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Jan-Robert Vogt; Jan Wilhelm  ; Anna-Sophia Hehn  



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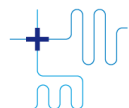
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Jan-Robert Vogt,¹ Jan Wilhelm,²  and Anna-Sophia Hehn^{1,a)} 

AFFILIATIONS

¹ Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Strasse 1, 24118 Kiel, Germany

² Institute of Theoretical Physics, University of Regensburg, 93053 Regensburg, Germany

^{a)} Author to whom correspondence should be addressed: hehn@pctc.uni-kiel.de

ABSTRACT

A comprehensive description of photo-chemical processes in materials, comprising spin-forbidden processes such as intersystem crossing and phosphorescence, implies taking into account spin-orbit coupling. We present an efficient implementation of a perturbative spin-orbit coupling correction for the Tamm-Dancoff approximation of linear-response time-dependent density functional theory within a mixed Gaussian and plane wave framework relying on spin-orbit coupling corrected pseudopotentials. The implementation is validated for a benchmark set of small aromatic molecules, with mean errors in excitation energies and spin-orbit coupling matrix elements being in the range of 0.1–0.6 eV and 1.0–14.4 cm⁻¹, respectively, in comparison with density functional theory and density functional theory multi-reference configuration interaction reference results. Computational timings are given for a bismuth-containing metal-organic framework.

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I. INTRODUCTION

The consideration of spin-orbit coupling is crucial for photochemistry,¹ enabling, even for light atoms, the coupling of energetically close lying excited states of different spin multiplicities, thus resulting in a splitting of spectral lines and inducing spin-forbidden transitions. The latter plays an emerging role in materials science, e.g., in light-induced excited-state spin trapping or upconversion processes. Sophisticated quantum-mechanical descriptions of spin-orbit coupling (SOC), the interaction between orbital angular momenta and spin angular momenta of electrons, based on the Dirac-Coulomb-Hamiltonian comprise four- or two-component approaches combined with various electronic-structure methods. Computational costs of existing relativistic schemes are, however, at least one order of magnitude larger than those of comparable non-relativistic or scalar-relativistic computations, motivating the use of perturbative SOC *Ansätze*.² Relying on (quasi) degenerate perturbation theory,³ spin-free states are thereby provided within a non-relativistic framework and coupled via approximate spin-orbit

Hamiltonians as the perturbation. A perturbative treatment of SOC was found to be reliable as long as SOC interactions are of small magnitude, which was found to be the case for molecules not containing 6p- or 7p-block elements.^{4,5} As highlighted by Cheng *et al.*, it was perturbative SOC *Ansätze* that pioneered the original description of intersystem crossing, and current implementations for the dynamic description of ISC relying on surface hopping non-adiabatic molecular dynamics are nearly exclusively formulated as perturbative corrections.^{6–14} Both spin-diabatic and adiabatic representations to include SOC in trajectory-based surface hopping procedures have been pioneered by Persico and Granucci.¹⁵

Within a perturbative description, common approximate spin-orbit Hamiltonians comprise Breit-Pauli and Douglas-Kroll transformed spin-orbit operators.¹ Furthermore, the perturbational expansion of the Dirac equation to the lowest order, the zero-order regular approximation (ZORA), is state-of-the-art, and the approximate ZORA Hamiltonian was shown to provide an accurate description of spin-orbit coupling effects on properties of heavy element diatomic molecules.¹⁶ van Wüllen furthermore proposed to

use a model potential to construct the ZORA kinetic energy operator, circumventing the intrinsic problems of the ZORA Hamiltonian of gauge noninvariance and nonstationarity of the energy.¹⁷ van Wüllen's model potential brings the advantage that the ZORA operator is no longer dependent on the Kohn–Sham orbitals and that the thereon based ionization potentials are improved, with remaining errors being comparable to those of the original ZORA computations, corrected with the electrostatic shift approximation and related to deficiencies of the exchange–correlation potential. Moreover, applying a model potential enables analytical expressions for nuclear gradients.

To apply the mentioned approximate Hamiltonians not only to all-electron computations but also to heavier-element chemistry relying on pseudopotentials, Kleinmann,¹⁸ Bachelet and Schlüter,¹⁹ and Hybertsen and Louie²⁰ pioneered the construction of pseudopotentials that account for spin–orbit coupling. Kleinman showed that the SOC-pseudopotentials correctly include not only core-electron orthogonality effects but also relativistic effects up to order α^2 , with α being the fine-structure constant.¹⁸ Following the suggested norm-conserving construction scheme of Bachelet and Schlüter, Hartwigsen *et al.* furthermore constructed dual-space Gaussian pseudopotentials,²¹ featuring the general advantage of the Goedecker–Tetter–Hutter potentials^{22,23} of being separable into a local and non-local part, with the integration of the latter scaling quadratically with system size. SOC-GTH pseudopotentials were parameterized with respect to two-component Dirac computations, thus including scalar-relativistic and SOC effects. They were shown to accurately reproduce bond lengths of an extended list of small molecules containing various heavy elements. In general, SOC-including PPs^{18–20,24–26} were also validated for a broader spectrum of molecular properties, e.g. yielding accurate predictions of spin–orbit splittings of band structures.²⁷

The combination of the mentioned approximate Hamiltonians with time-dependent density functional theory (TDDFT) poses the challenge that SOC matrix elements are defined with respect to many-electron wave functions. Tavernelli *et al.* therefore proposed the usage of so-called auxiliary many-electron wave functions (AMEWs) based on the Casida *Ansatz*,^{10,11} with the auxiliary functions being constructed relying on the TDDFT response functions and therein defined creation and annihilation operators. Corresponding implementations for the Sternheimer *Ansatz* of LR-TDDFT within the CPMD program package²⁸ were based on the Breit–Pauli Hamiltonian and conventional pseudopotentials without empirical reparameterization of the effective nuclear charges. Lowest-energy SOC matrix elements for formaldehyde were validated with respect to multi-configuration quasi-degenerate perturbation theory computations, and the implementation was extended to non-adiabatic molecular dynamics on spin-diabatic surfaces, not requiring nuclear forces due to the perturbative *Ansatz* but providing SOC-corrected transition probabilities using the Landau–Zener formula. Bussy and Hutter presented an analogous implementation for core excitations enabling the efficient modeling of x-ray absorption spectra under periodic boundary conditions,^{29,30} decoupling the investigated core states by considering only a small number of localized donor core orbitals. Through reduced resolution-of-the-identity basis sets located solely at the excited atom and acceleration by the auxiliary density matrix method, the authors demonstrated that the so-obtained SOC-corrected L-edge spectra are in agreement

with experimental data at sub-cubic scaling of computational cost. Malis and Luber^{31,32} presented perturbative spin–orbit couplings for the delta self-consistent field *Ansatz* analogously relying on the AMEW *Ansatz*. The implementation within a mixed Gaussian and plane wave framework implying pseudopotentials was validated for formaldehyde with respect to LR-TDDFT reference values obtained with the ORCA program package.³³

Within this context, we present an efficient implementation of a perturbative spin–orbit coupling *Ansatz* relying on AMEWs, as suggested by Tavernelli *et al.*,^{10,11} for the Tamm–Dancoff approximation (TDA) of linear-response time-dependent density functional perturbation theory, implemented within the mixed Gaussian and plane wave framework³⁴ of the CP2K program package.³⁵ The presented implementation is based on the mentioned related implementation for core excitations by Bussy and Hutter,²⁹ extending the formulation to valence excitations^{36,37} (Sec. II A) and SOC-corrected pseudopotentials of Hartwigsen *et al.*²¹ (Sec. II B). Spin–orbit couplings are validated with respect to all-electron computations performed with the ORCA program package³³ (Sec. III A) and benchmarked for a test set of 13 organic molecules against multi-reference configuration interaction (CI) reference data³⁸ (Sec. III B). Computational timings and comparison with experimental spectra are outlined for the bismuth-containing CAU-7-TATB metal–organic framework (MOF)^{39–42} (Sec. III D).

II. METHOD

A. Excited states and auxiliary wave functions within the Tamm–Dancoff approximation

The perturbative SOC *Ansatz* has been discussed in detail in Refs. 10, 11, and 29. We, therefore, restrict ourselves to a very short introduction of the most important equations. Within the Tamm–Dancoff approximation (TDA)^{43,44} of time-dependent density functional theory, the excitation energy Ω^N of the excited state N and the corresponding excitation amplitude $\mathbf{X}^N$ are given as the solution of a Hermitian eigenvalue problem,

$$\mathbf{A}\mathbf{X}^N = \Omega^N \mathbf{S}\mathbf{X}^N, \quad (1)$$

with $\mathbf{S}$ representing the atomic-orbital overlap matrix. For restricted closed-shell references with α (spin up) and β (spin down) spin components being degenerate, spin adaptation by unitary transformation enables us to define singlet excitation amplitudes and energies, $\mathbf{X}_{\text{sing}}^N$ and Ω_{sing}^N , with total spin $S = 0$ and spin quantum number $m_S = 0$, which are decoupled from the corresponding triplet excitation amplitudes and energies, $\mathbf{X}_{\text{trip}}^N$ and Ω_{trip}^N , with total spin $S = 1$ and $m_S = 0$. In the following, spin-adapted matrices will be indicated with lower indices, $\mathbf{M}_{S m_S}$, labeling total spin S and spin angular momentum m_S . The eigenvalue equations for singlet and triplet spins are given after spin summation within the Sternheimer formalism as

$$\sum_{\kappa j} [(\mathbf{F}_{S m_S})_{\mu\kappa} \delta_{ij} - (\mathbf{F}_{S m_S})_{ij} S_{\mu\kappa}] (\mathbf{X}_{S m_S}^N)_{\kappa j} + \sum_{\kappa\lambda} Q_{\mu\kappa}^T (\mathbf{K}_{S m_S}^N)_{\kappa\lambda} [\mathbf{D}^X] C_{\lambda i} = \sum_{\kappa} \Omega_{S m_S}^N S_{\mu\kappa} (\mathbf{X}_{S m_S}^N)_{\kappa i}, \quad (2)$$

with

$$(\mathbf{F}_{Sms})_{\mu\nu}[\mathbf{D}] = h_{\mu\nu} + \sum_{\kappa\lambda} D_{\kappa\lambda} [2(\mu\nu|\kappa\lambda) - a_{\text{EX}}(\mu\kappa|\nu\lambda)] + V_{\mu\nu}^{\text{XC},Sms}, \quad (3)$$

$$(\mathbf{K}_{Sms}^N)_{\kappa\lambda}[\mathbf{D}^X] = \sum_{\kappa\lambda} (\mathbf{D}^X)_{\kappa\lambda}^N [a_S(\mu\nu|\kappa\lambda) - a_{\text{EX}}(\mu\kappa|\nu\lambda) + f_{\mu\nu,\kappa\lambda}^{\text{XC},Sms}], \quad (4)$$

$$D_{\mu\nu} = 2 \sum_i C_{\mu i} C_{\nu i}^T, \quad (5)$$

$$(\mathbf{D}^X)_{\mu\nu}^N = 2 \sum_i (\mathbf{X}_{Sms}^N)_{\mu i} C_{\nu i}^T, \quad (6)$$

where $a_S = 2$ for singlet spin and $a_S = 0$ for triplet spin. The Kohn–Sham matrix contributions $\mathbf{F}$ and kernel contributions $\mathbf{K}$ depend on the chosen functional and comprise one-electron, Coulomb, and exchange–correlation (XC) contributions. The projection operator onto the virtual orbital space $\mathbf{Q}$ ensures orthonormality of the excitation amplitudes $\mathbf{X}^N$ with respect to the ground-state MO coefficients $\mathbf{C}$,

$$Q_{\mu\nu\sigma} = \delta_{\mu\nu} - \sum_{\kappa i} C_{\mu i} C_{\kappa i}^T S_{\kappa\nu}. \quad (7)$$

The global parameter a_{EX} scales the amount of exact exchange, and the two-electron repulsion integrals are defined in the Mulliken notation. $\mu, \nu, \kappa, \lambda, \dots$ indicate atomic orbitals; $i, j, k, l, \dots$ indicate occupied molecular orbitals. The remaining triplet states with spin angular momentum $m_S = 1$ and $m_S = -1$ require to take into account spin-flipped excitations, which are not accessible via the collinear TDA eigenvalue problem given in Eq. (1). Tavernelli *et al.*, therefore, suggested relying on auxiliary many-electron wave functions (AMEWs),^{11,45,46} which define singlet and triplet states as singly excited determinants,

$$|\Psi_{S=0,m_S=0}^N\rangle = \frac{1}{\sqrt{2}} \sum_{ia} (\mathbf{X}_{\text{sing}}^N)_{ia} (\hat{a}_{a\alpha}^\dagger \hat{a}_{i\alpha} + \hat{a}_{a\beta}^\dagger \hat{a}_{i\beta}) |\Psi^0\rangle, \quad (8)$$

$$|\Psi_{S=1,m_S=0}^N\rangle = \frac{1}{\sqrt{2}} \sum_{ia} (\mathbf{X}_{\text{trip}}^N)_{ia} (\hat{a}_{a\alpha}^\dagger \hat{a}_{i\alpha} - \hat{a}_{a\beta}^\dagger \hat{a}_{i\beta}) |\Psi^0\rangle, \quad (9)$$

$$|\Psi_{S=1,m_S=1}^N\rangle = \sum_{ia} (\mathbf{X}_{\text{trip}}^N)_{ia} \hat{a}_{a\alpha}^\dagger \hat{a}_{i\beta} |\Psi^0\rangle, \quad (10)$$

$$|\Psi_{S=1,m_S=-1}^N\rangle = \sum_{ia} (\mathbf{X}_{\text{trip}}^N)_{ia} \hat{a}_{a\beta}^\dagger \hat{a}_{i\alpha} |\Psi^0\rangle, \quad (11)$$

with $\mathbf{X}_{\text{sing}}^N$ and $\mathbf{X}_{\text{trip}}^N$ referring to the spin-adapted singlet and triplet excitation amplitudes and $a, b, c, d, \dots$ indicating virtual orbitals. $|\Psi^0\rangle$ denotes the KS reference Slater determinant built from the ground-state KS orbitals. As noted by Dinkelbach *et al.*,³⁸ Eqs. (8)–(11) can be obtained by choosing the AMEW with the maximum spin quantum number and generating the remaining states by applying the Wigner–Eckhart theorem.

B. Perturbative spin-orbit couplings with approximate Hamiltonians

Based on the unperturbed singlet and triplet excitation amplitudes $\mathbf{X}_{\text{sing}}^N$ and $\mathbf{X}_{\text{trip}}^N$ and the AMEWs of singlet and triplet states, a perturbative spin–orbit coupling correction can be derived using quasi-degenerate perturbation theory,³

$$H_{Sms,S'm'_s}^{\text{NM}} = \delta_{NM} \delta_{SS'} \delta_{m_S m'_S} \Omega_{Sms}^N + \langle \Psi_{Sms}^N | \hat{h}^{\text{SO}} | \Psi_{S'm'_s}^M \rangle. \quad (12)$$

While orthonormality of excitation amplitudes $\mathbf{X}_{Sms}^N$ of the same spin, as well as orthonormality of both amplitudes with the ground-state MO coefficients $\mathbf{C}$, is implied, an orthonormality for amplitudes of different spins, i.e., between $\mathbf{X}_{\text{sing}}^N$ and $\mathbf{X}_{\text{trip}}^N$, is not given due to the fact that both eigenvalue equations and the corresponding constraints are decoupled [Eq. (2)]. For mixed matrix elements, as given in Eq. (14), the Slater–Condon rules, therefore, do not apply, and Eq. (14) has to be solved relying on the more general Löwdin rules defining the required matrix elements, as outlined in Refs. 11, 30, 45, and 46. The one-electron SOC-Hamiltonian $\hat{h}^{\text{SO}}$ within the zero-order regular approximation (ZORA) is defined as

$$\hat{h}_{\text{ZORA}}^{\text{SO}} = \frac{c^2}{(2mc^2 - V)^2} \sigma_{\text{P}} \cdot (\nabla V \times \mathbf{p}), \quad (13)$$

with the potential V being approximated as van Wüllen’s model potential,¹⁷ c being the speed of light, $\mathbf{p} = -i\nabla$ being the momentum operator matrix, and σ_{P} representing the vector of Pauli spin matrices. Final resulting couplings between singlet and triplet states of different spin quantum numbers are given in the [supplementary material](#). Alternatively, if restricting the description to valence electrons only, a SOC-corrected pseudopotential, as parameterized by Hartwigsen *et al.*,²¹ can be used,

$$H_{Sms,S'm'_s}^{\text{NM}} = \delta_{NM} \delta_{SS'} \delta_{m_S m'_S} \Omega_{Sms}^N + \langle \Psi_{Sms}^N | \hat{h}_{\text{PP}}^{\text{SO}} | \Psi_{S'm'_s}^M \rangle, \quad (14)$$

where

$$\hat{h}_{\text{PP}}^{\text{SO}} = \frac{1}{2} \sum_l \Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}') \mathbf{L} \cdot \sigma_{\text{P}}, \quad (15)$$

with $\mathbf{L}$ representing the angular momentum matrix and $\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}')$ representing the non-local SOC correction pseudopotential contribution to the remaining scalar relativistic local and non-local terms. Explicit formulas are given in Ref. 21. The reduction to one-electron matrix elements over molecular orbitals relying on the Löwdin formula and integration of spin can be performed as for the all-electron Hamiltonian. Diagonalizing the resulting matrix of spin–orbit matrix elements (SOMEs) $H_{Sms,S'm'_s}^{\text{NM}}$ of dimension $\tilde{N} \times \tilde{N}$ with $\tilde{N} = (1 + N + 3N)$ gives the SOC-corrected excitation energies $\tilde{\Omega}^N$ as well as the perturbed eigenfunctions $\tilde{\Psi}^N$. Resulting SOC-corrected eigenvectors can be used to compute the corresponding oscillator strengths $f_{\tilde{N}}$ within the length or velocity representation,^{36,47}

$$f_{\tilde{N}}^{\text{len}} = \frac{2}{3} \tilde{\Omega}^N \sum_{\zeta=x,y,z} \left[\text{Re} \left[|\text{Tr}(\tilde{\Psi}^N | \hat{r}_{\zeta} | \tilde{\Psi}^0)|^2 \right] + i \text{Im} \left[|\text{Tr}(\tilde{\Psi}^N | \hat{r}_{\zeta} | \tilde{\Psi}^0)|^2 \right] \right], \quad (16)$$

$$f_N^{\text{vel}} = \frac{2}{3\tilde{\Omega}_N} \sum_{\zeta=x,y,z} \left[\text{Re} \left[\left| \text{Tr} \langle \tilde{\Psi}^N | \hat{p}_\zeta | \tilde{\Psi}^0 \rangle \right|^2 \right] + i \text{Im} \left[\left| \text{Tr} \langle \tilde{\Psi}^N | \hat{p}_\zeta | \tilde{\Psi}^0 \rangle \right|^2 \right] \right], \quad (17)$$

with $\hat{r}_\zeta$ indicating the dipole operator and $\hat{p}_\zeta$ indicating the momentum operator. Both representations are equal for exact wave functions not including a non-local potential at the complete basis-set limit or for approximate wave functions if fulfilling the Thomas–Reiche–Kuhn sum rule at the complete basis-set limit.^{48–50} Explicit working equations for the AMEW Ansatz are given in the [supplementary material](#).

III. RESULTS AND DISCUSSION

A. Validation of splittings and oscillator strengths

To validate the implementation within the CP2K program package, splittings and oscillator strengths relying on the all-electron ZORA-Hamiltonian of Eq. (13) were compared with the analogous implementation in ORCA featuring perturbative SOC relying on a Breit–Pauli Hamiltonian.^{51,52} The Breit–Pauli Hamiltonian includes next to spin-same also spin-other-orbit interactions, with the latter leading to a relatively large exchange contribution and resulting in a different sign in spin-orbit splittings in comparison with effective potential SOC operators, such as the all-electron ZORA

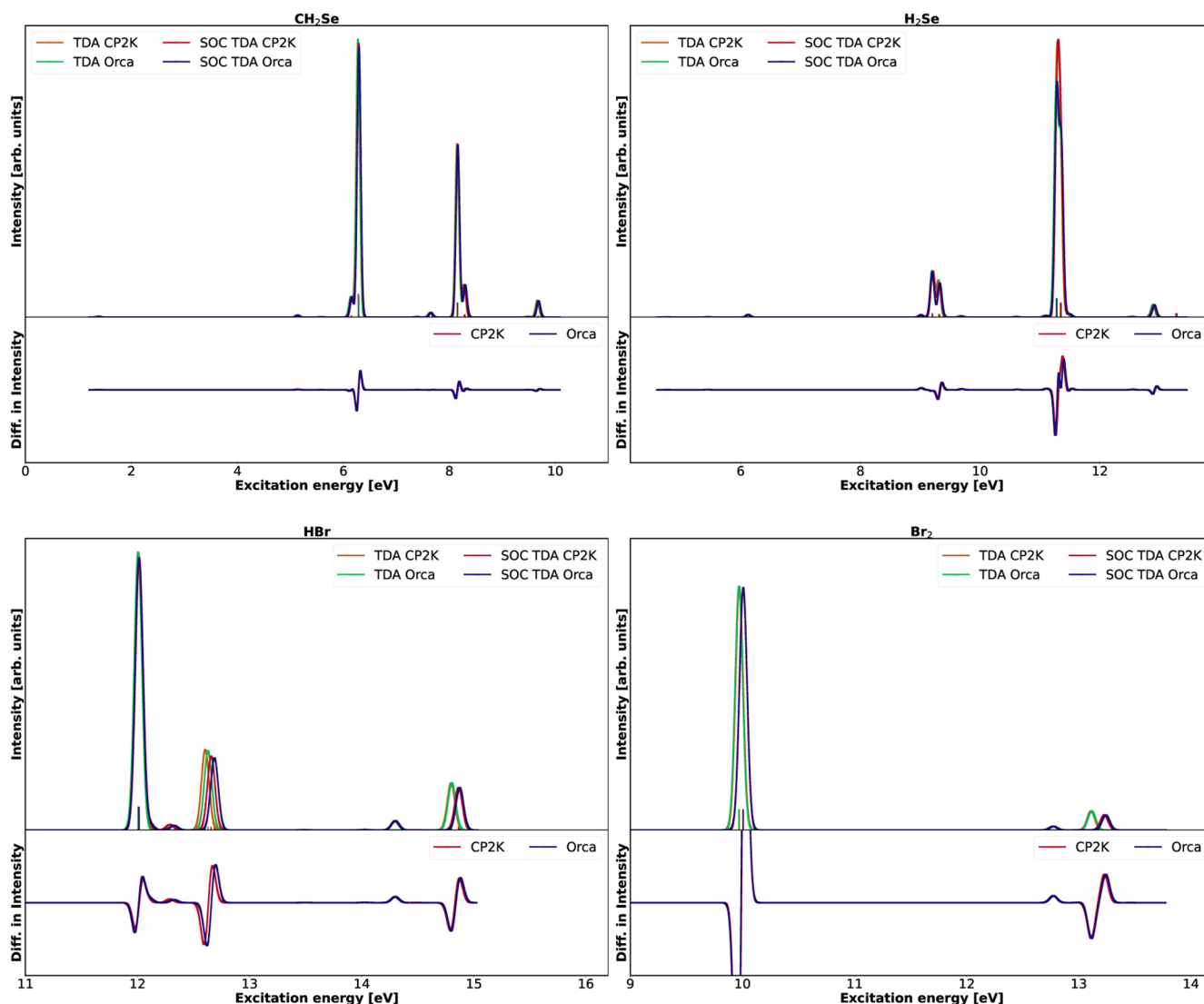


FIG. 1. Exemplary plots of absorption spectra for CH_2Se , H_2Se , HBr , and Br_2 , validating the all-electron ZORA implementation within the CP2K program package in comparison with a comparable perturbative SOC implementation within ORCA relying on a Breit–Pauli Hamiltonian. Plotted are excitation energies (in eV) and corresponding intensities (in arb. units) with spin–orbit coupling correction (SOC TDA) and without correction (TDA).

Hamiltonian. Ignoring spin-other-orbit effects in the case of the latter tends to overestimate the spin-orbit coupling effects.⁵² All calculations were performed using the Perdew–Burke–Ernzerhof with 25% Hartree–Fock exchange (PBE0) functional⁵³ and TZP-ZORA basis sets.⁵⁴ The computations with CP2K are furthermore relying on the Gaussian and augmented plane wave (GAPW) framework^{37,55} and all-electron potentials⁵⁶ to enable all-electron computations and a straightforward comparison. The first ten excited states of the homologue series of H₂O, H₂S, H₂Se, CH₂O, CH₂S, CH₂Se, HF, HCl, HBr, F₂, Cl₂, and Br₂ were considered for comparison. To highlight the overall agreement between the two program packages, corresponding root-mean-square deviations (RMSDs) for excitation energies and oscillator strengths are summarized in the [supplementary material](#). In total, we find an agreement with RMSDs of 0.13 eV for excitation energies and of $19.2 \cdot 10^{-3}$ a.u. for oscillator strengths. Corresponding spectra plots are visualized exemplarily for H₂Se, CH₂Se, HBr, and Br₂ in the upper half of the graphs of [Fig. 1](#). The obtained spin-orbit energy splittings are of meV magnitude, and thus, resulting spectra with or without the spin-orbit coupling correction mainly differ for the heavier homologues due to the slightly shifted peaks of the dominant singlet excitations as well as the non-zero oscillator strengths for the no longer spin-forbidden triplet excitations. Differences in intensities, highlighting the magnitude of the SOC-induced transitions and shifts, are shown in the lower half of the spectra plots of [Fig. 1](#). RMSDs in energy splittings for the comparison of the two program packages are smaller than 15.2 meV; spin-orbit induced differences in oscillator strengths deviate by a maximum of $4.6 \cdot 10^{-3}$ a.u.

B. Benchmarking spin-orbit coupling matrix elements

Spin-orbit coupling matrix elements (SOMEs) were furthermore validated for a benchmark set by Dinkelbach *et al.*³⁸ The

test set originally comprises 14 organic molecules. For two of the therein included structures, namely furan and thiophen, Dinkelbach *et al.* explicitly added diffuse basis functions centered at a dummy atom within the five-membered aromatic ring. For convenience and to enable an unbiased validation of all test structures, furan and thiophen were, therefore, excluded in our benchmark studies. The remaining 12 test molecules are shown in [Fig. 2](#), featuring C, O, N, S, and H atoms.

The performed TDA computations are compared with TDA and DFT/MRCI reference results of Ref. 38, with the latter representing an approach combining KS orbitals with restricted multi-reference configuration interaction (MRCI) expansions. For the TDA spin-orbit couplings, Dinkelbach *et al.* were also relying on the AMEW *Ansatz*, and thus, their TDA reference results are based on comparable wave functions. In contrast to the current implementation, the reference results are, however, based on an atomic mean-field approximation of the Breit–Pauli Hamiltonian, thus again including next to spin-same also spin-other-orbit interactions.

In analogy to the TDA reference results, computations were performed using the PBE0 functional.⁵³ As before, core electrons were taken into account by relying on GAPW and all-electron potentials. Triple- ζ basis functions with one polarization function from the def2 basis set family of the Ahlrichs group were used for all atoms of the first and second row of the periodic table (TZVP), while an additional polarization function was added for sulfur (TZVPP). In addition, augmented basis sets were used for formaldehyde, thioformaldehyde, and nitromethane to account for low-lying Rydberg states.

Since CP2K is not featuring an assignment of excited states regarding symmetry, the assignment of excited states was based on a comparison of CP2K results with analogous TURBOMOLE computations.⁵⁷ In general, it thus has to be highlighted that TDA and DFT/MRCI results were compared and the corresponding errors were computed based on the symmetry assignment and not on the

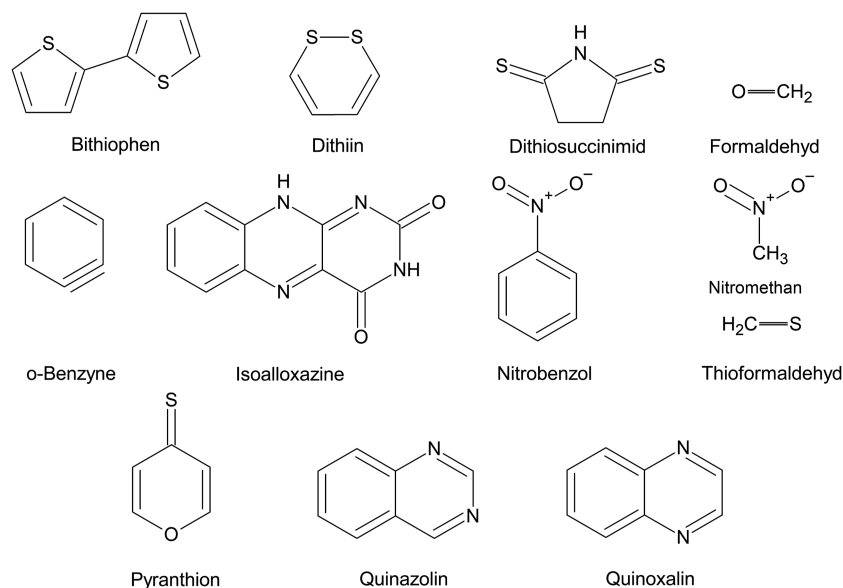


FIG. 2. Structures of the 12 considered molecules taken from the benchmark set of Ref. 38.

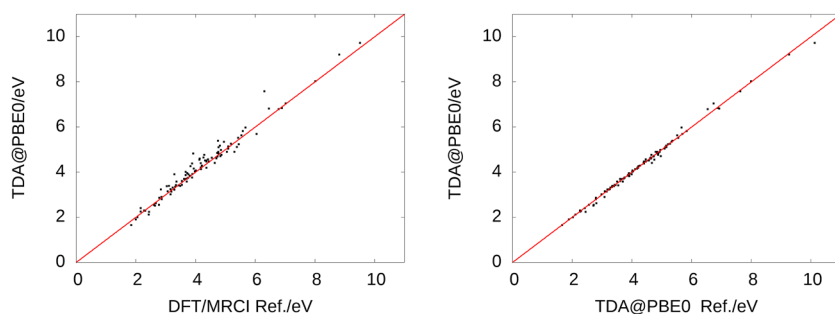
TABLE I. Root-mean-square deviations (RMSDs) in excitation energies Ω (eV) and spin-orbit coupling matrix elements (SOMEs) (cm^{-1}) of TDA results with respect to reference TDA and DFT/MRCI results taken from Ref. 38. For comparison, RMSDs comparing the reference TDA computations with the reference DFT/MRCI results are listed in the last column.

Molecule	TDA vs TDA Ref. 38		TDA vs DFT/MRCI Ref.		TDA Ref. 38 vs DFT/MRCI Ref. 38	
	Ω (eV)	SOME (cm^{-1})	Ω (eV)	SOME (cm^{-1})	Ω (eV)	SOME (cm^{-1})
1. Bithiophene	0.03	2.7	0.21	3.0	0.20	3.6
2. Dithiin	0.01	1.6	0.09	5.9	0.10	6.2
3. Dithiosuccinimide	0.19	3.2	0.18	8.1	0.21	7.8
4. Formaldehyde	0.20	3.1	0.23	4.7	0.34	6.4
5. Isoalloxazine	0.02	0.7	0.16	1.8	0.18	2.1
6. Nitrobenzene	0.05	2.1	0.40	3.3	0.38	2.9
7. Nitromethane	0.06	2.6	0.58	4.7	0.59	4.1
8. <i>o</i> -Benzyne	0.08	0.8	0.19	1.0	0.19	0.7
9. Pyranthione	0.05	3.2	0.33	13.6	0.34	14.4
10. Quinazoline	0.05	1.0	0.10	1.9	0.09	1.6
11. Quinoxaline	0.06	1.6	0.29	2.4	0.28	2.7
12. Thioformaldehyde	0.13	11.2	0.22	11.2	0.22	13.8
Total RMSD	0.10	3.7	0.28	5.9	0.25	5.8

energetic ordering. Only for dithiin, nitrobenzene, nitromethane, and *o*-benzyne, symmetry assignment was in full agreement with an ordering of excited states based on the excitation energy. For bithiophene, dithiosuccinimide, and isoalloxazine, the energetic ordering of two states, and for quinoxaline, the ordering of three pairs of states, differs from the reference assignment, increasing the listed error in the excitation energy. Resulting errors in the excitation energies amount up to 0.5 eV for both 1^1B_2 and 2^1A_2 of dithiosuccinimide and 1^1A_2 and 2^1A_2 for quinoxaline. Comparable deviations are discussed for full TDDFT not relying on the TDA in Ref. 38, suggesting the multireference character of these states to be significant. Further details on the assignment are given in the [supplementary material](#).

Overall errors of excitation energies and SOMEs with respect to the reference TDA and DFT/MRCI results³⁸ are summarized in [Table I](#). Corresponding correlation plots for excitation energies and spin-orbit coupling matrix elements are shown in [Figs. 3 and 4](#). It should be noted that the obtained spin-orbit energy splittings are again tiny in magnitude. In summary, total RMSDs with respect to the reference TDA results are 0.10 eV for excitation energies

and 3.7 cm^{-1} for spin-orbit coupling elements. Deviations with respect to DFT/MRCI references amount up to total RMSDs of 0.28 eV for excitation energies and 5.9 cm^{-1} for spin-orbit coupling elements. Due to the neglect of spin-other-orbit interactions in the Hamiltonian and differences in basis sets and setup, relying on the Gaussian and augmented plane wave implementation with all-electron potentials in comparison with all-electron implementations for both reference datasets, the TDA results of this work are considered less accurate by construction in comparison with the TDA reference. The nevertheless good agreement with the methodologically most accurate DFT/MRCI results must, therefore, rely on fortuitous error cancellation. In case of the SOME ([Fig. 4](#)), two data points at 137.2 and 83.6 cm^{-1} clearly deviate from the reference. These belong to matrix elements $\langle 1^3A_2 | H_{SO_z} | 1^1A_1 \rangle$ and $\langle 1^3B_2 | H_{SO_x} | 2^1A_1 \rangle$ of thioformaldehyde. For $\langle 1^3A_2 | H_{SO_z} | 1^1A_1 \rangle$, the deviation between DFT/MRCI and the reference TDA calculation is 37.1 cm^{-1} larger than the deviation of our calculation of only 8.4 cm^{-1} . For $\langle 1^3B_2 | H_{SO_x} | 2^1A_1 \rangle$, the difference in DFT/MRCI amounts up to 8.4 cm^{-1} for the reference TDA result, which is smaller than the error of 17.6 cm^{-1} of this work. Both errors

**FIG. 3.** Correlation plot comparing TDA excitation energies relying on the all-electron ZORA Hamiltonian with respect to DFT/MRCI (left) and TDA (right) reference results relying on a Breit-Pauli Hamiltonian.

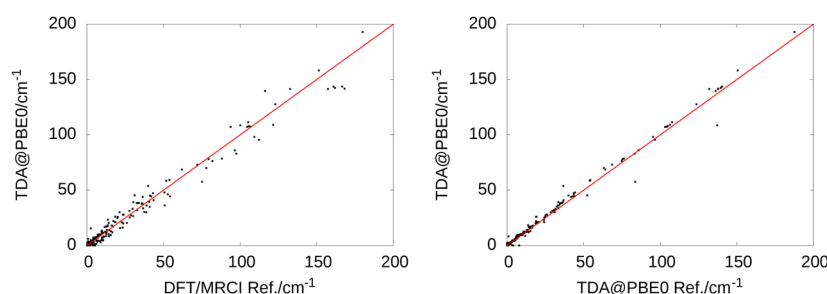


FIG. 4. Correlation plot comparing TDA spin-orbit coupling matrix elements relying on the all-electron ZORA Hamiltonian with respect to DFT/MRCI (left) and TDA (right) reference results relying on a Breit–Pauli Hamiltonian.

TABLE II. Root-mean-square errors in excitation energies (eV) and oscillator strengths (a.u.) for the comparison of pseudopotential (PP) TDA computations with respect to the all-electron TDA reference, with the latter relying on GAPW and the all-electron ZORA Hamiltonian. Errors of conventional PP-TDA results without spin-orbit coupling correction are listed for comparison.

Molecule	Conventional PP-TDA		SO-corrected PP-TDA		
	RMSD (Ω) (eV)	RMSD(f)/ 10^{-3} (a.u.)	RMSD (Ω) (eV)	RMSD(f)/ 10^{-3} (a.u.)	SOME (cm^{-1})
CH ₂ O	0.15	8.01	0.15	14.00	10.4
CH ₂ S	0.06	2.60	0.05	2.38	30.4
H ₂ O	0.09	2.09	0.08	2.19	12.4
H ₂ S	0.06	11.91	0.06	11.91	27.5
HF	0.17	5.66	0.17	5.96	46.9
HCl	0.08	3.87	0.08	3.80	81.6
F ₂	0.28	4.40	0.28	4.39	70.5
Cl ₂	0.17	4.48	0.17	4.37	114.5

could be due to the different setups, comparing Gaussian basis sets within TURBOMOLE with the Gaussian and augmented plane wave approach of CP2K.

C. Comparison of all-electron and pseudopotential computations

For computations on systems involving heavier elements, core electrons are treated by referring to the SOC-including pseudopotential of Eq. (15) and, thus, by treating solely valence electrons explicitly within the Gaussian and plane wave (GPW) framework.³⁴ An extensive benchmark of SOC-including pseudopotentials is beyond the scope of this work; however, the implementation was validated for the subset of small organic molecules discussed in Sec. III A. To enable a straightforward comparison, computations were performed using the aug-QZV2P-GTH basis sets, and we, therefore, restricted the validation to molecules containing solely atoms up to the third row of the periodic table. RMSDs in excitation energies for the comparison of pseudopotential computations with the all-electron reference, given in Table II, are smaller than 0.28 eV. RMSDs in SOMEs are in the range of 10.4–114.5 cm^{-1} .

D. Computational timings for a bismuth-containing metal-organic framework

Timings are presented for a metal-organic framework, called CAU-7-TATB,^{39,40,58} containing 184 atoms in the unit cell corresponding to 656 valence electrons and 2600 spherical basis functions. CAU-7-TATB (TATB³⁻ = triazine-2,4,6-triyl-tribenzaoate) is

a Bi-MOF that is isorecticular to CAU-7-BTB (BTB³⁻ = 1,3,5-benzenetrisbenzoate) with the inner phenyl ring formally replaced by a triazine linker. The structures contain Bi³⁺ ions that are ninefold coordinated by oxygen atoms of the TATB³⁻ ions, thereby forming threefold capped trigonal prisms. Face sharing of the BiO₉ polyhedra results in chains that are interconnected by the linker molecules to form a slightly distorted honeycomb network with one-dimensional channels about 1 nm wide. CAU-7 MOFs exhibit permanent porosity, catalytic activity, and are biocompatible and can be used for drug delivery.^{58,59} Computations were performed on a 512 Intel Xeon Gold 6426Y processor using in total 512 cores. Using a PBE/TZVP-MOLOPT-GTH basis set and the mentioned SOC-corrected GTH pseudopotentials and computing 200 excited states, the total computation time amounted up to 7 h 17 min 23.1 s. Computation of excitation energies and spin-orbit coupling matrix elements took only 14 min 58.1 s of the total computation time.

IV. CONCLUSIONS

Perturbative spin-orbit couplings were presented for the Tamm–Dancoff approximation of linear-response time-dependent density functional theory, relying on the AMEW Ansatz and a one-electron ZORA Hamiltonian, as well as SOC-corrected pseudopotentials. All-electron spin-orbit coupling corrected excitation energies and matrix elements are in agreement with DFT/MRCI reference results with errors in excitation energies and spin-orbit matrix elements being below 0.6 eV and 14.4 cm^{-1} , respectively. Relying on pseudopotentials, root-mean-square deviations increase

by an order of magnitude. Computation of the perturbative correction represents less than 3% of the overall computation time. The *Ansatz* could thus be beneficial for non-adiabatic molecular dynamics, in particular the description of intersystem crossing. More explicitly, a spin-diabatic formulation, relying on the unperturbed singlet and triplet eigenstates to compute the potential energy surfaces and the unperturbed nuclear forces, can be achieved by solely taking into account spin-orbit coupling corrected non-adiabatic coupling constants and thereon based transition probabilities.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) includes the formulas for the spin-orbit coupling matrix elements, formulas for oscillator strengths, a comparison between implementations in CP2K and ORCA, and further benchmark data on excitation energies and spin-orbit coupling matrix elements.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jan-Robert Vogt: Conceptualization (equal); Data curation (lead); Formal analysis (equal); Investigation (equal); Software (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jan Wilhelm:** Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Writing – review & editing (equal). **Anna-Sophia Hehn:** Conceptualization (equal); Data curation (supporting); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (lead); Software (equal); Supervision (lead); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The implementation is included in the open-source CP2K program package (<https://www.cp2k.org>). Input and relevant

data files for the computational results presented in this manuscript are available on Materials Cloud, <https://doi.org/10.24435/materialscloud:rd-wm>.

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