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Single Reference Coupled Cluster Theory for Multi-Reference Problems

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Abstract: Coupled-cluster (CC) theory is widely accepted as the most accurate and generally applicable approach in quantum chemistry. CC calculations are usually performed with single Slater-determinant references, e.g. canonical Hartree-Fock (HF) wavefunctions, though any single determinant can be used. This is an attractive feature because typical CC calculations are straightforward to apply, as there is no potentially ambiguous user input required. On the other hand, there can be concern that CC approximations give unreliable results when the reference determinant provides a poor description of the system of interest, i.e. when the HF or any other single determinant ground state has a relatively low weight in the full CI expansion. However, in many cases the reported "failures" of CC can be attributed to an unfortunate choice of reference determinant, rather than intrinsic shortcomings of CC itself. This is connected to well-known effects like spin-contamination, wavefunction instability and symmetry-breaking. In this contribution, a particularly difficult singlet/triplet splitting problem in two phenyldinitrene molecules is investigated, where single-reference CCSD(T) calculations were reported to give poor results. This is analyzed by using different reference determinants for CCSD(T), as well as performing higher level CCSDT-3 and CCSDT calculations. We show that doubly-ionized and electron attached equation-of-motion (DEA/DIP-EOM) approaches are a powerful alternative for treating such systems. These are operationally single-determinant methods that adequately take the multi-reference nature of these molecules into account. Our results indicate that CC remains a powerful tool for describing systems with both static and dynamic correlation, when pitfalls associated with the choice of the reference determinant are avoided.

I. Introduction

Coupled cluster (CC) theory is arguably the most accurate, general purpose method in quantum chemistry.[1–3] Thanks to significant advances in software and hardware, CC can now routinely be applied to small and mid-sized molecules, with linear-scaling techniques and massively parallel implementations promising even broader applicability.[4–8] CCSD's perturbative extension, CCSD(T), is the most commonly used CC approach, since it represents the best compromise between high accuracy and still manageable computational cost (non-iterative $O(n^7)$).[9–12] In addition to its high accuracy, a significant advantage of CCSD(T) is that it is essentially a black-box method, requiring little additional input from the user, apart from the initial geometry and basis set. This is because CC is generally used as a single-reference (SR) method, and simply requires some single-determinant (SD) reference wavefunction, e.g. a Kohn-Sham, B(rueckner), RHF, ROHF, UHF, QRHF, etc. determinant.

In some cases the reference determinant will be a poor approximation to the real system, particularly when occupied and virtual orbitals are nearly degenerate. Such systems are said to display static or non-dynamic correlation, meaning that the reference determinant has a relatively low weight in the full CI expansion of the wavefunction (or from a CC point of view, that the wavefunction displays at least one large T-amplitude). The conceptually straightforward solution to this problem is to use a linear combination of the most important configurations instead. This is done in multi-reference (MR) techniques like multiconfigurational/complete-active-space SCF,[13,14] MR-CI,[15] or MR-CC[16]. Systems with static correlation are therefore often described as having "multi-reference character".

SR CCSD(T) can display large errors for some multi-reference systems. Some failures (like in bond-breaking with improperly dissociating RHF references) are due to the perturbative nature of the (T) approximation and can be overcome to a degree by infinite-order approximations like CCSDT-3.[17] But there can be other difficulties. To overcome these issues, a more complete CC method like CCSDT or CCSDTQ can be applied, but this is often prohibitively expensive.[18,19] Alternatively, there are a number of genuine multi-reference approaches to CC theory,[16] but despite intensive research activity there is currently no "standard" MR-CC implementation available.[20–31] An additional problem is that MR-CC methods (and MR methods in general) tend to be computationally expensive and often require significant user input, especially in determining the active space. They are not generally black-box applications.

Fortunately, one can also turn to the family of equation-of-motion (EOM-) CC approaches.[32] These methods occupy the middle ground between "genuine" MR and SR-CC, in that they allow a balanced description of complicated electronic situations at a manageable computational cost and with a black-box character like SR-CC (i.e. they are "operationally single reference").[33–35] For singlet/triplet (S/T) gaps, this pertains especially to doubly-electron attached or doubly-ionized equation-of-motion (DEA/DIP-EOM) methods.[35–37] Here, a CC reference state with a different number of electrons (n±2) than the n-electron target state is used to define the similarity-transformed Hamiltonian $\overline{H}$. The EOM diagonalization of $\overline{H}$ then properly weights the four determinants in the (2×2) active space. Importantly, if a closed-shell reference is used, the DIP/DEA solutions are proper spin-eigenfunctions, which is a significant advantage relative to symmetry-breaking approaches.

In this contribution, we study the S/T gaps of two related phenyldinitrene biradicals (see Fig. 1), for which SR methods are reported to perform poorly.[38] The difficulty with describing this type of problem lies in the MR nature of their singlet biradical groundstate. The RHF singlet wavefunction is significantly too high in energy, and accordingly the S/T gap is far too large at this level. DePrince et al. showed that different CASSCF based methods can appropriately describe the situation, yielding S/T gaps in agreement with experiment and correctly finding the singlet to be the ground state.[38] They also claimed uncommonly large and unsystematic errors for CCSD and CCSD(T).

Since the RHF wavefunction is a poor approximation for open-shell biradicals, SR methods may not be expected to be suitable for this sort of problem. Fortunately, CC is relatively insensitive to the type of reference function used and can often compensate deficiencies of the reference determinant. Therefore, the high errors reported for CCSD(T) in ref. [38] (S/T gaps of -84.7 and -40.3 kcal mol^{-1} for **1** and **2**, respectively) are unexpected, likely indicating that the underlying SCF calculations for the singlet converged to an excited state solution (e.g., the reported CCSD total energy for **1** is ~ 200 kcal/mol higher than the one reported in this work).

The goal of this manuscript is twofold. First, the performance of SR-CC for these MR systems is thoroughly investigated. We find that dramatic failures of SR-CC can be attributed to problems with the reference determinant, rather than with the actual CC calculation. Second, we show that CCSDT-3 (an iterative ~$O(n^7)$ method) corrects its fourth-order approximation, CCSD(T), and is in quantitative agreement with experiment. The ΛCCSD(T)[39,40] generalization of CCSD(T) also provides good results at the same non-iterative ~$O(n^7)$ cost. Third, we see that CCSDT-3 and full CCSDT have the unusual property of giving a second determinant the same amplitude (~1.0) as the reference determinant in intermediate normalization. Though this is indicative of an extreme MR or two-determinant character, the fact the problem can still be described by SR-CC is impressive. Fourth, DEA/DIP methods are highly accurate and efficient tools for describing these systems.

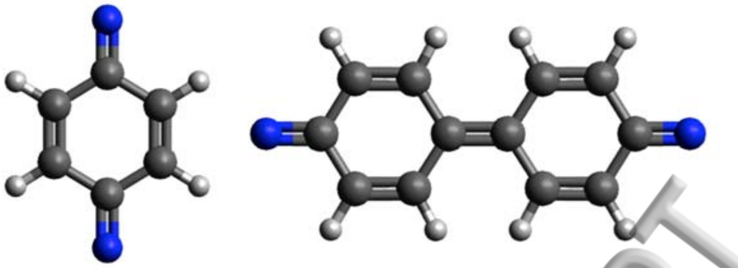

*Fig. 1: Geometries of the 1,4-phenylenedinitrene (**1**) and biphenyl-4,4'-dinitrene (**2**) biradicals investigated in this study.*

II. Computational Details

Calculations are performed with ACESII, ACES3, and CFOUR.[41–43] All reported calculations use the cc-pVDZ basis set, which was also used in ref. [38]. Test calculations with the larger cc-pVTZ basis show that the S/T gaps in these systems are relatively insensitive to basis set effects (see Supporting Information, Tables S1 and S2), as their magnitude is comparable for the singlet and triplet states of the same molecule. This is particularly true for the DEA/DIP-EOM calculations, whereas the S/T gaps for the SR methods are somewhat improved at the cc-pVTZ level.

S/T gaps are calculated as E_T-E_S, with positive values indicating that the singlet is more stable than the triplet. The CASSCF/cc-pVDZ geometries reported in the literature are used, to allow direct comparison with the S/T values reported therein.[38] SR CCSD(T) calculations are performed with RHF, UHF, ROHF, and Bruckner determinants. For the singlet states we also used spatially broken-symmetry UHF determinants. Additionally, the S/T gaps are determined with ΛCCSD(T), CCSDT-3, CCSDT, DEA-EOM-CCSD, DIP-EOM-CCSD, the similarity transformed DEA/DIP-STEOM-CCSD and DEA-EOM-CIS. The latter limits the EOM space to only singles.

The experimental S/T gaps of **1** and **2** are found to be below 1 kcal mol^{-1} in EPR[44,45] and magneto-optical[46] measurements, with the singlet being slightly more stable. The EPR experiments were performed by photolysis of diazide precursors in frozen 2-methyltetrahydrofuran solutions, while in the magneto-optical experiments an inert polymethylmethacrylate matrix was used. All simulations reported below (as well as the CASSCF simulations in the literature) yield vertical S/T gaps in the gas phase, so perfect agreement with the experimental values should, perhaps, not be expected. Consequently, we will not dissect the results to the last decimal point, but consider all gaps within ±2 kcal mol^{-1} as essentially in agreement with experiment.

III. Results and Discussions

*a) 1,4-phenylenedinitrene (**1**):*

Using a UHF reference for the triplet, we find an S/T gap of 16.5 kcal mol^{-1} for **1** with CCSD(T) (see Table 1). This is significantly in error relative to the experimental values, although it does correctly predict the singlet to be more stable. What is the origin of this error?

A possible issue with UHF calculations is spin-contamination. Indeed, the average multiplicity of the UHF triplet determinant is somewhat in error (3.2), while the singlet calculation converges to the RHF solution with the correct multiplicity. However, the projected multiplicity of the CCSD wavefunction is much improved (3.03), indicating that this is not a significant issue. To verify this, uncontaminated triplet reference determinants can be obtained within the restricted open-shell (ROHF) formalism, whose projected value has to be exact (although the expectation value of the CC solution itself will still be contaminated). This only leads to slightly improved results. Spin-contamination is evidently not crucial for this system. Similarly, the use of a Brueckner reference determinant (which often improves the performance of CC for difficult systems) does not lead to any benefit in this case.

The main problem lies with the description of the singlet state, not with the triplet. The lowest unoccupied molecular orbital (LUMO) in the RHF singlet determinant of **1** is very low in energy, with an eigenvalue of -3.0 eV (compared to -6.2 eV for the HOMO). As a consequence, the MBPT(2) and CCSD wavefunctions display enormous T2 amplitudes (0.88 and 0.66, respectively) corresponding to a double excitation into this orbital. This determinant, B, is quasi-degenerate to the reference determinant, A, and at the CCSD(T) level switching reference determinants shows only a ΔE=2.5 kcal mol^{-1} difference in total energies (see Supporting Information, Table S3). The electronic situation for the quasi-degenerate determinants A and B is illustrated in Fig. 2, together with the correlated IP/EA-EOM-CCSD ionization energies and electron affinities.

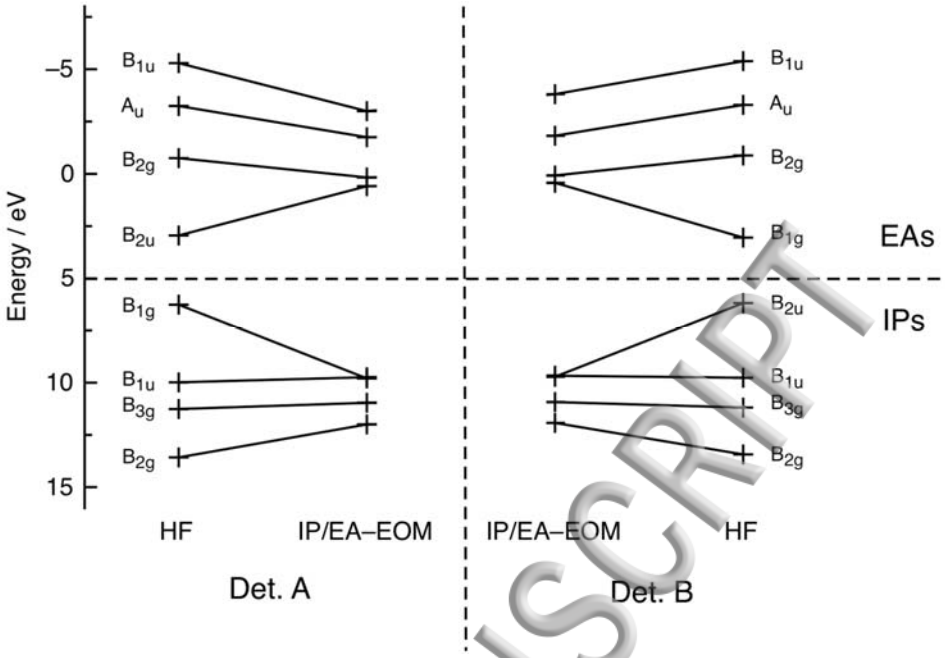

Fig. 2: HF molecular orbital energies and EOM-CCSD ionization potentials and electron affinities for the competing ground-state determinants of **1**.

As can be seen, the Koopmans' theorem energies are not even qualitatively correct, confirming the inadequacy of the HF description for these states (though one must be aware that the failure of the SR-CCSD can also affect the quality of the IP/EA-EOM-CC results). A purely perturbative correction to HF, as in MBPT(2), consequently provides very poor S/T gaps. As mentioned, using either A or B as the reference determinant does not significantly change the CC results (see the Supporting Information). In the following we will therefore focus on results obtained with reference determinant B, which is slightly more stable at the CCSD(T) level. The observation that the answers are very similar is another manifestation of the fact that CCSD (and beyond) is fairly insensitive to the particular reference determinant or its orbitals, as long as they correspond to the correct state.

A byproduct of this complicated electronic structure is that SCF calculations can easily converge to different excited determinants, which explains the erroneous results reported in ref. [38]. This can be avoided to some extent by performing a stability analysis of the HF wavefunction, which can reveal whether the HF solution is the appropriate reference determinant. Such stability tests should routinely be performed in this type of study.

Table 1. S/T splittings in **1** *calculated with single reference CC methods using the cc-pVDZ basis set.*

Reference S	**Reference T**	**Method**	**E_S / a.u.**	**E_T / a.u.**	**Δ / kcal mol^{-1}**
RHF[1]	*UHF*	*HF*	-338.11397	-338.37195	-161.88
RHF	*UHF*	*MBPT(2)*	-339.52537	-339.35341	107.90
RHF	*UHF*	*CCSD*	-339.37465	-339.43308	-36.67
RHF	*UHF*	*CCSD(T)*	-339.50687	-339.48061	**16.48**
RHF	*ROHF*	*HF*	-338.11397	-338.35464	-151.02
RHF	*ROHF*	*MBPT(2)*	-339.52537	-339.37118	96.75
RHF	*ROHF*	*CCSD*	-339.37465	-339.43281	-36.50
RHF	*ROHF*	*CCSD(T)*	-339.50687	-339.48122	**16.09**
Brueckner	*Brueckner*	*CCD(T)*	-339.50955	-339.48161	**17.53**
BS-UHF[2]	*UHF*	*HF*	-338.36013	-338.37195	-7.42
BS-UHF	*UHF*	*MBPT(2)*	-339.35347	-339.35341	0.04
BS-UHF	*UHF*	*CCSD*	-339.43186	-339.43308	-0.76
BS-UHF	*UHF*	*CCSD(T)*	-339.48135	-339.48061	**0.47**
RHF	*UHF*	*CCSDT*	-339.48517	-339.48358	**0.99**
RHF	*UHF*	*CCSDT-3*	-339.47753	-339.47760	**-0.05**
RHF	*UHF*	*ΛCCSD(T)*	-339.47581	-339.47805	**-1.40**

1) The RHF singlet numbers reported in this table correspond to determinant B in Fig. 2.

2) BS indicates unrestricted reference determinants with broken spatial symmetry were used for the singlet. The largest instability vector was followed repeatedly, until a determinant with no instabilities was found.

Stability analysis can also be used to find broken-symmetry (BS-) UHF solutions. In the case of **1**, using a BS-UHF reference for the singlet leads to fairly accurate S/T gaps even at the HF level, although the BS-CC solution for the singlet is heavily spin-contaminated (average multiplicity ~2.4). In this reference determinant, the HOMO-LUMO gap is much higher (> 10 eV, comparable to the IP/EA-EOM-CCSD gap), and consequently the T2 amplitudes are no longer quite as large (0.12 for CCSD). Overall, the BS-CCSD(T) S/T gap is within the experimental margin, with the significant caveat that the singlet is not actually a pure singlet state.

A more straightforward (albeit expensive) way of improving the SR-CC results is to go beyond CCSD(T). The objective of CC is rapid convergence to the full CI solution, at which point, the choice of reference determinant and orbitals is irrelevant (as long as the determinant overlaps the exact wavefunction). When using full CCSDT with a RHF reference for the singlet, the S/T gap is calculated to be ~1 kcal mol^{-1}, well within the expected error margin. More affordable alternatives to full CCSDT (~$O(n^8)$) are the CCSDT-3 (~$O(n^7)$) and the non-iterative ΛCCSD(T) (~$O(n^7)$) methods,[39] which also provide an accurate prediction of the S/T gap at a significantly reduced cost relative to CCSDT (see table 1 for details).

Interestingly, the CCSDT-3 and CCSDT wavefunctions display a T2 amplitude of ~1.0, indicating that in intermediate normalization the doubly excited determinant is as important to the wavefunction as the reference determinant. This is characteristic for a generalized valence bond (GVB)-type structure, and decidedly not an "open-shell singlet" that would correspond to a spin-flipped triplet. Accordingly, the usual two-determinant CC approach (TD-CCSD) is not applicable.[47] This feature of a GVB- or second highly weighted determinant also occurs in the famous methylene singlet-triplet separation problem. There, the triplet is the ground state, while the singlet is a similar two-determinant form. In prior MR-CC work, the GVB-CCSD approach was used in this context.[48]

The problems with the reference function can be avoided completely by using DEA-EOM methods, which use the closed-shell di-cation as a reference determinant. In this manner, all singlet and triplet configurations are treated on an equal footing, including the important doubly excited determinants. The results for different DEA-EOM methods are compiled in Table 2. All tested methods predict the singlet and triplet to be essentially equal in energy, in good agreement with the experimental results. This is even true for the DEA-EOM-CIS approach, which limits the EOM-space to singles. Hence, the description of the S/T gap does not depend on dynamical correlation effects (at least those beyond the ground state of $\overline{H}$).

*Table 2. S/T splitting in **1** calculated with DEA-EOM methods using the cc-pVDZ basis set.*

Method	**E$_S$ / a.u.**	**E$_T$ / a.u.**	**Δ / kcal mol^{-1}**
DEA-EOM-CCSD	-339.42417	-339.42413	**0.03**
DEA-EOM-CIS	-338.27520	-338.27531	**-0.07**
DEA-STEOM-CCSD	-339.44834	-339.44780	**0.34**

In agreement with the CCSDT results, the lowest DEA-EOM solution gives equal weight to the ground-state and doubly excited determinants. This is illustrated in Fig. 3, for the case of DEA-STEOM-CCSD. This figure shows that the "open-shell" singlet is 6 eV higher in energy than the ground state. This is the state that would be described by a two-determinant CC calculation. The “closed-shell” singlet lies even higher. Note that there are also many other excited states in this energy range, not depicted in the figure for clarity.

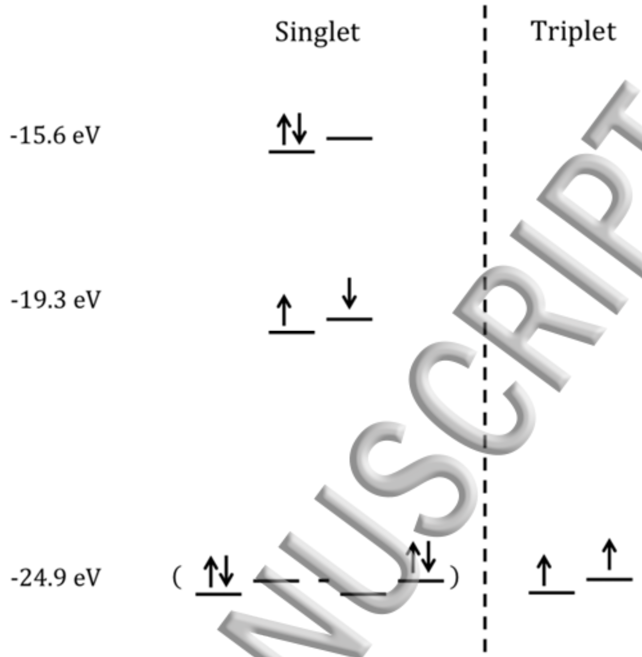

Figure 3. Schematic depiction of the energetic ordering of different DEA configurations at the DEA-STEOM-CCSD/cc-pVTZ level, using a di-cationic reference determinant. The displayed singlet configurations correspond to the naive “closed-shell”, “open-shell” and “double-excitation” wavefunctions discussed in the text, and illustrates the multireference character of the state. Note that there are also other states in this energy range (not depicted), but none that is lower lying than the ground state.

Alternatively, it is also possible to use the DIP-EOM-CC method for this system, with comparable results (see Table 3). This approach is more efficient computationally, since the DIP step scales with $O(n_o{}^5 n_v)$ (vs. $O(n_o n_v{}^5)$ for DEA). On the other hand, di-anionic reference states can be problematic, particularly if the basis set is relatively diffuse. These problems can be avoided, however, by using orbitals from a neutral SCF calculation and then constructing the di-anionic reference via the quasi-restricted HF (QRHF) procedure.[36] As can be seen in Table 3, the S/T gap is computed accurately independently of the type of orbital used (di-anion, neutral ground-state or neutral doubly excited state). Note however, that the total energies of the states do vary significantly with the choice of orbitals, in particular between the di-anionic and neutral references. In terms of total energies, the calculations using neutral orbitals are significantly closer to the CCSDT results, indicating that this is the appropriate choice for this system.

Table 3. S/T splitting in ***1*** *calculated with DIP-EOM-CCSD and different reference orbitals from di-anionic and neutral SCF wavefunctions. All calculations used the cc-pVDZ basis set.*

Reference Orbitals	**E_S / a.u.**	**E_T / a.u.**	**Δ / kcal mol^{-1}**
Dianion	-339.20829	-339.20856	**-0.17**
Neutral (det. A)	-339.31538	-339.31568	**-0.19**
Neutral (det. B)	-339.30977	-339.31000	**-0.14**

*b) Biphenyl-4,4'-dinitrene (**2**):*

Due to its relatively small size and high symmetry, **1** can be treated with full CCSDT. This is not feasible for **2**, but all other methods used above could be applied. Overall the results are very similar to what is found in the previous section, but the pathologies are more severe.

In terms of SR calculations, CCSD(T) correctly predicts the singlet to be the ground state, albeit with a too large S/T gap (~24 kcal mol^{-1}, see table 4). Here, spin contamination of the triplet does play a role (the projected multiplicity for UHF-CCSD is 3.2). Accordingly there is some benefit in using a ROHF reference for the triplet, which lowers the gap to ca. 21 kcal mol^{-1}.

As before, the main problem lies with the singlet, however. The HOMO-LUMO gap in the RHF reference is below 2 eV, and accordingly the maximum T2 amplitude is again extremely large (0.7 for CCSD). The RHF singlet wavefunction is unstable, and can be converted to a spin-contaminated UHF solution of the same spatial symmetry, or to a broken-symmetry solution. Only the BS reference allows obtaining qualitatively accurate S/T gaps for this system. As before, the corresponding singlet wavefunction is strongly spin contaminated (average multiplicity 2.7). More satisfyingly, the ΛCCSD(T) and CCSDT-3 methods also correct the error of UHF-CCSD(T) to a large extent, providing reasonable S/T gaps of 2.8 and 3.4 kcal mol^{-1}, respectively. With CCSDT-3, the largest T2-amplitude for the singlet state is again close to unity (0.96), confirming that the electronic structures of molecules **1** and **2** are analogous.

Table 4. S/T splitting in ***2*** *calculated with single reference CC methods using the cc-pVDZ basis set.*

Reference S	**Reference T**	**Method**	**E_S / a.u.**	**E_T / a.u.**	**Δ / kcal mol^{-1}**
RHF	*UHF*	*HF*	-567.62814	-567.92056	-183.50
RHF	*UHF*	*MBPT(2)*	-570.06091	-569.60883	283.68
RHF	*UHF*	*CCSD*	-569.70593	-569.76256	-35.54
RHF	*UHF*	*CCSD(T)*	-569.88792	-569.84948	**24.12**
RHF	*ROHF*	*HF*	-567.62814	-567.88790	-163.00
RHF	*ROHF*	*MBPT(2)*	-570.06091	-569.67549	241.85
RHF	*ROHF*	*CCSD*	-569.70593	-569.76558	-37.43
RHF	*ROHF*	*CCSD(T)*	-569.88792	-569.85372	**21.46**
Brueckner	*Brueckner*	*Brueckner-CCD(T)*	-569.88969	-569.85439	**22.15**
BS-UHF	*UHF*	*HF*	-567.91885	-567.92056	-1.07
BS-UHF	*UHF*	*MBPT(2)*	-569.58380	-569.60883	-15.71
BS-UHF	*UHF*	*CCSD*	-569.75118	-569.76256	-7.14
BS-UHF	*UHF*	*CCSD(T)*	-569.83830	-569.84948	**-7.01**
RHF	*UHF*	*CCSDT-3*	-569.84993	-569.84451	**3.40**
RHF	*UHF*	*ΛCCSD(T)*	-569.84906	-569.84464	**2.78**

Once again, the DEA approaches provide very accurate results at a moderate cost (see table 5). All tested methods predict that the singlet and triplet are nearly isoenergetic, in agreement with experimental data. Given the difficulties and ambiguities with converging the neutral wavefunction, it is particularly attractive to use the DEA approach here, which only requires the better behaved di-cation RHF solution and provides properly spin-adapted singlet and triplet energies in a single calculation. However, the basic results are the same for the DIP approaches, as can be seen, e.g. for DIP-STEOM-CCSD.

Table 5. S/T splittings in ***2*** *calculated with DEA/DIP-EOM methods using the cc-pVDZ basis set.*

	E_S / a.u.	E_T / a.u.	Δ / kcal mol^{-1}
DEA-EOM-CCSD	-569.78126	-569.78109	**0.11**
DEA-EOM-CIS	-567.69987	-567.69986	**0.01**
DEA-STEOM-CCSD	-569.75594	-569.75587	**0.05**
DIP-EOM-CCSD	-569.76467	-569.76457	**0.06**
DIP-STEOM-CCSD	-569.78745	-569.78720	**0.16**

IV. Conclusions

We have shown that CC methods can be used to obtain the singlet-triplet gaps in two highly multi-reference phenyldinitrene biradicals. These systems are difficult to describe because doubly excited determinants have a large weight in the wavefunctions of the singlet ground states. As a consequence, CCSD(T) is only qualitatively accurate when used with conventional HF reference determinants. Furthermore, it can fail completely (as reported in [38]) if the underlying SCF converges to the wrong state.

These problems can be solved in at least four ways within a fully SR-CC picture: (a) the extension to the infinite-order iterative CCSDT-3 that remains ~$O(n^7)$, (b) the extension to full CCSDT at ~$O(n^8)$, (c) the use of a broken-symmetry reference at the CCSD(T) level, (d) the ΛCCSD(T) method, which offers a good compromise having the same (non-iterative) scaling as CCSD(T), while predicting significantly more accurate S/T gaps.

Alternatively, the DEA/DIP methods accurately describe the system, by treating the ground state and doubly excited determinants on an equal footing. This approach is computationally efficient, requires no potentially ambiguous input from the user and leads to properly spin-adapted solutions (if the reference CC solution is for a closed shell). Furthermore, the relative singlet/triplet energies are fairly independent of the orbitals used, and the basis set-dependence is quite low. Overall, we recommend the DEA/DIP approach as the most accurate and economical approach to computing singlet/triplet gaps in difficult biradical systems.

Supplementary materials: This file includes additional data for the basis set dependence and a comparison the quasidegenerate determinants of **1**.

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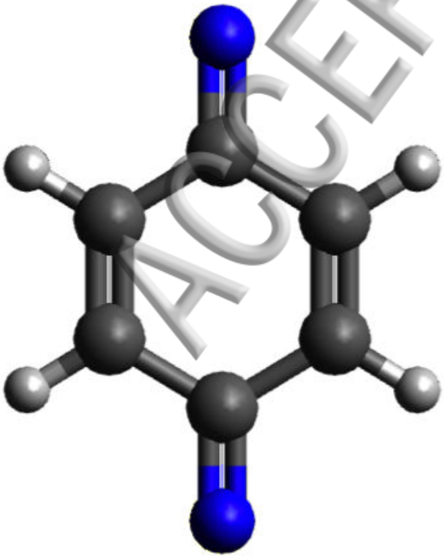

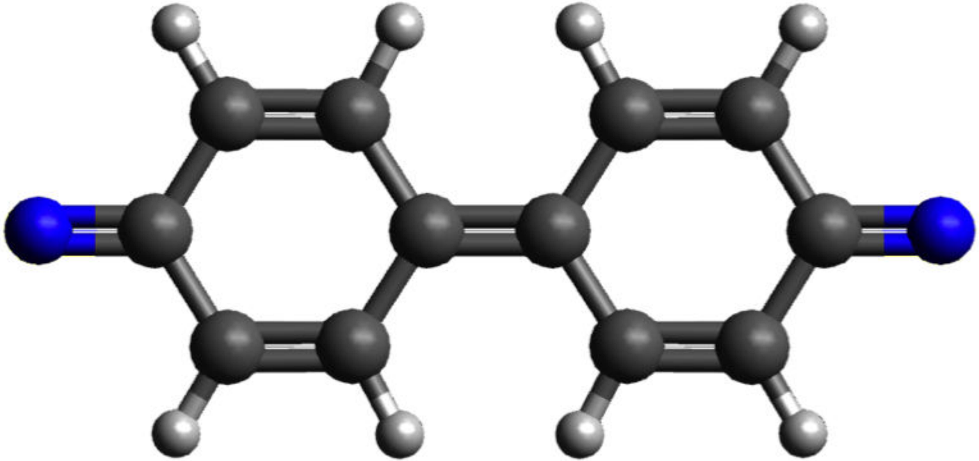

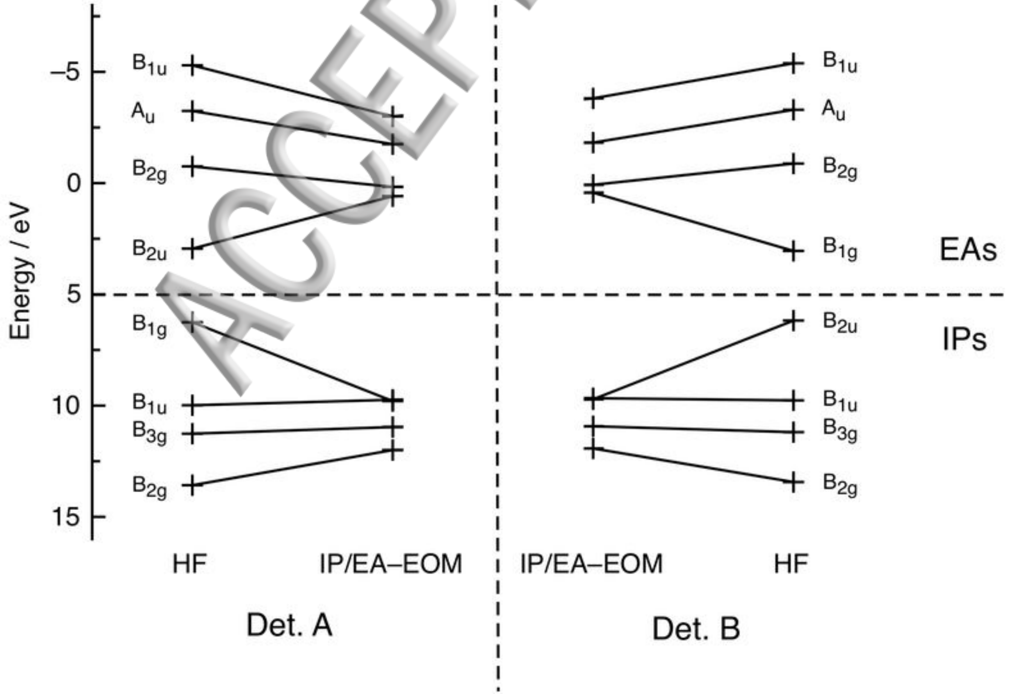
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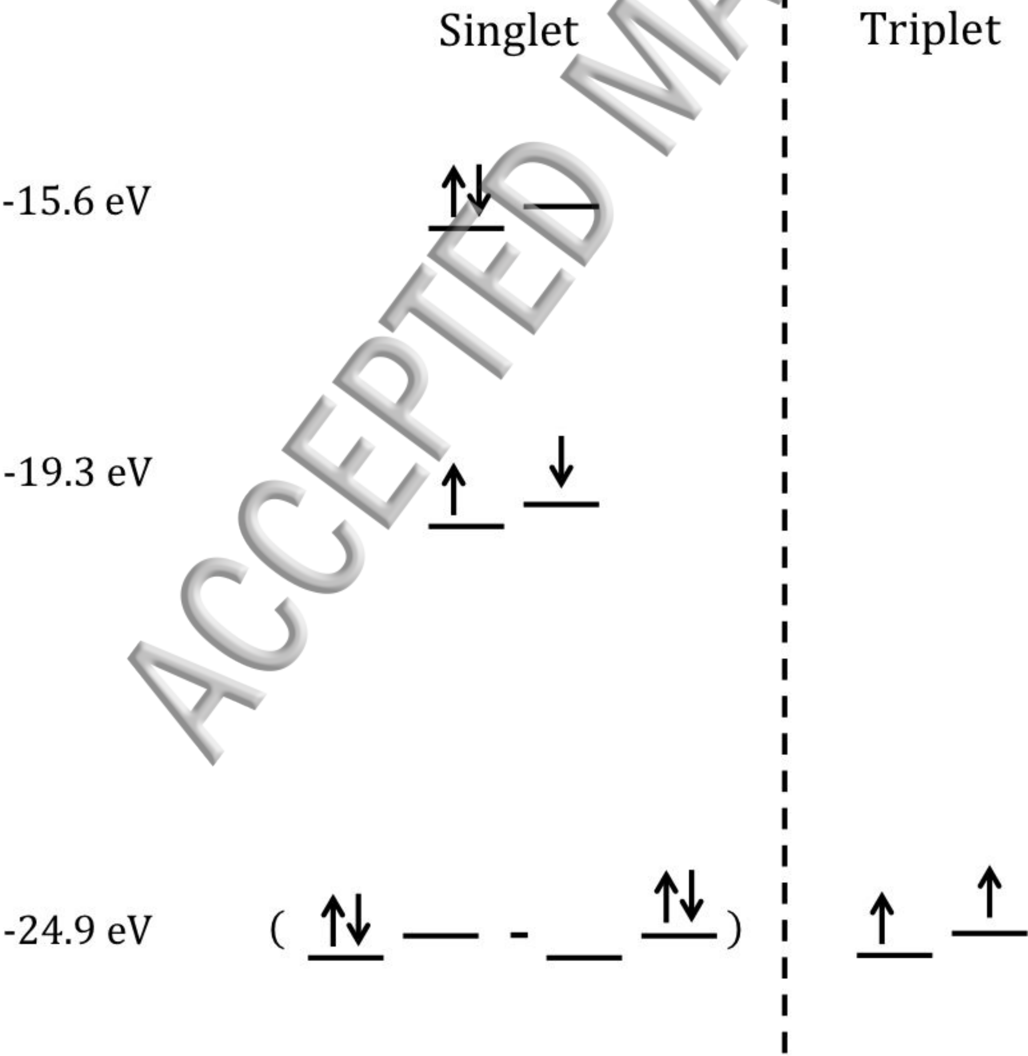
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