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Generalized Møller−Plesset Partitioning in Multiconfiguration Perturbation Theory

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Abstract: Two perturbation (PT) theories are developed starting from a multiconfiguration (MC) zero-order function. To span the configuration space, the theories employ biorthogonal vector sets introduced in the MCPT framework. At odds with previous formulations, the present construction operates with the full Fockian corresponding to a principal determinant, giving rise to a nondiagonal matrix of the zero-order resolvent. The theories provide a simple, generalized Møller−Plesset (MP) second-order correction to improve any reference function, corresponding either to a complete or incomplete model space. Computational demand of the procedure is determined by the iterative inversion of the Fockian, similarly to the single reference MP theory calculated in a localized basis. Relation of the theory to existing multireference (MR) PT formalisms is discussed. The performance of the present theories is assessed by adopting the antisymmetric product of strongly orthogonal geminal (APSG) wave functions as the reference function.

1. Introduction

Single-reference quantum chemical methods have achieved great success in describing molecular electronic structures at around equilibrium geometry. However, these methods fail in calculating systems which have near degeneracy around frontier orbitals, a situation often encountered at geometries far from equilibrium structures. For treating these latter systems, multireference (MR) variational theories have been proposed, such as multiconfigurational self-consistent field (MCSCF) theory,[1] complete active space self-consistent field (CASSCF) theory,[2] geminal-based theories including generalized valence bond (GVB) theory,[3] or the antisymmetric product of strongly orthogonal geminals (APSG) theory.[4−7] Although these methods can improve the description of degenerate systems qualitatively, they usually provide an insufficient amount of dynamic correlation energy, unless the variational space is extended to cover such a large portion of the configuration space, which in turn reduces the practical applicability of the approach. To achieve a significant inclusion of dynamic and static correlation at the same time it is well established to apply perturbation (PT) or coupled-cluster (CC) theories based on a multideterminantal wave function.

Multireference extension of PT theories has spawned a number of alternative formulations, the developments continuously being carried out. As a guiding rule, MR PT approaches can be categorized as being either (i) effective Hamiltonian theories with a model space of dimension higher than one ("perturb then diagonalize")[8,9] or (ii) theories that apply to a one-dimensional model space ("diagonalize then perturb"). Focusing on category ii, there is still a large variety of different formulations. For its obvious success in the realm of single-determinant dominated systems, the Møller−Plesset (MP) partitioning of standard Rayleigh−Schrödinger PT (the Fock operator playing the role of the unperturbed Hamilto-

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nian) was generalized to the MR case in particularly diverse ways. A common origin of several of these theories is the general expression of their zero-order Hamiltonian in the form

$$\hat{H}^{(0)} = E^{(0)}\hat{O} + \hat{P}\hat{F}\hat{P} \tag{1}$$

where $\hat{O}$ is the projector corresponding to the one-dimensional space spanned by the reference function and $\hat{P} = 1 - \hat{O}$ is the projector complementary and orthogonal to $\hat{O}$. Specific theories differ in the definition of the Fockian $\hat{F}$, the form of projector $\hat{O}$, the definition of the reference energy $E^{(0)}$, the functions applied to span space $\hat{P}$, and the treatment of their incidental overlap. It is also common to apply a decoupled form of eq 1, as will be discussed below.

In the present study, we devise a novel PT scheme that operates with the general form of eq 1 of the zero-order Hamiltonian and can be considered as the extension of the MP partitioning to the previously introduced multiconfiguration PT (MCPT) framework.[10,11] Previous variants of MCPT employed a diagonal zero-order Hamiltonian with a choice of zero-order energies. In the present formulation, this flexibility is left off by projecting the full Fockian into space $\hat{P}$ according to eq 1. The zero-order Hamiltonian is non-Hermitian, due to the application of biorthogonal vector sets specific to MCPT. Two alternatives of handling the overlap between excited determinants and the reference function lead to two MCPT variants with the MP partitioning. One will be referred to as projected or pMCPT; the other will be called unprojected or uMCPT.

To avoid any confusion, we note that acronym "u" in uMCPT is not the shorthand commonly used for unrestricted orbitals. In the present work, we consider restricted orbitals throughout. In principle, the determinant-based formalism presented below makes the extension of the theory straightforward for unrestricted orbitals. Such an extension shows relations with the USSG (unrestricted strongly orthogonal singlet-type geminals)-based perturbation theory developed by Rassolov and co-workers[12] and may be achieved without violation of the spin-symmetry.[13]

In this report, we first present the extension of MP partitioning to the MCPT framework in section 2. This is followed by a separate short section, section 3, devoted to the question of size-consistency, followed by a survey of related formulations in section 4. Finally, in section 5, we give a numerical assessment of the new method by applying it to the APSG reference wave function and show it as being superior to the diagonal partitioning applied previously.

2. Theory

We assume that the normalized zero-order wave function ψ satisfies the zero-order equation

$$\hat{H}^{(0)}|\psi\rangle = E^{(0)}|\psi\rangle \tag{2}$$

and we search the improvement to ψ and $E^{(0)}$ in an order-by-order expansion as

$$\Psi = \psi + \psi^{(1)} + ...$$

and

$$E = E^{(0)} + E^{(1)} + E^{(2)} + ...$$

where Ψ and E are the exact eigenstate and eigenenergy of the full Hamiltonian $\hat{H}$ partitioned as

$$\hat{H} = \hat{H}^{(0)} + \hat{W}$$

To define a Fermi vacuum, let us distinguish a principal determinant in ψ, denoted by $|\mathrm{HF}\rangle$ [depending on the molecular orbitals, $|\mathrm{HF}\rangle$ may or may not be the Hartee−Fock (HF) determinant]

$$|\psi\rangle = c_{\mathrm{HF}}|\mathrm{HF}\rangle + \sum_{K\in V_{\mathrm{R}}} c_K|K\rangle$$

and let us assume that c_{HF} is nonzero. Here and further on, notation $|K\rangle$, $|L\rangle$, etc. is used to indicate determinants excited with respect to $|\mathrm{HF}\rangle$. Occupied and virtual indices as well as the excitation level of determinants $|K\rangle$ will be also identified on the basis of the principal determinant $|\mathrm{HF}\rangle$. Set V_{R} collects indices of those excited determinants which have nonzero contribution to the reference function.

Provided that c_{HF} is nonzero, function ψ together with excited determinants $|K\rangle$ span the configuration space and form an overlapping basis. To construct a representation of the identity operator in terms of these vectors, we need to handle their overlap. This may be done by invoking any of the standard orthogonalization procedures which involve a numerical treatment of the overlap matrix. The overlap can be alternatively handled in an explicit manner if following a biorthogonal approach, due to the fact that the overlap matrix is invertible in a closed form. Two possible ways of a biorthogonal treatment are to

(a) Schmidt-orthogonalize $|K\rangle$'s to ψ as a first step, to obtain vectors

$$|K'\rangle = (1 - |\psi\rangle\langle\psi|)|K\rangle$$

In a second step, construct the reciprocal vectors to vectors $|K'\rangle$. This version of the theory is denoted pMCPT.

(b) Construct the reciprocal vector to the set formed by $|\psi\rangle$ and determinants $|K\rangle$. This version is denoted uMCPT.

Alternatives a and b lead to a different definition of the projector corresponding to the one-dimensional model space, namely

(a) $\hat{O} = |\psi\rangle\langle\psi|$ is a symmetrical projector if Schmidt-orthogonalization is applied first

(b) $\hat{O} = |\psi\rangle\langle\tilde{\psi}|$ is a skew projector if the reciprocal set is constructed right away. A tilde is used for denoting reciprocal vectors, i.e., $\langle\tilde{L}|K\rangle = \delta_{\mathrm{LK}}$

The sum $\hat{O} + \hat{P}$ is invariant to the choice of basis vectors; hence, a difference in the definition of $\hat{O}$ results in a difference in $\hat{P}$ as well. This is of importance since projectors $\hat{O}$ and $\hat{P}$ enter the definition of the zero-order Hamiltonian (eq 1). Consequently, the partitioning and the resulting PT series become different in the case of a and b. Before developing the PT treatment in the two cases, let us specify the Fockian, since it is common to both variants.

The Fockian $\hat{F}$ enters the zero-order Hamiltonian projected appropriately by $\hat{O}$ and $\hat{P}$ to ensure fulfillment of the zero-order Schrödinger—eq 2. We employ here a Fockian of the ordinary single reference form, constructed using the density matrix corresponding to the principal determinant. In the spin-orbital basis

$$\hat{F} = \sum_{ij} f_{ij} i^+ j^- = \sum_{ij} (h_{ij} + \sum_{k}^{\mathrm{occ}} \langle ik||jk\rangle) i^+ j^-$$

with $\langle ik||jk\rangle$ standing for antisymmetrized two-electron integrals in the $\langle 12|12\rangle$ convention. In accordance with the noncorrelated form of the Fockian, the zero-order energy of both variants is defined as

$$E^{(0)} = \langle \mathrm{HF}|\hat{F}|\mathrm{HF}\rangle$$

just like in ordinary single-reference MP theory.

Considering computational economy, it is obvious that the projection of $\hat{F}$ into space $\hat{P}$, as shown in eq 1, is impractical, since the matrix of $\hat{H}^{(0)}$ is nondiagonal, with offdiagonal elements coupling subspaces of different excitation levels. In the actual calculations, the expression of eq 1 is simplified, as detailed in section 4.

2.1. pMCPT: Schmidt-Orthogonalization Prior to Reciprocal Set Construction. Schmidt-orthogonalization of determinant $|K\rangle$ to ψ produces

$$|K'\rangle = |K\rangle - c_K|\psi\rangle \tag{3}$$

Obviously, $|K'\rangle = |K\rangle$ for $K \notin V_R$. Vectors $|K'\rangle$ together with ψ form a basis in the configuration space. This basis is not orthogonal, however, as projected determinants may exhibit nonzero overlap among themselves. Reciprocal vectors to $|K'\rangle$ are given by[11]

$$\langle \tilde{K}'| = \langle K| - \frac{c_K}{c_{\mathrm{HF}}}\langle \mathrm{HF}| \tag{4}$$

Again, $\langle \tilde{K}'| = \langle K|$ if $K \notin V_R$. Since the biorthogonal treatment affects only excited vectors, projector $\hat{O}$ is symmetrical

$$\hat{O} = |\psi\rangle\langle\psi|$$

The energy up to first order is also given by the symmetrical expression

$$E^{(0)} + E^{(1)} = \langle\psi|\hat{H}|\psi\rangle = E_{\mathrm{ref}} \tag{5}$$

Projector $\hat{P}$, expressed with excited determinants and their reciprocal counterparts, reads as

$$\hat{P} = \sum_K |K'\rangle\langle\tilde{K}'| \tag{6}$$

Note that in spite of $\hat{P}$ looking like a skew-projector, it is an ordinary Hermitean projector, since $\hat{P} = 1 - \hat{O}$. Given the expressions of $E^{(0)}$, $\hat{F}$, $\hat{O}$ and $\hat{P}$, the zero-order Hamiltonian is now well-defined by eq 1.

Imposing intermediate normalization for the wave function

$$\langle\psi|\Psi\rangle = 1 \tag{7}$$

implies that the first-order correction satisfies

$$\langle\psi|\psi^{(1)}\rangle = 0$$

giving rise to the expansion

$$|\psi^{(1)}\rangle = \sum_{K\in V_{\mathrm{I}}} t_K|K'\rangle \tag{8}$$

Here, V_{I} collects indices of those vectors which interact with $|\psi\rangle$ via the Hamiltonian, i.e., $\langle\tilde{K}'|\hat{H}|\psi\rangle \neq 0$. Set V_{I} is of course much larger than V_R. It includes HF and elements of V_R in the general case, while it may be reduced if introducing approximations. Coefficients t_K are determined from the first-order equation

$$(\hat{H}^{(0)} - E^{(0)})|\psi^{(1)}\rangle = (E^{(1)} - \hat{W})|\psi\rangle \tag{9}$$

projected by $\langle\tilde{L}'| \in V_{\mathrm{I}}$ to get

$$\sum_{K\in V_{\mathrm{I}}} \langle\tilde{L}'|\hat{F} - E^{(0)}|K'\rangle t_K = -\langle\tilde{L}'|\hat{H}|\psi\rangle \tag{10}$$

In obtaining eq 10, the zero-order Hamiltonian (eq 1) was substituted on the left-hand side; the zero-order equation (eq 2) and $\langle\tilde{L}'|\psi\rangle = 0$ were applied on the right-hand side.

In the general case, the linear system of eq 10 determines the first-order wave function. Upon substituting eq 3 for $|K'\rangle$ and eq 4 for $\langle\tilde{L}'|$ one obtains

$$\begin{aligned} &\sum_{K\in V_{\mathrm{I}}} \langle L|\hat{F} - E^{(0)}|K\rangle t_K - \langle L|\hat{F} - E^{(0)}|\psi\rangle \sum_{K\in V_{\mathrm{I}}} c_K t_K \\ &- \frac{c_L}{c_{\mathrm{HF}}} \sum_{K\in V_{\mathrm{I}}} \langle \mathrm{HF}|\hat{F} - E^{(0)}|K\rangle t_K + \frac{c_L}{c_{\mathrm{HF}}} \langle \mathrm{HF}|\hat{F} - E^{(0)}|\psi\rangle \sum_{K\in V_{\mathrm{I}}} c_K t_K \\ &= -\langle L|\hat{H}|\psi\rangle + c_L\tilde{E}_{\mathrm{ref}} \end{aligned} \tag{11}$$

where

$$\tilde{E}_{\mathrm{ref}} = \langle \mathrm{HF}|\hat{H}|\psi\rangle / c_{\mathrm{HF}}$$

It is possible to simplify eq 11 if restricting ourselves to APSG reference functions, which include exclusively doubly excited determinants expressed in the natural basis. This structure allows one to omit the fourth term on the left-hand side of eq 11. Furthermore, we restrict set V_{I} to include only index of doubly excited determinants. This approximation eliminates the third term on the left-hand side of eq 11. Altogether, this means that reciprocal vector $\langle\tilde{L}'|$ can be substituted by $\langle L|$ on the left-hand side of eq 10, leading to the equations

$$\sum_K^{2\times\,\mathrm{exc.}} \langle L|\hat{F} - E^{(0)}|K\rangle t_K - \langle L|\hat{F} - E^{(0)}|\psi\rangle \sum_K^{2\times\,\mathrm{exc.}} c_K t_K = -\langle L|\hat{H}|\psi\rangle + c_L\tilde{E}_{\mathrm{ref}} \tag{12}$$

The second-order equation

$$\hat{H}^{(0)}|\psi^{(2)}\rangle + \hat{W}|\psi^{(1)}\rangle = E^{(0)}|\psi^{(2)}\rangle + E^{(1)}|\psi^{(1)}\rangle + E^{(2)}|\psi\rangle \tag{13}$$

projected by $\langle\psi|$ gives the second-order energy

$$E^{(2)} = \langle\psi|\hat{H}|\psi^{(1)}\rangle = \sum_K^{2\times\,\mathrm{exc.}} \langle\psi|\hat{H} - c_K E_{\mathrm{ref}}|K\rangle t_K \tag{14}$$

having utilized the fact that $\langle\psi|$ is an eigenfunction of $\hat{H}^{(0)}$ from the left, normalization condition (eq 7), expansion (eq 8), eqs 3 and 5. Equations 12 and 14 are the working equations of the method MP-pMCPT(APSG) presented in the applications, where an APSG reference function is adopted.

2.2. uMCPT: Reciprocal Set Construction without Schmidt-Orthogonalization. Reciprocal vectors to the set formed by $|\psi\rangle$ and $|K\rangle$'s can be given by

$$\langle\tilde{\psi}| = \frac{1}{c_{\mathrm{HF}}}\langle\mathrm{HF}| \quad (15)$$

and

$$\langle\tilde{K}| = \langle K| - \frac{c_K}{c_{\mathrm{HF}}}\langle\mathrm{HF}|$$

With the use of the above vectors, one can put down skew-projector $\hat{O}$ in the form

$$\hat{O} = |\psi\rangle\langle\tilde{\psi}|$$

The sum of zero and first-order energies is also evaluated on the basis of the nonsymmetrical expression

$$E^{(0)} + E^{(1)} = \langle\tilde{\psi}|\hat{H}|\psi\rangle = \tilde{E}_{\mathrm{ref}}$$

This energy expression is equivalent to the symmetric form E_{ref} of eq 5 in the case where coefficients in the expansion of ψ are determined from diagonalization of $\hat{H}$ in a subspace of the configuration space. This holds true for an MCSCF wave functions or functions produced by single- or multi-reference CI procedures but not for the APSG wave function considered in the present applications. A skew-projector orthogonal and complementary to $\hat{O}$ is written as

$$\hat{P} = \sum_K |K\rangle\langle\tilde{K}| \quad (16)$$

With the above $\hat{O}$ and $\hat{P}$ definition and $E^{(0)}$ and $\hat{F}$ remaining unaltered, the zero order Hamiltonian of uMCPT is again defined by eq 1.

A suitable form of the intermediate normalization condition in this version of the theory is

$$\langle\tilde{\psi}|\Psi\rangle = 1 \quad (17)$$

Consequently, the first-order wave function should satisfy

$$\langle\tilde{\psi}|\psi^{(1)}\rangle = 0$$

Hence, in terms of vectors $|K\rangle$, it can be expanded as

$$|\psi^{(1)}\rangle = \sum_{K\in V_{\mathrm{I}}} t_K|K\rangle \quad (18)$$

In this formulation, HF is missing from V_{I}, due to the normalization (eq 17). Coefficients t_K are determined from the first-order eq 9, projected by $\langle\tilde{L}| \in V_{\mathrm{I}}$ to get

$$\sum_{K\in V_{\mathrm{I}}} \langle\tilde{L}|\hat{F} - E^{(0)}|K\rangle t_K = -\langle\tilde{L}|\hat{H}|\psi\rangle \quad (19)$$

In obtaining eq 19, the form of the zero-order Hamiltonian (eq 1) was applied, as well as the zero-order eq 2 and $\langle\tilde{L}|\psi\rangle = 0$. The general form of the equations determining function $\psi^{(1)}$ in this variant of the theory is eq 19.

Considering the approximation where V_{I} is restricted to doubly excited indices, term $-c_L\langle\mathrm{HF}|\hat{F} - E^{(0)}|K\rangle t_K/c_{\mathrm{HF}}$ stemming from the overlap of $\langle L|$ with $|\psi\rangle$ can be omitted on the left-hand side of eq 19, leading to

$$\sum_K^{2\times\,\mathrm{exc.}} \langle L|\hat{F} - E^{(0)}|K\rangle t_K = -\langle L|\hat{H}|\psi\rangle + c_L\tilde{E}_{\mathrm{ref}} \quad (20)$$

The second-order eq 13 projected by $\langle\tilde{\psi}|$ gives the second-order energy

$$E^{(2)} = \langle\tilde{\psi}|\hat{H}|\psi^{(1)}\rangle = \frac{1}{c_{\mathrm{HF}}}\sum_K^{2\times\,\mathrm{exc.}} \langle\mathrm{HF}|\hat{H}|K\rangle t_K \quad (21)$$

having utilized that $\langle\tilde{\psi}|$ is an eigenfunction of $\hat{H}^{(0)}$ from the left, normalization condition (eq 17), eq 15, and expansion (eq 18). Equations 20 and 21 are the working equations of the method denoted MP-uMCPT(APSG) in the applications, where an APSG reference function is adopted.

3. Size-Consistency

Among previous versions of the theory, where the zero-order Hamiltonian was assumed diagonal, uMCPT was shown to provide size-consistent correction at second order, if energy denominators were composed of one-particle indexed quantities.[11] We investigate here whether this property subsists in MP-uMCPT and find that canonical orbitals in the single-reference sense ensure a second-order energy behaving well in this respect. For noncanonical orbitals, deletion of the occupied-virtual block of the Fockian in the definition of $\hat{H}^{(0)}$ is necessary to obtain this behavior.

By size consistency, we understand the criterion of obtaining the energy as a sum of subsystem energies in the case where subsystems do not interact. To study this, let us suppose that the reference function is behaving well; i.e., it is given as a product [antisymmetrization being immaterial for noninteracting subsystems[14]] of noninteracting partner's reference functions

$$|\psi\rangle = |\psi_{\mathrm{A}}\psi_{\mathrm{B}}\rangle$$

where index A and B label the subsystems. As a consequence, the principal determinant is also given as the product

$$|\mathrm{HF}\rangle = |\mathrm{HF}_{\mathrm{A}}\mathrm{HF}_{\mathrm{B}}\rangle$$

appearing in the expansion of $|\psi\rangle$ with weight $c_{\mathrm{HF}}^{\mathrm{A}}c_{\mathrm{HF}}^{\mathrm{B}}$; hence, the reciprocal vector $\langle\tilde{\psi}|$ reads

$$\langle\tilde{\psi}| = \langle\mathrm{HF}_{\mathrm{A}}\mathrm{HF}_{\mathrm{B}}|/(c_{\mathrm{HF}}^{\mathrm{A}}c_{\mathrm{HF}}^{\mathrm{B}})$$

Since both the total Hamiltonian and the Fockian are given as a sum over noninteracting systems, the reference energy

$$\tilde{E}_{\mathrm{ref}} = \tilde{E}_{\mathrm{ref}}^{\mathrm{A}} + \tilde{E}_{\mathrm{ref}}^{\mathrm{B}}$$

and the zero-order energy

$$E^{(0)} = E^{(0)}_{\mathrm{A}} + E^{(0)}_{\mathrm{B}}$$

separate for terms corresponding to individual subsystems.

Determinants appearing in the expansion of $|\psi^{(1)}\rangle$ can be classified as doubly excited on system A, doubly excited on system B, or singly excited both on system A and B, giving rise to the form

$$|\psi^{(1)}\rangle = \sum_K^{\mathrm{A}} t^{\mathrm{AB}}_{K\mathrm{HF}} |K_{\mathrm{A}}\mathrm{HF}_{\mathrm{B}}\rangle + \sum_K^{\mathrm{B}} t^{\mathrm{AB}}_{\mathrm{HF}K} |\mathrm{HF}_{\mathrm{A}}K_{\mathrm{B}}\rangle + \sum_K^{\mathrm{A}} \sum_I^{\mathrm{B}} t^{\mathrm{AB}}_{KI} |K_{\mathrm{A}}I_{\mathrm{B}}\rangle \quad (22)$$

with self-explanatory notations. The above expansion substituted into the coefficients' equation (eq 20), we have to consider two distinct cases: (i) index L refers to a determinant doubly excited on one subsystem, say A, or (ii) index L belongs to a determinant singly excited on both subsystems. In case i, $\langle L|$ can be written as

$$\langle L| = \langle L_A \mathrm{HF}_B|$$

and by trivial derivation, one arrives at the coefficient equation

$$\sum_K^{\mathrm{A}} \langle L_{\mathrm{A}}|\hat{F}_{\mathrm{A}} - E^{(0)}_{\mathrm{A}}|K_{\mathrm{A}}\rangle t^{\mathrm{AB}}_{K\mathrm{HF}} + \sum_I^{\mathrm{B}} \langle \mathrm{HF}_{\mathrm{B}}|\hat{F}_{\mathrm{B}}|I_{\mathrm{B}}\rangle t^{\mathrm{AB}}_{LI} = -\langle L_{\mathrm{A}}|\hat{H}_{\mathrm{A}} - \tilde{E}^{\mathrm{A}}_{\mathrm{ref}}|\psi_{\mathrm{A}}\rangle c^{\mathrm{B}}_{\mathrm{HF}}$$

This equation should contain solely quantities belonging to subsystem A, which does not hold because of the second term on the left-hand side. (Coefficient $c^{\mathrm{B}}_{\mathrm{HF}}$ does not do any harm; in fact, it has a proper role as seen in eq 23.) In the study of case ii, it is seen that $\langle L|$ adopts the form

$$\langle L| = \langle L_{\mathrm{A}} J_{\mathrm{B}}|$$

and the coefficient equation is found to be

$$\langle J_{\mathrm{B}}|\hat{F}_{\mathrm{B}}|\mathrm{HF}_{\mathrm{B}}\rangle t^{\mathrm{AB}}_{L\mathrm{HF}} + \langle L_{\mathrm{A}}|\hat{F}_{\mathrm{A}}|\mathrm{HF}_{\mathrm{A}}\rangle t^{\mathrm{AB}}_{\mathrm{HF}J} + \sum_K^{\mathrm{A}} \langle L_{\mathrm{A}}|\hat{F}_{\mathrm{A}} - E^{(0)}_{\mathrm{A}}|K_{\mathrm{A}}\rangle t^{\mathrm{AB}}_{KJ} + \sum_I^{\mathrm{B}} \langle J_{\mathrm{B}}|\hat{F}_{\mathrm{B}} - E^{(0)}_{\mathrm{B}}|I_{\mathrm{B}}\rangle t^{\mathrm{AB}}_{LI} = -\langle L_{\mathrm{A}}|\hat{H}_{\mathrm{A}} - \tilde{E}^{\mathrm{A}}_{\mathrm{ref}}|\psi_{\mathrm{A}}\rangle c^{\mathrm{B}}_{J} - \langle I_{\mathrm{B}}|\hat{H}_{\mathrm{B}} - \tilde{E}^{\mathrm{B}}_{\mathrm{ref}}|\psi_{\mathrm{B}}\rangle c^{\mathrm{A}}_{L}$$

Due to A and B being noninteracting, coefficients of the type t^{AB}_{LJ} do not contribute to the second-order energy. The above equation—which corresponds to these rows—is therefore not important provided it is not coupled to columns corresponding to local excitations, e.g., $|L_{\mathrm{A}}\mathrm{HF}_{\mathrm{B}}\rangle$. Unfortunately, the first two terms on the left-hand side are just consistency-spoiling coupling terms. When the two cases are summarized, the coefficient matrix on the left-hand side of eq 20 can be depicted as shown in Figure 1.

Substituting expansion 22 into the second-order energy formula, one obtains

$$E^{(2)} = \sum_K^{\mathrm{A}} \langle \tilde{\psi}_A|\hat{H}_{\mathrm{A}}|K_{\mathrm{A}}\rangle t^{\mathrm{AB}}_{K\mathrm{HF}} \frac{1}{c^{\mathrm{B}}_{\mathrm{HF}}} + \{\mathrm{A} \leftrightarrow \mathrm{B}\ \text{exchanged}\} \quad (23)$$

indicating that size consistency would hold if the equation determining $t^{\mathrm{AB}}_{K\mathrm{HF}}/c^{\mathrm{B}}_{\mathrm{HF}}$ would be the same as the equation for t^{A}_{K}, when computed alone. This is spoiled by the coupling emerging in the blocks dotted in Figure 1. Nonzero elements of these blocks are solely occupied-virtual matrix elements of the Fockian and are zero only if the orbitals are canonical in the single-reference sense. In general, it certainly does not hold for multireference applications. To restore size consistency in such a case, one can modify the partitioning by allowing nonzero elements only in the occupied−occupied and virtual−virtual block of the Fockian.

4. Properties of MP-MCPT and Survey of Related Theories

Several MR extensions of MP theory are related to the MP-MCPT scheme detailed above. A characteristic feature unique to the MCPT framework is the biorthogonal treatment of the overlap among basis vectors. This is in contrast to the approach introduced by Wolinsky and co-workers[15,16] where internally contracted excited vectors are considered as basis vectors and Schmidt-orthogonalization is applied to keep subspaces of different excitation levels orthogonal to each other. Vectors belonging to the same excited subspace can be orthogonalized either by Löwdin's symmetrical[17] or canonical scheme[18,19] or by the Gram−Schmidt procedure.[20] Diagonalization of the overlap matrix can become a bottleneck of this approach, which induces the application of a partially contracted and partially uncontracted basis.[17,21] To avoid the overlap problem, Murphy and Messmer suggested the use of totally uncontracted configuration state functions (CSFs) as basis vectors in the excited space.[22,23] This theory has to cope with an increased dimension of the linear system of equations to solve in return. Both the approaches of Murphy and Messmer and the MRMP method introduced by Hirao et al.[24,25] assume the existence of a set of multiconfigurational basis vectors orthogonal and noninter-

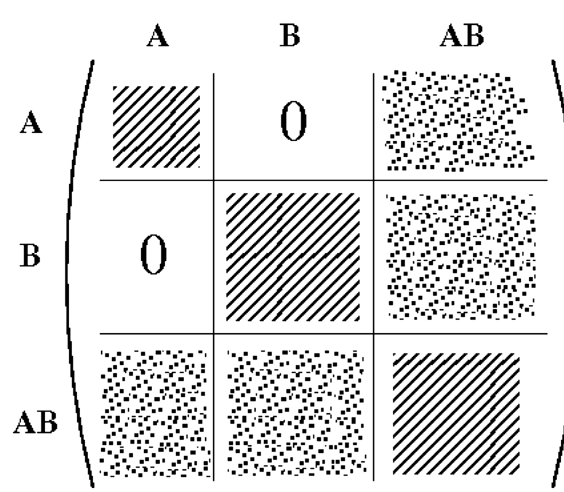

Figure 1. Block structure of the coefficient matrix of the first-order equation for noninteracting systems A and B.

acting through $\hat{H}$ with the reference function (e.g., excited CAS vectors). Explicit construction of these multiconfigurational basis vectors becomes necessary only beyond third order in energy, which was never investigated with these theories to the best of our knowledge. Within the MRMP framework, McDouall and Robinson have conducted extensive research in the line of lifting orbital optimization problems as well as reducing the size of the model space, see ref 26 and references therein.

Specific treatment of overlap among excited basis vectors is of course irrelevant as far as the zero-order Hamiltonian is of the form eq 1 and $E^{(0)}$ and $\hat{O}$ are defined alike. Most methods however do not apply the zero-order operator (eq 1) as it is. In their pioneering paper, Wolinsky et al.[15] suggested decoupling interactions at the zero order using the Hamiltonian

$$\hat{H}^{(0)} = E^{(0)}\hat{O} + \hat{P}_S\hat{F}\hat{P}_S + \hat{P}_D\hat{F}\hat{P}_D + ... \tag{24}$$

to break down the dimension of the inversion problem for smaller sub-blocks. Here, $\hat{P}_S$, $\hat{P}_D$, etc. refer to singly, doubly, etc. excited subspaces. With such a zero-order Hamiltonian, the definition of $\hat{P}_S$, $\hat{P}_D$, etc. clearly becomes of importance and affects the behavior of the PT series. Several different decoupling schemes have been investigated over time,[18,20] while Celani and Werner reported second-order energies with the nondecoupled zero order of eq 1.[21] It was also shown that increasing the block-diagonal character of $\tilde{H}^{(0)}$ reduces the size-consistency error of individual energy corrections.[20,27]

The MP-MCPT framework avoids the overlap problems present in internally contracted theories by adopting a determinant-based description and a biorthogonal treatment. At the same time, the dimension of the linear system of equations is kept at a manageable size by a decoupling of the type given in eq 24. In fact, restricting expansion of the first-order function to doubly excited determinants means that the zero-order Hamiltonian of MP-MCPT reads

$$\hat{H}^{(0)} = E^{(0)}\hat{O} + \hat{P}_D\hat{F}\hat{P}_D \tag{25}$$

where $\hat{P}_D$ is either of the form eq 6 or eq 16, with summation index K restricted to doubly excited determinants. This zero-order Hamiltonian is of course unfitted for calculating energies beyond third order. Even third-order results are omitted from the present study, where we intentionally aim to capture a significant portion of the dynamical correlation energy at the lowest order of a simple perturbation scheme. The error committed by decoupling of eq 25 as compared to eq 1 is expected to be negligible at order 2. At the same time, decoupling eq 25 means that the coefficient matrix on the left-hand side of eq 19 is of *exactly* the same form as the matrix appearing in single-reference MP calculations performed on a localized basis.[28−30] The inversion of this matrix is the rate determining step of MP-MCPT. Since the Fockian is a one-body operator, the structure of the coefficient matrix of the linear system of equations is comfortably sparse and easily invertible by iterative algorithms.[31,32] In the MP-pMCPT variant of the theory, a correction term on the left-hand side of eq 10 makes a difference with the coefficient matrix of single-reference MP theory. This correction affects those columns which correspond to the determinants present in the expansion of ψ but does not alter the size of the matrix.

The definition of the Fockian as well as the zero-order energy $E^{(0)}$ is an important question in MR MP theories, related to the sensitivity to intruder states. Most MP extensions use the generalized Fockian[33] built with the correlated one-body density matrix of the reference function and define the zero-order reference energy as the expectation value $\langle\psi|\hat{F}|\psi\rangle$. At odds with these, the density matrix of the principal determinant is used to construct the Fockian in MP-MCPT and we take $\langle \mathrm{HF}|\hat{F}|\mathrm{HF}\rangle$ as zero-order energy, both being the same constructions as in single-reference MP. Our choice is motivated partly by computational simplicity and partly by previous numerical experiences,[11] indicating a negligible difference in second-order results between using the uncorrelated or generalized Fockian. In fact, a generalized Fockian fits better to a multiconfiguration framework, and it is preferred particularly if orbital invariance of the theory is desirable. In our approach, however, a principal determinant is pinpointed at the stage of defining reciprocal vectors. This inhibits invariance to any orbital rotations and enhances the single-reference character of the theory, making it rather pointless to apply a generalized Fockian. Defining the ground state zero-order energy as in single-reference MP theory appears particularly dangerous due to the well-known quasi-degeneracy problem upon bond-dissociation. This fear, however, is just slightly justified according to the numerical experiences presented in section 5. On the other hand, working with a spectral representation of the Fockian built with CASSCF orbitals and orbital energies has been found to give a poor description of multireference problems if the reference function is a single configuration state function.[34]

As already alluded to, MP-MCPT is not invariant to orbital rotations that may leave the reference function unaffected. This is undesirable, but not unique among MR MP theories; e.g., assumption of a diagonal form of $\hat{H}^{(0)}$ destroys the invariance.[8,10,11,35] In the case of MP-MCPT, orbital non-invariance stems from the biorthogonal treatment and has the further consequence that MP-MCPT is not invariant to the choice of principal determinant either. This suggests that MP-MCPT is safely applicable only in the case where one of the determinants stands out in the expansion of the reference function, in terms of coefficient squared. The dissociation of the nitrogen molecule, where several determinants become equally weighted at the end of the process, is one test of this feature. As shown in section 5, performance of MP-MCPT is surprisingly acceptable in this example apart from the slight breakdown of the curve. In contrast to the nitrogen dissociation example, serious qualitative failure is in fact observed when the principal role is handed over from one determinant to another during the process studied. These are cases where MP-MCPT definitely should not be applied as it is. Averaging over principal determinants has been shown to be a possible cure to this problem.[36]

Choosing a suitable two-body zero-order Hamiltonian satisfying eq 2 instead of definition of eq 1 is certainly superior to any MP extension discussed here, and such theories were shown to produce excellent results,[37−40] at the price of coping with a more tedious task when obtaining the first-order coefficients. The present theory—being an uncomplicated version even among MP theories assuming a one-body zero-order Hamiltonian—obviously cannot compete with these methods either in accuracy or in desirable properties like size consistency or orbital invariance. On the other hand, we do observe an improvement in the numerical performance as compared to considering a diagonal zero-order Hamiltonian within the MCPT framework, suggested previously,[10,11,41] although in some cases the improvement in total energies may be rather small.

5. Assessments

We assessed the present MP-MCPT methods by adopting the APSG wave function expressed in the natural orbital basis as a reference. The APSG function can be written as the products of ground and pair-excited geminal functions as follows:

$$|\psi\rangle \equiv |\psi^{\mathrm{APSG}}\rangle = c_{\mathrm{HF}} \prod_{i}^{\mathrm{geminal}} \left(1 + \sum_{a \in \mathbf{S}(i)} \frac{c_i^a}{c_{\mathrm{HF}}} \hat{T}_{i_\alpha i_\beta}^{a_\alpha a_\beta}\right) |\mathrm{HF}\rangle$$

where $\mathbf{S}(i)$ is the set of the unoccupied orbitals of the geminal subset which has an occupied orbital i. We restricted the expansion of the first-order wave function within doubly excited determinants from $|\mathrm{HF}\rangle$, as discussed previously.

We selected the H_2O (water), HF (hydrogen fluoride), N_2 (nitrogen), and F_2 (fluorine) molecules as test systems and obtained potential energy curves for the bond dissociations. As a comparison, we present APSG, MP2, multireference MP2 (MRMP2), and a PT designed for the APSG wave function by Rosta and Surján (APSG-PT).[40,42] In addition, we also computed the equilibrium geometries of the diatomic molecules and calculated vibrational frequencies by the finite difference method. During the latter, we first determined equilibrium distances R_e up to the order of 0.1 pm and evaluated the frequencies from three points, namely, R_e and $R_e \pm 0.5$ pm structures. All calculations were performed with the 6-311G** basis set.[43] The APSG geminal subsets were defined to give six orbitals for each bonding geminal and three orbitals for each lone-pair geminal, around the equilibrium structure.

5.1. Dissociation Curves. We first calculated potential energy curves for two types of bond-breaking processes of the H_2O molecule: (i) a heterogeneous one-bond dissociation, with the other bond distance fixed to 95 pm, and (ii) a homogeneous two-bond dissociation. In both processes, the bond angle was fixed to 104.5°. The reference function underlying the MRMP2 calculation was a CASSCF wave function with four active electrons on four active orbitals, CASSCF(4,4) shortly.

Figure 2 shows the potential energy curves for one-bond dissociation of H_2O. The APSG curve is much worse in absolute energy than MRMP2. However, APSG can produce a qualitatively nice dissociation curve: nonparallelity error (NPE) with respect to MRMP2 is 0.0160 hartree. The single-reference perturbation approach (MP2) starts to diverge at about the 300 pm structure. Around equilibrium distance, both MP-pMCPT and MP-uMCPT are much improved from APSG in absolute energy, due to the consideration of dynamical correlation. As the bond length gets large, however, the two curves behave differently. The curve by MP-pMCPT becomes similar to the MP2 one up to 250 pm and levels out; hence, the dissociation energy is overestimated compared to MRMP2. On the other hand, MP-uMCPT reproduces the shape by MRMP2 or APSG-PT up to the dissociation limit. This may be attributed to the quasi size consistency of MP-uMCPT.

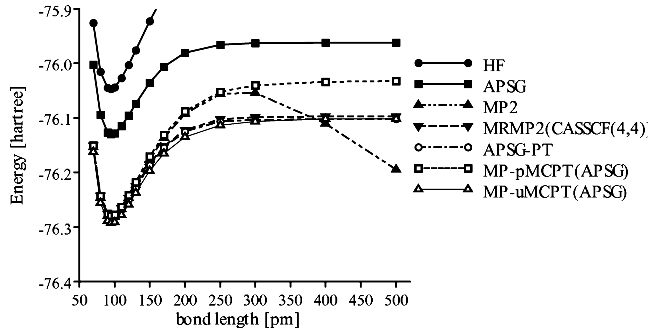

Figure 2. Potential energy curves for the heterogeneous one-bond dissociation of the H_2O molecule. The other O−H bond length is fixed to 95 pm and the bond angle is fixed to 104.5°.

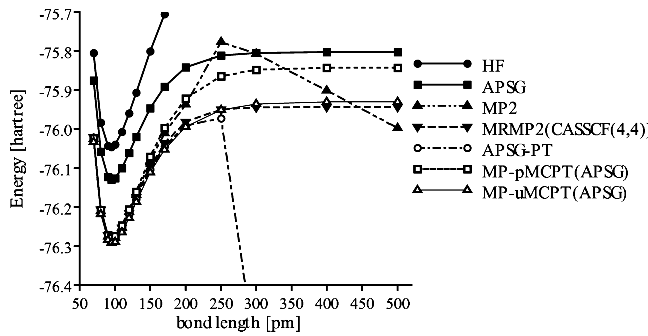

Figure 3. Potential energy curves for the homogeneous two-bond dissociation of the H_2O molecule. The bond angle is fixed to 104.5°.

Figure 3 shows the potential energy curves for two-bond homogeneous dissociation of the H_2O molecule. Although this sort of dissociation requires at least four-electron four-orbital active space, APSG still gives a qualitatively nice curve. APSG-PT cannot produce a correct dissociation curve shape in this case. On the other hand, MP-pMCPT and MP-uMCPT nicely level out with increasing bond length. The MP-pMCPT curve again follows MP2 up to 200 pm and overestimates the dissociation energy as compared to the MRMP2 result. The MP-uMCPT produces a potential curve similar to MRMP2 even for this multiple bond dissociation example.

Next, we assessed the dissociation potential energy surface for the bond-breaking process of the HF molecule, shown in Figure 4. In this system, the full-configuration interaction (FCI) results were obtained around equilibrium and dissociated structures by utilizing the sparse FCI algorithm of Rolik et al.[44] The behavior of the curves resembles that of Figure 2. In particular, MP-uMCPT reproduces the MRMP2 curve well, while MP-pMCPT follows the MP2 curve up to 250

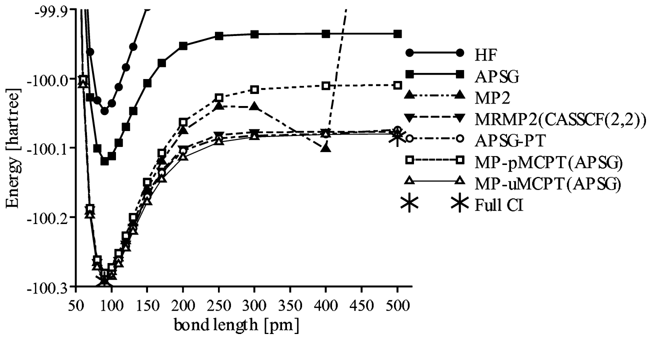

Figure 4. Potential energy curves for the dissociation of the HF molecule.

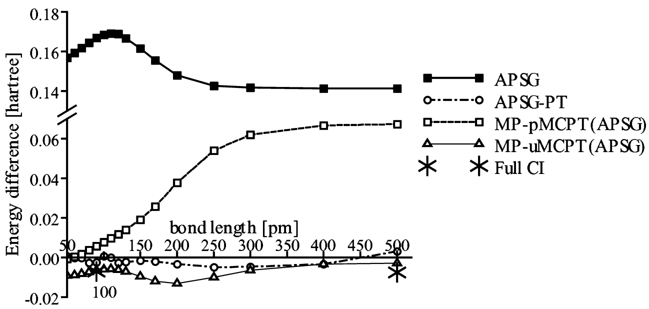

Figure 5. Energy difference from the MRMP2 results for the dissociation of the HF molecule.

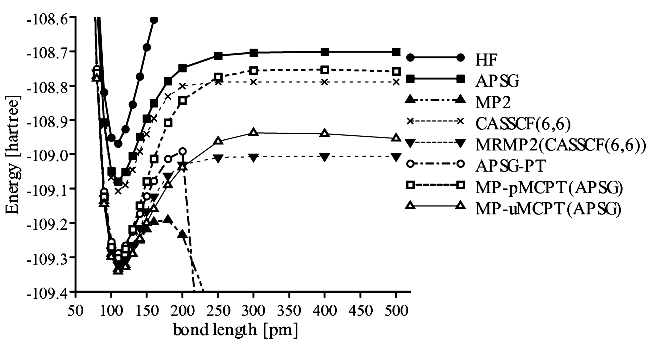

Figure 6. Potential energy curves for the dissociation of the N_2 molecule.

pm. Since the energy errors of MRMP2 with respect to FCI are comparable (0.0071 and 0.0075 hartree at 90 and 500 pm bond length, respectively), the energy difference from MRMP2 is a good indicator to assess the accuracy of the methods. These data are shown in Figure 5. Around equilibrium distance, the APSG energy error is larger than at the end of the process, due to the lack of dynamical correlation. The errors of MP-pMCPT and MP-uMCPT around equilibrium geometry are improved to less than 0.01 hartree by taking dynamical correlation into account. While the error of MP-pMCPT becomes large as the bond is stretched, MP-uMCPT remains fairly constant: NPEs of MP-pMCPT and MP-uMCPT are 0.0671 and 0.0102 hartree. The latter is comparable to the 0.0079 hartree error of APSG-PT.

Further, we assessed potential energy curves for the triple-bond-breaking process of the N_2 molecule, shown in Figure 6. The MRMP2 calculations for the N_2 molecule were based on a CASSCF(6,6) wave function as a reference. In this example, APSG-PT as well as MP2 diverge, as expected.

Table 1. Calculated Equilibrium Distances (R_e), Harmonic Vibrational Frequencies (f), and Dissociation Energies (D_e) of the HF Molecule Adopting the 6-311G** Basis Set

method	R_e [pm]	f [cm^{-1}]	D_e [eV]
HF	89.6	4496	22.14
APSG	91.0	4223	4.997
MP2	91.2	4247	
MRMP2(CASSCF(2,2))	91.9	4143	5.696
APSG-PT	91.8	4038	5.842
MP-pMCPT(APSG)	91.0	4280	7.368
MP-uMCPT(APSG)	91.6	4160	5.789
full CI	91.3	4213	5.679

Table 2. Calculated Equilibrium Distances (R_e), Harmonic Vibrational Frequencies (f), and Dissociation Energies (D_e) of the F_2 Molecule Adopting the 6-311G** Basis Set

method	R_e [pm]	f [cm^{-1}]	D_e [eV]
HF	133.1	1209	9.347
APSG	153.2	521	0.475
MP2	141.1	914	
MRMP2(CASSCF(2,2))	144.8	759	1.233
APSG-PT	146.1	711	1.068
MP-pMCPT(APSG)	136.8	1087	4.089
MP-uMCPT(APSG)	148.0	678	1.538
exptl.[a]	141.2	917	1.602

[a] Ref 45.

The MP-pMCPT and MP-uMCPT methods give qualitatively good dissociation profiles even for this triple-bond breaking, although slight bumps can be seen between the equilibrum and dissociated structures. It is to be noted here that the APSG reference wave function underlying MP-MCPTs is poorer than CASSCF(6,6) used for MRMP2, since sextuply excited deteminants appear as products of two-electron excitations in APSG. The imperfection of APSG to describle triple bond breaking as compared with CASSCF may be credited for the breakdown of MP-MCPT dissociation curves.

5.2. Parameters at Equilibrium Geometry. Next, we calculated parameters at an equilibrium geometry of diatomic molecules, i.e., equilibrium bond length (R_e), harmonic frequencies (f), and dissociation energies (D_e). Dissociation energy is evaluated as the energy difference between the equilibrium and 500 pm structures.

In Table 1, we summarize the parameters of the HF molecule. Equilibrium bond disstance as calculated by either of the present MP-MCPTs agrees with FCI within 0.3 pm. This is better than the R_e obtained by either MRMP2 or APSG-PT. The MP-pMCPT frequency is larger than f calculated by MP-uMCPT or MRMP2, which relates to the overestimation of the dissociation energy in MP-pMCPT. Both R_e and f are remarkably well estimated by APSG in this system.

The situation becomes different in the F_2 molecule, which has a much shallower potential than HF. Table 2 shows the parameters of F_2. For comparison, experimental data from ref 45 are also indicated. Compared to experimental values, APSG overestimates R_e by more than 10 pm and underestimates D_e by 70%, which is also reflected in the underestimation of f. As a contrast to this, MP-pMCPT underestimates R_e by about 5 pm, overestimates D_e by more than 200%, and consequently also overestimates the harmonic

Table 3. Calculated Equilibrium Distances (R_e), Harmonic Vibrational Frequencies (f), and Dissociation Energies (D_e) of the N_2 Molecule Adopting the 6-311G** Basis Set

method	R_e [pm]	f [cm^{-1}]	D_e [eV]
HF	107.0	2732	30.91
APSG	109.3	2455	10.11
MP2	111.9	2178	
CASSCF(6,6)	110.7	2349	8.646
MRMP2(CASSCF(6,6))	111.1	2295	8.597
MP-pMCPT(APSG)	109.3	2507	14.78
MP-uMCPT(APSG)	111.7	2231	10.53
exptl.[a]	109.8	2359	9.759

[a] Ref 45.

frequency. On the other hand, MP-uMCPT gives reasonable results: D_e is much improved from APSG, and R_e and f agree with those by APSG-PT or MRMP2 tolerably.

Finally, the parameters of N_2 are summarized in Table 3 and compared to experimental data from ref 45. The equilibrium bond length and the harmonic frequency are well reproduced within 2 pm and 150 cm^{-1} except for HF and MP2. Overestimation of R_e and slight underestimation of f is given by MP-uMCPT, showing resemblance to MRMP2 results. However, MP-uMCPT overestimates D_e, which is contrary to MRMP2. The overshooting of D_e is larger by MP-pMCPT, about 150%.

6. Concluding Remarks

Two simple extensions of single-reference MP theory to the multireference case were presented at the second order. The theories are strongly reminiscent of the single-reference MP2 procedure, particularly in what concerns the coefficient matrix of the linear system of equations determining the first-order wave function. Considering this equation, the present MR extensions practically affect only the inhomogeneous term, i.e., the right-hand side of the first-order equation. Numerical implementation of the theories is straightforward on the basis of an existing single-reference code adapted to a localized basis. Computational requirements of the approaches agree with single-reference MP2 calculation on a localized basis.

Among previous multireference MP theories, MP-MCPT shows the most similarity with multiference PT methods which apply a Fockian appropriately multiplied by Hilbert-space projectors to define the zero-order Hamiltonian. The novelty of the present scheme lies in the biorthogonal treatment of the overlap among basis vectors in the configuration space.

The simplicity of MP-MCPT methods is counterweighted by their failure to show desirable properties like orbital or principal determinant invariance. Size consistency is achievable only in MP-uMCPT, if assuming a block-diagonal form of the Fockian. Numerical assessment shows that in spite of their simplicity, the range of applicability does cover problems of significant multireference character, like the bond breaking process. Properties of equilibrium structures are also well estimated by MP-uMCPT.

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