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Relativistic Two-Component Particle–Particle Tamm–Dancoff Approximation

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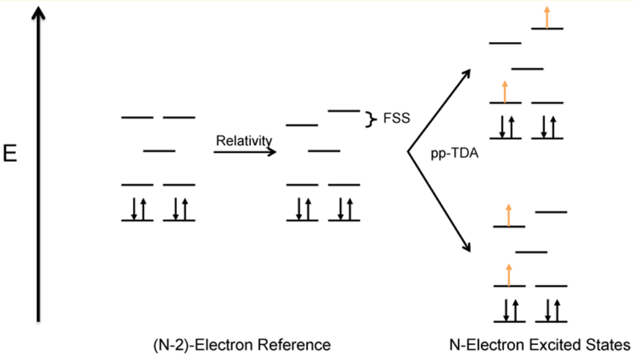
ABSTRACT: With the recent introduction of the particle–particle random-phase and Tamm–Dancoff approximations to *ab initio* theory, routine queries of traditionally difficult systems, such as diradicals and doubly excited states, have been made possible. However, although a wealth of inquiry has been directed to investigating these methods, the current formulations have been restricted to spin-collinear systems, leaving the methods incapable of treating noncollinearity and spin–orbit relativistic effects in excited states. In this work, we extend the particle–particle Tamm–Dancoff approximation to suit two-component Hamiltonians to explicitly treat relativistic effects in excited states. After reviewing the theory and computational implementation, we demonstrate the accuracy of this extension by evaluating the fine structure splittings some of atomic and molecular systems.



1. INTRODUCTION

The ability to accurately predict and characterize the electronically excited states of molecular systems is paramount to a complete understanding of many chemical phenomena. As such, excited states are the central focus of many fields of physical chemistry, the most prominent of which being spectroscopy. Due to this centralized importance and the need to efficiently and accurately predict excited-state properties, much effort has been devoted over the years toward the modeling of excitation energies and oscillator strengths.

Recently, the particle–particle random-phase approximation (pp-RPA) and Tamm–Dancoff approximation (pp-TDA), which have been standard trade tools of the nuclear physics community in the treatment of the many-body correlation energy for low matter density systems,[1] have been extended to the treatment the correlation energy and excitation energies of quantum molecular systems within a finite basis set.[2−8] Although this introduction into the quantum chemistry community is relatively recent, a wealth of effort has been afforded to the rigorous investigation of these methods in a variety of different contexts, involving the evaluation of excitation energies,[2−4] excited-state properties and geometry optimizations,[9] and the treatment of nonadiabatic phenomena such as nonadiabatic dynamics[10,11] and the description of conical intersections.[12] So far in their development, however, these methods have seen application only in molecular systems using strictly spin-collinear references, disallowing extension to systems with spin-noncollinear states, such as those that arise in spin-frustrated systems or whenever spin–orbit effects are included in the treatment. To the best of our knowledge, there has been no previous work to extend the implementation pp-TDA formalism to two-component or any relativistic wave functions for molecular systems.

Recent years have also seen new developments in the realm of relativistic quantum chemistry. Relativistic effects, while often neglected in most standard treatment of electronic structure, can have profound consequences in chemical systems.[13] Scalar relativistic effects cause the contraction of the core electron shells of heavy atoms, but perhaps of even more consequence is the introduction of spin couplings in the Hamiltonian. Spin–spin and spin–orbit interactions can affect the electronic spin dynamics even in light atoms, and a direct consequence of these couplings on excited states is the loss of degeneracies of spin-eigenstates, giving rise to fine structure splittings (FSS) in atoms and molecules with symmetry-induced degeneracies. It is therefore desirable to develop accurate and cost-effective relativistic electronic structure methods able to model such effects.

In this work, the pp-TDA formalism has been extended to two-component relativistic Hamiltonians, utilizing the single Slater determinant description for the two-component wave function. The presented formalism can, however, also be employed in the case of spin-frustrated systems with a noncollinear ground state even in the absence of relativistic effects.

2. THEORY

In the following presentation, we will use indices i, j, ... to refer to occupied molecular orbitals (MO), a, b,... to refer to virtual orbitals, and p, q, ... to refer to any orbital regardless of occupancy. All MOs are expanded in terms of real atomic-orbitals (AO).

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2.1. Exact Two-Component Method.

Relativistic quantum chemistry is based on the solution of the Dirac equation in lieu of the nonrelativistic Schrödinger equation.[14,15] The one-electron Dirac Hamiltonian takes the following form

$$\mathcal{H}_{\mathrm{D}} = \begin{pmatrix} V\sigma_0 & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & (V - 2mc^2)\sigma_0 \end{pmatrix} \tag{1}$$

where V collects all scalar potential terms, $\vec{p}$ is the momentum operator, $\vec{\sigma}$ is a vector whose components are the Pauli matrices, and σ_0 is the identity matrix of rank two. The relativistic wave function is separated into its large and small components. In the nonrelativistic limit, the large component approaches the nonrelativistic wave function while the small components goes to zero. Each component is separated into inseparable spin-up and spin-down parts

$$\psi^{4\mathrm{c}} = \begin{pmatrix} \psi_{\mathrm{L}} \\ \psi_{\mathrm{S}} \end{pmatrix} \tag{2}$$

$$\psi_{\mathrm{L}} = \begin{pmatrix} \psi_{\mathrm{L}}^{\alpha} \\ \psi_{\mathrm{L}}^{\beta} \end{pmatrix}; \quad \psi_{\mathrm{S}} = \begin{pmatrix} \psi_{\mathrm{S}}^{\alpha} \\ \psi_{\mathrm{S}}^{\beta} \end{pmatrix} \tag{3}$$

Although eq 1 may be solved for the four-component wave function directly, it is often advantageous from a practical as well an aesthetic perspective to transform the full four-component relativistic equations into a two-component form that closely resembles those found in nonrelativistic theory. Such a transformation allows one to employ the machinery of standard nonrelativistic electronic structure methods with only minor modifications.[16−20] In general, such a transformation is achieved by means of a unitary transformation, $\mathcal{U}$, such that

$$\mathcal{U}\mathcal{H}\mathcal{U}^{\dagger} = \begin{pmatrix} H_{+} & \mathbf{0}_2 \\ \mathbf{0}_2 & H_{-} \end{pmatrix}; \quad \mathcal{U}\begin{pmatrix} \psi_{\mathrm{L}} \\ \psi_{\mathrm{S}} \end{pmatrix} = \begin{pmatrix} \psi^{2\mathrm{c}} \\ 0 \end{pmatrix} \tag{4}$$

Here, the two-component transformed wave function $|\psi^{2c}\rangle$ is an eigenstate of the transformed Hamiltonian operator H_{+}. The exact transformation $\mathcal{U}$ for the full equation including the two-electron terms cannot, however, be found in most practical cases; therefore, one must introduce approximations for the decoupling of the large and small components. Several types of such decoupling methods have been described over the years. In this work, we employ only the exact two-component method (X2C), for which the precise form of the transformation matrix may be found elsewhere.[17,21−26] Here, the word "exact" refers to the fact that X2C is based on the diagonalization of the full one-electron four-component Hamiltonian, although the term X2C may also be used in general to describe methods with an effective Hamiltonian, such as the Dirac−Fock operator.[26−29]

Although the scalar potential, V, includes, for molecular systems, both electron−nuclei attraction and the electron−electron repulsion, a very common approximation is to neglect the transformation of the two-electron terms of the Dirac Hamiltonian. This approach greatly reduces the computational cost associated with the transformation; however, it neglects two-electron spin−orbit terms, some of which are of the same order as their one-electron counterparts. While several methods have been proposed to partially take two-electron spin−orbit couplings into account,[21,25,26,30,31] here we adopt a simple approach that employs scaling factors applied to the one-electron spin−orbit terms according to a scheme that depends on the angular momentum of the function.[32,33]

The total effective two-component Hamiltonian obtained with this procedure can be written in second quantized form

$$\mathcal{H} = V_{\mathrm{NN}} + h_{pq}^{\mathrm{X2C}} c_p^{\dagger} c_q + \frac{1}{2}\langle pq|rs\rangle c_p^{\dagger} c_r^{\dagger} c_s c_q \tag{5}$$

where $c_p^{\dagger}$ and c_p are the one-particle creation and annihilation operators that create and annihilate single-particle *spinor* Fock states, respectively. V_{NN} is the nuclear repulsion energy, $\mathbf{h}^{\mathrm{X2C}}$ is the effective one-electron core Hamiltonian matrix, and $\langle pq|rs\rangle$ is the Coulomb electron−electron repulsion integral over single-particle Fock states. The Einstein summation convention is implied. Note that in eq 5 the molecular orbitals are spinor quantities that cannot in general be classified as spin-up or spin-down. When written in terms of the AO basis, $\{\chi\}$, a generic MO is expanded as

$$\varphi_q(\vec{r}) = \sum_{\mu} \chi_{\mu}(\vec{r}) \begin{pmatrix} C_{\mu q}^{\alpha} \\ C_{\mu q}^{\beta} \end{pmatrix} \tag{6}$$

If the wave function is treated as a single determinant, then one may find the ground-state energy by means of the two-component Hartree−Fock (X2C-HF) method. Note however that once an approximate X2C decoupling is achieved, the quasi-relativistic Hamiltonian can be used with most electronic structure methods, provided a noncollinear formalism is employed.[16−19,26] If the Fock operator, $\mathbf{F}$, and the electron density, $\mathbf{P}$, are expanded in a basis of real spinor atomic orbitals, then one may write the X2C-HF equation as

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} \boldsymbol{\varepsilon} \tag{7}$$

$$\mathbf{F}^{\sigma\sigma'} = \mathbf{h}_{\mathrm{X2C}}^{\sigma\sigma'} + \delta_{\sigma\sigma'}\mathbf{J}(\mathbf{P}^{\alpha\alpha} + \mathbf{P}^{\beta\beta}) - \mathbf{K}(\mathbf{P}^{\sigma\sigma'}) \tag{8}$$

$$P_{\mu\nu}^{\sigma\sigma'} = \sum_{i} C_{\mu i}^{\sigma} C_{\nu i}^{\sigma' *} \tag{9}$$

Where $\mathbf{S}$ is the AO overlap matrix, $\boldsymbol{\varepsilon}$ is a diagonal matrix that collects the MO energies, $\mathbf{J}$ and $\mathbf{K}$ are the Coulomb and exchange matrices, respectively. In this equation, relativistic effects explicitly appear solely in the core Hamiltonian $\mathbf{h}^{\mathrm{X2C}}$, which has both a scalar and a spin−orbit components

$$\mathbf{h}^{\mathrm{X2C}} = \sigma_0 \mathbf{h}_{\mathrm{s}} + \vec{\sigma}\cdot\mathbf{h}_{\mathrm{so}} \tag{10}$$

Explicit two-electron relativistic and picture change effects are neglected in the Coulomb repulsion term. In the following section, we review the particle−particle formalism, keeping in mind that eq 7 can be applied to a system with any number of particles and thus allowing the application to reference shift of the pp-TDA.

2.2. Particle−Particle Tamm−Dancoff Approximation.

The pp-TDA approximation is a non-particle-number conserving method; i.e., the excitation operator does not commute with the number operator. To model a system with N electrons, it starts from the wave function of the system with $N - 2$ electrons and adds (removes) the electrons back using an appropriate "excitation" operator, for which an equation of motion may be written and solved. The ground and excited states of the N-particle system are thus obtained as "excited states" of the $N - 2$ electron reference, and the desired excitation energies can be written as simple energy differences. A general formalism for the treatment of the pp-TDA within a finite basis of molecular spin-orbitals has described rigorously elsewhere.[2,3,5] Here, we review this formalism for completeness and present the working expressions for the relativistic two-component pp-TDA (X2C-pp-TDA) within the basis of MO spinors as well as describe some caveats in the practical application of this method within the context of a two-component reference.

From an (exact) M-particle (in the case fermions) ground state, $|\Psi_0^M\rangle$, all ground and excited N-particle states ($|\Psi_0^N\rangle$ and $|\Psi_n^N\rangle$, respectively) may be regarded as "excitations" through the excitation operator $O_n^\dagger = |\Psi_n^N\rangle\langle\Psi_0^M|$,

$$|\Psi_n^N\rangle = O_n^\dagger|\Psi_0^M\rangle \tag{11}$$

Given such an ansatz, it is possible to construct an equation-of-motion (EOM)[1] for $O_n^\dagger$, affording some corresponding probing de-excitation operator δO, to obtain the eigenenergies of $|\Psi_n^N\rangle$

$$[\delta O, [\mathcal{H}, O_n^\dagger]] = (E_n^N - E_0^M)[\delta O, O_n^\dagger] \tag{12}$$

Equation 12 is formally exact and completely independent of the chosen reference, provided one has access to the exact N- and M-particle states. In practice, one may take the expectation value of eq 12 using some approximate M-particle ground state, $|\Phi_0^M\rangle$, to obtain *approximate* energy differences between N- and M-particle states given some explicit form of $O_n^\dagger$. As has been previously discussed, if the N and M systems differ by exactly two particles ($M = N - 2$), then the X2C-pp-TDA equation may be obtained by postulating that the excitation operator take the form of all (unique) two-particle additions to obtain N-particle states from an $(N - 2)$-particle reference

$$O_n^\dagger = \sum_{a<b} X_{ab}^n c_a^\dagger c_b^\dagger \tag{13}$$

while the de-excitation operator takes the form

$$\delta O = c_b c_a \tag{14}$$

Here, X_{ab}^n is an expansion coefficient that describes the contribution to the nth N-particle state of the addition of two particles into single-particle virtual states, a and b, of the $(N - 2)$-particle ground state reference. By taking the expectation value of eq 12 in a single X2C-HF Slater determinant given eq 13, one obtains the Hermitian eigenvalue problem of the X2C-pp-TDA

$$\sum_{c<d} A_{ab,cd} X_{cd}^n = \Omega_n X_{ab}^n \quad (a < b) \tag{15}$$

$$\Omega_n = (E_n^N - E_0^{N-2}) \tag{16}$$

$$A_{ab,cd} = \delta_{ac}\delta_{bd}(\epsilon_a + \epsilon_b) + \langle ab||cd\rangle \tag{17}$$

while $\langle\cdot||\cdot\rangle$ is the antisymmetrized two-electron integral tensor in Dirac integral notation and ϵ_p is a spinor-orbital eigenenergy obtained from solving the X2C-HF equation in eq 7. One may obtain neutral N-particle excitations from the eigen spectrum of eq 15 via a reference shift to the $(N - 2)$-particle system. By variationally optimizing the wave function of the $(N - 2)$-particle system via X2C-HF, both the N-particle ground- and excited-state energies are obtained via

$$E_n^N = E_0^{N-2} + \Omega_n \tag{18}$$

Thus, the excitation energy between N-particle ground and excited states, ω_n^N, described via the X2C-pp-TDA may be written as differences of the eigenenergies

$$\omega_n^N = \Omega_n - \Omega_0 \quad (n > 0) \tag{19}$$

These working expressions in eqs 15 and 17–19 are similar to those previously expressed for the spin-collinear reference.[2,3,5] The key difference is that all of the above equations are expressed in the spinor basis within the X2C picture frame rather than a spin-collinear spin–orbital basis and that the orbitals have been optimized in the presence of relativistic spin–orbit effects. Although eq 15 is a completely valid expression for the spin-noncollinear as well as the spin-collinear case, the spin-collinear case allows for significant simplification due to the spin-orthogonality of the spin-aligned reference.[2,4]

3. RESULTS AND DISCUSSION

All calculations were performed with a locally modified version of the Gaussian quantum chemistry suite of programs[34] and employed the taug-cc-pVTZ-DK basis set[35] with the diffuse f-functions removed. Relativistic effects were accounted for by means of the variational X2C method.[24,28,36−38] In order to partially account for two-electron spin–orbit interaction in the Hamiltonian, we employed a scheme based on the scaling of the nuclear charge according to the angular momenta.[32] The atomic nuclei, rather than being treated as point charges, were described using s-type Gaussian charge distribution.[39,40] The stability of the two-component ground-state wave function was also tested before X2C-pp-TDA calculations were performed.[41]

3.1. Single Excitations.

In order to highlight the capability of the method to describe excited states within a relativistic framework, in this section we look at the fine structure splittings of some atomic systems. The presence of spin–orbit couplings causes the total spin, $\vec{S}$, and orbital, $\vec{L}$, angular momentum operators to no longer commute with the Hamiltonian; therefore, they no longer generate good quantum numbers for the system. Instead, the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ is the fundamental quantity that should be considered when classifying the electronic states of the system. A direct consequence of spin–orbit couplings on the spectra of atoms is the lifting of some of the degeneracies that would be expected in the ground or excited electronic states. We therefore calculate the spectrum of selected atomic systems and compare the obtained fine structure splittings with experimental reference values[42] to asses the accuracy of the method. In this section, we restrict ourselves to states describable by single excitations (with respect to the N-electron system), which allows us to also compare our results with the results obtained using the two-component particle-hole random-phase approximation (X2C-ph-RPA), also known as time-dependent Hartree–Fock method (X2C-TDHF), as well as with results obtained using the X2C-ph-TDA method.[43] Results for these fine-structure splittings are collected in Table 1.

It can be seen that, in general, the three methods perform similarly with respect to the reference values insofar as the order of magnitude of the error is concerned. A general trend may be observed in that the X2C-pp-TDA consistently overestimates the splittings as the atomic charge of the underlying nucleus increases. This effect is magnified in the low energy transitions, whereas it is less apparent in the higher energy transitions. This is due to the fact that the frontier orbitals of the $(N - 2)$-reference being used become

Table 1. Calculated and Reference[42] Excited-State Fine Structure Splittings (in meV) of Some Atomic Systems[a]

method	level	Mg	Al^{+}	Si^{2+}
X2C-ph-RPA	$^{3}P^{\circ}_{1}-^{3}P^{\circ}_{0}$	4.89	10.49	19.85
X2C-ph-TDA		2.41	7.94	16.62
X2C-pp-TDA		2.77	9.13	18.97
ref		2.49	7.55	15.94
X2C-ph-RPA	$^{3}P^{\circ}_{2}-^{3}P^{\circ}_{1}$	9.75	21.02	39.96
X2C-ph-TDA		4.82	15.96	33.50
X2C-pp-TDA		5.55	18.40	38.40
ref		5.05	15.36	32.45
X2C-ph-RPA	$^{3}P^{\circ}_{1}-^{3}P^{\circ}_{0}$	0.33	1.82	4.43
X2C-ph-TDA		0.33	1.82	4.31
X2C-pp-TDA		0.42	2.17	5.08
ref		0.41	1.73	4.10
X2C-ph-RPA	$^{3}P^{\circ}_{2}-^{3}P^{\circ}_{1}$	0.67	3.67	9.09
X2C-ph-TDA		0.67	3.68	8.86
X2C-pp-TDA		0.84	4.50	11.04
ref		0.84	3.65	9.07
		MSE	MAE	
X2C-ph-RPA		2.32	2.28	
X2C-ph-TDA		0.32	0.19	
X2C-pp-TDA		1.55	1.55	

[a] The presence of a superscript "°" in the term symbol denotes an odd state with respect to space inversion. MSE (mean signed error) and MAE (mean absolute error) are also compared.

suboptimal in the proper description of the *N*-electron system due to a contraction in the presence of higher nuclear charge. This leads to an unphysically small energetic separation between the frontier orbitals of the *N*-electron system, which causes increasing errors due to an unphysical increase in mixing. This problem is less obvious in higher energy excitation because the higher lying orbitals are not as affected. These orbitals are properly optimized in X2C-ph-RPA/TDA due to the orbital occupancy of the resulting wave function. The general out-performance of X2C-ph-TDA over X2C-ph-RPA may be attributed to an over estimation of electron correlation in the excited states via the RPA.[44] The presence of the de-excitation amplitudes in X2C-ph-RPA allows for an overmixing for the low-lying excited states with the ground state, which gives rise to an overestimate of the FSS, much the same as the case for X2C-pp-TDA. The main advantage of the particle−particle over the particle−hole formalism is that, in the former, both the ground and electronically excited *N*-particle states are described on equal footing with respect to correlation, being a combination of several Slater determinants. Conversely, in the ph-TDA or ph-RPA method, the ground state is described as a single determinant, whereas excited states are described as linear combinations of single excitations (and possibly de-excitations). That being said, the excitation space spanned by the X2C-pp-TDA solutions does not include all chemically relevant excitations, many of which can be found using the more traditional ph-RPA or ph-TDA methods. This is due to the fact that the X2C-pp-TDA is, in its traditional form, incapable of accessing excitations that involve contributions from below the Fermi level. Some work has been done in attempts to resolve this problem,[2] but these alterations to the pp-TDA method have not been explored in this work.

3.2. Triplet References and Double Excitations. In this section, we highlight other advantages of X2C-pp-TDA over conventional X2C-ph-RPA. In the previous section, we presented results for atomic systems that are characterized by being closed shell in both the *N* and $N - 2$ systems. This is important because if the reference state has unpaired electrons then, as a consequence of the single-reference nature of the Hartree−Fock wave function, excited states will in general be spin-contaminated, affecting one's ability to extract meaningful fine structure splittings from the results, although adaptations to the general case exist.[45−49] By using X2C-pp-TDA, it is however possible to treat systems with *N* electrons with any odd spin multiplicity, provided they become closed shell upon the addition or removal of two electrons. Molecules that possess triplet ground states as well as diradical moieties may be taken as examples. To demonstrate this feature, we compare the FSS of one set of excited states of molecular oxygen with experimental data in Table 2. The difference between the calculated and measured value is just 2.5 meV, notwithstanding the approximations intrinsic in our method (e.g., the approximate treatment of electron correlation and the two-electron spin−orbit contributions, or the finite basis set). Of course, the same reasoning can also be applied in reverse: X2C-ph-RPA theory can be readily used to find excited-state FSS of systems with a singlet ground state; however, if the addition or removal of two electrons produces an open-shell molecule, then X2C-pp-TDA will present some spin-contamination in the computed excited-states.

Table 2. Excited-State Fine Structure Splittings (in meV)

system	level	X2C-pp-TDA	ref[42,50]
O_2	$^{3}\Delta_{3}-^{3}\Delta_{2}$	20.58	18.09
Al^{+}	$^{3}P_{1}-^{3}P_{0}$	9.20	7.75
	$^{3}P_{2}-^{3}P_{1}$	17.93	15.03
Si^{2+}	$^{3}P_{1}-^{3}P_{0}$	19.46	16.55
	$^{3}P_{2}-^{3}P_{1}$	37.88	32.06

One advantage that X2C-pp-TDA always has over X2C-ph-RPA theory, however, is its ability to describe double excitations. Table 2 compares calculated and reference excited-state FSS of doubly excited states of some atomic moieties. The performance of the method is similar to that in the case of single excitations presented in the previous section. Such states cannot be found among the excited states computed via X2C-ph-RPA.

4. CONCLUSIONS

In this work, a scheme for the extension of the pp-TDA method to relativistic two-component wave functions has been presented. This scheme involves the approximate decoupling of the large and small components of the relativistic wave function by means of the X2C method, followed by a Hartree−Fock SCF calculation on the system obtained by removing two electrons to obtain a set of complex spinor molecular orbitals. The two-component reference system is then used in the X2C-pp-TDA calculation that yields the ground and excited states for the *N*-electron system. The extension of the pp-TDA to a two-component reference comes at the cost of the employing complex spinor orbitals and not being able to separate the problem into smaller subproblems as is done in the case of

RHF or UHF references via spin integration. The increased computational cost highlights the ever pressing need for direct and parallel implementations of post-SCF electronic structure methods, which is exaggerated in the case of relativistic electronic structure calculations.

It has been shown that the X2C-pp-TDA method exhibits excellent results in the prediction of the fine-structure splittings of the atomic and molecular species considered here. The results are comparable and at times better than those obtained using X2C-ph-RPA.[43] In addition, X2C-pp-TDA is able to capture electronic excitations traditionally inaccessible by X2C-ph-RPA/TDA thanks to the two-particle reference shift, such as double excitations and those that would be described as spin-contaminated in particle-number conserving methods. While these results are promising, the general applicability of the X2C-pp-TDA method, as with the spin-collinear variant, is limited as it is traditionally unable to capture excitations that involve contributions of orbitals from below the Fermi level. That being said, there are many systems, such as triplet and diradical systems, for which X2C-pp-TDA provides a suitable method for the accurate description of the electronic manifold.

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Notes

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