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# Multiconfiguration perturbation theory: Size consistency at second order

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A modified version of a previously elaborated multiconfiguration perturbation theory (MCPT) [Rolik *et al.* J. Chem. Phys. **119**, 1922 (2003)] is presented. In the modified formulation size consistency is ensured at second order in energy, by omitting projectors from the zero order Hamiltonian operator. This MCPT formulation is abbreviated as SC2-MCPT (size consistent at second order). To ensure proper separability, we also require that energy denominators are constructed as differences of some one-particle energies. A similar choice for energy denominators also renders the well-known multireference Møller–Plesset (MRMP) energy size consistent at second order. The same thing applies to the related multireference perturbation theory by Witek, Nakano, and Hirao. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1862235]

## I. INTRODUCTION

Description of molecules at a wide range of atomic configurations, including stretched or dissociating bonds, continues to be a challenge for theory. To account for electron correlation all over the molecular potential surface in a well balanced manner, it is necessary to use multiconfiguration (MC) wave functions, built of several Slater determinants. A usual way to get such a wave function is to select a subspace of one-electron orbitals, called the active space, and determine a reference state containing excitations within the active space. Due to the unadvantageous scaling with increasing number of active orbitals and/or electrons of these procedures, there is no way to describe electron correlation with sufficient accuracy based on solely approaches like this.

Still, a MC function corresponding to a relatively small active space can describe the molecular potential surface qualitatively correctly and represents a good starting point for other, cheaper methods that can account for dynamical correlation, such as configuration interaction, coupled cluster, or perturbation theory (PT).

One of the simplest of the above families of methods is PT, which has the advantage over CI that possible size-consistent character of the reference MC function is not necessarily destroyed. Since it is not as straightforward to develop a PT treatment for a MC function, as it is for one single determinant, numerous formulations of multireference PT (MRPT) schemes have been elaborated. An important aspect of orientation among MRPT methodologies is whether or not PT corrections are obtained from the eigenvalue problem of an effective Hamiltonian operator. The so called "perturb then diagonalize" approaches fall into the former category, such as works by Robb and co-workers,[1] Freed and co-workers,[2] Nakano,[3] Davidson,[4] Malrieu and co-workers,[5] works by Mukherjee and co-workers,[6–9] Finley,[10] Angeli *et al.*,[11] and others. Examples for schemes operating without an effective operator are several studies by Davidson,[12–14] PT formulations worked out by Wolinski and co-workers,[15] Murphy and Messmer,[16] the complete active space PT (CASPT) methodology by Roos and co-workers,[17] studies by Werner,[18] Dyall,[19] Mitrushenkov,[20] the MRMP methodology of Hirao and co-workers,[21] works by Rosta and Surján,[22] Rassolov *et al.*,[23] the PT framework of Angeli *et al.*[24] and several others. Recently yet another MRPT scheme falling into the latter category has been proposed in our laboratory that was termed multiconfiguration perturbation theory, abbreviated as MCPT.[25]

The essence of MCPT is that perturbative corrections can be derived to an arbitrary reference (zero order) function, through the definition of virtual excited states. This way, no special character of the reference function is required; it does not have to be a CAS function, for instance. At the same time, the formulation of the theory remains simple; one does not need to apply a numerical orthogonalization procedure neither solve a linear system of equations to get the corrections. One more noteworthy feature of this scheme is the presence of free parameters that can tune the zero order operator. In other words, the partitioning in MCPT is not fixed *a priori*.[25–27] It is therefore rather a framework than one definite method that becomes well specified at the moment where free parameters—zero order excited state energies—get fixed.

There are some common difficulties that most MRPT formulations are faced with; the fulfillment of the criterion of size-consistency is one of such. Even though Rayleigh–Schrödinger perturbation theory may give size-consistent corrections at every finite order,[28] an unfortunate specification of the zero order Hamiltonian may destroy this behavior. This is the case with MRPT formulations that use projectors to define the zero order Hamiltonian.[16,18,29] The size-consistency issue of such MRPT methods has been discussed in more detail by Van Lenthe and co-workers,[30] pointing that the use of projectors in $\hat{H}^0$ need not necessarily violate size consistency. Initiated by their numerical experiences, Pulay and co-workers arrived to design a zero order Hamiltonian operator—through the application of projectors which correspond to excited subspaces sufficiently separated—that proved to give size-consistent results even if dissociating a system for open-shell fragments.[31] Complete elimination of projection operators from the zero order Hamiltonian does not solve the problem in itself, see, e.g., theories.[12,20] On the other hand, careful selection of the zero order quantities can result in a size-consistent theory, such as that of Rosta and Surján,[22] Rassolov,[23] or Angeli *et al.*[24] The approaches of Heully *et al.*[32] and Mukherjee and co-workers[33] also arrive to size-consistent PT corrections via well designed effective Hamiltonian operators.

Our recent MCPT formulation[25] has been shown to be slightly size inconsistent. In this study we present a reformulation of MCPT theory, so that size consistency of the initial function and energy is conserved at the first nonvanishing order. Energy corrections from third order on and wave function corrections from second order on remain consistency violating. This version of the theory will be referred to as SC2-MCPT.

We also show that by a careful selection of zero order excited energies, a similar situation can be achieved in the MRPT theory of Witek *et al.*[34] and in the closely related MRMP method of Hirao.[21]

## II. THEORY

### A. Multiconfiguration PT

According to the multiconfiguration perturbation theory described in Ref. 25, one starts with a function $|0\rangle$ that can be written as a weighted sum of a principal determinant $|\mathrm{HF}\rangle$ and several other Slater determinants $|k\rangle$:

$$|0\rangle = d_{\mathrm{HF}}|\mathrm{HF}\rangle + \sum_{k\neq \mathrm{HF}} d_k|k\rangle,$$

where the case $d_{\mathrm{HF}}=0$ is to be excluded.

In the spirit of perturbation theory, we consider $|0\rangle$ as the zero order ground state function and seek for perturbation corrections to it. For this end we define a formal zero order Hamiltonian

$$\hat{H}^0 = E_0|0\rangle\langle 0| + \sum_{k\neq \mathrm{HF}} E_k|k'\rangle\langle\tilde{k}'|, \tag{1}$$

where $\{|k'\rangle | k\neq \mathrm{HF}\}$ is an overlapping set of excited determinants from which the ground state $|0\rangle$ has been projected out:

$$|k'\rangle = \hat{P}|k\rangle = |k\rangle - d_k|0\rangle,$$

the projector $\hat{P}$ being

$$\hat{P} = 1 - |0\rangle\langle 0|.$$

The metric matrix of the projected excited determinants is

$$S_{k'l'} = \langle k|\hat{P}|l\rangle = \delta_{kl} - d_k d_l, \tag{2}$$

and vectors $\langle\tilde{k}'|$ are biorthogonal to $\{|k'\rangle | k\neq \mathrm{HF}\}$:

$$\langle\tilde{k}'| = \sum_{l\neq \mathrm{HF}} S^{-1}_{k'l'}\langle l'| = \langle k'| + \sum_{l\neq \mathrm{HF}} \frac{d_k d_l}{d_{\mathrm{HF}}^2}\langle l'| = \langle k| - \frac{d_k}{d_{\mathrm{HF}}}\langle \mathrm{HF}|. \tag{3}$$

We used the shorthand $S^{-1}_{k'l'}$ to denote the elements of the inverse of the metric matrix (2). This inverse can be given analytically due to the simple structure of $S_{k'l'}$. Tildes are used to denote reciprocal (biorthogonal) vectors throughout this work.

The zero order ground state energy is most practically chosen as $E_0=\langle 0|\hat{H}|0\rangle$, while the zero order excited energies $E_k$-s are parameters of the theory.

The perturbation operator is defined as

$$\hat{W} = \hat{H} - \hat{H}^0$$

and the second order PT correction looks:

$$E^2 = -\sum_{k\neq \mathrm{HF}} \frac{\langle 0|\hat{H}|k'\rangle\langle\tilde{k}'|\hat{H}|0\rangle}{E_k - E_0}. \tag{4}$$

The MCPT framework as detailed here is inherently size inconsistent. The main source of size inconsistency is the appearance of projector $\hat{P}$ in the zero order operator (1) that induces a coupling in $\hat{H}^0$ between noninteracting subsystems, similar to the problem encountered in the CASPT scheme.[29]

### B. Reformulation of MCPT: SC2-MCPT

In order to diminish consistency violation of the MCPT framework one needs to redefine the zero order Hamiltonian so that projector $\hat{P}$ is excluded. To reach this goal, let us use unprojected Slater determinants $|k\rangle$ instead of $|k'\rangle$ in $\hat{H}^0$:

$$\hat{H}^0_{\mathrm{SC2}} = E_0|0\rangle\langle\tilde{0}| + \sum_{k\neq \mathrm{HF}} E_k|k\rangle\langle\tilde{k}|. \tag{5}$$

Vectors $\langle\tilde{0}|$ and $\langle\tilde{k}|$ now stand for the reciprocal (biorthogonal) vectors of the overlapping set $\{|0\rangle\}\cup\{|k\rangle | k\neq \mathrm{HF}\}$. To construct the tilded vectors, let us build the metric matrix of the overlapping set:

$$S_{kl} = \delta_{kl} + d_k\delta_{l0}(1-\delta_{k0}) + d_l\delta_{k0}(1-\delta_{l0}). \tag{6}$$

(Case $k=0$ designates the multiconfiguration reference state $|0\rangle$.) The inverse of metric (6) can be expressed by the closed formula

$$S^{-1}_{kl} = \delta_{kl} - \delta_{k0}\delta_{l0} + e_k e_l, \tag{7}$$

with $e_0=d^{-1}_{\mathrm{HF}}$, $e_i=-d_i d^{-1}_{\mathrm{HF}}$ for $i\neq 0$, and $S^{-1}_{kl}$ being a shorthand for the elements of the inverse of the metric matrix (6). Inverse (7) results the reciprocal vectors

$$\langle\tilde{0}| = \frac{1}{d_{\mathrm{HF}}}\langle \mathrm{HF}|$$

and

$$\langle\tilde{k}| = \langle k| - \frac{d_k}{d_{\mathrm{HF}}}\langle \mathrm{HF}|.$$

It is interesting to compare the direct and reciprocal expansion states of MCPT and SC2-MCPT (see Table I). We see that bra excited vectors turn out to be the same in both formalisms. Thus, there is a difference in the ground state between the bra vectors, while the set of zero order ket vectors agree only in the ground state between the two versions.

The zero order ground state energy in this scheme is most practically taken as

TABLE I. Comparison of bra and ket expansion vectors used to construct $\hat{H}^0$ in MCPT and SC2-MCPT scheme. Slater determinants different from the Fermi vacuum are denoted by $k$. Number 0 stands for the multiconfigurational reference.

| | ket vectors | | bra vectors | |
|---|---|---|---|---|
| | Ground state | Excited states | Ground state | Excited states |
| MCPT | $\lvert 0\rangle$ | $\lvert k\rangle - d_k\lvert 0\rangle$ | $\langle 0\rvert$ | $\langle k\rvert - \frac{d_k}{d_{\mathrm{HF}}}\langle \mathrm{HF}\rvert$ |
| SC2-MCPT | $\lvert 0\rangle$ | $\lvert k\rangle$ | $\frac{1}{d_{\mathrm{HF}}}\langle \mathrm{HF}\rvert$ | $\langle k\rvert - \frac{d_k}{d_{\mathrm{HF}}}\langle \mathrm{HF}\rvert$ |

$$E_0 = \langle \tilde{0}|\hat{H}|0\rangle,$$

so that $E^1$ vanishes. The zero order excited energies $E_k$-s are still free parameters.

The reduced resolvent corresponding to the zero order Hamiltonian (5) is diagonal in the biorthogonal formulation:

$$\hat{Q}_{\mathrm{SC2}} = \sum_{k\neq \mathrm{HF}} \frac{|k\rangle\langle \tilde{k}|}{E_k - E_0}.$$

Corrections to $|0\rangle$ and $E_0$ in the SC2 variant of MCPT are straightforward to construct according to standard biorthogonal perturbation theory:

$$\langle \Psi^1_{\mathrm{SC2}}| = -\sum_{k\neq \mathrm{HF}} \frac{\langle \tilde{0}|\hat{H}|k\rangle}{E_k - E_0}\langle \tilde{k}|,$$

$$E^2_{\mathrm{SC2}} = -\sum_{k\neq \mathrm{HF}} \frac{\langle \tilde{0}|\hat{H}|k\rangle\langle \tilde{k}|\hat{H}|0\rangle}{E_k - E_0}, \tag{8}$$

etc.

Comparison of the second order formula Eq. (4) and Eq. (8) reveals that the latter is computationally cheaper than the former, since a sum for excited configurations is present in $\langle 0|$ not like in $\langle \tilde{0}|$. This might also give a warning that formula (8) may yield smaller corrections than Eq. (4)—this however is not found in our numerical tests presented in Sec. III.

A common property of both SC2-MCPT and MCPT is the noninvariance with respect to the choice of the Fermi vacuum $|\mathrm{HF}\rangle$. In cases where there is a dominant determinant in $|0\rangle$ it is natural to pick this as $|\mathrm{HF}\rangle$. If two or more determinants have (nearly) equal weight in $|0\rangle$ the choice is more arbitrary.

### C. Consistency at second order

In order to discuss size consistency, let us consider two systems $A$ and $B$ with no interaction in between:

$$\hat{H}_{AB} = \hat{H}_A\hat{I}_B + \hat{I}_A\hat{H}_B,$$

where $\hat{I}_A$ and $\hat{I}_B$ stand for the unit operator in the Hilbert space corresponding to system $A$ and $B$, respectively. Size consistency, as used by Pople,[35] requires additive separability of the energy over noninteracting partners,

$$E_{AB} = E_A + E_B,$$

while the wave function has to be multiplicatively separable:

$$\Psi_{AB} = \Psi_A\Psi_B.$$

It has been shown[28,30] that any finite order PT correction to the energy is size consistent, provided that the zero order operator is additive over independent subsystems, i.e.,

$$\hat{H}^0_{AB} = \hat{H}^0_A\hat{I}_B + \hat{I}_A\hat{H}^0_B. \tag{9}$$

In terms of zero order quantities, this requires additivity of zero order eigenvalues and multiplicative separability of zero order wave functions. (In the following discussion we will consider unit operators $\hat{I}_A$ and $\hat{I}_B$ as self-understood, and omit them to simplify formula.)

To examine the consistent or inconsistent nature of the SC2 variant of MCPT, let us look first at the zero order quantities for the joint system $AB$. We suppose that the reference function is product separable:

$$|0\rangle = |0_A0_B\rangle$$

just like its reciprocal vector

$$\langle \tilde{0}| = \frac{\langle \mathrm{HF}_A\mathrm{HF}_B|}{d_{\mathrm{HF}_A}d_{\mathrm{HF}_B}} = \langle \tilde{0}_A\tilde{0}_B|$$

giving rise to the additively separable zero order ground state energy

$$E_{0,AB} = \langle \tilde{0}_A\tilde{0}_B|\hat{H}_A + \hat{H}_B|0_A0_B\rangle = E_{0,A} + E_{0,B}.$$

Zero order excited state ket vectors are excited determinants, where the excitation may take place on one system, or the other, or both: $|\mathrm{HF}_Ak_B\rangle$, or $|k_A\mathrm{HF}_B\rangle$, or $|k_Al_B\rangle$. Unfortunately neither $|\mathrm{HF}_Ak_B\rangle$ nor $|k_A\mathrm{HF}_B\rangle$ is a product of a zero order vector on system $A$ and another on system $B$, since the vector $|\mathrm{HF}\rangle$ is not contained in the expansion set [cf. Eq. (5) and Table I]. This has unfavorable consequences on the consistency property of the energy from third order on.

Looking at zero order excited bra vectors, one finds:

$$\langle \widetilde{\mathrm{HF}_Ak_B}| = \langle \mathrm{HF}_Ak_B| - \frac{d_{k_B}}{d_{\mathrm{HF}_B}}\langle \mathrm{HF}_A\mathrm{HF}_B| = \langle \mathrm{HF}_A\tilde{k}_B|$$

similarly

$$\langle \widetilde{k_A\mathrm{HF}_B}| = \langle \tilde{k}_A\mathrm{HF}_B|$$

and

$$\langle \widetilde{k_Al_B}| = \langle k_Al_B| - \frac{d_{k_A}d_{l_B}}{d_{\mathrm{HF}_A}d_{\mathrm{HF}_B}}\langle \mathrm{HF}_A\mathrm{HF}_B| \neq \langle \tilde{k}_A\tilde{l}_B|.$$

Apart from the constant $d_{\mathrm{HF}_A}$, $\langle \widetilde{\mathrm{HF}_Ak_B}|$ is the product of zero order functions $\langle \tilde{0}_A|$ and $\langle \tilde{k}_B|$, which is desirable. However, this is not the case for $\langle \widetilde{k_Al_B}|$.

Zero order excited energies are considered in the form

$$E_k = E_0 + \Delta_k, \tag{10}$$

with $\Delta_k$ being constructed of one-particle energies that characterize the excitation taking from $|\mathrm{HF}\rangle$ to $|k\rangle$. By this

Møller–Plesset (MP) type construction one can avoid emergence of a coupling between independent subsystems in the energy denominators, since excited state energies then look:

$$E_{\mathrm{HF}_A k_B} = E_0 + \Delta_{k_B},$$

$$E_{k_A \mathrm{HF}_B} = E_0 + \Delta_{k_A},$$

and

$$E_{k_A l_B} = E_0 + \Delta_{k_A} + \Delta_{l_B}.$$

Using the above zero order functions and energies it is easy to see that the zero order Hamiltonian (5) is not additive over subsystems $A$ and $B$. Full size consistency of the SC2-MCPT scheme therefore cannot be expected. Still, we shall show that first nonvanishing corrections behave correctly. Let us start with the first order wave function:

$$\langle \Psi^1_{AB} | = - \sum_{k \neq \mathrm{HF}} \frac{\langle \widetilde{0_A} \widetilde{0_B} | \hat{H}_A + \hat{H}_B | k_A \mathrm{HF}_B \rangle}{\Delta_{k_A}} \langle \widetilde{k_A} \mathrm{HF}_B | + \{A \leftrightarrow B\}.$$

(Note that the contribution of $|k_A l_B\rangle$ is zero at this order.) Since $\langle \widetilde{0_A} | k_A \rangle = 0$, this formula simplifies to:

$$\langle \Psi^1_{AB} | = - \sum_{k \neq \mathrm{HF}} \frac{\langle \widetilde{0_A} | \hat{H}_A | k_A \rangle \langle \widetilde{0_B} | \mathrm{HF}_B \rangle}{\Delta_{k_A}} \langle \widetilde{k_A} \mathrm{HF}_B | + \{A \leftrightarrow B\}.$$

Integral $\langle \widetilde{0_B} | \mathrm{HF}_B \rangle$ gives $d^{-1}_{\mathrm{HF}_B}$, leading to:

$$\langle \Psi^1_{AB} | = - \sum_{k \neq \mathrm{HF}} \frac{\langle \widetilde{0_A} | \hat{H}_A | k_A \rangle}{\Delta_{k_A}} \langle \widetilde{k_A} \widetilde{0_B} | + \{A \leftrightarrow B\}.$$

The first order wave function therefore can be written as

$$\langle \Psi^1_{AB} | = \langle \Psi^1_A \widetilde{0_B} | + \langle \widetilde{0_A} \Psi^1_B |,$$

that is just the behavior required. (Note that this does not mean product separability of $\langle \Psi^1_{AB} |$.)

Looking at the second order energy

$$E^2_{AB} = \langle \Psi^1_A \widetilde{0_B} | \hat{H}_A + \hat{H}_A | 0_A 0_B \rangle + \{A \leftrightarrow B\}$$

and using the fact that $\langle \widetilde{k_A} | 0_A \rangle = 0$ for all $k \neq \mathrm{HF}$, one gets

$$E^2_{AB} = \langle \Psi^1_A | \hat{H}_A | 0_A \rangle \langle \widetilde{0_B} | 0_B \rangle + \{A \leftrightarrow B\},$$

that is

$$E^2_{AB} = E^2_A + E^2_B, \tag{11}$$

since $\langle \widetilde{0_B} | 0_B \rangle = 1$. This proves size consistency of the second order energy correction.

It is easy to check that the first order wave function correction written as a ket vector is already ill behaved from the point of view of size consistency. This is due to that determinant $|k_A l_B\rangle$ shows up in $|\Psi^1\rangle$ with the corresponding energy denominator $\Delta_{k_A} + \Delta_{l_B}$ that couples systems $A$ and $B$. Still, the second order energy as derived from $|\Psi^1\rangle$ matches Eq. (11):

$$\langle \Psi^1 | \hat{H} | 0 \rangle = \langle \tilde{0} | \hat{H} | \Psi^1 \rangle.$$

### D. Consistency violation at higher orders

Stepping to the next nonvanishing order, one recovers the unadvantageous consequence of the fact that certain zero order vectors are products of not exactly those vectors that would be needed. Inspecting the third order energy one gets:

$$E^3_{AB} = \sum_{k,l \neq \mathrm{HF}} \frac{\langle \widetilde{0_A} \widetilde{0_B} | \hat{H}_{AB} | k_A \mathrm{HF}_B \rangle \langle \widetilde{k_A} \mathrm{HF}_B | \hat{W}_{AB} | l_A \mathrm{HF}_B \rangle \langle \tilde{l}_A \mathrm{HF}_B | \hat{H}_{AB} | 0_A 0_B \rangle}{\Delta_{k_A} \Delta_{l_A}} \tag{12}$$

$$+ \sum_{k,l \neq \mathrm{HF}} \frac{\langle \widetilde{0_A} \widetilde{0_B} | \hat{H}_{AB} | k_A \mathrm{HF}_B \rangle \langle \widetilde{k_A} \mathrm{HF}_B | \hat{W}_{AB} | HF_A l_B \rangle \langle \mathrm{HF}_A \tilde{l}_B | \hat{H}_{AB} | 0_A 0_B \rangle}{\Delta_{k_A} \Delta_{l_B}} + \{A \leftrightarrow B\} \tag{13}$$

with $\hat{W}_{AB} = \hat{H}_A + \hat{H}_B - \hat{H}^0_{AB}$ .

Let us analyze the second bracket in the numerators of terms (12) and (13). Since both $|l_A \mathrm{HF}_B\rangle$ and $\langle \widetilde{k_A} \mathrm{HF}_B |$ are eigenvectors of the zero order Hamiltonian $\hat{H}^0_{AB}$, for term (12) we get

$$\langle \widetilde{k_A} \mathrm{HF}_B | \hat{W}_{AB} | l_A \mathrm{HF}_B \rangle = \langle \widetilde{k_A} | \hat{H}_A | l_A \rangle + \delta_{kl} ( \langle \mathrm{HF}_B | \hat{H}_B | \mathrm{HF}_B \rangle - \Delta_{k_A} - E_{0,A} - E_{0,B} ). \tag{14}$$

In the second bracket of Eq. (13) $\hat{H}_A$ and $\hat{H}^0_{AB}$ has zero contribution, as $\langle \mathrm{HF}_B | l_B \rangle = 0$ and $\langle \widetilde{k_A} \mathrm{HF}_B | \mathrm{HF}_A l_B \rangle = 0$, but $\hat{H}_B$ results the nonvanishing integral

$$\langle \widetilde{k_A} \mathrm{HF}_B | \hat{W}_{AB} | \mathrm{HF}_A l_B \rangle = \langle \widetilde{k_A} | \mathrm{HF}_A \rangle \langle \mathrm{HF}_B | \hat{H}_B | l_B \rangle. \tag{15}$$

The points where consistency is violated are apparent in formulas (14) and (15). First, $\langle \mathrm{HF}_B | \hat{H}_B | \mathrm{HF}_B \rangle$ does not cancel $E_{0,B}$ on the right-hand side (rhs) of Eq. (14), which would be necessary. Second, the integral $\langle \widetilde{k_A} \mathrm{HF}_B | \hat{W}_{AB} | \mathrm{HF}_A l_B \rangle$ establishes a coupling between independent zero order excited vectors $\langle \widetilde{k_A} \mathrm{HF}_B |$ and $|\mathrm{HF}_A l_B\rangle$, which is not allowed.

Let us note that both problems would disappear if internally contracted excitations were used for zero-order excited functions, just like in the CASPT2 scheme.[29] In this case however, the metric matrix would become too complicated to invert analytically.

It is further interesting to mention that redefining $E_0 = \langle \mathrm{HF}|\hat{H}|\mathrm{HF}\rangle$ does not solve the problem of Eq. (14), since in this case $\langle \tilde{0}|\hat{W}|0\rangle \neq 0$, and an additional term $\langle \tilde{0}|\hat{W}|\tilde{0}\rangle \times \langle \tilde{0}|\hat{H}\hat{Q}^2\hat{H}|0\rangle$ appears in $E^3$ that brings a coupling between subsystems $A$ and $B$. The fact that alteration of $E_0$ cannot possibly have any consequence on PT corrections is also clear from the invariance of Rayleigh–Schrödinger theory against any shift of the zero point of the energy scale.

### E. Consistency issue of the MRPT scheme of Witek, Nakano, and Hirao

We have seen in the previous sections that the exclusion of the projector from the zero order Hamiltonian facilitates the second order PT correction to become size consistent. This experience raises the question of whether multireference PT approaches where no projection operators appear show the same property. In a recent multireference Epstein–Nesbet study by Witek, Nakano, and Hirao[34] (WNH)—that lacks any reference to projection operators—size-consistency violation has been observed numerically. In this section we show that in the approach of WNH size inconsistency of the second order energy originates in the zero order excited energies and can be easily cured by using Møller–Plesset type energy denominators instead of the Epstein–Nesbet partitioning.

A multireference PT formalism in the Epstein–Nesbet partitioning, similar to the WNH approach,[34,36] was first proposed by Davidson,[12] then Mitrushenkov[20] and was used by several others. Zero order eigenvectors of this theory are multireference functions denoted by $|\Phi_0\rangle, |\Phi_1\rangle, \ldots$ that result from the diagonalization of the matrix of the Hamiltonian in a restricted reference space. This set is augmented by the nonredundant set of configurational state functions (CSF) $|q_1\rangle, |q_2\rangle, \ldots$ that arise by applying single, double, etc. excitations to the CSF spanning the reference space. With the use of these vectors, a zero order Hamiltonian is defined in the form:

$$\hat{H}^0_{\mathrm{WNH}} = \sum_i E_i \; |\Phi_i\rangle\langle\Phi_i| + \sum_i E_{q_i}|q_i\rangle\langle q_i|. \tag{16}$$

Zero order energies $E_i$ are the eigenvalues of the restricted diagonalization, while $E_{q_i}$'s are taken as $E_{q_i} = \langle q_i|\hat{H}|q_i\rangle$, in the spirit of the Epstein–Nesbet partitioning.

We would like to see how the second order energy correction

$$E^2_{\mathrm{WNH}} = -\sum_i \frac{\langle\Phi_0|\hat{H}|q_i\rangle\langle q_i|\hat{H}|\Phi_0\rangle}{E_{q_i} - E_0} \tag{17}$$

behaves, given two noninteracting subsystems $A$ and $B$. In this case excited CSF $|q_i\rangle$ may emerge as the product $|q_{j,A}k_{l,B}\rangle$, or $|k_{j,A}q_{l,B}\rangle$, or $|q_{j,A}q_{l,B}\rangle$, where $|k_i\rangle$ denotes CSF that belong to the reference space. Supposing that the zero order ground state function is product separable

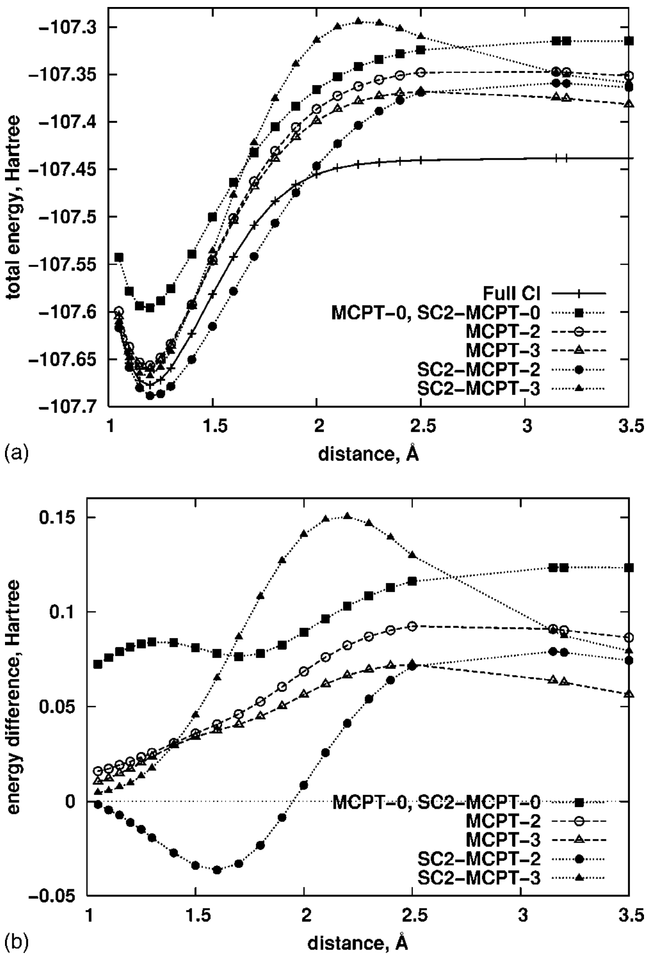

FIG. 1. Dissociation potential curve of the $N_2$ molecule in STO-3G basis set. (a) Total energy curves. (b) Difference curves of various PT formulations with respect to FCI.

$$|\Phi_0\rangle = |\Phi_{0,A}\Phi_{0,B}\rangle,$$

and making use of the orthogonality of $\langle\Phi_j|$ to $|q_i\rangle$, it is easy to see that no interaction occurs between $\langle\Phi_0|$ and $|q_{j,A}q_{l,B}\rangle$,

$$\langle\Phi_{0,A}\Phi_{0,B}|\hat{H}_A + \hat{H}_B|q_{j,A}q_{l,B}\rangle = 0$$

while the interaction between $\langle\Phi_0|$ and $|q_{j,A}k_{l,B}\rangle$ looks:

$$\langle\Phi_{0,A}\Phi_{0,B}|\hat{H}_A + \hat{H}_B|q_{j,A}k_{l,B}\rangle = \langle\Phi_{0,A}|\hat{H}_A|q_{j,A}\rangle\langle\Phi_{0,B}|k_{l,B}\rangle,$$

and $\langle\Phi_{0,A}\Phi_{0,B}|\hat{H}_A + \hat{H}_B|k_{j,A}q_{l,B}\rangle$ is completely analogous. This leads to the second order energy correction:

$$E^2_{\mathrm{WNH}} = -\sum_l |\langle\Phi_{0,B}|k_{l,B}\rangle|^2 \sum_j \frac{|\langle\Phi_{0,A}|\hat{H}_A|q_{j,A}\rangle|^2}{E_{q_{j,A}k_{l,B}} - E_0} + \{A \leftrightarrow B\}. \tag{18}$$

Supposing that $\Phi_{0,B}$ is normalized, we have $\sum_l |\langle\Phi_{0,B}|k_{l,B}\rangle|^2 = 1$. From Eq. (18) it is then apparent that $E^2_{\mathrm{WNH}}$ would be additive if the energy denominator on the rhs of Eq. (18) was independent of index $l$. This can be achieved by choosing zero order excited energies as

$$E_{q_i} = E_0 + \Delta_{q_i}, \tag{19}$$

where $\Delta_{q_i}$ depends only on the one-particle excitation indices that produce $|q_i\rangle$ out of a $|k_m\rangle$, such as in the Møller–Plesset partitioning. In principle, a $|q_i\rangle$ can be obtained from every $|k_m\rangle$ by appropriate excitation, there are therefore many ways of picking up such a $\Delta_{q_i}$ for a given level $q_i$.

To do this in an $l$-independent manner one can, e.g., specify a "principal determinant" of $|0\rangle$ to count the excitations from. Alternatively, one can fix $\Delta_{q_i}$ uniquely by selecting the smallest possible excitation level and MP-type excitation energy with respect to $|k_m\rangle$'s belonging to the CAS space. (In the latter case unphysically small denominators can be cured by, e.g., appropriate level shifts as proposed in Ref. 37.)

By any of the above choices the zero order excited energy becomes

$$E_{q_{j,A}k_{l,B}} = E_0 + \Delta_{q_{j,A}} \tag{20}$$

and Eq. (18) can be brought to the additively separable form:

$$E^2_{\mathrm{WNH}} = -\sum_j \frac{|\langle \Phi_{0,A}|\hat{H}_A|q_{j,A}\rangle|^2}{\Delta_{q_{j,A}}} + \{A \leftrightarrow B\}. \tag{21}$$

Similar to SC2-MCPT, the above choice for the energy denominators does not help the size inconsistency at the third oder. Inspecting

$$E^3_{\mathrm{WNH}} = \sum_{ijlm} \frac{\langle \Phi_{0,A}\Phi_{0,B}|\hat{H}_{AB}|q_{i,A}k_{l,B}\rangle\langle q_{i,A}k_{l,B}|\hat{W}_{AB}|q_{j,A}k_{m,B}\rangle\langle q_{j,A}k_{m,B}|\hat{H}_{AB}|\Phi_{0,A}\Phi_{0,B}\rangle}{\Delta_{q_{i,A}}\Delta_{q_{j,A}}} \tag{22}$$

$$+ \sum_{ijlm} \frac{\langle \Phi_{0,A}\Phi_{0,B}|\hat{H}_{AB}|q_{i,A}k_{l,B}\rangle\langle q_{i,A}k_{l,B}|\hat{W}_{AB}|k_{m,A}q_{j,B}\rangle\langle k_{m,A}q_{j,B}|\hat{H}_{AB}|\Phi_{0,A}\Phi_{0,B}\rangle}{\Delta_{q_{i,A}}\Delta_{q_{j,B}}} + \{A \leftrightarrow B\}, \tag{23}$$

and analyzing the second integral in terms (22) and (23) one gets

$$\begin{aligned}\langle q_{i,A}k_{l,B}|\hat{W}_{AB}|q_{j,A}k_{m,B}\rangle &= \delta_{ij}\langle k_{l,B}|\hat{H}_B|k_{m,B}\rangle \\ &\quad + \delta_{lm}\langle q_{i,A}|\hat{H}_A|q_{j,A}\rangle - \delta_{ij}\delta_{lm}(E_{0,A} \\ &\quad + E_{0,B} + \Delta_{q_{i,A}})\end{aligned} \tag{24}$$

for term (22) and

$$\langle q_{i,A}k_{l,B}|\hat{W}_{AB}|k_{m,A}q_{j,B}\rangle = 0$$

for term (23). In the latter case orthogonality of $\langle q_i|$ to $|k_l\rangle$ was utilized.

One can observe that a direct coupling between independent excitations on different subsystems is not established through $\hat{W}_{AB}$ in the WNH formulation, at difference with the third order formula of SC2-MCPT [cf., Eq. (15)]. There appear, however, consistency violating cross terms in Eq. (22) due to the fact that $\delta_{ij}\langle k_B|\hat{H}_B|l_B\rangle$ does not cancel $\delta_{ij}\delta_{kl}E_{0,B}$ on the rhs of Eq. (24). At this point the third order energy of Witek *et al.* shows a similarity with that of the SC2-MCPT scheme [cf. Eq. (14)]. Choosing the excited state energies according to Eq. (20) therefore ensures size consistency only at the first nonvanishing order in this MRPT formulation as well.

### F. Consistency issue of Hirao's MRMP

The well-known multireference MRMP methodology worked out by Hirao[21,37–40] is closely related to the method discussed in the preceding section. Though the zero order Hamiltonian of MRMP theory is defined with the use of projection operators, it can be easily rewritten to exclude any appearance of projectors, these therefore cannot spoil size consistency. Zero order eigenvectors in MRMP are the same as those discussed in Sec. II E, moreover, the spectral form of $H^{(0)}_{MRMP}$ in the first order interacting subspace (i.e., in the space of $|q_i\rangle$'s) also matches the corresponding part of Eq. (16). The second order energy correction in MRMP consequently has exactly the same form as Eq. (17). This is a favorable situation since only the energy denominators $E_{q_i} - E_0$ have to be investigated, if one wishes to see whether size consistency is ensured at second order in MRMP.

Due to the Møller–Plesset type partitioning, explicit expressions for $E_0$ and $E_{q_i}$ are already different in MRMP from what was discussed in Sec. II E. Let us consider again two noninteracting subsystems $A$ and $B$. In this case the zero order ground state energy in MRMP has the form

$$E_0 = \sum_{i \epsilon A} \epsilon_i^A D_{ii}^A + \sum_{i \epsilon B} \epsilon_i^B D_{ii}^B$$

with $D_{ii} = \Sigma_\sigma \langle 0|a^+_{i\sigma}a_{i\sigma}|0\rangle$ and $\epsilon_i$'s being orbital energies defined according to the MRMP recipe. According to Ref. 37, the zero order excited state energy for a state where the excitation has taken place on subsystem $A$ looks

$$E_{q_{i,A}k_{l,B}} = \sum_i^{\mathrm{occ}_{q_i}} \epsilon_i^A + \sum_i^{\mathrm{occ}_{k_l}} \epsilon_i^B.$$

Unfortunately the difference $E_{q_{i,A}k_{l,B}} - E_0$ apparently depends on orbital indices belonging to subsystem $B$, which spoils

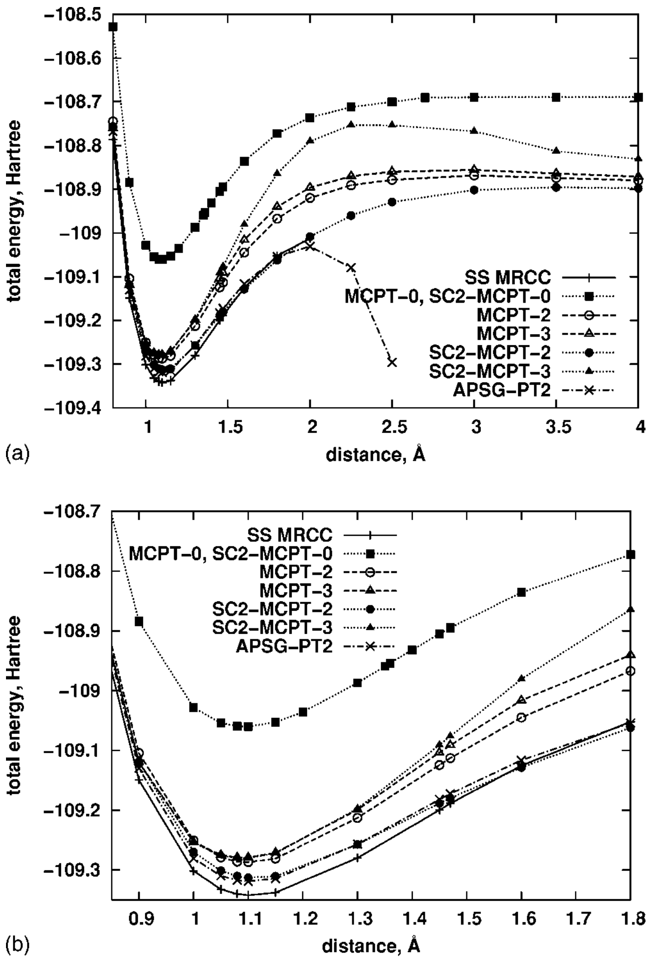

FIG. 2. Dissociation potential curve of the $N_2$ molecule in 6-311G** basis set. (a) Potential curve displayed in a wide range of diatomic distance. (b) Potential curve displayed at around equilibrium geometry.

size consistency of MRMP2. Just like in the case of the WNH approach, choice (19) for the zero order excited state energies ensures the size-consistent second order energy formula (21). The fact that by redefinition of excitation energies $E_{q_i}$ the very same formula is resulted from both MRMP and the WNH approach emphasizes that the second order energy of these theories are related by simple level shifts affecting zero order eigenvalues. For this reason choice (19) does not ensure size consistency of the third order energy neither if starting from MRMP.

## III. EXAMPLES

Illustrative applications reported in this section serve two purposes. Performance of the MCPT and SC2-MCPT schemes are compared on the dissociation potential curve of biatomic molecules $N_2$ and $F_2$, and on the example of the insertion of a Be atom in between two H atoms to form a $BeH_2$ molecule. Numerical check of size consistency is reported for both formulations using two noninteracting Be atoms and two noninteracting $H_2$ molecules with somewhat distorted geometry.

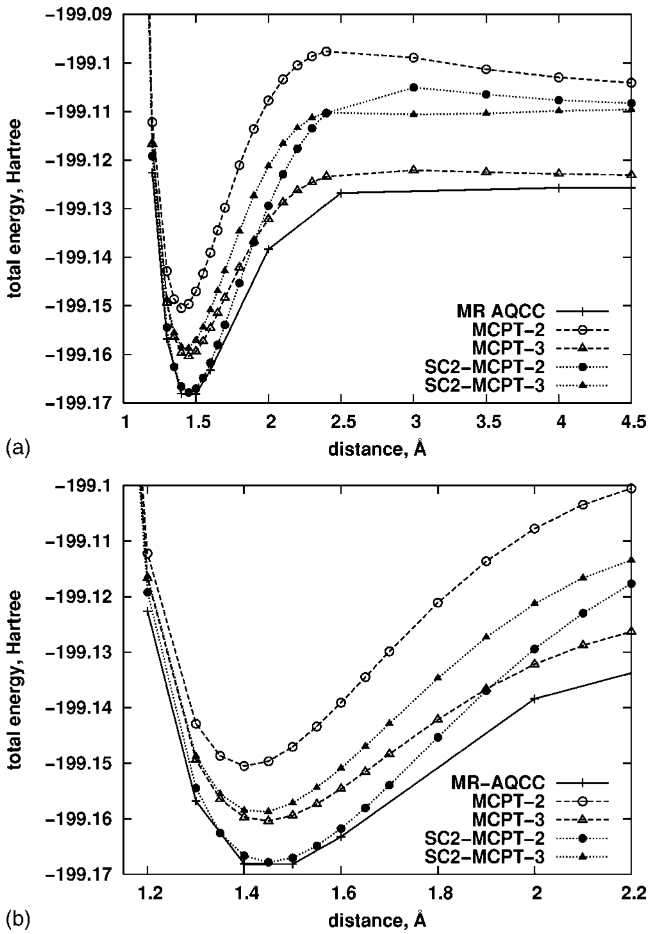

FIG. 3. Dissociation potential curve of the $F_2$ molecule in 6-311G** basis set. (a) Potential curve displayed in a wide range of diatomic distance. (b) Potential curve displayed at around equilibrium geometry.

We investigate two partitionings in the following examples. In the case of dissociation potential curves orbital energies used to construct the Møller–Plesset-like energy denominators $\Delta_k$, e.g.,

$$\Delta_{i,a} = \epsilon_a - \epsilon_i, \; i \in \text{occ}, \; a \in \text{virt}$$

are simply taken as the diagonal element of the Fock operator corresponding to the reference determinant $|\text{HF}\rangle$,

$$\epsilon_i = h_{ii} + \sum_{j}^{\text{occ}} \langle ij||ij\rangle. \tag{25}$$

In the case of the $BeH_2$ molecule and in size-consistency calculations we also checked the effect of using the diagonals of the generalized Fock operator

$$\epsilon_i = h_{ii} + \sum_{jk} \langle ij||ik\rangle P_{kj}, \tag{26}$$

with

$$P_{kj} = \langle 0|a_j^+ a_k|0\rangle.$$

This choice is, in principle, better suited to a multiconfigurational based PT approach, however it usually has only a slight effect in terms of numerical results, as we will see below.

TABLE II. Total energies in atomic units for the $BeH_2$ system in 6-31G** basis, at various nuclear arrangements. See geometry in text. Methods applied are MCPT and SC2-MCPT up to third order as well as the APSG-PT formalism. Partitioning in MCPT and SC2-MCPT is defined by either Eq. (25) or Eq. (26). Full CI energies are given for comparison.

| | $\epsilon_i$-s come from | | | | | |
|---|---|---|---|---|---|---|
| | Eq. (25) | Eq. (26) | Eq. (25) | Eq. (26) | Eq. (25) | Eq. (26) |
| Method | Point A | | Point B | | Point C | |
| MCPT-0 | −15.803 140 | | −15.770 403 | | −15.706 863 | |
| SC2-MCPT-0 | −15.803 139 | | −15.770 401 | | −15.706 850 | |
| MCPT-2 | −15.819 808 | −15.819 849 | −15.787 995 | −15.788 038 | −15.723 334 | −15.723 415 |
| MCPT-3 | −15.823 266 | −15.823 284 | −15.791 982 | −15.792 002 | −15.726 046 | −15.726 076 |
| SC2-MCPT-2 | −15.820 944 | −15.820 986 | −15.789 580 | −15.789 625 | −15.725 533 | −15.725 621 |
| SC2-MCPT-3 | −15.823 041 | −15.823 049 | −15.791 852 | −15.791 858 | −15.725 905 | −15.725 898 |
| APSG-PT2 | −15.824 415 | | −15.793 091 | | −15.726 117 | |
| FCI | −15.831 097 | | −15.800 286 | | −15.731 878 | |
| | Point D | | Point E | | Point F | |
| MCPT-0 | −15.650 441 | | −15.616 101 | | −15.615 634 | |
| SC2-MCPT-0 | −15.650 414 | | −15.616 067 | | −15.615 637 | |
| MCPT-2 | −15.666 955 | −15.667 110 | −15.632 959 | −15.633 184 | −15.641 700 | −15.643 665 |
| MCPT-3 | −15.669 425 | −15.669 487 | −15.636 205 | −15.636 316 | −15.646 599 | −15.647 344 |
| SC2-MCPT-2 | −15.669 167 | −15.669 323 | −15.634 720 | −15.634 928 | −15.642 592 | −15.643 769 |
| SC2-MCPT-3 | −15.668 983 | −15.668 981 | −15.635 277 | −15.635 301 | −15.645 930 | −15.648 995 |
| APSG-PT2 | −15.668 916 | | −15.635 444 | | −15.646 696 | |
| FCI | −15.675 800 | | −15.649 202 | | −15.656 667 | |
| | Point G | | Point H | | Point I | |
| MCPT-0 | −15.693 772 | | −15.734 123 | | −15.754 844 | |
| SC2-MCPT-0 | −15.693 781 | | −15.734 123 | | −15.754 843 | |
| MCPT-2 | −15.706 482 | −15.706 708 | −15.746 723 | −15.746 874 | −15.765 852 | −15.765 969 |
| MCPT-3 | −15.709 577 | −15.709 705 | −15.749 833 | −15.749 927 | −15.768 906 | −15.768 990 |
| SC2-MCPT-2 | −15.708 610 | −15.708 825 | −15.749 235 | −15.749 413 | −15.768 595 | −15.768 749 |
| SC2-MCPT-3 | −15.710 417 | −15.710 444 | −15.751 134 | −15.751 128 | −15.770 403 | −15.770 399 |
| APSG-PT2 | −15.709 671 | | −15.750 019 | | −15.769 933 | |
| FCI | −15.716 702 | | −15.757 323 | | −15.777 481 | |

### A. Dissociation potential curves

The case of the $N_2$ molecule is presented in Figs. 1 and 2. Basis sets used are STO-3G (Fig. 1) and 6-311G** (Fig. 2). Reference functions serving as starting point of the perturbation procedures are antisymmetrized product of strongly orthogonal geminals (APSG) in both cases.[41,42] Two orbitals were assigned to each noncore geminal in both basis sets, producing generalized valence bond (GVB) type reference states. Corrections by MCPT and SC2-MCPT are plotted at second at third order, using the diagonals of the ordinary Fock operator as orbital energies. Full configuration interaction (FCI, Full CI) curve is shown for comparison in Fig. 1 while a state-selective multiconfigurational coupled-cluster (SS-MRCC) (Ref. 43) energy was computed at some geometries in 6-311G** basis (Fig. 2).

The $F_2$ molecule was also treated in the 6-311G** basis. Here, as no full CI reference was affordable, we computed a multireference average quadratic coupled-cluster (MR AQCC) to test the perturbative results. Curves corresponding to the reference energies MCPT-0 and SC2-MCPT-0 are missing from the plot for purpose: they lie too far from the PT corrected lines to be displayed together in one plot. For the $F_2$ molecule we used simple (2, 2) CAS functions as zero order ground state reference.

Apart from the MCPT and SC2-MCPT formulations, the second order result obtained by the PT scheme of Rosta and Surján[22] is also shown in Fig. 2, labeled as APSG-PT2. In this method, following Dyall's idea,[19] a two-body zero order Hamiltonian is applied, whose eigenvectors are the APSG states. In Fig. 1(b) parallelity of the PT curves is plotted. Instead of a parallelity curve a zoom into the region at around equilibrium geometry helps to see the situation more clearly in Figs. 2(b) and 3(b).

Examining Figs. 1 and 2 one can observe that zero order energies in MCPT and SC2-MCPT formulations do not differ significantly in numerical terms. Second and third order results in the MCPT formulation lie close to each other in both basis sets. Third order MCPT slightly improves upon second order in the minimal basis set example, while it slightly worsens the second order in Fig. 2. On the other hand, SC2-MCPT second and third order curves differ significantly in both basis sets. Third order SC2-MCPT is worse than second order in both figures, showing a bump at around 2 Å. If

TABLE III. Energy differences in millihartrees between FCI and various PT formulations for the $BeH_2$ system in 6-31G** basis. Points A to I refer to the nuclear arrangement, see text for coordinates. Methods applied are MCPT and SC2-MCPT up to third order as well as the APSG-PT formalism. Partitioning in MCPT and SC2-MCPT is defined by either Eq. (25) or Eq. (26).

| | $\epsilon_i$-s come from | | | | | |
|---|---|---|---|---|---|---|
| | Eq. (25) | Eq. (26) | Eq. (25) | Eq. (26) | Eq. (25) | Eq. (26) |
| Method | Point A | | Point B | | Point C | |
| MCPT-0 | 27.96 | | 29.88 | | 25.01 | |
| SC2-MCPT-0 | 27.96 | | 29.89 | | 25.03 | |
| MCPT-2 | 11.29 | 11.25 | 12.29 | 12.25 | 8.54 | 8.46 |
| MCPT-3 | 7.83 | 7.81 | 8.30 | 8.28 | 5.83 | 5.80 |
| SC2-MCPT-2 | 10.15 | 10.11 | 10.71 | 10.66 | 6.35 | 6.26 |
| SC2-MCPT-3 | 8.06 | 8.05 | 8.43 | 8.43 | 5.97 | 5.98 |
| APSG-PT2 | 6.68 | | 7.20 | | 5.76 | |
| | Point D | | Point E | | Point F | |
| MCPT-0 | 25.36 | | 33.10 | | 41.03 | |
| SC2-MCPT-0 | 25.39 | | 33.13 | | 41.03 | |
| MCPT-2 | 8.84 | 8.69 | 16.24 | 16.02 | 14.97 | 13.00 |
| MCPT-3 | 6.37 | 6.31 | 13.00 | 12.89 | 10.07 | 9.32 |
| SC2-MCPT-2 | 6.63 | 6.48 | 14.48 | 14.27 | 14.08 | 12.90 |
| SC2-MCPT-3 | 6.82 | 6.82 | 13.93 | 13.90 | 10.74 | 7.67 |
| APSG-PT2 | 6.88 | | 13.76 | | 9.97 | |
| | Point G | | Point H | | Point I | |
| MCPT-0 | 22.93 | | 23.20 | | 22.64 | |
| SC2-MCPT-0 | 22.92 | | 23.20 | | 22.64 | |
| MCPT-2 | 10.22 | 9.99 | 10.60 | 10.45 | 11.63 | 11.51 |
| MCPT-3 | 7.13 | 7.00 | 7.49 | 7.40 | 8.58 | 8.49 |
| SC2-MCPT-2 | 8.09 | 7.88 | 8.09 | 7.91 | 8.89 | 8.73 |
| SC2-MCPT-3 | 6.29 | 6.26 | 6.19 | 6.19 | 7.08 | 7.08 |
| APSG-PT2 | 7.03 | | 7.30 | | 7.55 | |

comparing the second order of the two MCPT formulations, we see a notable decrease in energy stepping from MCPT2 to SC2-MCPT2. In STO-3G basis set the MCPT2 curve is about the same quality as the SC2-MCPT2 curve, deviating from full CI in the opposite direction at around equilibrium. In the triple $\zeta$ polarized basis overshooting of the SC2-MCPT2 curve is not seen, it represents a significant improvement upon the MCPT2 potential curve. The second order SC2-MCPT2 lies very close to APSG PT2 in this example at around equilibrium. This is remarkable taking into account that APSG-PT applies a more sophisticated zero order Hamiltonian than SC2-MCPT. Unfortunately APSG-PT2 starts to deviate from the good shape at around 2 Å due to the quasidegenerate character of the reference function that slowly builds up upon dissociation.

The example of $F_2$ molecule shown in Fig. 3 is somewhat different from the case of the $N_2$ molecule. Here we see a rather big deviation of MCPT second and third order results, third order improving on both the shape and the minimum value of the second order curve. In the case of SC2-MCPT, second order is hard to distinguish from MR AQCC at around equilibrium, but it gets worse as the dissociation takes place. Again at difference with the example of the $N_2$ molecule, third order SC2-MCPT does not simply worsen second order result, we see a better shaped curve at third order than at second, though the minimum is far better at second than at third order.

### B. $BeH_2$ system

The $C_{2v}$ insertion of a Be atom in between two H atoms with a simultaneous increase of the H–H distance presents various difficulties at different regions along the insertion path and has been a good test case of numerous multireference theories.[3,44–46] Nuclear arrangements (points A–I) along this path were borrowed from the work of Purvis and Bartlett.[47] The Be atom is put at the origin (0, 0, 0), the two H atoms lie symmetric to the $z$ axis, with coordinates in atomic units (0, ±2.54, 0), (0, ±2.08, 1.0), (0,±1.62, 2.0), (0, ±1.39, 2.5), (0, ±1.275, 2.75), (0, ±1.16, 3.0), (0, ±0.93, 3.5), (0, ±0.70, 4.0), and finally (0, ±7.70, 6.0) at points A, B, C, D, E, F, G, H, and finally I.

Basis set applied for this system was 6-31G**. We again used an APSG type zero order reference: three orbitals were assigned to both valence geminals, and the core geminal was left uncorrelated. Perturbation theory corrections to this function are collected in Table II, together with FCI results for comparison. Partitionings applying the diagonals of either the ordinary Fock operator [Eq. (25)] or the generalized

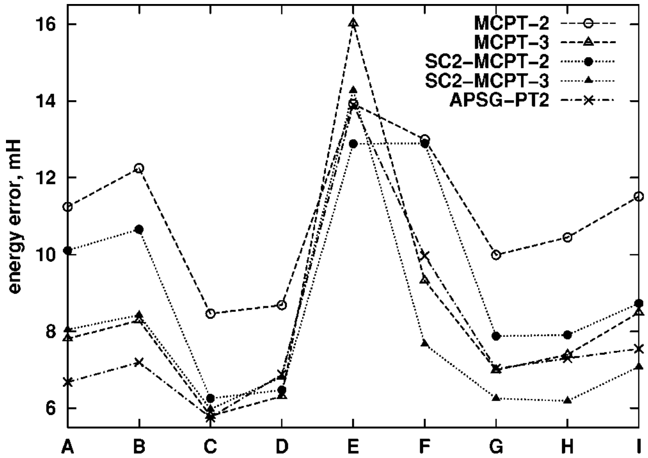

FIG. 4. Errors of total energies in millihartrees of the $BeH_2$ system obtained by MCPT, SC2-MCPT, and APSG-PT in 6-31G** basis. Labels A to I refer to the geometry, for coordinates see text.

one [Eq. (26)] as orbital energies were computed. In Table III deviation of these numbers from the FCI value are listed, in millihartrees. Energy errors of the PT corrected values, for partitioning corresponding to Eq. (26), are also plotted in Fig. 4 for a better overview.

Zero order energies MCPT-0 and SC2-MCPT-0 shown in Table II are very close to each other at each geometry, the largest difference between the two values is only 0.034 mhartrees, at point E. Errors of MCPT-0 and SC2-MCPT-0 vary between 20 and 30 mhartree along the sampling path, except for the peak of the barrier, points E and F. At these points the system shows a significant open-shell character that cannot be described by the APSG function,[41,42] hence the sudden increase of the error to around 40 mhartree.

Interestingly the largest error of PT corrected values is seen at point E, even though the zero order ground state energy is the worst at point F. Along the path from A to I MCPT-2 and SC2-MCPT-2 follow a similar trend, the SC2 variant being closer to the exact result typically by about a milliHartree. This does not hold for point F: here the two second order energies agree within 0.1 mhartree. Third orders improve upon second orders both in MCPT and SC2-MCPT, except for point E. Difference between the two variants of MCPT is smaller at third order than at second. The ordering of third orders changes along the path, at points from A to D MCPT-3 is slightly better than SC2-MCPT-3, at points from E to I this is just reversed, with the difference between SC2-MCPT-3 and MC-PT-3 becoming somewhat larger.

As expected, the second order of APSG-PT outperforms second orders of both MCPT formalism at most points. At points A, B, and C it is even better than either MCPT-3 or SC2-MCPT-3.

At most geometries it makes only a slight difference whether orbital energies building the energy denominators are related to the usual or the generalized Fock operator: Eq. (26) represents an improvement upon Eq. (25) only by a few tenths of a millihartree. Point F is again an exception, here Eq. (26) performs better than Eq. (25) by 1–3 mhartree. This behavior agrees with expectations, regarding that the multireference nature of the wave function is most expressed at point F, consequently the difference between the Hartree–Fock and the exact density matrix is the biggest at this geometry.

### C. Size-consistency studies

Two Be atoms and two $H_2$ molecules were selected for numerical size-consistency check. Internuclear distance of the $H_2$ molecules was 1.0 Å, noninteracting systems were put 100 Å away from each other. We used 6-311G** basis set in

TABLE IV. Total energies of one single $H_2$ molecule and two $H_2$ molecules forming a rectangle. For geometry see text. Energies obtained by PT in the MCPT and SC2-MCPT formulations, up to order three. Basis set applied was 6-311G**. The full CI solution is shown as reference. Size-inconsistency is tabulated in the last column.

| Method | Energy (hartree) | | Energy difference (millihartree) |
|---|---|---|---|
| | $E_{H_2}$ | $E_{H_2\ldots H_2}$ | $E_{H_2\ldots H_2}-2E_{H_2}$ |
| MCPT-0 | −1.128 780 | −2.257 559 | 0.000 |
| SC2-MCPT-0 | −1.128 780 | −2.257 559 | 0.000 |
| | Eq. (25) for $\epsilon_i$-s | | |
| MCPT-2 | −1.139 049 | −2.277 914 | 0.184 |
| MCPT-3 | −1.141 042 | −2.281 932 | 0.152 |
| SC2-MCPT-2 | −1.140 832 | −2.281 664 | 0.000 |
| SC2-MCPT-3 | −1.141 863 | −2.283 528 | 0.198 |
| | Eq. (26) for $\epsilon_i$-s | | |
| MCPT-2 | −1.139 113 | −2.278 043 | 0.183 |
| MCPT-3 | −1.141 069 | −2.281 989 | 0.149 |
| SC2-MCPT-2 | −1.140 906 | −2.281 812 | 0.000 |
| SC2-MCPT-3 | −1.141 860 | −2.283 519 | 0.201 |
| FCI | −1.141 748 | | |

TABLE V. Total energies of one single Be atom and two Be atoms 100 Å apart. Energies obtained by PT in the MCPT and SC2-MCPT formulations are given up to order three. Basis set applied was 6-311G**. The full CI solution is shown as reference. Size inconsistency is tabulated in the last column.

| Method | Energy (hartree) | | Energy difference (millihartree) |
|---|---|---|---|
| | $E_{\mathrm{Be}}$ | $E_{\mathrm{Be}\ldots\mathrm{Be}}$ | $E_{\mathrm{Be}\ldots\mathrm{Be}}-2E_{\mathrm{Be}}$ |
| MCPT-0 | −14.615 608 | −29.231 216 | 0.000 |
| SC2-MCPT-0 | −14.615 608 | −29.231 216 | 0.000 |
| | Eq. (25) for $\epsilon_i$-s | | |
| MCPT-2 | −14.631 011 | −29.261 810 | 0.212 |
| MCPT-3 | −14.632 906 | −29.265 688 | 0.123 |
| SC2-MCPT-2 | −14.632 479 | −29.264 957 | 0.000 |
| SC2-MCPT-3 | −14.633 773 | −29.267 322 | 0.224 |
| | Eq. (26) for $\epsilon_i$-s | | |
| MCPT-2 | −14.631 069 | −29.261 934 | 0.205 |
| MCPT-3 | −14.632 935 | −29.265 753 | 0.118 |
| SC2-MCPT-2 | −14.632 577 | −29.265 155 | 0.000 |
| SC2-MCPT-3 | −14.633 725 | −29.267 214 | 0.236 |
| FCI | −14.633 376 | | |

both examples. The reference function was a valence CAS with two active electrons and four active orbitals for a single Be atom, and correspondingly we used four active electrons and eight active orbitals for the noninteracting dimer. A simple (2, 2) CAS was computed as reference for the stretched $H_2$ molecule and (4, 4) CAS for the noninteracting dimer. Geometry of $H_4$ was a rectangle, the longer edge being 100 Å. Results collected in Tables IV and V include MCPT and SC2-MCPT corrections in two partitionings: we used the diagonals of either the ordinary or the generalized Fock operator to construct orbital energies $\epsilon_i$.

Numbers tabulated in Tables V and IV show that there is hardly any difference between zero order energies of formulations MCPT and SC2-MCPT, similar to the situation apparent in Figs. 1–3. Second and third order corrections are closer to the FCI value in the SC2-MCPT formulation than by MCPT. Second order in SC2-MCPT represents a significant improvement upon MCPT-2, while third orders in the two formulations are of similar quality. Third order of SC2-MCPT overshoots in both examples; this effect is not shown by MCPT-3. Still, the absolute value of the error of SC2-MCPT-3 is slightly smaller than that of MCPT-3. Partitioning with orbital energies taken from Eq. (26) performs slightly better than Eq. (25). However, this effect touches the numbers not at the relevant digit: while the error is in millihartree at second order, this choice improves only by a few hundredths of a millihartree.

Size inconsistency is of the order of magnitude of a tenth of a millihartree. It diminishes stepping from MCPT-2 to MCPT-3. Interestingly, size-consistency violation of the third order of the SC2-MCPT formulation is a little larger than size inconsistency of MCPT-2. Size-consistency violation as a function of the order of PT is plotted in Fig. 5 for the case of the $H_2$ molecules. Here one sees that consistency violation of the SC2-MCPT scheme remains slightly larger than that of MCPT at every order from third order on. Size inconsistency of the MCPT scheme diminishes faster, still the violation of the two schemes fall into the same order of magnitude at the third and higher orders.

## IV. SUMMARY

A modified formulation of the previously introduced multireference perturbation theory has been presented. In the modified theory the projector to the one-dimensional reference space has been left out from the zero order Hamiltonian. This has the consequence, that the first nonvanishing terms of the PT series, i.e., the first order wave function and the second order energy is strictly size consistent, provided that the zero order wave function is size consistent. Higher orders of this series, however, violate the size-consistency requirement.

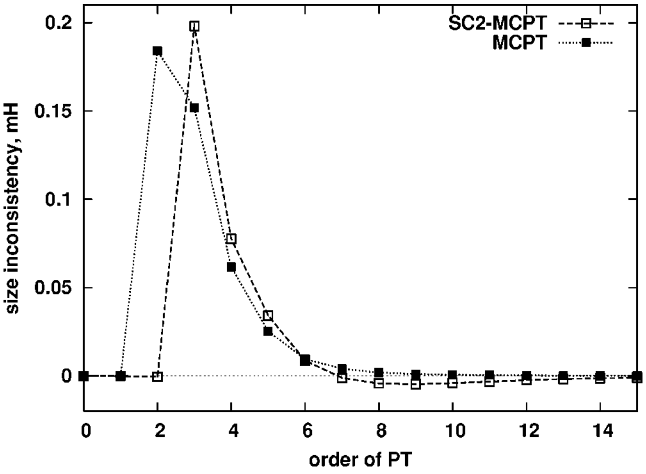

FIG. 5. Size inconsistency of MCPT and SC2-MCPT schemes on the example of two stretched $H_2$ molecules. For geometry see text. Numbers displayed are in millihartrees, basis set used is 6-311G**. Inconsistency is computed as $E_{H_2\ldots H_2}-2E_{H_2}$.

Numerical examples show that size-consistency violation of the MCPT and SC2-MCPT from third order on in energy fall into the same range. Violation of SC2-MCPT formulation at third and higher orders is slightly larger than that of MCPT. Second order energy of SC2-MCPT performs significantly better than MCPT-2 on the examples studied.

We have also shown that, by a special choice of the energy denominators, the second order formula of the recent MRPT formalism of Witek, Nakano, and Hirao can be also brought to be size consistent, just like Hirao's MRMP. Similarly to SC2-MCPT, this modification of the partitioning does not cure size-consistency violation of higher orders of these formalisms.

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