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A Jeziorski-Monkhorst fully uncontracted multi-reference perturbative treatment. I. Principles, second-order versions, and tests on ground state potential energy curves

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The present paper introduces a new multi-reference perturbation approach developed at second order, based on a Jeziorski-Mokhorst expansion using individual Slater determinants as perturbers. Thanks to this choice of perturbers, an effective Hamiltonian may be built, allowing for the dressing of the Hamiltonian matrix within the reference space, assumed here to be a CAS-CI. Such a formulation accounts then for the coupling between the static and dynamic correlation effects. With our new definition of zeroth-order energies, these two approaches are strictly size-extensive provided that local orbitals are used, as numerically illustrated here and formally demonstrated in the Appendix. Also, the present formalism allows for the factorization of all double excitation operators, just as in internally contracted approaches, strongly reducing the computational cost of these two approaches with respect to other determinant-based perturbation theories. The accuracy of these methods has been investigated on ground-state potential curves up to full dissociation limits for a set of six molecules involving single, double, and triple bond breaking together with an excited state calculation. The spectroscopic constants obtained with the present methods are found to be in very good agreement with the full configuration interaction results. As the present formalism does not use any parameter or numerically unstable operation, the curves obtained with the two methods are smooth all along the dissociation path. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4984616]

I. INTRODUCTION

The research of the ground-state wave function of closed-shell molecules follows well-established paths. The perturbative expansions from the mean-field Hartree-Fock single determinant usually converge and may be used as basic tools, especially when adopting a mono-electronic zero-order Hamiltonian known as the Møller-Plesset Hamiltonian.[1] In this approach, the wave function and the energy may be understood in terms of diagrams, which lead to the fundamental linked-cluster theorem.[2] The understanding of the size-consistency problem led to the suggestion of the coupled cluster approximation,[3–7] which is now considered as the standard and most efficient tool in the study of such systems in their ground state, especially in its CCSD(T) version where linked corrections by triple excitations are added perturbatively.[8] The situation is less evident when considering excited states, chemical reactions, and molecular dissociations, since it then becomes impossible to find a relevant single determinant zero-order wave function. These situations exhibit an intrinsic Multi-Reference (MR) character. A generalized linked-cluster theorem has been established by Brandow,[9] which gives a basis to the understanding of the size-consistency problem in this context, but the conditions for establishing this theorem are severe. They require a Complete Active Space (CAS) model space and a mono-electronic zero-order Hamiltonian. Consequently, the corresponding Quasi-Degenerate Perturbation Theory (QDPT) expansion cannot converge in most of the molecular MR situations.[10–12] The research of theoretically satisfying (size-consistent) and numerically efficient MR treatments remains a very active field in quantum chemistry, as summarized in recent review articles concerning either perturbative[13] or coupled-cluster[14] methods.

The present work concentrates on the search of a new MR perturbative approach at second order (MRPT2). Of course, pragmatic proposals have been rapidly formulated, consisting first in the identification of a reference model space, defined on the set of single determinants having large components in the desired eigenstates of the problem. Diagonalizing the Hamiltonian in this reference space delivers a zero-order wave function. Then one must define the vectors of the outer space to be used in the development and, in a perturbative context, choose a zero-order Hamiltonian. The simplest approach consists in using single determinants as outer-space eigenvectors, and this has been used in the CIPSI method[15,16] which is iterative, increasing the model space from the selection of the perturbing determinant of largest coefficients and their addition to the model space. From a practical point of view, this method is very efficient and is now employed to reach near

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exact Full Configuration Interaction (FCI) energies on small molecules[17,18] and also as trial wave function in the context of quantum Monte Carlo.[19–22] But the method suffers two main defects: (i) it is not size-consistent and (ii) it does not revise the model-space component of the wave function under the effect of its interaction with the outer-space. This last defect is avoided if one expresses the effect of the perturbation as a change of the matrix elements of the model space CI matrix, according to the Intermediate Effective Hamiltonian (IEH) theory,[23] as done in the state-specific[24] or multi-state[25] versions. Other methods which start from a CAS model space and use multi-determinantal outer-space vectors have been proposed later on and are now broadly used. The first one is the CASPT2 method,[26,27] which employs a mono-electronic zero-order Hamiltonian. The method suffers from intruder state problems, to be cured in a pragmatic manner through the introduction of some parameters, and is not strictly size-consistent. The NEVPT2 method[28–30] also uses multi-determinantal perturbers [defined in two different ways in its partially (pc-NEVPT2) and strongly contracted (sc-NRVPT2) versions], it makes use of a more sophisticated bi-electronic Hamiltonian (the Dyall Hamiltonian[31]) to define the zero-order energies of these perturbers, it is parameter-free, intruder-state free, and size-consistent. Both methods are implemented in several popular codes and use a contracted description of the model space component of the desired eigenfunction (fixed by the diagonalization of the Hamiltonian in the model space). Still in the spirit of the NEVPT2 approaches, a recent work of Sokolov and Chan[32] has allowed one to remove any contractions in the perturber space, thanks to the use of matrix product states and time-dependent perturbation theory (see Sec. III A for a comparison with the present work). Multi-state versions exist to give some flexibility to the model space component, in particular around weakly avoided crossings, but this flexibility is very limited.[33,34] If one returns to methods using single-determinant perturbers, the origin of their size-inconsistency problem has been identified as due to the unbalance between the multi-determinant character of the zero-order wave function and the single determinant character of the perturbers.[35] It is in principle possible to find size consistent formulations but they require rather complex formulations[36–39] and face some risk of numerical instabilities since they involve divisions by possibly small coefficients, the amplitudes of which may be small. Finally, one should mention the approaches based on the linearized internally contracted multi-reference coupled cluster (MRCC) theory using matrix product states[40,41] and stochastic techniques.[42] Such approaches use a much richer zeroth-order Hamiltonian (the Fink Hamiltonian) which provides very accurate results, to the price of a higher computational cost than the methods based on the Dyall Hamiltonian.

The present paper is composed as follows. In Sec. II, the here-proposed formalism is presented, whose main features are as follows:

1. it considers a CAS model space (to achieve the strict separability requirement), usually obtained from a preliminary CASSCF calculation;
2. the perturbers are single determinants (the method is externally non-contracted, according to the usual terminology);
3. it is state-specific and strictly separable when localized active MOs are used (see formal demonstration in the Appendix);
4. it makes use of the Dyall Hamiltonian to define the excitation energies appearing in the energy denominators;
5. it is based on a Jeziorski-Monkhorst[43] (JM) expression of the wave operator and proceeds through reference-specific partitionings of the zero-order Hamiltonian, as it has been previously suggested in the so-called Multi-Partitionning[44–46] (MUPA) and also in the UGA-SSMPRT2.[39] Consequently, it does not define a unique zero-order energy to the outer-space determinants (see a brief discussion in the Appendix);
6. it can be expressed either as a second-order energy correction or as a dressing of the CAS-CI matrix, which offers a full flexibility in the treatment of the feed-back effect of the post-CAS-CI correlation on the model space component of the wave function;
7. the contributions of the various classes of excitations are easily identified (as in the CASPT2 and NEVPT2 methods);
8. thanks to our definition of the zeroth-order energies, all processes involving double excitations can be treated by using only the one- and two-boy density matrices, avoiding to loop on the perturbers;
9. given a set of molecular orbitals, it is parameter free and does not contain any threshold to avoid numerical instabilities.

After having presented the working equations of the present formalism in Sec. II, Sec. III proposes a comparison with other existing MR approaches, such as some special cases of multi-reference coupled cluster (MRCC) and MRPT2. Section IV discusses the computational aspects of the two methods proposed here. Then, Sec. V presents the numerical results for the ground state potential energy curves of six molecules involving single, double, and triple bond breaking together with an excited state calculation with both the JM-MRPT2 and JM-HeffPT2 methods. A numerical test of size-extensivity is provided, together with the investigation of the dependency of the results on the locality of the active orbitals. Finally, Sec. VI summarizes the main results and presents its tentative developments. The reader can find in Sec. VI B a mathematical proof of strong separability of the JM-MRPT2 method.

II. WORKING EQUATIONS FOR THE PERTURBATION AND EFFECTIVE HAMILTONIAN AT SECOND ORDER

As demonstrated previously by one of the present authors and his collaborators,[35] the size-consistency problem in any multi-reference perturbative expansion using single Slater determinants as perturbers comes from the unbalanced zeroth order energies that occur in the denominators. More precisely, if the zeroth order wave function is a CAS-CI eigenvector, the zeroth order energy is stabilized by all the interactions within the active space. A perturber treated as a single Slater determinant does not take into account the correlation effects included in the zeroth order wave function, and consequently its zeroth order energies are unbalanced with respect to the one of the CAS-CI eigenvector. Nevertheless, if instead of a

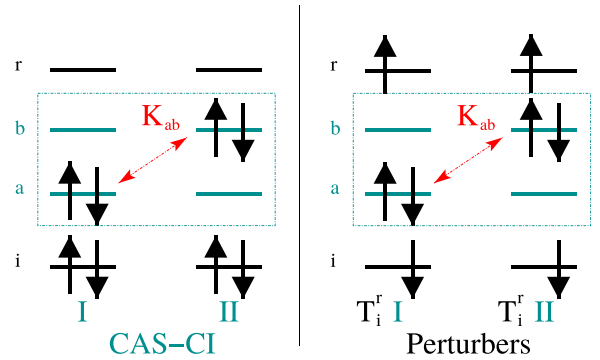

FIG. 1. Example of interactions: the two determinants of the CAS interact through a bi-electronic operator involving the two active orbitals a and b, just as the two perturber determinants generated by the same excitation operator T_i^r on the two CAS determinants.

unique perturber determinant, one considers the wave function created by the application of a given excitation operator on the whole CAS-CI wave function, most of the interactions found within the active space will also occur within this excited wave function (see Fig. 1 for a pictorial example). Therefore, the use of linear combinations of Slater determinants as perturbers together with a bi-electronic zeroth order operator, as it is the case in the NEVPT2 framework which uses the Dyall zeroth order operator, leads to balanced energy differences and removes the size-consistency problem.

On the basis of such considerations, the present work proposes an approach that uses single Slater determinants as perturbers and takes benefits of a new definition of energy denominators as expectation values of the Dyall zeroth order Hamiltonian over a specific class of linear combinations of Slater determinants. We first expose the definition of this perturbation theory, namely, the JM-MRPT2 method, which is strictly separable provided that local orbitals are used.

A large benefit from this new definition is that one may go beyond the sole calculation of the energy and improve the reference wave function by taking into account, in a strictly size-consistent way, the correlation effects brought by the perturbers on the reference space. In a second step, we reformulate the approach as a dressing of the Hamiltonian matrix within the set of Slater determinants belonging to the reference wave function, which is diagonalized. This approach will be referred to as the JM-HeffPT2 method.

A. The JM-MRPT2 method

1. First-order perturbed wave function and second-order energy

The formalism presented here is state specific and is not therefore restricted to ground state calculations. Nevertheless, for the sake of clarity and compactness, we omit the index referring explicitly to a specific eigenstate.

The zeroth order wave function $|\psi^{(0)}\rangle$ is assumed to be a CAS-CI eigenvector expanded on the set of reference determinants $|\mathrm{I}\rangle$,

$$|\psi^{(0)}\rangle = \sum_{\mathrm{I}\in\mathrm{CAS-CI}} c_{\mathrm{I}}\,|\mathrm{I}\rangle\,. \tag{1}$$

Such a wave function has a variational energy $e^{(0)}$,

$$e^{(0)} = \frac{\langle\psi^{(0)}|H|\psi^{(0)}\rangle}{\langle\psi^{(0)}|\psi^{(0)}\rangle}. \tag{2}$$

Starting from a normalized $|\psi^{(0)}\rangle$ (i.e., $\langle\psi^{(0)}|\psi^{(0)}\rangle = 1$), we assume that the exact wave function can be expressed as

$$|\Psi\rangle = |\psi^{(0)}\rangle + \sum_{\mu\notin\mathrm{CAS-CI}} c_\mu|\mu\rangle\,, \tag{3}$$

where $|\mu\rangle$ are all possible Slater determinants not belonging to the CAS-CI space. One should notice that such a form is in principle not exact, as some changes of the coefficients within the CAS-CI space can formally occur when passing from the CAS-CI eigenvector to the FCI one, but such an approximated form for the exact wave function is the basis of many MRPT2 approaches like NEVPT2, CASPT2, or CIPSI.

As in any projection technique, the exact energy can be obtained by projecting the Schrödinger equation on $|\psi^{(0)}\rangle$,

$$E = \langle\psi^{(0)}|H|\Psi\rangle = e^{(0)} + \sum_{\mu\notin\mathrm{CAS-\,CI}} c_\mu\,\langle\psi^{(0)}|H|\mu\rangle\,, \tag{4}$$

and one only needs to compute the coefficients of $|\mu\rangle$ that interact with $|\psi^{(0)}\rangle$, which consist in all individual Slater determinants being singly or doubly excited with respect to any Slater determinant in the CAS-CI space. From now on, we implicitly refer to $|\mu\rangle$ as any single Slater determinant belonging to such a space.

The coefficients c_μ are then written according to the JM ansatz,[43] whose general expression for wave function is not explicitly needed here, and will be therefore given in Sec. III B when the comparison of the present method with other multi-reference methodologies will be investigated. The JM ansatz introduces the genealogy of the coefficients c_μ with respect to the Slater determinants within the CAS-CI space

$$c_\mu = \sum_{\mathrm{I}} c_{\mathrm{I}}\; t_{\mathrm{I}\mu}, \tag{5}$$

where the quantity $t_{\mathrm{I}\mu}$ is the excitation amplitude related to the excitation process $T_{\mathrm{I}\mu}$ that leads from $|\mathrm{I}\rangle$ to $|\mu\rangle$,

$$T_{\mathrm{I}\mu}\,|\mathrm{I}\rangle = |\mu\rangle\,. \tag{6}$$

Here, we restrict $T_{\mathrm{I}\mu}$ to be a single or double excitation operator. Within this JM formulation of c_μ, a very general first order approximation of the amplitudes $t^{(1)}_{\mathrm{I}\mu}$ can be expressed as

$$t^{(1)}_{\mathrm{I}\mu} = \frac{\langle\mathrm{I}|H|\mu\rangle}{e^{(0)} - E^{(0)}_{\mathrm{I}\mu}} = \frac{\langle\mathrm{I}|H|\mu\rangle}{\Delta E^{(0)}_{\mathrm{I}\mu}}, \tag{7}$$

where the excitation energy $\Delta E^{(0)}_{\mathrm{I}\mu}$ depends explicitly on the couple $(|\mathrm{I}\rangle, |\mu\rangle)$. In that regard, a given Slater determinant $|\mu\rangle$ will have different zeroth-order energies according to the parent $|\mathrm{I}\rangle$ from which it is generated, implying that the zeroth-order Hamiltonian explicitly depends on the reference determinant $|\mathrm{I}\rangle$, just as was initially proposed in the MUPA approaches[44–46] (the interested reader could find in the Appendix a more detailed discussion of that aspect). Such a definition is different from other determinant-based MRPT2 like the CIPSI or shifted-B_k where the excitation energy does not depend on the couple $(|\mathrm{I}\rangle, |\mu\rangle)$ but only on $|\mu\rangle$. With this

definition of $t^{(1)}_{\mathrm{I}\mu}$, one can write the second-order correction to the energy $e^{(2)}$ as

$$e^{(2)} = \langle\psi^{(0)}|H|\psi^{(1)}\rangle = \sum_{\mu}\sum_{\mathrm{I}} c_{\mathrm{I}} \frac{\langle \mathrm{I}|H|\mu\rangle}{\Delta E^{(0)}_{\mathrm{I}\mu}} \langle\psi^{(0)}|H|\mu\rangle$$
$$= \sum_{\mu}\sum_{\mathrm{IJ}} c_{\mathrm{I}} \frac{\langle \mathrm{I}|H|\mu\rangle \langle\mu|H|\mathrm{J}\rangle}{\Delta E^{(0)}_{\mathrm{I}\mu}} c_{\mathrm{J}}, \tag{8}$$

and the total second-order energy $E^{(2)}$,

$$E^{(2)} = \langle\psi^{(0)}|H|\psi^{(0)}\rangle + \langle\psi^{(0)}|H|\psi^{(1)}\rangle = e^{(0)} + e^{(2)}. \tag{9}$$

2. Definition of the energy denominators

The first-order wave function can be written explicitly in terms of the excitation operators $T_{\mathrm{I}\mu}$,

$$|\psi^{(1)}\rangle = \sum_{\mu} c^{(1)}_{\mu}|\mu\rangle = \sum_{\mu}\sum_{\mathrm{I}} c_{\mathrm{I}} \frac{\langle \mathrm{I}|H\ T_{\mathrm{I}\mu}|\mathrm{I}\rangle}{\Delta E^{(0)}_{\mathrm{I}\mu}} T_{\mathrm{I}\mu}|\mathrm{I}\rangle. \tag{10}$$

However, one can notice that

1. the excitation operators $T_{\mathrm{I}\mu}$ do not explicitly depend on $|\mathrm{I}\rangle$ as they are general single or double excitation operators, just as in the Hamiltonian for instance;
2. a given excitation operator T contributes to the coefficients of several $|\mu\rangle$ ($T_{\mathrm{I}\mu} = T_{\mathrm{J}\nu} = T$);
3. the application of all the single and double excitation operators T on each $|\mathrm{I}\rangle$ generates the entire set of $|\mu\rangle$ as the reference is a CAS.

Therefore one can rewrite the first-order perturbed wave function directly in terms of excitation operators T applied on the each CAS-CI Slater determinant as

$$|\psi^{(1)}\rangle = \sum_{T} |\psi^{(1)}_{T}\rangle, \tag{11}$$

where $|\psi^{(1)}_{T}\rangle$ is the part of the first-order wave function associated with the excitation process T,

$$|\psi^{(1)}_{T}\rangle = \sum_{\mathrm{I}} c_{\mathrm{I}} \frac{\langle \mathrm{I}|H\ T|\mathrm{I}\rangle}{\Delta E^{(0)}_{\mathrm{I}\,T\mathrm{I}}} T|\mathrm{I}\rangle. \tag{12}$$

In order to fully define our perturbation theory and intermediate Hamiltonian theory, one needs to select an expression for the energy denominators occurring in the definition of $|\psi^{(1)}_{T}\rangle$. We propose to take a quantity that does not depend explicitly on the reference determinant $|\mathrm{I}\rangle$ but only depends on the excitation process T,

$$\Delta E^{(0)}_{\mathrm{I}\,T\mathrm{I}} = \Delta E^{(0)}_{T} \quad \forall\ \mathrm{I}. \tag{13}$$

Consequently, in the expression of $|\psi^{(1)}_{T}\rangle$ [see Eq. (12)], the energy denominator can be factorized

$$|\psi^{(1)}_{T}\rangle = \frac{1}{\Delta E^{(0)}_{T}} \sum_{\mathrm{I}} c_{\mathrm{I}}\ \langle \mathrm{I}|H\ T|\mathrm{I}\rangle\ T|\mathrm{I}\rangle = \frac{1}{\Delta E^{(0)}_{T}} |\tilde{\psi}^{(1)}_{T}\rangle, \tag{14}$$

where $|\tilde{\psi}^{(1)}_{T}\rangle$ is simply

$$|\tilde{\psi}^{(1)}_{T}\rangle = \sum_{\mathrm{I}} c_{\mathrm{I}}\ \langle \mathrm{I}|H\ T|\mathrm{I}\rangle\ T|\mathrm{I}\rangle. \tag{15}$$

Also, one can notice that as $|\tilde{\psi}^{(1)}_{T}\rangle$ and $|\psi^{(1)}_{T}\rangle$ differ by a simple constant factor, they have the same normalized expectation values

$$\frac{\langle\psi^{(1)}_{T}|H^{D}|\psi^{(1)}_{T}\rangle}{\langle\psi^{(1)}_{T}|\psi^{(1)}_{T}\rangle} = \frac{\langle\tilde{\psi}^{(1)}_{T}|H^{D}|\tilde{\psi}^{(1)}_{T}\rangle}{\langle\tilde{\psi}^{(1)}_{T}|\tilde{\psi}^{(1)}_{T}\rangle}. \tag{16}$$

Then, the excitation energy $\Delta E^{(0)}_{T}$ is simply taken as the difference of the normalized expectation values of the Dyall Hamiltonian H^{D} over $|\psi^{(0)}\rangle$ and $|\tilde{\psi}^{(1)}_{T}\rangle$,

$$\Delta E^{(0)}_{T} = \frac{\langle\psi^{(0)}|H^{D}|\psi^{(0)}\rangle}{\langle\psi^{(0)}|\psi^{(0)}\rangle} - \frac{\langle\tilde{\psi}^{(1)}_{T}|H^{D}|\tilde{\psi}^{(1)}_{T}\rangle}{\langle\tilde{\psi}^{(1)}_{T}|\tilde{\psi}^{(1)}_{T}\rangle}$$
$$= \frac{\langle\psi^{(0)}|H^{D}|\psi^{(0)}\rangle}{\langle\psi^{(0)}|\psi^{(0)}\rangle} - \frac{\langle\psi^{(1)}_{T}|H^{D}|\psi^{(1)}_{T}\rangle}{\langle\psi^{(1)}_{T}|\psi^{(1)}_{T}\rangle}. \tag{17}$$

This ensures the strong separability when localized orbitals are used, as will be illustrated numerically in Sec. V.

The Dyall Hamiltonian is nothing but the exact Hamiltonian over the active orbitals and a Møller-Plesset type operator over the doubly occupied and virtual orbitals. If one labels a, b, c, and d as the active spin-orbitals, i, j the spin-orbitals that are always occupied, and v, r the virtual spin-orbitals, the Dyall Hamiltonian can be written explicitly as

$$H^{D} = H^{D}_{iv} + H^{D}_{a}, \tag{18}$$

$$\begin{cases} H^{D}_{a} = \sum_{ab} h^{\mathrm{eff}}_{ab} a^{\dagger}_{a} a_{b} + \frac{1}{2}\sum_{abcd} (ad|bc)\ a^{\dagger}_{a} a^{\dagger}_{b} a_{c} a_{d} \\ H^{D}_{iv} = \sum_{i} \epsilon_{i}\ a^{\dagger}_{i} a_{i} + \sum_{v} \epsilon_{v}\ a^{\dagger}_{v} a_{v} + C \end{cases}, \tag{19}$$

where ϵ_i and ϵ_v are defined as the spin-orbital energies associated with the density given by $|\psi^{(0)}\rangle$, and the effective active one-electron operator $h^{\mathrm{eff}}_{ab} = \langle a|h + \sum_i (J_i - K_i)|b\rangle$. With a proper choice of the constant C in Eq. (19),

$$C = \sum_{i} \langle i|h|i\rangle + \frac{1}{2}\sum_{i,j} ((ii|jj) - (ij|ij)), \tag{20}$$

one has

$$\frac{\langle\psi^{(0)}|H^{D}|\psi^{(0)}\rangle}{\langle\psi^{(0)}|\psi^{(0)}\rangle} = \frac{\langle\psi^{(0)}|H|\psi^{(0)}\rangle}{\langle\psi^{(0)}|\psi^{(0)}\rangle} = e^{(0)}. \tag{21}$$

Because the Dyall Hamiltonian acts differently on the active and inactive-virtual orbitals, the excitation energy $\Delta E^{(0)}_{T}$ is the sum of an excitation energy $\Delta E^{(0)\,iv}_{T}$ associated with the inactive and virtual orbitals and of an excitation energy $\Delta E^{(0)\,a}_{T}$ associated with the active orbitals

$$\Delta E^{(0)}_{T} = \Delta E^{(0)\,a}_{T} + \Delta E^{(0)\,iv}_{T}. \tag{22}$$

Also, it is useful to differentiate the active part from the inactive-virtual part of the excitation T,

$$T = T_{a} T_{iv}. \tag{23}$$

The inactive-virtual excitation energy $\Delta E^{(0)\,iv}_{T}$ is simply

$$\Delta E^{(0)\,iv}_{T} = \sum_{i\in T} \epsilon_{i} - \sum_{v\in T} \epsilon_{v}, \tag{24}$$

where $i \in T$ and $v \in T$ refer to, respectively, the inactive and virtual spin-orbitals involved in the excitation operator T.

Conversely, the active excitation energy $\Delta E_T^{(0)\,a}$ has a more complex expression, namely,

$$\Delta E_T^{(0)\,a} = e^{(0)} - \frac{\sum_{\mathrm{I\,J}} \left(c_{\mathrm{I}} \langle \mathrm{I}|H\,T|\mathrm{I}\rangle\right) \langle \mathrm{I}|T_a^\dagger\, H^D\, T_a|\mathrm{J}\rangle \left(c_{\mathrm{J}} \langle \mathrm{J}|H\,T|\mathrm{J}\rangle\right)}{\sum_{\mathrm{I}} \left(c_{\mathrm{I}} \langle \mathrm{I}|H\,T|\mathrm{I}\rangle\right)^2 \langle \mathrm{I}|T^\dagger T|\mathrm{I}\rangle}. \tag{25}$$

3. Practical consequences: The difference between single and double excitation operators

From Eq. (25), one must differentiate the class of the pure single excitation operators from the pure double excitation operators. For the sake of clarity, we define the spin-adapted bielectronic integrals $((mn|pq))$ as

$$((mn|pq)) = \begin{cases} (mn|pq) & \text{if } \sigma(m,p) \neq \sigma(n,q) \\ (mn|pq) - (mp|nq) & \text{if } \sigma(m,p) = \sigma(n,q) \end{cases}, \tag{26}$$

where $\sigma(m,p)$ is the spin variable of the spin orbitals m and p. If one considers a given double excitation involving four different spin orbitals m, n, p, and q,

$$T_{mp}^{nq} = a_n^\dagger a_q^\dagger a_p a_m \qquad m \neq n \neq p \neq q, \tag{27}$$

one can notice that the Hamiltonian matrix elements associated with this double excitation only depend, up to a phase factor, on the four indices m, n, p, and q involved in T_{mp}^{nq}. Indeed, if T_{mp}^{nq} is possible on both $|\mathrm{I}\rangle$ and $|\mathrm{J}\rangle$, one has

$$\begin{aligned} \langle \mathrm{I}|H\ T_{mp}^{nq}|\mathrm{I}\rangle &= ((mn|pq))\ \langle \mathrm{I}|\left(T_{mp}^{nq}\right)^\dagger T_{mp}^{nq}|\mathrm{I}\rangle, \\ \langle \mathrm{J}|H\ T_{mp}^{nq}|\mathrm{J}\rangle &= ((mn|pq))\ \langle \mathrm{J}|\left(T_{mp}^{nq}\right)^\dagger T_{mp}^{nq}|\mathrm{J}\rangle, \end{aligned} \tag{28}$$

and as

$$\begin{aligned} \langle \mathrm{I}|\left(T_{mp}^{nq}\right)^\dagger T_{mp}^{nq}|\mathrm{I}\rangle &= \langle \mathrm{J}|\left(T_{mp}^{nq}\right)^\dagger T_{mp}^{nq}|\mathrm{J}\rangle \\ &= 1, \end{aligned} \tag{29}$$

it becomes

$$\langle \mathrm{J}|H\ T_{mp}^{nq}|\mathrm{J}\rangle = \langle \mathrm{I}|H\ T_{mp}^{nq}|\mathrm{I}\rangle. \tag{30}$$

Therefore, as the Hamiltonian matrix elements of type $\langle \mathrm{J}|H\ T_{mp}^{nq}|\mathrm{J}\rangle$ can be factorized both in the numerator and the dominator of the expression of the active part of the excitation energy [see Eq. (25)]. Finally, the expression of the active part of the excitation energy for a given double excitation T_{mp}^{nq} is simply

$$\begin{aligned} \Delta E_{T_{mp}^{nq}}^{(0)\,a} &= e^{(0)} - \frac{\sum_{\mathrm{I\,J}} c_{\mathrm{I}}\ \langle \mathrm{I}|T_a^\dagger\, H^D\, T_a|\mathrm{J}\rangle\ c_{\mathrm{J}}}{\sum_{\mathrm{I}} c_{\mathrm{I}}^2 \langle \mathrm{I}|T_a^\dagger\ T_a|\mathrm{I}\rangle} \\ &= e^{(0)} - \frac{\langle \psi^{(0)}|T_a^\dagger\, H^D\, T_a|\psi^{(0)}\rangle}{\langle \psi^{(0)}|T_a^\dagger T_a|\psi^{(0)}\rangle}. \end{aligned} \tag{31}$$

As a consequence, the amplitudes $t_{\mathrm{I}T_{mn}^{qp}\mathrm{I}}$ and $t_{\mathrm{J}T_{mn}^{qp}\mathrm{J}}$ associated with the same excitation T_{mn}^{qp} for different parents $|\mathrm{I}\rangle$ and $|\mathrm{J}\rangle$ are also equal,

$$\begin{aligned} t_{\mathrm{I}T_{mn}^{qp}\mathrm{I}} &= \frac{\langle \mathrm{I}|H\ T_{mn}^{qp}|\mathrm{I}\rangle}{\Delta E_{T_{mn}^{qp}}^{(0)}}, \\ t_{\mathrm{J}T_{mn}^{qp}\mathrm{J}} &= \frac{\langle \mathrm{J}|H\ T_{mn}^{qp}|\mathrm{J}\rangle}{\Delta E_{T_{mn}^{qp}}^{(0)}}, \end{aligned} \tag{32}$$

and one can define a unique excitation operator $\mathcal{T}_{mn}^{qp\,(1)}$ which does not depend on the reference determinant on which it acts. The explicit form of the reference-independent excitation operator $\mathcal{T}_{mn}^{qp\,(1)}$ is

$$\mathcal{T}_{mn}^{qp\,(1)} = \frac{((mq|np))}{\Delta E_{T_{mn}^{qp}}^{(0)}} a_q^\dagger a_p^\dagger a_n a_m. \tag{33}$$

In the case where T is a pure single excitation operator, the term $\langle \mathrm{I}|H\,T|\mathrm{I}\rangle$ may strongly depend on $|\mathrm{I}\rangle$ and Eq. (25) cannot be simplified.

4. Precaution for spin symmetry

As the formalism proposed here deals with Slater determinants, it cannot formally ensure to provide spin eigenfunctions. In order to ensure the invariance of the energy with the S_z value of a given spin multiplicity, we introduced a slightly modified version of the Dyall Hamiltonian which does not consider the following:

1. any exchange terms in the Hamiltonian matrix elements when active orbitals are involved,
2. any exchange terms involving two electrons of opposite spins (namely, $a_{b\alpha}^\dagger a_{a\beta}^\dagger a_{b\beta} a_{a\alpha}$ and $a_{b\beta}^\dagger a_{a\alpha}^\dagger a_{b\alpha} a_{a\beta}$).

B. The JM-HeffPT2 method

An advantage of a determinant-based multi-reference perturbation theory is that it can be easily written as a dressing of the Hamiltonian matrix within the reference space. Starting from the Schrödinger equation projected on a given reference determinant $|\mathrm{I}\rangle$, one has

$$c_{\mathrm{I}} \langle \mathrm{I}|H|\mathrm{I}\rangle + \sum_{\mathrm{J}\neq I} c_{\mathrm{J}} \langle \mathrm{I}|H|\mathrm{J}\rangle \sum_{\mu} c_\mu^{(1)} \langle \mathrm{I}|H|\mu\rangle = E^{(2)} c_{\mathrm{I}}. \tag{34}$$

Using the expression for the first order coefficients $c_\mu^{(1)}$, it becomes

$$c_{\mathrm{I}} \left(\langle \mathrm{I}|H|\mathrm{I}\rangle + \sum_{\mu} \frac{\langle \mathrm{I}|H|\mu\rangle^2}{\Delta E_{\mathrm{I}\mu}^{(0)}} \right) + \sum_{\mathrm{J}\neq I} c_{\mathrm{J}} \left(\langle \mathrm{I}|H|\mathrm{J}\rangle + \frac{\langle \mathrm{I}|H|\mu\rangle \langle \mu|H|\mathrm{J}\rangle}{\Delta E_{\mathrm{J}\mu}^{(0)}} \right) = E^{(2)} c_{\mathrm{I}}. \tag{35}$$

Therefore, one can define an non-Hermitian operator $\Delta H^{(2)}$,

$$\langle \mathrm{I}|\Delta H^{(2)}|\mathrm{J}\rangle = \sum_{\mu} \frac{\langle \mathrm{I}|H|\mu\rangle \langle \mu|H|\mathrm{J}\rangle}{\Delta E_{\mathrm{J}\mu}^{(0)}}, \tag{36}$$

and a dressed Hamiltonian $\mathcal{H}$ as

$$\langle \mathrm{I}|\mathcal{H}^{(2)}|\mathrm{J}\rangle = \langle \mathrm{I}|H|\mathrm{J}\rangle + \langle \mathrm{I}|\Delta H^{(2)}|\mathrm{J}\rangle, \tag{37}$$

such that Eq. (35) becomes a non-symmetric linear eigenvalue equation within the CAS-CI space

$$c_{\mathrm{I}} \langle \mathrm{I}|\mathcal{H}^{(2)}|\mathrm{I}\rangle + \sum_{\mathrm{J}\neq I} c_{\mathrm{J}} \langle \mathrm{I}|\mathcal{H}^{(2)}|\mathrm{J}\rangle = E^{(2)} c_{\mathrm{I}}. \tag{38}$$

The second-order correction to the energy $e^{(2)}$ can be simply obtained as the expectation value of $\Delta H^{(2)}$ over the zeroth-order wave function

$$\begin{aligned} e^{(2)} &= \langle \psi^{(0)}|\Delta H^{(2)}|\psi^{(0)}\rangle \\ &= \sum_{\mu} \sum_{\mathrm{I\,J}} c_{\mathrm{I}}\ \frac{\langle \mathrm{I}|H|\mu\rangle \langle \mu|H|\mathrm{J}\rangle}{\Delta E_{\mathrm{J}\mu}^{(0)}}\ c_{\mathrm{J}}. \end{aligned} \tag{39}$$

Finally, one can define a Hermitian operator $\tilde{H}^{(2)}$,

$$\langle \mathrm{I}|\tilde{H}^{(2)}|\mathrm{J}\rangle = \frac{1}{2}\left(\langle \mathrm{I}|\mathcal{H}^{(2)}|\mathrm{J}\rangle + \langle \mathrm{J}|\mathcal{H}^{(2)}|\mathrm{I}\rangle\right), \tag{40}$$

and a corresponding eigenpair $(|\tilde{\Psi}_2\rangle, \tilde{E}^{(2)})$ verifying

$$\tilde{H}^{(2)}|\tilde{\Psi}_2\rangle = \tilde{E}^{(2)}|\tilde{\Psi}_2\rangle. \tag{41}$$

The diagonalization of such a Hamiltonian allows then to improve the CAS-CI wave function by treating the coupling that can exist between the correlation effects within and outside the CAS-CI space.

III. LINKS WITH OTHER MULTI-REFERENCE METHODS

A. MRPT2 based on the Dyall Hamiltonian

It is interesting to understand the similarities and differences between the present JM-MPRT2 and other strictly size-consistent MRPT2 methods based on the Dyall zeroth-order Hamiltonian. The most flexible solution of such MRPT2 makes use of the exact solution for the Dyall Hamiltonian with $N+1$, $N+2$, $N-1$, and $N-2$ electrons in the active space (where N is the number of electrons in the active space) as perturbers. Such a formulation is totally uncontracted in the perturber space, which implies a high computational cost, but a solution as been recently proposed by Sokolov and Chan.[32] using a time-dependent formulation and matrix product state techniques. Then, one can use the partially contracted NEVPT2 (pc-NEVPT2) which is computationally less demanding and provides very similar results, as shown by Sokolov and Chan.[32] Finally, when comparing JM-MRPT2, the nearest version of NEVPT2 is certainly the strongly contracted one and the present paragraph focusses on their differences and similarities.

JM-MRPT2 uses perturbers that are individual Slater determinants, whereas all versions of NEVPT2 use linear combinations of Slater determinants. However, in SC-NEVPT2, the contraction coefficients are closely related to the Hamiltonian matrix elements, just as in the JM-MRPT2 method. In order to better understand the differences between SC-NEVPT2 and JM-MRPT2, let us take a practical example. Here, i, j are the inactive spin-orbitals, a, b are the active spin-orbitals, and r, s are the virtual spin-orbitals. Considering a given semi-active double excitation $T_{ij}^{av} = a_a^\dagger a_v^\dagger a_j a_i$, the first-order amplitude $t_{ij}^{av(1)}$ associated with T_{ij}^{av} in the JM-MRPT2 formalism is given by

$$t_{ij}^{av(1)} = \frac{((ia|jv))}{\epsilon_i + \epsilon_j - \epsilon_v + \Delta E^{(0)}_{a_a^\dagger}}, \tag{42}$$

where the active part of the excitation energy $\Delta E^{(0)}_{a_a^\dagger}$ directly comes from Eq. (31)

$$\Delta E^{(0)}_{a_a^\dagger} = e^{(0)} - \frac{\langle \psi^{(0)}|a_a H^D a_a^\dagger|\psi^{(0)}\rangle}{\langle \psi^{(0)}|a_a a_a^\dagger|\psi^{(0)}\rangle}. \tag{43}$$

Note that such a quantity can be thought as an approximation of the electron affinity of the molecule, as it is the change in energy when one introduces "brutally" an electron in spin orbital a without relaxing the wave function. Consequently, as it has been emphasized in Sec. II A [see Eq. (33)], one can consider the part of the first-order perturbed wave function generated by the excitation T_{ij}^{av},

$$|\psi^{(1)}_{T_{ij}^{av}}\rangle = \sum_{\mathrm{I}} c_{\mathrm{I}}\, t_{ij}^{av(1)}\, T_{ij}^{av}|\mathrm{I}\rangle, \tag{44}$$

which turns out to be

$$\begin{aligned}|\psi^{(1)}_{T_{ij}^{av}}\rangle &= \frac{((ia|jv))}{\epsilon_i + \epsilon_j - \epsilon_v + \Delta E^{(0)}_{a_a^\dagger}} \sum_{\mathrm{I}} c_{\mathrm{I}}\, T_{ij}^{av}\, |\mathrm{I}\rangle \\ &= \frac{((ia|jv))}{\epsilon_i + \epsilon_j - \epsilon_v + \Delta E^{(0)}_{a_a^\dagger}} T_{ij}^{av}|\psi^{(0)}\rangle. \end{aligned} \tag{45}$$

In the SC-NEVPT2 framework, one does not consider explicitly a given T_{ij}^{av} but has to consider a unique excitation $\mathcal{T}_{ij}^{v}$ which is a linear combination of all possible T_{ij}^{av} for all active spin orbitals a, with proper contraction coefficients. To be more precise, the first-order perturbed wave function associated with $\mathcal{T}_{ij}^{v}$ is

$$|\psi^{(1)}_{\mathcal{T}_{ij}^{v}}\rangle = \frac{1}{\Delta E^{(0)}_{\mathcal{T}_{ij}^{v}}} \sum_a ((ia|jv))\, T_{ij}^{av}\, |\psi^{(0)}\rangle, \tag{46}$$

where the excitation energy $\Delta E^{(0)}_{\mathcal{T}_{ij}^{v}}$ associated with $\mathcal{T}_{ij}^{v}$ is unique for all the excitation operators T_{ij}^{av} and can be thought as an average excitation energy over all a. Consequently, one can express the part of $|\psi^{(1)}_{\mathcal{T}_{ij}^{v}}\rangle$ that comes from the T_{ij}^{av} as

$$|\psi^{(1)}_{T_{ij}^{av}}\rangle^{(\text{SC- NEVPT2})} = \frac{((ia|jv))}{\Delta E^{(0)}_{\mathcal{T}_{ij}^{v}}} T_{ij}^{av}\, |\psi^{(0)}\rangle, \tag{47}$$

which we can compare to Eq. (45) in the case of the JM-MRPT2 method. Then, the only difference between SC-NEVPT2 and JM-MRPT2 is the definition of the excitation energy occurring in Eqs. (45) and (47). In the SC-NEVPT2 method, the excitation energy $\Delta E^{(0)}_{\mathcal{T}_{ij}^{v}}$ is closely related to the excitation energy defined in JM-MRPT2

$$\begin{aligned}\Delta E^{(0)}_{\mathcal{T}_{ij}^{v}} &= e^{(0)} - \frac{\langle \psi^{(1)}_{\mathcal{T}_{ij}^{v}}|\, H^D\, |\psi^{(1)}_{\mathcal{T}_{ij}^{v}}\rangle}{\langle \psi^{(1)}_{\mathcal{T}_{ij}^{v}}|\psi^{(1)}_{\mathcal{T}_{ij}^{v}}\rangle} \\ &= \epsilon_i + \epsilon_j - \epsilon_v + \Delta E^{(0)\mathrm{SC-NEVPT2}}_{a^\dagger}, \end{aligned} \tag{48}$$

where the quantity $\Delta E^{(0)\mathrm{SC-NEVPT2}}_{a^\dagger}$ is the same for all active orbitals and defined as

$$\begin{aligned}&\Delta E^{(0)\mathrm{SC-NEVPT2}}_{a^\dagger} \\ &\quad = e^{(0)} - \frac{\sum_a \sum_b ((ia|jv))((ib|jv))\,\langle \psi^{(0)}|a_b\, H^D\, a_a^\dagger|\psi^{(0)}\rangle}{\sum_a ((ia|jv))^2\,\langle \psi^{(0)}|a_a a_a^\dagger|\psi^{(0)}\rangle}. \end{aligned} \tag{49}$$

Under this perspective, one sees that the quantity $\Delta E^{(0)\mathrm{SC-NEVPT2}}_{a^\dagger}$ is related to $\Delta E^{(0)}_{a_a^\dagger}$ defined in Eq. (43):

- in the JM-MRPT2 method, the quantity $\Delta E^{(0)}_{a_a^\dagger}$ explicitly refers to the "brutal" addition of an electron in orbital a, whatever the inactive orbitals i, j or virtual orbitals v involved in T_{ij}^{av};

- the quantity $\Delta E^{(0)\text{SC–NEVPT2}}_{a^\dagger}$ involved in SC-NEVPT2 is an average electronic affinity over all possible excitation processes $a^\dagger_a$ within the active space, but keeping a trace of the inactive and virtual excitation processes involved in T^{av}_{ij}, thanks to the interaction $(ia|jv)$.

Consequently, the quantity $\Delta E^{(0)\text{SC–NEVPT2}}_{a^\dagger}$ contains also the interactions between various $a^\dagger_a\,|\psi^{(0)}\rangle$. To summarize, on one hand, JM-MRPT2 gives a different but rather crude excitation energy for each T^{av}_{ij}, and on the other hand, SC-NEVPT2 has a unique and sophisticated excitation energy for all T^{av}_{ij}. Of course, one can extend this comparison to all the other classes of double excitations.

Finally, one should notice that the effective Hamiltonian formulation of JM-MRPT2 leads to the revision of the zeroth-order wave function, which is not allowed by the NEVPT2 framework, whatever its degree of contraction in the perturber space.

B. Multi-reference coupled cluster methods

The present formalism has also several links with other multi-reference methods. First of all, as it uses a JM genealogical definition for the coefficients $c^{(1)}_\mu$ [see Eqs. (5) and (7)], the wave function corrected at first order $|\Psi^{(1)}\rangle$ can be written as

$$\begin{aligned}|\Psi^{(1)}\rangle &= |\psi^{(0)}\rangle + |\psi^{(1)}\rangle \\ &= \sum_{\mathrm{I}} c_{\mathrm{I}}\,|\mathrm{I}\rangle + \sum_{\mu}\sum_{\mathrm{I}} c_{\mathrm{I}}\; t^{(1)}_{\mathrm{I}\mu}\; T_{\mathrm{I}\mu}|\mathrm{I}\rangle \\ &= \sum_{\mathrm{I}} c_{\mathrm{I}} \left(1 + \sum_{\mu} t^{(1)}_{\mathrm{I}\mu}\; T_{\mathrm{I}\mu}\right)|\mathrm{I}\rangle\,. \end{aligned} \tag{50}$$

By introducing the excitation operator $T^{(1)}_{\mathrm{I}}$ acting only on $|\mathrm{I}\rangle$ as

$$T^{(1)}_{\mathrm{I}} = \sum_{\mu} t^{(1)}_{\mathrm{I}\mu}\; T_{\mathrm{I}\mu}, \tag{51}$$

the expression of $|\Psi^{(1)}\rangle$ in Eq. (50) becomes

$$|\Psi^{(1)}\rangle = \sum_{\mathrm{I}} c_{\mathrm{I}} \left(1 + T^{(1)}_{\mathrm{I}}\right)|\mathrm{I}\rangle\,. \tag{52}$$

Such a parameterization for the first-order corrected wave function $|\Psi^{(1)}\rangle$ recalls immediately a first-order Taylor expansion of the general JM-MRCC ansatz

$$|\mathrm{JM-MRCC}\rangle = \sum_{\mathrm{I}} c_{\mathrm{I}}\; e^{T_{\mathrm{I}}}\;|\mathrm{I}\rangle. \tag{53}$$

Nevertheless, based on the JM-MRPT2 expression for the amplitudes, one might imagine to divide the general T_{I} operator into a reference-dependent single excitation operator and a reference-independent double excitation operator. The JM-MRPT2 amplitudes might be used as a guess to start the iterative research of the MRCC equations.

Also, within the present formalism, the class of the double excitations can be factorized as shown in Sec. II A [see Eq. (33)]. Therefore, using the reference-independent amplitudes defined in Eq. (33), one can define a unique double excitation operator $\mathcal{T}^{(1)}_D$ as

$$\mathcal{T}^{(1)}_D = \sum_{m,n,p,q} \mathcal{T}^{qp(1)}_{mn}, \tag{54}$$

recalling thus the formalism of the internally contracted-MRCC[58–61] (ic-MRCC) which uses a unique excitation operator $\mathcal{T}$ as in the single-reference coupled-cluster

$$|\mathrm{ic-MRCC}\rangle = e^{\mathcal{T}}|\psi^{(0)}\rangle = e^{\mathcal{T}}\sum_{\mathrm{I}} c_{\mathrm{I}}\;|\mathrm{I}\rangle\,. \tag{55}$$

In such a perspective, as the energy provided by the JM-MRPT2 equations is size-extensive, it can be seen as a linearized coupled cluster version using a hybrid parameterization of the wave function: internally contracted ansatz for the double excitation operators and JM ansatz for the single excitation operators.

C. Determinant-based multi-reference perturbation theories

JM-MRPT2 presented here can be directly compared to the CIPSI method, just as the JM-HeffPT2 can be directly compared to the shifted-B_k method.[48–50] Indeed, by using the following amplitudes:

$$t^{\mathrm{CIPSI}}_{\mathrm{I}\mu} = \frac{\langle \mathrm{I}|H|\mu\rangle}{e^{(0)} - \langle \mu\,|H|\,\mu\rangle}, \tag{56}$$

in the equation of the second-order correction on the energy [see Eq. (8)], one obtains the CIPSI energy, and by introducing $t^{\mathrm{CIPSI}}_{\mathrm{I}\mu}$ in the definition of the dressed Hamiltonian $\tilde{H}^{(2)}$, one obtains

$$\langle \mathrm{I}|H^{(2)}_{\mathrm{Shifted}-B_k}|\mathrm{J}\rangle = \langle \mathrm{J}\,|H|\,\mathrm{J}\rangle + \sum_{\mu} \frac{\langle \mathrm{I}|H|\mu\rangle\,\langle \mu\,|H|\,\mathrm{J}\rangle}{e^{(0)} - \langle \mu\,|H|\,\mu\rangle}, \tag{57}$$

which defines the shifted-B_k Hamiltonian and corresponding energy once $H^{(2)}_{\mathrm{Shifted}-B_k}$ is diagonalized. As mentioned previously, it has been shown that the size-consistency error of these methods comes from the unbalanced treatment between the variational energy of a multi-reference wave function such as $|\psi^{(0)}\rangle$ and the variational energy of the single Slater determinant $|\mu\rangle$. Such an error is not present within the definitions of the excitation energies in the JM-MRPT2 method as the latter introduces expectation values of the Hamiltonian over linear combinations of perturber Slater determinants.

In a similar context, one can compare the JM-HeffPT2 method to the Split-GAS[47] of Li Manni *et al.* whose definition of the amplitude is

$$t^{\mathrm{Split-GAS}}_{\mathrm{I}\mu} = \frac{\langle \mathrm{I}|H|\mu\rangle}{e^{(0)} + e^{(2)} - \langle \mu\,|H|\,\mu\rangle}. \tag{58}$$

In the Split-GAS framework, the correlation energy $e^{(2)}$ brought by the perturbers is included in the energy denominator, which introduces self consistent equations as in the Brillouin-Wigner perturbation theory.[51] However, the size-consistency error in such a method is even more severe than in the shifted-B_k as the excitation energies are much larger due to the presence of the total correlation energy $e^{(2)}$.

IV. COMPUTATIONAL COST

A. Mathematical complexity and memory requirements

Compared to other size-extensive MRPT2 methods, a clear advantage of JM-MRPT2 is its simplicity. The NEVPT2 approach requires to handle the four-body density matrix and

the CASPT2 needs to handle the three-body density matrix. Both of these computationally intensive phases can be skipped in our formalism as one only needs to compute expectation values whose number is relatively small compared to NEVPT2 and CASPT2. The most involved quantity to be computed is

$$\Delta E_{ir}^{(0)} = e^{(0)} - \frac{\sum_{\mathrm{I}} \sum_{\mathrm{J}} c_{\mathrm{I}} \langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle \langle \mathrm{I}|H|\mathrm{J}\rangle \langle \mathrm{J}|H\ a_r^\dagger a_i|\mathrm{J}\rangle c_{\mathrm{J}}}{\left(\sum_{\mathrm{I}} c_{\mathrm{I}} \langle \mathrm{I}|H\ a_r^\dagger a_i\,|\mathrm{I}\rangle\right)^2}, \tag{59}$$

for all pairs (i, r) where i is an inactive orbital and r is a virtual orbital. These quantities need to be only computed once since they can all fit in memory. Each $\Delta E_{ir}^{(0)}$ is, from the computational point of view, equivalent to an expectation value over the CASSCF wave function. As all $\Delta E_{ir}^{(0)}$ are independent, the computation of these quantities can be trivially parallelized. Regarding the memory footprint of the JM-MRPT2 method, it scales as $\mathcal{O}(n_a^3)$ (n_a being the number of active orbitals) for the storage of the $\Delta E^{(0)}_{a_a^\dagger a_b^\dagger a_c}$ and $\Delta E^{(0)}_{a_a^\dagger a_b a_c}$ quantities.

Regarding the complexity of the equations for the amplitudes, it is clear that once computed the active part of the denominator, JM-MRPT2 is just a simple sum of contributions. This is in contrast with the UGA-SSMRPT2 equations which involve the handling of coupled amplitude equations.

B. Removal of the determinant-based computational cost

The present formalisms are formally determinant-based methods, which implies that the computational cost should be proportional to the number of perturbers $|\mu\rangle$ that one has to generate to compute the corrections to the energy or the dressing of the Hamiltonian matrix, just as in the CIPSI, shifted-B_k, or UGA-SSMRPT2 methods. To understand the main computational costs, one can divide the excitation classes according to the difference dedicated CI (DDCI) framework,[52] which classifies the Slater determinants in terms of numbers of holes in the doubly occupied orbitals and particles in the virtual orbitals. If N_{CAS} is the number of Slater determinants of the CAS-CI zeroth order wave function, n_o, n_a, and n_v, respectively, the number of doubly occupied, active and virtual orbitals, one can then classify each excitation class according to the number of perturbers needed to compute their contribution to the second-order perturbation correction to the energy:

1. the *two-holes-two-particles* excitation class (2h2p) which scales as $N_{\mathrm{CAS}} \times n_o^2 \times n_v^2$;
2. the *one-hole-two-particles* excitation class (1h2p) which scales as $N_{\mathrm{CAS}} \times n_o \times n_a \times n_v^2$;
3. the *two-holes-one-particle* excitation class (2h1p) which scales as $N_{\mathrm{CAS}} \times n_o^2 \times n_a \times n_v$;
4. the *two-particles* excitation class (2p) which scales as $N_{\mathrm{CAS}} \times n_v^2$;
5. the *two-holes* excitation class (2h) which scales as $N_{\mathrm{CAS}} \times n_o^2$;
6. the *one-hole-one-particle* excitation class (1h1p) which scales as $N_{\mathrm{CAS}} \times n_o \times n_v$;
7. the *one-particle* excitation class (1p) which scales as $N_{\mathrm{CAS}} \times n_v$;
8. the *one-hole* excitation class (1h) which scales as $N_{\mathrm{CAS}} \times n_o$.

Nevertheless, our formalism presents several mathematical simplifications that allow one to basically remove any browsing over the Slater determinants $|\mu\rangle$, and once more there is a difference between the single and double excitations processes.

C. Factorization of the most numerous double excitation processes

As the five most computationally demanding excitation classes involve only double excitation operators in their equations, their contribution can be formalized directly, thanks to the one- and two-body density matrices of the zeroth-order wave function. To understand how one can write the second-order correction to the energy as

$$\begin{aligned} e^{(2)}_{\text{double exc.}} &= \sum_{m,n,p,q} \sum_{\mathrm{I}} c_{\mathrm{I}} \langle \psi^{(0)}|H\ a_q^\dagger a_p^\dagger a_n a_m|\mathrm{I}\rangle \frac{((mq|np))}{\Delta E^{(0)}_{a_q^\dagger a_p^\dagger a_n a_m}} \\ &= \sum_{m,n,p,q} \sum_{\mathrm{I,\,J}} c_{\mathrm{I}} c_{\mathrm{J}} \langle \mathrm{J}|H\ a_q^\dagger a_p^\dagger a_n a_m|\mathrm{I}\rangle \frac{((mq|np))}{\Delta E^{(0)}_{a_q^\dagger a_p^\dagger a_n a_m}}. \end{aligned} \tag{60}$$

Consequently, as $\langle \mathrm{J}\,|H\ a_q^\dagger a_p^\dagger a_n a_m|\mathrm{I}\rangle$ is necessarily of type

$$\langle \mathrm{J}|H\ a_q^\dagger a_p^\dagger a_n a_m|\mathrm{I}\rangle = ((ef|gh))\,\langle \mathrm{J}|a_f^\dagger a_h^\dagger a_g a_e\ a_q^\dagger a_p^\dagger a_n a_m|\mathrm{I}\rangle\,, \tag{61}$$

one can reformulate the second-order correction to the energy in terms of many-body density matrices

$$\begin{aligned} e^{(2)}_{\text{double exc.}} = &\sum_{m,n,p,q,e,f,g,h} \langle \psi^{(0)}|a_f^\dagger a_h^\dagger a_g a_e\ a_q^\dagger a_p^\dagger a_n a_m|\psi^{(0)}\rangle \\ &\times \frac{((mq|np))\ ((ef|gh))}{\Delta E^{(0)}_{a_q^\dagger a_p^\dagger a_n a_m}}. \end{aligned} \tag{62}$$

Such a formulation avoids completely to run over Slater determinants and consequently kills the prefactor in N_{CAS} involved in each of the excitation classes, just as in the internally contracted formalisms. Of course, because of the restrictions in terms of holes and particles in the inactive and virtual orbitals, the handling of the four-body density matrix never occurs in our formalism. We report here the explicit equations for the energetic corrections of the five most numerous double excitation classes

$$e^{(2)}_{\mathrm{2h2p}} = \frac{1}{2} \sum_{i,j,v,r} \frac{3(iv|jr)^2 + (ir|jv)^2 - 2(iv|jr)(ir|jv)}{\epsilon_i + \epsilon_j - \epsilon_v - \epsilon_r}, \tag{63}$$

$$e^{(2)}_{\mathrm{1h2p}} = \frac{1}{2} \sum_{i,v,r,a,b} \langle \psi^{(0)}|a_a a_b^\dagger|\psi^{(0)}\rangle \frac{((ir|av))((ir|bv))}{\epsilon_i + \Delta E^{(0)}_{a_a^\dagger} - \epsilon_r - \epsilon_v}, \tag{64}$$

$$e^{(2)}_{\mathrm{2h1p}} = \frac{1}{2} \sum_{i,j,r,a,b} \langle \psi^{(0)}|a_a^\dagger a_b|\psi^{(0)}\rangle \frac{((ir|aj))((ir|bj))}{\epsilon_i + \epsilon_j + \Delta E^{(0)}_{a_a} - \epsilon_r}, \tag{65}$$

$$e^{(2)}_{\mathrm{2p}} = \frac{1}{2} \sum_{r,v,a,b,c,d} \langle \psi^{(0)}|a_a^\dagger a_b^\dagger a_c a_d|\psi^{(0)}\rangle \frac{((ar|bv))((cr|dv))}{\Delta E^{(0)}_{a_c a_d} - \epsilon_r - \epsilon_v}, \tag{66}$$

TABLE I. Geometries used for the ethane and ethylene molecules.

Geometrical parameters	C_2H_6	C_2H_4
C–H (Å)	1.103	1.089
H–C–C (°)	111.2	120.0
H–C–H (°)	107.6	120.0
H–C–C–H (°)	180.0	180.0

$$e^{(2)}_{2h} = \frac{1}{2}\sum_{i,j,a,b,c,d} \langle \psi^{(0)}|a_a a_b a_c^\dagger a_d^\dagger|\psi^{(0)}\rangle \frac{((ai|bj))((ci|dj))}{\epsilon_i+\epsilon_j+\Delta E^{(0)}_{a_c^\dagger a_d^\dagger}}. \tag{67}$$

D. Simplification for the 1h1p excitation class

Thanks to the factorization of the most numerous double excitations processes, the remaining main computational cost comes from the single excitations involved in the 1h1p excitation class. In the case of single excitation processes, the factorization cannot be applied as the Hamiltonian matrix elements depend on the Slater determinant on which the single excitation is applied. The total energetic correction brought by the single excitation processes involved in the 1h1p excitation class can be expressed as follows:

$$\begin{aligned} e^{(2)\ \text{Single exc.}}_{1h1p} &= \sum_{i,r}\sum_{\mathrm{I}} \langle \psi^{(0)}|H\ a_r^\dagger a_i|\mathrm{I}\rangle\, c_\mathrm{I} \frac{\langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle}{\Delta E^{(0)}_{ir}} \\ &= \sum_{i,r}\sum_{\mathrm{I,J}} c_\mathrm{J}\, \langle \mathrm{J}|H\ a_r^\dagger a_i|\mathrm{I}\rangle\, c_\mathrm{I} \frac{\langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle}{\Delta E^{(0)}_{ir}}. \end{aligned} \tag{68}$$

As the Hamiltonian matrix elements $\langle \mathrm{J}|H\ a_r^\dagger a_i|\mathrm{I}\rangle$ are simply

$$\langle \mathrm{J}|H\ a_r^\dagger a_i|\mathrm{I}\rangle = ((ir|ab))\,\langle \mathrm{J}|a_b^\dagger a_a|\mathrm{I}\rangle\,, \tag{69}$$

one can reformulate the sum as

$$e^{(2)\ \text{Single exc.}}_{1h1p} = \sum_{\mathrm{I,J}} c_\mathrm{J} c_\mathrm{I} \sum_{a,b} \mathcal{F}^\mathrm{I}_{ab}\ \langle \mathrm{J}|a_b^\dagger a_a|\mathrm{I}\rangle\,, \tag{70}$$

where the quantity $\mathcal{F}^\mathrm{I}_{ab}$ is the effective Fock operator associated with the Slater determinant $|\mathrm{I}\rangle$ involving the active orbitals a and b,

$$\mathcal{F}^\mathrm{I}_{ab} = \sum_{i,r}((ir|ab)) \frac{\langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle}{\Delta E^{(0)}_{ir}}. \tag{71}$$

Of course, as $\langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle$ depends on the occupation of $|\mathrm{I}\rangle$, there is one effective Fock operator for each reference determinant $|\mathrm{I}\rangle$ which would suggest to compute explicitly these quantities for each Slater determinant within the CAS-CI space. Nevertheless, one can notice that $\langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle$ is just a sum of terms

$$\langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle = \sum_{m \text{ occupied in } |\mathrm{I}\rangle} ((ir|mm)). \tag{72}$$

Considering that the inactive orbitals are always doubly occupied in $|\mathrm{I}\rangle$, this sum can be split into an inactive and an active contribution, namely,

$$\langle \mathrm{I}|H\ a_r^\dagger a_i|\mathrm{I}\rangle = F^{\mathrm{c.s.}}_{ir} + F^\mathrm{I}_{ir}, \tag{73}$$

where F^{cs}_{ir} and F^I_{ir} are defined as

$$F^{\mathrm{cs}}_{ir} = \sum_{j \text{ doubly occupied in } |\mathrm{I}\rangle} 2(ir|jj) - (rj|ij), \tag{74}$$

$$F^\mathrm{I}_{ir} = \sum_{c \text{ occupied in} |\mathrm{I}\rangle} ((ir|cc)). \tag{75}$$

Therefore, one can first compute the effective Fock operator associated with the closed shell orbitals

$$\mathcal{F}^{\mathrm{cs}}_{ab} = \sum_{i,r}((ir|ab)) \frac{F^{\mathrm{cs}}_{ir}}{\Delta E^{(0)}_{ir}}, \tag{76}$$

TABLE II. Non-parallelism errors and spectroscopic constants computed from the potential energy curves obtained at different computational levels for the F_2, C_2H_6, and FH molecules. NPE and D_0 are reported in mH, R_{eq} in Å, and k in hartree/Å^2.

	F_2				C_2H_6				FH			
	NPE	D_0	R_{eq}	k	NPE	D_0	R_{eq}	k	NPE	D_0	R_{eq}	k
CASSCF	30.7	22.1	1.53	0.43	27.7	154.0	1.55	0.99	35.3	180.0	0.92	2.15
JM-MRPT2	6.7	46.3	1.44	0.85	2.5	179.0	1.53	1.06	9.7	220.4	0.93	2.11
JM-MRPT2 (deloc)	11.4	51.1	1.43	0.93	4.5	181.6	1.54	1.06	13.1	224.3	0.93	2.13
SC-NEVPT2	8.5	48.1	1.44	0.88	2.6	179.2	1.54	1.07	9.5	220.5	0.93	2.11
PC-NEVPT2	8.5	48.2	1.44	0.88	2.5	179.2	1.54	1.07	9.5	220.5	0.93	2.11
CASPT2 (IPEA = 0)	2.6	44.1	1.46	0.74	3.6	175.0	1.53	1.08	3.1	214.1	0.92	2.16
CASPT2 (IPEA = 0.25)	3.9	44.3	1.46	0.75	3.4	177.8	1.53	1.09	4.0	214.5	0.92	2.17
Mk-MRPT2[a]	...	47.2	1.44	0.60	...	...	...	...	...	...	...	...
Mk-MRPT2 (deloc)[a]	...	48.4	1.44	0.71	...	...	...	...	...	...	...	...
JM-HeffPT2	7.4	50.1	1.45	0.87	2.4	179.4	1.53	1.05	8.9	221.9	0.93	2.11
JM-HeffPT2 (deloc)	14.2	56.2	1.44	0.94	5.4	182.2	1.54	1.05	14.5	226.1	0.94	2.14
Shifted B_k	6.6	50.1	1.48	0.80	8.6	136.4	1.64	0.75	44.3	216.4	0.93	2.11
Shifted B_k (deloc)	5.7	91.8	1.41	1.26	4.7	220.5	1.53	1.09	26.7	236.1	0.94	2.31
FCI[b]	...	45.1	1.46	0.77	...	177.7	1.53	1.06	...	214.4	0.92	2.16

[a]Results from Ref. 62.
[b]Results obtained with CIPSI calculations converged up to a second-order perturbative correction lower than 10^{-4} hartree.

which is common for all the Slater determinants $|\mathrm{I}\rangle$ within the CAS-CI space. Then, what differentiates the effective Fock operator between two different determinants $|\mathrm{I}\rangle$ and $|\mathrm{J}\rangle$ is the active part

$$F^{\mathrm{I}}_{ab} = \sum_{i,r} ((ir|ab)) \frac{F^{\mathrm{I}}_{ir}}{\Delta E^{(0)}_{ir}}. \tag{77}$$

One can then notice that the active part of the Fock operator F^{I}_{ir} is just a sum over all active orbitals occupied in $|\mathrm{I}\rangle$ of quantities that only depend on the active orbitals

$$F^{\mathrm{I}}_{ab} = \sum_{c \text{ occupied in } |\mathrm{I}\rangle} F^{c}_{ab}, \tag{78}$$

where F^{c}_{ab} is nothing but

$$F^{c}_{ab} = \sum_{i,r} ((ir|ab)) \frac{((ir|cc))}{\Delta E^{(0)}_{ir}}. \tag{79}$$

Therefore, by computing and storing all possible F^{c}_{ab} together with $\mathcal{F}^{\mathrm{cs}}_{ab}$, one can then easily rebuild the total effective operator of a given Slater determinant $|\mathrm{I}\rangle$,

$$\mathcal{F}^{\mathrm{I}}_{ab} = \mathcal{F}^{\mathrm{cs}}_{ab} + \sum_{c \text{ occupied in } |\mathrm{I}\rangle} F^{c}_{ab}, \tag{80}$$

and consequently compute the total second-order correction to the energy $e^{(2)\ \mathrm{Single\ exc.}}_{\mathrm{1h1p}}$ as a simple expectation value. To summarize, a computational step scaling as $N^2_{\mathrm{CAS}} \times n_o \times n_v$ [see Eq. (68)] is replaced by a first calculation scaling as $n^3_{act} \times n_o \times n_v$ [see Eq. (79)], followed by the computation of an expectation value scaling as N^2_{CAS}, independent of the number of doubly occupied and virtual orbitals.

V. NUMERICAL RESULTS

The present section spells out the numerical results obtained for the potential energy curves and corresponding spectroscopic constants of six molecules involving a single, double, and triple bond breaking, which are F_2, FH, C_2H_6, C_2H_4, H_2O, and N_2. We also report the computation of the ${}^1A_g \rightarrow {}^1B_{1u}$ excitation energy of the ethylene molecule and compare it to the near FCI value obtained by Daday and coworkers[53] with the FCI-Quantum Monte Carlo (FCI-QMC) approach. A numerical test of strong separability is also provided in the case of the $F_2 \cdots FH$ molecule.

A. General computational details

The cc-pVDZ basis set has been used in all cases, except for the FH molecule for which the aug-cc-pVDZ basis set was retained, and pure spherical harmonics were used for all calculations. The frozen core approximation has been used, and consequently the 1*s* electrons were systematically frozen for all non-hydrogen atoms. The near FCI reference values were obtained using the CIPSI algorithm developed in the program *Quantum Package*[54] and all calculations were converged below 0.1 mH. The shifted-B_k, JM-MRPT2, and JM-HeffPT2 have been implemented in the *Quantum Package*, and all CASSCF calculations were performed using the GAMESS(US)[55] software. The CASPT2 calculations were performed with MOLCAS 7.8,[56] while the NEVPT2 results were obtained using stand-alone codes developed at the University of Ferrara and interfaced with MOLCAS 7.8. The geometrical parameters used for the C_2H_6 and C_2H_4 molecules can be found in Table I, and the H–O–H angle of the H_2O molecule has been set to 110.6°. Concerning the excitation energy calculation of the ethylene molecule, we used the experimental geometry and the ANO-L-VDZ basis set[57] in order to compare to one of the values obtained within the FCI-QMC method in Ref. 53.

In order to compare the performance of the here proposed formalisms with other determinant-based MPRT2 methods, we have also performed calculations using the shifted-B_k method using an Epstein-Nesbet zeroth order Hamiltonian, and we also report results obtained at the Mk-MPRT2[62] and UGA-SSMRPT2[39] level of theories when available. For

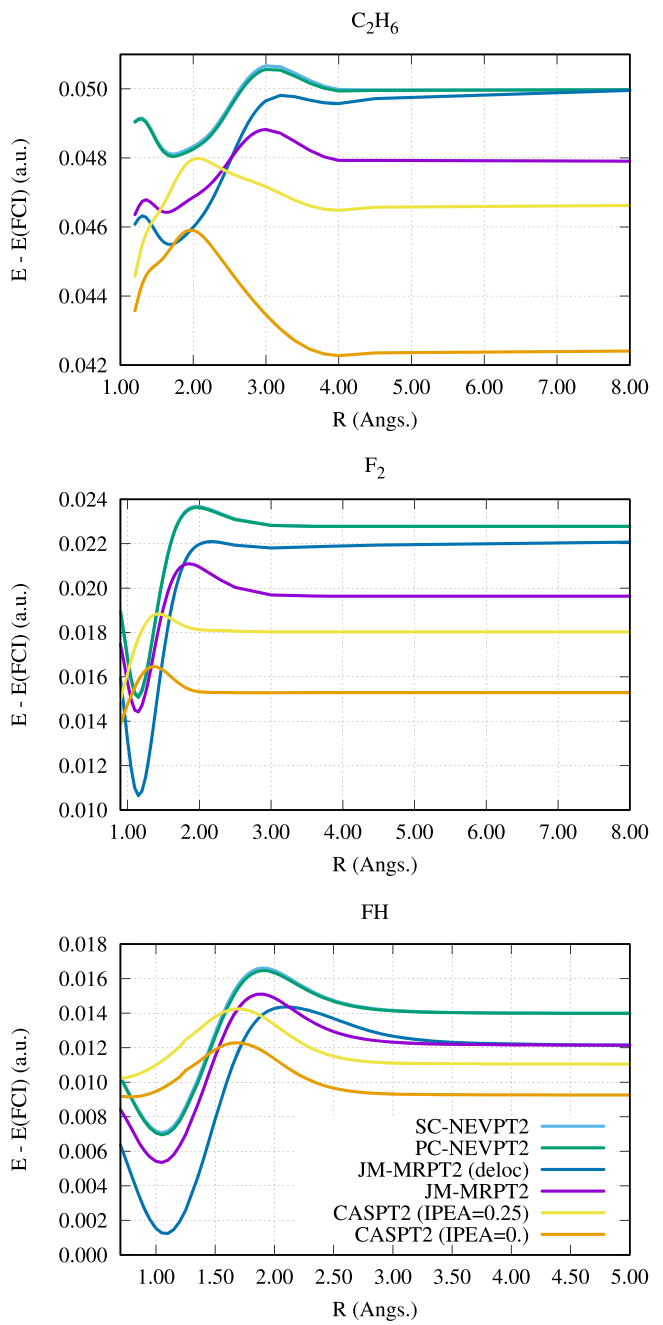

FIG. 2. Comparison of different MR-PT2 schemes with the FCI energy along the potential energy curves of C_2H_6, F_2, with the cc-pVDZ basis set, and FH with the aug-cc-pVDZ basis set. Energy differences in atomic units.

the sake of comparison with other state-of-the-art methods, we also report the spectroscopic constants and the error with respect to FCI obtained at the strongly contracted (SC-NEVPT2) and partially contracted (PC-NEVPT2) NEVPT2 using delocalized orbitals, together with CASPT2 with two different IPEA values. The IPEA values were chosen as 0 as in the original formulation of CASPT2, and 0.25 corresponding to the nowadays standard CASPT2 method.

B. Definition of the active spaces and localized orbitals

All MRPT2 calculations started with a minimal valence CASSCF involving the bonding and anti-bonding orbitals of each bond being broken along the potential energy curve. In the case of the single bond breaking, it simply implies a CASSCF(2,2) with the σ and σ^* orbitals. The following minimal valence active spaces are used for the three systems involving multiple bond breaking: for the H_2O molecule, a CASSCF(4,4) with four orbitals of valence character (using the C_{2v} symmetry point group, two orbitals of the A_1 irrep and two orbitals of the B_2 irrep having a C–H bonding character); for the C_2H_4 molecule, a CAS(4, 4) has been performed using the bonding and anti-bonding orbitals of both the σ and π C–C bonds; and for the N_2 molecule, a CAS(6, 6) has been used with the bonding and anti-bonding orbitals of the σ and the two π bonds.

Nevertheless, as it is the case for many multi-reference perturbation theories, our formalism is not invariant through orbital rotations within each orbital space (active, inactive, and virtual). Therefore one can choose to use delocalized orbitals, as the canonical ones, or localized orbitals. The present formalism is strictly separable when localized orbitals are used, so it seems therefore natural to use localized active orbitals rather than the canonical ones. In the case, F_2, N_2, C_2H_6, and C_2H_4, these orbitals are simply obtained by a rotation of $\pi/4$ between the bonding and anti-bonding active orbitals (σ and σ^* for the σ bond, π and π^* for the π bonds, and so on). In the case of the FH and H_2O molecules, the active orbitals were obtained, thanks to a rotation of the canonical active MOs in order to maximize the overlap with reference localized orbitals following chemical intuition: for the FH molecule, they consist in the $2p_z$ atomic orbital of the fluorine and $1s$ atomic orbital of the hydrogen atom, and for the H_2O molecule they consist in the two $1s$ atomic orbitals of the hydrogen atoms and of two simple linear combinations of the $2p_x$ and $2p_y$ orbitals, each one pointing to a given hydrogen atom.

Even if the present formalism is strictly separable only using localized orbitals, we nevertheless investigate the dependency of the choice of the active orbitals for the three molecules involving a single bond breaking (F_2, FH and C_2H_6) for which we report calculations both with canonical delocalized active orbitals (which are referred as "deloc") and localized active orbitals.

C. Single bond breaking

Table II presents the spectroscopic constants, namely, equilibrium distance (R_{eq}), the bond energy (D_0), and the second derivative (k) at R_{eq}, for the F_2, C_2H_6, and FH molecules at different computational levels. Also, we represent in Fig. 2 the difference of the FCI energy along the potential energy curves of those systems. From these data, several trends can be observed, both regarding the quality of the potential energy curves and the dependency on the choice of the active orbitals.

1. Dependency on the locality of the active orbitals

From the error of the potential energy curve to the FCI reference, it appears that the JM-MRPT2 method gives systematically better spectroscopic constants and a lower error with respect to the full-CI energy when localized orbitals are chosen. This is consistent with the fact that these methods are strictly separable when localized orbitals are used. Therefore, from now on we shall only refer to the results obtained with localized orbitals. One can remark that in the case of the F_2 molecule where Mk-MRPT2 calculations are available in the literature,[62] the JM-MRPT2 method gives very similar results.

2. Quality of the potential energy curves

From Table II, one can observe that the results obtained with the JM-MRPT2 method are comparable to those obtained

TABLE III. Non-parallelism errors and spectroscopic constants computed from the potential energy curves obtained at different computational levels for the H_2O, C_2H_4, and N_2 molecules. NPE and D_0 are reported in mH, R_{eq} in Å and k in hartree/Å^2.

	H_2O				C_2H_4				N_2			
	NPE	D_0	R_{eq}	k	NPE	D_0	R_{eq}	k	NPE	D_0	R_{eq}	k
CASSCF	40.9	289.3	0.96	3.74	26.2	252.6	1.36	2.03	18.2	313.7	1.11	5.34
JM-MRPT2	3.0	332.7	0.96	3.89	3.7	279.5	1.35	2.07	3.4	316.9	1.12	5.05
SC-NEVPT2	2.4	329.2	0.96	3.81	2.4	278.2	1.36	2.09	2.3	317.2	1.12	5.10
PC-NEVPT2	2.5	329.5	0.96	3.81	3.2	279.3	1.35	2.10	1.3	318.2	1.12	5.10
CASPT2 (IPEA = 0)	5.5	325.4	0.96	3.86	6.0	271.9	1.35	2.10	9.6	310.2	1.12	5.07
CASPT2 (IPEA = 0.25)	3.0	327.9	0.96	3.86	4.5	278.0	1.35	2.11	4.4	318.8	1.12	5.14
JM-HeffPT2	4.8	333.9	0.96	3.85	4.0	280.2	1.35	2.08	4.5	317.1	1.12	4.99
Shifted B_k	30.8	304.3	0.98	3.37	7.6	238.5	1.40	1.73	5.9	277.7	1.14	4.42
FCI[a]	...	330.3	0.96	3.89	...	277.0	1.35	2.09	...	319.4	1.12	5.04

[a]Results obtained with CIPSI calculations converged up to a second-order perturbative correction lower than 10^{-4} hartree.

with the well-established CAS-PT2 and NEVPT2 methods. The largest deviation on D_0 is of 6 mH for the FH molecule, representing less than 3% of error on the total binding energy, whereas it is of 1.2 mH and 1.3 mH which represents an error of less than 3% and 1% on the binding energy for the F_2 and C_2H_6 molecules, respectively. The equilibrium geometries obtained at the JM-MRPT2 level are always within 1% of error with respect to the FCI estimates, and so are the k values except for the F_2 molecule for which a significant deviation of 10% is observed. Except for the quality of the results, one can observe a systematic overestimation of the binding energy at the JM-MRPT2 level.

The non-parallelism error (NPE) is, within the computed points, the difference between the maximum and minimum absolute errors with respect to FCI energies. In addition to the the spectroscopic constants, the NPE is also a good indicator of the quality of the results of a given method. Using localized orbitals, the NPE obtained at JM-MRPT2 is of 6.7 mH for the F_2 molecule, 2.5 mH for C_2H_6, and 9.7 mH for the FH molecule. The maximum NPE is then for the FH molecule, which has also the largest energetic variation among the three molecules studied here.

D. Numerical results for double and triple bond breaking

Table III presents the spectroscopic constants obtained for the H_2O, C_2H_4, and N_2 molecules and Fig. 3 shows the difference of the FCI energy along the potential energy curves. From Table III, it appears that the results obtained with the JM-MRPT2 method follow a trend similar to what has been observed with the study of the three molecules involving a single bond breaking: the spectroscopic constants obtained at this level of theory are globally in good agreement with the FCI ones, D_0 obtained at the JM-MRPT2 level tends to be overestimated. Also, the absolute error on D_0 obtained at JM-MRPT2 is quite constant: 2.4 mH, 2.4 mH, and 2.5 mH, representing 0.7%, 0.9%, and 0.8% of the total binding energy for the H_2O, C_2H_4, and N_2 molecules, respectively.

Regarding the curves displaying errors with respect to the FCI energies, it appears that the JM-MRPT2 curves are smooth and do not present any intruder state problems, with an NPE between 3 and 4 mH.

E. Comparison of JM-HeffPT2 with shifted-B_k

Figure 4 shows the difference of the FCI for all the previously studied systems, for the JM-HeffPT2 and the shifted-B_k methods. It is clear that in all the cases, the potential energy curves obtained with the JM-HeffPT2 are much more parallel to the FCI curve than the shifted-B_k ones. Also, it is worth mentioning that the JM-HeffPT2 curves are smooth and do not present any intruder state problems. The spectroscopic constants and NPEs calculated with both methods are given in Tables II and III.

In general, the energetic values obtained after diagonalizing the effective Hamiltonian are not better than those obtained with the JM-MRPT2 method. But the main advantage of JM-HeffPT2 over JM-MRPT2 is that it provides improved CI-coefficients on the reference space, like the shifted-B_k method. To illustrate the quality of the improved wave functions, we report in Table IV the ratios c_i/c_n where c_i and c_n are the CI-coefficients of the determinants relative to the ionic and neutral structures of F_2 obtained at the CAS-CI, JM-HeffPT2, shifted-B_k, and CIPSI levels. As a reference, CIPSI calculations were carried out in the frozen-core FCI space, and the number of determinants (N_{det}) selected in the variational wave function are given in Table IV. For such large wave functions, the CI-coefficients on the reference determinants are expected to be very close to the FCI limit. Both the JM-HeffPT2 and shifted-B_k methods show a significant improvement of the wave function, and JM-HeffPT2 is in very good agreement with the FCI especially at the equilibrium distance. Similarly, we report in Table V computations of the dipole moment along the internuclear axis for the FH molecule and compare it to

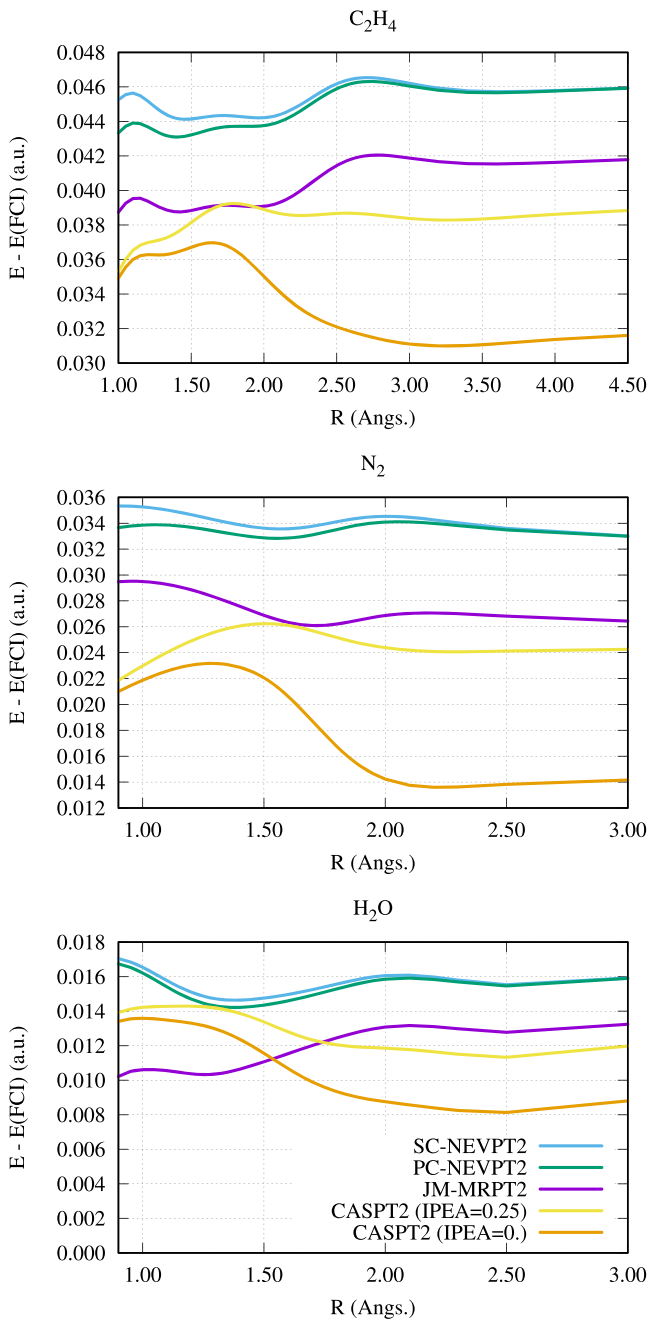

FIG. 3. Comparison of different MR-PT2 schemes with the FCI energy along the potential energy curves of C_2H_4, N_2, and H_2O with the cc-pVDZ basis set. Energy differences in atomic units.

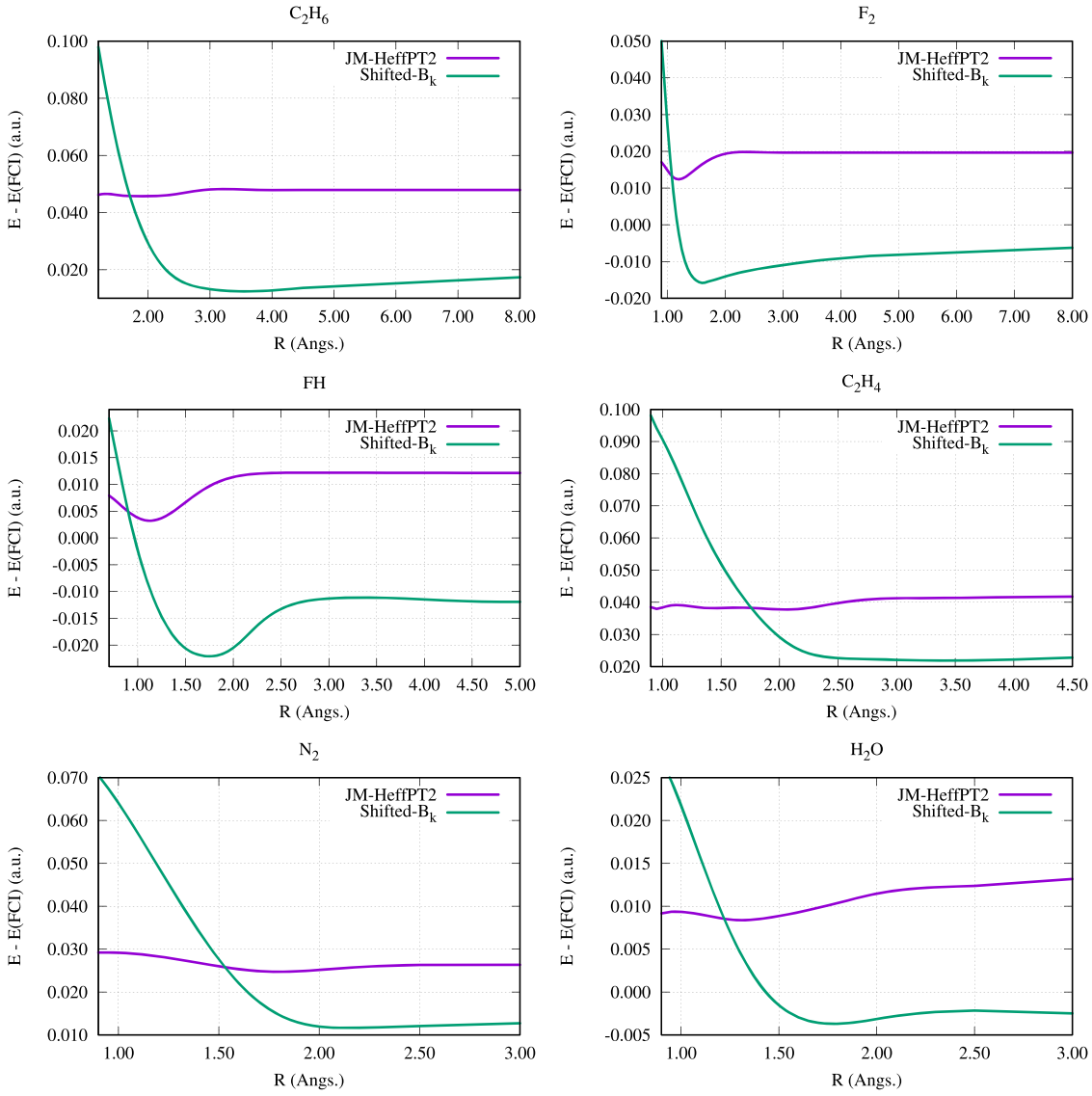

FIG. 4. Energy difference of JM-HeffPT2 and shifted-B_k with respect to the FCI energy along the potential energy curves of C_2H_6, F_2, C_2H_4, N_2, and H_2O with the cc-pVDZ basis set, and FH with the aug-cc-pVDZ basis set. Energy differences in atomic units.

values obtained by projecting and normalizing large CIPSI wave functions on the CAS-CI space (referred hereafter as CIPSI-proj-CAS). Therefore, the dipole moment computed with a given method only depends on the relative coefficients of the four Slater determinants belonging to the CAS-CI space. From these results, it clearly appears that the JM-HeffPT2 method allows one to obtain values for the dipole moment that are in excellent agreement with that obtained at the CIPSI-proj-CAS level of theory. Also, one can notice a significant improvement of the description of the dipole moment going from the CAS-CI wave function to the JM-HeffPT2 wave function, implying that the diagonalization of the dressed Hamiltonian leads to coefficients within the CAS-CI space that are closer to the ones of the FCI wave function, which is not the case for the shifted-B_k method.

TABLE IV. Ratios c_i/c_n at different internuclear distances, for the F_2 molecule (cc-pVDZ). The last row indicates in italics the number of Slater determinants in the CIPSI wave functions.

F2	1.4119 Å	2 Å	3 Å
CAS-CI	0.572	0.212	0.024
JM-HeffPT2	0.646	0.273	0.033
Shifted-B_k	0.707	0.274	0.030
CIPSI	0.638	0.259	0.030
N_{det}	*6 321 822*	*7 889 806*	*12 748 141*

TABLE V. Dipole moment (reported in a.u.^{2}) along the internuclear axis obtained at various computational levels for the FH molecule (aug-cc-pVDZ). The last row indicates in italics the number of Slater determinants in the CIPSI wave functions.

FH	0.95 Å	1.4 Å	1.9 Å
CAS-CI	1.07	1.87	3.20
JM-HeffPT2	1.04	1.70	2.88
Shifted-B_k	1.01	1.47	2.19
CIPSI-proj-CAS	1.05	1.71	2.92
N_{det}	*2 677 789*	*2 545 448*	*2 153 580*

TABLE VI. Excitation energy of the ethylene molecule for the $^1B_{1u}$ singlet state computed in the ANO-L-VDZ basis set.

	ΔE (eV)
CASSCF(2,2)	8.83
JM-MRPT2 (loc)	8.38
JM-MRPT2 (deloc)	8.47
JM-HeffPT2 (loc)	8.42
JM-HeffPT2 (deloc)	8.53
Shifted-B_k (loc)	7.97
Shifted-B_k (deloc)	7.62
FCI-QMC[a]	8.25(1)

[a]Results obtained from Ref. 53.

F. The excited state $^1B_{1u}$ of the ethylene molecule

The excited state of the ethylene molecule $^1B_{1u}$ of singlet spin symmetry has been the subject of intense debates, both from a theoretical and experimental point of views. The excited state $^1B_{1u}$ resulting from the singlet coupling of the single $\pi \rightarrow \pi^*$ excitation has a strong ionic character. Consequently, the electronic correlation effects are much larger in such a state than in the ground state where the neutral forms dominate, explaining the high dependency of the excitation energy to the level of treatment of electronic correlation.[63,64] In order to test the applicability of the JM-MRPT2 method for the computation of excited states, we performed state-specific calculations on both the ground and the singlet $^1B_{1u}$ states and compare it to the near FCI values obtained by Daday *et al.*[53] As $^1B_{1u}$ is the lowest singlet of the B_{1u} symmetry (using the D_{2h} point group), we optimize the orbitals of both the ground and excited states at the CASSCF level using two electrons in the two π and π^* orbitals. We used the ANO-L-VDZ basis set[57] and performed the calculation both with symmetry adapted and localized active orbitals. The results are reported in Table VI. From this table, one can notice that the maximum deviation from the FCI-QMC result is of 0.31(1) eV using JM-HeffPT2 with delocalized orbitals, whereas the minimum deviation of 0.13(1) is obtained with JM-MRPT2 with localized orbitals.

G. Numerical evidence of strong separability

A given method based on the definition of active orbitals is said to be strongly separable when the energy computed for a system composed of two non interacting fragments A $\cdots$ B with active orbitals both on system A and B coincides with the sum of the energies of each sub system computed individually with the corresponding active orbitals on the fragments A and B. The present definitions of JM-MRPT2 and JM-HeffPT2 respect the property of strong separability when localized orbitals are used. A formal proof of the strict separability is given in the Appendix. In order to give a numerical example of the strong separability property, we report in Table VII calculations on F_2 (F–F = 1.45 Å), FH (F–H = 0.90 Å), and on the super-system of $F_2 \cdots$ FH at an intermolecular distance of 100 Å. As the two subsystems are different, the orbitals obtained by the CASSCF method are localized on each system, which is a necessary condition for the strong separability in our formalism. From Table VII, it appears that the deviations on the computed correlated energy $e^{(2)}$-JM-MRPT2 [see Eq. (8)] between the super system with non-interacting fragments and the sum of the two systems is lower than 10^{-13} hartree, which is actually smaller than the non-additivity of the CASSCF energies. For JM-HeffPT2, the relative error remains in the same order of magnitude than that for the CASSCF. This shows that the effective Hamiltonian does not introduce non-separability error. Finally, one should notice the strong non-separability error of the shifted-B_k approach.

VI. CONCLUSIONS AND PERSPECTIVES

A. Summary of the main results

The present work has presented a new MRPT2 approach, the JM-MRPT2 method, that uses individual Slater determinants as perturbers and allows for an intermediate Hamiltonian formulation, which is the JM-HeffPT2 approach. These methods are strictly size-consistent when localized orbitals are used, as has been numerically illustrated here. The link of these two new methods with other existing multi-reference theories has been established, specially in the case of the SC-NEVPT2 level of theory. The accuracy of the methods has been investigated on a series of ground state potential energy curves up to the full dissociation limit for a set of six molecules involving single (F_2, FH, and C_2H_6), double (H_2O, C_2H_4), and triple bond breaking (N_2), using the cc-pVDZ basis set and the aug-cc-pVDZ basis set in the case of FH. The two methods proposed here have been compared to near FCI energies, thanks to large CIPSI calculations converged bellow 0.1 mH, whose values can be found in the supplementary material. The quality of the results has been investigated by means of the non-parallelism error and three spectroscopic constants (R_{eq}, D_0, and k) together with absolute errors with respect to FCI energies along the whole potential energy curves. Among the six molecules studied here, the largest error found on the

TABLE VII. Total energies (a.u.) for the numerical separability check on $F_2 \cdots$ FH.

	CASSCF	Shifted-B_k	$e^{(2)}$-JM-MRPT2	JM-HeffPT2
F_2	−198.746 157 368 569	−199.122 170 300	−0.337 009 510 134 933	−199.085 305 155 169 4
FH	−100.031 754 985 880	−100.289 784 498	−0.230 422 886 638 017	−100.262 424 667 296 7
F_2 + FH	−298.777 912 354 448	−299.411 954 798	−0.567 432 396 772 949	−299.347 729 822 466 0
$F_2 \cdots$ FH	−298.777 912 354 443	−299.396 752 116	−0.567 432 396 773 035	−299.347 729 822 461 6
Absolute error (a.u.)	5.0×10^{-12}	1.5×10^{-2}	8.6×10^{-14}	4.4×10^{-12}
Relative error	1.7×10^{-14}	5.1×10^{-5}	1.5×10^{-13}	1.4×10^{-14}

binding energy at the JM-MRPT2 level of theory is of 6 mH for the FH molecule, representing a deviation lower than 3% with respect to the FCI value. In all other cases, the errors on D_0 are much smaller, ranging from 1.3 mH to 2.5 mH, which represents deviations between 1% and 3% with respect to the FCI estimates. The equilibrium distance is also found to be always within 1% of the FCI values. These results are very encouraging, specially considering the simplicity of this second-order perturbation theory, and its low computational cost. Regarding the JM-HeffPT2 method, its intermediate Hamiltonian formulation allows one to take into account the dominant part of the coupling between the static and dynamic correlation effects. From what has been observed in the present calculations, the diagonalization of the symmetrized intermediate Hamiltonian yields improved CI-coefficients on the reference determinants, together with a very small NPE compared to the shifted-B_k method.

B. Perspectives

Due to its flexibility, the present formalism offers a broad field of perspectives. First, the JM-MRPT2 and JM-HeffPT2 methods can be formalized with a zeroth order wave function that does not need to be a CAS-CI eigenvector. This opens the way of treating much larger active spaces as one can select the dominant configurations of a given CAS-CI space, thanks to the use of a perturbative criterion (as in the CIPSI algorithm) or by using localized orbitals. Second, the reasons of the systematic slight overestimation of the binding energy at the JM-MRPT2 level of theory can also be investigated, taking benefit from localized active orbitals and of the clear reading of the reference wave function that they offer. Moreover, this allows one to use as zeroth-order wave function quasi diabatic states obtained, for instance, by a unitary transformation of a few CI eigenvectors[65] (either of a CAS-CI or from a more general CI). Also, as it has been shown that the present formulation is connected to multi-reference coupled-cluster formalisms, it is possible to derive the working equations starting from the JM-MRCC ansatz. This will allow one to obtain higher order terms which may correct the slight overestimation of the binding energies. The coupling of the present formalism with multi-reference coupled cluster models follows naturally. For instance, the treatment of the most numerous excitation classes at the JM-MRPT2 level can easily be combined with the recently introduced JM-MRCC ansatz of some of the present authors.[66] This will allow for a drastic lowering of the computational costs of the JM-MRCC ansatz, and opens the way to the treatment of larger systems at high level of *ab initio* theory.

SUPPLEMENTARY MATERIAL

See supplementary material for all the near FCI energies obtained with the CIPSI calculations.

ACKNOWLEDGMENTS

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APPENDIX: PROOF OF STRONG SEPARABILITY AND LINK WITH THE MUPA APPROACH

The present appendix provides analytical derivations in order to demonstrate analytically the size consistency property of the JM-MRPT2 and JM-HeffPT2 methods (see part 1), and also to show the link of these two methods with the multi-partitioning of the Hamiltonian (see part 2).

1. Proof of separability

The present section proposes an analytical proof of strong separability of the JM-MRPT2 method. In a MRPT2 framework, the strong separability requires that an excitation T_A located on a system A gives the same contribution to the correlation energy with or without the presence of another system B whose zeroth-order wave function contains correlation effects. To be more specific, let us define the zeroth-order wave function and energy of a system A,

$$|\psi^{(0)A}\rangle = \sum_{\mathrm{I_A}} c_{\mathrm{I_A}} \, |\mathrm{I_A}\rangle \,, \tag{A1}$$

$$E^{(0)A} = \frac{\langle \psi^{(0)A} \, | H_A \, | \psi^{(0)A} \rangle}{\langle \psi^{(0)A} \, | \psi^{(0)A} \rangle}, \tag{A2}$$

and the same quantities for the system B,

$$|\psi^{(0)B}\rangle = \sum_{\mathrm{I_B}} c_{\mathrm{I_B}} \, |\mathrm{I_B}\rangle \,, \tag{A3}$$

$$E^{(0)B} = \frac{\langle \psi^{(0)B} | H_B | \psi^{(0)B} \rangle}{\langle \psi^{(0)B} \, | \psi^{(0)B} \rangle}. \tag{A4}$$

Let us consider now a given excitation T_A acting only on a system A. According to the definition of Eq. (14), the corresponding contribution to the first-order perturbed wave function is

$$|\psi^{(1)A}_{T_A}\rangle = \frac{1}{\Delta E^{(0)A}_{T_A}} \; |\tilde{\psi}^{(1)A}_{T_A}\rangle \,, \tag{A5}$$

$$|\tilde{\psi}^{(1)A}_{T_A}\rangle = \sum_{\mathrm{I_A}} \mathrm{c_{I_A}} \; \langle \mathrm{I_A} \, | H_A \; T_A \, | \mathrm{I_A} \rangle \; T_A \, | \mathrm{I_A} \rangle \,, \tag{A6}$$

and the excitation energy $\Delta E^{(0)A}_{T_A}$ characteristic of the excitation T_A is defined according to Eq. (17) as

$$\Delta E^{(0)A}_{T_A} = E^{(0)A} - \frac{\langle \tilde{\psi}^{(1)A}_{T_A} | H_A \, | \tilde{\psi}^{(1)A}_{T_A} \rangle}{\langle \tilde{\psi}^{(1)A}_{T_A} | \tilde{\psi}^{(1)A}_{T_A} \rangle}. \tag{A7}$$

Therefore, its contribution to the correlation energy of A is

$$e^{(2)A}_{T_A} = \langle \psi^{(0)A} | H | \psi^{(1)A}_{T_A} \rangle = \frac{\langle \psi^{(0)A} | H_A \, | \tilde{\psi}^{(1)A}_{T_A} \rangle}{\Delta E^{(0)A}_{T_A}}. \tag{A8}$$

A necessary and sufficient mathematical condition for the strong separability property of the energy is that a given excitation process T_A involving only the orbitals of the system A gives the same contribution to the energy when it is considered on the sole system A or on the super non interacting system $A \cdots B$. To reach such a condition, one first needs that the zeroth-order wave function be the product of the zeroth-order wave function of the two sub-systems A and B,

$$|\psi^{(0)A+B}\rangle = |\psi^{(0)A}\rangle \otimes |\psi^{(0)B}\rangle \,, \tag{A9}$$

which ensures that its corresponding zeroth-order energy is the sum of zeroth-order energies of the sub-systems A and B,

$$\begin{aligned} E^{(0)A+B} &= \frac{\langle \psi^{(0)A+B}|H_A + H_B|\psi^{(0)A+B}\rangle}{\langle \psi^{(0)A+B}|\psi^{(0)A+B}\rangle} \\ &= \frac{\langle \psi^{(0)A}|H_A|\psi^{(0)A}\rangle \langle \psi^{(0)B}|\psi^{(0)B}\rangle}{\langle \psi^{(0)A}|\psi^{(0)A}\rangle \langle \psi^{(0)B}|\psi^{(0)B}\rangle} \\ &\quad + \frac{\langle \psi^{(0)B}|H_B|\psi^{(0)B}\rangle \langle \psi^{(0)A}|\psi^{(0)A}\rangle}{\langle \psi^{(0)B}|\psi^{(0)B}\rangle \langle \psi^{(0)A}|\psi^{(0)A}\rangle} \\ &= E^{(0)A} + E^{(0)B}, \end{aligned} \tag{A10}$$

as the total Hamiltonian can be written as the sum of H_A acting only on the orbitals of A and the corresponding H_B acting only on the orbitals of B. A CAS-CI wave function respects of course the property of the additivity of the energy.

Starting from $|\psi^{(0)A+B}\rangle$, one can generate the contribution to the first-order perturbed wave function $|\psi^{(1)A}_{T_A}\rangle$ associated with T_A in the super-system $A\cdots B$,

$$|\psi^{(1)A+B}_{T_A}\rangle = \frac{1}{\Delta E^{(0)A+B}_{T_A}} \; |\tilde{\psi}^{(1)A+B}_{T_A}\rangle, \tag{A11}$$

$$\begin{aligned} |\tilde{\psi}^{(1)A+B}_{T_A}\rangle &= \sum_{\mathrm{I_A}\,\mathrm{I_B}} c_{\mathrm{I_A}} c_{\mathrm{I_B}} \; T_A \; |\mathrm{I_B}\rangle \otimes |\mathrm{I_A}\rangle \\ &\quad \langle \mathrm{I_A}| \otimes \langle \mathrm{I_B}| (H_A + H_B) \; T_A \, |\mathrm{I_B}\rangle \otimes |\mathrm{I_A}\rangle, \end{aligned} \tag{A12}$$

with the following excitation energy $\Delta E^{(0)A+B}_{T_A}$:

$$\Delta E^{(0)A+B}_{T_A} = E^{(0)A+B} - \frac{\langle \tilde{\psi}^{(1)A+B}_{T_A}|H_A + H_B|\tilde{\psi}^{(1)A+B}_{T_A}\rangle}{\langle \tilde{\psi}^{(1)A+B}_{T_A}|\tilde{\psi}^{(1)A+B}_{T_A}\rangle}. \tag{A13}$$

Then, the contribution of T_A to the correlation energy of the super system $A\cdots B$ is simply

$$e^{(2)A+B}_{T_A} = \frac{\langle \psi^{(0)A+B}|H_A + H_B|\tilde{\psi}^{(1)A+B}_{T_A}\rangle}{\Delta E^{(0)A+B}_{T_A}}. \tag{A14}$$

One can then notice that as T_A only acts on the orbitals of A, one has

$$\langle \mathrm{I_A}| \otimes \langle \mathrm{J_B}| (H_A + H_B) \; T_A |\mathrm{J_B}\rangle \otimes |\mathrm{I_A}\rangle = \langle \mathrm{J_B}|\mathrm{J_B}\rangle \langle \mathrm{I_A}| H_A \; T_A |\mathrm{I_A}\rangle, \tag{A15}$$

and consequently the zeroth-order wave function of system B can be factorized in Eq. (A12)

$$\begin{aligned} |\tilde{\psi}^{(1)A+B}_{T_A}\rangle &= \sum_{\mathrm{I_B}} c_{\mathrm{I_B}} |\mathrm{I_B}\rangle \otimes \sum_{\mathrm{I_A}} c_{\mathrm{I_A}} \langle \mathrm{I_A}| H_A \; T_A |\mathrm{I_A}\rangle \; T_A \; |\mathrm{I_A}\rangle \\ &= |\psi^{(0)B}\rangle \otimes |\tilde{\psi}^{(1)A}_{T_A}\rangle. \end{aligned} \tag{A16}$$

This form for $|\tilde{\psi}^{(1)A+B}_{T_A}\rangle$ is crucial, as it has a product structure, implying that it will not suffer from any size consistency and separability issues. Indeed, the numerator of Eq. (A14) simply reduces to

$$\langle \psi^{(0)A+B}|H_A + H_B|\tilde{\psi}^{(1)A+B}_{T_A}\rangle = \langle \psi^{(0)A}|H_A|\tilde{\psi}^{(1)A}_{T_A}\rangle, \tag{A17}$$

and the denominator of the same Eq. (A14) is then

$$\begin{aligned} \Delta E^{(0)A+B}_{T_A} &= E^{(0)A+B} - \frac{\langle \tilde{\psi}^{(1)A}_{T_A}|H_A|\tilde{\psi}^{(1)A}_{T_A}\rangle}{\langle \tilde{\psi}^{(1)A}_{T_A}|\tilde{\psi}^{(1)A}_{T_A}\rangle} - E^{(0)B} \\ &= E^{(0)A} - \frac{\langle \tilde{\psi}^{(1)A}_{T_A}|H_A|\tilde{\psi}^{(1)A}_{T_A}\rangle}{\langle \tilde{\psi}^{(1)A}_{T_A}|\tilde{\psi}^{(1)A}_{T_A}\rangle} \\ &= \Delta E^{(0)A}_{T_A}, \end{aligned} \tag{A18}$$

and therefore,

$$e^{(2)A+B}_{T_A} = e^{(2)A}_{T_A}. \tag{A19}$$

Consequently, the JM-MRPT2 is strictly separable provided that a partition of the Hamiltonian in terms of H_A and H_B can be done, which supposes local orbitals.

2. Multi-partitioning of the Hamiltonian

In contrast with the CIPSI or shifted-B_k approaches, a given perturber determinant $|\mu\rangle$ has as much zeroth-order energies as reference determinants $|\mathrm{I}\rangle$ with which it interacts (i.e., $\langle \mu|H|\mathrm{I}\rangle \neq 0$) within the JM-MRPT2 framework. This formally implies that the zeroth-order Hamiltonian depends on the reference determinant $|\mathrm{I}\rangle$, just as in the MUPA approach. The present paragraph proposes to briefly highlight the link existing between these two approaches.

Using the JM ansatz for the wave function [see Eq. (53)] and projecting the Schrödinger equation onto a given perturber $|\mu\rangle$ lead to

$$\sum_{\mathrm{I}} c_{\mathrm{I}} \left(\langle \mu|H|\mathrm{I}\rangle + \sum_{\mu'} \langle \mu|H|\mu'\rangle \, t_{\mathrm{I}\mu'} \right) + \mathcal{R} = E \sum_{\mathrm{I}} c_{\mathrm{I}} t_{\mathrm{I}\mu}, \tag{A20}$$

where $\mathcal{R}$ contains all terms in the coupled cluster equation containing higher or equal powers of T_{I} than $(T_{\mathrm{I}})^2$. Retaining all terms of first order in $t_{\mathrm{I}\mu'}$ in Eq. (A20) leads to the equations of linearized coupled cluster type

$$\sum_{\mathrm{I}} c_{\mathrm{I}} \left(\langle \mu|H|\mathrm{I}\rangle + \sum_{\mu'} \langle \mu|H|\mu'\rangle \, t_{\mathrm{I}\mu'} \right) = e^{(0)} \sum_{\mathrm{I}} c_{\mathrm{I}} t_{\mathrm{I}\mu}, \tag{A21}$$

which can be written as

$$\sum_{\mathrm{I}} c_{\mathrm{I}} \left(\langle \mu|H|\mathrm{I}\rangle + \sum_{\mu'} \langle \mu|H|\mu'\rangle \, t_{\mathrm{I}\mu'} - e^{(0)} t_{\mathrm{I}\mu} \right) = 0. \tag{A22}$$

Just as in the spirit of the UGA-SSMPRT2 of Mukherjee *et al.*, Eq. (A22) is solved independently for all references $|\mathrm{I}\rangle$, leading to

$$\langle \mu|H|\mathrm{I}\rangle + t_{\mathrm{I}\mu} \langle \mu|H|\mu\rangle + \sum_{\mu'\neq\mu} \langle \mu|H|\mu'\rangle \, t_{\mathrm{I}\mu'} = e^{(0)} t_{\mathrm{I}\mu}. \tag{A23}$$

As each equation is solved independently, one can use a different partitioning of the Hamiltonian according to the reference determinants $|\mathrm{I}\rangle$,

$$\begin{aligned} H &= H^{(0)}_{\mathrm{I}} + \lambda V_{\mathrm{I}}, \\ H^{(0)}_{\mathrm{I}} &= e^{(0)} |\mathrm{I}\rangle\langle \mathrm{I}| + \sum_{\mu} e^{(0)}_{\mathrm{I}\mu} |\mu\rangle\langle \mu|. \end{aligned} \tag{A24}$$

In Eq. (A24), retaining all terms at first order in λ leads to

$$\langle \mu|V_{\mathrm{I}}|\mathrm{I}\rangle + t^{(1)}_{\mathrm{I}\mu} \langle \mu|H^{(0)}_{\mathrm{I}}|\mu\rangle + \sum_{\mu'\neq\mu} \langle \mu|H^{(0)}_{\mathrm{I}}|\mu'\rangle \, t^{(1)}_{\mathrm{I}\mu'} = e^{(0)} t^{(1)}_{\mathrm{I}\mu}. \tag{A25}$$

By defining the zeroth-order energies $e^{(0)}_{\mathrm{I}\mu}$ as

$$e^{(0)}_{\mathrm{I}\mu} = \frac{\langle \tilde{\psi}^{(1)}_{T_{\mathrm{I}\mu}} | H^D | \tilde{\psi}^{(1)}_{T_{\mathrm{I}\mu}} \rangle}{\langle \tilde{\psi}^{(1)}_{T_{\mathrm{I}\mu}} | \tilde{\psi}^{(1)}_{T_{\mathrm{I}\mu}} \rangle}, \tag{A26}$$

where $|\tilde{\psi}^{(1)}_{T_{\mathrm{I}\mu}}\rangle$ is defined in Eq. (15) with the excitation operator $T_{\mathrm{I}\mu}$ which connects $|\mathrm{I}\rangle$ and $|\mu\rangle$ [see Eq. (6)], one can recover the expression of the amplitudes used in the JM-MRPT2 approach

$$t^{(1)}_{\mathrm{I}\mu} = \frac{\langle \mu | H | \mathrm{I} \rangle}{e^{(0)} - e^{(0)}_{\mathrm{I}\mu}}. \tag{A27}$$

Also, one can notice that the zeroth-order energies of the MUPA and JM-MRPT2 methods coincide for the 2h2p but also for the 1h2p and 2h1p. Indeed, the energy denominators appearing in the two latter classes imply the generalization of ionization potential [see Eq. (43)] and electronic affinities whose definition is identical in the MUPA and JM-MRPT2 methods. Therefore, in the case of the double excitations amplitudes, one can see the JM-MRPT2 method as the generalization of the MUPA method to all possible operations appearing in the active space for the definition of energy denominators.

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