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Spin-adapted multipartitioning perturbation theory

Andréi Zaitsevskii, Jean-Paul Malrieu

IRSAMC, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex, France
F-31062 Toulouse Cedex, France

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Abstract. The multireference generalization of the Møller-Plesset perturbation theory employing multiple partitionings of the total Hamiltonian is revised in order to avoid spin contaminations and non-physical dependence of the results on the *z* projection of the total spin. The novel formulation retains the main advantages of the original approach (computational simplicity, numerical stability, uncontracted treatment of the reference-space part of wavefunctions, size consistency of second-order results for complete model spaces). The results of pilot calculations on the transitions between electronic states with different spin multiplicities in CH_2, SiH_2, ScH, Sc_2 and Cu_2 are reported.

Key words: Electron correlations in molecules – Multireference perturbation theory – Spin eigenfunctions

1 Introduction

The multireference perturbation theory (MRPT) is usually considered as one of the most promising approaches to molecular electronic structure calculations, and in particular as a potentially powerful tool for the study of excited states and large deviations from equilibrium geometries [1–6]. In a perfect agreement with the chemical intuition, the MRPT may take advantage from the separation of the electron correlation effects into internal (non-dynamic) correlations associated with the interactions of model-space configurations and remainder (dynamic) effects arising from the couplings between the model and outer spaces [7]. In contradistinction to the non-degenerate multiconfigurational perturbative schemes, which follow the so-called “diagonalize-then-perturb” strategy [8–12], the MRPT-based methods are capable of describing the interferences between dynamic and non-dynamic correlations properly [7, 13].

The fundamental problem of MRPT treatment of molecular electronic states arises from the difficulties in combining numerical stability (especially for large model spaces) and satisfactory low-order results with the strict size consistency. The conventional Bloch-Brandow MRPT [14–16], being size-consistent for complete model spaces, suffers from instabilities owing to nearly zero energy denominators in the presence of intruder states [5, 17, 18]. The elimination of small denominators by applying appropriate shift techniques [3, 4, 6, 19–21] restores the numerical stability at least in low orders but usually destroys the size consistency [6, 13, 21].

In a recent publication [22] we proposed a state-selective second-order MRPT method based on the simultaneous use of several partitionings of the total Hamiltonian into a one-electron zero-order part and a perturbation (multi-partitioning MRPT). This method can be considered as a consistent generalization of the famous Møller-Plesset many-body perturbation theory [23] for multidimensional model spaces. It combines numerical stability in the presence of intruders with strict size consistency, provided that complete model spaces are used. A series of numerical tests demonstrated its accuracy in excited-state calculations in rather complicated situations.

A serious deficiency of this approach consists in an incorrect treatment of spin eigenfunctions. Even if spin-restricted spin-orbital bases are used, the zero-order operators defined in [22] are generally not spin scalars. This can result in spin contaminations of the eigenvectors of effective Hamiltonians and non-physical dependence of the energy estimates for the states with non-zero spin on the choice of the reference *z*-axis. Therefore, the method is not well suited for the study of electronic states with different spin multiplicities.

In this paper we reformulate the state-selective multipartitioning MRPT in a spin-adapted manner, introducing the sets of zero-order operators commuting with the total spin. Several applications to molecular electronic states with different spin values are presented and discussed.

Correspondence to: A. Zaitsevskii

2 Theory

Let us first recall the general principles of the multipartitioning multireference perturbation theory [22, 24, 25]. We start with splitting the total space L of N-electron wave functions into the model space L_P with its projector P and the outer space L_Q projected by $Q = 1 - P$ and choosing an orthonormal basis $\{|J\rangle\}$ in $L_P (P = \sum_J |J\rangle\langle J|)$. An effective Hamiltonian $\tilde{H}$ acting in L_P and the associated wave operator Ω should satisfy the generalized Bloch equation [16]

$$\Omega P \tilde{H} = H \Omega P \tag{1}$$

Provided that the intermediate normalization of Ω [16] is accepted, this equation can be written in the form

$$\tilde{H} = PH\Omega P \tag{2}$$

$$QH\Omega P = Q\Omega PH\Omega P \tag{3}$$

The use of intermediate normalization, which implies the non-hermiticity of $\tilde{H}$, is not compulsory; an alternative formulation of the multipartitioning MRPT yielding a Hermitian effective Hamiltonian is given in the Appendix.

To construct $\tilde{H}$ and Ω perturbatively, we split Eqs. (2, 3) into projections on the basis functions

$$\tilde{H}|J\rangle\langle J| = PH\Omega|J\rangle\langle J| \tag{4}$$

$$QH\Omega|J\rangle\langle J| = Q\Omega PH\Omega|J\rangle\langle J| \tag{5}$$

and define, for each projection separately, a partitioning of the total Hamiltonian H into the zero-order part $H_0(J)$ and the perturbation $V(J)$

$$H = H_0(J) + V(J), \quad H_0(J)P = PH_0(J) \quad \forall J : |J\rangle \in L_P \tag{6}$$

Substituting the partitionings in Eq. (5), one gets

$$Q[\Omega, H_0(J)]|J\rangle\langle J| = Q(V(J)\Omega - \Omega PV(J)\Omega)|J\rangle\langle J| \ . \tag{7}$$

At present we shall assume that each operator $H_0(J)$ commutes with the corresponding one-dimensional projector $|J\rangle\langle J|$:

$$H_0(J)|J\rangle\langle J| = |J\rangle\langle J|H_0(J) = |J\rangle e_J \langle J| \ . \tag{8}$$

Then the Liouvilleans in Eq. (7) are easily inverted and after the summation over the model states we obtain

$$Q\Omega P = \sum_J \frac{Q}{e_J - H_0(J)} (V(J)\Omega - \Omega PV(J)\Omega)|J\rangle\langle J| \ . \tag{9}$$

Iterating Eq. (9) from $\Omega^{(0)} = P$ and regrouping the terms according to their overall power in $V(J)(|J\rangle \in L_P)$, one arrives at the recursive formula for perturbative corrections

$$\Omega^{(n)} = \sum_J \frac{Q}{e_J - H_0(J)} \times \left(V(J)\Omega^{(n-1)} - \sum_{m=1}^{n-1} \Omega^{(m-1)} PV(J)\Omega^{(m)} \right) |J\rangle\langle J| \ . \tag{10}$$

Equation (4) readily provides the corresponding expansion of $\tilde{H}$

$$\tilde{H}^{(0)} = \sum_J |J\rangle e_J \langle J| \tag{11}$$

$$\tilde{H}^{(n)} = \sum_J PV(J)\Omega^{(n-1)}|J\rangle\langle J| \ . \tag{12}$$

Taking into account that $PV(J)Q = PHQ \ \forall J : |J\rangle \in L_P$, at second order we get

$$\tilde{H}^{(2)} = \sum_J PH \frac{Q}{e_J - H_0(J)} H|J\rangle\langle J| \ . \tag{13}$$

The extension of the present perturbative approach to a more general class of zero-order operators, which do not satisfy Eq. (8), is rather straightforward. In this case the explicit recursive formulas (9, 10, 12) are replaced by recursive commutator relations. Provided that a matrix or second quantized representation of the involved operators is used, these relations are readily transformed into systems of linear equations for matrix elements or second-quantization amplitudes.

Now we turn to the state-selective formulation of the theory for a many-electron system, assuming for instance that we are interested in a single-target state $|\psi_\mu\rangle$. Suppose that the spin-orbital set is obtained from an orthogonal set of space orbitals; the spin orbitals will be labeled by the indices of their space parts $(r, s, t, \ldots)$ and spin factors $(\sigma, \tau, \ldots = \alpha \text{ or } \beta)$. The model space is defined by the choice of its basis composed of Slater determinants. The zero-order operator $H_0(J)$ corresponding to the model determinant $|J\rangle$ is specified as

$$H_0(J) = \sum_{\substack{s\sigma \\ (s\sigma)\text{ occupied} \\ \text{in } |J\rangle}} \varepsilon^+_{s\sigma} a^\dagger_{s\sigma} a_{s\sigma} + \sum_{\substack{t\tau \\ (t\tau)\text{ empty} \\ \text{in } |J\rangle}} \varepsilon^-_{t\tau} a^\dagger_{t\tau} a_{t\tau} \tag{14}$$

[14]. The entities $\{\varepsilon^+_{s\sigma}\}$ and $\{\varepsilon^-_{s\sigma}\}$ are the Koopmans-like spin-orbital ionization potentials (IP) and electron affinities (EA) with opposite signs, defined with respect to the multiconfigurational state $|P\psi_\mu\rangle$ (i.e. the target vector of $\tilde{H}$):

$$\varepsilon^+_{s\sigma} = \left\langle P\psi_\mu | H | P\psi_\mu \right\rangle - \left\langle P\psi_\mu | a^\dagger_{s\sigma} H a_{s\sigma} | P\psi_\mu \right\rangle \left(n^\mu_{s\sigma}\right)^{-1} \tag{15}$$

$$\varepsilon^-_{s\sigma} = \left\langle P\psi_\mu | a_{s\sigma} H a^\dagger_{s\sigma} | P\psi_\mu \right\rangle \left(1 - n^\mu_{s\sigma}\right)^{-1} - \left\langle P\psi_\mu | H | P\psi_\mu \right\rangle \ . \tag{16}$$

Here $\left|P\psi_\mu\right\rangle$ is supposed to be normalized and

$$n^\mu_{s\sigma} = \left\langle P\psi_\mu | a^\dagger_{s\sigma} a_{s\sigma} | P\psi_\mu \right\rangle \tag{17}$$

are spin-orbital occupation numbers. It should be underlined that the dependence of the zero-order operators on an eigenvector of the operator $\tilde{H}$, which should be determined, suggests the use of self-consistency principle in practical implementations of the theory.

Introducing the spin-orbital particle and hole Fock operators

$$f^+_{s\sigma,t\sigma} = a^\dagger_{s\sigma}[a_{t\sigma}, H] \ , \tag{18}$$

$$f^-_{s\sigma,t\sigma} = -a_{s\sigma}\left[a^\dagger_{t\sigma}, H\right] \ , \tag{19}$$

one can write down the definitions (15–16) in the form

$$\varepsilon_{s\sigma}^{+}=\left\langle P\psi_{\mu}\middle|f_{s\sigma,s\sigma}^{+}\middle|P\psi_{\mu}\right\rangle\left(n_{s\sigma}^{\mu}\right)^{-1}\ ,\tag{20}$$

$$\varepsilon_{s\sigma}^{-}=\left\langle P\psi_{\mu}\middle|f_{s\sigma,s\sigma}^{-}\middle|P\psi_{\mu}\right\rangle\left(1-n_{s\sigma}^{\mu}\right)^{-1}\ .\tag{21}$$

The energy denominators appearing in the expansion (10) will always be composed of the differences between IP-like and EA-like entities, in a strict analogy with the conventional (single-reference) Møller-Plesset perturbation theory. Note that this analogy does not hold for the multiconfiguration perturbation theories employing any common set of orbital energies and can be restored only by introducing appropriate denominator shifts [6].

Further, the $\varepsilon_{s\sigma}^{+}$ and $\varepsilon_{s\sigma}^{-}$ values are separable with respect to the fragmentation of the many-electron system provided that the model space is complete and no orbital can be delocalized between separated fragments. As has been shown in [22, 24], this feature ensures the separability and therefore the size consistency at least for the second-order results.

Note that the $\varepsilon_{s\sigma}^{+}$ values are not defined for secondary spin orbitals; similarly, no EA-like entity can be associated with a core spin orbital. However, this does not give rise to any problems since such values do not enter the expressions for perturbative corrections. For reasonable choices of a model space, the differences $\varepsilon_{s\sigma}^{+}-\varepsilon_{t\tau}^{-}$ for any core or active spin orbital $(s\sigma)$ and any active or secondary spin orbital $(t\tau)$ are not expected to be small or positive, and ill-defined energy denominators cannot appear at any order. It is worth discussing the potentially dangerous situation when the occupation number of an active spin-orbital approaches 0 (or 1). Taking into account the peculiar importance of double (rather than single) excitations to correlating spin orbitals [27], one realizes that the annihilation of one electron on an early empty (correlating) spin-orbital normally yields a highly excited ionic wavefunction. The associated $\varepsilon_{s\sigma}^{+}$ value should be very low (see numerical illustrations in Sect. 3 and [22]), giving rise to large negative energy denominators and ensuring the smallness of corresponding perturbative corrections. This result should be considered as reasonable because no correction of this type appears for purely empty (secondary) spin orbitals. Similarly, one should expect to obtain small contributions from excitations to almost filled orbitals characterized by rather high EA-like energies.

It should be underlined that the elimination of small denominators is not sufficient to ensure the convergence of perturbative expansions. For large complete model spaces the choice (14–16) results in strong diagonal perturbations, which enter the numerators of $\tilde{H}^{(n)}, n\geq 3$ and can induce the divergence in higher orders. As has been pointed out in [22], in such situations the convergent analogues of expansions (9–12) can be obtained in the frame of intermediate Hamiltonian theory [6, 19] via replacing the starting Bloch equation (1) by the so-called shifted Bloch equation [21, 26]. The price to be paid is the loss of information on all the states except the target one and the difficulties in achieving a strict size consistency in the third and higher finite orders. With a reasonable choice of shift operator, this transformation does not affect $\tilde{H}^{(n)}, n\leq 2$. Since we are concentrating on the second-order method, we prefer to skip the detailed description of the intermediate Hamiltonian form of the multipartitioning theory, which can be found elsewhere [22].

One of the main drawbacks of the spin-orbital formulation of the method presented above consists in an incorrect treatment of spin eigenstates. If the projection of the total spin on z axis (S_z) differs from zero, then $\varepsilon_{s\alpha}^{+}\neq\varepsilon_{s\beta}^{+}$ and $\varepsilon_{s\alpha}^{-}\neq\varepsilon_{s\beta}^{-}$. This leads to spin contaminations of the perturbed wave vector. Moreover, the calculated energies for the states with non-zero spin will depend on the particular choice of S_z.

Another logical and practical aspect of this problem, which apparently blocks the passage from the determinant basis to that of spin-adapted configuration state functions (CSF), manifests itself even for $S_z=0$ states. The second-order energy denominator associated with a substitution operator $|J\rangle\rightarrow|A\rangle, |J\rangle\in L_P,\ |A\rangle\in L_Q$ depends explicitly on its spin part, as is illustrated by the following example. Consider a model-space Slater determinant $|J\rangle=a_{s\alpha}^{\dagger}a_{t\beta}^{\dagger}|\mathrm{core}\rangle$ and two outer space determinants, $|A\rangle=a_{t\beta}^{\dagger}a_{n\alpha}^{\dagger}|\mathrm{core}\rangle$ and $|A'\rangle=a_{t\alpha}^{\dagger}a_{n\beta}^{\dagger}|\mathrm{core}\rangle$, and suppose that the z projection of the total spin is zero (i.e. $\varepsilon_{s\alpha}^{+}=\varepsilon_{s\beta}^{+}=\varepsilon_{s}^{+}$ etc.). Since the space parts of $|A\rangle$ and $|A'\rangle$ coincide, these determinants should enter the spin-adapted wavefunction with equal weights, but in fact the energy denominators corresponding to the substitutions $|J\rangle\rightarrow|A\rangle$ and $|J\rangle\rightarrow|A'\rangle$ will differ by the value $\varepsilon_{t}^{+}-\varepsilon_{t}^{-}$.

In this work we propose a spin-adapted version of the method that retains the attractive features of the previous formulation but avoids the spin contaminations and ensures necessary spin invariances. It is natural to suppose that the model space is defined by a set of spatial electron configurations and therefore the model space projector commutes with all spin operators. The central point of the new approach consists in replacing the spin-orbital Fock-like operators and occupation numbers in Eqs. (20, 21) by their orbital (spin-free) analogues:

$$\varepsilon_{s}^{+}=\left\langle P\psi_{\mu}\middle|F_{ss}^{+}\middle|P\psi_{\mu}\right\rangle\left(N_{s}^{\mu}\right)^{-1}\ ,\tag{22}$$

$$\varepsilon_{s}^{-}=\left\langle P\psi_{\mu}\middle|F_{ss}^{-}\middle|P\psi_{\mu}\right\rangle\left(2-N_{s}^{\mu}\right)^{-1}\ ,\tag{23}$$

where

$$F_{st}^{+}=f_{s\alpha,t\alpha}^{+}+f_{s\beta,t\beta}^{+},\ F_{st}^{-}=f_{s\alpha,t\alpha}^{-}+f_{s\beta,t\beta}^{-},\ N_{s}^{\mu}=n_{s\alpha}^{\mu}+n_{s\beta}^{\mu}\ .\tag{24}$$

Furthermore, one should avoid the dependence of an energy denominator on the spin part of the corresponding substitution operator. This requirement is easily fulfilled if we admit the appearance of several two-body terms in $H_0(J)$

$$H_0(J)=\sum_{\substack{r\\ \text{2-occ.}\\ \text{in }|J\rangle}}\varepsilon_{r}^{+}\hat{E}_{r}^{r}+\sum_{\substack{s\\ \text{1-occ.}\\ \text{in }|J\rangle}}\left(\varepsilon_{s}^{+}\hat{E}_{s}^{s}+\frac{1}{2}\left(\varepsilon_{s}^{-}-\varepsilon_{s}^{+}\right)\hat{e}_{ss}^{ss}\right)+\sum_{\substack{t\\ \text{empty}\\ \text{in }|J\rangle}}\varepsilon_{t}^{-}\hat{E}_{t}^{t}\ .\tag{25}$$

Here we used the standard notation for one- and two-particle excitation operators

$$\hat{E}_s^s = a_{s\alpha}^\dagger a_{s\alpha} + a_{s\beta}^\dagger a_{s\beta}, \quad \hat{e}_{ss}^{ss} = 2a_{s\alpha}^\dagger a_{s\beta}^\dagger a_{s\beta} a_{s\alpha} \ . \tag{26}$$

The operator (25) is completely defined by the set of spatial occupancies $\{N_s^J\}$ associated with the determinant $|J\rangle$. It is worth noting that Eq. (25) uses essentially the OPT2 Ansatz for H_0 [29, 30] with J-dependent parameters:

$$H_0(J) = \sum_r \varepsilon_r'(J)\hat{E}_r^r - \sum_{\substack{s \\ \text{1-occ} \\ \text{in } |J\rangle}} \eta_s \hat{E}_s^s \left(2 - \hat{E}_s^s\right) \ ,$$

$$\varepsilon_r'(J) = \left(N_r^J \varepsilon_r^+ + \left(2 - N_r^J\right)\varepsilon_r^-\right)/2, \quad \eta_s = \left(\varepsilon_s^+ - \varepsilon_s^-\right)/2 \ . \tag{27}$$

Owing to the spin-scalar nature of $H_0(J)$ and P, no spin contamination can occur in finite-order calculations. Moreover, the new formulation enables us to replace the basis of determinants by any spin-adapted CSF basis. Provided that the spatial occupancy distributions (spatial electron configurations) of model-space and outer-space determinants cannot coincide, each of the zero-order operators is spin-independent and no spin contaminations can occur. Moreover, the invariance of $H_0|J\rangle$'s with respect to rotations within the subspaces corresponding to given sets of orbital occupancies (spin flips) enables us to replace the basis of determinants by the spin-adapted CSF basis.

One readily verifies that the energy denominator associated with a substitution $|J\rangle \rightarrow |A\rangle$, which now depends only upon the changes in spatial occupancies, is still composed of the differences between IP-like and EA-like entities:

$$\langle J|H_0(J)|J\rangle - \langle A|H_0(J)|A\rangle = \sum_{\substack{s: \\ N_s^A \langle N_s^J}} \left(N_s^J - N_s^A\right)\varepsilon_s^+ - \sum_{\substack{t: \\ N_t^A \rangle N_t^J}} \left(N_t^A - N_t^J\right)\varepsilon_t^- \ , \tag{28}$$

where N_s^A stands for the occupancy of the spatial orbital s in the outer-space basis vector $|A\rangle$.

As well as for the initial spin-orbital formulation, the use of diagonal zero-order operators (25) ensures the maximum computational simplicity of the second-order scheme. The corresponding shortcoming consists in the lack of invariance of the finite-order results under orbital rotations conserving the model space (e.g. under the rotations with inactive, active and secondary orbital subspaces when the model space is complete).

3 Pilot applications

In this section we present several applications of the spin-adapted multi-partitioning perturbation theory restricted to second order [MPMRPT(2)] to calculations of energy splitting between molecular electronic states with different spin multiplicities. In all cases complete model spaces optimized by the CASSCF method [31, 32] were used. In the contradistinction with the CASSCF energy functional, the zero-order operators (22–25), and therefore the resulting effective Hamiltonians, are not invariant with respect to orbital rotations within inactive, active and secondary subspaces, and the orbitals should be specified unambiguously. A priori it seems advantageous to employ the CASSCF canonical MO (CMO), which diagonalizes the inactive, active and secondary subblocks of the generalized Fock operator [9–11]. Taking into account that this operator coincides with the one-particle part of the Hamiltonian written in the generalized normal form [33] with respect to multiconfigurational vacuum state (CASSCF wavefunction), this choice should reduce the risk of large non-diagonal perturbations. In order to estimate the stability of the results with respect to MO rotations, we also used the bases of CASSCF natural MO (NMO), which were assumed to coincide with CMO in the inactive and secondary subspaces.

As has been pointed out in Sect. 2, the dependence of the orbital energies $\{\varepsilon_s^+, \varepsilon_s^-\}$ on the target eigenvector of $\tilde{H}$ implies the use of iterative computational procedure. In addition to the self-consistent results, we also present those obtained by a simplified non-iterative scheme based on replacing the $\tilde{H}$ eigenvectors in Eqs. (22, 23) by corresponding solutions to the CASSCF problem.

3.1 $^1A_1$-$^3B_1$ separations in CH_2 and SiH_2

The adiabatic singlet-triplet splittings in CH_2 and SiH_2 radicals provide a sensible test for perturbative approaches owing to a particular importance of differential correlation effects. Although fortuitously good estimates of the 1^1A_1-1^3B_1 energy separations are readily obtained at the valence CASSCF level, attempts to incorporate the dynamic correlations by second-order procedures usually lead to a serious deterioration of results, (see [34] and references therein).

To enable the direct comparison of the MPMRPT(2) estimates with the full CI data of Bauschicher and Taylor [35, 36], we used the same atomic basic sets ([2s] H, [4s2p1d] C, and [5s3p1d] Si) and equilibrium geometries. The splittings were also computed for symmetrically distorted $SiH_2(r(\text{Si-H}) = 1.5r_e$ and $2r_e)$. While such splittings are not directly related to any physical characteristics, this offered the possibility to simulate the situations with strong configuration mixing. Only six electrons were correlated. The active MO subspaces were spanned by six MOs correlating with valence atomic orbitals. The behavior of IP- and EA-like energies is illustrated in Fig. 1.

The results of our calculations are summarized in the Table 1. In all cases the deviations of the MPMRPT(2) splittings from the corresponding full CI values were less than 1 kcal/mol, with a slight underestimation of relative energies of singlet state. This accuracy and a regular behavior of the deviations stand in contrast with the poor results obtained within the standard CASPT(2) approach [10], which also uses the spinless Fock operator at zeroth order. The simplified version of our method employing the CASSCF wavefunction for the computation of

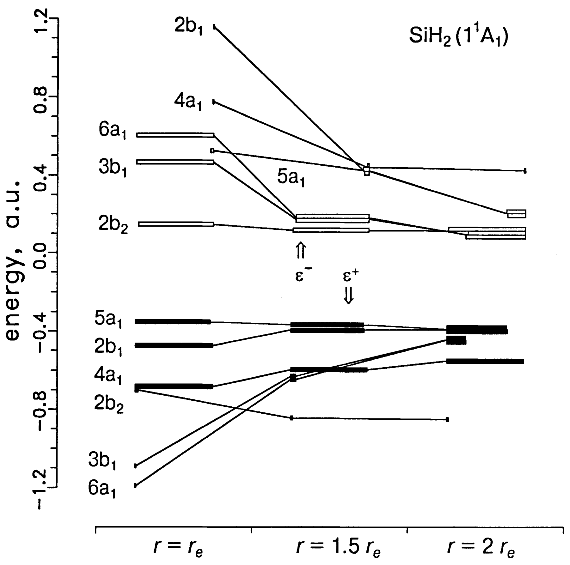

Fig. 1. IP-like orbital energies (*filled rectangles*) and EA-like orbital energies for the SiH_2 canonical MOs. The size of the symbols for ε^+ and ε^- is proportional to particle (N_s^μ) and hole ($2-N_s^\mu$) occupancies, respectively

IP- and EA-like orbital energies yields essentially the same estimates as the full (self-consistent) procedure. This might be explained by a relatively weak interference between the model-space and remainder correlation effects: the maximal rotation angle of the target model-space vector caused by the incorporation of second-order terms was only 3.7°($^3B_1$ state of SiH_2 at r (Si-H) $= 1.5r_e$). The results were also relatively stable with respect to replacing the canonical MOs by natural MOs.

3.2 ScH

A proper account for dynamic correlations, including those involving the core $3sp$-shell, is known to be of crucial importance even for a qualitatively correct description of the low-lying states of the molecules containing transition-metal atoms. The simplest example is provided by the ScH molecule, where the neglect of dynamic correlations results in wrong symmetry type and spin multiplicity of the ground state [37, 38].

Table 1. The singlet-triplet separations in CH_2 and SiH_2, kcal/mol

	CH_2	SiH_2		
Geometry	r_e	r_e	$1.5r_e$	$2r_e$
Full CI[a]	−11.97	17.50	17.18	4.32
CASSCF	−12.82	16.38	18.49	6.57
MPMRPT(2):				
CMO[b]	−12.82	17.22	17.06	3.53
CMO	−12.84	17.24	17.06	3.56
NMO[b]	−12.92	17.22	16.97	3.44
NMO	−12.93	17.22	16.99	3.47
CASPT(2)[c]	−15.43	15.12	15.63	3.64
CASPT(2)[d]	−12.95 ÷ −13.20	16.70 ÷ 16.84		

[a] [35, 36]

[b] Simplified non-iterative scheme ($\{\varepsilon_s^+, \varepsilon_s^-\}$ were defined with respect to the CASSCF wavefunctions)

[c] Non-degenerate multiconfiguration perturbation theory with CASSCF zero-order wavefunctions, [10]

[d] The zero-order Fock-like operator was modified in order to enlarge the energy gap between active and secondary orbitals, [34]

We calculated the energies of the two lowest states of ScH ($1^1\Sigma^+$ and $1^3\Delta$) at their equilibrium geometries ($r_e = 3.41$ and 3.66 a.u. respectively, [37]). The Sc basis comprised the $(14s11p6d)/[8s7p3d]$ set of Watchers and Hay with uncontracted $3p$ component, diffuse s, p, d functions (exponential parameters $\alpha_s = \alpha_p = 0.01$, $\alpha_d = 0.012$) and two sets of f-functions ($\alpha_f = 1.40$, $\alpha_f = 0.27$) recommended by Anglada et al. [34]. For the hydrogen atom we used the $(7s3p)/[3s2p]$ basis from [41] extended by a single d-manifold ($\alpha_d = 0.6$). The model spaces were obtained by the CASSCF calculations with 7 active MO arising from valence AO ($4s$, $3d$ Sc and 1s H). Note that in order to preserve the valence-like character of active MOs, we had to freeze the core orbitals 1σ–5σ, 1π–2π ($1s$-$3s$, $2p$-$3p$ Sc) after the spin-restricted SCF calculations. At the MPMRPT(2) step, 12 electrons (excepting the inner $1s2s2p$ core of Sc) were correlated.

Both SCF and valence CASSCF methods place the singlet state above the triplet one. The inclusion of dynamic correlations via the MPMRPT(2) procedure reverse the ordering of these states and bring the estimate of adiabatic transition energy in a reasonable agreement with the results of much more sophisticated and expensive calculations (Table 2). Note that the singlet-triplet splitting value is small in comparison with the total correlation energies, and this agreement indicates a well-balanced treatment of correlations in the states of different physical nature. As well as in previous examples, the simplified non-iterative scheme provides essentially the same results as the full self-consistent calculations and the effect of replacing the canonical MOs by CASSCF NMOs is negligible.

3.3 Sc_2

The relative energies of the low-lying electronic states of the diatomic cluster of scandium are essentially governed

Table 2. Correlation and relative energies for the $X^1\Sigma^+$ and $1^3\Delta$ states of the ScH molecule

	Correlation energy, eV		ΔE, eV
	$X^1\Sigma^+$	$1^3\Delta$	
SCF	0	0	−0.761
CASSCF	1.29	0.73	−0.198
MPMRPT(2):			
CMO[a]	8.85	7.88	0.216
CMO	8.86	7.88	0.227
NMO[a]	8.85	7.88	0.211
NMO	8.86	7.88	0.222
MRD CI + extrp[b]	9.52	8.40	0.34
MCPF[c]			0.19

[a] Simplified non-iterative scheme

[b] Extrapolation to full CI, [38]

[c] Modified coupled pair functional method, [37]

by correlation effects. A peculiarity of this system consists in that the high-spin ground state ($X^5\Sigma_u^-$) is strongly favored by the dynamic correlations, while the low-lying singlet and triplet states are much less correlated [38–40].

We used the same Sc basis set as in the calculations on ScH. Two electronic states were studied, the ground $X^5\Sigma_u^-$ state and the state $1^3\Delta_u$, which appears to be the lowest one according to the valence-like MCSCF approach [44]. The equilibrium geometries were taken from [44]. Active spaces were spanned by 12 MO correlating with 4*s* and 3*d* orbitals of Sc atoms. As well as in the previous case, only the inner (1*s*2*s*2*p*) core was excluded from correlation treatment.

At the spin-restricted SCF level, the $1^5\Sigma_u^-$ state is characterized by a rather high energy with respect to the $1^3\Delta_u$ one (Table 3). The valence-like CASSCF calculations reduced the gap but the state ordering remained incorrect. The subsequent MPMRPT(2) treatment rectified the error and yielded the $X^5\Sigma_u^- - 1^3\Delta_u$ excitation energy values, which are in good agreement with the most trustworthy estimate of Åkeby and Pettersson [44]. It is interesting to note that the differential dynamic correlation energy was as large as 1 eV. The rotations of target eigenvectors associated with the incorporation of dynamic correlations were not negligible (7° and 6.5° for the $X^5\Sigma_u^-$ and $1^3\Delta_u$ states respectively) and corresponded to the increase in the weights of dominant configurations.

3.4 *Cu*$_2$

The structure of the ground ($X^1\Sigma_g^+$) and the lowest excited ($a^3\Sigma_u^+$) electronic states of the Cu$_2$ cluster can be qualitatively described in terms of bonding and antibonding combinations of 4*s*-orbitals in the presence of [Ar]$3d^{10}$ atomic cores. However, the neglect of dynamic correlations involving these rather diffuse and high-energy cores leads to very poor quantitative results. We computed the adiabatic $X^1\Sigma_g^+–a^3\Sigma_u^+$ splitting using the experimental equilibrium geometries [45] and standard [6s5p4d2f] ANO basis set [45]. At the SCF level the singlet-triplet separation was estimated to be 0.941 eV, i.e. less than half of the well-established experimental value (1.903 eV, [45]). The CASSCF calculations with two active MO ($4s\sigma_g, 4s\sigma_u^*$), which included the right-left correlations but completely ignored the dynamic ones lowered the singlet energy only by 0.252 eV, providing the energy splitting 1.193 eV (the triplet state is not affected by right-left correlations). The MPMRPT(2) method starting with the CASSCF model spaces and correlating 38 electrons (including the 3*s*, 3*p* and 3*d* shells) yielded the splitting estimate with an accuracy ca 0.1 eV (2.025 and 2.026 for simplified and complete procedures respectively). The interference of dynamic and right-left correlations manifested itself in favoring the bonding structure of the ground state (the formal bond order increased from the CASSCF value 0.938 to 0.967).

Table 3. Correlation and relative energies for the $X^5\Sigma_u^-$ and $1^3\Delta_u$ states of the Sc$_2$ molecule

	Correlation energy, eV		ΔE, eV
	$X^5\Sigma_u^-$	$1^3\Delta_u$	
SCF	0	0	−1.857
CASSCF	2.06	0.75	−0.541
MPMRPT(2):			
CMO[a]	17.92	15.57	0.494
CMO	17.95	15.59	0.507
NMO[a]	17.94	15.58	0.505
NMO	17.96	15.59	0.515
ACPF[b]			0.391

[a] Simplified non-iterative scheme

[b] Averaged coupled pair functional method with CASSCF reference function, [40]

4 Conclusions

A spin-adapted version of the state-selective multipartitioning perturbation theory is presented. As well as in the original (spin-orbital) formulation [22], several partitionings of the total Hamiltonian into a zero-order part and a perturbation are employed simultaneously. Each zero-order operator $H_0(J)$ is completely defined by the set of spatial orbital occupancies of the corresponding basis function $|J\rangle$ (Slater determinant or CSF), commutes with the total spin and is degenerate within each subspace associated with a definite spatial electron configuration. Owing to these properties of zero-order operators, the eigenvectors of the second-order effective Hamiltonian are pure spin functions; therefore, the method offers the possibility of qualitatively correct treatment of electronic states with different spin multiplicities.

Avoiding the spin contaminations and spurious dependence of calculation results on the choice of the reference *z* axis, the novel formulation retains the main attractive features of the conventional state-selective multipartitioning MRPT. The energy denominators are still composed of differences between IP-like and EA-like one-electron energies; the separability of second-order results for complete model spaces is ensured, provided that no orbital is delocalized between the separated subsystems. As was demonstrated in a series of pilot applications, the method does not suffer from illdefined energy denominators even in calculations with relatively large complete model spaces.

The second-order estimates of energy separations between the electronic states with different spin multiplicities were obtained for several systems. The accuracy of the results appears to be encouraging, taking into account the low computational cost. One should note an adequate description of differential correlation effects associated with 3*d*-shells, which is known to be a particularly difficult task for ab initio methods. While the method is not invariant under MO rotations, the calculated energy differences were found to be relatively stable with respect to transformations from canonical to natural active MO basis sets.

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Appendix

To obtain an Hermitian effective Hamiltonian, it is convenient to employ the wave operator obeying the isometry requirements [46]

$$P\Omega^{\dagger}\Omega P = P, \quad (P\Omega P)^{\dagger} = P\Omega P \ . \tag{29}$$

Let us first consider the model space part of the Bloch equation

$$PH\Omega P = P\Omega P\tilde{H} \tag{30}$$

and split it into "symmetrized" projections on model space vectors $\{|J\rangle\}$

$$|J\rangle\langle J|H\Omega P + PH\Omega|J\rangle\langle J| = |J\rangle\langle J|\Omega P\tilde{H} + P\Omega P\tilde{H}|J\rangle\langle J|, \quad |J\rangle \in L_P \ . \tag{31}$$

When introducing the J-dependent partitioning (6–8) and switching off the perturbations, one immediately arrives at the expression (11) for $\tilde{H}^{(0)}$. The extraction of linear terms yields

$$\tilde{H}^{(1)} = \frac{1}{2}\sum_J \left(|J\rangle\langle J|V(J)P + PV(J)|J\rangle\langle J|\right) = PHP - \tilde{H}^{(0)} \ . \tag{32}$$

At n-th order ($n > 1$) we get

$$\begin{aligned} &|J\rangle\langle J|\left[\Omega^{(n)}, H_0(J)\right]P + P\left[\Omega^{(n)}, H_0(J)\right]|J\rangle\langle J| \\ &\quad = |J\rangle\langle J|\left(V(J)\Omega^{(n-1)}P - \sum_{m=0}^{n-1}\Omega^{(m)}P\tilde{H}^{(n-m)}\right) \\ &\qquad + P\left(V(J)\Omega^{(n-1)} - \sum_{m=0}^{n-1}\Omega^{(m)}P\tilde{H}^{(n-m)}\right)|J\rangle\langle J| \ . \end{aligned} \tag{33}$$

Since $P\Omega^{(0)}P$ and $\{H_0(J)\}, |J\rangle \in L_P$ are Hermitian operators, the l.h.s. of Eq. (33) is anti-Hermitian. Adding to Eq. (33) its Hermitian conjugate, one eliminates the commutators and obtains the expression for $\tilde{H}^{(n)} = \tilde{H}^{(n)\dagger}$ in terms of lower-order entities:

$$\begin{aligned} \tilde{H}^{(n)} &= \frac{1}{4}\sum_J \Big(|J\rangle\langle J|\left(G_J^{(n)} + G_J^{(n)\dagger}\right) \\ &\qquad + \left(G_J^{(n)} + G_J^{(n)\dagger}\right)|J\rangle\langle J|\Big) \ , \\ G_J^{(n)} &= PV(J)\Omega^{(n-1)}P - \sum_{m=1}^{n-1}P\Omega^{(m)}P\tilde{H}^{(n-m)} \end{aligned} \tag{34}$$

(cf. [46, 47]). The multipartitioning perturbative treatment of the Q-P block of Eq. (1) analogous to that described in the Sect. 2 gives

$$\begin{aligned} Q\left[\Omega^{(n)}, H_0(J)\right]|J\rangle\langle J| = Q\Bigg(&V(J)\Omega^{(n-1)}. \\ &- \sum_{m=1}^{n-1}\Omega^{(m)}\tilde{H}^{(n-m)}\Bigg)|J\rangle\langle J| \ . \end{aligned} \tag{35}$$

Equations (34, 35) together with the order-by-order form of the isometry conditions (28)

$$P\Omega^{(n)}P = -\frac{1}{2}\sum_{m=1}^{n-1}P\Omega^{(m)\dagger}\Omega^{(n-m)}P \tag{36}$$

[43] completely define the multipartitioning perturbation expansions for the Hermitian effective Hamiltonian and the corresponding wave operator. Note that the second-order correction

$$\tilde{H}^{(2)} = \frac{1}{2}\sum_{JJ'}|J\rangle\langle J|H\left(\frac{Q}{e_J - H_0(J)} + \frac{Q}{e_{J'} - H_0(J')}\right)H|J'\rangle\langle J'| \tag{37}$$

coincides with the symmetrized form of Eq. (13), in analogy with the conventional quasidegenerate perturbation theory [1].

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