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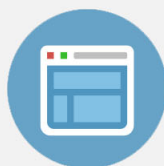
Analysis of and remedies for unphysical ground states of the multireference averaged coupled-pair functional

David B. Krisiloff,[1] Victor B. Oyeyemi,[2] Florian Libisch,[3] and Emily A. Carter[4]

[1]*Department of Chemistry, Princeton University, Princeton, New Jersey 08544-1009, USA*

[2]*Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544-5263, USA*

[3]*Institute for Theoretical Physics, Vienna University of Technology, Vienna, Austria*

[4]*Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544-5263, USA; Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544, USA; and Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08544-5263, USA*

A Multireference Configuration Interaction (MRCI) wavefunction includes both static and dynamic electron correlation. MRCI's well-known flaw, a lack of size extensivity, can be ameliorated with the Multireference Averaged Coupled-Pair Functional (MRACPF). However, the original MRACPF is frequently unstable, sometimes producing unphysical results. The more Multireference Averaged Quadratic Coupled-Cluster and MRACPF2 functionals also occasionally exhibit unphysical behavior. We find that these instabilities are avoided crossings with unphysical solutions to the MRACPF equations. We present two approaches to avoid the undesirable unphysical solutions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4861035]

I. INTRODUCTION

Multireference Configuration Interaction (MRCI) simultaneously includes both static and dynamic electron correlation. However, unlike Coupled Cluster (CC) or Many-Body Perturbation Theory (MBPT), MRCI is not size extensive,[1] which results in an error proportional to system size. A multitude of methods exist to approximately correct the MRCI size extensivity error. *A posteriori* corrections[2–5] provide a correction after wavefunction optimization, while *a priori* methods[6–8] provide a correction during wavefunction optimization. The latter should be more accurate because they optimize the wavefunction in the presence of the correction, though neither is exact.[9]

The Multireference Averaged Coupled-Pair Functional (MRACPF) is an *a priori* size extensivity corrected form of Multireference Singles and Doubles Configuration Interaction (MRSDCI).[6,7] MRACPF corrects MRSDCI by modified wavefunction normalization. Unfortunately, MRACPF's approximate size extensivity correction tends to overestimate the correction for single excitations. This overemphasis of single excitations can cause unphysical behavior, though to our knowledge only two first-hand accounts exist.[10,11] MRACPF variants, Multireference Averaged Quadratic Coupled-Cluster (MRAQCC) and MRACPF2, are more stable since they reduce the correction to single excitations. Nevertheless, we have observed cases where MRACPF2 produces unstable results, mostly when using small active spaces (see the supplementary material[12] for examples).

MRACPF's overestimation of single excitations does not completely explain the unphysical solutions since MRACPF always overestimates the singles contribution but does not always produce unphysical behavior. In this work, we show that the chemically relevant solution of the MRACPF functional

may not be its lowest energy solution. The overestimated single excitation correction can unphysically lower the energy of high lying MRACPF solutions. An avoided crossing occurs if the high lying state is decreased in energy below the physical ground state. Under these circumstances, (i) minimization of the MRACPF functional yields the unphysical state and (ii) the MRACPF solutions become unacceptably distorted at the crossing. We conjecture that these avoided crossings are the instabilities observed in the literature. We can recover physically reasonable MRACPF solutions with root following far away from the avoided crossing and with degenerate perturbation theory close to the avoided crossing. Furthermore, we examine the previous suggestion[10] to handle unphysical MRACPF results using a larger active space in light of this new analysis.

II. THE MRACPF EQUATIONS

The MRSDCI wavefunction contains a series of reference configuration state functions (CSFs, spatial/spin eigenfunctions), Ψ_{ref}, and all singly and doubly excited CSFs from each reference in Ψ_{ref}. Orbitals which are always doubly occupied (always empty) in Ψ_{ref} are called inactive (virtual) orbitals, while active orbitals have varying occupation. The MRACPF correlation energy is calculated with the functional:[7]

$$E_{corr}[\Psi] = \frac{\langle \Psi | H - E_{ref} | \Psi \rangle}{\sum_{k=1}^{5} g_k \langle \psi_k | \psi_k \rangle}. \quad (1)$$

H is the many-electron Hamiltonian and Ψ is the MRSDCI wavefunction. E_{ref} is the variationally minimal energy of a linear combination of the reference CSFs. The g values $\{g_k\}_{k=1}^{5}$ modify the normalization in the MRSDCI

energy functional by assigning different weights to five different classes of CSFs in the wavefunction. ψ_1 contains only the reference CSFs. ψ_2 consists of those CSFs involving excitations within only the active orbitals. ψ_3 comprises CSFs derived from single and double excitations from the inactive orbitals to the active orbitals. ψ_4 and ψ_5 contain those CSFs consisting of all single and double excitations into virtual orbitals, respectively. If $g_k = 1 \ \forall \ k$, we recover MRSDCI. Different flavors of MRACPF are distinguished by different values for the set $\{g_k\}_{k=1}^5$. The *g* values define the size extensivity correction. MRACPF defines $g_1, g_2 = 1$ and $g_3, g_4, g_5 = 2/N$ where *N* is the number of correlated electrons. $2/N$ comes from an analysis of double excitations in a system of non-interacting correlated electron pairs.[6] No similar rationalization exists for using $2/N$ to correct single excitations. The use of $2/N$ tends to overestimate the contribution of single excitations (g_3, g_4).[7,13,14] Multiple MRACPF variants reduce this overestimation.[7] MRAQCC uses

$$g_3, g_4, g_5 = \frac{4}{N}\left[1 - \frac{1}{2(N-1)}\right]. \tag{2}$$

These g values reduce the single excitation size extensivity correction compared to MRACPF. MRACPF2 uses a combination of MRAQCC and MRACPF,

$$g_3, g_4 = \frac{4}{N}\left[1 - \frac{1}{2(N-1)}\right] g_5 = \frac{2}{N}. \tag{3}$$

Wennmohs and Neese later suggested a modification of MRACPF2, MRACPF2a where $g_3, g_4 = 4/N$, which shows the same asymptotic behavior as MRACPF2.[15]

To solve for the MRACPF energy, we variationally minimize the energy functional. Variational minimization of Eq. (1) yields the MRACPF equations:

$$[H - E_{ref}I + \Delta)]\Psi = E_{corr}\Psi, \tag{4}$$

$$\Delta = E_{corr}(I - G). \tag{5}$$

The G matrix containing the g values ($G = \sum_{k=1}^5 g_k |\psi_k\rangle\langle\psi_k|$) is diagonal in an orthogonal orbital basis. *I* is the unit matrix while Δ is the diagonal shift. The diagonal shift equation (Eq. (4)) is the most common form of the MRACPF equations.[16,17] However, Eq. (4) can also be rewritten as a generalized eigenvalue problem, removing the self-consistency in Δ:

$$[H - E_{ref}I]\Psi = E_{corr}G\Psi. \tag{6}$$

Additionally, the equations can be directly cast into a Hermitian eigenvalue problem. While less useful computationally, the Hermitian form will be useful in subsequent analysis:

$$[G^{-\frac{1}{2}}(H - E_{ref}I)G^{-\frac{1}{2}}](G^{\frac{1}{2}}\Psi) = E_{corr}(G^{\frac{1}{2}}\Psi). \tag{7}$$

Note that $G^{\frac{1}{2}}$ and $G^{-\frac{1}{2}}$ are well defined in an orthonormal basis as G is a diagonal matrix of the g values, which are always bounded by $0 < g_k \le 1 \forall k$. All three variations produce

the same MRACPF energies and can be solved using modified forms of Davidson's method.[17–19]

The lowest energy eigenvalue of Eq. (4) is the MRACPF ground state energy. Unlike MRSDCI, the higher energy eigenvalues have no meaning because they are not excited states. Calculating a MRACPF excited state requires the excited state's reference energy in Eq. (4) instead of the ground state. See Ref. 16 on "state specific" MRACPF for further discussion. The ground state energy is dominated by the reference CSFs because dynamic correlation accounts for a small fraction of the total energy. Therefore, the reference CSFs should contribute significantly to the ground state eigenvector. We denote such states as physical; accordingly, we denote ground state eigenvectors with very small reference contributions as unphysical.

III. CALCULATION DETAILS

We have probed the MRACPF instability using a simple test case, stretching the C–O bond in methanol (see the supplementary material[12] for the methanol geometry). For each C–O distance we performed a complete active space self-consistent field, CASSCF(2e,2o) [i.e., an active space of two electrons in two orbitals] calculation using the cc-pVDZ basis set with the C–O σ and σ^* orbitals as the CASSCF active space. The MRACPF ($g_3, g_4, g_5 = 2/N$) correlation energy was then calculated using the CASSCF orbitals. In the region around 3 Å, a larger active space is necessary to prevent the σ and σ^* from rotating out of the complete active space (CAS) space. However, using a larger CAS removes the instability (*vide infra*), so we restrict ourselves to CAS(2e,2o) and exclude the region around 3 Å. Integral and orbital calculations were performed using the MOLCAS quantum chemistry code.[20] For all calculations the two-electron integrals were decomposed using a Cholesky Decomposition with a threshold of 1.0×10^{-8}. The MRACPF calculations were performed using TigerCI.[19,21–24] For simplicity, we did not relax the nuclear positions as the bond was stretched.

IV. METHANOL TEST CASE

Our discussion takes place as follows. We calculate the bond dissociation curve of our methanol test case. The fully dissociated molecule has an unphysical MRACPF ground state. Examination of the dissociated molecule reveals a higher energy state consistent with the expected physical state. We conjecture that the instability is an avoided crossing which has reordered the physical and unphysical eigenstates. Such an avoided crossing indicates that the ground state MRACPF solution is not always the chemically relevant one. We demonstrate that away from the avoided crossing a root following approach obtains the chemically relevant solution. Close to the avoided crossing we use degenerate perturbation theory to generate a stable solution. Finally, we use our new analysis to understand why expanding the CAS in a MRACPF calculation can also remove the avoided crossing.

We have calculated the bond dissociation curve for the C–O bond in methanol. For each bond length, we solved Eq. (6) (the generalized eigenvalue form) for the
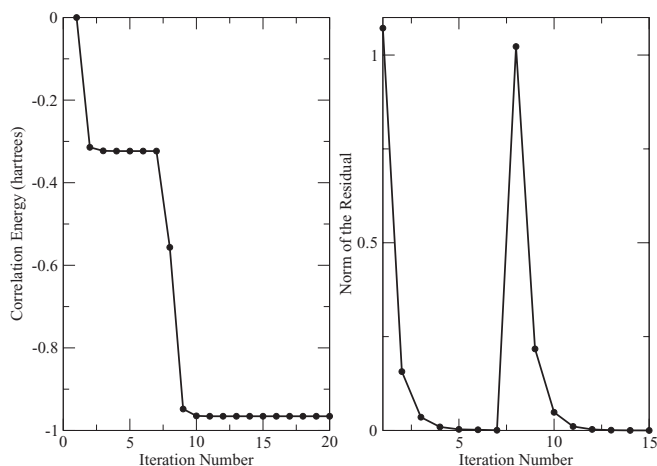
FIG. 1. CAS(2,2) MRACPF correlation energy (left) and norm of the residual (right) as a function of iteration number. At the seventh iteration step, the energies appear to converge (to a physical solution, with substantial weight on the original references) before suddenly collapsing to an unphysical lower energy state (with minimal weight on the references). The two minima in the norm of the residual confirm that the first and second solutions are both eigenvalues.
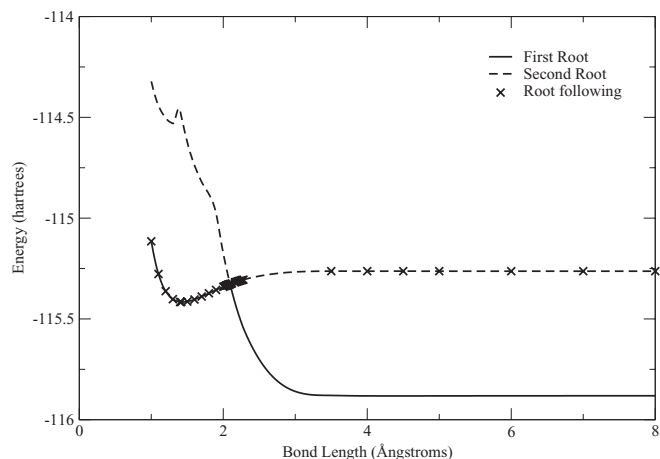

FIG. 2. CAS(2,2)-MRACPF encounters an avoided crossing when dissociating the methanol C–O bond. The avoided crossing occurs because MRACPF overestimates the size extensivity correction for single excitations, thereby spuriously reducing the energy of the second root (dominantly a single excitation). The physical solution can be recovered via a root following approach.

lowest energy eigenvalue using Davidson's iterative eigenvalue method. MRACPF produces a physical solution for the equilibrium bond length, $L_B = 1.42$ Å, and an unphysical solution for a fully dissociated C–O bond, $L_B = 10.0$ Å. The physical solution (1.42 Å) contains a large weight on the reference CSFs. The total weight of the reference CSFs (sum of the reference coefficients squared) is 0.90. The unphysical solution ($L_B = 10.0$ Å) contains a very small weight on the reference CSFs of 2.0×10^{-14} and exhibits unusual features. The dominant configurations in the unphysical solution are single excitations from an oxygen lone pair to one of the active space orbitals (total weight 0.96). The contribution of the oxygen lone pair electrons, while important, should not outweigh the contribution of the broken C–O bond.

Examination of the unphysical solution reveals unusual behavior: Davidson's method first finds a higher-energy solution before collapsing to the lower energy, unphysical eigenvalue (Figure 1, left). To analyze the different solutions we use the norm of the residual $\| [H - E_{ref}I] \Psi_{guess} - E_{corr}^{guess} G \Psi_{guess} \|$, which measures how close the calculated Ψ_{guess} is to a numerically exact eigenvector. The higher energy solution produces a very small norm of the residual (Figure 1, right), indicating that it is an eigenvalue (but not the ground state). Davidson's method often produces this behavior when the method's starting guess is close to an excited state eigenvector. This excited state solution contains a large weight on the reference coefficients. We argue that this is the chemically relevant solution, even though it is not the lowest energy solution to the MRACPF equations. Bond dissociation energies computed with the high energy, physical solution compare reasonably well with experiment. Bond dissociation energies computed with the lowest energy solution are absurd.

These results suggest an avoided crossing or conical intersection. On one side of the crossing, the physical state is the ground state; on the other side, the eigenval-

ues are reordered and the physical state is a higher energy eigenvalue. To validate this hypothesis we have solved the MRACPF equations for the lowest two eigenvalues across the bond dissociation curve (Figure 2). We find an avoided crossing in the MRACPF bond dissociation curve around $L_B = 2.1$ Å. Since the MRACPF solutions satisfy a Hermitian eigenvalue problem (Eq. (7)), the Wigner-von Neumann non-crossing theorem[25] applies. Electronic states of the same symmetry cannot cross. Any time two states would cross an avoided crossing occurs. Furthermore, the adiabatic eigenstates corresponding to the ground ($|\psi_0\rangle$) and excited ($|\psi_1\rangle$) state solutions of the MRACPF equations exchange characteristics at the avoided crossing according to the evolution of the diabatic states (i.e., the physical,$|\phi_{phys}\rangle$, and unphysical,$|\phi_{unphys}\rangle$, solutions). From these results, we conjecture that MRACPF always overestimates the contribution of single excitations[7,13,14] because single excitations are lower in energy than they should be. The MRACPF instability occurs when this overestimation reduces the energy of a single excitation dominated state below the physical ground state producing an avoided crossing or conical intersection.

MRACPF solutions near the avoided crossing are clearly perturbed (Figure 3); however, the eigenvalues do not appear to be perturbed far away from the avoided crossing (Figure 2). Away from the crossing we propose calculating the higher energy, physical root to obtain the MRACPF energy using root following. A root following approach has been used in similar situations, such as MRACPF excited states[16] and other applications.[14] Root following solves for the eigenvector with maximum overlap with the reference wavefunction instead of the lowest energy eigenvector. If the reference wavefunction resembles the physical ground state, root following avoids the unphysical solution (Figure 2). However, root following does not repair the perturbation at the crossing (Figure 3).

Near the avoided crossing we can reconstruct the MRACPF solutions with first-order degenerate perturbation theory. A similar approach has been taken for coupled-cluster methods near conical intersections.[26] First we make
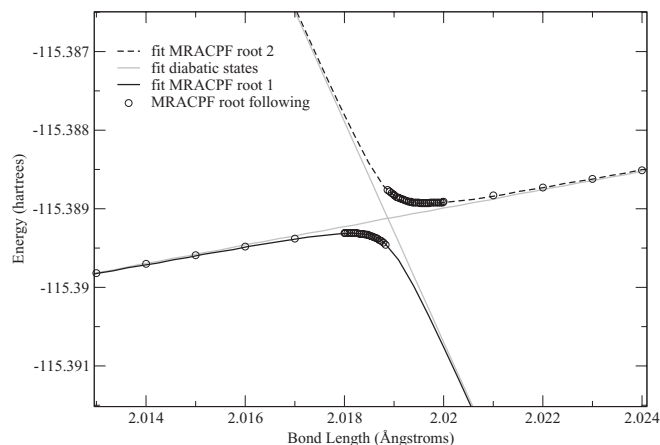
FIG. 3. Zoom-in on the avoided crossing of Fig. 2 when dissociating the methanol C–O bond (distorted geometry described in the text). The MRACPF solutions are highly perturbed near the avoided crossing. The lines in light grey are the unperturbed solutions generated from first order degenerate perturbation theory (Eq. (9)). Near the avoided crossing the MRACPF solutions (both the 1st and 2nd root) show large deviations.

the ansatz:

$$\begin{pmatrix} E_{\text{phys}}(L_B) & V \\ V & E_{\text{unphys}}(L_B) \end{pmatrix} \psi = E\psi, \qquad (8)$$

where $E_{\text{phys}}(L_B)$ and $E_{\text{unphys}}(L_B)$ are the diabatic energies of the physical and unphysical states, respectively, L_B is the varying bond length, and V is the coupling matrix element between the two diabatic solutions $\langle V = \langle \psi_{\text{phys}}^{\text{diab}} | H | \psi_{\text{unphys}}^{\text{diab}} \rangle$. Solving this simple 2×2 system allows for accurately fitting V (Figure 3) and for recovering $E_{\text{phys}}(L_B)$. For the perfectly symmetric methanol molecule, we find an exceedingly small crossing (approximately 10^{-6} hartrees), since the coupling matrix element V is very small. The small crossing prevents a convincing demonstration of the perturbation theory

approach. By breaking the symmetry (twisting the H–C–O–H dihedral angle $10°$ and adding a $2e$ point charge 4 Å from the C atom, perpendicular to the C–O bond, see the supplementary material[12] for geometry and inputs), V increases to 0.35 mHa. The first-order perturbation theory ansatz correctly reproduces both the original curves and the coupling (Figure 3). We note that more complicated molecules might feature broader and more numerous avoided crossings requiring a more sophisticated approach, such as local diabatization.[27]

Finally, we reexamine the previous solution to MRACPF instabilities by using a larger CAS.[10] Using a large active space for MRACPF has multiple effects. First, the CASSCF orbital shapes will improve. Second, a larger number of references are used during the MRACPF calculation, increasing the number of CSFs in the wavefunction. Third, the classification of orbitals change (there are more active orbitals). The reclassification indirectly affects the calculation. The size extensivity correction (g value) assigned to different excitations will change if the orbital type changes (e.g., a virtual orbital becomes an active orbital). This creates subtle differences in the size extensivity correction. To distinguish these effects, we performed a full valence CASSCF(12e,11o) calculation to generate an improved set of orbitals. Then we ran two MRACPF calculations, a CAS(12e,11o)-MRACPF and a CAS(2e,2o)-MRACPF, both using the orbitals from the full valence CASSCF(12e,11o) calculation. In the CAS(12e,11o)-MRACPF calculation, we used the active orbitals and important references from the CAS(12e,11o) (i.e., those with CI coefficients greater than 0.05). In the CAS(2e,2o)-MRACPF, we used the active space definition and the three references from the CAS(2e,2o) consisting of the C–O σ and σ^* orbitals. The CAS(12e,11o)-MRACPF does not produce an unphysical ground state, but the CAS(2e,2o)-MRACPF does (Figure 4). Since both calculations used the same orbitals, the improved orbitals are not responsible for removing the instability. The
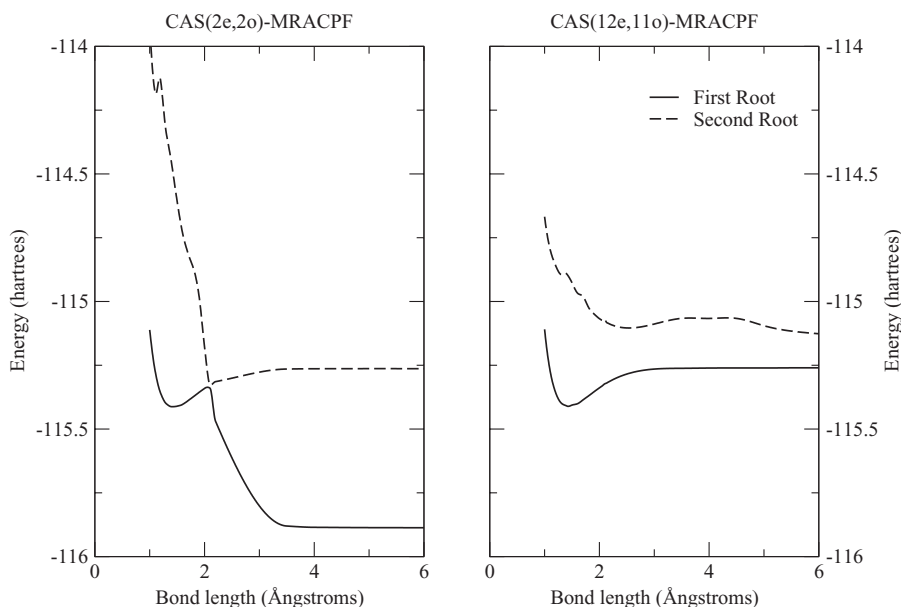

FIG. 4. Using a large CASSCF space in the MRACPF calculation removes the unphysical solution. The CAS(2e,2o)-MRACPF calculation (left) using CASSCF(12e,11o) orbitals demonstrates that improved orbitals do not remove the unphysical solution. The CAS(12e,11o)-MRACPF (right) does not provide a (overestimated) size extensivity correction to any single excitation in the active space, thereby removing the unphysical solution.

larger CAS space removes the instability by the aforementioned shift in the size extensivity correction. The important oxygen internal to active orbital excitation becomes an active to active orbital excitation in the CAS(12e,11o)-MRACPF. Active to active orbital excitations do not receive a size extensivity correction ($g_2 = 1$). Therefore, CAS(12e,11o)-MRACPF does not incorrectly lower the excitation's energy and no avoided crossing occurs. This change in the size extensivity correction, and not improved orbitals, explains why increasing the CAS size remedies MRACPF instabilities.

V. CONCLUSIONS

MRACPF instabilities have been previously associated with MRACPF's overestimation of single excitation contributions.[10] We have shown that this overestimation results in an avoided crossing or conical intersection, which reorders the eigenvectors. Beyond such a region on the potential energy surface, MRACPF appears unstable because the lowest eigenvector is not the physical state. Away from the crossing we can recover the correct eigenvector with root following. We also reevaluated the suggestion to avoid MRACPF instabilities by using larger active spaces. A large active space hides low lying single excitations in the active space where they receive no correction and cannot cause instabilities. We recommend root following as the default approach for MRACPF (except near the crossing), since increasing the CAS scales exponentially. If MRACPF results near a crossing are required, one can use a larger CAS to avoid the instability problem. Alternatively, to avoid the necessity of a large CAS for the entire potential energy surface, we showed that one can also successfully fit to an avoided crossing using degenerate perturbation theory.

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