

Using the charge-stabilization technique in the double ionization potential equation-of-motion calculations with dianion references

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The charge-stabilization method is applied to double ionization potential equation-of-motion (EOM-DIP) calculations to stabilize unstable dianion reference functions. The auto-ionizing character of the dianionic reference states spoils the numeric performance of EOM-DIP limiting applications of this method. We demonstrate that reliable excitation energies can be computed by EOM-DIP using a stabilized resonance wave function instead of the lowest energy solution corresponding to the neutral + free electron(s) state of the system. The details of charge-stabilization procedure are discussed and illustrated by examples. The choice of optimal stabilizing Coulomb potential, which is strong enough to stabilize the dianion reference, yet, minimally perturbs the target states of the neutral, is the crux of the approach. Two algorithms of choosing optimal parameters of the stabilization potential are presented. One is based on the orbital energies, and another – on the basis set dependence of the total Hartree-Fock energy of the reference. Our benchmark calculations of the singlet-triplet energy gaps in several diradicals show a remarkable improvement of the EOM-DIP accuracy in problematic cases. Overall, the excitation energies in diradicals computed using the stabilized EOM-DIP are within 0.2 eV from the reference EOM spin-flip values. © 2011 American Institute of Physics. [doi:10.1063/1.3626149]

I. INTRODUCTION

The double ionization potential equation-of-motion (EOM-DIP) method^{1–3} has emerged more than a decade ago as a non-particle-conserving variant of the EOM coupled cluster (EOM-CC) scheme^{4,5} targeting diradicals. In EOM-CC, multiple target states of a system, $\Psi_k = R_k \Phi_0$, are found as the solutions of a non-Hermitian eigenvalue problem

$$\bar{H} R_k = E_k R_k, \quad (1)$$

where \bar{H} is a similarity transformed Hamiltonian,

$$\bar{H} = e^{-T} H e^T, \quad (2)$$

and T is a general excitation operator determined from the CC equations for the reference state. The choice of the excitation operator R is specific for different EOM-CC models,⁶ e.g., it is a particle-conserving operator in the excitation energy variant (EOM-EE),⁷ particle-annihilating operator in EOM-IP,⁸ and particle-creating operator in the electron attachment EOM (EOM-EA).⁹ The EOM-DIP model employs R that generates determinants that have two fewer electrons than the reference function, Φ_0 . The excitation level in T and R can be varied (inclusion of higher excitations improves accuracy but is, of course, more computationally demanding). Our study considers only EOM-CC methods that employ the operators restricted to the single and double substitutions (with respect to the reference Φ_0), that is, 1h1p+2h2p (h for hole, p for particle) in T and in R in particle-conserving EOM models, whereas the respective excitation level of R in EOM-DIP is 2h+3h1p. Thus, EOM-DIP refers to a model in which

T includes single and double substitutions and satisfies the coupled-cluster singles and doubles (CCSD) equations for the reference state, and amplitudes R are found by diagonalizing \bar{H} in the 2h+3h1p space.

The EOM-DIP method provides an improved description of the electronic structure in the cases when the spin-conserving EOM (EOM-EE) method suffers from an unbalanced treatment of near-degenerate configurations,⁶ such as diradicals and bond-breaking. The EOM-DIP offers an alternative approach to the spin-flip (SF) method,^{10,11} which is also capable of treating these chemical problems.^{6,12} When the wave functions of interest can be described as two electrons in two orbitals, the quality of the SF and DIP sets of target configurations is comparable, as illustrated in Fig. 1. The two frontier orbitals belong to the occupied subspace (when using triplet or dianion reference functions) and the leading determinants of the target wave functions are treated on the equal footing as they both are single excitations generated from the respective references. This balanced treatment ensures that the energy differences between the target states derived from these configurations are accurately described by both EOM-DIP and EOM-SF. The EOM-EE method, however, fails for diradicals because: (i) these nearly degenerate orbitals are split between the occupied and virtual subspaces; and (ii) the two leading determinants engaged in the 1A_1 states appear at different excitation levels, i.e., as the reference and doubly excited ones, which leads to a preferential treatment of one leading determinant, and hence, an unbalanced description of the two 1A_1 states.

For more complex degeneracy patterns, however, DIP has an advantage over SF, as illustrated in Fig. 2 showing target states derived by distributing four electrons over three

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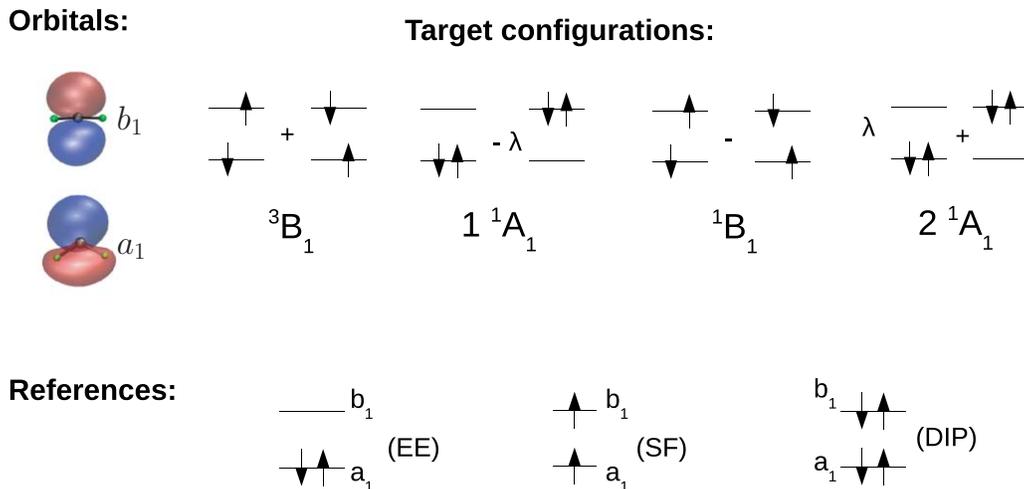


FIG. 1. Four configurations arising from distributing two electrons in two near-degenerate orbitals of methylene. All four target states are described correctly by the SF and DIP methods because: (1) their leading determinants are treated on the same footing; (2) the two orbitals are engaged in the reference state equally. The spin-conserving EOM-CCSD method fails for this system because: (1) the frontier orbitals are treated differently, i.e., one belongs to the occupied and another – to the virtual subspaces; (2) in the 1A_1 states, one of the leading determinants is doubly excited with respect to the reference state.

orbitals. These wave functions include two types of configurations. Those denoted as type A can be described as a diradical manifold derived from the two highest orbitals and, therefore, can be accurately described by both SF and DIP. However, the configurations of type B belong to two other diradical manifolds derived from the lowest orbital and one of the higher orbitals. From the SF point of view, these configurations would require another triplet reference (or a higher excitation level). Thus, SF cannot describe both groups of configurations on the same footing using the same reference state. In EOM-DIP, however, all these configurations appear as primary excitations (2-hole) from the dianion reference. This type of electronic structure occurs in oxygen-containing diradicals^{13–16}

formed in the reactions of triplet oxygen with unsaturated compounds,¹⁷ which are relevant to combustion. Other examples of electronic states for which SF runs out of steam can be found in oxyallyl¹⁸ and trimethylmethane (TMM).¹⁹

Additional attractive features of DIP are its reduced computational cost, naturally spin-pure wave functions, and the lack of reference spin-contamination. The cost reduction is due to o^4v^2 scaling of the EOM-DIP diagonalization procedure, which is superior to that of its SF and spin-conserving counterparts of the same excitation level. Moreover, EOM-DIP does not require constructing the four-virtual block of \hat{H} , which further reduces the cost and storage requirements.

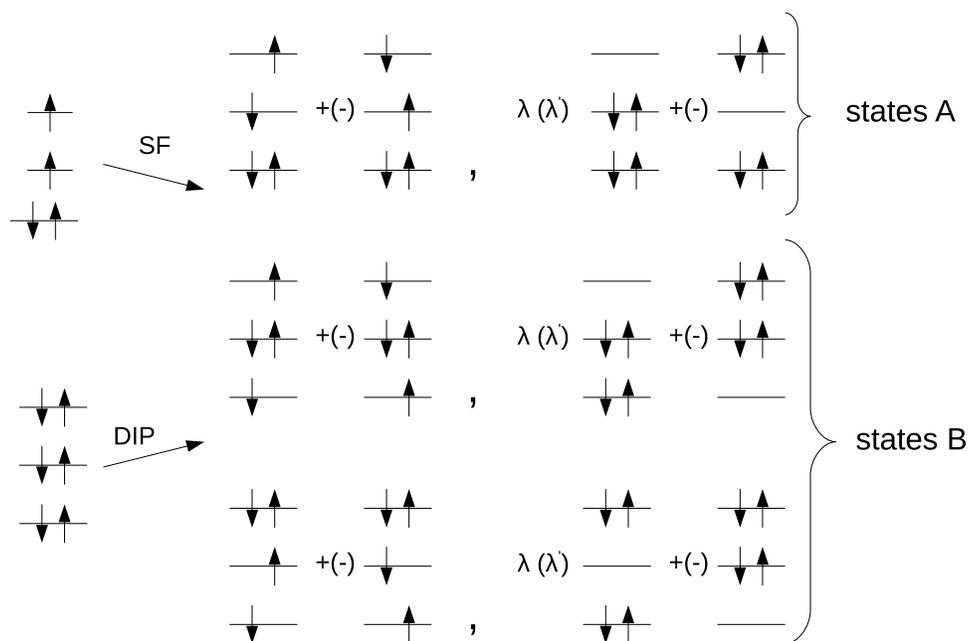


FIG. 2. Twelve electronic configurations arising from distributing four electrons over three orbitals. The states of type A are described equally well by both methods; however, for the states of type B, the DIP method is superior to SF due to the balanced treatment of the leading determinants.

Despite these attractive features, only a limited number of applications of EOM-DIP have been reported so far, e.g., studies of NO_3 ,² ozone,³ O_2 , and F_2 .²⁰ Recent papers benchmarked the performance of several DIP models for dications (H_2O , CO , and C_2H_2), ethylene torsion and cyclobutadiene interconversion.^{21,22}

This seeming lack of interest is due to the complications arising from using anionic or dianionic reference states. Negatively charged species (especially dianions) are often unstable (in the gas phase) with respect to the electron detachment. In small bases, these states behave like normal bound states; however, as more diffuse functions are added, the wave function becomes more and more diffuse approximating a continuum state corresponding to an electron-detached system and a free electron (or electrons). This behavior is well known in the context of metastable (or quasi-bound) states (so-called resonances).

Resonances are states that belong to the continuum spectrum of the Hamiltonian, but whose wave functions resemble normal bound states. For example, a non-stationary state derived by attaching an electron to a high-energy valence MO is a resonance. Such states are encountered in dissociative electron attachment,^{23,24} electron scattering,^{25,26} or high-energy ionization processes.²⁷ These states also play a role in biological systems, e.g., the initial step in the DNA damage induced by free electrons involves resonance anionic states.^{28,29} Another example of a resonance state is an excited state lying above the ionization continuum, such as $\pi\pi^*$ excited states in the anionic forms of the model GFP and PYP chromophores^{30,31} (in GFP, the excitation energy of the $\pi\pi^*$ state is 2.6 eV, whereas the electron detachment energy from the π orbital is 2.5 eV).

A number of theoretical methods have been developed to describe such resonance states.^{32–35} One set of methods is based on the stabilization approach in which the original Hamiltonian is perturbed such that the resonance state is lowered (stabilized) below the onset of the continuum and its wave function becomes L^2 -integrable that can be described by standard approaches using finite basis sets. From the DIP point of view, such stabilized resonance state of the dianion would provide an appropriate reference state for the DIP expansion. For accurate description of the target (doubly detached) states, the orbitals of the reference state should not be too diffuse so they provide a reasonable basis for describing neutral states, and the core correlation effects in the reference described by T_1 and T_2 should be transferable to the target states.

Using a small basis set, which is equivalent to forcing the electron to stay in the valence region, amounts to a form of stabilization,³⁶ and numeric performance of DIP in relatively small basis sets is indeed very good²¹ (as compared to higher level methods, for example). However, using large basis sets is mandatory for obtaining reliable results with correlated wave functions, and the electron-detached dianion reference states that appear in sufficiently large bases provide a poor starting point for generating target configurations of the neutral system. Indeed, if the highest-occupied molecular orbital (HOMO) in the dianion reference becomes too diffuse in its attempt to detach two extra electrons, as illustrated in

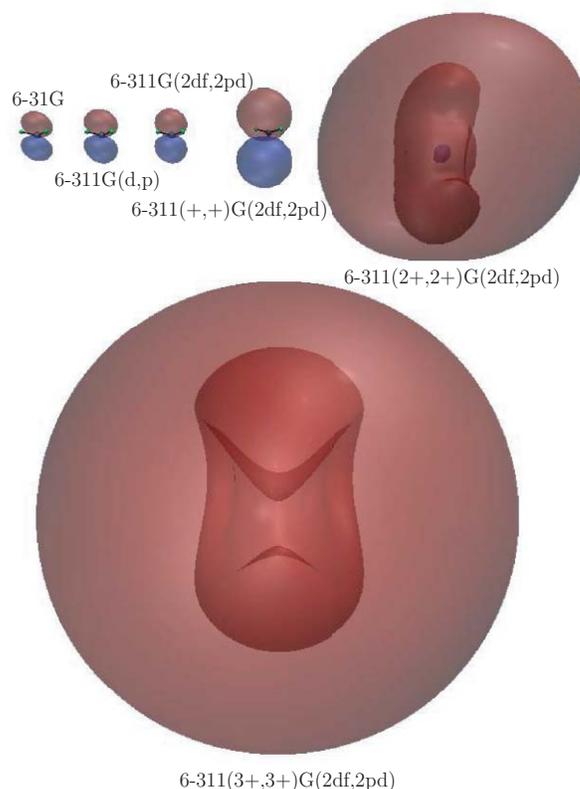


FIG. 3. The shape of the HOMO of CH_2^{2-} in different basis sets. The orbitals are visualized using a contour value enclosing 70% of the electron density.

Fig. 3 for CH_2^{2-} , only one target determinant from Fig. 1 is adequately described (i.e., the one that corresponds to removing two electrons from the HOMO). The second “closed-shell” type determinant (derived by removing two electrons from the HOMO-1) corresponds to a doubly ionized state of the neutral (two remaining electrons occupy a very diffuse orbital) and is not a valence-like determinant needed for a diradical wave function. Likewise, open-shell determinants also become unphysical (roughly, they correspond to a singly ionized state of the neutral). Thus, the description of all states from Fig. 1 (except, possibly, the 1^1A_1 state, if λ is sufficiently small) is spoiled, which is reflected in the energy differences (the energies of open-shell singlet and triplet states are pushed up, relative to the lowest closed-shell state).

One may attempt to avoid these pseudo-continuum states by employing different orbitals,²² e.g., obtained from Hartree-Fock (HF) solution for a neutral system using, for example, the quasi-restricted HF method.³⁷ This type of strategy has been employed in the first work exploiting the DIP ideas within the similarity transformed EOM-CC method.¹ The authors constructed their reference dianion determinant by using $N - 2$ orbitals of the neutral and an additional orbital (the HOMO of the dianion) computed using the \tilde{V}^{N-1} potential.³⁸ Indeed, the reference determinant in EOM-CC does not have to be the lowest energy HF solution for the reference state, which is often exploited in problematic CC/EOM-CC calculations.^{22,37,39} However, using the reference determinant that corresponds to a highly excited state is numerically

unstable, as the T_1 operator can, in principle, rotate the orbitals such that CCSD equations converge to the lowest correlated state of the system. Since the diffuse pseudo-continuum state is not an artifact of the HF procedure, but is indeed the lowest state of the correlated system, preventing CCSD equations from collapsing to the physically lowest state is problematic and would require modifications in the standard DIIS (direct inversion of the iterative subspace) scheme.^{40,41} In several cases that we investigated, we observed a rapid divergence of the CCSD equations when using in dianion's calculations orbitals corresponding to the N-2 system (i.e., HF orbitals of the singlet or triplet state of the neutral). Thus, fixing the reference orbitals alone does not provide a robust solution to the problem.

This work explores the possibility of employing stabilization approach using an additional Coulomb potential in DIP calculations. We modify the Hamiltonian in such a way that the resonance state solution is shifted down (i.e., stabilized) below the manifold of the $N + FE$ states (throughout this paper, the label $N + FE$ denotes a state of a dianion that approximates the continuum. In contrast to quasi-bound resonance states characterized by relatively localized wave functions, the $N + FE$ states are maximally diffuse). Alternatively, one can say that the electron-detached continuum is shifted up by the stabilizing potential. This can be achieved by adding positive charges that lower the energy of the anionic states and, therefore, increase the electron-detachment energy. When the detachment energy becomes sufficiently high, the resonance state drops below the detachment continuum and becomes a well-behaved bound state. Hence, the stabilized resonance state becomes computationally available as the lowest energy solution of HF and CC equations. We consider two variants of the charge-stabilization method, i.e., modifying nuclear charges and adding a positively charged sphere.

The stabilized resonance state is a good starting point for the DIP expansion; however, one faces a problem of quantifying the effect of stabilization potential on the target states. Ideally, the strength of the stabilizing potential should be just sufficient to stabilize the dianion state and not too strong such the target neutral states are perturbed too much. We quantify this perturbation by performing SF calculations with the stabilizing potential. We then develop a procedure of choosing parameters for stabilization method that provide sufficient stabilization of the reference without large perturbations of the target states. If all target states are perturbed to a similar extent, the errors in energy differences that are computed by EOM directly may largely cancel out. In a subsequent work, we will develop a state-specific correction to eliminate the remaining errors.

The first stabilization technique is based on embedding a negative ion in a positively charged cage.^{42–45} The method has been used, for example, to study the resonance $^2\Sigma_u^+$ states of H_2^- .^{42,43} In these studies, the charged cage was used to carry out self-consistent field (SCF) calculations determining the resonance orbital (occupied by the excess electron). After performing CI calculations, the manifold of CI states was filtered out by the projection operator to exclude the $N + FE$ states. These calculations also involved a procedure reducing the

undesirable effect of the charged cage on the core orbitals. Another application of the charged sphere method involved calculations of the shape resonances in N_2^- and Mg^- using the multireference CI (MRCI) method.⁴⁶

The second stabilization method exploited in this paper is the variation of nuclear charges. In this approach, the charge of each nucleus (Z_i) is scaled as $(1 + \gamma)Z_i$, where γ is a small parameter (the same for all nuclei).³³ This generates an additional positive potential that stabilizes the unstable resonance state. This approach was used to study two resonances of N_2^- ($^2\Pi_g$ and $^2\Pi_u$) within the SCF and MRCI frameworks.

For benchmark purposes, we consider diradicals and focus on the singlet-triplet (ST) energy gaps. The benchmark set consists of CH_2 , NH , ortho-, meta-, and para-benzynes (o-, m-, and p-benzyne), and TMM. These systems have been studied by the SF method and benchmarked against the experimental data.^{19,47} The results suggest that the typical accuracy of EOM-SF-CCSD is below 1 kcal/mol, with the largest error of 3 kcal/mol.¹² Hence, the SF gaps are used as the reference values. The size of the molecules is diverse enough to test whether the proposed strategy is universal and that the choice of optimal stabilization parameters works well for the systems of varying size.

The paper is organized as follows. First, we compare the performance of EOM-DIP with SF for well-behaved neutral references. We then analyze the behavior of the EOM-DIP method using $N + FE$ reference states. This is followed by the presentation of the results obtained with the stabilization method. Then the algorithm of choosing the optimal values of stabilization parameters is presented and verified by additional EOM-DIP calculations. Finally, we discuss pros and cons of the proposed method and its prospects.

II. COMPUTATIONAL DETAILS

We focus on vertical ST gaps computed at the best available geometries from the previous studies,^{19,47} or at the experimentally derived geometries (NH).⁴⁸ The Cartesian coordinates are summarized in the supplementary materials.⁴⁹ For benzynes and TMM, the core orbitals were frozen in the correlated calculations. For other systems, all electrons were active. The calculations were performed using the Q-CHEM electronic structure package.⁵⁰

III. BENCHMARK CALCULATIONS

The SF method provides reliable reference values for the ST gaps in diradicals.^{11,12,51,52} For simple diradicals (two electrons in two orbitals) that are studied in this paper both SF and DIP should yield accurate results, provided that the DIP results are not affected by the quality of the reference state. To validate this assessment, we performed DIP calculations for well-behaved (i.e., non-resonance) references. We considered neutral HF references, so the target states are those of the double cation. We computed the ST separation between the states involving two lowest occupied orbitals for three small dications derived from H_2O , NH_3 , and N_2 . We used the following geometries: $R_{OH} = 0.9572$ Å, $\alpha_{HOH} = 104.52$ (H_2O),⁵³ $R_{NH} = 1.0116$ Å, $\alpha_{HNN} = 106.7$ (NH_3),⁵⁴ and $R_{NN} = 1.09768$ Å

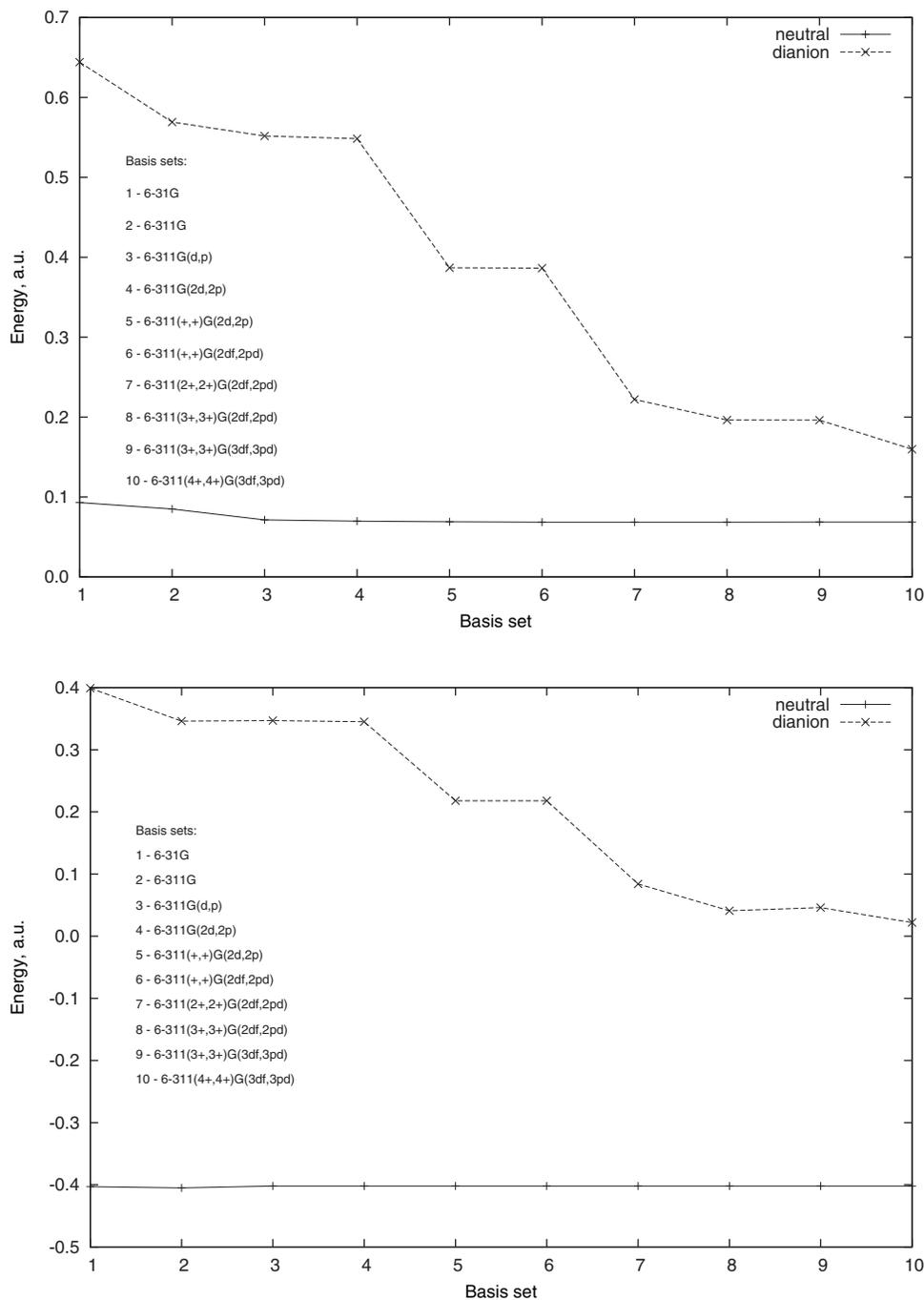


FIG. 4. Top: The HF energy (hartree) of the 1A_1 state of the methylene dianion compared with the 3B_1 state of the neutral using the split-valence Pople basis sets with an increasing number of diffuse functions. The energy is reported as $E + 39$. Bottom: The HOMO energies of the dianion 1A_1 reference and the 3B_1 neutral state.

(N_2),⁴⁸ and the 6-311(2+,2+)G(2df,2pd) basis set. The discrepancies between DIP and SF are -0.17 , -0.17 , and 0.07 eV, respectively. This confirms that the accuracy of the two methods is similar and indicates that the discrepancies of about 0.1 – 0.2 eV are natural, and the perfect agreement between SF and DIP should not be expected. These results are similar to the benchmark DIP calculations of dications reported in Ref. 21.

To investigate the performance of DIP with unstable reference states, we begin with the methylene diradical. The problem becomes apparent as one computes the HF energy

of CH_2^{-2} using basis sets with an increasing number of diffuse functions as shown in Fig. 4(a). We compute HF energies of the lowest triplet state of neutral CH_2 and the ground state of the dianion using ten basis sets of increasing size. Whereas the neutral curve is relatively flat, the dianion energy exhibits strong basis set dependence. An important observation is that the energy decrease is not uniform – energy drops are considerably larger whenever a set of diffuse functions is added such that the two extra electrons can move further away from the neutral core by occupying a more diffuse orbital. For the largest basis set used [6-311(4+,4+)G(3df,3pd)], the

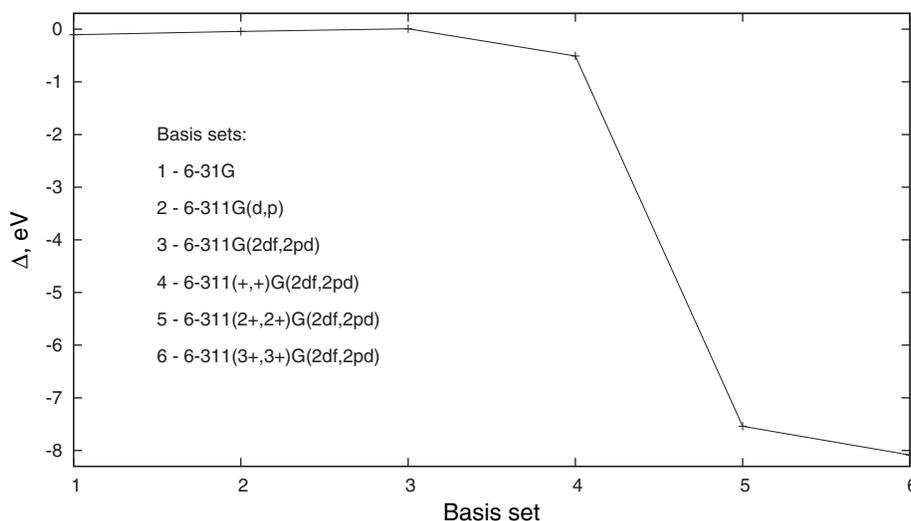


FIG. 5. The errors (eV) in the ST gap in methylene computed by the DIP method relative to SF ($E_{\text{DIP}} - E_{\text{SF}}$) for different basis sets.

two curves are separated by only about 0.09 hartree indicating that the dianion wave function approaches an electron-detached state. Since the lowest state of methylene with two extra electrons, a methylene anion and a continuum electron cannot be described by the restricted HF wave function in which the two electrons are forced to occupy the same orbital, the HF procedure converges to a higher energy singlet neutral +2 free electrons state (N+2FE). The increasing diffuseness of the dianion's HOMO is illustrated in Fig. 3. The energy of the HOMO [Fig. 4(b)] tells the same story. In a small basis, the HOMO energy is positive (which corresponds to a negative value of the electron detachment energy in the Koopmans approximation) reflecting the unstable character of the dianion. As the basis set increases, the energy of the HOMO decreases approaching zero for a fully electron-detached wave function. In contrast, the HOMO of the stable neutral triplet state is rather insensitive to the basis set.

Next, we compare the ST gaps computed with DIP and SF using the bases of increasing sizes and assess how the deteriorating quality of the reference state affects the DIP excitation energies. The results are presented in Fig. 5, which shows the relative accuracy of DIP for the ST energy gap for a number of basis sets. The discrepancy between DIP and SF is small (between -0.1 and 0.008 eV) in the three smallest basis sets; it increases when the first diffuse functions are added (to about -0.5 eV) and then, with an addition of the next set of diffuse functions, it plummets to about -7.5 eV. This is the point where the reference state, although not yet pure N + 2FE, becomes inadequate for the DIP expansion. Subsequent addition of more diffuse functions causes further deterioration of the DIP results.

This example demonstrates how much the accuracy of the DIP method can be impaired by using an electron-detached reference state. To investigate how general this phenomenon is, we computed DIP and SF ST gaps in different systems using large basis sets. The results indicate that the magnitude of the effect varies. Some molecules are affected very strongly. These are o- and m- benzynes [errors of 3.49 and 1.55 eV in 6-311(+,+)G(2df)], and NH [errors of 10.60 eV in 6-311(3+,3+)G(3df,2pd)]. Other systems are affected less.

For example, for p-benzynes [6-311(+,+)G(2df)] and TMM [6-311(2+,2+)G(2df,2p)], the absolute discrepancies are 0.07 and -0.45 eV, respectively. The observed range of errors needs to be taken into account such that the stabilization method is tested not only for problematic cases, but also for the well-behaved ones.

While heavily augmented bases (with more than one set of diffuse functions) are not required for low-lying electronic states of neutral molecules (such as singlet and triplet states of diradicals), the above problem shows up in much smaller bases. Let us, for example, revisit the cyclobutadiene example from Ref. 21. Using the geometries from Ref. 21 and the cc-pVDZ basis set, we observe that relative state ordering at the square geometry is reversed, and the lowest singlet state is open-shell $^1B_{2g}$. Thus, the reported interconversion barrier of 10.05 kcal/mol, which appears to be in excellent agreement with higher level methods,^{11,21} corresponds to the wrong electronic state (the barrier for the closed-shell $^1B_{1g}$ state is 45.7 kcal/mol). In a larger basis set (aug-cc-pVDZ), the calculations are complicated by multiple HF solutions that affect the state ordering. If the lowest energy HF solution is employed, the correct ordering of the open and closed-shell states is restored (albeit for a wrong reason – the open-shell state is destabilized more than the closed-shell diradical state, and their symmetries are incorrect), and the computed barrier is 21.2 kcal/mol, which is twice higher than the reference value. However, if one uses the higher energy HF solution of the correct symmetry (in which the HOMO and HOMO-1 are b_{2g} and b_{3g} at the rectangular geometry, and e_g at the square geometry), the interconversion barrier corresponding to the correct closed-shell state is 54.1 kcal/mol, while the barrier corresponding to the open-shell state is 20.2 kcal/mol. So for the correct symmetry solution, the two singlet states are ordered incorrectly at the square geometry (for more details, see supplementary materials⁴⁹). Thus, an unstable reference state may affect the DIP results even when using modest basis sets such as cc-pVDZ and aug-cc-pVDZ. Hence, a good accuracy of DIP methods using dianion references observed in relatively small basis sets²¹ cannot be reliably achieved in realistic calculations.

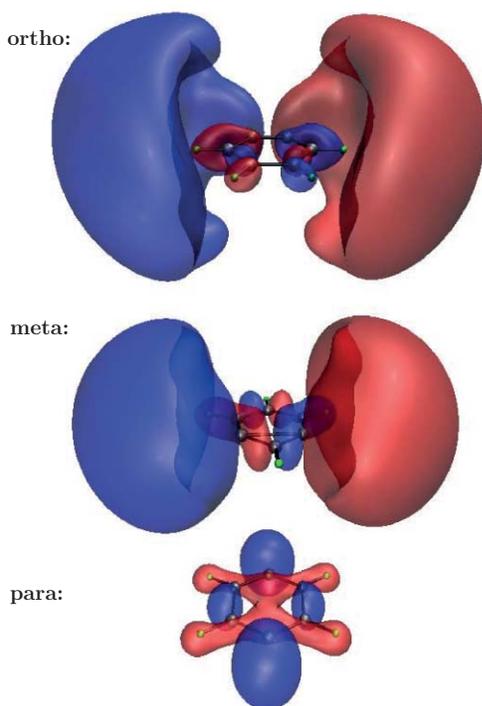


FIG. 6. The HOMO of the dianion reference in o-, m-, and p-benzyne. The orbitals are visualized using a contour value that encloses 70% of the electron density. The contour value corresponding to the desired density value is computed with the OpenCubMan program (Ref. 55). The degree of the diffuseness of the HOMO correlates with the relative instability of the dianion reference.

While magnitude of errors obviously depends on the basis set size, a more important factor is relative stability (or, rather, instability) of the dianion states in different systems, as demonstrated by the comparison of the three benzyne isomers for which the errors calculated with the same basis set vary from -3.49 to 0.07 eV. To understand these variations in the DIP accuracy, we visualized the respective dianion's HOMOs [computed using the 6-311(+,+) $G(2df)$ basis set, see Fig. 6]. The picture demonstrates that the errors correlate with the degree of the orbital diffuseness. The size of the HOMO is significantly larger for o- and m-benzynes than for p-benzyne because the extra electrons are further apart in p-benzyne, which reduces their repulsion. Thus, the dianion state of p-benzyne is less unstable, which is also indicated by a less negative double electron affinity (-0.34 and -0.13 hartree for o-benzyne and p-benzyne, respectively, computed at the HF/6-311G level). The HOMO energy exhibits a similar trend (0.268 and 0.164 hartree for o-benzyne and p-benzyne, respectively, computed by HF/6-311G). Because the p-benzyne dianion is less unstable than other benzynes, its wave function is affected less by the interaction with the continuum leading to smaller DIP errors. Overall, we expect the DIP method to perform well without stabilization for stable or nearly stable dianions. The above example demonstrates that the size and energy of the HOMO can provide a diagnostic for whether stabilization is required or not such that the systems with stable references can be identified and treated without stabilization.

A. DIP calculations using stabilization by Coulomb potential

We begin an analysis of the different stabilization approaches using CH_2 and the three benzyne isomers. In the charged cage method, the charge and size of the cage need to be carefully analyzed; however, the shape of the cage should be of less concern. Ideally, the cage should be spherical. However, as demonstrated in Refs. 42 and 46, the distribution of 26 or 20 point charges effectively simulates the charged sphere. We verified this by performing two sets of calculations using the same total charge. First, we distributed 20 point charges placed at the vertices of a dodecahedron (cf. Ref. 46); then we placed a large number of points (more than 100,000) on the sphere of the same radius as that of the dodecahedron. The two calculations yielded identical results for larger spheres. As we decreased the radius, small differences (≤ 0.01 eV) appeared. Only for very small radii (for example, 1.0 Å and less in the case of methylene), significant discrepancies of about 0.2 eV develop. Moreover, using such small dodecahedron cages brakes spatial symmetry and, consequently, orbital/state degeneracies. However, these problems occur only in very small cages that are not necessary for stabilization calculations. Thus, in the subsequent calculations we employ the dodecahedral cage built of 20 point charges. Using the point charges instead of an analytical potential allows us to test the technique without modification of the integral code with the current version of the Q-CHEM package.⁵⁰

Using cages of varying size and charge as well as scaled nuclear charges, we test the accuracy of the stabilized DIP method versus the reference SF values (same basis, no charges). We also assess the degree of perturbation of the neutral states by the stabilization potential by performing SF calculations with the charged cage. The discrepancies in the SF values computed with and without additional potential allow us to quantify the degree of perturbation. The results for the charged cage and scaled nuclear charges methods are collected in Tables I and II, respectively. The values in parenthesis indicate the perturbation of the SF values by the stabilizing potential.

We note that the HOMO energy provides a good indication of the degree of stabilization. For example, we observe a significant drop in errors when the HOMO energy becomes sufficiently negative.

As the potential becomes stronger (i.e., the radius decreases or the total charge increases, or the nuclear charge increases), the DIP values approach those of SF, being practically the same at certain points. In p-benzyne, which is affected very little, the relative accuracy of the two methods remains almost constant.

Contrary to a naive expectation that 2 excess electrons can be stabilized by an additional +2 charge, we observe that a reasonable DIP results are obtained using stronger potentials, i.e., +5 charge and a relatively small sphere of 2–3 Å (although the HOMO energy is negative in all calculations using +2 charge). In the scaled nuclear charges approach, a smaller extra charge is required for sufficient stabilization (total extra charge slightly above +1).

TABLE I. The errors (eV) in ST gaps for the DIP method stabilized by the charged cage. The errors are computed as $E_{\text{DIP}} - E_{\text{ref}}$, where E_{ref} is the SF value computed without the stabilization potential and in the same basis set. In parenthesis, the perturbation of the SF energies by the stabilization potential is reported (computed as $E_{\text{SF}} - E_{\text{ref}}$, where E_{SF} is the SF value computed with the same basis and with the stabilizing potential). E_{HOMO} is the HOMO energy (hartree). The 6-311(2+,2+)G(2df,2pd) basis set is used for methylene and the 6-311(+,+)G(2df) basis set is used for benzyne. The cage parameters are the total charge and radius (in Å).

Cage	CH ₂	E_{HOMO}	o-benzyne	E_{HOMO}	m-benzyne	E_{HOMO}	p-benzyne	E_{HOMO}
...	-7.54 (0.000)	0.08	-3.49 (0.000)	0.15	-1.55 (0.000)	0.15	-0.06 (0.000)	0.11
+2, 3.5	-0.81 (0.001)	-0.10	-0.82 (0.013)	-0.09	-0.53 (0.019)	-0.10	-0.09 (-0.046)	-0.18
+2, 3.0	-0.58 (0.004)	-0.12	-0.45 (0.029)	-0.12	-0.35 (0.018)	-0.13	-0.08 (-0.044)	-0.21
+5, 3.0	-0.32 (0.008)	-0.63	-0.17 (0.072)	-0.63	-0.15 (0.008)	-0.63	-0.02 (-0.037)	-0.72
+5, 2.5	-0.18 (0.024)	-0.76	0.01 (0.162)	-0.75	-0.10 (-0.013)	-0.73	-0.02 (-0.051)	-0.84
+5, 2.0	-0.06 (0.064)	-0.95	0.08 (0.226)	-0.85	-0.11 (-0.067)	-0.84	-0.09 (-0.107)	-0.94

Judging by the SF calculations performed with the stabilizing potential, the perturbation of the neutrals' states by the charged cage appears to be relatively uniform giving rise to errors in ST gaps of 0.001–0.2 eV (the sign of the errors changes). The scaled nuclear charges appear to perturb the target neutral states to a larger extent. For example, for the values of stabilization potential when the DIP errors (against SF) become acceptable, the changes in the SF gaps due to the additional potential are 0.02–0.7 eV. Thus, in this work we will focus on the charged cage method, for which we aim to develop an algorithm for finding optimal stabilization parameters.

The results from Table I show that a good agreement between stabilized DIP and the reference SF values is achieved for the cages with +3 – +5 charge with relatively small radii (2–3 Å). Most importantly, the results improve dramatically in the cases when unstabilized DIP fails. For all these cases, there is a range of stabilization parameters that reduce the absolute relative error of DIP to about 0.2 eV or less. Unfortunately, those optimal stabilization parameters are system-dependent. Hence, we need a criterion allowing one to determine optimal values of the stabilization parameters *a priori*. The rest of the paper is devoted to establishing the algorithm determining optimal stabilization parameters for both stabilization methods.

B. A procedure for determining optimal stabilization parameters

To develop a practical procedure of choosing stabilization parameters, one needs to identify a convenient molecular property that depends strongly on the stabilization parameters. One such quantity has been used to distinguish between resonances and N + FE states^{42,46} – it is the $\langle z^2 \rangle$ expectation value, which describes the spatial extend of the electron density. Indeed, $\langle z^2 \rangle$ (or, more generally, $\langle r^2 \rangle$) is larger for a N + FE state because of the detached electron occupying the most diffuse orbital.

Although $\langle r^2 \rangle$ value depends on the stabilization parameters, its utility to measure the degree of stabilization turns out to be rather limited. In previous applications, the $\langle z^2 \rangle$ was computed for the wave function of just three electrons. When all electrons are taken into account, the changes in $\langle r^2 \rangle$ become less pronounced. For example, our results for methylene and benzyne indicate a relatively weak dependence of $\langle r^2 \rangle$ on the stabilization potential, i.e., the $\langle r^2 \rangle$ values computed at the CCSD level for the three benzyne isomers in the 6-311(+,+)G(2df) basis set (the orbitals shown in Fig. 6) vary in the range of 598–416, 574–420, and 494–422 bohr², respectively, between no potential and the charged cage of the 2.0 Å radius and +5 total charge. Although these differences may seem considerable, variations of the $\langle r^2 \rangle$ values in the range of optimal stabilization potential are much smaller.

TABLE II. The errors (eV) in ST gaps for the DIP method stabilized by the increased nuclear charge. The errors are computed as $E_{\text{DIP}} - E_{\text{ref}}$, where E_{ref} is the SF value computed without the stabilization potential and in the same basis set. In parenthesis, the perturbation of the SF energies by the stabilization potential is reported (computed as $E_{\text{SF}} - E_{\text{ref}}$, where E_{SF} is the SF value computed with the same basis and with the stabilizing potential). E_{HOMO} is the HOMO energy (hartree). The 6-311(2+,2+)G(2df,2pd) basis set is used for methylene and the 6-311(+,+)G(2df) basis set is used for benzyne. The charge variation parameter characterizes the total positive charge added to a molecule.

Charge	CH ₂	E_{HOMO}	o-benzyne	E_{HOMO}	m-benzyne	E_{HOMO}	p-benzyne	E_{HOMO}
...	-7.54 (0.00)	0.08	-3.49 (0.000)	0.15	-1.55 (0.000)	0.15	-0.06 (0.000)	0.11
0.2	-1.35 (0.08)	0.08	-2.85 (0.020)	0.13	-1.24 (0.036)	0.13	-0.05 (0.025)	0.08
0.6	-0.72 (0.24)	0.06	-1.24 (0.064)	0.08	-0.68 (0.114)	0.07	-0.04 (0.025)	-0.01
0.8	-0.31 (0.33)	0.01	-0.62 (0.087)	0.05	-0.35 (0.155)	0.03	-0.03 (0.024)	-0.05
1.0	0.07 (0.43)	-0.05	-0.42 (0.112)	0.00	-0.18 (0.197)	-0.01	-0.03 (0.023)	-0.09
1.2	0.26 (0.52)	-0.12	-0.24 (0.138)	-0.04	-0.08 (0.244)	-0.06	-0.03 (0.022)	-0.14
1.4	0.40 (0.62)	-0.19	-0.14 (0.165)	-0.09	-0.00 (0.286)	-0.10	-0.03 (0.021)	-0.18
1.6	0.54 (0.72)	-0.28	-0.07 (0.193)	-0.13	0.06 (0.331)	-0.15	-0.03 (0.021)	-0.23

Even for o-benzyne, which exhibits the largest variation of $\langle r^2 \rangle$ among the three benzyne, the values for stabilization potentials of $+5/3.0$, $+5/2.5$, $+5/2.0$ (the total charge/radius in Å) are 449, 436, and 416 bohr², respectively. For methylene [CCSD/6-311(2+,2+)G(2df,2pd), see Fig. 3], the $\langle r^2 \rangle$ value changes more significantly, from 371 (no potential) to 42 bohr² ($+5/2.0$ Å). The above results illustrate that the changes in the diffuse character of the wave function due to the two electrons being detached is blurred by other electrons making the $\langle r^2 \rangle$ -based analysis system-dependent, which undermines its utility as a general diagnostic.

Alternatively, one can consider energy-based criteria. We developed two schemes, one based on the HOMO energy and another – on the HF energy. The HOMO criterion leads to a simple yet effective scheme based on an analysis of the HOMO energies for unstabilized and stabilized HF calculations. The second route leads to a more sophisticated algorithm involving the analysis of the total HF energy that provides the so-called stabilization coefficients allowing one to quantify the degree of stabilization.

Let us begin with the HOMO criterion. Tables I and II report values of the HOMO energies for different stabilizing potentials. Comparing the two stabilization approaches, we note that the scaled nuclear charge method requires smaller lowering of the HOMO energies to achieve a good accuracy of the DIP energies. For the nuclear charge stabilization method, the DIP errors in the range from -0.03 to -0.24 eV are achieved when HOMO energies become negative and approach values around -0.05 hartree. We observe a similar correlation between the HOMO energy and DIP accuracy for the charged cage method, e.g., good accuracy is achieved for HOMO energies of range -0.6 to -0.75 hartrees. Furthermore, the energy difference between the unstabilized and stabilized HOMOs (denoted by Δ_{HOMO}) provides even better diagnostic than just the HOMO energy. We observe the errors below 0.18 eV when $\Delta_{\text{HOMO}} \approx 0.8$ hartree.

Let us now consider an alternative measure of stabilization based on the total HF energy. We observe a strong correlation between the HF energy and the degree of stabilization as illustrated by the plots in Fig. 7. They show the changes in the HF energy in a series of basis sets as one applies the charged cages of the total charge $+3$ and of different sizes. As expected, the smaller the radius is, the flatter the curve becomes. When compared with the neutral curve, starting from the radius of 2.0 Å, the shape of the dianion curves becomes similar to the one of the neutral.

The analogous behavior is observed when the total charge of the cage is increased (Fig. 8). The curves flatten as the charge grows; however, the stabilization increases as the cage shrinks. Although each parameter increases the stabilization, none of them alone is sufficient to achieve a desired level of stabilization. They have to be considered together in the course of preliminary calibration.

The plots of the HF energy indicate that the shape of the curves is, indeed, strongly linked to the stabilization. To develop a more quantitative criterion, one needs a procedure which can compare a given curve with the neutral reference. To establish such a procedure, we first shift the curves to a maximum alignment, as demonstrated for o-benzyne in Fig. 9.

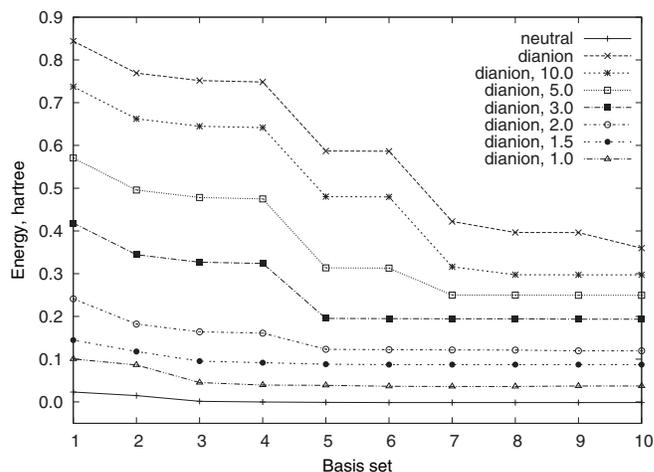


FIG. 7. The total HF energy (hartree) of the 1A_1 state of the dianion and the 3B_1 state of the neutral methylene for the split-valence Pople basis sets with an increasing number of diffuse functions (see Fig. 4). The 1A_1 state is stabilized by the charged cage of the total charge $+3$ varying in the radii (in Å). The energies of the neutral, unstabilized dianion, and dianion stabilized by charged spheres of decreasing radii are shifted by 38.93, 39.2, 39.23, 39.2, 39.23, 39.25, 39.2, and 38.75 hartree, respectively.

One can see that up to a point, which is the largest basis set not containing any diffuse functions, the curves, although not identical, are very similar. After that point they start to diverge proportionally to the degree of the stabilization. Encouraged by this observation, we established the following algorithm of expressing the stabilization numerically:

1. We compute the HF energy difference between the last common point (the point up to which the curves have a similar shape) and the last point (the HF energy in the largest basis set used). The quantity is denoted as Δ_{HF} .
2. We compute the ratio between Δ_{HF} for a given cage and the reference value (in our case it is Δ_{HF} for the lowest

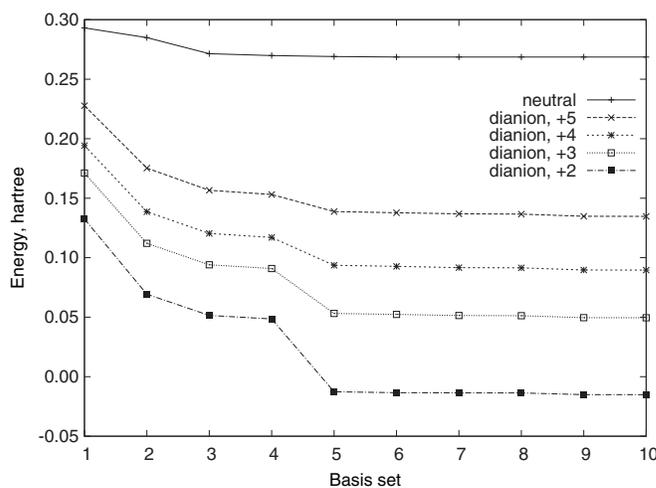


FIG. 8. The HF energy (hartree) of the 1A_1 state of the dianion and the 3B_1 state of the neutral methylene for the split-valence Pople basis sets with an increasing number of diffuse functions (see Fig. 4). The 1A_1 state is stabilized by the charged cage of the radius 2.0 Å varying in the total charge. The energies of the neutral and dianion stabilized by charged spheres of decreasing charge are shifted by 39.2, 38.67, 39.02, 39.18, and 39.12 hartree, respectively.

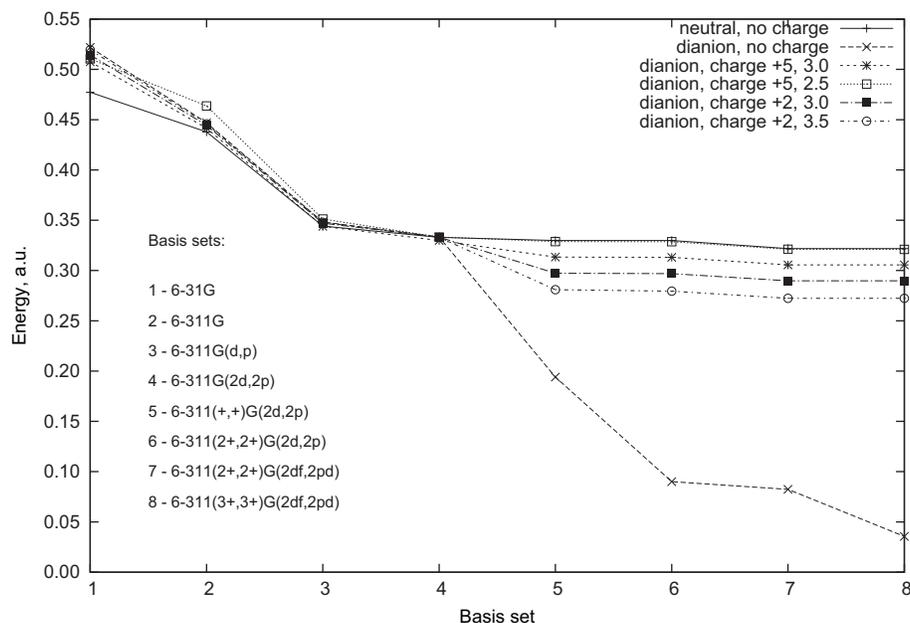


FIG. 9. The HF energy (hartree) of the 1A_1 state of the dianion and the 3B_1 state of neutral o-benzyne for the split-valence Pople basis sets with an increasing number of diffuse functions. The 1A_1 state is stabilized by the charged cage of the total charge +5 varying in the radii (in Å). The curves are shifted vertically for maximum overlap.

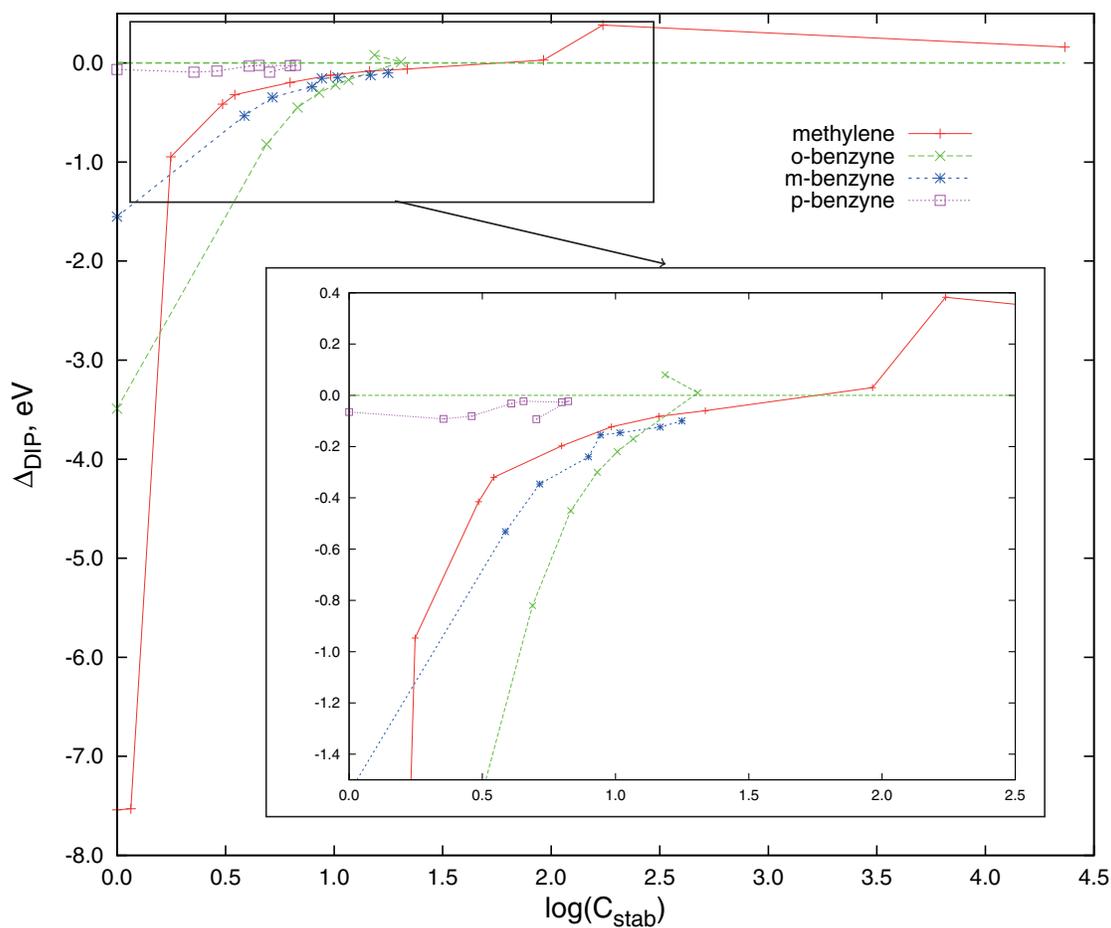


FIG. 10. The dependence of the DIP error on the stabilization coefficient (logarithmic scale) for methylene and benzenes. For methylene, C_{stab} is determined for the 6-311G(2d,2p) and 6-311(4+,4+)G(3df,3pd) basis sets, and for benzenes the basis sets are 6-311G(2d,2p) and 6-311(3+,3+)G(2df,2pd).

triplet state of the neutral). Values much larger than 1.0 indicate no stabilization. The ratio decreases when stabilization increases, and approaches 1.0 for very strong stabilization. The quantity is denoted as D_{Δ} .

3. We compute D_{Δ} for several charged cages and relate them to D_{Δ}^0 , which is unstabilized D_{Δ} . The quantity, called the stabilization coefficient and denoted as C_{stab} , is defined as $C_{\text{stab}} = D_{\Delta}^0/D_{\Delta}$.

To determine the relation between the so defined stabilization coefficient and the DIP accuracy, we perform a number of calculations for our benchmark systems, methylene, and benzyne. We vary the stabilizing potential, compute the respective stabilization coefficients, and calculate the resulting DIP errors. The stabilization coefficient computations employ the 6-311G(2*d*,2*p*) and 6-311(4+,4+)G(3*df*,3*pd*) basis sets for methylene, and 6-311G(2*d*,2*p*) and 6-311(3+,3+)G(2*df*,2*pd*) for benzyne (the two basis sets listed refer to the two calculations required to compute Δ_{HF}). The respective plot is shown in Fig. 10 demonstrating that there is a consistency between the results for different systems, which suggests that a prediction of the optimum stabilization parameters for an arbitrary system is possible. For all the cases except p-benzyne, the DIP errors become smaller than 0.2 eV when C_{stab} is about 10. Therefore, for different systems, there is a regularity in the relation between the stabilization and the DIP accuracy. The p-benzyne example shows that no stabilization is required in this case as the DIP accuracy is not affected by the strength of stabilization potential. Also, C_{stab} does not reach 10 for p-benzyne and, therefore, the algorithm cannot be applied.

The above algorithm produces similar magnitude of errors when applied to other systems, as demonstrated below.

C. Benchmark calculations using optimal stabilization parameters

Finally, we apply the same algorithms for calculating the ST gaps in NH and TMM. The stabilization parameters are determined using the procedure described above, and the C_{stab} values closest to 10 are used for the charged cage method. To compute the stabilization parameters, we use the 6-311G(2*d*,2*p*) and 6-311(3+,3+)G(3*df*,2*pd*) basis sets for NH, and the 6-311G(2*df*,2*pd*) and 6-311(3+,3+)G(2*df*,2*pd*) basis sets for TMM. The DIP calculations are performed us-

TABLE III. Errors (eV) in the ST gaps computed by the DIP method stabilized by the charged cage. The errors are computed as $E_{\text{DIP}} - E_{\text{ref}}$, where E_{ref} is the SF value computed without the stabilization potential and in the same basis set. The errors are computed for the stabilization parameters such that $C_{\text{stab}} \approx 10$. In parenthesis, the radius of the charged cage (\AA) used and its total charge (a.u.) is reported.

System	C_{stab}	E_{HOMO}	DIP/not stabilized	DIP/stabilized
CH ₂ (2.0, +3)	9.6	-0.46	-7.54	-0.12
o-benzyne (3.0, +4)	10.2	-0.46	-3.49	-0.22
m-benzyne (2.75, +4)	10.4	-0.50	-1.55	-0.15
NH (1.65, +3)	9.6	-0.59	-10.60	-0.07
TMM (2.75, +4)	9.5	-0.57	-0.45	-0.03

TABLE IV. Errors (eV) in the vertical excitation energies computed by the DIP method stabilized by the charged cage. The errors are computed as $E_{\text{DIP}} - E_{\text{ref}}$, where E_{ref} is the SF value computed without the stabilization potential and in the same basis set. The errors are computed for the stabilization parameters such that $C_{\text{stab}} \approx 10$. In parenthesis, the radius of the charged cage (\AA) used and its total charge (a.u.) is reported.

System (cage)	E_{HOMO}			
CH ₂ (2.0, +3)	-0.46	1A_1	1B_1	2^1A_1
		-0.12	-0.06	0.02
		1A_1	1B_2	2^1A_1
TMM (2.75, +4)	-0.57	-0.03	-0.17	-0.07
		$^1\Delta$		$1^1\Sigma^+$
		-0.07		-0.11

ing the 6-311(3+,3+)G(3*df*,2*pd*) basis set for NH and 6-311(2+,2+)G(2*df*,2*p*) for TMM. The results are presented in Table III, which also collects the results for previously discussed systems. A spectacular improvement occurs for NH, for which the error exceeding 10 eV is brought down to only -0.07 eV. For TMM the accuracy is also very good. This system is similar to p-benzyne as the error for unstabilized calculations is relatively small. These results confirm the effectiveness of the stabilization technique presented as for all systems the DIP versus SF discrepancies are minimized to about the same level as for a well-behaved reference state.

The HOMO criterion is also working well. Using $\Delta_{\text{HOMO}} \approx 0.8$, we obtain similar improvement in NH and TMM as in methylene and benzyne. The DIP errors (eV) and Δ_{HOMO} 's (hartree, in parenthesis) for CH₂, o-benzyne, m-benzyne, p-benzyne, NH, and TMM, are -0.18 (0.84), -0.17 (0.78), -0.15 (0.78), -0.02 (0.83), -0.11 (0.78), and -0.02 (0.83), respectively. Moreover, the range of Δ_{HOMO} for which the DIP accuracy is satisfactory appears to be relatively broad. Analyzing the HOMO energies reported in Tables III and IV, one can see that the DIP errors are brought down to a range from -0.03 to -0.22 eV by Δ_{HOMO} smaller than 0.8, starting with 0.55 hartree (methylene). Hence, there is a relatively broad range of Δ_{HOMO} , about 0.5-0.8 hartree for which the stabilization is effective enough to provide DIP energies with errors of about 0.2 eV or smaller.

We also consider other electronic states of TMM, methylene, and NH (Table IV). The same optimal stabilization potentials as described above are used. For the three states considered (two in the case of NH as the two singlet states are degenerate), the average absolute error against SF is only 0.08 eV, with the largest deviation of 0.17 eV. Thus, the stabilizing potential appears to perturb different electronic states of the neutral to a similar extent. These results suggest that DIP stabilized by an optimum stabilization potential provides results of a similar quality to the SF method.

IV. CONCLUSIONS

We investigated problematic behavior of the EOM-DIP method employing unstable dianion reference states. As the basis set increases, the lowest energy solution (of both HF

and CCSD equations) becomes more and more diffuse approximating an electron-detached state of the system. Such reference wave functions are ill suited for the DIP expansion, which manifests itself numerically in very large errors in energy differences between the target states of the neutral (e.g., sometimes 10 eV and more). This presents a serious stumbling block for practical applications of DIP.

The problems with unstable references go beyond HF procedure and cannot be easily and reliably addressed by using alternative (localized) HF solutions, as the e^{T_1} part of the CC operator expansion is able to perform a unitary transformation of HF orbitals yielding a delocalized dianionic wave function, which usually results in a divergent CCSD procedure.

To overcome these problems, we employ the charge stabilization technique. We adopt two schemes, scaled nuclear charges and charged cage methods. Our numerical examples illustrate that accuracy of DIP can be improved by using stabilized references, however, errors in the target state energy differences may be introduced due to perturbation of the neutral states by the stabilizing potential. We found that errors in energy differences between the target states of about 0.2 eV can be induced by the stabilizing charged sphere. Thus, ideally one should use the weakest stabilizing potential.

We propose two algorithms for determining optimal stabilization parameters *a priori*. One algorithm is based on the analysis of the dianion HF energy. The results demonstrate that following this numerical recipe, one can compute DIP energies with the accuracy of about 0.2 eV or better. The additional cost of this calibration is a negligible part of the overall cost of the DIP calculations as only several additional HF computations are required. The second approach is based on the HOMO energy. We observe an optimal stabilization when the HOMO energy becomes sufficiently negative. We find that the stabilization resulting in 0.5–0.8 hartree change in the HOMO energy yields accurate results.

Although stabilization approach described here offers a solution to unstable references, a number of issues remain. Ideally, one would need to develop an automated procedure of determining the optimal stabilization parameters and an algorithm for estimating perturbation due to stabilization, such that a correction can be applied to the target neutral states. This will be addressed in a future work. As indicated by our results, the errors due to the stabilizing potential are not very large in virtue of error cancellation when vertical energy differences are computed. However, one may expect larger errors in a different type of calculations, e.g., adiabatic excitation energies when the two states would correspond to different molecular geometries and, therefore, could be affected differently by the stabilization potential. Another problem with using stabilization is derivative and properties calculations.

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