Singlet–Triplet Energy Gaps for Diradicals from Particle–Particle Random Phase Approximation

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Supporting Information

ABSTRACT: The particle–particle random phase approximation (pp-RPA) for calculating excitation energies has been applied to diradical systems. With pp-RPA, the two nonbonding electrons are treated in a subspace configuration interaction fashion while the remaining part is described by density functional theory (DFT). The vertical or adiabatic singlet–triplet energy gaps for a variety of categories of diradicals, including diatomic diradicals, carbene-like diradicals, disjoint diradicals, four-π-electron diradicals, and benzynes are calculated. Except for some excitations in four-π-electron diradicals, where four-electron correlation may play an important role, the singlet–triplet gaps are generally well predicted by pp-RPA. With a relatively low O(r4) scaling, the pp-RPA with DFT references outperforms spin-flip configuration interaction singles. It is similar to or better than the (variational) fractional-spin method. For small diradicals such as diatomic and carbene-like ones, the error of pp-RPA is slightly larger than noncollinear spin-flip time-dependent density functional theory (NC-SF-TDDFT) with LDA or PBE functional. However, for disjoint diradicals and benzynes, the pp-RPA performs much better and is comparable to NC-SF-TDDFT with long-range corrected ωPBE functional and spin-flip configuration interaction singles with perturbative doubles (SF-CIS(D)). In particular, with a correct asymptotic behavior and being almost free from static correlation error, the pp-RPA with DFT references can well describe the challenging ground state and charge transfer excitations of disjoint diradicals in which almost all other DFT-based methods fail. Therefore, the pp-RPA could be a promising theoretical method for general diradical problems.

INTRODUCTION

Diradicals are molecules with two electrons in degenerate or nearly degenerate molecular orbitals.1,2 They can be short-lived reactive species that play an important role in chemical reactions, such as carbenes.3 They can also be relatively stable species that can possibly be used in material sciences, such as graphene fragments.4 In a diradical, the various possibilities of alignments for the two nonbonding electrons give rise to its versatile chemistry behaviors. Therefore, it is of particular interest to study diradicals both experimentally and theoretically.

In the simplest two-orbital diradical model, there are six possible occupation configurations corresponding to six determinants (Figure 1). Through linear combination, six spin-adapted configurations can be generated. Of these six spin-adapted ones, there are three triplet states with the same energy and three singlet states usually with different energies.

In a simple Hartree–Fock (HF) analysis, the alignment of these four energy levels depends on the orbital energies, the coulomb repulsion energy within the same orbital and between the two orbitals, as well as the exchange energy between the two orbitals.

In general, if we ignore the symmetry and consider all the possible configuration interactions within the two-orbital two-electron model, there is a general form for the three singlet states,

$$\Psi = c_α|αα⟩ + c_β|ββ⟩ + \frac{c_{αβ}}{\sqrt{2}}(|αβ⟩ + |βα⟩)$$

$$= \frac{c_α + c_β}{2}(|αα⟩ + |ββ⟩) + \frac{c_α - c_β}{2}(|αβ⟩ + |βα⟩) + \frac{c_{αβ}}{\sqrt{2}}(|αβ⟩ - |βα⟩)$$

$$= C_1Φ_1 + C_2Φ_2 + C_3Φ_3,$$  (1)

with

$$Φ_1 = \frac{|αα⟩ + |ββ⟩}{\sqrt{2}}$$  (2a)

$$Φ_2 = \frac{|αβ⟩ - |βα⟩}{\sqrt{2}}$$  (2b)

$$Φ_3 = \frac{|αβ⟩ + |βα⟩}{\sqrt{2}}$$  (2c)

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Under an orbital transformation, for example, the following one,

\[ |A⟩ = \frac{|a⟩ + |b⟩}{\sqrt{2}} \]  
\[ |B⟩ = \frac{|a⟩ - |b⟩}{\sqrt{2}} \]

the three component terms become

\[ \Phi_1 = \frac{|AA⟩ + |BB⟩}{\sqrt{2}} \]  
\[ \Phi_2 = \frac{|AB⟩ - |BA⟩}{\sqrt{2}} \]  
\[ \Phi_3 = \frac{|AA⟩ - |BB⟩}{\sqrt{2}} \]

The form of the first term is unchanged and so are the triplet terms not shown here. This holds true for general unitary transformations. These transformed orbitals are useful for understanding and analyzing results in specific systems, although these orbitals do not necessarily diagonalize any one-electron Hamiltonian and cannot be assigned orbital energies from eigenvalues.

Usually, the most interesting states to chemists are the three triplet states and the one low-lying singlet states. This singlet state can be either a closed-shell singlet (for example, methylene\(^5\)), or possibly an open-shell singlet (for example, cyclobutadiene). The energy difference between the triplets and the low-lying singlet differs from species to species, and can be used to predict the electronic properties and chemical reactivities of a given diradical.

Despite the long history of diradical problems,\(^6,8\) it still remains a hot topic to pursue a theoretical method that can efficiently and accurately describe a diradical system, especially its open-shell singlet state. Because of the energy near-degeneracy of the orbitals that diagonalize the one-body effective Hamiltonian, the open-shell singlet state has strong static correlation. In other words, the state has a strong multiconfiguration nature, and in order for it to be theoretically well described, multireference methods are required. The commonly used multireference wave function methods include the complete active space self-consistent-field (CASSCF) and its second order perturbative treatment (CASSPT2),\(^9\) the multireference configuration interaction (MR-CI),\(^10\) and the multireference coupled cluster theory (MR-CC).\(^11,12\) These methods are generally accurate. However, they are computationally demanding and therefore limited to relatively small systems. Another category of methods that are commonly used is usually called the broken-symmetry (BS) approach.\(^13–16\) In this approach, instead of directly describing the challenging open-shell singlet state, one uses unrestricted density functional theory (UDFT) or unrestricted coupled cluster theory (UCC) to describe one of the broken-symmetry states (Figure 1), which is roughly a half open-shell singlet contaminated by a half triplet state and energetically lies approximately half way in between the triplets and the open-shell singlet state. The amount of spin-contamination can be further corrected by spin-projection.\(^17,18\) Despite its low cost and great popularity, the broken-symmetry approach is an indirect method of obtaining the open-shell singlet, whose SCF calculation only targets on the spin-contaminated BS state; moreover, the spin projected DFT is also reported to lead to degraded potential energy surfaces.\(^19\)

In the past few years, some new methods were developed and showed their strength in describing diradical systems. One of them is the fractional-spin method\(^20\) or the variational fractional-spin method.\(^21\) They are able to directly obtain the open-shell singlet state without spin contamination using a fractionally occupied state. This category of methods is the fractional-spin version of delta-SCF approach,\(^13,22\) and it can obtain good singlet–triplet (ST) gaps \((E_S − E_T)\) for many types of diradicals,\(^20,21\) however, because of the limitations of current density functional approximations (DFAs), the (variational) fractional-spin method suffers from DFA’s intrinsic static correlation error\(^23,24\) and therefore cannot well describe diradicals with disjoint features.\(^21\) Another category of new methods uses the concept of spin flip.\(^25,26\) These methods include spin-flip equation-of-motion coupled cluster theory (SF-EOM-CC),\(^27–29\) spin-flip configuration interaction (SF-CI),\(^30,31\) restricted active space spin-flip configuration interaction (RAS-SF-CI)\(^32,33\) and spin-flip time-dependent density

![Figure 1. Two-orbital diradical model. Of the six possible configurations, there are two singlets, two triplets, and two broken-symmetry configurations. The broken-symmetry configurations can linearly combine and form a singlet and a triplet. The true singlet wave functions can be obtained through configuration interaction of the singlet configurations.](Image)
functional theory (SF-TDDFT) with either collinear\textsuperscript{34} or noncollinear kernel.\textsuperscript{35–37} These spin-flip methods start with an open-shell high-spin triplet and obtain singlet states through spin-flip excitation operators. With an unrestricted initial reference, these spin-flip methods can obtain improved results over the BS approach for diradicals\textsuperscript{31,32,34,38–41} with a tolerably small amount of spin contamination. Among these methods, SF-CIS and SF-TDDFT are able to achieve low $O(r^4)$ scaling, which makes them applicable to large systems. The introduction of noncollinear kernel\textsuperscript{35–37} improved the original collinear SF-TDDFT, although at the cost of being more functional sensitive.\textsuperscript{42} With a restricted open-shell calculation and by applying spin-adapted operators and the tensor reference, one can formulate spin-pure and spin-complete SF-TDDFT.\textsuperscript{43–45}

Recently, we employed the pairing matrix fluctuation\textsuperscript{46} or the time-dependent density functional theory with pairing field (TDDFT-P)\textsuperscript{47} to solve excitation problems. Results show that time-dependent density functional theory with pairing can describe diradicals well with a low cost. The diabatic excitation problem and the employment of single-determinant references makes it computationally more practical to large systems. Through direct diagonalization, the whole excitation spectrum can be obtained with an $O(r^6)$ scaling, where $r$ is the number of occupied orbitals, or the number of virtual ones, depending on which number is larger. However, an iterative Davidson method with a lower $O(r^4)$ scaling can be implemented to capture the lowest few excitations.\textsuperscript{48}

In a diradical system, when we remove the two nonbonding electrons, the remaining ($N-2$)-electron system is usually a well-behaved closed-shell singlet species without dramatic static correlation. Therefore, the ($N-2$)-electron reference can be well described by some well-known density functionals, such as B3LYP\textsuperscript{57,58} or PBE.\textsuperscript{59} In contrast, the two nonbonding electrons, which dominate the chemical behavior of a diradical, show strong static correlation and need more accurate multireference descriptions, such as CASSCF, CASPT2, or MR-CI. Through a seamless combination of DFT for the ($N-2$)-electron reference and a subspace CI for the two nonbonding electrons (Figure 2), the pp-RPA is expected to describe diradicals well with a low cost.

In this paper, we adopt the convention that $a,b,c,d$ are for unoccupied molecular orbitals, $i,j,k,l$ for occupied orbitals, and $pq,rs$ for general orbitals. The eigenvalues $\omega$'s can represent two-electron addition energies if the normalization sign of the corresponding eigenvector is positive or two-electron removal energies if the normalization sign is negative.

Starting from an $(N-2)$-electron (two-electron deficient) reference, through the two-electron addition process, the system can reach a series of its $N$-electron states (neutral states), including both the ground state and excited states. The eigenvalues in eq 5 represent the transition energy from the $(N-2)$-reference to the final neutral states. Then if we subtract two transition energies, the difference will be the energy gap between the two involved neutral states. Specifically, if one neutral state is the ground state $|0,N\rangle$, and the other is an excited state $|n,N\rangle$, then the energy difference is the excitation energy,

$$E_n^N - E_0^N = (E_n^N - E_{\text{ref}}^{N-2}) - (E_0^N - E_{\text{ref}}^{N-2}) = \omega_n - \omega_0$$

It is worth noting that in wave function theory, the double electron-attachment equation-of-motion coupled cluster theory (DEA-EOM-CC)\textsuperscript{55,56} has also been applied to excitation problems with the same philosophy. The difference is that pp-RPA can use DFT to describe the $(N-2)$-electron system, and the employment of single-determinant references makes it computationally more practical to large systems. Through direct diagonalization, the whole excitation spectrum can be obtained with an $O(r^6)$ scaling, where $r$ is the number of occupied orbitals, or the number of virtual ones, depending on which number is larger. However, an iterative Davidson method with a lower $O(r^4)$ scaling can be implemented to capture the lowest few excitations.\textsuperscript{48}

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Our spin-adapted pp-RPA\textsuperscript{60} is implemented in the local QM4D package.\textsuperscript{61} A Davidson algorithm is used to calculate the lowest few excitations.\textsuperscript{46} We report our results on four

![Figure 2. Pp-RPA combines DFT with wave function methods. The (N-2)-electron system is described by single reference DFT. The two electrons added in can form any two-electron configuration within the virtual space, resembling a subspace configuration interaction singles and doubles (CISD).](https://example.com/figure2.png)
Table 1. Adiabatic Singlet-Triplet Gaps (in kcal/mol) for Diatomic Diradicals 

<table>
<thead>
<tr>
<th></th>
<th>exp¹b</th>
<th>pp-HF</th>
<th>pp-B3LYP</th>
<th>pp-PBE</th>
<th>(V)FS-PBE</th>
<th>SF-CIS²d</th>
<th>SF-CIS(D)²d</th>
<th>SF-LDA²d</th>
<th>SF-PBE²d</th>
<th>SF-B3LYP⁴d</th>
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<tbody>
<tr>
<td>CH₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH</td>
<td>35.9</td>
<td>30.9</td>
<td>38.5</td>
<td>40.5</td>
<td>41.1</td>
<td>40.7</td>
<td>37.1</td>
<td>35.6</td>
<td></td>
<td></td>
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<tr>
<td>OH¹</td>
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<td>45.5</td>
<td>52.3</td>
<td>54.2</td>
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<td>53.6</td>
<td>50.2</td>
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<tr>
<td>NF</td>
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<td>28.6</td>
<td>28.7</td>
<td>28.3</td>
<td>34.0</td>
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<td>30.3</td>
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<td></td>
</tr>
<tr>
<td>O₂</td>
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<td>23.1</td>
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<td>23.5</td>
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<td></td>
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<td>MAE</td>
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<td>2.8</td>
<td>3.8</td>
<td>3.4</td>
<td>6.3</td>
<td>1.1</td>
<td>1.8</td>
<td></td>
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The geometries for pp-RPA calculations are adopted from ref 20. Aug-cc-pVDZ basis set is used for all pp-RPA calculations. The adiabatic gap correction is based on eq 10a. Experimental values from ref 74. (Variational) fractional-spin results from ref 21 with 6-311+G(2d,2p) basis set. Spin-flip CI results from ref 38 with cc-pVQZ basis set. *Spin-flip TDDFT with noncollinear kernel results from ref 36 with TZ2P basis set.

Table 2. Adiabatic Singlet–Triplet Gaps (in kcal/mol) for Carbene-like Diradicals

<table>
<thead>
<tr>
<th></th>
<th>ref ¹b</th>
<th>ref ²c</th>
<th>pp-HF</th>
<th>pp-B3LYP</th>
<th>pp-PBE</th>
<th>(V)FS-PBE</th>
<th>SF-CIS²d</th>
<th>SF-CIS(D)²d</th>
<th>SF-LDA²d</th>
<th>SF-PBE²d</th>
<th>SF-B3LYP⁴d</th>
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<tbody>
<tr>
<td>CH₂</td>
<td>1Å</td>
<td>9.0</td>
<td>9.7</td>
<td>−2.4</td>
<td>3.7</td>
<td>5.9</td>
<td>15.7</td>
<td>20.4</td>
<td>14.1</td>
<td>11.8</td>
<td>12.3</td>
</tr>
<tr>
<td>NH₂+</td>
<td>1Å</td>
<td>31.7</td>
<td>32.5</td>
<td>26.3</td>
<td>32.0</td>
<td>33.3</td>
<td>36.2</td>
<td>43.2</td>
<td>38.0</td>
<td>30.7</td>
<td>32.3</td>
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<tr>
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<td>1Å</td>
<td>29.0</td>
<td>29.8</td>
<td>12.8</td>
<td>23.1</td>
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<td>1Å</td>
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<td>72.5</td>
<td>e</td>
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<td>83.8</td>
<td>81.2</td>
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<td>−24.9</td>
<td>−28.7</td>
<td>−28.3</td>
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<td>MAE¹b</td>
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<td>10.8</td>
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</table>

The geometries for pp-RPA calculations are adopted from ref 38. Aug-cc-pVDZ basis set is used for all pp-RPA calculations. The adiabatic gap correction is based on eq 10a. Experimental values from CH₂ from ref 70. MR-CI values for NH₂ from ref 71. Experimental values for SiH₂ from refs 72 and 73. Experimental values for PH₂ from ref 74. *EOM-SF-CCSD(dT)/aug-cc-pVQZ results from ref 42. (Variational) fractional-spin results from ref 21 with 6-311+G(2d,2p) basis set. *Spin-flip CI results from ref 38 with TZ2P basis set. *Spin-flip TDDFT with noncollinear kernel results from ref 42 with cc-pVTZ basis set. *Due to limited data in ref 1, 2Å data are not counted in when MAE is calculated. *All excitation values are taken into account when comparing with data from ref 2. Error for (V)FS-PBE is not calculated because of the lack of 2Å data.

diatomic diradicals (NH, OH⁺, NF, O₂), four carbene-like diradicals (CH₂, NH⁺, SiH₂⁺, PH₂⁺), three disjoint diradicals (CH₂,CH₂CH₂, CH₂CH₂CH₂, CH₂CH₂CH₂, CH₂CH₂CH₂CH₂, CH₂CH₂CH₂CH₂), two-four electron diradicals (cyclobutadiene (C₄H₂) and TMM (C₃H₄)), and three benzenes (α-, m-, β-). The optimized geometries are adopted from their original references and summarized in the Supporting Information. 62 ST gaps for these diradicals are calculated through pp-RPA with HF, B3LYP, and PBE functionals, which include different percentages of HF exchange. The aug-cc-pVDZ basis set, which has been shown in our previous paper 48 to give converged excitation energies, is adopted in all pp-RPA calculations. Vertical ST gaps Eg are directly calculated with eq 9, while adiabatic gaps Eg are calculated from Eg, plus a correction on the potential energy curves obtained from SCF calculations for the N-electron system. Two flavors of correction can be employed, either on the triplet energy curve 10a or on the singlet energy curve 10b, depending on which N-electron spin state can be better described by the functional used.

\[
E_g = E_{S,Sgeo} - E_{T,Tgeo} = E_{g,Sgeo} + (E_{T,Sgeo} - E_{T,Tgeo}) \\
\text{(10a)}
\]

\[
E_g = E_{S,Sgeo} - E_{T,Tgeo} = E_{g,Sgeo} + (E_{S,Sgeo} - E_{S,Tgeo}) \\
\text{(10b)}
\]

In most cases, the N-electron triplet state is better described by single reference methods. Therefore, the correction based on eq 10a is adopted unless specifically specified.

### RESULTS AND DISCUSSIONS

#### Diatomic Diradicals

The test set of diatomic diradicals are adopted from a previous fractional-spin study. 20 This set of diradicals was also well investigated and benchmarked earlier by spin-flip methods. 36,38 There are four diradicals in this set: NH, OH⁺, NF, and O₂, which are two pairs of isoelectronic species. Although their geometries are simple and characterized by a single bond length, their electronic structures are nontrivial. For these diradicals, the configuration Φ₁ and Φ₂ in eq 2a and 3a span a degenerate irreducible representation, generating a 2-fold degenerate singlet Δ state. The triplet Σ state is below the 1Δ state, while the singlet Σ state is above it. The calculated singlet–triplet (1Δ−Σ) gaps are summarized in Table 1. Overall, there is a good agreement between pp-RPA calculations and experimental results. With the aug-cc-pVDZ basis set, the pp-RPA with HF reference (pp-RPA-HF), or pp-HF for short), which has no dynamic correlations for the (N = 2)-reference, also performs well for these small molecules with a small underestimation of the ST gaps. The pp-RPA with DFT references performs better and the mean absolute error for pp-RPA-B3LYP is as small as 2.8 kcal/mol. These pp-RPA results are better than SF-CIS (MAE 6.3 kcal/mol) and comparable.
with (V)FS-PBE (MAE 3.4 kcal/mol). However, SF-CIS(D)/cc-pVDZ and SF-TDLDA/TZ2P with noncollinear kernel (NC-SF-TDLDA) have mean absolute error even below 2 kcal/mol, which shows their good performances in these very small diradicals.

**Carbene-like Diradicals.** Carbene and carbene-like diradicals are important species that are widely used in organic chemistry.\(^1\) Here we choose a well-studied set\(^{20,21,38,42}\) for testing purposes. This set includes CH\(_2\), NH\(_2\), SiH\(_2\), and PH\(_2\), which are also two pairs of isoelectronic molecules. Unlike the previous diatomic diradicals, carbene-like diradicals have nondegenerate frontier orbitals—one \(\sigma\) orbital and one \(\pi\) orbital—with different symmetry, which means the open-shell singlet (\(\sigma^+ \pi^+\)) and closed-shell singlet (\(\sigma^\pi\)) cannot further mix through configuration interaction. Take methylene as an example. The lowest state is triplet \(^3B_1\) with one electron occupying \(\sigma\) and another one occupying \(\pi\). Then the closed-shell singlet \(^1A_1\) comes next with mostly the \(\sigma\) orbital doubly occupied and a small contribution from \(\pi\) orbital doubly occupied. The open-shell singlet \(^1B_1\) with singly occupied \(\sigma\) and \(\pi\) is the third state and finally there is another closed-shell \(^1A_1\), which is mostly the \(\pi\) orbital doubly occupied. Despite the relatively simple orbital picture, the energy alignment might change greatly depending on the center atom and the surrounding environments. For example, in PH\(_2\) and SiH\(_2\), the order of \(^1B_1\) and the first \(^1A_1\) is switched compared to CH\(_2\) and NH\(_2\), resulting in a negative ST gap; Chen et al.\(^5\) also have theoretically attempted to lower the energy of the \(\pi\)-doubly occupied \(^1A_1\) state to make it the ground state by a proper choice of ligand groups.

The pp-RPA results for these carbene-like diradicals are summarized in Table 2. For methylene, the first adiabatic ST gap historically\(^{64,65}\) had been a puzzle, in which the value was finally agreed by experiments and calculations to be as small as only 9 kcal/mol.\(^{65,67}\) The pp-RPA with B3LYP and PBE references reasonably predicts the adiabatic gap to be 3.7 and 5.9 kcal/mol, respectively. For the HF reference, the gap is predicted to be negative (−2.4 kcal/mol), which shows that here the HF reference is not as good as DFT references. The (variational) fractional-spin method overestimates the gap (15.7 kcal/mol) and so do SF-CI (20.4 kcal/mol) and SF-CIS(D) (14.1 kcal/mol). The SF-TDDFT with noncollinear kernels greatly depends on functionals, with the hybrid B3LYP functional greatly underestimating the gap, while the local LDA and PBE functional well predict the gap. For the next gap between \(^3B_1\) and \(^1B_1\) states, the result of pp-RPA with DFT references (32.0 kcal/mol for B3LYP and 33.5 kcal/mol for PBE), together with SF-TDLDA (30.7 kcal/mol) and SF-TDPBE (32.3 kcal/mol), is even closer to the reference value (31.7 kcal/mol) than that of SF-CIS(D) (38.0 kcal/mol). SF-CIS and SF-B3LYP still have large systematic errors. The gap between \(^3B_1\) and the second \(^1A_1\) is similar, with pp-RPA and SF-TDLDA performing the best.

It is also worth noting that many existing works\(^{67–69}\) show that at the optimized singlet geometry for methylene, the singlet energy is very close to or even lower than the triplet energy. Therefore, a very small or negative vertical gap is expected. With pp-RPA, we also observed this phenomenon, with −7.3 and −4.5 kcal/mol vertical ST gap obtained by B3LYP and PBE references, respectively (see Supporting Information\(^{62}\) for detailed data).

For other carbene-like molecules, the results are similar to methylene. Interestingly, the pp-RPA results with B3LYP reference—more HF exchange than PBE and less HF exchange than HF—mostly lie between the results with PBE and those with HF references. This phenomenon implies that the amount of HF exchange and its related virtual orbital energy alignments may play an important role in achieving good accuracy. Overall, for this test set, pp-RPA with DFT references—with no or a small amount of HF exchange—perform well with 4.3 kcal/mol MAE for the B3LYP reference and 3.5 or 3.7 kcal/mol for the PBE reference. Although they are still not as good as SF-TDLDA (2.4 or 3.2 kcal/mol) and SF-TDPBE (1.9 or 2.7 kcal/mol), they are much better than SF-CIS (10.7 or 15.5 kcal/mol) and SF-TDB3LYP (9.7 or 10.8 kcal/mol), and similar to or slightly better than (V)FS-PBE (4.2 kcal/mol) and SF-CIS(D) (4.2 or 6.2 kcal/mol).

**Disjoint Diradicals.** Disjoint diradicals are problematic for the (variational) fractional-spin method because of the static correlation error intrinsic to commonly used DFTs.\(^{21,23}\) For \(\text{CH}_2\text{CH}_2\text{CH}_2\), the reference vertical ST gap is 1.8 kcal/mol. Fractional-spin LDA (12.8 kcal/mol) and fractional-spin PBE (20.4 kcal/mol) greatly overestimate the gaps.\(^{21}\) In contrast, pp-RPA with DFT references give a reasonably small gap, with 4.4 and 5.4 kcal/mol for B3LYP and PBE, respectively (Table 3). The pp-RPA-HF also reasonably predicts a vertical gap of 2.4 kcal/mol. The advantage of pp-RPA is even more clear for two longer disjoint diradicals, that is, \(\text{CH}_2(\text{CH}_2)_2\text{CH}_2\) and \(\text{CH}_2(\text{CH}_2)_2\text{C}(\text{CH}_3)\text{H}\). The pp-RPA with DFT references cannot only well describe the lowest singlet−triplet gap, but also well predict the higher excitations with charge transfer character.

These disjoint diradicals can be viewed as two electrons connected by a \((\text{CH}_2)_n\) bridge. If we ignore the bridge, the systems resemble the stretched \(\text{H}_2\) molecule. It is well-known that the stretched \(\text{H}_2\) has strong static correlation, and most
single reference methods will fail to describe the stretching process.24 Meanwhile, it is also a challenge for DFAs to describe the charge transfer excitation in stretched H$_2$ because of common DFAs' large delocalization error. Similarly, with an additional (CH$_2$)$_3$ bridge, these long disjoint diradicals become even more challenging. Fortunately, the subspace CISD treatment frees pp-RPA from static correlation and enables it to well describe the lowest $^1$A$_2$ and $^1$A$_1$ states. The full coulomb kernel enables pp-RPA to correctly capture the asymptotic behavior of charge-transfer excitations.22 For spin-flip TDDFT, the employment of high spin references and spin-flip excitation operators also frees it from static correlation error, thus the $^1$A$_1$/$^3$A$_1$ gap is well described by all functionals. However, when it comes to excitations, the erroneous DFA kernels in SF-TDDFT account for the greatly underestimated charge transfer excitations. Only when the long-range corrected functional (for example, ωPBEh) is employed can the problem be relieved.

### Four-Electron Diradicals

Diradicals with four π electrons also have a long history. They were discussed in detail in Borden and Davidson's work.75 The non-Kekule molecule trimethylenemethane (TMM) is one of the examples.76−82 In a single reference picture, TMM has four electrons occupying four π atomic orbitals. If there is D$_{3h}$ geometry, these four π orbitals form one molecular orbital lying at the bottom, one at the top and two degenerate ones in the middle. Therefore, two electrons form a pair and occupy the lowest molecular orbital and two remaining electrons occupy the two degenerate orbitals, forming a diradical. A further mix of open-shell and closed-shell singlet determinants is allowed with D$_{3h}$ geometry because of the proper symmetry of the degenerate orbitals. Therefore, the picture is much like the diatomic cases. According to Hund's rule, which is obeyed in this case, the triplets show lower energy than the singlets. When the D$_{3h}$ symmetry is not preserved, the state degeneracy is broken. One state finds its global minimum at a twisted nonplanar geometry, and this state is assigned the symbol $^1$B$_1$. The other state has a local minimum with the restricted planar geometry, and it is assigned as the $^1$A$_1$ state.77 The calculated adiabatic ST gaps for TMM are summarized in Table 4. It can be seen that the lowest adiabatic ST gap ($^1$B$_1$−$^3$A$_1$) is well predicted by pp-RPA with errors even less than 1 kcal/mol. However, for the second ST gap ($^1$A$_1$−$^3$A$_2$), the pp-RPA greatly overestimates the result. One cause is very likely to be related to the two bonding electrons treated with DFT. Even though in a single-reference picture these two electrons form a pair and occupy a $b_1$ orbital that seems to play a less important role in determining the chemical properties of the diradical, this $b_1$ orbital is very sensitive to the chemical environment at the optimized $^1$A$_1$ geometry. With a restricted B3LYP SCF calculation for the singlet neutral system, in which the four electrons line up as $1b_1^2$ $1a_2^2$, the $b_1$ orbital mostly localizes as a π bond between the central atom and the closest carbon atom (Figure 3a). However, a calculation for the (N − 2)-electron reference shows it to be much more diffuse onto the other two farther carbon atoms (Figure 3b). An unrestricted triplet calculation for the neutral system gives pictures between these two cases (Figure 3 orbitals c and d). Overall, from the most localized one to the most diffuse one, the order is neutral singlet orbital, neutral triplet beta orbital, neutral triplet alpha orbital, and finally the (N−2)-electron singlet orbital. The frozen $b_1$ orbital for the (N−2)-electron reference might be too diffuse compared to the real picture, making the (N−2)-electron core not well described. This inaccurate description of the core leads to the large error. Interestingly, in contrast, this $b_1$ orbital is not quite sensitive to the chemical environment at the optimized $^1$B$_1$ geometry (Figure 3 orbitals e−h). Therefore, the frozen core should be close to the real picture and the vertical gap ($^1$B$_1$−$^3$A$_1$) at the optimized $^1$B$_1$ is well described, finally making the adiabatic gap also well predicted by pp-RPA.

Spin-flip TDDFT with LDA, PBE, and B3LYP functionals can also well predict the lowest $^1$B$_1$−$^3$A$_1$ gap. However, they greatly underestimate the two higher $^1$A$_1$−$^3$A$_2$ gaps. Unlike pp-RPA, SF-TDDFT can correlate the lower non-HOMO excitation configurations, and therefore the error for SF-TDDFT mostly lies in the functional that is employed. When the long-range corrected functional ωPBEh with a larger portion of Hartree–Fock exchange is employed, the error gets smaller.

Another typical four-π-electron system is cyclobuta
diene.27,29,83−85 It has similar single-reference orbital picture...
The pp-RPA describes diradical systems by starting from an SCF \((N-2)\)-electron reference, and then adding two electrons with explicit correlation. The relatively simpler \((N-2)\) system can be well described by a single-determinant DFT reference, while the two electrons are described in a subspace CI fashion. The combination of DFT with correlated wave function methods, as well as the treatment of all neutral states on the same footing, enables pp-RPA to describe diradicals both accurately and efficiently. The bare coulomb kernel of pp-RPA ensures a correct description of charge separated and charge transferred state. In this work, we showed the pp-RPA results with HF, B3LYP, and PBE functionals for a variety of categories of diradicals, including diatomic diradicals, carbene-like diradicals, disjoint diradicals, four-\(\pi\)-electron diradicals and larger benzene diradicals. The difference between different functional references shows that the amount of HF exchange affects the final results by affecting the virtual orbital energies. As to the results, except for some states for the four-\(\pi\)-electron diradicals with important correlation contributions from more than the two nonbonding electrons, the pp-RPA with DFT references generally gives rise to good results, which shows that pp-RPA is much more accurate than SF-CIS. It is comparable or better than (variational) the fractional-spin method. In some small diradical systems, such as diatomic diradicals and carbene-like diradicals, the error for pp-RPA is slightly larger than that of SF-TDDFT with LDA and PBE functionals. However, when it comes to more difficult disjoint diradicals and benzyne, the pp-RPA with DFT reference performs much better, and it becomes comparable to SF-CIS(D) and SF-TDDFT.

Moreover, the pp-RPA is an inexpensive \(O(n^4)\) scaling that is newly applied to molecular systems. Although further exploration of functionals and kernels may further improve the results and a better converging method may relieve some SCF convergence problems for the \((N-2)\) system, the pp-RPA is already now a reliable theoretical method for describing diradical systems and could be promising in solving much larger and more challenging diradical-related problems.

### CONCLUSION

The pp-RPA describes diradical systems by starting from an SCF \((N-2)\)-electron reference, and then adding two electrons with explicit correlation. The relatively simpler \((N-2)\) system can be well described by a single-determinant DFT reference, while the two electrons are described in a subspace CI fashion. The combination of DFT with correlated wave function methods, as well as the treatment of all neutral states on the same footing, enables pp-RPA to describe diradicals both accurately and efficiently. The bare coulomb kernel of pp-RPA ensures a correct description of charge separated and charge transferred state. In this work, we showed the pp-RPA results with HF, B3LYP, and PBE functionals for a variety of categories of diradicals, including diatomic diradicals, carbene-like diradicals, disjoint diradicals, four-\(\pi\)-electron diradicals and larger benzene diradicals. The difference between different functional references shows that the amount of HF exchange affects the final results by affecting the virtual orbital energies. As to the results, except for some states for the four-\(\pi\)-electron diradicals with important correlation contributions from more than the two nonbonding electrons, the pp-RPA with DFT references generally gives rise to good results, which shows that pp-RPA is much more accurate than SF-CIS. It is comparable or better than (variational) the fractional-spin method. In some small diradical systems, such as diatomic diradicals and carbene-like diradicals, the error for pp-RPA is slightly larger than that of SF-TDDFT with LDA and PBE functionals. However, when it comes to more difficult disjoint diradicals and benzyne, the pp-RPA with DFT reference performs much better, and it becomes comparable to SF-CIS(D) and SF-TDDFT.

Moreover, the pp-RPA is an inexpensive \(O(n^4)\) scaling that is newly applied to molecular systems. Although further exploration of functionals and kernels may further improve the results and a better converging method may relieve some SCF convergence problems for the \((N-2)\) system, the pp-RPA is already now a reliable theoretical method for describing diradical systems and could be promising in solving much larger and more challenging diradical-related problems.

### ASSOCIATED CONTENT

#### Supporting Information

Geometries, detailed calculation procedure, and detailed data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jp512727a.

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**Notes**

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