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Explicitly correlated multireference configuration interaction with multiple reference functions: Avoided crossings and conical intersections

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We develop an explicitly correlated multireference configuration interaction method (MRCI-F12) with multiple reference functions. It can be routinely applied to nearly degenerate molecular electronic structures near conical intersections and avoided crossings, where the reference functions are strongly mixed in the correlated wave function. This work is a generalization of the MRCI-F12 method for electronic ground states, reported earlier by Shiozaki *et al.* [J. Chem. Phys. **134**, 034113 (2011)]. The so-called F12b approximation is used to arrive at computationally efficient formulas. The doubly external part of the wave function is expanded in terms of internally contracted configurations generated from all the reference functions. In addition, we introduce a singles correction to the CASSCF reference energies, which is applicable to multi-state calculations. As examples, we present numerical results for the avoided crossing of LiF, excited states of ozone, and the $H_2 + OH$ ($A^2\Sigma^+$) reaction. © *2011 American Institute of Physics*. [doi:10.1063/1.3587632]

I. INTRODUCTION

The internally contracted multireference configuration interaction (MRCI) method of Werner and Knowles[1,2] has been a powerful tool for computing global potential energy surfaces (PESs) and electronically excited states, and for describing nearly degenerate electronic structures of molecules. Even for quasi-degenerate electronic states around conical intersections and avoided crossings,[3] where reference functions are strongly mixed in the correlated wave functions, the internally contracted MRCI based on multiple reference functions can be routinely used (see Ref. 4). One known problem is, however, that the correlation energy is only slowly convergent with respect to the basis size; therefore, one needs to use a large basis set (sometimes quintuple-ζ or even larger basis sets[5]) to perform predictive calculations.

Recently, we have developed an explicitly correlated MRCI (MRCI-F12) method[6] and implemented it for electronic ground states within the so-called F12b approximation.[7,8] MRCI-F12 accelerates the basis-set convergence of the underlying MRCI method with very little additional computational effort. As in other explicitly correlated F12 methods,[9–11] MRCI-F12 introduces a term into the wave function that has an explicit dependence on the electron–electron distances r_{ij}. The MRCI-F12 method has been based on our earlier development of an explicitly correlated complete active space second-order perturbation (CASPT2-F12) method,[12] which in turn has employed modern F12 techniques such as the resolution of the identity approximation[13,14] using auxiliary basis sets,[15,16] a Slater-type geminal function [$F_{12} = -e^{-\gamma r_{12}}/\gamma$],[17] geminal amplitudes fixed at the values from the first-order cusp conditions,[18] efficient formulas for F12 intermediates,[19,20] and density fitting for the F12 integrals.[21,22]

There are also approaches by others to multireference F12 theories. Gdanitz was the first to combine the explicitly correlated methods with multireference correlation models,[23,24] using a linear R12 correlation factor and the so called standard approximation (i.e., using the orbital basis to represent resolutions of the identity). Ten-no has introduced internally contracted geminal excitations in his study on an explicitly correlated multireference perturbation method.[25] Valeev and co-workers have studied a perturbative correction that utilizes the two-particle reduced density matrix of the underlying correlated models,[26,27] and Varganov and Martínez have proposed to combine an F12 function with CASSCF.[28]

In this study we generalize the aforementioned MRCI-F12 method[6] to incorporate multiple reference functions required in the presence of conical intersections and avoided crossings. Internally contracted conventional and geminal doubles functions are generated from several reference functions, and wave functions for all the states of interest are obtained as eigenfunctions of the resulting Hamiltonian matrix. We also introduce a complementary auxiliary basis set (CABS) singles correction which is applicable to multiple state calculations. Numerical examples are presented to demonstrate the much improved basis set convergence of MRCI-F12 compared to the conventional MRCI.

II. THEORY

A. Multi-state MRCI-F12

The index notation is as follows: i, j, k, l, m, n label occupied orbitals, a, b virtual orbitals in the orbital basis set (OBS), α, β virtual orbitals in the complete basis, κ, λ any orbitals, x, y virtual orbitals in the CABS,[16] and L, M, N reference wave functions. All the orbitals are normalized and the occupied, virtual, and CABS orbitals are orthogonal to each other.

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We use the Werner–Knowles partial internal contraction scheme (i.e., doubly external configurations are internally contracted, while singly external and internal configurations remain uncontracted).[1] This mixed scheme has been chosen for convenience, but the method could straightforwardly be extended to more strongly contracted wave function ansätze, as, e.g., proposed in the context of CASPT2 by Celani and Werner,[29] or completely contracted MRCI as first used by Werner and Reinsch.[30] In this work the MRCI-F12 wave functions of the Mth state is parametrized as in the single-state MRCI-F12 method with the scaled fixed (SFIX) ansatz;[6] the only difference is that the geminal configurations, as well as conventional doubly external configurations, are generated from all the reference functions:

$$\Psi^M_{\mathrm{MRCI-F12}} = \Psi^M_{\mathrm{MRCI}} + \sum_N t^{MN}_{\mathrm{F12}} \hat{Q}\hat{F}|N\rangle, \tag{1}$$

where the conventional MRCI wave function is defined as

$$\Psi^M_{\mathrm{MRCI}} = \sum_I t^M_I |\Phi_I\rangle + \sum_{S,a} t^{S,M}_a \left|\Phi^a_S\right\rangle + \frac{1}{2}\sum_N \sum_{ij} \sum_{ab} T^{ij,MN}_{ab} \left|\Phi^{ab}_{ij,N}\right\rangle. \tag{2}$$

Here, $|\Phi_I\rangle$ and $|\Phi^a_S\rangle$ are standard spin-adapted configuration state functions (CSFs) with zero and one electron, respectively, in the external orbital space. The internally contracted doubly excited configurations $|\Phi^{ab}_{ij,N}\rangle$ are generated by applying spin-free excitation operators $\hat{E}^{ab}_{ij}$ to the complete reference functions $|N\rangle$,

$$|N\rangle = \sum_R c^N_R |\Phi_R\rangle, \tag{3}$$

$$\left|\Phi^{ab}_{ij,N}\right\rangle = \hat{E}^{ab}_{ij}|N\rangle. \tag{4}$$

Thus, the internally contracted configurations are state specific, and the contraction coefficients c^N_R are kept fixed in the MRCI calculation. Using the union of the internally contracted configurations of all considered states effectively allows for a relaxation of the contraction coefficients and makes it possible to describe all states in a balanced way.

The reference configurations are a subset of the internal configurations $|\Phi_I\rangle$, i.e., $\{R\} \subseteq \{I\}$. Note that the coefficients t^M_R of the reference configurations are fully relaxed in the MRCI wave function. They are only fixed in the definition of the internally contracted configurations as explained above. We will further discuss the choice of the reference functions $|N\rangle$ later in this section.

In the SFIX ansatz, the coefficients t^{MN}_{F12} are variationally optimized to minimize the energy expectation value. The SFIX ansatz is essential for deriving the multi-state MRCI-F12, since it allows us to optimize the amplitudes by a Davidson-like diagonalization procedure, which is not the case for the FIX ansatz[6] in which these coefficients are set to 1. The geminal excitation operator $\hat{F}$ is defined as

$$\hat{F} = \frac{1}{2}\sum_{ij}\sum_{\alpha\beta} \mathscr{F}^{ij}_{\alpha\beta}\hat{E}^{\alpha\beta}_{ij} + \sum_{ijk}\sum_{\alpha} \mathscr{F}^{ij}_{\alpha k}\hat{E}^{\alpha k}_{ij}, \tag{5}$$

where $\mathscr{F}^{ij}_{\alpha\beta}$ are two-electron integrals over the Slater-type geminal function[17] multiplied by fixed amplitudes[18]

$$\mathscr{F}^{ij}_{\alpha\beta} = \frac{3}{8}\langle\alpha\beta|F_{12}|ij\rangle + \frac{1}{8}\langle\alpha\beta|F_{12}|ji\rangle. \tag{6}$$

In our implementation, the $F_{12} = -e^{-\gamma r_{12}}/\gamma$ correlation factor is fitted to a linear combination of six Gaussian geminals whose coefficients and exponents are determined by a weighted fit.[20] Throughout this work, the length parameter γ is set to 1.0 a_0^{-1}.

The strong orthogonality projector is defined as

$$\hat{Q} = \hat{Q}_{\alpha\beta,ij} - \hat{Q}_{ab,ij} + \hat{Q}_S \equiv \hat{Q}_P + \hat{Q}_S, \tag{7}$$

where $\hat{Q}_{\alpha\beta,ij}$ is a projector onto a complete space spanned by the internally contracted configurations $|\Phi^{\alpha\beta}_{ij,N}\rangle$. $\hat{Q}_P$ eliminates from the geminal excitations the internally contracted double excitations that are present in the conventional MRCI wave function. $\hat{Q}_S$ projects out the contributions of internally contracted singly excited configurations

$$\left|\Phi^x_{i,M}\right\rangle = \hat{E}^x_i|M\rangle, \tag{8}$$

as well as the semi-internal doubles present in the conventional MRCI:

$$\hat{Q}_S = \sum_S \sum_x |\Phi^x_S\rangle\langle\Phi^x_S| \left[1 - \sum_{ij}\sum_{MN} \left|\Phi^x_{i,M}\right\rangle (\boldsymbol{\gamma}^{-1})^{MN}_{ij} \left\langle\Phi^x_{j,N}\right|\right]. \tag{9}$$

The overlap of the internally contracted singles is given by the first-order reduced transition density matrix (1RDM)

$$\gamma^{MN}_{ij} = \left\langle\Phi^x_{i,M}\middle|\Phi^x_{j,N}\right\rangle = \langle M|\hat{E}^i_j|N\rangle. \tag{10}$$

The inverse of this matrix in Eq. (9) appears since the internally contracted singles are not orthonormal to each other. According to the above definition, the singly external terms in the geminal operator are directly approximated by using the CABS orbitals x. In our previous work[6] we have shown that this does not deteriorate the convergence of the correlation energy with basis set size.

In this work, we use the MRCI-F12b approximation to arrive at computationally efficient working equations,[6] which is analogous to the F12b approximation in coupled-cluster theory.[7,8] The geminal–geminal part of the Hamiltonian matrix is approximated as

$$\langle M|\hat{F}^\dagger\hat{Q}\hat{H}\hat{Q}\hat{F}|N\rangle \approx \langle M|\hat{F}^\dagger\hat{Q}\left(\hat{f} + \tfrac{1}{2}E^{(1)}_M + \tfrac{1}{2}E^{(1)}_N\right)\hat{Q}\hat{F}|N\rangle, \tag{11}$$

with $E^{(1)}_M = \langle M|\hat{H} - \hat{f}|M\rangle$. This definition is consistent with the previously reported ground-state formulation[6] and analogous to the multireference quasi-degenerate perturbation theories (MCQDPT or MS-CASPT2)[31,32] based on the Bloch wave operator formalism. The state-averaged Fock operator is used,

$$\hat{f} = \left[h_{\kappa\lambda} + \sum_{ij}\gamma^{(\mathrm{sa})}_{ij}\left(J^{ij}_{\kappa\lambda} - \tfrac{1}{2}K^{ij}_{\kappa\lambda}\right)\right]\hat{E}^\kappa_\lambda \equiv f_{\kappa\lambda}\hat{E}^\kappa_\lambda, \tag{12}$$

where $\gamma_{ij}^{(sa)}$ is the state-averaged one-particle density matrix (using equal weights for all states) and $J_{\kappa\lambda}^{ij}$ and $K_{\kappa\lambda}^{ij}$ are Coulomb and exchange operators, $J_{\kappa\lambda}^{ij} = \langle i\kappa|r_{12}^{-1}|j\lambda\rangle$, $K_{\kappa\lambda}^{ij} = \langle\kappa\lambda|r_{12}^{-1}|ij\rangle$. The couplings between geminal and conventional excitations are also approximated as in the ground-state MRCI-F12.[6]

This approximation to the geminal–geminal block, however, breaks the invariance of the multi-state MRCI-F12 with respect to the rotations in the reference space. Although the most straightforward choice for the reference functions is to use the CASSCF functions, this turned out to lead to humps on the PESs; this is due to the fact that the $E^{(1)}$ values dramatically change around the crossing points of the CASSCF PESs. We note that this also causes humps on the MS-CASPT2 PESs. A better set of reference functions can be generated by diagonalizing the Fock operator within the reference space, so that

$$\langle M|\hat{f}|N\rangle = \delta_{MN} f_{MM}, \tag{13}$$

$$|M\rangle = \sum_N |N^{\mathrm{CASSCF}}\rangle U_{NM}. \tag{14}$$

The rotation of the reference functions only affects the F12 contributions since the underlying MRCI is invariant. The importance of this procedure is presented for the ozone case (see below). It also generates smooth MS-CASPT2 potentials.

Davidson's correction, which approximately corrects the size consistency error of the MRCI and MRCI-F12 methods, is computed as

$$\Delta E_{+\mathrm{Q}}^M = \left(E^M - \tilde{E}_{\mathrm{ref}}^M\right)\left[\left(c_0^M\right)^{-2} - 1\right], \tag{15}$$

where

$$\left(c_0^M\right)^2 = \frac{1}{N}\sum_R \left(t_R^M\right)^2, \tag{16}$$

with t_I^M being the internal (relaxed reference) coefficients in the final MRCI-F12b wave function of the Mth state, and

$$N = \left\langle \Psi_{\mathrm{MRCI-F12}}^M \middle| \Psi_{\mathrm{MRCI-F12}}^M \right\rangle. \tag{17}$$

$\tilde{E}_{\mathrm{ref}}^M = \langle\tilde{M}|\hat{H}|\tilde{M}\rangle$ is the reference energy of the rotated reference $|\tilde{M}\rangle$ of the Mth state, which is a unitary transformation of the original reference functions that maximizes the overlap with the final MRCI-F12 wave functions:

$$|\tilde{M}\rangle = |N\rangle[\mathbf{T}(\mathbf{T}^\dagger\mathbf{T})^{-1/2}]_{NM}, \tag{18}$$

$$T_{NM} = \left\langle N \middle| \Psi_{\mathrm{MRCI-F12}}^M \right\rangle. \tag{19}$$

See Ref. 5 for more details.

B. CABS singles correction

Although the MRCI-F12 method is efficient for achieving near CBS limit correlation energies, the basis set errors of the CASSCF contributions remain uncorrected.[6,26] Recently, Kong and Valeev proposed a scheme to rectify such errors, which was applied to multireference single-state calculations.[27] In the following, we introduce a generalization of the CABS singles correction[7,33] that is generally applicable to multireference, multi-state calculations. In our work the correction is computed for each state separately through a singles CI. The reason that we prefer a CI-based approach is that the introduction of the Fock operator in the singles correction may amplify the breaking of degeneracies of states when spatial symmetries are present.

The singles wave function is expanded by the reference function and internally contracted CABS singles configurations $|\tilde{\Phi}_{i,N}^x\rangle = \hat{E}_i^x|\tilde{N}\rangle$ generated from all the references:

$$\left|\Psi_S^M\right\rangle = |\tilde{M}\rangle + \sum_N \sum_i \sum_x t_x^{i,MN} \left|\tilde{\Phi}_{i,N}^x\right\rangle. \tag{20}$$

Note that the first term is state specific and uses the rotated reference wave function $|\tilde{M}\rangle$ that has largest overlap with the MRCI-F12 wave function for state M [cf. Eq. (18)]. The internally contracted CABS singles configurations are orthogonal to the space considered in MRCI-F12, owing to the projection Eq. (9).

The amplitudes in Eq. (20) are optimized by minimizing this energy, i.e., by solving the eigenvalue equation

$$\left\langle\tilde{\Phi}_{i,N}^x\middle|\hat{H} - E_{\mathrm{S}}^M\middle|\Psi_S^M\right\rangle = 0, \tag{21}$$

where $E_{\mathrm{S}}^M = \langle\Psi_S^M|\hat{H}|\Psi_S^M\rangle/\langle\Psi_S^M|\Psi_S^M\rangle$ is the energy expectation value. The necessary matrix elements are:

$$\langle\tilde{M}|\hat{H}\left|\tilde{\Phi}_{i,N}^x\right\rangle = \sum_j \tilde{\gamma}_{ji}^{MN} h_{xj} + \sum_{jkl} \tilde{\Gamma}_{ji,kl}^{MN} J_{xj}^{kl}, \tag{22}$$

$$\left\langle\tilde{\Phi}_{i,N}^x\middle|\hat{H}\middle|\tilde{\Phi}_{j,L}^y\right\rangle = h_{xy}\tilde{\gamma}_{ij}^{NL} + \sum_{kl}\left(\tilde{\Gamma}_{ij,kl}^{NL} J_{xy}^{kl} + \tilde{\Gamma}_{kj,il}^{NL} K_{xy}^{kl}\right) + \delta_{xy}\sum_{kl}\tilde{\Gamma}_{ij,kl}^{NL} h_{kl} + \frac{1}{2}\delta_{xy}\sum_{klmn}\tilde{\Gamma}_{ij,kl,mn}^{NL} J_{mn}^{kl}. \tag{23}$$

The transition density matrices $\tilde{\gamma}_{ij,MN}$, $\tilde{\Gamma}_{ij,MN}^{kl}$, and $\tilde{\Gamma}_{ijk,MN}^{lmn}$ are computed using the rotated reference functions:

$$\tilde{\gamma}_{ij}^{MN} = \langle\tilde{M}|\hat{E}_j^i|\tilde{N}\rangle, \tag{24}$$

$$\tilde{\Gamma}_{ij,kl}^{MN} = \langle\tilde{M}|\hat{E}_{jl}^{ik}|\tilde{N}\rangle, \tag{25}$$

$$\tilde{\Gamma}_{ij,kl,mn}^{MN} = \langle\tilde{M}|\hat{E}_{jln}^{ikm}|\tilde{N}\rangle. \tag{26}$$

The singles correction is then defined as

$$\Delta E_{\mathrm{S}}^M = E_{\mathrm{S}}^M - \langle\tilde{M}|\hat{H}|\tilde{M}\rangle. \tag{27}$$

We note in passing that the singles corrections can be alternatively defined perturbatively by minimizing the Hylleraas functional $\langle\tilde{\Phi}_S^M|\hat{H}^{(0)}|\tilde{\Phi}_S^M\rangle + 2\langle\tilde{\Phi}_S^M|\hat{H}|\tilde{M}\rangle$. For single state calculations this reduces to the method by Kong and Valeev.[27] Despite the aforementioned shortcoming, the perturbative approach has the advantage that one can avoid the evaluation of K and J integrals with two CABS indices. Another choice would be to include the CABS singles configurations in the MRCI-F12 (with some approximation to Hamiltonian matrix elements). These possibilities will be explored in future work.

TABLE I. The effect of singles corrections to the singlet-triplet separation of CH_2 and the dissociation energy of ozone in kcal/mol. ΔE_S denotes the singles corrections to the energy differences. The geometries have been optimized for each method and basis set.

OBS	CASSCF	MRCI	MRCI-F12[a]	MRCI-F12+ΔE_S
		CH_2 singlet–triplet splitting (full valence)		
VDZ-F12	10.58	10.12	9.29	8.78
VTZ-F12	10.12	9.01	8.57	8.53
VQZ-F12	10.11	8.73	8.51	8.50
CBS[56]		8.49		
		CH_2 singlet–triplet splitting [(7,4,3,1) orbitals]		
VDZ-F12	11.21	10.35	9.35	9.01
VTZ-F12	10.61	9.33	8.93	8.86
VQZ-F12	10.54	9.07	8.85	8.84
CBS[56]		8.83		
		O_3 dissociation energy (full valence)		
VDZ-F12	9.01	17.62	23.43	25.01
VTZ-F12	10.27	22.72	25.38	25.64
VQZ-F12	10.55	24.86	26.01	26.03
CBS[56]		26.12		

[a]Values from Ref. 6.

III. NUMERICAL RESULTS

A. CABS singles correction

Table I demonstrates the effect of the singles corrections for the singlet–triplet splitting of CH_2 and the dissociation energy of ozone computed with single-state MRCI-F12 as in Ref. 6 (all the computational details can be found there). When the full valence active space is used, the singles corrections closely reproduce the basis set truncation errors of CASSCF for both systems. Moreover, when the extended active space consisting of the full valence + C($3s$, $3p$, $3d$) orbitals is used, where the basis errors of CASSCF and the correlation energies of MRCI-F12 do not seem additive, the CABS singles corrected energies provide similar accuracy as in the full valence cases. Similar improvements are also found in the examples presented in the following sections.

B. Avoided crossing of LiF

The potential energy curves of two lowest $^1\Sigma^+$ states of LiF are known to have an ionic-covalent avoided crossing at a long distance, and the CASSCF curves have the avoided crossing at a much shorter distance (see Fig. 1). The reason is that dynamical correlation effects lower the ionic state relative to the neutral one, thus moving the crossing point to longer distances. This effect is sensitive to the basis set. If one naively follows the lowest energy state in a single-state calculation for ca. $R = 10.6$–13.8 bohr, the ionic MRCI wave function will be expanded by the internally contracted configurations generated from the covalent CASSCF reference, which leads to large errors. Therefore, a multi-state treatment is vital for this molecule.

Following a recent extensive work of Varandas,[34] we use the cc-pVXZ and aug-cc-pVXZ (X = D, T, Q) basis sets[35–37] for Li and F (denoted as VXZ), respectively, and the active space consisting of six electrons in three a_1, two b_2, and two b_1 orbitals. These correspond to the Li($2s$) and F($2p$, $3p$) atomic orbitals. The $1s$ orbitals and the $2s$ orbital of F are doubly occupied in the CASSCF reference, and the $1s$ orbitals are not correlated in the MRCI and MRCI-F12b calculations. The corresponding JKFIT and MP2FIT basis sets[38–40] are used for density fitting (DF) and resolution of the identity (RI). Since for Li no JKFIT basis is available, the QZVPP/JKFIT set[41] is used in this case. For this molecule, the Davidson correction to MRCI has been reported to give less accurate results (compared to the full configuration interaction) than the uncorrected ones;[34] it is therefore not included in this work.

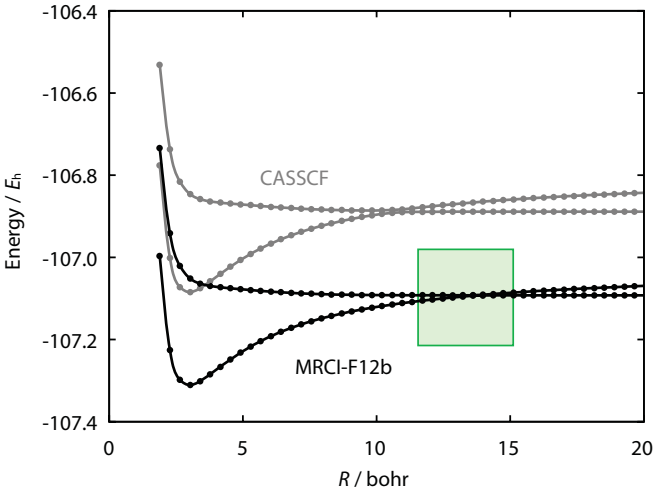

FIG. 1. The global potential energy curves of LiF computed by CASSCF (grey) and MRCI-F12b (black) with VQZ. The rectangle indicates the region expanded in Fig. 2.

The potential energy curves (R = 12.0–15.0) computed by MRCI and MRCI-F12b are shown in Fig. 2. Those computed by MRCI have an avoided crossing (where the energy difference between the ground and excited states is minimized) at 12.83, 13.12, and 13.48 bohr with VDZ, VTZ, and

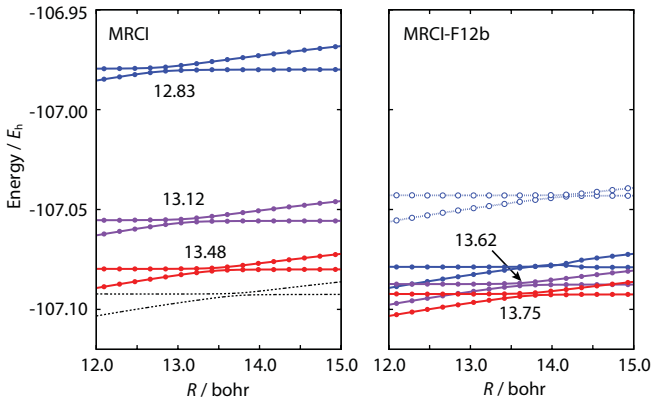

FIG. 2. The potential energy curves of LiF computed by MRCI and MRCI-F12b with the VDZ (blue), VTZ (purple), and VQZ (red) basis sets. Dotted lines in the left panel are the results from MRCI-F12b/VQZ. Dotted blue lines with open circles in the right panel are the results from MRCI-F12/VDZ without the singles correction.

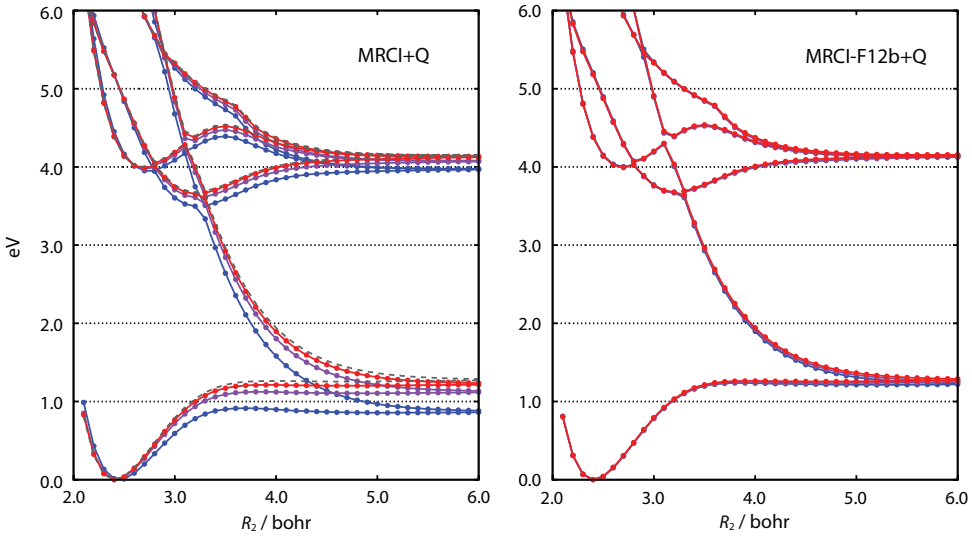

FIG. 3. PESs of low-lying singlet A' states of ozone computed by MRCI+Q (the left panel) and MRCI-F12b+Q (the right panel). One dimensional cuts are made at one $R_1 = 2.4$ and $\angle_{OOO} = 116.8$. The aug-cc-pVDZ (blue), aug-cc-pVTZ (purple), and aug-cc-pVQZ (red) basis sets are used. Dotted lines in the left panel are those computed by MRCI-F12b+Q with aug-cc-pVQZ.

VQZ, respectively, while the MRCI-F12b crossings are at 13.62 and 13.75 bohr with VTZ and VQZ, respectively. The MRCI-F12b/VDZ curve has small irregular behavior around the crossing due to the large *a posteori* CABS singles correction. Probably, this can only be solved by integrating the CABS singles into the MRCI-F12b wavefunction, which will be considered in the future. The empirical value for the crossing point is 13.7 bohr, which is derived by using the Rittner potential for the ionic state[42,43]

$$R_c = \frac{1}{\Delta_{\mathrm{IPEA}}} + \frac{\alpha(\mathrm{Li}^+) + \alpha(\mathrm{F}^-)}{2\Delta_{\mathrm{IPEA}} R_c^3}, \tag{28}$$

where Δ_{IPEA} is the difference between the ionization potential (IP) of Li and electron affinity (EA) of F, and α's are the polarizabilities. From this formula, we ascribe the quicker basis set convergence of MRCI-F12b mainly to the improved description of the electron affinity of F. It should be noted that one cannot expect that our calculation reproduces the empirical crossing distance exactly. For this one would have to include, e.g., core correlation effects and higher-order excitations. Most notably, taking into account the core-valence correlation effect in the Li atom would reduce the computed crossing distance by about 0.34 bohr. On the other hand, taking into account higher order excitations in the F atom would increase the electron affinity, thereby increasing the crossing distance by about 0.34 bohr. Thus, there is some very favorable error compensation which leads to the good agreement of our computed MRCI-F12 values with the empirical value.

C. Excited states of Ozone

The photodissociation of ozone has been theoretically studied to provide insights into atmospheric chemistry of the ozone layer (see, for instance, Ref. 44 and references therein). The excited-state dynamics after photoexcitations of 1–6 eV goes through multiple conical intersections. Here we demonstrate them by MRCI+Q and MRCI-F12b+Q calculations with various basis sets.

We used the full valence active space with frozen core approximation, that is, the three 1s orbitals are doubly occupied in the CASSCF references and not correlated in the MRCI calculations. Dunning's aug-cc-pVXZ basis sets were used for the OBS and Weigend's auxiliary basis sets for DF and RI.[38,39] The calculations were carried out in C_s symmetry, and five A' and six A'' states were averaged in the CASSCF, but only the five A' states have been calculated by MRCI+Q and MRCI-F12b+Q. The two O-O bond distances are denoted R_1 and R_2. Figure 3 compiles the one-dimensional cuts of PESs as a function of the distance R_2, keeping $R_1 = 2.4$ bohr and $\angle_{OOO} = 116.8°$ fixed.

Although the vertical excitation energies from the equilibrium geometry of the ground state are quickly

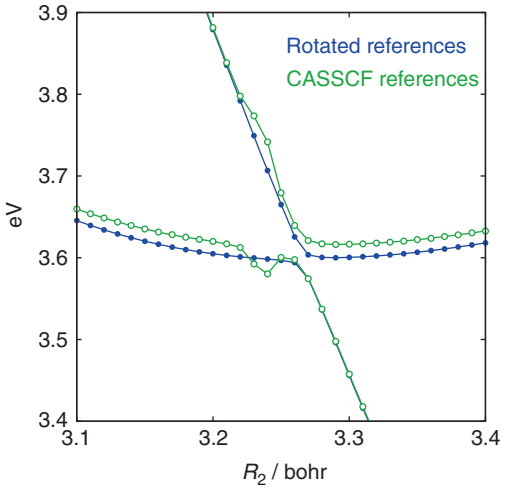

FIG. 4. PESs of excited states of ozone computed by MRCI-F12b using the CASSCF (open circles) and the rotated (full circles) reference functions. The aug-cc-pVDZ basis set is used.

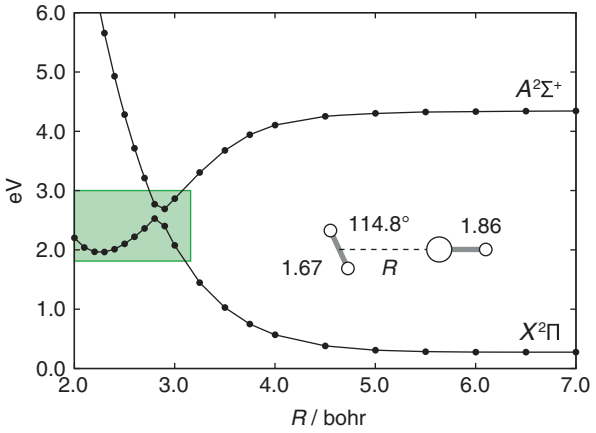

FIG. 5. One-dimensional cut of the ground and first excited A' PES of the H_2 +OH reaction computed by MRCI-F12b+Q with aug-cc-pVQZ. The rectangle indicates the region expanded in Fig. 6.

convergent to their complete basis limits with MRCI+Q (which were presented by Schinke and co-workers to validate their results[44,45]), this is partly due to error cancellations between the basis-set truncation errors of the ground and excited states. Such fortunate error cancellation is not present in general; the dissociation energies and the positions of the avoided crossings (associated with the conical intersections at C_{2v} geometries) are very sensitive to the size of the basis set, as we already observed in our earlier work[6] for the dissociation energies of the ground state. To achieve quantitative agreements, one needs to use larger than the quadruple-ζ basis sets. MRCI-F12b+Q remedies this problem to a large extent, and even the PESs computed with the double-ζ basis set are hardly distinguishable on the scale of the figure from those calculated with the quadruple-ζ basis set.

The choice of the reference functions discussed in Sec. II is also investigated on this system. Figure 4 is the expanded view of the avoided crossing in the same cut computed by MRCI-F12b and aug-cc-pVDZ with the CASSCF and the rotated references. The Davidson correction is not included, since it may lead to unphysical humps on the potentials in the crossing region. The results support the use of rotated reference functions to define the approximate geminal–geminal Hamiltonian matrix elements.

D. H_2 + OH reaction

The photoquenching of OH ($A^2\Sigma^+$) by H_2 has been extensively studied both experimentally and theoretically (see Refs. 46–48 and references therein). Notably, Hoffman and Yarkony have located 13 conical intersections of the PESs of this reaction.[47] The construction of the global PES of this reaction requires more than 20 000 energy calculations,[48] which would be greatly facilitated by the cost-effective MRCI-F12 method presented in this work.

In order to demonstrate the performance of the MRCI-F12b method, we follow the work of Fu *et al.*[48] and compute a one-dimensional cut through the six-dimensional PESs to illustrate one of the conical intersections in C_s symmetry. Fig. 5 shows the energy profiles along this cut. The geometrical parameters are also presented in the figure. The energy zero is set to the energy of H_2 +OH ($X\,^2\Pi$) using the experimental geometries:[49] $r_{HH} = 1.831$ bohr, $r_{OH} = 1.400$ bohr.

As in Ref. 48, we have performed a state-averaged CASSCF using two states in A' and one state in A'' within C_s symmetry. The full valence active space (which consists of six a' and one a'' orbitals) has been used. The 1s orbital of oxygen was kept doubly occupied and not correlated. The subsequent MRCI and MRCI-F12b calculations have been performed for two states in A' symmetry. The basis set used was the same as in the ozone calculation (see Sec. III C).

The basis set dependence of the PES near the conical intersection computed by MRCI+Q and MRCI-F12b+Q is shown in Fig. 6. The MRCI+Q curves have a significant basis set dependence, giving basis errors of more than 0.1 eV with the aug-cc-pVDZ basis for short distances, while the MRCI-F12b+Q curves computed with the aug-cc-pVXZ (X = D, T, Q) basis sets are hardly distinguishable from each other. In other words, MRCI+Q/aug-cc-pVQZ accuracy can be achieved with MRCI-F12b+Q/aug-cc-pVDZ. The cost reduction observed between MRCI+Q/aug-cc-pVQZ and MRCI-F12b+Q/aug-cc-pVDZ is more than one order of magnitude

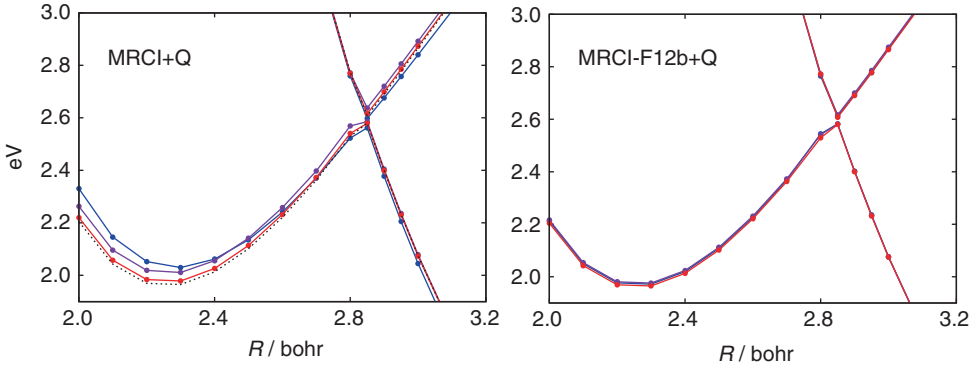

FIG. 6. Expanded view of the one-dimensional cut of H_2 + OH PES with a conical intersections in C_s symmetry, computed by MRCI+Q and MRCI-F12b+Q. The aug-cc-pVDZ (blue), aug-cc-pVTZ (purple), and aug-cc-pVQZ (red) basis sets are used. Dotted lines in the left panel are those computed by MRCI-F12b+Q with aug-cc-pVQZ.

(318 and 13 seconds excluding the CASSCF step, respectively, on 1 CPU, Xeon 3.33 GHz).

IV. CONCLUSIONS

We have developed an MRCI-F12 method for multiple state calculations, which expands the wave functions using the union of internally contracted configurations generated from all the reference functions. This allows us to apply it to nearly degenerate electronic structures around conical intersections and avoided crossings, which play an important role, for instance, in photochemistry. As in our earlier development, the so-called F12b approximation has been used to arrive at efficient working equations. The specific choice of the reference functions that diagonalize the Fock operator yields smooth global PESs. Compared to the underlying MRCI method, the additional computational cost is small, whereas the basis set convergence is much improved. Especially for the ozone excited states and the $H_2 + OH$ reaction studied here, results comparable in accuracy to the conventional MRCI with quadruple-ζ basis sets are obtained by MRCI-F12b using double-ζ basis sets. This leads to the vast reduction of the computational costs while achieving the same accuracy. The computer codes have been implemented into the MOLPRO package,[50] and will be made available for general use in the next release.

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