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Size consistent formulations of the perturb-then-diagonalize Møller-Plesset perturbation theory correction to non-orthogonal configuration interaction

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In this paper we introduce two size consistent forms of the non-orthogonal configuration interaction with second-order Møller-Plesset perturbation theory method, NOCI-MP2. We show that the original NOCI-MP2 formulation (Yost, S. R. and Kowalczyk, T. and Van Voorhis, T. *J. Chem. Phys.* **193**, 174104 (2013)), which is a perturb-then-diagonalize multi-reference method, is not size consistent. We also show that this causes significant errors in large systems like the linear acenes. By contrast, the size consistent versions of the method give satisfactory results for singlet and triplet excited states when compared to other multi-reference methods that include dynamic correlation. For NOCI-MP2 however, the number of required determinants to yield similar levels of accuracy is significantly smaller. These results show the promise of the NOCI-MP2 method, though work still needs to be done in creating a more consistent black-box approach to computing the determinants that comprise the many-electron NOCI basis.

Keywords: Acenes, Multi-reference Perturbation Theory, Non-Orthogonal Configuration Interaction

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I. INTRODUCTION

In electronic structure theory, the mean field Hartree-Fock (HF) method captures almost 99% of the total electronic energy with its single determinant wavefunction. The last 1% is defined as the correlation energy, and while the correlation energy is small relative to the total energy, it nonetheless contains many important physical effects in molecular systems¹⁻³. The electron correlation energy can be roughly categorized into two types. The first is called static/strong electron correlation, and is associated with strong mixing between different determinants, so that when such effects are present, the use of just one determinant (i.e. HF theory) is qualitatively incorrect. Examples of molecular systems with strong correlations include antiferromagnetically coupled transition metal atoms⁴, single biradicaloid organic molecules⁵, and some conjugated organics such as the longer acenes^{6,7}. The second type of correlation energy is called dynamic/weak electron correlation, and it is associated with the dynamic instantaneous interaction of electrons with each other beyond a mean field approximation. Effects of dynamic correlation range from contributions of about 1 eV per electron pair, to chemical bond energies, to the entire long-range Van der Waals attraction^{8,9}.

Since the correlation energy in many systems is a small fraction of the total energy, it is often a reasonable approximation to apply perturbation theory, where the perturbation is the instantaneous interaction between electrons. The commonly used form of perturbation theory is Møller-Plesset perturbation theory, which mainly captures dynamic correlations^{10,11}. Other methods that describe dynamic correlations include the coupled-cluster (CC) and configuration-interaction (CI) methods, though unlike perturbation theory and CC theory the truncated CI methods are not size consistent^{12,13}. These methods can be truncated at many different excitation levels that include single, double, triple, or higher excitations out of the HF reference. In molecular systems without strong correlation, CC methods that include at least triple substitutions can approach quantitative results for the energy and molecular properties^{14,15}.

In order to adequately describe strong correlation in a molecular system one needs to go beyond single determinant based methods. The most common way to go beyond a single determinant approximation is to use active space based methods either within molecular orbital theory or in valence bond methods. The many-electron basis functions in the valence bond approach^{16,17} often resemble Lewis structures and can be very effective for breaking

chemical bonds and describing other strong correlation effects, but going beyond small numbers of strongly coupled pairs of electrons can become computationally prohibitive without additional approximations^{18,19}. The typical active space method within molecular orbital theory is the complete active space self consistent field method (CASSCF)^{20,21}. In CAS methods, a set of active orbitals is selected, and a full CI expansion is carried out within the resulting active space. Similarly the Spin-Flip (SF) method defines the active space by starting with a high spin reference and using the singly occupied orbitals as the active space orbitals^{22–26}. For example, a triplet reference yields a (2,2) active space, which is the same active space size as CAS(2,2) but with different orbitals.

Quantitative treatment of both types of correlation energy requires a combination of the strong and weak correlation methods mentioned above. In the SF approach there are a variety of methods that use CC theory^{27,28}, or take a perturbation approach^{24,29,30}. CASSCF also uses perturbation theory to include the weak correlation energy with a diagonalize-then-perturb approach, called the CASPT2 method^{31,32}. These multi-reference correlation theories can be quite accurate for many different molecular systems^{33–35}.

All of the correlation methods mentioned are capable of computing excited states as well. In the case of CC theory and SF-CC one can apply the equation of motion approximation to compute the excited states^{23,36}. For CASSCF/CASPT2 the excited states are often computed by “state averaging”, where the optimized electronic energy during the CASSCF procedure is a weighted average of the ground state and one or more selected excited states³⁷. Even so, to compute excited states near conical intersections and avoided-crossings the multi-state CASPT2 method is required because the perturb-then-diagonalize approach in CASPT2 collapses the different states at these points on the potential energy surface^{38,39}.

But a problem for any of these active space methods is the cost as the size of the active space grows; exponentially with the number of active space orbitals/electrons. One potential solution is to use a restricted active space approach, such as RASSCF for CASSCF and RAS-SF for SF, to reduce the number of configurations^{25,26,40}. Reduced active space methods can be just as accurate as their non-reduced counterparts because complete active spaces often include many unnecessary determinants in the total wavefunction that do not contribute significantly to the desired energy or property. In general, it would be very useful to avoid the extra computational work required from including all of the “deadwood” determinants^{41,42}.

All of the methods mentioned use a single set of orbitals to construct all determinants

used to describe the ground and excited states. For the case of the excited states, this typically means the excited state determinant is constructed from ground state orbitals, and thus there is a lot of neglected orbital relaxation that needs to be captured by the correlation method. One method that treats the excited states more equally with the ground states and captures the missing orbital relaxation in the excited state is the non-orthogonal configuration interaction (NOCI) method^{43,44}. In the NOCI method each determinant is optimized at the HF level, yielding a different set of orbitals for each determinant. As a result, many of the weakly correlated determinants that are necessary in other multi-reference methods are not needed in the NOCI case because the effect of those determinants has been wrapped up in the orbital relaxation in each determinant. In favorable cases, the retained non-orthogonal determinants can resemble diabatic states (e.g. ionic and covalent determinants) so that simple NOCI wavefunctions may also have quite clear physical content. It is worth noting that the use of non-orthogonal orbitals has also been studied in the valence bond framework. The breathing orbital valence bond (BOVB) method allows the orbitals to relax and differ between different valence bond basis states, and it shows much improvement over other valence bond methods^{45,46}.

The NOCI method has been shown to do very well for excited states when compared to other methods that use a much larger set of determinants. Sundstrom et al. showed that with 10 HF determinants they obtained results comparable to SF-XCIS and CASCI-MRMP⁴⁴. But while the orbital relaxation in each NOCI determinant captures some of the missing electron correlation energy it cannot capture it all when using a small number of NOCI states. The missing correlation energy will be primarily dynamical in nature as long as the set of NOCI determinants includes all essential correlations. Efficiently recovering this missing correlation energy is a suitable task for perturbation theory.

The perturbation expansion for NOCI has been previously worked out in a perturb-then-diagonalize approach^{47,48}. The NOCI-MP2 method (also called Δ SCF(2)) has been shown to compute excited states with similar accuracy to CASPT2. Since NOCI-MP2 is a perturb-then-diagonalize method, it can properly treat avoided crossings and conical intersections^{48,49}, unlike standard CASPT2. But while the NOCI and NOCI-MP2 methods require far fewer determinants than typical CAS methods, each of those determinants needs to be picked and individually optimized. This requires the user to provide *a priori* information about the desired electronic states. In cases where one knows the types of excitations

that are relevant this is not a major drawback and the NOCI-MP2 method can yield very good results. However, NOCI-based methods are generally not black-box in nature.

A potentially serious problem is that unlike NOCI itself, the original formulation of the NOCI-MP2 method is not size consistent. Size consistency is often an issue in multi-reference perturbation theory methods^{50,51}. Even though multi-reference methods like CASSCF and NOCI are size consistent, and perturbation theory methods like MP2 are size consistent; the combination of the two are not guaranteed to be size consistent. The original formulations of multi-reference perturbation theory (MR-PT) were indeed not size consistent⁵². But with the right choice of the zeroth-order Hamiltonian⁵³ methods like the n -electron valence perturbation theory⁵⁴ method and others^{55,56} can be formally size consistent. The issue of size consistency for NOCI-MP2 is addressed in the theory section of this paper, where we show the origin of the size inconsistency, and how that problem can be removed. Then we will present numerical results to show how the size consistent variants of NOCI-MP2 compare to the size inconsistent version, and discuss the accuracy of these approaches relative to other highly correlated methods.

II. THEORY

The notation used in the rest of this paper is as follows. The NOCI determinants are labeled as Ψ and superscripts $A, B, C, \dots$ will be used to indicate different HF states that each have their own set of unique orbitals. Indices $i, j, \dots$ are used for occupied orbitals; $a, b, \dots$ are used for virtual orbitals; and $p, q, \dots$ are used for all orbitals. All repeated indices are implicitly summed over, following the Einstein convention.

A. The NOCI-MP2 method

The NOCI-MP2 method starts from a set of non-orthogonal HF determinants, $\{|\Psi^{(0)}\rangle\}$. The Hamiltonian and overlap matrices are then formed and the secular equation, $\mathbf{HC} = \mathbf{SCE}$, is solved to obtain the final energies and wavefunctions. Since each determinant in the NOCI basis is a solution to its own HF equation, each HF wavefunction can be expanded in the typical Møller-Plesset perturbation theory fashion. Retaining just the reference and the lowest order correction to the wavefunction yields a set of corrected wavefunctions,

$\{|^A\Psi\rangle\} = \{|^A\Psi^{(0)}\rangle + |^A\Psi^{(1)}\rangle\}$. The CI Hamiltonian and overlap matrix elements then become

$$\langle ^A\Psi|\hat{H}|^B\Psi\rangle = \langle ^A\Psi^{(0)}|\hat{H}|^B\Psi^{(0)}\rangle + \langle ^A\Psi^{(0)}|\hat{H}|^B\Psi^{(1)}\rangle + \langle ^A\Psi^{(1)}|\hat{H}|^B\Psi^{(0)}\rangle + \langle ^A\Psi^{(1)}|\hat{H}|^B\Psi^{(1)}\rangle \quad (1)$$

$$\langle ^A\Psi|^B\Psi\rangle = \langle ^A\Psi^{(0)}|^B\Psi^{(0)}\rangle + \langle ^A\Psi^{(0)}|^B\Psi^{(1)}\rangle + \langle ^A\Psi^{(1)}|^B\Psi^{(0)}\rangle + \langle ^A\Psi^{(1)}|^B\Psi^{(1)}\rangle \quad (2)$$

In order to keep the computational cost on the order of conventional MP2, we keep the leading correction terms (which are second order) and drop the last (third order) term on the RHS of Eq. (1). Similarly in the overlap matrix element, we drop the final (second order) term in Eq. (2). The correction terms are then averaged to ensure that the diagonal of the Hamiltonian is the MP2 energy for the given determinant, and that the Hamiltonian and overlap matrices are Hermitian. This gives the original NOCI-MP2 ansatz and working set of equations

$$\langle ^A\Psi|\hat{H}|^B\Psi\rangle = \langle ^A\Psi^{(0)}|\hat{H}|^B\Psi^{(0)}\rangle + \frac{1}{2} \left(\langle ^A\Psi^{(0)}|\hat{H}|^B\Psi^{(1)}\rangle + \langle ^A\Psi^{(1)}|\hat{H}|^B\Psi^{(0)}\rangle \right) \quad (3)$$

$$\langle ^A\Psi|^B\Psi\rangle = \langle ^A\Psi^{(0)}|^B\Psi^{(0)}\rangle + \frac{1}{2} \left(\langle ^A\Psi^{(0)}|^B\Psi^{(1)}\rangle + \langle ^A\Psi^{(1)}|^B\Psi^{(0)}\rangle \right) \quad (4)$$

To evaluate the correlation corrections in the above matrix elements we insert the identity, $1 = |^A\Psi\rangle\langle ^A\Psi| + |^A\Psi_i^a\rangle\langle ^A\Psi_i^a| + |^A\Psi_{ij}^{ab}\rangle\langle ^A\Psi_{ij}^{ab}| + \dots$, so we can solve the Hamiltonian matrix elements with the same state for the bra and the ket. The final set of working equations for the MP2 like terms are

$$H_{MP2} = \langle ^A\Psi^{(0)}|\hat{H}|^B\Psi^{(1)}\rangle = \frac{1}{4}t_{ij}^{ab}E_A^{HF}\langle ^A\Psi^{(0)}|^B\Psi_{ij}^{ab}\rangle + \frac{1}{16}\langle kl||cd\rangle t_{ij}^{ab}\langle ^A\Psi_{kl}^{cd}|^B\Psi_{ij}^{ab}\rangle \quad (5)$$

$$S_{MP2} = \langle ^A\Psi^{(0)}|^B\Psi^{(1)}\rangle = \frac{1}{4}t_{ij}^{ab}\langle ^A\Psi^{(0)}|^B\Psi_{ij}^{ab}\rangle \quad (6)$$

where $t_{ij}^{ab} = \frac{\langle ia||jb\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$. This yields what will be referred to in the rest of the paper as NOCI-MP2 version 0. The details of how to compute the NOCI and NOCI-MP2 energies have been given in earlier work^{44,48}. While NOCI itself has been shown to be size consistent⁴⁴, the question of whether or not after the MP2 correction is the method still size consistent has not been addressed.

B. Size consistency

For size consistent methods, the total energy of a system of non-interacting molecules is just the sum of the energies of each molecule. This is a seemingly trivial requirement,

but many truncated CI methods fail to be size consistent (e.g. consider CISD which is exact for a single H_2 molecule, but not exact for two non-interacting H_2 molecules since its exact wavefunction is CISDTQ). Many multi-reference perturbation theories also fail to be size consistent⁵². Size consistency is a key property that useful electronic structure methods should satisfy. Because bimolecular chemical reactions involve two different molecules coming together, possibly forming intermediates, passing through one or more transition structures, and finally yielding one or more product molecules.

Consider a model system composed of two non-interacting atoms, Be and He. We will assume that there are two different non-aufbau states where the non-aufbau occupations occur only on Be. Because the atoms are non-interacting the total wavefunction is a product of the He and Be wavefunctions ($\Psi_{tot} = \Psi_{(Be)} \otimes \Psi_{(He)}$), so all wavefunctions have the same set of He orbitals. The question of size consistency can be answered by examining how the Hamiltonian and overlap matrices change for Be when the He atom is added to the system. The diagonal of the Hamiltonian and overlap matrices are just the total supersystem energy and 1, respectively, due to HF and MP2 being size consistent methods. The off-diagonal terms are not as obvious.

First let us look at the correlation contribution to the off-diagonal overlap matrix element in Eq. (6). Since both HF states have common orthonormal He orbitals, non-zero contributions to Eq. (6) can arise only when all excitation indices are on the Be atom. For instance, if the excitations occur on the He atom, the overlap between states A and B becomes

$$\frac{1}{4}t_{ij}^{ab}\langle^A\Psi^{(0)}|^B\Psi_{ij}^{ab}\rangle = \frac{1}{4}t_{ij}^{ab}\langle^A\Psi_{(Be)}^{(0)}\Psi_{(He)}^{(0)}|^B\Psi_{(Be)}^{(0)}\Psi_{(He)ij}^{ab}\rangle \quad (7)$$

As He has common orthonormal orbitals in both states, the overlap is zero from the He term. The non-zero case is when the double excitation is on the Be atom, which yields the unchanged MP2 off-diagonal overlap for Be. Therefore the overlap is unchanged by the introduction of the non-interacting He atom.

The MP2 coupling in Eq. (5) is composed of two parts: the first is just the MP2 overlap multiplied by the total HF energy, and the second is the more complicated term with four different electron excitations. The first part is only changed by the fact that the HF energy becomes the sum of the He and Be HF energies, so we only need to consider the second term:

$$\frac{1}{16}\langle kl||cd\rangle t_{ij}^{ab}\langle^A\Psi_{kl}^{cd}|^B\Psi_{ij}^{ab}\rangle \quad (8)$$

In Eq. (8) there are two different two electron integrals, and so we have four different non-trivial cases, shown in Table I, that need to be considered. In the first case, where all excitations occur on the Be atom, Eq. (8) is unchanged and we just get back the MP2 Hamiltonian matrix element for Be, H_{MP2}^{Be} . Now if all of the excitations are on He, the only situation where the coupling is non-zero is when $i = k, j = l, a = c, b = d$, and this just yields the MP2 energy of He times the HF overlap of the two states. Finally for cases 3 and 4 of Table I, Eq. (8) is equal to 0 because (as in the case of the MP2 overlap) the overlap of the He wavefunction will be 0.

Combining the different contributions yields the modified secular equation after the addition of a non-interacting He atom

$$(\mathbf{H}_{MP2}^{\text{Be}} + E_{HF}^{\text{He}} (\mathbf{S}_{\text{HF}} + \mathbf{S}_{MP2}^{\text{Be}}) + E_{MP2}^{\text{He}} \mathbf{S}_{\text{HF}}) \mathbf{c} = (\mathbf{S}_{MP2}^{\text{Be}} + \mathbf{S}_{\text{HF}}) \mathbf{c} \mathbf{E} \quad (9)$$

where E_{HF}^{He} and E_{MP2}^{He} are the He HF and MP2 energy, respectively, and the bold labels indicate matrix quantities. The matrix elements of $\mathbf{H}_{MP2}^{\text{Be}}$ and $\mathbf{S}_{MP2}^{\text{Be}}$ are defined in Table I and by Eq. (6), respectively, and the matrix elements of $\mathbf{S}_{\text{HF}}$ are just the NOCI overlap matrix elements. It is easy to see that the HF energy of He can be moved to the RHS of Eq. (9) and just subtracted from the total energy $\mathbf{E}$. But the MP2 energy of He is only multiplied by the HF NOCI overlap, $\mathbf{S}_{\text{HF}}$. The MP2 energy of He is never multiplied by the MP2 overlap because that contribution is a third-order term, which was dropped when the third-order term in the coupling was dropped.

The non-size consistency of NOCI-MP2 version 0 is illustrated numerically by the results for the energies of Be + N_{He} non-interacting (i.e. remote) He atoms, shown in Figure 1. The set of NOCI determinants consists of the ground state, the two HOMO→LUMO single excitations, and the HOMO→LUMO double excitation on Be, which is equivalent to a (2,2) CAS active space. Figure 1 plots the size consistency error, defined as

$$\Delta E = E_{\text{total}}(\text{Be} + N_{\text{He}}) - E_{\text{Be}} - N_{\text{He}} * E_{\text{He}} \quad (10)$$

versus N_{He} . The results, which should be zero, instead show a linear dependence on the number of He atoms. In the simple case of only two NOCI states on Be, the size consistency error can be worked out to $\Delta E = -E_{MP2}^{\text{He}} \left(\frac{S_{MP2}}{1+S_{MP2}} \right)$. E_{MP2}^{He} is the MP2 correlation energy of He and S_{MP2} is the MP2 overlap between the two Be states. This is why we see a linear dependence on the size consistency error with the number of He atoms.

In the original reports^{47,48} on NOCI-MP2, the method was tested on a number of small systems. For those cases, no significant size consistency error is evident. This is mainly due to the fact that the error in the original method is proportional to the MP2 correlation energies of the systems multiplied by the MP2 overlap. In the test cases reported, this is a relatively small number and does not cause major problems in the accuracy of the results. But as we have shown, the method is formally size inconsistent with errors that may grow with the magnitude of the MP2 correlation energy.

There are two different ways to fix the size consistency issues in NOCI-MP2. The simplest way, which in the rest of the paper will be referred to as version 1, is to just set the MP2 overlap, Eq. (6), to zero. The MP2 coupling is then just equal to Eq. (8). Another option to make the NOCI-MP2 method size consistent is to add the third order coupling term back into the Hamiltonian. The full third order term is computationally prohibitive, but an approximate form of the term will suffice to restore size consistency. To solve the third order coupling matrix element, as before, one must first insert the resolution of the identity as the expansion in the basis $^A\Psi$ as $1 = |^A\Psi\rangle\langle^A\Psi| + |^A\Psi_i^a\rangle\langle^A\Psi_i^a| + |^A\Psi_{ij}^{ab}\rangle\langle^A\Psi_{ij}^{ab}| + \dots$ to give

$$\begin{aligned} \langle^A\Psi^{(1)}|\hat{H}|^B\Psi^{(1)}\rangle &= \langle^A\Psi^{(1)}|\hat{H}|^A\Psi\rangle\langle^A\Psi|^B\Psi^{(1)}\rangle + \langle^A\Psi^{(1)}|\hat{H}|^A\Psi_k^c\rangle\langle^A\Psi_k^c|^B\Psi^{(1)}\rangle \\ &\quad + \langle^A\Psi^{(1)}|\hat{H}|^A\Psi_{kl}^{cd}\rangle\langle^A\Psi_{kl}^{cd}|^B\Psi^{(1)}\rangle + \dots \end{aligned} \quad (11)$$

The simplest approximation to this term is to terminate the RHS of Eq. (11) after the first term, which yields

$$\langle^A\Psi^{(1)}|\hat{H}|^B\Psi^{(1)}\rangle \cong t_{kl}^{cd}t_{ij}^{ab}\langle^A\Psi_{kl}^{cd}|\hat{H}|^A\Psi\rangle\langle^A\Psi|^B\Psi_{ij}^{ab}\rangle = E_{MP2}^A t_{ij}^{ab}\langle^A\Psi|^B\Psi_{ij}^{ab}\rangle \quad (12)$$

This is interesting because it gives exactly the term missing from the NOCI-MP2 equations to make it size consistent. Adding this term gives what will be called in this paper version 2 of the NOCI-MP2 method. The form of the MP2 corrections to the NOCI-MP2 Hamiltonian and overlap for all three versions are summarized in Table II.

As discussed by Sundstrom et. al. for the NOCI method⁴⁴, the size consistent versions of the NOCI-MP2 method can also be size intensive for excitation energies. But to keep the method size intensive for interacting subsystems requires a non-linear increase in the number of required NOCI states. For example, in the case of two identical interacting systems, to keep the excitation energies size intensive requires the square of the original number of NOCI states.

C. NOCI States

Like the NOCI method, the NOCI-MP2 method requires one to first define and converge all the different HF states that are relevant to the multi-reference states of interest. For many simple excited states it is easy to determine which non-aufbau states are required to obtain the minimum description of the desired ground or excited state, as most dramatically exemplified by single non-aufbau HF determinant descriptions of excited states⁵⁷⁻⁶². But this is not always the case, particularly for multi-reference problems. Furthermore it can also be difficult to converge the non-aufbau states. One established way to converge a non-aufbau state is to use the maximum overlap method (MOM) to force the occupation of the orbitals to be based on the best overlap with the previous iteration (or a given starting state) instead of energy ordering⁵⁹. In many cases, we have found this to work quite well to obtain the desired state.

To go further, it is desirable to make the NOCI-MP2 method easier to reproduce and more black-box. We would also like to have the option of being able to specify in a straightforward manner which non-aufbau states are potentially important before starting a given calculation. One way to do so is via a connection to orbital active spaces, and for this purpose we utilize the Spin-Flip (SF) method. A SF calculation begins with a high spin reference that is converged in restricted open shell HF (ROHF). To target a multi-reference ground state, the ROHF state is chosen to be the highest multiplicity configuration that is low in energy. The active space is defined by the singly occupied orbitals of the ROHF determinant.

From the ROHF state, we flip enough spins within the active space to access the lowest M_S value, and all determinants obtained this way are converged as HF states, relaxing the core orbitals whilst freezing the active orbitals. These determinants are straightforward to converge, and are those used as the NOCI states in the SF-NOCI method⁶³. Once those states are converged, we unfreeze the active orbitals and do an unrestricted HF (UHF) calculation to compute the fully optimized NOCI states. All calculations reported in the Results section are based on single spin flip calculations (i.e. a triplet high spin reference). In all cases this step-wise convergence approach is able to converge all of the HF states. Most states converged with the DIIS algorithm⁶⁴ without MOM, and the rest converged with the addition of MOM or by changing the SCF algorithm to other methods such as GDM⁶⁵.

III. RESULTS AND DISCUSSION

Most electronic structure methods focus on the ground state. An advantage of the NOCI-MP2 method is that the ground and excited states are treated on a relatively equal footing because orbital optimization is performed for each NOCI determinant, rather than for a target state such as a multi-reference ground state. While the NOCI-MP2 method can also be used to compute strongly correlated ground states, it is just as appropriate to use the method to model excited states (i.e. conical intersections). In this section we focus on the accuracy of the NOCI-MP2 method for different triplet and singlet excited states in the linear acenes and a set of small and medium-sized diradicaloid molecules. All calculations were performed using a development version of the Q-Chem program package^{66,67}.

A. Linear Acenes

The first system we look at is a set of linear acenes ranging in size from naphthalene to pentacene. The relative energy of the lowest triplet and singlet excited state energies in the linear acenes are very important to their function in organic electronic devices. Their relative energies shift as a function of the number of fused rings, such that the larger acenes, tetracene and pentacene, undergo singlet fission within picoseconds upon photo-excitation^{68,69}. Singlet fission is the process where a singlet excited state decays into two lower energy triplet states on separate molecules^{70,71}. Using these molecules in photovoltaic devices makes it possible to go beyond the Shockley-Queisser⁷² limit by doubling the current for a given photon^{73,74}. Here we look at NOCI-MP2 calculations of the triplet and singlet excitation energies in the acenes and compare the results with CASPT2 values^{33,75}, shown in Table III. All of the NOCI-MP2 calculations were done using the def2-TZVP basis, which should be adequate to describe the ground state and these valence excitations. Benzene was not included in this set because the (2,2) active space we use is not large enough to correctly treat the degeneracy in its HOMO and LUMO levels.

The first set of results corresponding to the top half of Table III correspond to the direct implementation of the three versions of NOCI-MP2 discussed above. There is a very pronounced failure of NOCI-MP2 v0 and NOCI-MP2 v2 for naphthalene. This is due to a very small HOMO→LUMO gap in the doubly excited non-aufbau determinant. In

naphthalene this HOMO→LUMO gap is 0.007 Hartrees, while in other molecules the gap is typically greater than 0.4 Hartrees. It is only the size consistent version of NOCI-MP2 that does not include the MP2 overlap term (NOCI-MP2 v1) that yields reasonable results for the small gap systems. Typically the issue of a small gap is addressed in perturbation theory by either using quasi-degenerate forms of perturbation theory^{76,77} or introducing an empirical energy level shift to regularize the amplitude equations^{78,79}. While we won’t focus on this here, it is encouraging to see that NOCI-MP2 v1 is significantly less sensitive to very small orbital energy gaps, and we note that more reasonable results can be obtained through some type of level shift correction.

The bottom half of the results in Table III are obtained by deleting all double substitutions that take place solely in the two orbital active space that is defined by the SF method. For these triplet reference cases, this means there are no double excitations that only occur between the HOMO and LUMO of the molecule. Since at the NOCI level we are performing Full CI within a determinant space that is derived by relaxation from the two orbital active space, the MP2 corrections within the active space have, to a considerable extent, already been treated at the reference level. Indeed, if the NOCI relaxation was zero, these terms would be strictly double-counted, and thus should be excluded. In the presence of relaxation of the individual determinants, it is not clear on formal grounds whether or not to include MP2 terms that lie entirely within the active orbitals. It is therefore interesting to test the numerical consequences of excluding these “double-counting” terms, particularly because we can anticipate that their exclusion will also remove the small orbital energy gap in the doubly excited non-aufbau determinant of naphthalene from the MP2 expansion. We will refer to this as a restricted NOCI-MP2 calculation and use the short hand of rvX for the different restricted version of NOCI-MP2.

Comparing the top versus the bottom part of Table III reveals that NOCI-MP2 v0 and v2 behave dramatically better for naphthalene with the double-counting terms removed. This is obviously because we are removing the small orbital energy gap from the MP2 expansion. While the removal of the double-counting terms in the MP2 expansion doesn’t fix the size consistency issue, it is interesting that it greatly improves the NOCI-MP2 v0 results. NOCI-MP2 v0 with all terms included performed very poorly not only for naphthalene, but also for the larger acenes which did not actually suffer from the near zero HOMO-LUMO gap in the doubly excited determinant. In these cases the excited singlet is actually located below

the triplet with qualitatively poor excitation energies. But once the active space correlation is removed, NOCI-MP2 v0 gives qualitatively similar results to the size consistent versions.

Focusing on the singlet excitation energies ($1^1A_g \rightarrow 1^1B_{2u}$) from the bottom part of Table III, there are several comments to be made. First, the singlet excitation energies for all the acenes are quite accurate, with small deviations of only about 0.2 eV from CASPT2 results. Considering that these systems have increasing levels of biradicaloid character in the ground state, and are therefore more difficult for conventional single reference methods, these are encouraging results. It is particularly encouraging that the NOCI-MP2 results use only the 4 determinants derived from the (2,2) active space, while the CASPT2 results use up to a (22,22) active space, which has over 10^{11} determinants. These 4 relaxed determinants are appropriate for a balanced description of the singlet ground state and the 1^1B_{2u} singlet excited state in the acene series. 1^1B_{2u} is the lowest excited state in all of the acenes except naphthalene, where the 1^1B_{3u} state at 4.24 eV is lower. To properly capture this state we would have needed to use the relaxed determinants corresponding to a (4,4) active space⁸⁰, and this also holds true for the lowest triplet excited state.

For the excitation energies from the 1^1A_g ground state to the 1^3B_{2u} triplet excited state, NOCI-MP2 rv1 and rv2 have similar errors of 0.2 to 0.4 eV with respect to the CASPT2 results. In all cases the MP2 correction lowers the triplet excitation energy by approximately 0.2 eV, while the NOCI error decreases as the acenes get larger. This indicates that for the larger acenes the contribution of the HOMO→LUMO excitation in the 1^3B_{2u} state increases. Indeed we find that at the CIS level, the percent of HOMO→LUMO excitation in the 1^3B_{2u} state rises from 70% to 80% from naphthalene to pentacene.

The single reference high spin, $M_s = \pm 1$, unrestricted and restricted-open-shell MP2 triplet energies are given alongside the NOCI-MP2 rv1 and CASPT2 results in Table IV. The restricted-open-shell MP2 triplet energies compare surprisingly well with the multi-reference methods. Not surprisingly, unrestricted MP2 does very poorly because of the spin contamination that grows with the size of the acene. Even though NOCI-MP2 is constructed from unrestricted determinants, the multi-reference low spin triplet state, which is composed of the HOMO→LUMO excited determinants, does not suffer from the same spin contamination issues as UMP2.

It is well-known that the character of the 1^3B_{2u} states are covalent, while the 1^1B_{2u} states are ionic⁸⁰. This leads to systematic differences in the behavior of the NOCI and NOCI-

MP2 results for triplet and singlet excitations. At the NOCI level, all excitation energies are overestimated, but we find better results for the covalent 1^3B_{2u} states relative to the ionic 1^1B_{2u} states. This can be understood as arising due to better cancellation of correlation effects between the covalent ground state and the covalent triplet excited states. On the other hand, the NOCI-MP2 rv1 and rv2 results are able to yield a much better balanced description of both the singlet and triplet excitations, as referenced against CASPT2. Errors at the NOCI-MP2 level are in fact slightly smaller for the singlet excitations than the triplet excitations. Thus MP2 stabilization of the ionic states is correctly greater than for the covalent states.

Summarizing, the first lesson of these NOCI-MP2 calculations on the acenes is that it is essential to remove “double-counting” errors in cases where the HOMO-LUMO gap becomes smaller than a critical value, perhaps on the order of 0.3 Hartree. It is probably desirable to do so in general when the NOCI configurations are derived from a spin-flipping active space, as we consistently do in this paper. Second, in the restricted size consistent versions of NOCI-MP2 we see that the minimal (2,2) active space is capable of approaching CASPT2 results that used a significantly larger active space size for both the singlet and triplet excited states. A third observation is that for the larger acenes there is essentially no difference between the two different size consistent versions of NOCI-MP2 (v1 and v2). Due to this surprising fact, and that the NOCI-MP2 v1 appears to be significantly less sensitive to small orbital energy gaps and any double-counting effects, we suggest to use the NOCI-MP2 v1 form. In the next section we will only present results for NOCI-MP2 v1, though version 2 also gives similar results.

B. Triplet diradicals and singlet diradicaloids

Organic diradicals and diradicaloids are very interesting molecules for both organic chemists, due to their prevalent nature as an intermediate in chemical reactions, and for theoretical chemists, due to the weakly interacting pair of electrons^{34,81–84}. The weakly interacting pair of electrons can form a singlet or a triplet ground state and which is the lower energy state is very system-dependent. Predicting the correct ground state in these diradical systems requires both strong and weak correlation energy because of the open-shell nature of the electronic states. The multi-reference nature and the fact that the most rel-

evant electronic states are intuitive makes this a promising application for the NOCI-MP2 method.

As noted above we use the SF approach to obtain a (2,2) active space with a total of four different HF determinants that are individually relaxed to form the NOCI state basis. We use the set of molecules created by the authors in reference 85 as our test set, shown in Figure 2. This test set of diradicals contains the different linear alkane and benzyne based molecules shown in Figure 2, as well as C, O, Si, S, CH₂, NH₂, SiH₂, and PH₂. The geometries and SF-EOM-CC energies used are all taken from reference 85. Our final test set did not include N and P because they are a doublet-quartet gap, and we did not include the molecule labeled rC6Cr because the geometry given in the supporting information is not for the same molecule. Finally, trimethylenemethane is not included because the symmetry of the molecule makes it unsuitable for the (2,2) active space we are using. This leaves a total of 23 singlet-triplet gaps, which are composed of vertical and adiabatic gaps as well as singlet and triplet ground states. All of the calculations were run with the same basis set as the SF-EOM-CCSD(dt) results in reference 85, though no frozen core was used in our calculations. The singlet-triplet gaps are computed with NOCI-MP2 v1 and NOCI-MP2 rv1, where again the rv1 form is where no MP2 excitations solely in the active space are included.

One of the molecules in the test set, labeled rC6rC, only contained two HF determinants in the NOCI-MP2 v1 calculation. For this molecule, which has nearly no singlet/triplet gap, the closed shell doubly occupied ground state is a delocalized UHF state that at the NOCI level has a large overlap, 0.5, with the localized open shell states. The localized open shell states have the two unpaired electrons localized on opposite ends of the molecule, which for this molecule are the lowest energy UHF states. In NOCI-MP2 v1 the delocalized doubly occupied state is artificially lowered by 0.2 Hartree by the HOMO→LUMO double excitation due to its 0.07 Hartree gap. We therefore exclude the delocalized closed shell doubly occupied determinant and the doubly excited closed shell determinant to obtain well-behaved NOCI-MP2 v1 results. This approximation is reasonable for rC6rC where the two radical centers are far enough apart that the only two essential determinants are the open shell ones. However, a typical singlet biradicaloid is stabilized by some closed shell contribution, for instance o-benzyne, the lowest singlet state is composed of a mixture of the closed shell doubly occupied determinants and open shell determinants. Just like for the

acenes, this troublesome issue does not occur in the NOCI-MP2 rv1 method since the low gap excitations in the active space are not included in the MP2 expansion.

Table IV shows the full set of singlet-triplet gaps at the highest available level, SF-EOM-CCSD(dt). The singlet-triplet gaps are defined as $E_{ST} = E_S - E_T$, so a positive singlet-triplet gap indicates that the triplet is the lower electronic state. For the other methods, Table IV shows the individual differences relative to the benchmark, as well as the RMSD and average error relative to SF-EOM-CCSD(dt). A positive deviation thus indicates that the method gives a smaller (larger) singlet-triplet gap when the singlet (triplet) is the ground state. The NOCI method shows a significantly positive average deviation of 0.17 eV, reflecting a relative underestimation of the singlet state energy. The RMS value of 0.32 eV is nearly twice as large indicating that there is also significant scatter. The measure of success for NOCI-MP2 is the reduction that can be obtained in both these values.

From Table IV it is clear that the dynamic correlation captured by the NOCI-MP2 correction stabilizes the singlet state more than the triplet state because the average error has the opposite sign as NOCI. Encouragingly, the average error for the rv1 form is six times smaller in magnitude than the NOCI average error (the reduction is a factor of 5 for the v1 correction). The RMSD is also reduced by a factor of more than 4, and is less than twice as large as the error for SF-EOM-CCSD. The near kcal/mol accuracy of NOCI-MP2 rv1 is very promising when considering its scaling of N^5 compared to the N^6 and N^7 scaling of SF-EOM-CCSD and SF-EOM-CCSD(dt), respectively. The main source of the RMSD error is from just a few molecules in the test set, the largest being p-benzyne. If p-benzyne is removed then the RMSD of NOCI-MP2 v1 is reduced to 0.057 eV, which is a 30% reduction.

It should be noted that despite the improvements in converging the NOCI states by using the combined SF/MOM approach there are still cases that require careful inspection to treat correctly. For the o-benzyne molecule we find two different singlet-triplet gaps from using two different initial ROHF triplet guesses. In this case it is the higher energy ROHF triplet that gives a better initial guess for the NOCI states and yields the correct singlet-triplet gap. In general, the molecules with high symmetry are the ones that cause the most difficulties in converging the NOCI states. Overall, like the acenes, Table IV indicates that the NOCI-MP2 rv1 method provides near-quantitative results when correctly applied (i.e. with an appropriate basis of NOCI determinants), and is very robust for a perturbation theory based method. In addition, its lower computational cost makes it very promising for

applications to larger polyradical and polyradicaloid molecules.

IV. CONCLUSION

In this paper we have shown that the original formulation^{47,48} of the NOCI-MP2 method (version 0) is not size consistent and when applied to larger systems this size inconsistency can create catastrophic errors. We presented two different revised formulations (versions 1 and 2) that restore size consistency. We then compared their accuracies for predicting singlet and triplet excitations in acenes ranging between naphthalene and pentacene, and singlet-triplet gaps in a range of biradicaloid atoms and molecules. The difference between NOCI-MP2 version 1 and NOCI-MP2 version 2 is typically less than 1 kcal/mol. Furthermore, NOCI-MP2 version 1, which does not include the contribution due to the MP2 overlap, is more stable when the HOMO→LUMO gap approaches zero.

For singlet-triplet gaps in molecules with biradicaloid character, a (2,2) active space is physically appropriate. We use the (2,2) active space associated with a single determinant restricted open shell Hartree-Fock reference to define 4 determinants which are individually relaxed in order to provide the NOCI determinant basis. This algorithm can quite reliably determine different NOCI states of interest, provided that the usual criterion for validity of SF-CAS is satisfied (namely, there should only be one low-lying triplet state). This algorithm also provides an easy way to define and remove double-counting terms in the MP2 expansion (specifically the active-active correlations), which avoids the need for level shifts to stabilize against small energy denominators. Overall, we recommend using the NOCI-MP2 rv1 method (i.e. version 1 with double counting terms removed) based on its similar accuracy to other size consistent versions and its more robust behavior.

We showed that the NOCI-MP2 rv1 method yields accurate results for the singlet and triplet excited state energies for the acene series using many orders of magnitude fewer reference determinants than CASPT2 results in much larger active spaces. This shows the effectiveness of relaxing the orbitals differently for each determinant in the NOCI basis. For example, ionic and covalent determinants with very different charge distributions are naturally described by different orbitals. NOCI-MP2 rv1 also shows accuracy approaching SF-EOM-CCSD for singlet-triplet gaps in diradical molecules. In the end the size consistent versions of the NOCI-MP2 method (particularly version 1 in its rv form) shows well behaved

and accurate results in a number of system, and is a promising low scaling alternative to other multi-reference perturbation methods. It is now amongst the few analytical size consistent perturb-then-diagonalize perturbation theory methods. The principal limitation is the necessity to obtain appropriate NOCI reference determinants. While we have made progress on this issue for the states of biradicaloid systems discussed here, further improvements would be tremendously beneficial for treating a broader range of excited states.

$ijab \quad klcd$	$\frac{1}{16} \langle kl cd \rangle t_{ij}^{ab} \langle {}^A\Psi_{kl}^{cd} {}^B\Psi_{ij}^{ab} \rangle$
Case 1 $\in \text{Be} \in \text{Be}$	$H_{MP2}^{\text{Be}} = \frac{1}{16} \langle kl cd \rangle t_{ij}^{ab} \langle {}^A\Psi_{(\text{Be})kl}^{cd} {}^B\Psi_{(\text{Be})ij}^{ab} \rangle \langle \Psi_{(\text{He})}^{(0)} \Psi_{(\text{He})}^{(0)} \rangle$
Case 2 $\in \text{He} \in \text{He}$	$E_{MP2}^{\text{He}} \langle {}^A\Psi^{(0)} {}^B\Psi^{(0)} \rangle$
Case 3 $\in \text{Be} \in \text{He}$	0
Case 4 $\in \text{He} \in \text{Be}$	0

TABLE I. NOCI-MP2 off diagonal Hamiltonian matrix elements for the model system of non-interacting BeHe.

	$\langle {}^A\Psi^{(0)} \hat{H} {}^B\Psi^{(1)} \rangle$	$\langle {}^A\Psi^{(0)} {}^B\Psi^{(1)} \rangle$
Version 0	$\frac{1}{4} t_{ij}^{ab} E_{HF}^A \langle {}^A\Psi^{(0)} {}^B\Psi_{ij}^{ab} \rangle + \frac{1}{16} \langle kl cd \rangle t_{ij}^{ab} \langle {}^A\Psi_{kl}^{cd} {}^B\Psi_{ij}^{ab} \rangle$	$\frac{1}{4} t_{ij}^{ab} \langle {}^A\Psi^{(0)} {}^B\Psi_{ij}^{ab} \rangle$
Version 1	$\frac{1}{16} \langle kl cd \rangle t_{ij}^{ab} \langle {}^A\Psi_{kl}^{cd} {}^B\Psi_{ij}^{ab} \rangle$	0.0
Version 2	$\frac{1}{4} t_{ij}^{ab} (E_{HF}^A + E_{MP2}^A) \langle {}^A\Psi^{(0)} {}^B\Psi_{ij}^{ab} \rangle + \frac{1}{16} \langle kl cd \rangle t_{ij}^{ab} \langle {}^A\Psi_{kl}^{cd} {}^B\Psi_{ij}^{ab} \rangle$	$\frac{1}{4} t_{ij}^{ab} \langle {}^A\Psi^{(0)} {}^B\Psi_{ij}^{ab} \rangle$

TABLE II. Second order Hamiltonian and overlap matrix elements for the different versions of NOCI-MP2 used in the text.

FIG. 1. Size consistency error, ΔE defined in the manuscript, in the NOCI-MP2 version 0 method for Be with N_{He} non-interacting He atoms. The NOCI space consists of a (2,2) active space on Be.

4-State										
Molecule	1^3B_{2u}					1^1B_{2u}				
	NOCI	+MP2 v0	+MP2 v1	+MP2 v2	CASPT2	NOCI	+MP2 v0	+MP2 v1	+MP2 v2	CASPT2
Napthalene ^a	3.88	>100	2.85	>100	3.20	5.85	>100	3.70	>100	4.77
Anthracene ^b	2.90	37.75	2.63	2.64	2.32	4.54	27.33	3.66	3.68	3.45
Tetracene ^b	2.15	28.36	1.89	1.90	1.70	3.70	14.36	2.84	2.85	2.71
Pentacene ^b	1.63	28.11	1.42	1.43	1.22	3.09	10.83	2.31	2.32	2.17

4-State minus (2,2) active space HOMO/LUMO double excitations

Molecule	1^3B_{2u}					1^1B_{2u}				
	NOCI	+MP2 rv0	+MP2 rv1	+MP2 rv2	CASPT2	NOCI	+MP2 rv0	+MP2 rv1	+MP2 rv2	CASPT2
Napthalene ^a	3.88	3.47	3.63	3.62	3.20	5.85	5.25	4.89	4.88	4.77
Anthracene ^b	2.90	2.52	2.68	2.68	2.32	4.54	4.08	3.68	3.68	3.45
Tetracene ^b	2.15	1.82	1.93	1.93	1.70	3.70	3.20	2.85	2.85	2.71
Pentacene ^b	1.63	1.47	1.47	1.46	1.22	3.09	2.50	2.31	2.31	2.17

^aCASPT2 values taken from reference 33 using the TZVP basis

^bCASPT2 values taken from reference 75 using the cc-pVTZ(-f) basis

TABLE III. Comparison of the NOCI-MP2 excitation energies from the 1^1A_g ground state to the 1^1B_{2u} singlet and 1^3B_{2u} triplet excited states in the linear acene series with CASPT2. All NOCI calculations are done with 4 relaxed determinants derived from the (2,2) active space in the def2-TZVP basis, while the CASPT2 active space ranges from all valence in napthalene, (12,12), to all π orbitals in the larger acenes like pentacene, (22,22).

Molecule	NOCI	NOCI-MP2 rv1	UMP2	RMP2	CASPT2
Napthalene ^a	3.88	3.63	2.98	3.35	3.20
Anthracene ^b	2.90	2.68	1.92	2.31	2.32
Tetracene ^b	2.15	1.93	1.07	1.76	1.70
Pentacene ^b	1.63	1.47	0.49	1.20	1.22

^aCASPT2 values taken from reference 33 using the TZVP basis

^bCASPT2 values taken from reference 75 using the cc-pVTZ(-f) basis

TABLE IV. Comparison of the multi-reference triplet energies for the 1^3B_{2u} state with the high spin, $M_s = \pm 1$, unrestricted and restricted-open-shell MP2 triplet excitation energies. All energies are given in eV.

FIG. 2. Molecules included in the diradical test set. The set also includes C, O, Si, S, CH₂, NH₂, SiH₂, and PH₂ and is taken from Reference 85

Molecule	SF-EOM-CCSD(dt)	SF-EOM-CCSD	NOCI	NOCI-MP2 v1	NOCI-MP2 rv1
C	1.271	-0.022	0.171	0.028	0.028
O	1.972	-0.009	0.167	-0.040	-0.044
Si	0.766	-0.033	0.127	-0.028	-0.024
S	1.138	-0.027	0.158	-0.026	-0.028
CH ₂	0.420	0.027	0.472	0.074	0.074
NH ₂	1.253	0.02	0.528	0.003	0.020
SiH ₂	-0.892	0.018	0.414	-0.052	-0.042
PH ₂	-0.794	0.016	0.266	-0.025	-0.016
C6rr	-0.614	0.027	0.395	0.005	0.015
C7rr	-0.623	0.027	0.395	0.006	0.016
C6rrC	-0.696	0.035	0.430	-0.018	-0.004
rC6r	0.000	0.000	0.000	0.000	0.000
rC6rC	-0.007	-0.005	-0.004	-0.006	-0.009
o-benzyne	-1.619	0.041	0.704	-0.074	-0.073
m-benzyne	-0.892	0.11	-0.338	-0.058	-0.026
p-benzyne	-0.172	0.025	-0.023	-0.263	-0.217
α ,2-didehydrotoluene	0.247	0.041	-0.130	-0.147	-0.147
α ,3-didehydrotoluene	-0.066	-0.06	0.053	0.076	0.076
α ,4-didehydrotoluene	0.250	0.033	-0.121	-0.116	-0.116
m-xylylene	0.454	0.043	-0.333	-0.005	-0.028
Average		0.018	0.166	-0.033	-0.026
RMSD		0.042	0.323	0.081	0.073

TABLE V. Single-triplet gaps for a series of small diradicals and diradicaloids. The gaps are defined as $\Delta E_{ST} = E_S - E_T$, so that if the triplet is lower in energy the difference is positive. The singlet triplet gaps are explicitly given for SF-EOM-CCSD(dt), while for all other methods, the deviations are reported with respect to the reference SF-EOM-CCSD(dt) results. The average values are the unsigned average error. All energies are given in eV, and the SF-EOM-CCSD and SF-EOM-CCSD(dt) results are from reference 85. Basis sets were also chosen following reference 85.

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