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Perturbative correction for the basis set incompleteness error of complete-active-space self-consistent field

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To reduce the basis set incompleteness of the complete-active-space self-consistent field (CASSCF) wave function and energy we develop a second-order perturbation correction due to single excitations to complete set of unoccupied states. Other than the one- and two-electron integrals, only one- and two-particle reduced density matrices are required to compute the correction, denoted as $[2]_S$. Benchmark calculations on prototypical ground-state bond-breaking problems show that only the aug-cc-pVXZ basis is needed with the $[2]_S$ correction to match the accuracy of CASSCF energies of the aug-cc-pV(X+1)Z quality. © 2010 American Institute of Physics.
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I. INTRODUCTION

Contemporary *ab initio* quantum chemistry methods represent the Hamiltonian operator and the wave function in a n -electron basis set of an antisymmetrized tensor products of one-electron basis functions. The tensor product form greatly simplifies evaluation of the matrix elements and allows application of advanced correlation methods, such as the coupled-cluster method,¹ to small and medium-sized molecules. One significant drawback of the tensor product basis sets is the resulting slow convergence of the electron correlation energy with respect to the one-particle basis.² This problem is due to the inefficient emulation of the Coulomb hole by a linear combination of any finite number of tensor products of one-electron functions; such linear combinations lack the electron-electron cusp.^{3,4} The Coulomb hole can be described efficiently, however, in terms of the interelectronic distances, which are the natural coordinates for description of this local feature of the wave function. Explicitly correlated methods are characterized by the direct use of the interelectronic distances in the wave function expansion.⁵ Among all explicitly correlated wave function methods the R12 (or F12) methods pioneered by Kutzelnigg⁶ are currently the only general and systematically improvable methods.

The R12 methods have witnessed significant progress over the past two decades.⁷ Early work focused on exploration of the R12 idea at the second order perturbation level (MP2-R12),^{8,9} and the extension to coupled cluster methods (CC-R12)^{10–12} is also undergoing active development. To obtain high accuracy, it is important to significantly reduce both the method error via incorporating high-level correlation effects and the basis set error via R12 methods.¹³ Application of the R12 approach to the popular CCSD(T) method can proceed directly, by incorporating the r_{12} terms into the cluster operator^{14–18} or by an *a posteriori* perturbative treatment.^{19–21} The R12 approach has also been used with the

multireference configuration-interaction method (MRCI),^{22,23} and state-specific second-order multireference perturbation theory (MR-MP2) methods,²⁴ as well as a state-specific *a posteriori* correction to a multireference wave function.²⁵ The R12 method has also been applied in the framework of equation of motion coupled cluster and linear response theory to describe excited states²⁶ and response properties.^{27,28}

One somewhat surprising feature of modern R12 methods is that they reduce the basis set error for the correlation energy to such an extent that the basis set error of the reference (usually, Hartree–Fock) energy becomes a limiting factor. To reduce that error, an additional correction for the incompleteness of the Hartree–Fock energy [known as “the complementary auxiliary basis set (CABS) singles” correction^{17,29–33}] is often employed in applications of R12 methods. The CABS singles correction is a second-order energy correction due to the extension of the basis to include the basis functions missing in the orbital basis set. Note that the CABS singles correction has been employed in other contexts under the name “dual basis” method.^{34–45}

The objective of this work is to extend the idea of the CABS singles correction to the case of a multiconfiguration reference [(specifically complete-active-space self-consistent field (CASSCF)]. We have explored second-order perturbative correction to reduce the basis set error of the CASSCF wave function and energy. The primary motivation of this work is the $[2]_{R12}$ method, which was recently developed by Torhyden and Valeev²⁵ in our group. $[2]_{R12}$ is an explicitly correlated perturbative approach generally applicable to any electronic state. In Ref. 25, the authors have shown that with the addition of the two-particle geminal functions, only an aug-cc-pVDZ basis is enough to compute correlation energies of an aug-cc-pVQZ quality. For their calculations, the wave function is generated from MRCI, which is preceded by a CASSCF calculation to optimize the orbitals. The accuracy of the correlation energy is so high that the error in the reference CASSCF wave function energy due to the incomplete basis (aug-cc-pVDZ) becomes the dominant source of

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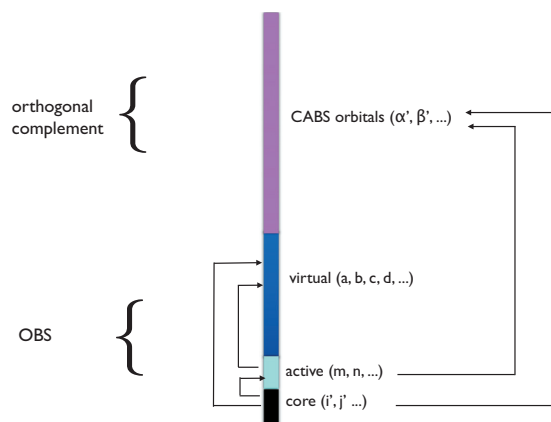


FIG. 1. Illustration of the orbital spaces defined in Sec. II and orbital rotations for CASSCF orbital optimization.

error. Therefore, it is desirable to improve the accuracy of the reference energy so that it matches that of the correlation energy.

A straightforward solution to reducing the CASSCF basis set error is to perform calculations in larger bases. The use of large basis sets, however, can become impossible for sufficiently large systems due to the uncontrollable effects of basis set linear dependencies and loss of precision due to large condition numbers of operator matrices in large basis sets. Our hope is to avoid these difficulties by replacing iterative CASSCF in a large basis with a one-step noniterative perturbative correction. In addition, in the context of [2]_{R12}, even if such calculations in large bases are affordable in certain cases, separate calculations of CASSCF and MRCI in different bases are not desirable when energy derivatives are needed for structure optimization or the computation of response properties.

II. THEORY

The orbitals in the CASSCF wave function $|\psi\rangle$ are optimized in such a way that the following conditions are met:

$$\langle\psi|a_m^i\hat{H}|\psi\rangle=0, \quad \forall i', m, \quad (1)$$

$$\langle\psi|a_a^i\hat{H}|\psi\rangle=0, \quad \forall i, a, \quad (2)$$

where we adopt the standard tensor notation used in electronic structure literature (refer to Appendix A for a brief summary). Note that i stands for an occupied orbital, which can be either core or active, hence Eq. (2) represents the residual equations corresponding to both core to virtual and active to virtual excitations. If the orbitals were expanded in complete basis set (CBS), not in orbital basis set (OBS), the following additional residual equations would be satisfied (see Fig. 1):

$$\langle\psi|a_{\alpha'}^i\hat{H}|\psi\rangle=0, \quad \forall i, \alpha'. \quad (3)$$

The basis set incompleteness error (BSIE) is defined as the difference between the CASSCF energies calculated in the given OBS and in the CBS (“the CBS limit”).

To reduce BSIE via a perturbative approach it is natural to choose as zeroth-order the CASSCF wave function repre-

sented in OBS, $|\psi^{(0)}\rangle$. Although this wave function does not satisfy Eq. (3), the Hamiltonian can be partitioned so that it is satisfied to zeroth-order

$$\langle\psi^{(0)}|a_{\alpha'}^i\hat{H}^{(0)}|\psi^{(0)}\rangle=0, \quad \forall i, \alpha', \quad (4)$$

$$\langle\psi^{(0)}|a_{\alpha'}^i\hat{H}^{(1)}|\psi^{(0)}\rangle\neq 0, \quad \forall i, \alpha'. \quad (5)$$

This is possible by, for example, selecting as the first-order all parts of \hat{H} that, when applied to $\psi^{(0)}$, promote one electron from an occupied to a CABS orbital

$$\hat{H}^{(1)}=h_{\alpha'}^i a_i^{\alpha'} + \frac{1}{2}v_{\alpha'k}^{ij} a_{ij}^{\alpha'k}, \quad (6)$$

where h and v are the usual one- and two-electron integrals. However, to compute a second-order energy based on this partitioning would require high-rank reduced density matrices (RDMs) and would be relatively expensive. Here we define $\hat{H}^{(1)}$ as

$$\hat{H}^{(1)}=f_{\alpha'}^i a_i^{\alpha'}, \quad (7)$$

where $f_{\alpha'}^i=h_{\alpha'}^i+v_{\alpha'k}^{ij}\gamma_j^k$; parts of Eq. (6) that are not present in Eq. (7) are classified as second-order in perturbation and will not affect the second-order energy.

With $\hat{H}^{(1)}$ defined in Eq. (7), the first order interaction space contains the configurations $\{a_i^{\alpha'}|\psi^{(0)}\rangle=|i^{\alpha'}\rangle, \forall i, \alpha'\}$. In addition, as will be discussed in the next section, we would specify $\hat{H}^{(0)}$ so that it couples OBS virtual orbitals with CABS orbitals; due to the coupling, the configurations induced by single excitations from an occupied to an OBS virtual orbital, $\{a_i^a|\psi^{(0)}\rangle=|i^a\rangle, \forall i, a\}$, will also emerge in the first order wave function $|\psi^{(1)}\rangle$. Therefore, the first order interaction space is defined as $\{a_i^{\alpha}|\psi^{(0)}\rangle=|i^{\alpha}\rangle, \forall i, \alpha\}$ (α stands for any virtual orbital in CBS. See Appendix A for details).

The set of configurations $\{|i^{\alpha}\rangle, \forall i, \alpha\}$ is neither orthogonal nor normalized, since $\langle i^{\alpha}|j^{\beta}\rangle=\delta_{\alpha}^{\beta}\gamma_i^j$. We can introduce a set of orthonormal configurations $\{|\bar{i}^{\alpha}\rangle\}$ via the matrix $\gamma^{-1/2}$ in the following way:

$$|\bar{i}^{\alpha}\rangle=(\gamma^{-1/2})_i^k |i^{\alpha}\rangle, \quad (8)$$

therefore

$$|i^{\alpha}\rangle=(\gamma^{1/2})_i^k |\bar{i}^{\alpha}\rangle. \quad (9)$$

The projector on the first-order interaction space is defined as

$$\hat{P}=|\bar{i}^{\alpha}\rangle\langle\bar{i}^{\alpha}|=(\gamma^{-1})_i^k |i^{\alpha}\rangle\langle i^{\alpha}|. \quad (10)$$

A. The zeroth-order Hamiltonian

The choice of $\hat{H}^{(0)}$ is crucial, and it is guided by both formal and computational cost considerations. One option is to define $\hat{H}^{(0)}$ as the one-body Fock operator

$$\hat{H}_F^{(0)}=E^{(0)}+f_{\alpha}^q \tilde{a}_q^{\alpha}+f_{\beta'}^{\alpha'} \tilde{a}_{\alpha'}^{\beta'}+(f_{\alpha}^{\alpha'} \tilde{a}_{\alpha'}^{\alpha}+f_{\alpha'}^{\alpha} \tilde{a}_{\alpha'}^{\alpha}), \quad (11)$$

where $f_{\alpha}^{\alpha'}=h_{\alpha}^{\alpha'}+v_{\alpha'}^{\alpha i}\gamma_i^{\alpha'}$, and \tilde{a} denotes the multireference normal ordering developed by Mukherjee and Kutzelnigg^{46–48} (in MK order, $\tilde{a}_{\beta}^{\alpha}=a_{\beta}^{\alpha}-\gamma_{\beta}^{\alpha}$). In the CABS singles approach cor-

recting the basis set incompleteness of the Hartree–Fock wave function, it is preferable to include in $\hat{H}^{(0)}$ the coupling between OBS virtual orbitals and CABS orbitals. To reproduce this single reference limit, the terms in parentheses in Eq. (11) are included to take care of the coupling effect.

We also attempted a more complete $\hat{H}^{(0)}$

$$\hat{H}_D^{(0)} = \hat{H}_{\text{OBS}} + f_{\alpha'}^{\beta'} a_{\beta'}^{\alpha'} + (f_a^{\alpha'} a_a^{\alpha'} + f_a^{\alpha'} a_{\alpha'}^a), \quad (12)$$

where \hat{H}_{OBS} stands for the full Hamiltonian in OBS: $h_p^q a_p^q + \frac{1}{4} v_{pq}^{qs} a_{pq}^{pr}$. D refers to the connection with the Dyll Hamiltonian,⁴⁹ since the terms making nonzero contributions to the correction are similar to those in the Dyll Hamiltonian. Clearly, Eqs. (1)–(3) are valid with $\hat{H}_D^{(0)}$. In addition

$$\langle \psi^{(0)} | a_q^p \hat{H}_D^{(0)} | \psi^{(0)} \rangle = E^{(0)} \gamma_q^p, \quad (13)$$

where $\gamma_q^p = \langle \psi^{(0)} | a_q^p | \psi^{(0)} \rangle$ (refer to Appendix B for a proof). The indices p and q can be any index in OBS. This property will play an important role later. For both $\hat{H}_F^{(0)}$ and $\hat{H}_D^{(0)}$, $E^{(0)} = \langle \psi^{(0)} | \hat{H}^{(0)} | \psi^{(0)} \rangle = \langle \psi^{(0)} | \hat{H}_{\text{OBS}} | \psi^{(0)} \rangle$, i.e., the CASSCF energy in OBS.

B. Perturbation corrections

According to the Rayleigh–Schrödinger perturbation theory, the first order wave function, $|\psi^{(1)}\rangle = C_{\alpha}^y a_y^{\alpha} |\psi^{(0)}\rangle = C_{\alpha}^y |y\rangle^{\alpha}$, is obtained by solving the following equation:

$$\hat{P}(\hat{H}^{(0)} - E^{(0)})\hat{P}|\psi^{(1)}\rangle = -\hat{H}^{(1)}|\psi^{(0)}\rangle. \quad (14)$$

After projecting over the first order interaction space, the above equation can be written in a matrix form

$$B_{\beta y}^{x\alpha} C_{\alpha}^y = -\gamma_{j\gamma'}^x f_{\gamma'}^{\beta'} \delta_{\beta}^{\alpha'}, \quad (15)$$

where $B_{\beta y}^{x\alpha} \equiv \langle x | (\hat{H}^{(0)} - E^{(0)}) | y \rangle^{\alpha} = \langle \psi^{(0)} | a_{\beta}^x (\hat{H}^{(0)} - E^{(0)}) a_y^{\alpha} | \psi^{(0)} \rangle$.

The second-order energy correction is then calculated as

$$E^{(2)} = \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(1)} \rangle = C_{\alpha'}^j f_i^{\alpha'} \gamma_j^i. \quad (16)$$

Now let us look at the computation of the B matrix. If we use $\hat{H}_F^{(0)}$

$$B_{\beta y}^{x\alpha} = \langle \beta | (\hat{H}_F^{(0)} - E^{(0)}) | y \rangle^{\alpha} \quad (17)$$

$$= \delta_{\beta j}^{\alpha i} (\lambda_{yi}^{xj} - \gamma_i^x \gamma_y^j) + f_{\beta}^{\alpha} \gamma_y^x. \quad (18)$$

λ here stands for the 2-RDM *cumulant* ($\lambda_{rs}^{pq} = \gamma_{rs}^{pq} - \gamma_r^p \gamma_s^q + \gamma_s^p \gamma_r^q$);⁵⁰ it is nonzero only when the four indices are all active orbital indices.

If we use $\hat{H}_D^{(0)}$

$$B_{\beta y}^{x\alpha} = \langle \psi^{(0)} | a_{\beta}^x (\hat{H}_D^{(0)} - E^{(0)}) a_y^{\alpha} | \psi^{(0)} \rangle, \quad (19)$$

$$= -E^{(0)} \delta_{\beta}^{\alpha} \gamma_y^x + \langle \psi^{(0)} | a_{\beta}^x \hat{H}_D^{(0)} a_y^{\alpha} | \psi^{(0)} \rangle. \quad (20)$$

A direct evaluation of the second term would require 3-RDM, but that can be avoided by extracting a commutator as follows

$$B_{\beta y}^{x\alpha} = -E^{(0)} \delta_{\beta}^{\alpha} \gamma_y^x + \langle \psi^{(0)} | a_{\beta}^x \hat{H}_D^{(0)} a_y^{\alpha} | \psi^{(0)} \rangle, \quad (21)$$

$$= -E^{(0)} \delta_{\beta}^{\alpha} \gamma_y^x + \langle \psi^{(0)} | a_{\beta}^x a_y^{\alpha} \hat{H}_D^{(0)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | a_{\beta}^x [\hat{H}_D^{(0)}, a_y^{\alpha}] | \psi^{(0)} \rangle, \quad (22)$$

$$= -E^{(0)} \delta_{\beta}^{\alpha} \gamma_y^x + \delta_{\beta}^{\alpha} \langle \psi^{(0)} | a_y^{\alpha} \hat{H}_D^{(0)} | \psi^{(0)} \rangle + \langle \psi^{(0)} | a_{\beta}^x [\hat{H}_D^{(0)}, a_y^{\alpha}] | \psi^{(0)} \rangle, \quad (23)$$

$$= -E^{(0)} \delta_{\beta}^{\alpha} \gamma_y^x + \delta_{\beta}^{\alpha} \gamma_y^x E^{(0)} + \langle \psi^{(0)} | a_{\beta}^x [\hat{H}_D^{(0)}, a_y^{\alpha}] | \psi^{(0)} \rangle \quad (\text{using Eq. 13}), \quad (24)$$

$$= \langle \psi^{(0)} | a_{\beta}^x [\hat{H}_D^{(0)}, a_y^{\alpha}] | \psi^{(0)} \rangle. \quad (25)$$

With this expression, we do not need 3-RDM to calculate B , since the commutator is at most a two-body operator, and then one index from the commutator needs to be contracted with the external index β . More explicitly

$$B_{\beta y}^{x\alpha} = -\delta_{\beta}^{\alpha} (f_y^i \gamma_i^x + \frac{1}{2} v_{yk}^{ij} \lambda_{ij}^{xk}) + f_{\beta}^{\alpha} \gamma_y^x. \quad (26)$$

Let us now compare the two versions of perturbation theory.

- To compare the cost, let us use o , v , and A to denote the number of occupied orbitals, OBS virtual orbitals, and virtual orbitals from both OBS and CABS, respectively. For both variants, B assumes a factorized form. With $\hat{H}_F^{(0)}$, B contains an intermediate $f_j^i (\lambda_{yi}^{xj} - \gamma_i^x \gamma_y^j)$; With $\hat{H}_D^{(0)}$, B contains $(f_y^i \gamma_i^x + \frac{1}{2} v_{yk}^{ij} \lambda_{ij}^{xk})$. The cost of calculating both intermediates is negligible in the context of a CASSCF calculation. The second term of B , $f_{\beta}^{\alpha} \gamma_y^x$, scales as $o^2 A^2$, roughly the fourth power of the system. In comparison, solving the CASSCF residual equations scales at least as $v o^4$, roughly the fifth power of the size of the system. Therefore, the cost of the perturbative correction is small compared to the CASSCF procedure.
- In the single reference limit, for both variants B reduces to the form $-\delta_{\beta}^{\alpha} f_y^i \delta_i^x + f_{\beta}^{\alpha} \delta_y^x = f_{\beta}^{\alpha} \delta_y^x - \delta_{\beta}^{\alpha} f_y^i$; Eq. (15) reduces to $(f_{\beta}^{\alpha} \delta_y^x - \delta_{\beta}^{\alpha} f_y^i) C_{\alpha}^y = -f_{\gamma'}^{\beta'} \delta_{\beta}^{\alpha'}$. Therefore, both variants reduce to the CABS singles approach.
- In typical single reference situations, where γ_y^x is close to δ_y^x and the cumulant is small, the two versions shall behave similarly; as the bond is stretched, the orbital occupation pattern complicates, and a more complete zeroth-order Hamiltonian beyond the one-particle Fock operator would be advantageous. Overall, we expect a somewhat superior behavior of $\hat{H}_D^{(0)}$ over $\hat{H}_F^{(0)}$.
- For both variants, the index pairs (x, β) and (y, α) must have the same spin (otherwise B vanishes), as is clear from Eqs. (18) and (26). Therefore, the equations for the alpha and beta spin components of the C vector are decoupled.

The described second-order correction to the energy will be denoted as $[2]_S$. The $[2]_S$ method with the two choices of zeroth-order Hamiltonian has been implemented in the developmental version of the MPQC quantum chemistry package.⁵¹

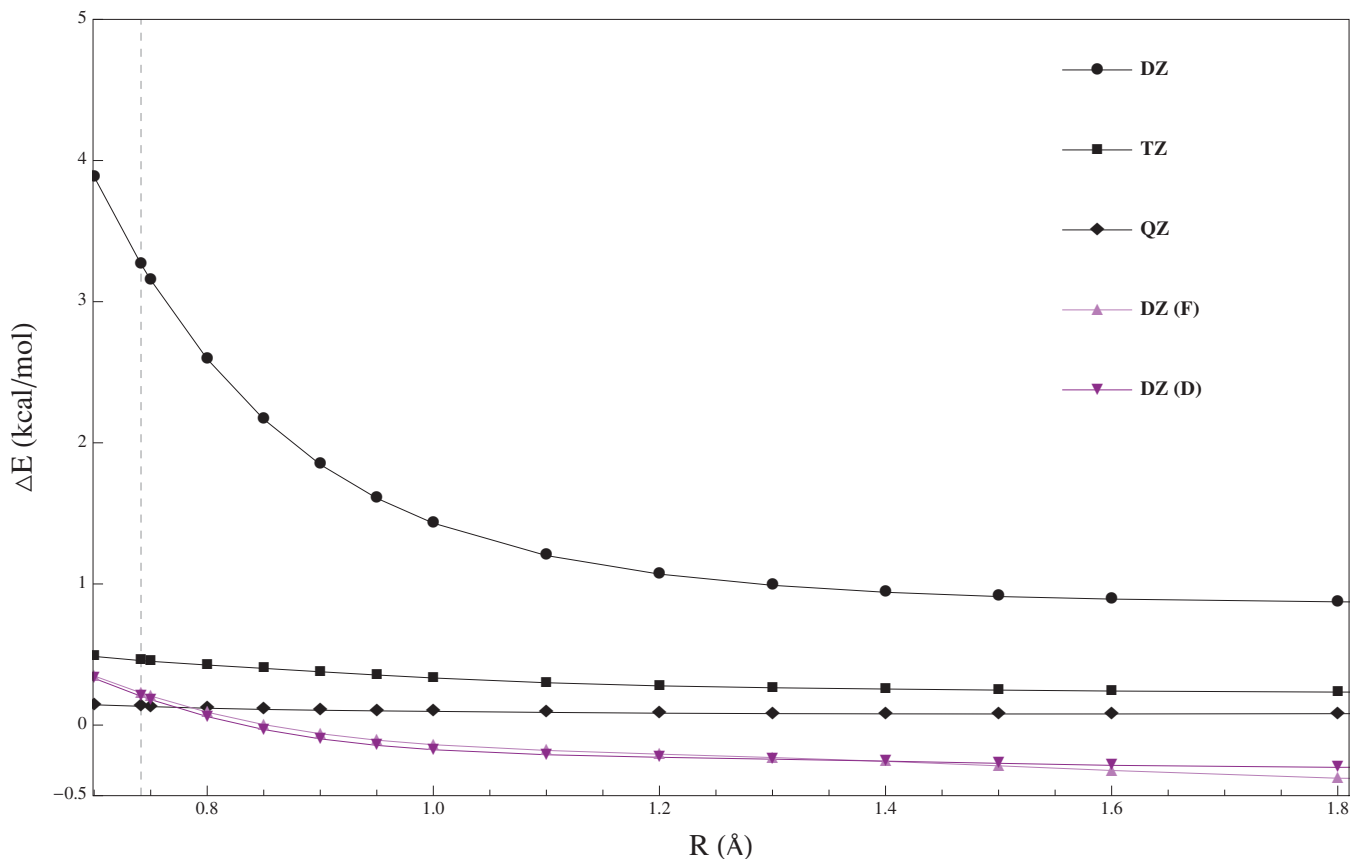


FIG. 2. The basis set incompleteness of valence CASSCF energy for H_2 molecule. XZ stands for the aug-cc-pVXZ basis. (F) and (D) refer to the $[2]_S$ results with the zeroth-order Hamiltonian of Eqs. (11) and (12), respectively. The dashed line marks the equilibrium geometry ($R_e=0.74144$ Å).

III. RESULTS AND DISCUSSION

To test the efficacy of the perturbative correction, we have computed the CASSCF energies and $[2]_S$ corrections for H_2 , HF, H_2O , and N_2 molecules using Dunning's aug-cc-pVXZ basis sets ($X=2, 3, 4$, and 5).^{52,53} The basis set limit is obtained from the three-point extrapolation $A+Be^{-XC}$ with $X=3, 4$, and 5 . Since the $[2]_{R12}$ in the aug-cc-pVDZ basis is already very efficient in accounting for the basis set incompleteness of the dynamical correlation energy, in the current work we mainly focus on the CASSCF perturbative correction also in the same basis. Valence active spaces are used in all computations: (2e, 2o), (8e, 5o), (8e, 6o) and (10e, 8o) for H_2 , HF, H_2O and N_2 , respectively. For all the calculations, the core orbitals are fixed by the restricted Hartree-Fock calculation and kept unchanged in CASSCF. We use a union of the uncontracted cc-pV6Z basis set and the corresponding OBS as the basis set from which the CABS orbitals are computed. The CASSCF calculations are carried out with the PSI3 package⁵⁴ and the $[2]_S$ calculations are done with the MPQC package.⁵¹ The results are plotted in Figs. 2–5. The mean absolute errors (MAE) and the nonparallelity errors [(NPE), defined as the absolute value of the difference between the maximum error and the minimum error] are tabulated in Table I, based on the data from the equilibrium geometry to the most stretched geometry.

The most conspicuous observation from Fig. 2 is the large variation of BSIE in the aug-cc-pVDZ basis for H_2 .

This is clearly reflected in the large NPE of 2.42 kcal/mol. In aug-cc-pVTZ, both the absolute and the relative errors are significantly reduced: the MAE decreases from 1.50 to 0.32 kcal/mol, and the NPE decreases by an order of magnitude, from 2.42 to 0.22 kcal/mol. In aug-cc-pVQZ, both MAE and NPE are below 0.1 kcal/mol, and the BSIE curve is almost flat. The $[2]_S$ correction greatly reduces the large basis set error of aug-cc-pVDZ, as apparent from the figure. With the use of $\hat{H}_F^{(0)}$ the NPE is reduced to 0.50 kcal/mol, five times smaller than the uncorrected value. For $\hat{H}_D^{(0)}$ the NPE is further reduced to 0.28 kcal/mol, an order of magnitude improvement with respect to the uncontracted value. From Fig. 1, when the bond is stretched beyond 1.5 Å, the curve for $\hat{H}_D^{(0)}$ deviates from the $\hat{H}_F^{(0)}$ curve and varies more slowly. This suggests that $\hat{H}_D^{(0)}$ may be a better choice of a zeroth-order Hamiltonian when the multireference character of the system becomes pronounced.

Similar conclusions are drawn for HF (Fig. 3). The error curve for aug-cc-pVDZ lies high above all the other ones, indicating the large absolute error (the MAE is 22.85 kcal/mol). For the relative error, its NPE is 2.11 kcal/mol, comparable to that for H_2 . In aug-cc-pVTZ, it is greatly reduced to 0.4 kcal/mol. The curve for aug-cc-pVQZ is already very flat. The error for aug-cc-pVDZ decreases substantially via the introduction of the $[2]_S$ correction. With $\hat{H}_F^{(0)}$, the NPE is 0.58 kcal/mol, close to the aug-cc-pVTZ result. The use of

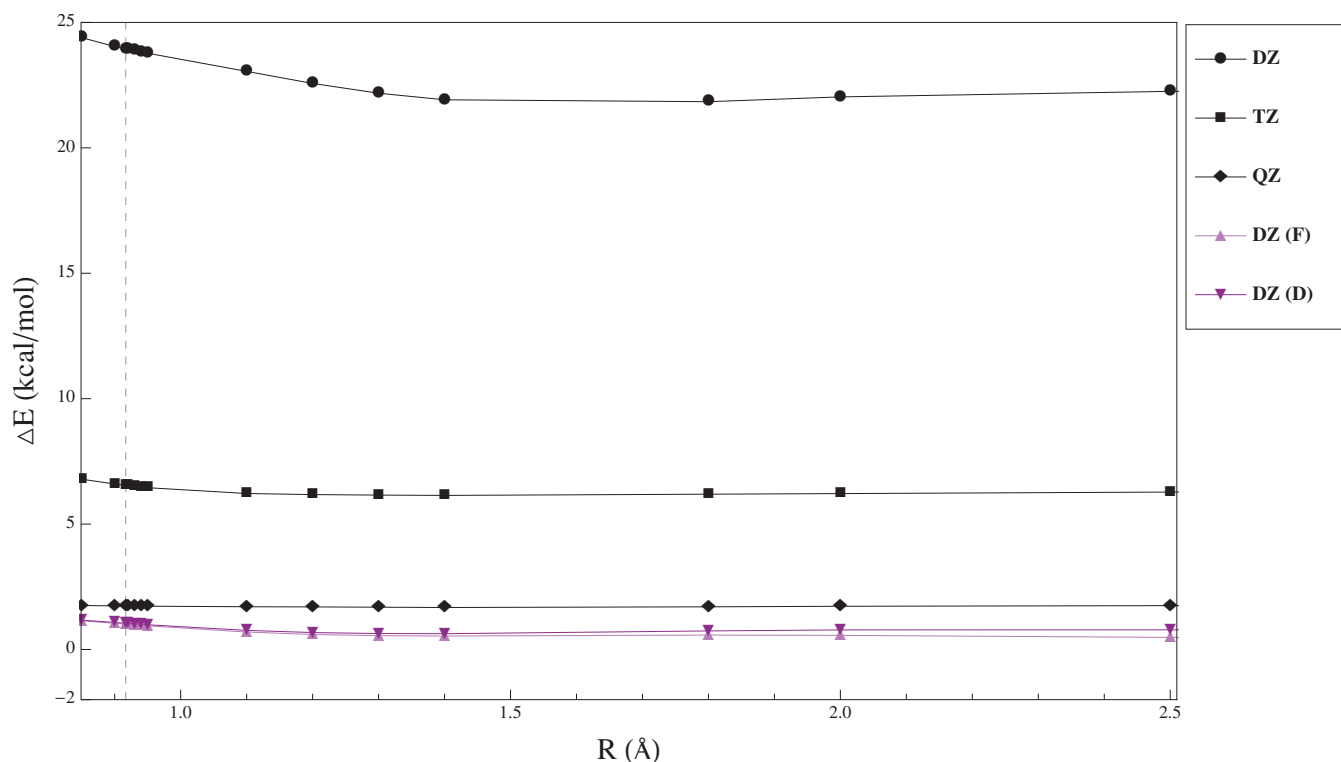


FIG. 3. The basis set incompleteness of valence CASSCF energy for HF molecule. XZ stands for the aug-cc-pVXZ basis. (F) and (D) refer to the $[2]_S$ results with the zeroth-order Hamiltonian of Eqs. (11) and (12), respectively. The dashed line marks the equilibrium geometry ($R_e=0.9168$ Å).

$\hat{H}_D^{(0)}$ further reduces the NPE to 0.42 kcal/mol, roughly the same as the aug-cc-pVTZ result. As for H_2 , we observe in Fig. 3 a more mild fluctuation of the error in the $\hat{H}_D^{(0)}$ curve than that for $\hat{H}_F^{(0)}$, at greatly stretched geometries.

Again, similar trends are observed for H_2O and N_2 . For H_2O , the large NPE in aug-cc-pVDZ of 3.10 kcal/mol is brought down to 0.85 and 0.72 kcal/mol, for $\hat{H}_F^{(0)}$ and $\hat{H}_D^{(0)}$, respectively. N_2 has a much larger NPE of 6.85 kcal/mol in

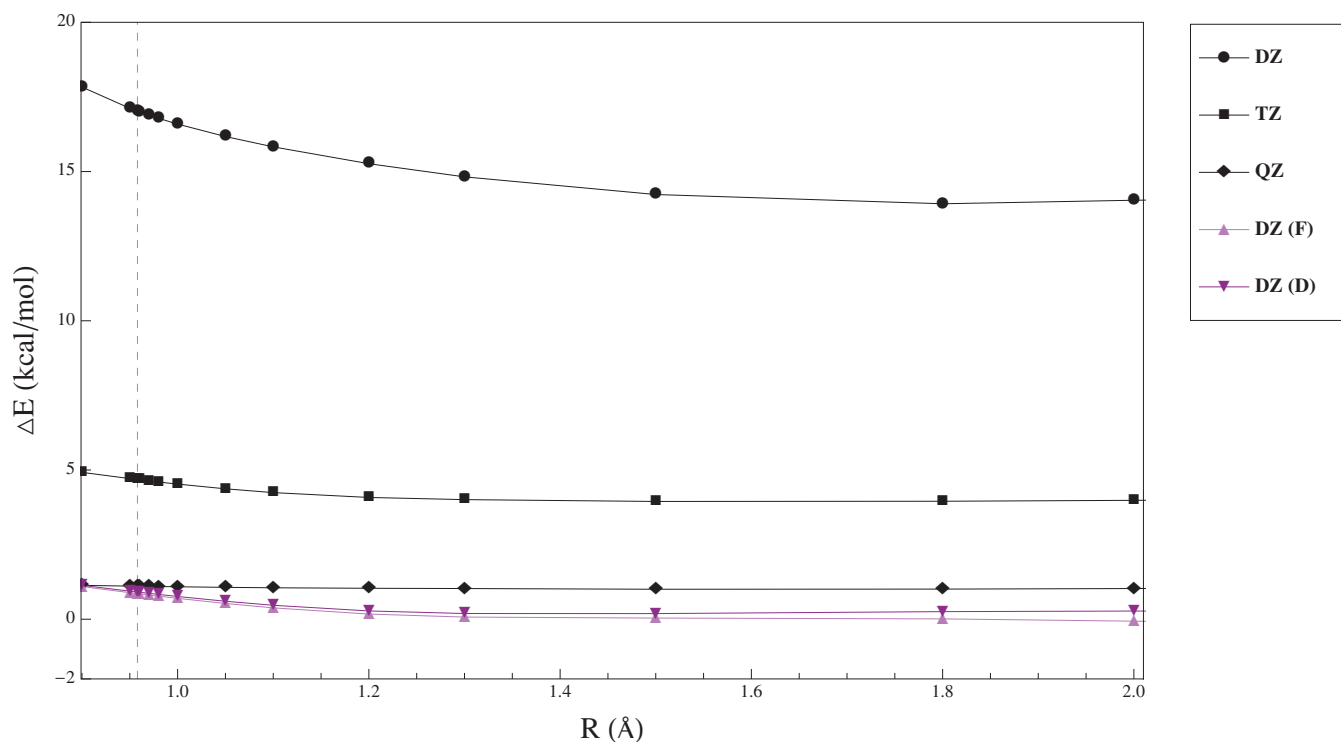


FIG. 4. The basis set incompleteness of valence CASSCF energy for H_2O molecule. XZ stands for the aug-cc-pVXZ basis. (F) and (D) refer to the $[2]_S$ results with the zeroth-order Hamiltonian of Eqs. (11) and (12), respectively. $\angle HOH=109.57^\circ$ and O–H bonds are stretched symmetrically. The dashed line denotes the equilibrium geometry ($R_e=0.958$ Å).

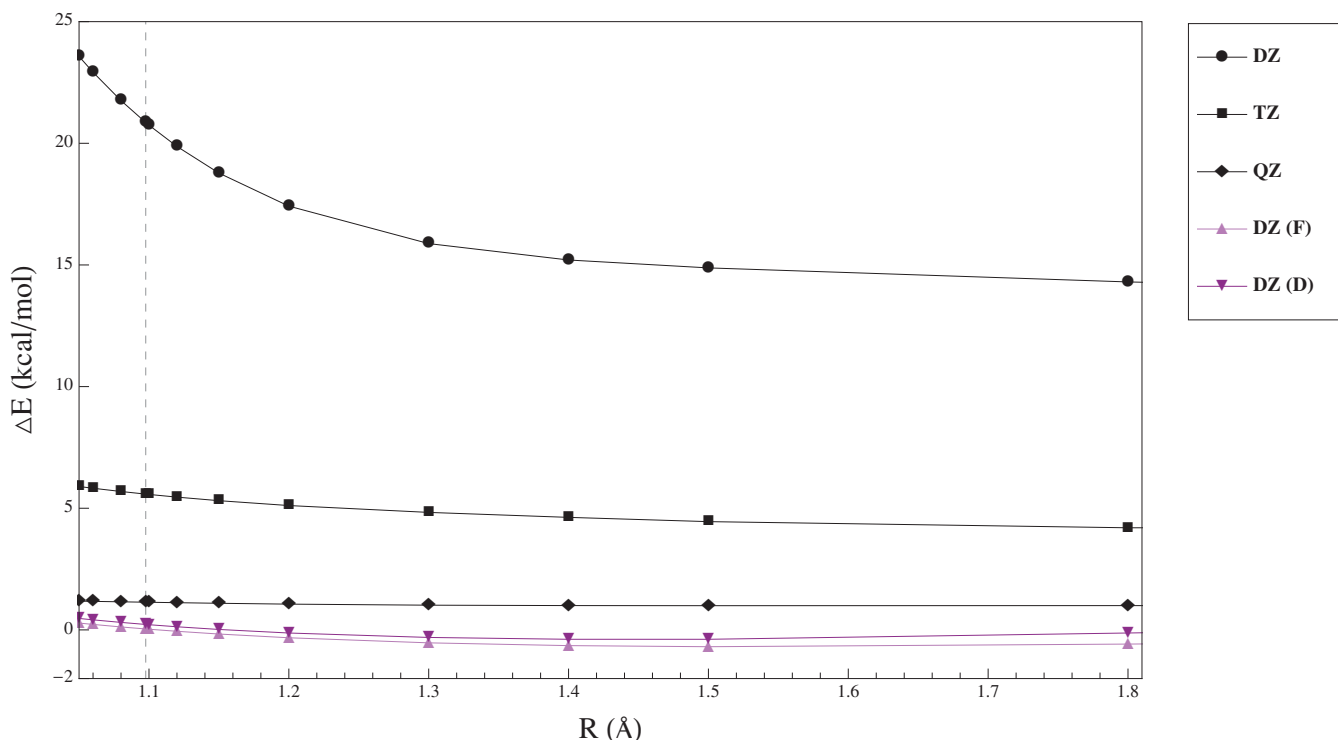


FIG. 5. The basis set incompleteness of valence CASSCF energy for N_2 molecule. XZ stands for the aug-cc-pVXZ basis. (F) and (D) refer to the $[2]_S$ results with the zeroth-order Hamiltonian of Eqs. (11) and (12), respectively. The dashed line marks the equilibrium geometry ($R_e=1.09768 \text{ \AA}$).

aug-cc-pVDZ, but the $[2]_S$ correction reduces it to 0.66 and 0.37 kcal/mol, for $\hat{H}_F^{(0)}$ and $\hat{H}_D^{(0)}$, respectively. They are even smaller than the aug-cc-pVTZ result.

Overall, the $[2]_S$ correction yields substantial improvement in both the absolute and the relative basis set errors. For the corrected results based on CASSCF calculations in aug-cc-pVDZ, both variants of the correction reduce the NPE to below 1 kcal/mol. The $\hat{H}_F^{(0)}$ -based $[2]_S$ correction reduces the NPE by about roughly four times for H_2 , HF, and H_2O and by an order for N_2 . Use of $\hat{H}_D^{(0)}$ further improves upon $\hat{H}_F^{(0)}$. In terms of NPE, the $\hat{H}_D^{(0)}$ -based $[2]_S$ correction in aug-cc-pVDZ yields results of quality the same as or better than that for aug-cc-pVTZ without the correction.

Since results in aug-cc-pVTZ are already fairly accurate, we expect very small BSIE for perturbation corrected computations in aug-cc-pVTZ (see Table I). The aug-cc-pVTZ $[2]_S$ result is of similar quality to the standard aug-cc-pVQZ results.

For all the calculations, we employed a large uncontracted cc-pV6Z basis to construct CABS. To investigate whether the computational cost of the perturbation calculation can be reduced, we carried out a series of calculations with CABS of reduced dimensions. The result is plotted in Fig. 6. We reduce CABS by gradually truncating the high angular momentum basis functions in the cc-pV6Z basis. For example, in Fig. 6, the x -coordinate p means that only s and

TABLE I. MAE and NPE of valence CASSCF energies with respect to their complete basis set limits, based on the data from the equilibrium geometry to the most stretched geometry (a bond distance of 10 Å for H_2 , HF, and N_2 , and 3 Å for the O–H bonds in H_2O). For H_2 , the active space is (2e, 2o); for HF, it is (8e, 5o); for H_2O , it is (8e, 6o), $\angle HOH=109.57^\circ$, and O–H bonds are stretched symmetrically; for N_2 , it is (10e, 8o). XZ in the first column refers to the aug-cc-pVXZ basis set [“(F)” and “(D)” refer to the $[2]_S$ results with the zeroth-order Hamiltonian of Eqs. (11) and (12), respectively].

	H_2	HF	H_2O	N_2	H_2	HF	H_2O	N_2
	MAE (kcal/mol)				NPE (kcal/mol)			
DZ	1.50	22.84	15.62	16.46	2.42	2.10	3.10	6.85
TZ	0.32	6.32	4.29	4.79	0.22	0.40	0.73	1.38
QZ	0.10	1.72	1.06	1.05	0.05	0.10	0.10	0.15
5Z	0.03	0.47	0.26	0.23	0.01	0.04	0.03	0.04
DZ(F)	0.24	0.70	0.43	0.38	0.50	0.58	0.85	0.66
TZ(F)	0.03	0.50	0.29	0.16	0.04	0.05	0.14	0.23
DZ(D)	0.21	0.83	0.52	0.19	0.28	0.42	0.72	0.37
TZ(D)	0.04	0.51	0.31	0.19	0.03	0.04	0.10	0.19

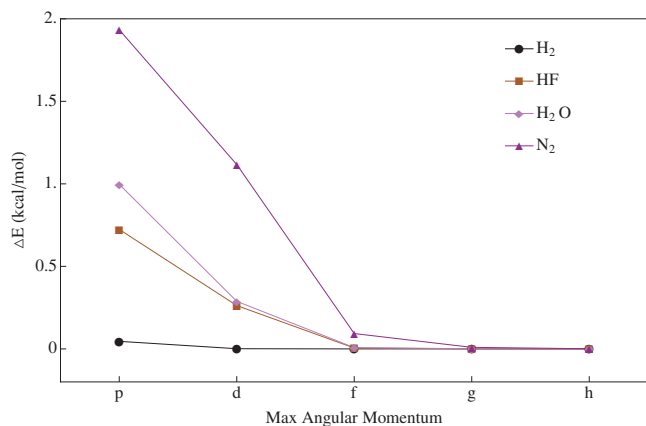


FIG. 6. Convergence of the $[2]_S$ correction with respect to the maximum angular momentum of the basis functions kept in CABS. Zero is defined as the $[2]_S$ correction obtained with the full uncontracted cc-pV6Z basis set containing up to h functions for H and i functions for N, O, and F.

p functions are included in CABS. The geometries adopted for this test are $R=1.00$ Å for H₂, $R=1.20$ Å for HF, $R(OH)=1.20$ Å for H₂O ($\angle HOH=109.57^\circ$) and $R=1.40$ Å for N₂. For easy comparison, we take the BSIE of the perturbation corrected results (in aug-cc-pVDZ) with the untruncated CABS as the reference point. Quick convergence with respect to CABS is observed for all the tests. Once f functions are included in CABS, the difference from the complete CABS is smaller than 0.1 kcal/mol. If even higher angular momentum functions are included, the result is essentially indistinguishable from the complete CABS. Therefore, it seems to suffice to include up to f function in CABS for practical purposes, provided that only up to $2p$ functions are strongly occupied.

IV. SUMMARY AND CONCLUSIONS

In this work we have presented a second-order perturbative correction for the basis set incompleteness of CASSCF. The need for such a correction naturally arises in the context of the explicitly correlated $[2]_{R12}$ method. The basis set error of correlation energy is reduced in the $[2]_{R12}$ method via the introduction of the two-particle geminal functions to such an extent that the basis set error in the CASSCF reference energy becomes a major source of the residual error when small double-zeta basis set is used.

In the current approach the CASSCF wave function obtained in a small orbital basis (e.g., aug-cc-pVDZ) is taken as the zeroth order wave function $|\psi^{(0)}\rangle$. A large auxiliary basis set is introduced, in combination with OBS, to approximate the complete basis set. The one-particle excitation operator from an occupied (core or active) to a CABS orbital, $f_\alpha^i a_i^\alpha$, is taken as the first order Hamiltonian $\hat{H}^{(1)}$, which captures the missing orbital rotation effect due to the incomplete basis. Two variants of the zeroth order Hamiltonian are attempted; one is the one-particle Fock operator $\hat{H}_F^{(0)}$, and the other, $\hat{H}_D^{(0)}$, is a two-particle operator, which includes the full Hamiltonian in OBS. (Note that the former is identical to the zeroth-order operator used in our $[2]_{R12}$ method). The com-

putational cost for both variants scales as $o^2 A^2$. This correction, denoted as $[2]_S$ reduces to the CABS singles approach¹⁷ in the single reference limit.

Benchmark calculations are carried out on the systems H₂, HF, H₂O, and N₂ to test the approach. We found that the $[2]_S$ correction greatly reduces the basis set error of CASSCF. The error in the absolute energy in aug-cc-pVDZ, measured in terms of MAE, has been reduced to below that of standard aug-cc-pVQZ CASSCF. More importantly, significant improvement for relative energies is observed. Measured in terms of NPE, the error of aug-cc-pVDZ CASSCF + $[2]_S$ in relative energies is below 1 kcal/mol. $\hat{H}_D^{(0)}$ performs better than $\hat{H}_F^{(0)}$; with the use of $\hat{H}_D^{(0)}$, the accuracy in aug-cc-pVDZ exceeds aug-cc-pVTZ. If we employ aug-cc-pVTZ as OBS, the accuracy upon the perturbative correction exceeds aug-cc-pVQZ. The dependence on CABS is also tested, and quick convergence is observed. It seems reasonable to expect that including up to f functions in CABS suffice for the level of accuracy achievable in aug-cc-pVDZ, provided that only up to $2p$ functions are strongly occupied.

The proposed perturbation theory is rather simple and of general applicability, not confined to the context of explicitly correlated computations. Other than one- and two-electron integrals, only up to two-particle RDMs are needed to compute the correction. Encouraged by the reasonable performance of the perturbation theory, we might explore the possibility of treating the diffuse functions perturbatively in CASSCF, since those functions may lead to linear dependency and convergence issues in the iterative procedure of CASSCF, while those difficulties may be suppressed in the one-step noniterative perturbation procedure.

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APPENDIX A: NOTATION

The OBS is defined as the computational basis in which the CASSCF calculation is carried out. Conventionally, this basis is divided into three sets: core orbitals (denoted by i', j'), (partially occupied) active orbitals (denoted by m, n), and virtual orbitals (denoted by a, b, c , and d). The occupied orbitals, which are either core or active orbitals, are denoted by i, j, k, l . Orbitals in OBS are collectively denoted by p, q, r , and s . To compose a CBS, OBS needs to be supplemented by its orthogonal complement, which is clearly a space of infinite dimension. In this work the orthogonal complement is approximated by the CABS approach;⁵⁵ i.e., CBS \approx OBS \cup CABS. CABS is constructed using the CABS + approach: a sufficiently large auxiliary basis set is chosen, OBS is added to it, and the part that overlaps with OBS is projected out. We will use α' and β' to denote CABS orbitals. They are the additional virtual orbitals with respect to the occupied orbitals in OBS, and together with the virtual orbit-

als in OBS, they form the complete virtual orbital space. Orbitals in this space are denoted by α and β . The orbitals in CBS are denoted by κ and ρ . The relationships between orbital spaces are illustrated in Fig. 1.

Standard tensor notation is used throughout the work, i.e., $H_p^q \equiv \langle \phi_p(1) | \hat{H}(1) | \phi_q(1) \rangle$ and $G_{pq}^{rs} \equiv \langle \phi_p(1) \phi_q(2) | \hat{G}(1, 2) | \phi_r(1) \phi_s(2) \rangle$. Labels h, f, v , and γ denote the matrix elements of the one-electron (core) Hamiltonian, Fock operator, Coulomb operator, and reduced density operators, respectively. The Einstein summation convention is adopted, i.e., summation is implied over every index that appears in subscript and superscript of a given term. The particle-number-conserving operators are defined as: $a_q^p = a_p^\dagger a_q$, $a_{qs}^{pr} = a_p^\dagger a_r^\dagger a_s a_q$.

APPENDIX B: PROOF

Here we verify that $\langle \psi^{(0)} | a_q^p \hat{H}_D^{(0)} | \psi^{(0)} \rangle = E^{(0)} \gamma_q^p$. According to the definition of $\hat{H}_D^{(0)}$

$$\langle \psi^{(0)} | a_q^p \hat{H}_D^{(0)} | \psi^{(0)} \rangle = \langle \psi^{(0)} | a_q^p (\hat{H}_{\text{OBS}} + f_{\alpha'}^{\beta'} a_{\beta'}^{\alpha'} + (f_{\alpha'}^{\alpha'} a_{\alpha'}^{\alpha'} + f_{\alpha'}^{\alpha'} a_{\alpha'}^{\alpha'})) | \psi^{(0)} \rangle, \quad (\text{B1})$$

$$= \langle \psi^{(0)} | a_q^p \hat{H}_{\text{OBS}} | \psi^{(0)} \rangle, \quad (\text{B2})$$

where in last step we used the fact that only core and active orbitals are occupied in $|\psi^{(0)}\rangle$. As long as either p or q is a nonactive index, it is straightforward to show that the equality to be verified holds. The only nontrivial part is when p and q are both active. In this case, let us first define a CAS Hamiltonian as follows

$$\hat{H}_{\text{CAS}} = h_{i'}^{i'} a_{i'}^{i'} + \frac{1}{2} v_{i'j'}^{i'j'} a_{i'j'}^{i'j'} + h_m^n a_n^m + \frac{1}{4} v_{mm_1}^{mm_1} a_{mm_1}^{mm_1} + v_{mi'}^{ni'} a_{mi'}^{ni'}. \quad (\text{B3})$$

This Hamiltonian is essentially the *Dyall* Hamiltonian. It has $|\psi^{(0)}\rangle$ as its eigenfunction; i.e., $\hat{H}_{\text{CAS}} |\psi^{(0)}\rangle = E^{(0)} |\psi^{(0)}\rangle$. Therefore $\langle \psi^{(0)} | a_q^p \hat{H}_{\text{CAS}} | \psi^{(0)} \rangle = E^{(0)} \gamma_q^p$. It is not hard to show that

$$\langle \psi^{(0)} | a_q^p \hat{H}_{\text{OBS}} | \psi^{(0)} \rangle = \langle \psi^{(0)} | a_q^p \hat{H}_{\text{CAS}} | \psi^{(0)} \rangle = E^{(0)} \gamma_q^p. \quad (\text{B4})$$

This completes the proof.

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