

Intruder State Avoidance Multireference Møller–Plesset Perturbation Theory

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Abstract: A new perturbation approach is proposed that enhances the low-order, perturbative convergence by modifying the zeroth-order Hamiltonian in a manner that enlarges any small-energy denominators that may otherwise appear in the perturbative expansion. This intruder state avoidance (ISA) method can be used in conjunction with any perturbative approach, but is most applicable to cases where small energy denominators arise from orthogonal-space states—so-called intruder states—that should, under normal circumstances, make a negligible contribution to the target state of interests. This ISA method is used with multireference Møller–Plesset (MRMP) perturbation theory on potential energy curves that are otherwise plagued by singularities when treated with (conventional) MRMP; calculation are performed on the $1^3\Sigma_u^-$ state of O_2 ; and the $2^1\Delta$, $3^1\Delta$, $2^3\Delta$, and $3^3\Delta$ states of AgH. This approach is also applied to other calculations where MRMP is influenced by intruder states; calculations are performed on the $^3\Pi_u$ state of N_2 , the $^3\Pi$ state of CO, and the $2^1A'$ state of formamide. A number of calculations are also performed to illustrate that this approach has little or no effect on MRMP when intruder states are not present in perturbative calculations; vertical excitation energies are computed for the low-lying states of N_2 , C_2 , CO, formamide, and benzene; the adiabatic $^1A_1-^3B_1$ energy separation in CH_2 , and the spectroscopic parameters of O_2 are also calculated. Vertical excitation energies are also performed on the Q and B bands states of free-base, chlorin, and zinc–chlorin porphyrin, where somewhat larger couplings exists, and—as anticipated—a larger deviation is found between MRMP and ISA-MRMP.

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Key words: multireference perturbation theory; intruder state problem; excitation energy; potential energy surface (PES)

Introduction

Multireference Perturbation theory is a useful *ab initio* tool for treating open-shells, excited state, and potential energy surfaces (PESs). Unfortunately, these methods are not as widely used as, for example, the single-reference Møller–Plesset Perturbation Theory.^{1–3} One reason for this shortcoming is the occurrence of convergence difficulties that may negatively influence the low-order energies. Although methods exists for improving perturbative convergence, these approaches frequently require some kind of analysis and are, therefore, usually only employed by “specialists.” Our objective is to modify multireference perturbative methods in a manner that improves the accuracy of low-order energies, but does not require any analysis. These approaches can be used by the nonspecialists for routine calculations involving chemical applications.

The valence universal multireference perturbation theory based on a reference space spanned by a complete active space (CAS)^{4–7} is known to suffer from “near-singularities” caused by very small

or vanishing energy denominators. This problem often occurs because high-lying states within the CAS frequently have zeroth-order energies that are quasidegenerate with zeroth-order states in the orthogonal space. In such cases, orthogonal-space states that are quasidegenerate with reference-space states and are disrupting perturbative convergence are sometimes called *intruder states*, even though this differs from the original definition.^{8,9}

The H^v method of Freed and coworkers¹⁰ removes these vanishing energy denominators by forcing the active orbitals to be degenerate. This approach has been demonstrated to yield accurate

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excitation energies and potential energy surfaces for a wide range of systems.^{11–16} Unfortunately, forcing active-orbital degeneracies can sometimes introduce new small—but nonvanishing—energy denominators that can lead to convergence problems. By using a redefinition of the zeroth-order Hamiltonian H_0 —corresponding to orbital–energy shifts—these new small energy denominators can be removed and convergence improved.¹¹ Unfortunately, this requires some analysis, making this approach more tailored for the specialist.¹⁷

The intermediate Hamiltonian formalism^{18,19} is an attractive method that avoids intruder states, in part, by employing a formalism that only considers a subset of the reference space states. The incomplete model space method of Hose and Kaldor^{20,21} avoids intruder states by having a greater flexibility in the choice of the reference space. Both of these methods can remove intruders at most internuclear distances. However, there is often *not* one incomplete or intermediate model space that can be used over an entire PES.

Instead of using a reference space spanned by a CAS, the Hilbert space approaches use a *single* CAS self-consistent field (SCF) reference states.^{22–25} These approaches avoid intruder states, in part, by possessing energy denominators involving only the single CASSCF state, instead of all the determinantal states within the CAS. Three methods that have shown the most applicability are the (second-order) complete active space perturbation theory (CASPT2),^{26,27} diagrammatic CASPT2,^{28–31} and the (second-order) multireference Møller–Plesset (MRMP) Perturbation Theory.^{32–35} These approaches, however, are not immune from intruder states, especially when applied to PESs. For example, the Cr_2 ground state has numerous singularities—from vanishing energy denominators—on its PES that can be treated by introducing energy denominator shifts into CASPT2.^{36,37} Recently, intruder states yielding small energy denominators have been shown to disrupt convergence for MRMP calculations of the $^3\Pi_u$ state of N_2 , and the $^3\Pi$ state of CO .³⁸ These states have Rydberg character and are so weakly coupled with the CASSCF reference state that they can simply be removed from the perturbative expansion.

In this article we employ a simple modification of any (diagonal) H_0 that automatically removes vanishingly small energy denominators in perturbation expansions, and can be used in conjunction with almost any perturbative approach. This intruder state avoidance (ISA) method can treat the most serious convergence problems that may adversely affect multireference perturbative methods in *low* orders, by modifying the energy denominators in a manner that introduces large shifts *only* into energy denominators that would otherwise be very small, while other energy denominators are changed only slightly. This method is most applicable whenever the intruder state—under normal circumstance—makes a negligible contribution to the target state, because ISA effectively removes the intruder state from the perturbation expansion.

The ISA method is used in conjunction with multireference Møller–Plesset (MRMP) perturbation theory on potential energy curves that are otherwise plagued by singularities when treated with (conventional) MRMP; calculations are performed on the $1^3\Sigma_u^-$ state of O_2 ; and the $2^1\Delta$, $3^1\Delta$, $2^3\Delta$, and $3^3\Delta$ states of AgH . This approach is also applied to other calculations where MRMP is influenced by intruder states; calculations are performed on the $^3\Pi_u$ state of N_2 , the $^3\Pi$ state of CO , and the $2^1A'$ state of

formamide. A number of calculations are also performed to illustrate that this approach has little or no effect on MRMP when intruder states are not present in perturbative calculations; vertical excitation energies are computed for the low-lying states of N_2 , C_2 , CO , formamide, and benzene; the adiabatic $^1A_1\text{--}^3B_1$ energy separation in CH_2 , and the spectroscopic parameters of O_2 are also calculated. Vertical excitation energies are also calculated for the Q and B bands states of free-base, chlorin, and zinc–chlorin porphyrin, where somewhat large couplings exists, and—as anticipated—a larger deviation is found between MRMP and ISA-MRMP.

Theory

Multireference Møller–Plesset Perturbation Theory

The multireference Møller–Plesset (MRMP) method is a single-root perturbative technique based on the Rayleigh–Schrödinger perturbation theory. The total Hamiltonian H is split into the zeroth-order Hamiltonian H_0 and the perturbation V :

$$H = H_0 + V \quad (2.1)$$

where

$$H_0 = |\alpha\rangle E_\alpha^{(0)} \langle\alpha| + \sum_k |k\rangle E_k^{(0)} \langle k| + \sum_q |q\rangle E_q^{(0)} \langle q|; \quad (2.2)$$

$|\alpha\rangle$ is the CASSCF reference state, $|q\rangle$ are the single-determinantal states outside the CAS, and $|k\rangle$ are the multideterminantal states from the CAS that are orthogonal to $|\alpha\rangle$. The zeroth-order energies: $E_\alpha^{(0)}$, $E_k^{(0)}$, and $E_q^{(0)}$, are defined by

$$E_\lambda^{(0)} = \sum_i D_{ii}^{(\lambda)} \varepsilon_i, \quad \lambda = \alpha, k, q, \quad (2.3)$$

where $D_{ii}^{(\lambda)}$ are the diagonal elements of the one-electron, spinless density matrix³⁹ for the state λ . The orbital energies ε_i are defined by

$$\varepsilon_i = \langle \varphi_i | F | \varphi_i \rangle, \quad (2.4)$$

where F is a generalized Fock operator, given by

$$F_{ij} = h_{ij} + \sum_{kl} D_{kl}^a \left[(ij|kl) - \frac{1}{2} (ik|lj) \right]. \quad (2.5)$$

The set of canonical orbitals φ_i in eq. (2.4) is obtained by block-diagonalizing the matrix F_{ij} within the inactive, active, and virtual orbital subspaces. The CASSCF reference state $|\alpha\rangle$ is invariant to this type of orbital transformation.

The energy of $|\alpha\rangle$ through the first-order of perturbation calculation $E_\alpha^{(0-1)}$ is given by

$$E_\alpha^{(0-1)} = \langle \alpha | H_0 | \alpha \rangle + \langle \alpha | V | \alpha \rangle = \langle \alpha | H | \alpha \rangle, \quad (2.6)$$

and is equal to the CASSCF energy of $|\alpha\rangle$. The first-order wave function $|\Psi_\alpha^{(1)}\rangle$ is given by

$$|\Psi_\alpha^{(1)}\rangle = -\sum_q \frac{\langle q|H|\alpha\rangle}{E_q^{(0)} - E_\alpha^{(0)}} |q\rangle, \quad (2.7)$$

where the summation includes all singly and doubly excited configurations generated from the reference configurations within the CAS. The energy of $|\alpha\rangle$ through the second-order $E_\alpha^{(0-2)}$ is given by

$$E_\alpha^{(0-2)} = \langle \alpha|H|\alpha\rangle + E_\alpha^{(2)}, \quad (2.8)$$

where the second-order (correction to the) energy is given by

$$E_\alpha^{(2)} = -\sum_q \frac{|\langle q|H|\alpha\rangle|^2}{E_q^{(0)} - E_\alpha^{(0)}}. \quad (2.9)$$

Explicit expression for $E_\alpha^{(2)}$ in terms of the density matrices, orbital energies, and one- and two-electron integrals can be found elsewhere.^{40,41}

**Small Energy-Denominators Problem:
Intruder States in MRMP**

Consider a singly or doubly excited state, say $|s\rangle$, that is coupled and quasidegenerate with the reference state $|\alpha\rangle$:

$$\langle s|H|\alpha\rangle \neq 0, \quad (2.10)$$

$$E_s^{(0)} \cong E_\alpha^{(0)}. \quad (2.11)$$

In that case, the second-order energy gives

$$E_\alpha^{(2)} \rightarrow \begin{cases} +\infty & \text{if } E_s^{(0)} - E_\alpha^{(0)} \rightarrow 0^- \\ -\infty & \text{if } E_s^{(0)} - E_\alpha^{(0)} \rightarrow 0^+, \end{cases} \quad (2.12)$$

where the singularity in $E_\alpha^{(2)}$ is caused by a poor choice of either $E_s^{(0)}$ or $E_\alpha^{(0)}$. In the limit ($E_s^{(0)} = E_\alpha^{(0)}$), the second-order energy $E_\alpha^{(2)}$ is infinite, while for the quasidegenerate case, ($E_s^{(0)} \cong E_\alpha^{(0)}$), it is very large, positive or negative, yielding usually poor results. For example, for a state with ($\langle s|H|\alpha\rangle = 0.0005$ a.u.)—a weak coupling case—the error is larger than 0.05 a.u. (1.36 eV), when ($E_s^{(0)} - E_\alpha^{(0)}$) lies within ± 0.000005 a.u.

For our purposes, the state $|s\rangle$, in the above example, is defined as an intruder state. We believe that intruder states are more likely to occur in MRMP when the reference state $|\alpha\rangle$ is a high-lying state, and when a basis set with diffuse functions is used.

**Intruder State Avoidance Multireference Møller–Plesset
(ISA-MRMP) Perturbation Theory**

To avoid the problem of intruder states caused by very small energy denominators, we propose a modified MRMP perturbation theory, called intruder state avoidance MRMP (ISA-MRMP). This approach uses a modified zeroth-order Hamiltonian \tilde{H}_0 for which the zeroth-order energies of the reference state is never quasidegenerate with any orthogonal space states. This approach employs the following \tilde{H}_0 :

$$\tilde{H}_0 = |\alpha\rangle E_\alpha^{(0)} \langle \alpha| + \sum_k |k\rangle \tilde{E}_k^{(0)} \langle k| + \sum_q |q\rangle \tilde{E}_q^{(0)} \langle q|, \quad (2.13)$$

where

$$\tilde{E}_\lambda^{(0)} = E_\lambda^{(0)} + \Delta_\lambda, \quad \lambda = k, q; \quad (2.14)$$

the energy–denominator shifts are given by

$$\Delta_\lambda = \frac{b}{E_\lambda^{(0)} - E_\alpha^{(0)}}, \quad \lambda = k, q, \quad (2.15)$$

and $E_\alpha^{(0)}$, $E_k^{(0)}$, and $E_q^{(0)}$ are given by eq. (2.3). The parameter b is at our disposal, and is chosen to be 0.02. We believe that this value of b is large enough to remove intruder states associated with very small energy denominators, but small enough to have a minimum influence on other states.

The energy of $|\alpha\rangle$ through the first-order $\tilde{E}_\alpha^{(0-1)}$ does not depend on the choice of the zeroth-order Hamiltonian:

$$\tilde{E}_\alpha^{(0-1)} = \langle \alpha|H|\alpha\rangle = E_\alpha^{(0-1)}. \quad (2.16)$$

The second-order energy is given by

$$\tilde{E}_\alpha^{(2)} = -\sum_q \frac{|\langle q|H|\alpha\rangle|^2}{\tilde{E}_q^{(0)} - E_\alpha^{(0)}} = -\sum_q \frac{|\langle q|H|\alpha\rangle|^2}{E_q^{(0)} - E_\alpha^{(0)} + \Delta_q}. \quad (2.17)$$

Let us now consider how ISA-MRMP treats a quasidegeneracy involving the intruder state $|s\rangle$ defined by eqs. (2.10) and (2.11). The energy-denominator shift Δ_s for $|s\rangle$ is then given by

$$\Delta_s \rightarrow \begin{cases} +\infty & \text{if } E_s^{(0)} - E_\alpha^{(0)} \rightarrow 0^+ \\ -\infty & \text{if } E_s^{(0)} - E_\alpha^{(0)} \rightarrow 0^-, \end{cases} \quad (2.18)$$

and the portion of the second-order energy arising from $|s\rangle$ approaches zero,

$$\frac{|\langle s|H|\alpha\rangle|^2}{E_s^{(0)} - E_\alpha^{(0)} + \Delta_s} \rightarrow 0, \quad \text{if } E_s^{(0)} - E_\alpha^{(0)} \rightarrow 0. \quad (2.19)$$

Subsequently, the second-order energy $\tilde{E}_\alpha^{(2)}$ becomes

$$\tilde{E}_\alpha^{(2)} \rightarrow -\sum_{q \neq s} \frac{|\langle q|H|\alpha\rangle|^2}{E_q^{(0)} - E_\alpha^{(0)} + \Delta_q} \quad \text{if } E_s^{(0)} - E_\alpha^{(0)} \rightarrow 0. \quad (2.20)$$

(Note the summation restriction.) Hence, in the limit ($E_s^{(0)} = E_\alpha^{(0)}$), the state $|s\rangle$ is simply removed from the perturbation expansion. For the quasidegenerate case ($E_s^{(0)} \cong E_\alpha^{(0)}$), the energy contribution to $\tilde{E}_\alpha^{(2)}$ from $|s\rangle$ is small, and scales linearly with ($E_s^{(0)} - E_\alpha^{(0)}$):

$$\frac{|\langle s|H|\alpha\rangle|^2}{E_s^{(0)} - E_\alpha^{(0)} + \Delta_s} \cong \frac{|\langle s|H|\alpha\rangle|^2}{b} (E_s^{(0)} - E_\alpha^{(0)}). \quad (2.21)$$

On the other hand, for large ($E_s^{(0)} - E_\alpha^{(0)}$) we have

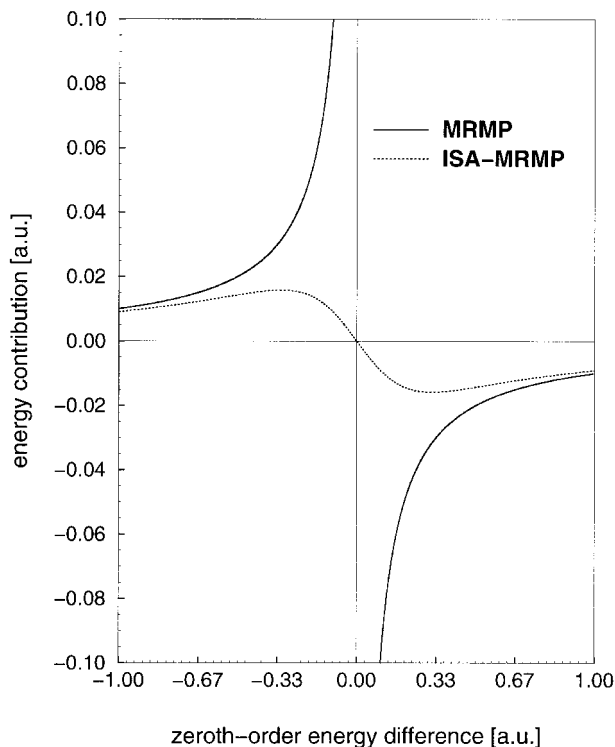


Figure 1. Energy contribution from single state $|s\rangle$ to the second order energy of $|\alpha\rangle$ as a function of $(E_s^{(0)} - E_\alpha^{(0)})$ for the MRMP and ISA-MRMP methods.

$$\frac{|\langle s|H|\alpha\rangle|^2}{E_s^{(0)} - E_\alpha^{(0)} + \Delta_s} \cong \frac{|\langle s|H|\alpha\rangle|^2}{E_s^{(0)} - E_\alpha^{(0)}}, \quad (2.22)$$

and the energy contribution from the state $|s\rangle$ is approximately the same as it is for MRMP. The difference between the MRMP and ISA-MRMP is illustrated by Figure 1, where the contribution from state $|s\rangle$ to the second-order energy is plotted as a function of $(E_s^{(0)} - E_\alpha^{(0)})$. The MRMP contribution, either positive or negative, is becoming infinite when $(E_s^{(0)} - E_\alpha^{(0)})$ goes to zero. The ISA-MRMP contribution, however, is always finite and changes smoothly with $(E_s^{(0)} - E_\alpha^{(0)})$, that guarantees smooth potential energy surfaces. Note, that the ISA-MRMP method does not produce any singularities, because $(E_s^{(0)} - E_\alpha^{(0)} + \Delta_s)$ never approaches zero: Δ_s is large for small $(E_s^{(0)} - E_\alpha^{(0)})$, and vice versa.

Note that when the intruder state makes a significant contribution to the target state, removing it from the perturbation expansion in the region of the singularity results in a noticeable error in the second-order energy $\tilde{E}_\alpha^{(2)}$. Such situation occurs when the intruder and reference states are strongly coupled, i.e., when the intruder state makes a significant contribution to the reference state. However, in our previous calculation of the ${}^3\Pi_u$ state of N_2 , and the ${}^3\Pi$ state of CO,³⁸ we have found that the intruders have Rydberg character and are so weakly coupled with the (valence-like) CASSCF reference state that they can simply be removed from the

perturbative expansion. If the intruder state does significantly contribute to the reference state, other approaches can be employed. For example, the CAS can be enlarged to include the intruder state into the zeroth-order wavefunction or the zeroth-order energy of the intruder state can be chosen in an optimal manner.^{17,42}

Higher order terms for ISA-MRMP differ from the terms that appear in MRMP only slightly: the energy denominators are changed from $(E_s^{(0)} - E_\alpha^{(0)})$ to $(E_s^{(0)} - E_\alpha^{(0)} + \Delta_s)$, and some additional terms are present. The explicit equations for the third- and fourth-order ISA-MRMP energies are given by

$$\tilde{E}_\alpha^{(3)} = \sum_{q_1, q_2} \frac{\langle \alpha|H|q_1\rangle\langle q_1|V|q_2\rangle\langle q_2|H|\alpha\rangle}{(E_{q_1}^{(0)} - E_\alpha^{(0)} + \Delta_{q_1})(E_{q_2}^{(0)} - E_\alpha^{(0)} + \Delta_{q_2})} - \sum_q \frac{\langle \alpha|V|\alpha\rangle\langle q|H|\alpha\rangle^2}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)^2} \quad (2.23)$$

$$- \sum_q \frac{\langle q|H|\alpha\rangle^2}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)} \left(\frac{\Delta_q}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)} \right) \quad (2.24)$$

and

$$\tilde{E}_\alpha^{(4)} = - \sum_{q_1, r, q_2} \frac{\langle \alpha|H|q_1\rangle\langle q_1|V|r\rangle\langle r|V|q_2\rangle\langle q_2|H|\alpha\rangle}{(E_{q_1}^{(0)} - E_\alpha^{(0)} + \Delta_{q_1})(E_r^{(0)} - E_\alpha^{(0)} + \Delta_r)(E_{q_2}^{(0)} - E_\alpha^{(0)} + \Delta_{q_2})} \quad (2.25)$$

$$+ 2 \sum_{q_1, q_2} \frac{\langle \alpha|V|\alpha\rangle\langle \alpha|H|q_1\rangle\langle q_1|V|q_2\rangle\langle q_2|H|\alpha\rangle}{(E_{q_1}^{(0)} - E_\alpha^{(0)} + \Delta_{q_1})^2(E_{q_2}^{(0)} - E_\alpha^{(0)} + \Delta_{q_2})} \quad (2.26)$$

$$+ \sum_{q_1, q_2} \frac{\langle q_1|H|\alpha\rangle^2\langle q_2|H|\alpha\rangle^2}{(E_{q_1}^{(0)} - E_\alpha^{(0)} + \Delta_{q_1})^2(E_{q_2}^{(0)} - E_\alpha^{(0)} + \Delta_{q_2})} - \sum_q \frac{\langle \alpha|V|\alpha\rangle^2\langle q|H|\alpha\rangle^2}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)^3} \quad (2.27)$$

$$+ 2 \sum_{q_1, q_2} \frac{\langle \alpha|H|q_1\rangle\langle q_1|V|q_2\rangle\langle q_2|H|\alpha\rangle}{(E_{q_1}^{(0)} - E_\alpha^{(0)} + \Delta_{q_1})(E_{q_2}^{(0)} - E_\alpha^{(0)} + \Delta_{q_2})} \left(\frac{\Delta_{q_1}}{(E_{q_1}^{(0)} - E_\alpha^{(0)} + \Delta_{q_1})} \right) \quad (2.28)$$

$$- 2 \sum_q \frac{\langle \alpha|V|\alpha\rangle\langle q|H|\alpha\rangle^2}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)^2} \left(\frac{\Delta_q}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)} \right) \quad (2.29)$$

$$- \sum_q \frac{\langle q|H|\alpha\rangle^2}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)} \left(\frac{\Delta_q}{(E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)} \right)^2. \quad (2.30)$$

where, for the simplicity of notation, we assume real arithmetics. The additional terms, eq. (2.24) and eqs. (2.28)–(2.30), introduced by modifying the perturbation V , contain shift parameters Δ_s in the numerator. It may introduce some singularities, because Δ_s becomes infinite when $E_s^{(0)}$ approaches $E_\alpha^{(0)}$. However, it is possible to show that

$$0 < \frac{\Delta_s}{E_s^{(0)} - E_\alpha^{(0)} + \Delta_s} \leq 1 \quad (2.31)$$

for all values of $E_s^{(0)}$. Therefore, the components of eqs. (2.23)–(2.24) and (2.25)–(2.30) with Δ_s in the numerator are finite. Moreover, they are rather small, because the function in eq. (2.31) is very small only unless $E_s^{(0)}$ and $E_\alpha^{(0)}$ are very close to each other, i.e., for intruder states.

An alternative method to introduce energy denominator shifts into a perturbation expansion is to begin with the MRMP expansion and expand out the energy denominators in a similar manner that is employed in the valence universal multireference perturbation theory with a flexible energy denominator.⁴³ For example, the second-order energy for MRMP can be expanded out using the following identity:

$$\frac{|\langle q|H|\alpha\rangle|^2}{E_q^{(0)} - E_\alpha^{(0)}} = \frac{|\langle q|H|\alpha\rangle|^2}{E_q^{(0)} - E_\alpha^{(0)} + \Delta_q} \left(1 + \frac{\Delta_q}{E_q^{(0)} - E_\alpha^{(0)} + \Delta_q} + \left[\frac{\Delta_q}{E_q^{(0)} - E_\alpha^{(0)} + \Delta_q} \right]^2 + \dots \right). \quad (2.32)$$

Instead of using the MRMP energy denominator, given by the lhs of eq. (2.32), the second-order energy is given by the first factor on the rhs and the other terms produce higher order corrections: $|\langle q|H|\alpha\rangle|^2 \Delta_q^{N-1} / (E_q^{(0)} - E_\alpha^{(0)} + \Delta_q)^N$ makes a contribution to the N th order. This approach is a type of reordering of the perturbative expansion that can improve the perturbative convergence, and is equivalent to using the modified zeroth-order. Hamiltonian \tilde{H}_0 , given by eq. (2.13).

Results

In the following calculations we use MOLPRO quantum chemistry package^{44–47} for the CASSCF calculations. The HONDO quantum chemistry package^{48,49} is used for the MRMP calculations that is augmented with the ISA approach.

Removing of Intruder States from Potential Energy Curves

The $1^3\Sigma_u^-$ potential energy curve of O_2 is computed with the MRMP and ISA-MRMP methods. We use the $(10s5p2d1f)/[4s3p2d1f]$ cc-pVTZ basis set.⁵⁰ A 10-orbital active space is used, consisting of the $2s$, $2p$, and $3s$ atomic orbitals of oxygen. The number of electrons in the active space is 12. State averaged CASSCF calculations are performed with the six lowest triplet states. The calculated curves are presented in Figure 2. A singularity is present in the MRMP curve at the interatomic separation of 0.9 Å. The shape of the curve in the neighborhood of the singularity is consistent with eq. (2.12): one branch is bent down, the other one is bent up. The singularity is avoided in the ISA-MRMP curve: the potential curve is smooth.

The potential energy curves are also computed for four states of AgH: $2^1\Delta$, $3^1\Delta$, $2^3\Delta$, and $3^3\Delta$. A $(18s15p9d2f)/[10s8p5d2f]$ Gropen⁵¹ basis set is employed for Ag that is modified on a

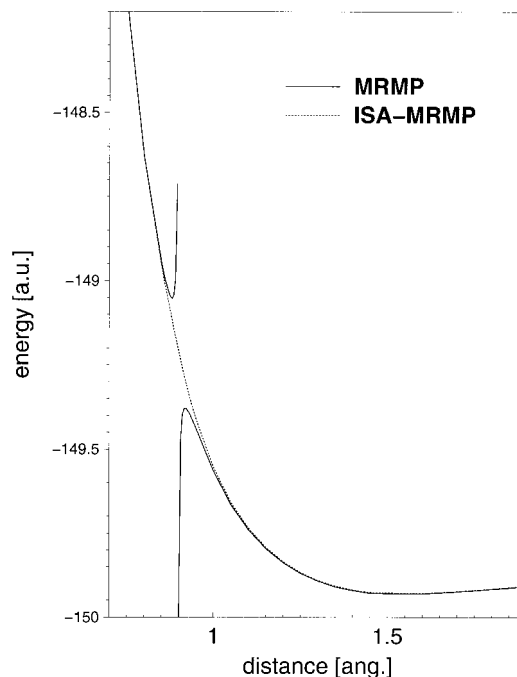


Figure 2. Potential energy curve for the $1^3\Sigma_u^-$ state of O_2 calculated using the MRMP and ISA-MRMP methods.

manner described by Nakajima and coworkers.^{52,53} For the hydrogen atom, we use the $(9s2p)/[6s2p]$ basis set of Lie and Clementi.⁵⁴ The active space includes 12 electrons and 10 orbitals that originate from the following atomic orbitals: the $4d$, $5s$, $5p$ of Ag and the $1s$ of H. A state-averaged CASSCF optimization is performed that uses the 12 electronic states, corresponding to the three lowest dissociation channels of AgH. The relativistic effects are neglected. The curves for the $2^1\Delta$ and $3^1\Delta$ states are plotted in Figure 3; the curves for the $2^3\Delta$ and $3^3\Delta$ states are in Figure 4. A large number of singularities are found for the MRMP calculations: eight for $2^1\Delta$, eleven for $3^1\Delta$ (four singularities are located in 1.40–1.45 Å, but appear as one), 10 for $2^3\Delta$, and six for $3^3\Delta$. The ISA technique removes all singularities, and the resultant curves are smooth.

As indicated previously, when the intruder state is important in the description of its target state, the ISA method possess an error, because the intruder state's contribution to the target state is entirely removed in the vicinity of the singularity. To determine if any of the 35 intruder states—that are present in the AgH potential curves—are important in the description of their target states, we have performed an analysis of each intruder state's contribution. This analysis is identical to the one performed for excited states of N_2 ($^3\Pi_u$) and CO ($^3\Pi$),³⁸ and involves estimating, using various methods, the contribution the intruder states make to their target states. These estimations use other partitioning methods—Epstein–Nesbet and maximum radius of convergence (MAXR_c) perturbation theory⁵⁵—and a two-state model constructed from the intruder state and the reference state. Using this approach, we find that 34 of the 35 states—under normal circumstances—make a negligible contribution to their target state;

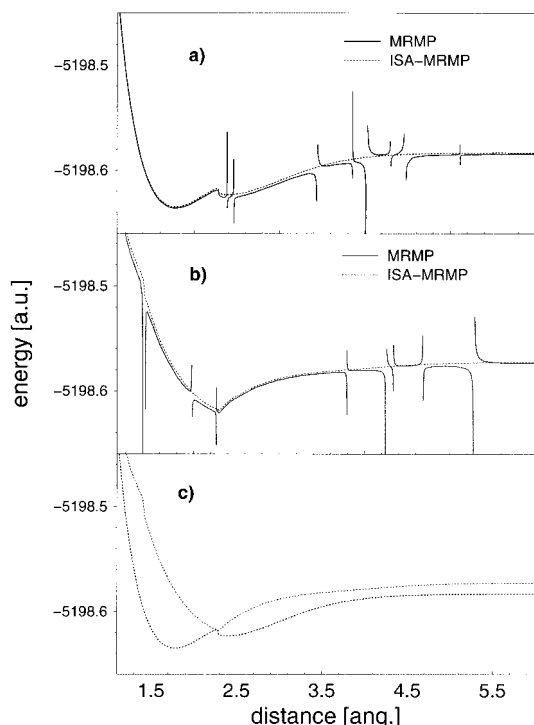


Figure 3. Potential energy curves for the $2^1\Delta$ (a) and $3^1\Delta$ (b) states of AgH calculated using the MRMP and ISA-MRMP methods. Graph (c) presents the ISA-MRMP curves for both states.

explicitly, the contributions from the intruder states arising from the two-state model, Epstein–Nesbet, and $\text{MAX}R_c$ perturbation theory is always less than 0.0002 a.u. Hence, for all these 34 cases, we believe it is appropriate to use the ISA method to correct the deficiencies present in the MRMP method.

However, one of the intruder state—which is present for the $3^1\Delta$ state at the internuclear distance of 1.40 Å—does make a significant contribution to its target state. All estimation methods—the two-state model, Epstein–Nesbet, and $\text{MAX}R_c$ partitioning—yield a 0.01-a.u. contribution to the target state from this intruder. In addition, the distortion in the $3^1\Delta$ state in the vicinity of 1.40 Å is due, in part, to an avoided crossing involving the $4^1\Delta$ state. (This avoided crossing is clearly visible on the CASSCF curves.) Hence, an accurate description of this region of the potential curve requires a multistate approach.^{40,41} In addition, as mentioned above, because the intruder state in this region makes a significant contribution to the target state, this intruder states cannot be handled by ISA, but instead require a larger active space to include the coupled state or a different partitioning method. Nevertheless, except for this very repulsive part of these two potential curves, the ISA method appears to treat the the $3^1\Delta$ potential curves satisfactory.

The ISA-MRMP Method for Diatomic and Triatomic Systems

To establish ISA-MRMP as a standard quantum chemistry tool, it is necessary to test it on many systems. Vertical excitation energies

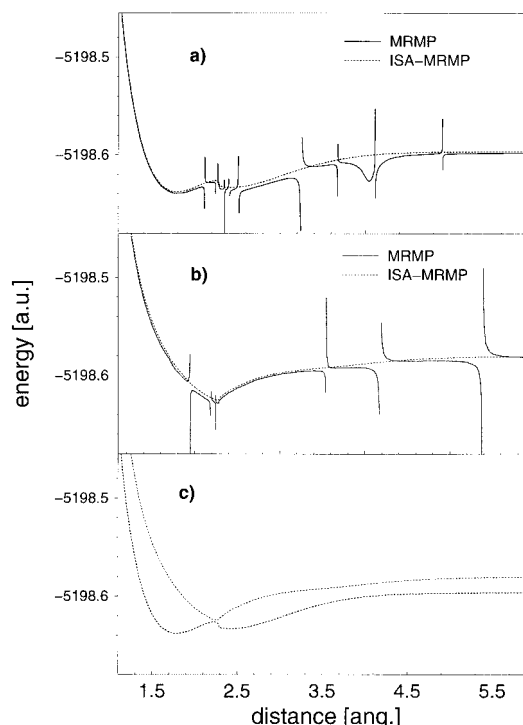


Figure 4. Potential energy curves for the $2^3\Delta$ (a) and $3^3\Delta$ (b) states of AgH calculated using the MRMP and ISA-MRMP methods. Graph (c) presents the ISA-MRMP curves for both states.

Table 1. Vertical Excitation Energies (eV) for Eight States of N_2 and Seven States of CO Calculated Using the MRMP and ISA-MRMP Methods.

Molecule	State	MRMP ²⁹	ISA-MRMP	Exp. ³⁷
N_2	$1\Sigma_u^-$	9.93	9.96	9.92
	$1\Pi_g$	9.19	9.25	9.31
	$1\Delta_u$	10.23	10.28	10.27
	$3\Sigma_u^+$	7.37	7.50	7.75
	$3\Sigma_u^-$	9.47	9.56	9.67
	$3\Pi_g$	7.84	7.87	8.04
	$3\Pi_u$	10.47	10.95	11.19
	$3\Delta_u$	8.78	8.82	8.88
	Error	0.22	0.12	
CO	$1\Sigma^-$	9.90	9.90	9.88
	1Π	8.56	8.40	8.51
	1Δ	9.98	9.99	10.23
	$3\Sigma^+$	8.22	8.24	8.54
	$3\Sigma^-$	9.62	9.64	9.88
	3Π	5.86	6.02	6.32
	3Δ	9.23	9.16	9.36
	Error	0.21	0.20	

Error is computed as an average absolute deviation from experiment. The basis sets (6s5p1d for N_2 and Sadlej's pVTZ for CO), active spaces (eight orbitals and 10 electrons for both systems) and geometries are described in ref. 29 for N_2 and in ref. 30 for CO.

Table 2. Vertical Excitation Energies (eV) for Four States of C₂ Calculated Using the MRMP and ISA-MRMP Methods.

Molecule	State	MRMP	ISA-MRMP	FCI ⁵⁸
C ₂	¹ Π _u	1.48	1.48	1.38
	¹ Δ _g	2.47	2.47	2.29
	¹ Π _g	4.52	4.54	4.49
	¹ Σ _u ⁺	5.59	5.61	5.60
	Error	0.08	0.08	

Error is computed as an average absolute deviation from the full CI results. The basis set (Dunning's cc-pVDZ), active space (eight electrons distributed among eight orbitals) and geometry are discussed elsewhere.³⁰

are computed for the lowest lying states of N₂, C₂, and CO. The adiabatic ¹A₁ – ³B₁ energy separation in CH₂, and the spectroscopic parameters of O₂ are also computed. The basis set and active space for the O₂ calculations are identical to the ³Σ_u[−] state of O₂ calculation, described in the previous section. For other systems, we repeat previously performed MRMP calculations. Information regarding active spaces and basis sets for these calculations appear in the tables.

Vertical excitation energies of N₂ and CO are presented in Table 4. The ISA-MRMP results are characterized by a small average deviation from experiment: 0.12 and 0.20 eV for N₂ and CO, respectively. We have shown previously that the presence of intruder states in the MRMP calculations for the ³Π state of CO, and the ³Π_u state of N₂, deteriorates the results.³⁸ The MRMP results for these states differ by 0.72 and 0.46 eV, respectively.

After removing the intruder states from the perturbation expansion,³⁸ the MRMP vertical excitation energies differ from experiment by only 0.35 and 0.23 eV, respectively. These values are very close to the ISA-MRMP values: 0.30 and 0.24 eV. Hence—as in our previous approach—the ISA-MRMP method is able to remove the influence of these intruder states. However—in contrast to our previous approach—no analysis is required.

Table 6 presents vertical excitation energies of C₂. The accuracy of MRMP and ISA-MRMP is very similar. The largest ISA-MRMP deviation from the FCI results is 0.18 eV for the ¹Δ_g state of C₂. Harmonic vibrational frequencies and equilibrium distances using MRMP and ISA-MRMP for the seven lowest

Table 4. Adiabatic Singlet-Triplet Energy Separation (kcal/mol) in CH₂.

Active Space	MRMP	ISA-MRMP	Exp. ⁵⁶
(6,6)	14.44	14.38	9.37
(6,12)	10.49	10.46	

Two types of active space are used, denoted as (6,6) and (6,12), where six electrons is distributed among 6 and 12 active orbitals, respectively. Detailed information on the active spaces, basis sets (cc-pVTZ of Dunning) and geometry may be found elsewhere.⁵⁶

states of O₂ are listed in Table 6. They give very similar results for ω_e (±3 cm^{−1}) and r_e (±0.0021 Å), except for the c¹Σ_u[−] state. The ISA-MRMP values for this state are closer to experiment. In both methods, the overall agreement with experiment is not very satisfactory. (Perhaps some improvement can be gained if individual CASSCF orbitals are used for each state, instead of a single set of orbitals obtained from a single state-average CASSCF calculation.)

The adiabatic ¹A₁ – ³B₁ separation in CH₂ has a large differential correlation effects that gives a challenging test for correlation methods, because these states have different spin multiplicity.⁵⁶ The MRMP and ISA-MRMP values for this separation are given in Table 6. Both methods give very similar results. The separation calculated using the larger active space is only about 1.2 kcal/mol different from the experimental value.

The ISA-MRMP Method for Larger Systems

Excitation energies for the low-lying states of formamide and benzene are given in Table 6. For formamide, the agreement of the result with experiment is not satisfactory for the 2¹A' calculations using MRMP. This poor MRMP result probably arises from the presence of an intruder state. ISA-MRMP is apparently able to avoid this intruder state by enlarging the energy denominator corresponding to this state. For benzene, both methods have similar accuracy. A smaller average deviation appears for ISA-MRMP (0.18 eV). The largest single-state deviation for ISA-MRMP is 0.37 eV.

Porphyrin systems are large systems that possess 18 conjugate π-electrons making the calculations on the excited states very challenging. Table 6 presents vertical excitation energies of free-

Table 3. Harmonic Vibrational Frequencies ω_e (cm^{−1}) and Equilibrium Distances r_e (Å) for Seven Lowest States of O₂ Calculated Using the MRMP and ISA-MRMP Methods.

State	ω _e			r _e		
	MRMP	ISA-MRMP	exp.	MRMP	ISA-MRMP	exp.
X ³ Σ _g [−]	1702	1704	1580	1.2109	1.2108	1.2075
a ¹ Δ _g	1632	1632	1484	1.2183	1.2181	1.2156
b ¹ Σ _g ⁺	1507	1507	1433	1.2366	1.2363	1.2269
c ¹ Σ _u [−]	916	852	794	1.5032	1.5086	1.517
A' ³ Δ _u	866	868	(850)	1.5072	1.5067	(1.48)
A ³ Σ _u ⁺	804	805	799	1.5251	1.5245	1.5215
B ³ Σ _u [−]	872	869	709	1.5413	1.5434	1.6042

Experimental values are taken from Herzberg and Huber.⁵⁹ (Data in parenthesis is uncertain.)

Table 5. Vertical Excitation Energies (eV) for Three States of Formamide and Eight States of Benzene.

Molecule	State	MRMP	ISA-MRMP	Exp. ^{30,29}
Formamide	1 ¹ A''	5.59	5.62	5.5
	2 ¹ A'	6.50	7.11	7.4
	1 ³ A''	5.23	5.32	5.30
	Error	0.35	0.14	
Benzene	1 ¹ B _{1u}	6.05	6.08	6.20
	3 ³ B _{1u}	3.90	3.92	3.95
	1 ¹ B _{2u}	4.58	4.65	4.90
	3 ³ B _{2u}	5.40	5.43	5.60
	1 ¹ E _{1u}	7.35	6.57	6.94
	3 ³ E _{1u}	4.42	4.46	4.76
	1 ¹ E _{2g}	7.73	7.82	7.80
	3 ³ E _{2g}	6.96	7.04	6.83
	Error	0.21	0.18	

Error is computed as an average absolute deviation from experiment. In formamide calculations, following basis sets are used: aug-cc-pVDZ for C, N, and O and cc-pVDZ for H. In the calculations on benzene, we use Widmark's ANO-type basis for both C and H atoms. Detailed informations on basis sets, active spaces (six electrons and six orbitals for both systems) and geometries are described in ref. 30 for formamide and in ref. 29 for benzene.

base, chlorin, and zinc–chlorine porphyrin. The MRMP and ISA-MRMP results from Table 6 correspond well to the experiment. The largest average deviation is 0.22 eV for both methods. The largest single-state deviations are 0.35 eV for MRMP and 0.41 eV for ISA-MRMP. The overall accuracy of both methods is very similar. The excitation energies for ISA-MRMP are typically larger than MRMP by roughly 0.05–0.15 eV.

Discussion

The ISA-MRMP method is a useful approach for removing intruder states caused by very small energy denominators when the intruder is weakly coupled to the reference state. This is probably the case—at least to a certain extent—for the AgH and O₂ curves we have examined, because we have obtained surfaces that look

Table 6. Vertical Excitation Energies (eV) for the Q and B Bands States of Free-Base Porphine, Chlorin, and Zinc Chlorin.

Molecule	State	MRMP	ISA-MRMP	Exp. ^{61–63}
Free-base porphine	1 ¹ B _{3u}	1.63	1.70	1.98 ^a
	1 ¹ B _{2u}	2.55	2.60	2.42 ^a
	2 ¹ B _{3u}	3.10	3.34	3.33 ^a
	2 ¹ B _{2u}	3.25	3.40	3.33 ^a
	Error	0.20	0.14	
Chlorin	1 ¹ B ₂	1.68	1.74	1.98 ^b
	2 ¹ A ₁	2.43	2.50	2.29 ^b
	2 ¹ B ₂	3.01	3.15	3.18 ^b
	3 ¹ A ₁	3.44	3.59	3.18 ^b
	Error	0.22	0.22	
Zn-Chlorin	1 ¹ B ₂	1.99	2.10	2.04 ^c
	2 ¹ A ₁	2.15	2.24	2.33 ^c
	2 ¹ B ₂	3.06	3.24	3.29 ^c
	3 ¹ A ₁	3.33	3.50	3.13 ^c
	Error	0.16	0.19	

Error is computed as an average absolute deviation from experiment. The basis sets, active space, and geometries are specified elsewhere.⁶⁰

^aIn gas phase.

^bIn C₆H₆.

^cIn CH₃OH.

reasonable. However, in higher orders, divergence in regions of the potential energy surface are assured to occur from incorrect energy ordering,¹⁷ because the *sign* of the energy denominator involving the intruder state ($E_s^{(0)} - E_\alpha^{(0)}$) will always be different to the one obtained from Epstein–Nesbet partitioning ($\langle s|H|s \rangle - \langle \alpha|H|\alpha \rangle$), on one side of the singularity point. This discrepancy must occur since the energy denominator ($E_s^{(0)} - E_\alpha^{(0)}$) changes the sign at the singular point, and ISA-MRMP does not correct this problem. (Incorrect ordering appears when the sign of an energy denominator factor differs from what it is in Epstein–Nesbet partitioning, leading usually to a divergent expansion.)

Conclusion

The ISA-MRMP method yields very similar results as MRMP when no intruder states are present that are associated with small energy denominators. When intruders are present, ISA-MRMP removes their negative influence in the low-order expansion and yields satisfactory results as long as the intruder is weakly coupled to the reference state. We have applied this approach by augmenting MRMP, but it is applicable to any valence universal or Hilbert space perturbative method that is susceptible to small energy denominator problems.

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