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The deviations of the second-order state-specific effective Hamiltonian method from the strict size consistency are analyzed. Provided that complete or separable model spaces are used, these deviations can be suppressed by a proper choice of nonuniform shifts of energy denominators. © *1996 American Institute of Physics.* [S0021-9606(96)01539-5]

I. INTRODUCTION

The second-order state-specific effective Hamiltonian methods such as the ''shifted B_k'' scheme,[1] intermediate-Hamiltonian generalized degenerate perturbation theory,[2,3] state-selective QDPT (quasidegenerate perturbation theory) of Hoffmann,[4] MROPT-n techniques,[5–7] etc., have become an extremely popular tool for intermediate accuracy calculations on ground and excited electronic states of molecules. These methods combine several attractive features such as low computational cost, numerical stability and proper account for the outer-space correlation effects on the reference space part of the wave functions. Unfortunately, all the approaches of this group suffer from the lack of size consistency of resulting energy estimates even when complete model spaces are used. This problem does not bear such a catastrophic character as for the predecessor second-order Brillouin–Wigner–type (B_k) method.[8–10] Nevertheless, it is in no way of purely theoretical interest; for instance, the deviations from size consistency can be one of the main sources of errors in the calculations on excitation energies even for medium-size molecules.[11]

While the size inconsistency of approximate state-specific effective Hamiltonians has been a subject of several numerical studies,[5,11–13] up until now only a special aspect of this problem concerning the separation of a closed-shell fragment has been analyzed theoretically.[5,14]

In the present article we propose a simple interpretation of the origin of size inconsistency of second-order state-specific effective Hamiltonians in complete model spaces. The understanding of this origin enables to force the exact separability (and therefore size consistency) by a proper modification of energy denominators.

II. THEORY

Assume that we are searching for a single eigenstate $|\psi_\mu\rangle$ of a many-electron system with its Hamiltonian H:

$$H|\psi_\mu\rangle = E_\mu|\psi_\mu\rangle. \tag{1}$$

We start with splitting the total space of N-electron wave functions into the model space L_P and the outer space L_Q projected by the operators P and $Q=1-P$ respectively. Both L_P and L_Q are supposed to be spanned by appropriate sets of Slater determinants ($\{|j\rangle\}$ and $\{|\alpha\rangle\}$):

$$P=\sum_j |j\rangle\langle j|, \quad Q=\sum_\alpha |\alpha\rangle\langle\alpha|. \tag{2}$$

We shall restrict our attention to complete model spaces uniquely defined by the partitioning of the spinorbital set into core, active and secondary subsets. Let us introduce a zero-order operator H_0 which is diagonal in the basis of the determinants

$$H_0=\sum_j |j\rangle e_j\langle j| + \sum_\alpha |\alpha\rangle e_\alpha\langle\alpha| \tag{3}$$

and a perturbation $V=H-H_0$. The second-order state-specific effective Hamiltonian $\tilde{H}$ corresponding to the target eigenstate $|\psi_\mu\rangle$ is usually defined[1–7] as

$$\tilde{H}=PHP+\tilde{H}^{(2)}=PHP+PV\frac{Q}{E_\mu^0-H_0}VP. \tag{4}$$

The choice of the parameter E_μ^0 is rather arbitrary and usually related to the model space eigensolution which is believed to correlate with $|\psi_\mu\rangle$. Let us separate a closed non-diagonal part of the total Hamiltonian written in the normal form with respect to the core vacuum

$$W=\sum_a \sum_{\substack{b \\ a\neq b}} f_{ab}a_a^\dagger a_b + \tfrac{1}{2}\sum_{ab}\sum_{\substack{cd \\ ab\neq cd}} \langle ab|cd\rangle a_a^\dagger a_b^\dagger a_d a_c, \tag{5}$$

where the indices a, b, c, d correspond to active spinorbitals and $f_{ab}, \langle ab|cd\rangle$ are the one- and two-particle amplitudes of the normal-ordered H, and specify the parameter E_μ^0 as an appropriate eigenvalue of the operator $P(H_0+W)P$:

$$P(H_0+W)P|\chi_\mu\rangle = E_\mu^0|\chi_\mu\rangle, \tag{6}$$

$$|\chi_\mu\rangle=\sum_j c_{j\mu}|j\rangle. \tag{7}$$

Note that for an Epstein–Nesbet–type zero-order operator[15,16] $P(H_0+W)P=PHP$ and E_μ^0 is an eigenvalue of the model-space problem as it is usually assumed in the shifted B_k scheme. It should also be noticed that with any reasonable choice of H_0 and L_P our definition should not cause the appearance of ill-defined denominators in Eq. (4) provided that $|\psi_\mu\rangle$ is a low-lying state.

The expansion coefficients of $|\chi_\mu\rangle$ in the basis of determinants should satisfy the matrix eigenvalue equation which may be written as

$$\sum_{\substack{k \\ k\neq j}} \langle j|W|k\rangle c_{k\mu} + (e_j - E^0_\mu) c_{j\mu} = 0 \quad \forall j: \ |j\rangle \in L_p . \tag{8}$$

Provided that all the coefficients $c_{j\mu} \neq 0$, we can represent any matrix element of the second-order effective interaction $\tilde{H}^{(2)}$ [Eq. (3)] in the form

$$\langle k|\tilde{H}^{(2)}|j\rangle = \sum_\alpha \frac{\langle k|H|\alpha\rangle\langle\alpha|H|j\rangle}{e_j - e_\alpha + c^{-1}_{j\mu} \sum\limits_{\substack{l \\ l\neq j}} \langle j|W|l\rangle c_{l\mu}} . \tag{9}$$

Let us now analyze the separability properties of the second-order effective Hamiltonian. Consider a system AB composed of two noninteracting fragments A and B with its Hamiltonian $H^{AB} = H^A + H^B$ and assume that each spin–orbital is completely localized on one of the fragments. The sets of active orbitals localized on A and B define the complete model spaces of the fragments (L^A_P and L^B_P); we shall denote the determinants spanning those spaces by $|j_A\rangle$, $|k_A\rangle$,... and $|j_B\rangle$, $|k_B\rangle$,... . All the possible antisymmetrized products $|j_A j_B\rangle = \mathscr{A}|j_A\rangle|j_B\rangle$ span a subspace $L^A_P \otimes L^B_P$ of the complete model space of the whole system which does not interact with other (charge-transfer) model states and therefore can be considered separately. Suppose that we are interested in a state $|\psi_{\mu\nu}\rangle$ of the supersystem arising from the states μ and ν of the fragments.

Any matrix element of the state-specific effective interaction as given by Eqs. (4) and (9) is a sum of contributions from individual outer-space states. Without loss of generality, we can restrict our attention to outer space states arising from localized substitutions

$$|j_A \alpha_B\rangle = \mathscr{A}|j_A\rangle|\alpha_B\rangle \quad \text{or} \quad |\alpha_A j_B\rangle = \mathscr{A}|\alpha_A\rangle|j_B\rangle$$

because the configurations $|\alpha_A \alpha_B\rangle = \mathscr{A}|\alpha_A\rangle|\alpha_B\rangle$ and charge transfer states do not interact directly with $L^A_P \otimes L^B_P$.

Assume, for instance, that the substitution producing the outer-space determinant is localized on A. Since the total Hamiltonian H^{AB} is simply the sum of fragment Hamiltonians H^A and H^B, an outer-space determinant $|\alpha_A j_B\rangle$ contributes only to the matrix elements $\langle k_A j_B|\tilde{H}^{(2)AB}|j_A j_B\rangle$ by

$$\langle k_A j_B|\tilde{H}^{(2)AB}(\alpha_A j_B)|j_A j_B\rangle = \frac{\langle k_A j_B|H^{AB}|\alpha_A j_B\rangle\langle\alpha_A j_B|H^{AB}|j_A j_B\rangle}{e_{j_A j_B} - e_{\alpha_A j_B} + c^{-1}_{j_A j_B,\mu\nu} \sum\limits_{\substack{l_A l_B \\ l_A l_B \neq j_A j_B}} \langle j_A j_B|W^{AB}|l_A l_B\rangle c_{l_A l_B,\mu\nu}} . \tag{10}$$

Let us first note that the numerator in Eq. (10) does not depend on j_B

$$\langle k_A j_B|H^{AB}|\alpha_A j_B\rangle\langle\alpha_A j_B|H^{AB}|j_A j_B\rangle = \langle k_A|H^A|\alpha_A\rangle\langle\alpha_A|H^A|j_A\rangle \tag{11}$$

Further, it is natural to assume the separability of the eigenvalues of zero-order operators

$$e_{j_A j_B} = e_{j_A} + e_{j_B}, \quad e_{\alpha_A j_B} = e_{\alpha_A} + e_{j_B}, \tag{12}$$

which holds automatically for Epstein–Nesbet and conventional generalized Møller–Plesset[17–19] H_0. Since $W^{AB} = W^A + W^B$, the eigenvectors of the model-space problems [Eq. (8)] can always be chosen consistently such that

$$c_{j_A j_B,\mu\nu} = c_{j_A\mu} c_{j_B\nu} . \tag{13}$$

Taking into account Eqs. (12) and (13), one can write down the denominator in Eq. (10) as

$$e_{j_A} - e_{\alpha_A} + \Sigma_1 + \Sigma_2 , \tag{14a}$$

$$\Sigma_1 = c^{-1}_{j_A\mu} \sum_{\substack{l_A \\ l_A \neq j_A}} \langle j_A|W^A|l_A\rangle c_{l_A\mu} , \tag{14b}$$

$$\Sigma_2 = c^{-1}_{j_B\nu} \sum_{\substack{l_B \\ l_B \neq j_B}} \langle j_B|W^B|l_B\rangle c_{l_B\nu} . \tag{14c}$$

Omitting in Eq. (13) the last term (Σ_2) explicitly depending on the model-state label of the fragment B, one could arrive at the equation

$$\langle k_A j_B|\tilde{H}^{(2)AB}(\alpha_A j_B)|j_A j_B\rangle = \langle k_A|\tilde{H}^{(2)A}(\alpha_A)|j_A\rangle, \tag{15}$$

which guarantees the separability of the effective interaction under the fragmentation of AB into A and B. Therefore the lack of separability may be directly associated with the appearance of j_B-dependent term Σ_2 in the denominator of perturbative correction [Eq. (10)] and this term should be considered as spurious.

Taking into account this fact, one may try to restore the separability of state-specific effective Hamiltonians by discarding from the energy denominators in Eq. (9) all the terms $c^{-1}_{j\mu}\langle j|W|k\rangle c_{k\mu}$ which can enter the separability-violating sum Σ_2 [Eq. (14c)] at least for one possible fragmentation channel. An exception can be made for the cases when the numerator of corresponding contribution tends to zero at the fragmentation limit.

Let us consider two substitution operators, $D^\dagger(j\to l)$: $|l\rangle = D^\dagger(j\to l)|j\rangle$ and $D^\dagger(j\to\alpha)$: $|\alpha\rangle = D^\dagger(j\to\alpha)|j\rangle$, and assume that each of these operators change the occupancy of a

certain active spin–orbital, in other words, $D^{\dagger}(j\rightarrow l)|\alpha\rangle=0$. Suppose that for a certain fragmentation channel the substitution $D^{\dagger}(j\rightarrow\alpha)$ is completely localized on one of the fragments (otherwise the numerator of the corresponding contribution to $\langle k|\widetilde{H}^{(2)}|j\rangle$ is zero). One readily realizes that the matrix element $\langle j|W|l\rangle$ which might enter the Σ_2-like sum in Eq. (14) vanishes because of connectivity of W.

This observation gives rise to a general rule enabling to discard the separability-violating terms in the denominators and to arrive at the following analogue of $\widetilde{H}^{(2)}$ [Eqs. (4) and (9)]

$$\langle k|\widetilde{H}^{(2)}_{\mathrm{Sep}}|j\rangle=\sum_{\alpha}\ \frac{\langle k|H|\alpha\rangle\langle\alpha|H|j\rangle}{e_j-e_\alpha+A^{\mu}_{j\alpha}}, \tag{16a}$$

$$A^{\mu}_{j\alpha}=c^{-1}_{j\mu}\sum_{l:}\ \langle j|W|l\rangle c_{l\mu}, \quad D^{\dagger}(j\rightarrow l)|\alpha\rangle=0 \tag{16b}$$

An analysis of a second-order contribution to $\widetilde{H}^{(2)}_{\mathrm{Sep}}$ similar to that presented by Eqs. (10)–(14) readily shows that the separability-violating sum, Eq. (14c), is now empty and the analog of Eq. (15) is really satisfied. Therefore Eq. (16) defines a strictly separable approximate effective Hamiltonian.

It should be noted that the whole set of energy denominators in Eq. (16) for all possible values j,k: $|j\rangle,|k\rangle\in L_P$ cannot be represented in terms of any unique manifold of zero-order energies. Therefore the identification of this approximation with a second-order correction of the conventional perturbation theory with any unique zero-order operator at least is not straightforward. In contrast, Eq. (16) is readily interpreted as a second-order approximation of the multipartitioning perturbation theory (MPPT).[20] The zero-order operator corresponding to the jth basis determinant may be defined as

$$H_0(j)=\sum_{\substack{k\\ |k\rangle\in L_P}}|k\rangle e_k\langle k|+\sum_{\substack{\alpha\\ |\alpha\rangle\in L_Q}}|\alpha\rangle(e_\alpha-A_{j\alpha})\langle\alpha| \tag{17}$$

and the expression for the second-order MPPT correction

$$\widetilde{H}^{(2)}_{\mathrm{MPPT}}=\sum_{j}\ PV(j)\ \frac{Q}{\langle j|H_0(j)|j\rangle-H_0(j)}\ V(j)|j\rangle\langle j|, \tag{18}$$

where $V(j)=H-H_0(j)$, immediately yields Eq. (16). It is interesting to note that the MPPT has already provided another solution to the problem of constructing a separable state-specific second-order Hamiltonian.[21]

III. DISCUSSION

It is worth comparing the matrix element (16) with the corresponding second-order contribution to the Bloch state-universal effective Hamiltonian.[22] They have the same numerators while the denominators differ by the terms $A^{\mu}_{j\alpha}$. On the other hand, one may refer to the original expression of the second-order state-specific effective Hamiltonian (4) which also involves the same numerators and introduces $E^{\mu}_0-e_\alpha$ as j-independent energy denominators. The following discussion shows that both limits may be reached by the denominators in Eq. (16).

A. Inactive double excitations

Suppose that an outer-space determinant $|\alpha\rangle$ is obtained from a given reference determinant $|j\rangle$ by an inactive double substitution, i.e., a substitution $D^{\dagger}_r$ involving two core spin–orbitals and two secondary spin–orbitals: $|\alpha\rangle=D^{\dagger}_r|j\rangle$. In this case $|\alpha\rangle$ interacts only with one model state $|j\rangle$. Since for any $l\neq j$ $D^{\dagger}(j\rightarrow l)|\alpha\rangle\neq0$, $A^{\mu}_{j\alpha}=0$ and the second-order effect of $|\alpha\rangle$ reduced to a diagonal correction

$$\langle j|\widetilde{H}^{(2)}_{\mathrm{Sep}}(\alpha)|j\rangle=\frac{\langle j|H|\alpha\rangle\langle\alpha|H|j\rangle}{e_j-e_\alpha}, \tag{19}$$

which is identical to the second-order contribution to the state-universal effective Hamiltonian.[22] If we choose the Møller–Plesset definition of H_0, the denominators become independent on $|j\rangle$ and the effect of inactive excitations is a uniform shift of all diagonal matrix elements. This is an explicit manifestation of separability of the definition (16) for the cases where the active orbitals are localized on one of the subsystem (weak separability[14,23]). Notice that the occupied and virtual inactive MO's being well separated in energy for any reasonable choice of the model space, these excitations cannot produce any intruder problem.

B. Case of two active electrons in two active orbitals

Consider the breaking of homopolar bond or the rotation around the C–C bond of ethylene. In these problems it is natural to span the active space by two active MO's ϕ and φ^* of different symmetries (σ_g, σ^*_u for the first problem, π_u, π^*_g for the second one). The corresponding fully symmetric sector of the complete model space involves only two determinants $|1\rangle=|\mathrm{core}\ \varphi\overline{\varphi}|$ and $|2\rangle=|\mathrm{core}\ \varphi^*\overline{\varphi^*}|$. One easily sees that any model space substitution [$D^{\dagger}(1\text{–}2)$ and $D^{\dagger}(2\text{–}1)$] involves all the active spin–orbitals. Therefore for any outer-space determinant $|\alpha\rangle$, except those obtained by inactive substitutions, the energy denominators in Eq. (16) reduce to those from Eqs. (4) and (9), i.e., $E^{\mu}_0-e_\alpha$. For the ground state study ($\mu=1$), the gap $E^{\mu}_0-e_\alpha$ remains large whatever the bond length of the homopolar single bond or the twisting angle of the double bond. Hence the intruder states which make the conventional effective Hamiltonian expansion[22] divergent through the occurrence of small e_2-e_α denominators do not cause any trouble.

As a simple numerical illustration we investigated the accuracy of formula (16) in describing the ground-state potential curve of F_2. We used the same $[9s5p1d]/[4s3p1d]$ basis set as Laidig, Saxe, and Bartlett[24] in their thorough study on this system. The model space was generated by the CASSCF (complete active space self-consistent field) calculations[25] with only two MO's ($3\sigma_g$, $3\sigma^*_u$) in the active space. To specify the Møller–Plesset–type zero-order Hamiltonian, CASSCF pseudocanonical MO's and generalized orbital energies[19] were used. Our results along with those from some previous second-order calculations and ''nearly full-CI'' data from[24] are given in Table I.

TABLE I. Spectroscopic constants for the F_2 ground state calculated within the $[4s3p1d]$ basis set (Ref. 24).

	r_e (Å)	D_e (eV)	ω_e (cm^{-1})
MCSCF	1.500	0.562	583
Second-order PT:			
Ref. 27[a]	1.368	2.411	1115
Ref. 27[b]	1.392	1.784	997
Ref. 4[b,c]	1.434	1.621	
Present work[d]	1.438	1.451	850
Nearly full-CI data			
Ref. 24			
MRDCI	1.436[e]	1.275[e]	821[c]
MR LCCM	1.439[e]	1.257[e]	842[c]

[a]State-universal effective Hamiltonian, degeneracy of the model space is forced by averaging the active orbital energies.
[b]Size-inconsistent state-specific effective Hamiltonian.
[c]The model space is extended to 10 configurations.
[d]Size-consistent state-specific effective Hamiltonian.
[e]The model space is extended to 32 configurations.

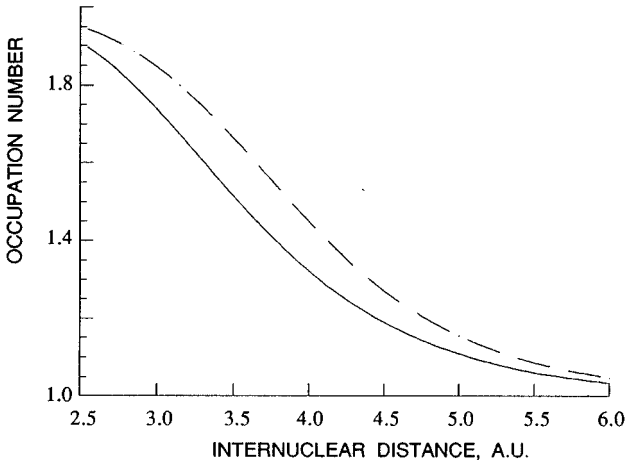

FIG. 1. Occupation number of the bonding $3\sigma_g$-MO F_2 as a function of the internuclear separation. Solid line: MCSCF. Dashed line: size-consistent second-order effective Hamiltonian method.

The $(3\sigma_g, 3\sigma_u^*)$ CASSCF approximation recovers only 44–45 % of the bonding energy which can be reproduced within the given basis set. Straightforward application of the conventional effective Hamiltonian PT (Ref. 22) is meaningless because of several crossing between the model and outer zero-order levels near the equilibrium geometry. The second-order degenerate PT treatment with averaged active orbital energies[26,27] provides a smooth potential curve but markedly overshoots the dissociation energy and the vibrational frequency. The size-inconsistent state-specific effective Hamiltonian procedures deriving the zero-order model-space energy from the solution of the reference space problem[4,27] seem to yield more reliable curves although the dissociation energy is still too large. Our method gives a considerably better approximation to nearly full-CI spectroscopic constants of Laidig, Saxe, and Bartlett.[24] The remaining slight overestimation of the bond energy may be attributed to the systematic error inherent to the second-order treatment with the chosen form of one-particle zero-order operator (see Ref. 28 for a detailed discussion).

It should be mentioned that the decontracted treatment of the model space part of the wavefunction is essential for a proper description of the F–F bonding, since the starting CASSCF model substantially underestimates the occupancy of the bonding $3\sigma_g$ MO (see Fig. 1).

C. Practical aspects

While the present analysis aimed essentially to reveal the origins of the size inconsistency of conventional state-specific effective Hamiltonian approach, it can also give rise to a practically valuable tool for molecular electronic structure computations. The direct use of the approximation defined by Eq. (16) is limited by the risk of numerical instabilities which should appear when some of $c_{j\mu}$ coefficients are small or zero. These problems may be circumvented via an appropriate denominator averaging over the model space, i.e., by replacing the set of j-dependent denominators $\{(e_j - e_\alpha + A_{j\alpha}^\mu)\}$, $|j\rangle \in Lp$, by a single denominator

$$\mathrm{den}(\mu,\alpha) = \sum_j \rho_{j\alpha}^\mu (e_j - A_{j\alpha}^\mu) + e_\alpha , \tag{20}$$

where the weights $\rho_{j\alpha}^\mu$ are scaled on the contributions of the determinants $|j\rangle$ to the target wave function. For instance, $\rho_{j\alpha}^\mu$ can be identified with the genealogical weights[29]

$$\rho_{j\alpha}^\mu = \frac{\langle \alpha|H|j\rangle c_{j\mu}}{\Sigma_k \langle \alpha|H|k\rangle c_{k\mu}} . \tag{21}$$

One can verify that the averaging procedure with $\rho_{j\alpha}^\mu$ defined as in Eq. (21) preserves the separability of resulting effective Hamiltonian.

It should be noticed that the denominators (20) may be also used in nondegenerate formalisms which perturb a multiconfiguration wave function (an eigenfunction of PHP) by the effect of the outer space determinants.[30] One may demonstrate that these contracted procedures then become size consistent (strictly separable when localized orbitals are used) provided that the model space is complete.

Let us note finally that the additional computational efforts arising from the necessity to evaluate the shift values $A_{j\alpha}^\mu$ can be drastically reduced by an appropriate preliminary partial summations, and the procedure may be competitive with conventional second-order schemes.

IV. CONCLUSIONS

We presented an analysis of the conventional second-order state-specific effective Hamiltonians revealing the origin of their inherent size inconsistency in the situations where the complete or separable model spaces are used. Discarding the separability-violating term from the energy denominators, one can arrive at a strictly size-consistent expression which admits a simple interpretation in terms of the second-order multipartitioning perturbation theory. The numerical instability of this expression can be in principle avoided by a proper averaging of the energy denominator without destroying the separability.

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