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Letter

On the role of single excitations in quasi-degenerate perturbation theory

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Abstract. In multiconfiguration perturbation theory, the generalized Brillòuin theorem is normally fulfilled, which imposes constraints on the matrix elements involved in the description of single excitations. This can be considered as guaranteeing coherence of the configurations and orbitals describing the zeroth order wavefunction. In quasi-degenerate perturbation theory (QDPT) single excitations are treated independently, which causes a loss of coherence. It is argued that a loss of orbital coherence leads to unreasonable QDPT correlation energies.

Key words: Quasi-degenerate perturbation theory – Multireference methods – Correlation energy – Single excitations – Orbital coherence

1 Introduction

There is an ongoing interest in developing new multiconfiguration perturbation theory (MCPT) methods that provide the correct starting wavefunction for a given electronic system with the help of multiconfiguration self-consistent field (MCSCF) theory [1]. The dynamic electron correlation effects of a system are then considered using perturbation theory (PT) [2]. The roots of this work date back to the pioneering work of Brandow, Kaldor, Davidsson and others on quasi-degenerate perturbation theory (QDPT) [3–10] that was developed to handle systems with nearly degenerate states while practical versions of MCPT methods benefitted from Pulay's work on generalized valence bond second order Møller-Plesset perturbation theory (GVB-MP2) [11]. Today, one can distinguish two basically different approaches to MCPT [12, 13].

1. The first approach [11, 14–27] can be characterized as a *diagonalize and then perturb* (*DP*) *method,* that is just a generalization of MP theory for single reference Hartree-Fock (HF) wavefunctions [28]. In MCPT-DP methods, first the MCSCF wavefunction (zeroth order wavefunction) is optimized: (a) with regard to the configuration interation (CI) expansion coefficients, which requires the diagonalization of the Hamiltonian (the D in the abbreviation DP) in the model space spanned by a selected number of determinants, and (b) with regard to orbital rotations, which implies diagonalization of the Fock operators [1]. In the second step, a suitable set of functions is constructed that can be used for describing electron excitations from the zeroth order wavefunction to excited state wavefunctions. Then, after defining the zeroth order Hamiltonian, perturbation theory of the Rayleigh-Schrödinger (Møller-Plesset [28]) or Brillòuin-Wigner (Epstein-Nesbet [29]) type is carried out.

2. The second approach to MCPT uses a *perturb and then diagonalize* (*PD*) *procedure* [12, 13, 30–37]. For MCPT-PD methods, instead of finding an appropriate set of functions for describing electron excitations, the diagonalization of the Hamiltonian in the model space is postponed, in the sense that the Hamiltonian is improved in the perturbation-like manner (the construction of an effective Hamiltonian) and then diagonalized.

MCPT-PD methods are directly based on QDPT but, despite the early formulation of QDPT, the development of generally applicable MCPT-PD methods has been considerably delayed. To the best of our knowledge, the first application of MCPT-PD was performed by Nakano [34, 35]. In the following, we will no longer distinguish between QDPT and MCPT-PD since the underlying concepts are the same.

There seems to be no formal way to compare MCPT-DP with MCPT-PD methods and to predict which method provides a better description of an electronic system with both dynamic and nondynamic (static) electron correlation. It is the general understanding that the advantages or disadvantages of the two approaches can only be unravelled by applying them and then comparing the calculated results [33]. In this work, however, we will show that the two approaches differ in the way they handle single excitations and that this difference can be used to decide which of the two approaches should be better suited for the description of electron correlation in typical multireference systems.

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2 Theory

In the case of single determinant perturbation theory such as MP [28], the contribution of single excitations to the second-order energy is exactly zero. This is a consequence of the Brillouin theorem [38], which one can consider as a "reward" for the optimization of the orbitals. The absence of single excitation contributions may improve the convergence of the perturbation series. There are two problems which make a generalization of HF-MP approach to MCPT-DP methods difficult. First, it is not clear how to define the single excitation space in MCPT and, second, there is no clear method to construct a perturbation theory which leads to zero contributions from single excitations once the latter have been introduced.

Wolinski et al. [25] have suggested a procedure for defining a single excitation space within MCPT theory:

$$\Psi^{s}_{r} = (\hat{E}^{s}_{r} - \hat{E}^{r}_{s})\Psi_0 \tag{1a}$$

$$\hat{E}^{s}_{r} = s^{\dagger}r + \bar{s}^{\dagger}\bar{r}. \tag{1b}$$

Since the generalized Brillouin theorem [39] holds:

$$\langle \Psi_0 | H | \Psi^{s}_{r} \rangle = 0, \tag{2}$$

there are no single excitation contributions to the second-order energy.

An extension of Pulay's approach to MCPT-PD [12, 34] is not possible since single excitations will always give non-vanishing contributions to the second-order energy within any MCPT method as will be shown in the following. Of course, a priori it is not clear whether nonvanishing single excitation contributions are physically unreasonable and, therefore, have to be avoided in any way. There is no quantum chemical law that requires vanishing single excitation contributions in the second-order PT energy. However, we present arguments in this work that nonvanishing single excitation contributions indicate a deficiency of the multiconfiguration (MC) wavefunction used.

We use the two configuration wavefunction of Eq. (3) as a simple example of a MC wavefunction.

$$\Psi_0 = A\Phi_1 + B\Phi_2 \tag{3}$$

where

$$\Phi_1 = |(core)n\bar{n}|, \quad \text{and} \quad \Phi_2 = |(core)m\bar{m}|. \tag{4}$$

The notation (*core*) indicates core orbitals while *n,m,...* denote valence orbitals and *a,b,...* virtual orbitals.

The QDPT Hamiltonian $\hat{H} = \hat{H}_0(QDPT) + \hat{V}(QDPT)$ for wavefunction (3) can be written according to Eqs. (5a, b):

$$\hat{H}_o(QDPT) = \sum_i \epsilon_i(i^{\dagger}i + \bar{i}^{\dagger}\bar{i}) + \epsilon_n(n^{\dagger}n + \bar{n}^{\dagger}\bar{n}) + \epsilon_m(m^{\dagger}m + \bar{m}^{\dagger}\bar{m}) + \sum_a \epsilon_a(a^{\dagger}a + \bar{a}^{\dagger}\bar{a}), \tag{5a}$$

$$\hat{V}(QDPT) = \hat{H} - \hat{H}_0(QDPT), \tag{5b}$$

with $\hat{V}$ being the perturbation operator.

The second-order effective Hamiltonian $\hat{H}^{(2)}_{eff}$ is defined in Eq. (6) [3]:

$$H^{(2)}_{eff}(J,I) = \sum_{\alpha} \langle \Phi_J | \hat{V}(QDPT) | \Phi_\alpha \rangle (E^{0}_{I} - E^{0}_{\alpha})^{-1} \langle \Phi_\alpha | \hat{V}(QDPT) | \Phi_I \rangle, \tag{6}$$

where Φ_α indicates a set of functions used to describe the complement of the space spanned by Φ_1 and Φ_2. After diagonalizing the effective Hamiltonian $\hat{H}_{eff}$ of Eq. (7),

$$\begin{pmatrix} H_{eff}(1,1) & H_{eff}(1,2) \\ H_{eff}(2,1) & H_{eff}(2,2) \end{pmatrix} \begin{pmatrix} \tilde{A} \\ \tilde{B} \end{pmatrix} = E_{QDPT} \begin{pmatrix} \tilde{A} \\ \tilde{B} \end{pmatrix}, \tag{7}$$

the second-order contribution to the energy is obtained by Eq. (8):

$$E^{(2)}_{QDPT} = \tilde{A}^2 H^{(2)}_{eff}(1,1) + \tilde{B}^2 H^{(2)}_{eff}(2,2) + \tilde{A}\tilde{B}\left[H^{(2)}_{eff}(1,2) + H^{(2)}_{eff}(2,1)\right]. \tag{8}$$

For the set Φ_α only those functions presenting single excitations will be considered:

$$\{\Phi_\alpha(Single)\} = \{\Phi^{a}_{n}, \Phi^{\bar{a}}_{\bar{n}}; \Phi^{a}_{m}, \Phi^{\bar{a}}_{\bar{m}}; \Phi^{n}_{i}, \Phi^{\bar{n}}_{\bar{i}}; \Phi^{m}_{i}, \Phi^{\bar{m}}_{\bar{i}}; \Phi^{m}_{n}, \Phi^{\bar{m}}_{\bar{n}}; \Phi^{a}_{i}, \Phi^{\bar{a}}_{\bar{i}}; \}, \tag{9}$$

where Φ can be Φ_1 or Φ_2. In Eq. (9), only those wavefunctions are considered that are unique in the sense that they do not represent linear combinations of other members of the set. There is no unique way of defining single excitations for a MC wavefunction. In the case of set Eq. (9), the single excitations are chosen to comply with the generalized Brillouin theorem given in Eq. (2).

Provided the MC wavefunction is variationally optimized with regard to orbital rotations, contribution from single excitations vanish in the second-order energy [17]. Since any function Ψ^{s}_{r} can be written as a linear combination of the members of Eq. (9), the choice of a QDPT single excitation space according to Eq. (9) is justified.

With the help of Eq. (9), the energy $E^{(2)}_{QDPT}$ given in Eq. (8) can be partitioned into contributions from different single excitations:

$$E^{(2)}_{QDPT}(Single) = \sum_{a,\bar{a}} E^{(2)}(\Phi^{a}_{n}, \Phi^{\bar{a}}_{\bar{n}}) + \sum_{a,\bar{a}} E^{(2)}(\Phi^{a}_{m}, \Phi^{\bar{a}}_{\bar{m}}) + \sum_{i,\bar{i}} E^{(2)}(\Phi^{n}_{i}, \Phi^{\bar{n}}_{\bar{i}}) + \sum_{i,\bar{i}} E^{(2)}(\Phi^{m}_{i}, \Phi^{\bar{m}}_{\bar{i}}) + E^{(2)}(\Phi^{m}_{n}, \Phi^{\bar{m}}_{\bar{n}}) + \sum_{i,a,\bar{i},\bar{a}} E^{(2)}(\Phi^{a}_{i}, \Phi^{\bar{a}}_{\bar{i}}). \tag{10}$$

For wavefunction Eq. (3), Φ^{a}_{n} (or $\Phi^{\bar{a}}_{\bar{n}}$) covers only one singly excited configuration Φ^{a}_{1n}(or $\Phi^{\bar{a}}_{1\bar{n}}$). Considering this and Eqs. (8) and (6), the first energy term of Eq. (10) can be written according to Eq. (11):

$$E^{(2)}(\Phi^{a}_{n},\Phi^{\bar{a}}_{\bar{n}}) = E^{(2)}(\Phi^{a}_{1n}) + E^{(2)}(\Phi^{\bar{a}}_{1\bar{n}}) = 2E^{(2)}(\Phi^{a}_{1n})$$
$$= 2\left[\tilde{A}^2\frac{\langle\Phi_1|\hat{H}|\Phi^{a}_{1n}\rangle\langle\Phi^{a}_{1n}|\hat{H}|\Phi_1\rangle}{E^{0}_{1}-E^{0a}_{1n}} + \tilde{B}^2\frac{\langle\Phi_2|\hat{H}|\Phi^{a}_{1n}\rangle\langle\Phi^{a}_{1n}|\hat{H}|\Phi_2\rangle}{E^{0}_{2}-E^{0a}_{1n}} + \tilde{A}\tilde{B}\langle\Phi_1|\hat{H}|\Phi^{a}_{1n}\rangle\langle\Phi^{a}_{1n}|\hat{H}|\Phi_2\rangle\left(\frac{1}{E^{0}_{2}-E^{0a}_{1n}}+\frac{1}{E^{0}_{1}-E^{0a}_{1n}}\right)\right]. \quad (11)$$

Using the generalized Brillouin theorem [Eq.(2)], Eq. (12) can be obtained:

$$A\langle\Phi_1|\hat{H}|\Phi^{a}_{1n}\rangle + B\langle\Phi_2|\hat{H}|\Phi^{a}_{1n}\rangle = 0. \quad (12)$$

The denominators of Eq. (11) can be determined by Eqs. (13a, b)

$$E^{0}_{1} - E^{0a}_{1n} = \epsilon_n - \epsilon_a, \quad (13a)$$

$$E^{0}_{2} - E^{0a}_{1n} = 2\epsilon_m - \epsilon_n - \epsilon_a. \quad (13b)$$

Finally, using Eqs. (11), (12), and (13), Eq. (14) follows:

$$E^{(2)}(\Phi^{a}_{n},\Phi^{\bar{a}}_{\bar{n}}) = E^{(2)}(\Phi^{a}_{1n}) + E^{(2)}(\Phi^{\bar{a}}_{1\bar{n}}) = 2E^{(2)}(\Phi^{a}_{1n})$$
$$= 2\left(1-\frac{\tilde{B}A}{\tilde{A}B}\right)\left\langle\Phi_1|\hat{H}|\Phi^{a}_{1n}\right\rangle^2 \left[\frac{\tilde{A}^2}{\epsilon_n-\epsilon_a} - \frac{\tilde{A}\tilde{B}A}{B(2\epsilon_m-\epsilon_n-\epsilon_a)}\right]. \quad (14)$$

In the same way as described above, one can obtain explicit expressions for other energy terms of Eq. (10):

$$E^{(2)}(\Phi^{a}_{m},\Phi^{\bar{a}}_{\bar{m}}) = E^{(2)}(\Phi^{a}_{2m}) + E^{(2)}(\Phi^{\bar{a}}_{2\bar{m}}) = 2E^{(2)}(\Phi^{a}_{2m})$$
$$= 2\left(1-\frac{\tilde{A}B}{\tilde{B}A}\right)\left\langle\Phi_2|\hat{H}|\Phi^{a}_{2m}\right\rangle^2 \left[\frac{\tilde{B}^2}{\epsilon_m-\epsilon_a} - \frac{\tilde{A}\tilde{B}B}{A(2\epsilon_n-\epsilon_m-\epsilon_a)}\right], \quad (15)$$

$$E^{(2)}(\Phi^{m}_{i},\Phi^{\bar{m}}_{\bar{i}}) = E^{(2)}(\Phi^{m}_{1i}) + E^{(2)}(\Phi^{\bar{m}}_{1\bar{i}}) = 2E^{(2)}(\Phi^{m}_{1i})$$
$$= 2\left(1-\frac{\tilde{B}A}{\tilde{A}B}\right)\left\langle\Phi_1|\hat{H}|\Phi^{m}_{1i}\right\rangle^2 \left[\frac{\tilde{A}^2}{\epsilon_i-\epsilon_m} - \frac{\tilde{A}\tilde{B}A}{B(\epsilon_m+\epsilon_i-2\epsilon_n)}\right], \quad (16)$$

$$E^{(2)}(\Phi^{n}_{i},\Phi^{\bar{n}}_{\bar{i}}) = E^{(2)}(\Phi^{n}_{2i}) + E^{(2)}(\Phi^{\bar{n}}_{2\bar{i}}) = 2E^{(2)}(\Phi^{n}_{2i})$$
$$= 2\left(1-\frac{\tilde{A}B}{\tilde{B}A}\right)\left\langle\Phi_2|\hat{H}|\Phi^{n}_{2i}\right\rangle^2 \left[\frac{\tilde{B}^2}{\epsilon_i-\epsilon_n} - \frac{\tilde{A}\tilde{B}B}{A(\epsilon_n-\epsilon_i-2\epsilon_m)}\right], \quad (17)$$

$$E^{(2)}(\Phi^{m}_{n},\Phi^{\bar{m}}_{\bar{n}}) = E^{(2)}(\Phi^{m}_{1n}) + E^{(2)}(\Phi^{\bar{m}}_{1\bar{n}}) = 2E^{(2)}(\Phi^{m}_{1n})$$
$$= 2\tilde{A}^2\left(1-\frac{\tilde{B}A}{\tilde{A}B}\right)\left(1+\frac{\tilde{B}A}{\tilde{A}B}\right)\frac{\langle\Phi_1|\hat{H}|\Phi^{m}_{1n}\rangle^2}{\epsilon_n-\epsilon_m}, \quad (18)$$

where we have used the fact that $\Phi^{m}_{1n} = \Phi^{n}_{2m}$ (or $\Phi^{\bar{m}}_{1\bar{n}} = \Phi^{\bar{n}}_{2\bar{m}}$). Eqs. (14–18) reveal that the single contributions are proportional to the factors $(1-\frac{\tilde{B}A}{\tilde{B}A})$ and $(1-\frac{\tilde{A}B}{\tilde{A}B})$, respectively. If $\tilde{A}$ were equal to A and $\tilde{B}$ equal to B, then the single contributions would not contribute to the second-order energy.

All that remains is to analyse the last term of Eq. (10), which is given by Eq. (19)

$$E^{(2)}(\Phi^{a}_{i},\Phi^{\bar{a}}_{\bar{i}}) = E^{(2)}(\Phi^{a}_{1i}) + E^{(2)}(\Phi^{\bar{a}}_{1\bar{i}}) + E^{(2)}(\Phi^{a}_{2i}) + E^{(2)}(\Phi^{\bar{a}}_{2\bar{i}})$$
$$= 2\left[E^{(2)}(\Phi^{a}_{1i}) + E^{(2)}(\Phi^{a}_{2i})\right] = 2\left(\tilde{A}^2 + \frac{\tilde{B}^2A^4}{B^4}\right)\frac{\langle\Phi_1|\hat{H}|\Phi^{a}_{1i}\rangle^2}{\epsilon_i-\epsilon_a}, \quad (19)$$

since $\langle\Phi_2|\hat{H}|\Phi^{a}_{1i}\rangle = \langle\Phi_1|\hat{H}|\Phi^{a}_{2i}\rangle = 0$.

Clearly, the right side of Eq. (19) will not vanish even if $\tilde{A} = A$ and $\tilde{B} = B$. On the other hand, one has to realize that Φ^{a}_{i} corresponds to the hidden double excitation Φ^{na}_{in} (or Φ^{ma}_{im}) (see, e.g., Murray and Davidson [22]) and, therefore, should make a contribution to the second-order energy as correctly predicted by Eq. (19). Hence, we come to the conclusion that all genuine single-excitation contributions in Eq. (10) will vanish for $\tilde{A} = A$ and $\tilde{B} = B$. However, they will be different from zero and contribute to the second-order energy (despite the fact that all orbitals are variationally optimized) if $\tilde{A} \neq A$ and $\tilde{B} \neq B$ holds or, in other words, if $\tilde{A}$ and $\tilde{B}$ appear in the energy formula Eq. (6) rather than coefficients A and B of wavefunction Eq. (3). The question is whether single excitation contributions of Eq. (10) have any physical relevance or whether they are an artefact of the theory. There are two possible scenarios (which do not necessarily exclude each other):

1. The orbitals of the two determinants Φ_1 and Φ_2 are simultaneously optimized and, therefore, their final forms depend on each other. We say that they are "coherent" and speak of the coherence of the two states associated with Φ_1 and Φ_2. This coherence should be kept when applying perturbation theory. However, the non-zero contributions of the single excitations of Eq. (10) indicate that the diagonalization procedure, which leads to $\tilde{A} \neq A$ and $\tilde{B} \neq B$, destroys this coherence. This is simply a result of the fact that during the perturbation part of MCPT-PD theory the two determinants are decoupled from each other and are treated independently.

2. The coefficients A and B change to $\tilde{A}$ and $\tilde{B}$ because of the projection of the exact eigenfunctions onto the model space. Accordingly, the orbitals have to be rerotated slightly to accommodate for this change. This rerotation of orbitals is described by the nonvanishing single excitation contributions.

The first scenario corresponds to a physically unreasonable situation characterized by an uncontrolled loss of orbital and state coherence, which will probably be enhanced in higher orders of perturbation theory. The second scenario should be unproblematic since it requires just some reoptimization of the orbitals by appropriate orbital rotations. However, there could be a

more serious problem hidden in the second situation. Coefficients $\tilde{A}$ and $\tilde{B}$ depend on the effective Hamiltonian and, thereby, on higher orders of PT. On the other hand, the single excitation energies of Eq. (10) are fixed functions of $\tilde{A}$ and $\tilde{B}$ [see, e.g., Eq.(11)]. Therefore, the single excitation contributions depend on higher orders of PT through the values of $\tilde{A}$ and $\tilde{B}$. The form of Eq. (11) does not change with higher orders of PT. This means that second-order orbital mixing is largely decoupled from higher orders of PT. Since $\tilde{A}$ and $\tilde{B}$ are used in the calculation rather than A and B, a value for $E^{(2)}_{QDPT}(Single)$ different from zero results. This could indicate a loss of coherence owing to improper treatment of higher orders. Of course, one could think of using Brueckner orbitals in this situation to eliminate single excitations [40, 41]; however no use of Brueckner orbitals in QDPT has been reported so far.

We conclude that QDPT (MCPT-PD) used to add dynamic correlation effects to MC wavefunctions suffers from a loss of coherence of orbitals. This is indicated by nonzero contributions of single excitations in second-order PT, which are physically unreasonable. As a consequence, MCPT-PD energies are no longer comparable to MCPT-DP energies, which represent more reasonable correlation energies.

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