where the scaling is optimal.

runs the local disk storage requirements for the ADC matrix are reduced by a factor of $1/M$, where M is the number of cores. For considerably larger problems where the $\mathbf{H}b_j$ step and matrix storage become serious bottlenecks, the parallel version reveals its true value.

5. CONCLUSIONS

In this work we presented a detailed analysis of the effect of spin–orbit coupling on excitation energies, transition moments, and spectral structure for various systems together with an outline of the corresponding implementation available in the Dirac program package.⁵⁵ In the relativistic case the mathematical and computational frames have to be extended due to the occurrence of fermionic irreps. This introduces complex molecular two-electron integrals also leading to complex transition moments and a substantially increased numerical effort. It could be demonstrated for $\text{H}_2\text{Os}(\text{CO})_4$ that SO effects alone introduce major changes in the expected absorption spectrum which will similarly hold for other metal complexes of the 5d series, such as iridium used in OLEDs. The polarization propagator in a four-component framework together with a suitable parallelization strategy provides a useful method to obtain excitation spectra of large systems with heavy centers where a perturbational treatment of SO effects

may fail and where electron correlation and SO coupling need to be treated on an equal footing.

■ APPENDIX

The x, y, z geometry of the osmium complex in C_{2v} structure obtained at the DFT level is listed in Table 4.

Table 4. Cartesian Coordinates of $\text{H}_2\text{Os}(\text{CO})_4$ in Angstroms

atom	x	y	z
Os	0.00000	0.00000	0.00000
O	2.41214	0.00000	−1.98152
O	−2.41214	0.00000	−1.98152
O	0.00000	−3.03655	0.59571
O	0.00000	3.03655	0.59571
C	0.00000	−1.93462	0.31819
C	0.00000	1.93462	0.31819
C	1.51252	0.00000	−1.28285
C	−1.51252	0.00000	−1.28285
H	1.10331	0.00000	1.25671
H	−1.10331	0.00000	1.25671

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Markus.Pernpointner@pci.uni-heidelberg.de.

ORCID

Markus Pernpointner: 0000-0002-4618-1359

Lucas Visscher: 0000-0002-7748-6243

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Notes

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(55) Authors: Visscher, L.; Jensen, H. J. Aa.; Bast, R.; Saue, T. Contributors: Bakken, V.; Dyall, K. G.; Dubillard, S.; Ekström, U.; Eliav, E.; Enevoldsen, T.; Faßhauer, E.; Fleig, T.; Fossgaard, O.; Gomes, A. S. P.; Hedegård, E. D.; Helgaker, T.; Henriksson, J.; Iliaš, M.; Jacob, Ch. R.; Knecht, S.; Komorovský, S.; Kullie, O.; Lærdahl, J. K.; Larsen, C. V.; Lee, Y. S.; Nataraj, H. S.; Nayak, M. K.; Norman, P.; Olejniczak, G.; Olsen, J.; Olsen, J. M. H.; Park, Y. C.; Pedersen, J. K.; Pernpointner, M.; di Remigio, R.; Ruud, K.; Salek, P.; Schimmelpfennig, B.; Shee, A.; Sikkema, J.; Thorvaldsen, A. J.; Thyssen, J.; van Stralen, J.; Villaume, S.; Visser, O.; Winther, T.; Yamamoto, S. *DIRAC, a Relativistic ab Initio Electronic Structure Program*, release DIRAC17; 2017. <http://www.diracprogram.org>.