Unitary perturbation theory applied to multiconfigurational reference functions

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Abstract

Unitary parametrization of the wave operator in the form suggested by Mayer is studied in the multireference framework. The investigated unitary perturbation theory (UPT) constructs a first correction in terms of the functions having nonzero interaction with the reference state via the Hamiltonian. Parameters in the exponential of the wave operator are determined by two dimensional eigenvalue equations. Due to the unitary mapping, UPT is unaffected by the quasi-degeneracy problem, making it an ideal tool for correcting multireference starting functions. Lack of size-consistency is however a shortcoming of the method.

Applications of UPT as well as the related degeneracy-corrected PT (DCPT) are presented on intruder prone examples like the symmetric dissociation of the water molecule, the BeH_2 system and the two lowest lying states of the scandium dimer. Size consistency violation is analysed and evaluated on the example of the water dimer. Tractability of excited states by UPT is examined by computing the singlet-triplet splitting of the CH_2 molecule.

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INTRODUCTION

Describing dynamic along with static correlation of the electrons in molecules has been a persisting challenge of electronic structure theory. Among the strategies commonly used, perturbation theory (PT) applied to a multi-determinantal reference function represents an important branch. Although a multitude of methods have been developed in this field, the technique that would confidently fulfill the basic expectations of extensivity, consistency, intruder-free character and invariance to orbital rotations (in case the reference function exhibits this property) seems to be yet missing.

Widespread methods of the "diagonalize then perturb" type *e.g.* CASPT2[1,2] or MRMP[3,4] struggle with size-inconsistency[5,6]. More importantly, this class of techniques are prone to the intruder-state problem, inducing the need of active spaces larger than warranted by static correlation. This latter problem can be managed by applying level-shifts[7–11] which however renders a hand tailored character to the theory. Application of two-body zero-order Hamiltonians is a promising alternative, offering balanced description of correlation effects at a larger cost[12–17].

"Perturb then diagonalize" (also termed quasi-degenerate PT) approaches constitute an other major field of development[18,19]. The chief benefit of these methods is their potential of being size-extensive[20]. A drawback, particularly of the effective Hamiltonian theories studied in the early days is their breakdown if *any* of the model functions become quasi-degenerate with an external function. In response to this serious intruder-state problem the model space has got partitioned into a primary and a secondary subspace in intermediate Hamiltonian theories[21,22] as well as in generalized Van Vleck PT[23,24]. State-specific perturbation approaches emerge by taking the idea of primary model space to the extreme of one single target state[25,26]. Multipartitioning in the context of effective Hamiltonians has been advocated as another workaround to tackle the intruder problem[27,28]. This latter theory however requires further refinement to ensure spatial symmetry conservation[29].

The above brief and necessary incomplete summary only serves to highlight some fundamental concepts and problems of multireference PT (MRPT). For more detailed account on this subject we refer to review articles[30–35].

In the present work we explore a non-standard, perturbation-like approach advocated by Mayer[36]. Forerunners of the idea appeared in a work by Lepetit and Malrieu[37] as well as in a study by Assfeld et al.[38]. Both of the latter papers investigate the handling of the quasi-degeneracy problem in PT by constructing two-by-two Hamiltonian matrices with the use of an excited function, say i, and the reference function. Expansion coefficient of function i in the first order wavefunction is taken to match the exact solution of the two-by-two matrix. This approach avoids the problem of close to zero PT denominators by substituting the well-known Rayleigh-Schrödinger amplitude formula

$$c_i = \frac{V_{0i}}{E_0^{(0)} - E_i^{(0)}} \tag{1}$$

for the divergence free expression

$$c_i = \frac{\sin\varphi_i}{\cos\varphi_i} \tag{2}$$

with

$$\varphi_i = \frac{1}{2}\arctan\left(\frac{2H_{0i}}{H_{00} - H_{ii}}\right) , \tag{3}$$

angle φ_i lying in the interval $[-\pi/4, \pi/4]$. By this modification the essential feature of first order PT is conserved, *i.e.* just one excited state is addressed at a time, interaction of the excited states is regarded as a higher order effect. The approach has a clear connection to Jacobi-rotations: Eq.(2) derives from the Jacobi angle of the rotation involving state i and the reference state, using intermediate normalization. Both Lepetit et al.[37] and Assfeld et al.[38] studied the above idea in the context of single-reference PT, taking the Hartree–Fock (HF) determinant as zero-order function. Assfeld and coworkers coined the name degeneracy-corrected PT (DCPT), a terminology we adopt presently. An application of DCPT in the context of generalized Van Vleck PT has been published by Khait et al.[24] in the multi-reference framework.

Several approximation methods are based on the technique of Jacobi rotations. Hoffmann in the 90's explored a trigonometric parametrization of the wave operator of canonical Van Vleck PT[39]. Jacobi-rotations also inspired Mayer[36] who proposed a correction scheme which handles Jacobi angles involving the reference state on an equal footing. Obviously, the outcome of a Jacobi sweep over the first row of the Hamiltonian depends on the ordering of excited states i. In Mayer's approach Jacobi-angles induced by every state i are first computed, then utilized to carry out one single rotation step, producing a corrected wavefunction that makes no distinction among states i whatsoever. Construction of the corrected wavefunction is fully analytical and involves only those states which have nonzero interaction with the reference via the Hamiltonian. The latter property is reminiscent of a standard first order wavefunction, hence the name unitary PT (UPT). This approach also avoids energy denominators, amplitudes of the corrected wavefunction emerging from the unitary mapping instead of Eq.(1). This feature has been demonstrated on the bond dissociation profile of the hydrogen molecule, starting from the HF reference function.

Carrying out Jacobi rotations successively on the first row represents an iterative procedure leading to an exact eigenvector, eigenvalue pair upon convergence. Mayer's UPT can also be performed in an iterative manner. In the latter case only the elements of the first order interacting subspace (first order configuration interaction, FOCI) contribute to the corrected function in the first step. A second step requires a MR generalization of the method, *e.g.* along the lines described presently. In this second step the expansion of the wavefunction over determinants grows considerably, since all determinants which interact with any element of the FOCI space may emerge. As the iteration proceeds, the wavefunction rapidly extends in the full-CI space. Convergence behavior of the interative application of UPT is yet under study in our laboratory. The present work does not investigate this issue, but focuses on the performance of one single correction step taken by UPT.

We consider a multi-determinantal wavefcuntion as a starting function for UPT. This situation has not been addressed previously. The motivation of such a survey is to explore whether the intruder-free nature of UPT may provide a simple method, reliable in difficult MR situations. An immediate drawback of the theory is given by its violation of size-consistency. Though size-consistency is a highly desirable property, only a few of the MRPT methods possess it. For this reason we still consider it desirable to seize the performance of UPT, accompanied by a numerical evaluation of size-inconsistency.

METHODOLOGY

Correction schemes UPT and DCPT2 are summarized briefly in the following. For deeper insight we refer to the original works by Mayer[36] and Assfeld et al.[38].

Unitary perturbation theory

As the starting point of our approach, let us consider a normalized reference function, Ψ_0. In order to develop a correction for the reference, we can take the normalized function Ψ_i (commonly called an excited function), orthogonal to Ψ_0. Adopting the standard notation $H_{ij} = \langle\Psi_i|H|\Psi_j\rangle$, the Hamiltonian written in the basis of Ψ_0, Ψ_i takes the form:

$$\boldsymbol{h}_i = \begin{pmatrix} H_{00} & H_{0i} \\ H_{i0} & H_{ii} \end{pmatrix} .$$

The description given by Ψ_0 and Ψ_i can be improved if combining them according to:

$$\begin{aligned} \Psi_0' &= \cos\varphi_i\,\Psi_0 + \sin\varphi_i\,\Psi_1 \\ \Psi_i' &= -\sin\varphi_i\,\Psi_0 + \cos\varphi_i\,\Psi_1 . \end{aligned} \tag{4}$$

Taking angle φ_i from Eq.(3), transformed functions Ψ_0' and Ψ_i' diagonalize matrix $\boldsymbol{h}_i$, *i.e.* $H_{0i}' = 0$.

Transformation between Ψ_0, Ψ_i and Ψ_0', Ψ_i' is governed by the two dimensional rotation matrix:

$$\boldsymbol{u}_i = \begin{pmatrix} \cos\varphi_i & -\sin\varphi_i \\ \sin\varphi_i & \cos\varphi_i \end{pmatrix} \tag{5}$$

which can be expressed as a matrix exponential

$$\boldsymbol{u}_i = \exp \boldsymbol{a}_i$$

with the antisymmetric $\boldsymbol{a}_i$ involving the rotation angle:

$$\boldsymbol{a}_i = \begin{pmatrix} 0 & -\varphi_i \\ \varphi_i & 0 \end{pmatrix} .$$

Usually, in a space one works with, state Ψ_i is not the only state orthogonal to Ψ_0. Considering N orthogonal functions, interacting with Ψ_0 via the Hamiltonian, matrix $\boldsymbol{a}_i$ has to be padded with zeros, accommodating φ_i in the $(i+1)$st row and column:

$$\boldsymbol{A}_i = \begin{pmatrix} 0 & 0 & \dots & -\varphi_i & \dots & 0 \\ 0 & 0 & \dots & 0 & \dots & 0 \\ \vdots & & & & & \vdots \\ \varphi_i & 0 & \dots & 0 & \dots & 0 \\ \vdots & & & & & \vdots \\ 0 & 0 & \dots & 0 & \dots & 0 \end{pmatrix} . \tag{6}$$

In the traditional Jacobi-diagonalization approach, transformations are performed successively with unitary matrices

$$\boldsymbol{U}_i = \exp \boldsymbol{A}_i \tag{7}$$

in such a way that the off-diagonal matrix elements of the Hamiltonian are decreased. Since

$$[\boldsymbol{U}_i, \boldsymbol{U}_j] \neq 0 \ ,$$

that is, two-by-two rotations do not commute, the outcome of a series of Jacobi-rotations, *e.g.* a sweep on the first row

$$\prod_{i=1}^{N} \boldsymbol{U}_i \tag{8}$$

is sequence-dependent, unless convergence is reached.

In his seminal paper^{36} Mayer suggested to replace the transformation given by Eq.(8) with a mapping which treats excited states Ψ_i on an equal footing. This was obtained by summing first the logarithms of matrices $\boldsymbol{U}_i$ to get

$$\boldsymbol{A} = \begin{pmatrix} 0 & -\varphi_1 & -\varphi_2 & \dots & -\varphi_N \\ \varphi_1 & 0 & 0 & \dots & 0 \\ \varphi_2 & 0 & 0 & \dots & 0 \\ \vdots & & & & \vdots \\ \varphi_N & 0 & 0 & \dots & 0 \end{pmatrix} ,$$

and then taking its exponential

$$\boldsymbol{U} \quad = \quad \exp \boldsymbol{A} \ .$$

In general it may not be possible to give a closed form for a matrix exponential. Due to the simple structure of matrix $\boldsymbol{A}$ however, its exponential is expressible with the use of trigonometric functions:

$$\boldsymbol{U} = \begin{pmatrix} \cos\varphi & -x_1 \sin\varphi & -x_2 \sin\varphi & \dots & -x_i \sin\varphi \dots & \\ x_1 \sin\varphi & 1 + x_1^2(\cos\varphi - 1) & x_1 x_2(\cos\varphi - 1) & \dots & x_i x_1(\cos\varphi - 1) & \dots \\ x_2 \sin\varphi & x_1 x_2(\cos\varphi - 1) & 1 + x_2^2(\cos\varphi - 1) & \dots & x_i x_2(\cos\varphi - 1) & \dots \\ \vdots & & \vdots & & \vdots & \\ x_i \sin\varphi & x_1 x_i(\cos\varphi - 1) & x_2 x_i(\cos\varphi - 1) & \dots & 1 + x_i^2(\cos\varphi - 1) & \dots \\ \vdots & & \vdots & & \vdots & \\ x_N \sin\varphi & x_1 x_N(\cos\varphi - 1) & x_2 x_N(\cos\varphi - 1) & \dots & x_i x_N(\cos\varphi - 1) & \dots \end{pmatrix} , \tag{9}$$

adopting the notations

$$\varphi = \left(\sum_{i=1}^{N} \varphi_i^2 \right)^{1/2} \tag{10}$$

and

$$x_i = \frac{\varphi_i}{\varphi} \ . \tag{11}$$

The structure of the unitary matrix Eq.(9) clearly reflects the fact that no distinction is made among basis functions Ψ_i for $i \geq 0$. The first column of $\boldsymbol{U}$ gives the corrected function, expanded on the basis $\{\Psi_i\}_{i=0}^{N}$ according to

$$\Psi_{\mathrm{UPT}} \quad = \quad \cos\varphi \, \Psi_0 \ + \ \sum_{i=1}^{N} \frac{\varphi_i}{\varphi} \sin\varphi \, \Psi_i \ . \tag{12}$$

With angles φ_i determined from Eq.(3) and φ taken from Eq.(10), Ψ_{UPT} of Eq.(12) is the wavefunction behind the method referred to as UPT. The corresponding energy expression reads

$$\begin{aligned} E_{\mathrm{UPT}} \quad &= \quad \langle \Psi_{\mathrm{UPT}} | H | \Psi_{\mathrm{UPT}} \rangle \qquad (13) \\ &= \quad \cos^2\varphi \, H_{00} \ + \ 2 \cos\varphi \sin\varphi \sum_{i=1}^{N} x_i \, H_{i0} \ + \ \sin^2\varphi \sum_{i,j=1}^{N} x_i \, H_{ij} \, x_j \ . \end{aligned}$$

As noted by Mayer, angle φ can also be considered a parameter, subject to optimization. (Doing so, quantities x_i do not change, since, based on Eq. (10), scaling of φ by α induces the scaling of φ_i by α as well, leaving Eq. (11) uneffected.) The straightforward procedure is to define φ based on the variational condition

$$\langle \Psi_{\mathrm{UPT}} | H | \Psi_{\mathrm{UPT}} \rangle = \mathrm{min}.$$

resulting

$$\varphi_{\mathrm{opt}} = \frac{1}{2} \arctan \left(\frac{2 \sum\limits_{i=1}^{N} H_{0i}\, x_i}{H_{00} - \sum\limits_{i,j=1}^{N} x_i\, H_{ij}\, x_j} \right) . \tag{14}$$

The wavefunction of Eq.(12) calculated with the optimized angle φ_{opt} is designated as OPTUPT in what follows.

Excited functions used in multiconfigurational UPT

In order to compute the wavefunction of either UPT or OPTUPT, excited functions Ψ_i have to be specified. In the single reference approach, where Ψ_0 is the HF determinant, Ψ_i's are simply the doubly substituted determinants. Considering a model space spanned by $M+1$ orthonormal determinants $\{\Phi_i\}_{i=0}^{M}$ and a reference function expanded in the model space as:

$$\Psi_0 \;\; = \;\; \sum_{i=0}^{M} c_i \; \Phi_i \ , \tag{15}$$

excited determinants Φ_i, $1 \leq i \leq M$ are not orthogonal to Ψ_0 (unless $c_i = 0$). This situation can be handled either by introducing the overlap into the expressions of UPT, or by finding M orthonormal functions in the model space, orthogonal to Ψ_0. The latter option is particularly suited for UPT, since the wavefunction correction scheme of UPT can be regarded an orthogonalization algorithm as well (called Mayer's orthogonalization here).

To make this point apparent, we note, that the exponential of matrix $\boldsymbol{A}$, Eq.(9) provides not only the corrected function, Ψ_{UPT}, but a set of vectors orthogonal to it. These are defined by the second, third *etc.* columns of matrix $\boldsymbol{U}$. Let us now abandon the idea of determining angles φ_i from Eq.(3), and make instead the mapping

$$\begin{aligned}\cos\varphi &= c_0 \\ \sin\varphi &= \sqrt{1-c_0^2} \\ x_i &= c_i/\sin\varphi\ , \qquad i=1,\ldots,M\ .\end{aligned}$$

In words, the first column of matrix $\boldsymbol{U}$ is identified with Ψ_0, expanded on $\{\Phi_i\}_{i=0}^M$. Having quantities x_i and φ determined from this condition, columns $2,\ldots,M+1$ of matrix $\boldsymbol{U}$ define functions Ψ_i. Expansion on the basis of $\{\Phi_i\}_{i=0}^M$ is readily obtained as

$$\Psi_i \;=\; -c_0\ \Phi_0\ +\ \Phi_i\ -\ \frac{c_i}{1+c_0}\sum_{j=1}^{M} c_j\ \Phi_j\ , \qquad i=1,\ldots,M\ . \tag{16}$$

It was shown recently, that functions produced by Mayer's orthogonalization are exactly those, which would be generated if projecting Ψ_0 out of functions Φ_i, $i=1,\ldots,M$ and orthogonalizing the thus produced set by Löwdin's symmetrical scheme[40]. In the applications presented below, Ψ_i's of Eq.(16) are considered in the multiconfigurational (MC) UPT and OPTUPT schemes.

For indices $i>M$, Φ_i are trivially orthogonal to Ψ_0, as they are orthogonal to the entire model space. For this reason determinants Φ_i are considered as basis vectors Ψ_i for $i>M$.

Size-consistency issue of UPT

Let us first discuss the simplest case, the question of size-consistency of UPT in the single reference framework, without optimizing angle φ. We shall assume two closed shell systems A and B, and suppose that the Hamiltonian of the supersystem involves no inter-system interaction:

$$H^{AB} \;=\; H^A + H^B\ .$$

Quantities corresponding to subsystems are labeled by upper index, *e.g.* Φ_i^A and Φ_i^B are determinants of the subsystems. Functions in the configuration interaction (CI) space of the supersystem can be considered to be simple products of subsystem determinants, $\Phi_i^A\Phi_j^B$, since antisymmetrization is immaterial in the lack of interaction[41]. Starting from the reference function $\Phi_0^A \Phi_0^B$, the UPT wavefunction for the supersystem involves excited determinants of the type $\Phi_0^A \Phi_i^B$ and $\Phi_i^A \Phi_0^B$

$$\Psi_{\mathrm{UPT}}^{AB} \;=\; \cos\varphi^{AB}\,\Phi_0^A\Phi_0^B \;+\; \sum_{i=1}^{N^A} \frac{\varphi_i^A}{\varphi^{AB}} \sin\varphi^{AB}\,\Phi_i^A\Phi_0^B \;+\; \sum_{i=1}^{N^B} \frac{\varphi_i^B}{\varphi^{AB}} \sin\varphi^{AB}\,\Phi_0^A\Phi_i^B \;.$$

with the shorthands

$$\varphi^{AB} \;=\; \sqrt{\left(\varphi^A\right)^2 + \left(\varphi^B\right)^2}\;, \tag{17}$$

and

$$\varphi^A \;=\; \sqrt{\sum_{i=1}^{N^A} \left(\varphi_i^A\right)^2}\;.$$

Function Ψ_{UPT}^{AB} gives rise to the UPT energy for the supersystem

$$\begin{aligned} E_{\mathrm{UPT}}^{AB} \;&=\; \left(\cos^2\varphi^{AB} \;+\; \frac{\left(\varphi^B\right)^2 \sin^2\varphi^{AB}}{\left(\varphi^{AB}\right)^2}\right) H_{00}^A \\ &+\; 2\frac{\cos\varphi^{AB}\sin\varphi^{AB}}{\varphi^{AB}} \sum_{i=1}^{N^A} \varphi_i^A H_{i0}^A \;+\; \frac{\sin^2\varphi^{AB}}{\left(\varphi^{AB}\right)^2} \sum_{i,j=1}^{N^A} \varphi_i^A H_{ij}^A \varphi_j^A \\ &+\; \{A \leftrightarrow B\}\;. \end{aligned}$$

The above formula is to be compared with the UPT energy of a subsystem, *e.g.* A alone, which reads

$$E_{\mathrm{UPT}}^A \;=\; \cos^2\varphi^A\, H_{00}^A \;+\; 2\frac{\cos\varphi^A \sin\varphi^A}{\varphi^A} \sum_{i=1}^{N^A} \varphi_i^A H_{i0}^A \;+\; \frac{\sin^2\varphi^A}{\left(\varphi^A\right)^2} \sum_{i,j=1}^{N^A} \varphi_i^A H_{ij}^A \varphi_j^A\;.$$

Apparently, even in this simplest case, angle φ^{AB} brings a mixing of quantities in E_{UPT}^{AB}, spoiling the trigonometric coefficients. Taking the case of identical subsystems, the inconsistency error is given by $E_{\mathrm{UPT}}^{AA} - 2E_{\mathrm{UPT}}^A$. In this expression, the trigonometric factors in front of the three terms oscillate with φ^A and often happen to be of opposite sign. This indicates that a cancellation of errors takes place, though it is hard to judge its extent, based on the formulae.

Optimizing angle φ^{AB} brings a further mixing of subsystem quantities according to

$$\tan\left(2\varphi_{\mathrm{opt}}^{AB}\right) \;=\; \left(\frac{\frac{2}{\varphi^{AB}}\left(\sum\limits_{i=1}^{N^A} H_{0i}^A\varphi_i^A \;+\; \sum\limits_{i=1}^{N^B} H_{0i}^B\varphi_i^B\right)}{H_{00}^{AB} - \frac{1}{\left(\varphi^{AB}\right)^2}\left(\sum\limits_{i,j=1}^{N^A} \varphi_i^A\left(H_{ij}^A + \delta_{ij}H_{00}^B\right)\varphi_j^A \;+\; \sum\limits_{i,j=1}^{N^B} \varphi_i^B\left(H_{ij}^B + \delta_{ij}H_{00}^A\right)\varphi_j^B\right)}\right)$$

while for an isolated system A we have

$$\tan\left(2\varphi_{\mathrm{opt}}^{A}\right) = \left(\frac{\frac{2}{\varphi^{A}}\sum\limits_{i=1}^{N^{A}} H_{0i}^{A}\varphi_{i}^{A}}{H_{00}^{A} - \frac{1}{(\varphi^{A})^{2}}\sum\limits_{i,j=1}^{N^{A}} \varphi_{i}^{A} H_{ij}^{A}\varphi_{j}^{A}}\right) \tag{18}$$

Examining again the prefactor of the three terms in $E_{\mathrm{OPTUPT}}^{AA} - 2E_{\mathrm{OPTUPT}}^{A}$ they vary in a narrower range and follow a less oscillatory pattern.

Finally, the effect of orthogonalization in the MC case is to be accounted for. The orthogonalization described above happens to be a third source of consistency violation. In the case of two noninteracting subsystems, the direct product nature of the starting function, $\Psi_{0}^{A}\Psi_{0}^{B}$ does not ensure a product form of the orthogonal functions, $\Psi_{i}^{A}\Psi_{0}^{B}$ or $\Psi_{0}^{A}\Psi_{i}^{B}$. (This would hold if *e.g.* eigenvectors of the Hamiltonian operating in the model space would be considered.)

To gain an impression on the eventual size inconsistency, arising from the above sources, a numerical evaluation is presented among the results.

Degeneracy corrected perturbation theory

The key point of the degeneracy corrected theory by Assfeld et al.[38] is the formula for the exact correlation energy of a 2×2 system

$$E_{\mathrm{corr}} = \frac{1}{2}\left(\Delta E_{10}^{(0)} - \sqrt{\left(\Delta E_{10}^{(0)}\right)^{2} + 4V_{10}^{2}}\right)$$

with $\Delta E_{10}^{(0)} = H_{11} - H_{00}$ being the Epstein–Nesbet (EN) type[42,43] zero-order excitation energy. If there are more excited levels, the above formula is taken for each of the levels. This means a complete neglect of the interaction of excited states. Summing up for states i, the second order correction of DCPT reads

$$E_{\mathrm{DCPT}}^{(2)} = \frac{1}{2}\sum_{i\neq 0}\left(\Delta E_{i0}^{(0)} - \sqrt{\left(\Delta E_{i0}^{(0)}\right)^{2} + 4V_{i0}^{2}}\right) . \tag{19}$$

The first order wavefunction behind the DCPT2 energy expression is given by:

$$\Psi_{\mathrm{DCPT}} = \Psi_{0} + \sum_{i\neq 0}\frac{\sin\varphi_{i}}{\cos\varphi_{i}}\,\Psi_{i} \tag{20}$$

Angles φ_i play a central role both in DCPT2 and UPT, however parametrization of the wavefunctions by φ_i angles differ considerably (compare Eqs. (20) and (12)).

The motivation behind DCPT2 was to find an expression free from the divergence of PT as $\Delta E_{i0}^{(0)} \to 0$. Obviously, Eq.(19) is unaffected by this problem, irrespective of the actual definition of $\Delta E_{i0}^{(0)}$. In their test calculations, Assfeld et al. considered two choices for $\Delta E_{i0}^{(0)}$: defined by either the EN or the Møller–Plesset[44] (MP) partitioning.

Application of DCPT2 in the multireference framework is straightforward, once an orthonormal basis in the configuration space is defined. In the calculations presented below, we apply EN zero-order energies

$$\Delta E_{i0}^{(0)} = H_{ii} - H_{00} \ .$$

Khait el al.[23] analysed the MP version of DCPT in the context of Van Vleck PT and found it unsatisfactory as it gives an overcorrection for those levels which are characterized by negative or zero excitation energy at the zero order: $\Delta E_{i0}^{(0)} \leq 0$. For this reason Khait el al. introduced a damping by the hyperbolic tangent function in the DCPT2 formula. Malrieu et al.[37] also noted, that DCPT2 is expected to fall below the exact solution, since the interaction of excited states brings a considerable positive contribution to the correlation energy. Malrieu and coworkers stepped beyond DCPT2 by introducing the concept of minimal dressing, an initiative that led to the development of size-consistent, self-consistent CI[45].

RESULTS AND DISCUSSION

Symmetric dissociation of H_2O

Simultaneous stretching of the two OH bonds in the water molecule is a typical example where the quasi-degeneracy problem may show up. This affects theories that rely on a generalized valence bond type function (*e.g.* the antisymmetrized product of strongly orthogonal geminals, APSG[46]) and neglect interaction of the dissociating bonds at zero-order[13].

In the present example we adopt the APSG wavefunction as reference, with two basis functions on each OH bonds. All other geminals are kept at the HF level. This gives rise to a reference function composed of four determinants, constructed in energy optimized, natural basis. Dunning's double-zeta polarized basis set is applied[47].

Total energies and energy errors with respect to full CI (FCI) are displayed in Fig.1 as a function of the OH bond distance. The intruder free character of MC-DCPT and the MC-UPT approaches is apparent in the Figure. All three methods give a reliable description of the bond dissociation process. The overestimating character of MC-DCPT is also obvious. Interestingly MC-DCPT represents the best estimation among the three methods above 2 Å . The largest error is committed by MC-UPT without optimizing angle φ: between 18 mE$_h$ and 60 mE$_h$ in the bond distance range examined. Optimizing angle φ brings an improvement, the error of MC-OPTUPT is reduced to lie between 10 mE$_h$ and 38 mE$_h$. Apart from the opposite sign, this is comparable to the [-4,-30] mE$_h$ error range of MC-DCPT.

Size-inconsistency

To assess the extent of nonadditivity over two noninteracting subsystems, we present the results obtained for two distant water molecules in Dunning's polarized valence triple-zeta basis[48]. The OH bonds are slightly stretched to warrant a multireference based PT treatment. Tables 1 and 2 collect total energies, errors with respect to FCI as well as size-consistency errors. The reference wavefunction in Table 1 is an APSG function while the results collected in Table 2 were obtained with a complete active space (CAS) reference function. The latter choice for the reference opens the possibility to compare the errors of MC-UPT with the second order corrections by MRMP[3,4] and NEVPT[14,49]. In both Tables results by the second order of multiconfigurational PT (MCPT) are also displayed[50–52].

Comparing the energy errors of MC-UPT and MC-OPTUPT obtained with the two reference functions, a definite improvement is observed when stepping from APSG to CAS. This is not the case for the size-consistency errors though: these remain on the same order. Optimizing angle φ has practically no effect on size-inconsistency. For the APSG reference (Table 1) the last three columns of MC-UPT and MC-OPTUPT fall in the same order, while for the CAS reference (Table 2) the last column is already disturbingly large. In particular, the energy error of the dimer by MC-OPTUPT in Table 2 can be essentially attributed to the size-inconsistent nature of the theory. Large size-inconsistency in proportion to the energy error is especially striking for MC-OPTUPT and pMCPT2, since these two theories result markedly small energy errors.

Keeping in mind the balanced treatment of both the monomer and the dimer, NEVPT2 with either contraction schemes outperforms all other methods listed in Table 2. The energy error of both MRMP and MC-UPT are ten times larger than that of NEVPT2. In spite of its size-consistent nature, uMCPT2 also drops behind due to the relatively large errors committed in energy. In view of Tables 1 and 2 MC-OPTUPT and pMCPT appear to be promising alternatives of NEVPT2, provided that size-inconsistency of the former theories can be reduced.

Ground state of BeH_2

The BeH_2 system with the geometry points defined by Purvis and Bartlett[53] has been the test system of many MR based PT methods. Illustration of the geometry points is shown in Figure 3. Here we compute the molecule in a basis matching with Ref.[34] to facilitate comparison with GVVPT2[24] and SS-MRPT[26,54]. Reference function is provided by a CAS(4,4) model, with two active orbitals of a_1 and two of b_1 symmetry (classified in C_{2v}). Energy error curves of MRPT methods plotted in Fig.2 run in the range of [5,20] mE_h for MP partitioning and [-5,5] mE_h for EN partitioning. Error curves of MC-DCPT and the MC-UPT schemes are similar to EN partitioning. The difference between MC-UPT and MC-OPTUPT is hardly visible in Fig.2. It is notable that MC-UPT schemes give the least nonparallelity error: difference between the largest and smallest error along the curve is only 2.3 mE_h.

Singlet-triplet splitting of CH_2

The example of the methylene molecule was selected to test the applicability of MC-UPT methods for excited states. A CAS(6,6) model was computed as reference function, adopting the valence double zeta basis of Dunning and Hay[55], with one set of d functions on the carbon atom. Separate orbital optimization was carried out for the ground state (triplet) and the first excited state (singlet). In Table 3 we present the results for energies and energy errors. Singlet-triplet splittings listed in the last column reflect that all methods get the order of this quantity correctly. Comparing MC-DCPT with the two MC-UPT methods, MC-DCPT proves to be the less balanced. Optimizing angle φ brings a slight but systematic improvement if contrasting MC-UPT with MC-OPTUPT. According to expectations, MC-DCPT falls below FCI for both states. Although the smallest error is achieved by MC-DCPT in Table 3, it is the least balanced theory. The error of MC-OPTUPT is somewhat larger (around 10%) but it gives the best estimate for the singlet-triplet splitting with a *cca.* 3% error.

Scandium dimer

As a final example we study the intriguing case of the scandium dimer. This system has received considerable attention recently[56], due to the fact that the ordering of the two lowest states is highly sensitive to the choice of the CAS and the level shift parameters applied in CASPT2 and MRMP[57–59]. Among numerous previous works, a recent third-order NEVPT[60], a second-order GVVPT2[61] and a multireference configuration interaction (MRCI)[62] study address this question with high numerical precision and including comparison with experiment. Accurate numerical calculations agree on the symmetry of the lowest lying states being ${}^5\Sigma_u^-$ for the ground state and ${}^3\Sigma_u^-$ for the first excited state. By taking the example of Sc_2 presently, we aim to show that MC-UPT type methods give reliable answer for the question of ordering of these states. It is not our purpose however, to reproduce experimental data, as this goal would require a more extensive study.

We adopt the basis set denoted TZVP+G(3df,2p), specified in detail in the Method section of the report of Matxain et al.[63]. Matxain et al. in fact applied a smaller basis set in their MRPT calculations[64]. Based on the studies of Miranda and Kaplan[62], relativistic corrections were not considered in our model. To select the orbitals included in the reference CAS wavefunction, natural orbital occupation numbers of a full valence CAS(18,6) were computed. Based on this, 9 active orbitals were determined as the smallest model space necessary for describing non-dynamical correlation. Among the 9 active orbitals there are three a_g's, one b_{3u}, one b_{2u}, two b_{1u}'s, one b_{2g} and one b_{3g}, classified in D_{2h} point group. (All calculations were carried out under this symmetry constraint.) The totally symmetric combination of the $4p_z$ orbitals is included in the active space, in accordance with the suggestions of Camacho et al.[60] and Soto et al.[58].

Single point energies and energy difference of the two states are shown in Table 4 for MC-UPT methods, second order NEVPT and MRMP. The reported calculations were carried out at the internuclear distance of 2.65 Å , as most methods gave a minimum close around this geometry, for both of the lowest states. Results by MC-CDPT are not included in the Table as this curve reaches its minimum below 2.5 Å .

It is apparent in Table 4 that the CAS(9,6) reference fails to reproduce the correct ordering of the states. However, the energy of the two lowest states is fairly close by CAS(9,6) (-0.003 eV) if comparing it to the value that is expected to be correct in this basis: somewhere between 0.08 and 0.12 eV[60]. As Table 4 reflects, all PT methods based on this reference set the order of the states right, indicating that the CAS(9,6) reference is an acceptable starting point. Comparing the different MRPT methods, MC-OPTUPT outperforms the MC-UPT variant. The 0.06 eV state energy difference given by MC-OPTUPT is comparable in quality to the results of MRMP and NEVPT2 in this model and fairly close to the $0.08-0.12$ eV range expected based on third order NEVPT calculations[60]. Both MRMP and the partially contracted version of NEVPT2 give an energy spacing larger than expected, while NEVPT2 with the strongly contracted scheme seems to produce an adequate result here.

CONCLUSION

Unitary perturbation theory has been combined with Mayer's orthogonalization and applied to multireference starting functions to give a robust, intruder free first correction. The method does not rely on the concept of a CAS starting function, it is applicable to a reference of any type. Computational cost of MC-DCPT agrees with that of a second-order theory (proportional to $(M+1)\, n_{occ}^2\, n_{virt}^2$, where $M+1$ is the dimension of the model space) while MC-UPT and MC-OPTUPT is of third-order cost (proportional to $(M+1)\, n_{occ}^2\, n_{virt}^4$), due to the symmetrical energy formula Eq.(13). Energy errors and chemical energy differences of MC-OPTUPT are typically similar to those of well-behaving MR PT techniques. Though errors of MC-DCPT and MC-UPT are also encouraging, energy differences computed by these theories are less satisfactory.

Size-inconsistency is a weak point of MC-UPT approaches. Consistency violation dominates the error already for a 20-electron system. This prompts against using MC-UPT when the system is decomposed into noninteracting parts, and marks the path of further research studies in connection with MC-UPT.

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The APSG (GVB) reference functions were generated by the Budapest version of the MUNGAUSS program package[65]. The CAS functions were computed by the GAMESS program suite[66] and the Dalton package[67]. The MRMP corrections were also obtained by GAMESS, NEVPT2 results were produced by Dalton. The MCUPT results were obtained by a code developed in our laboratory, using the supercomputing facility of the National Information Infrastructure Development Institute.

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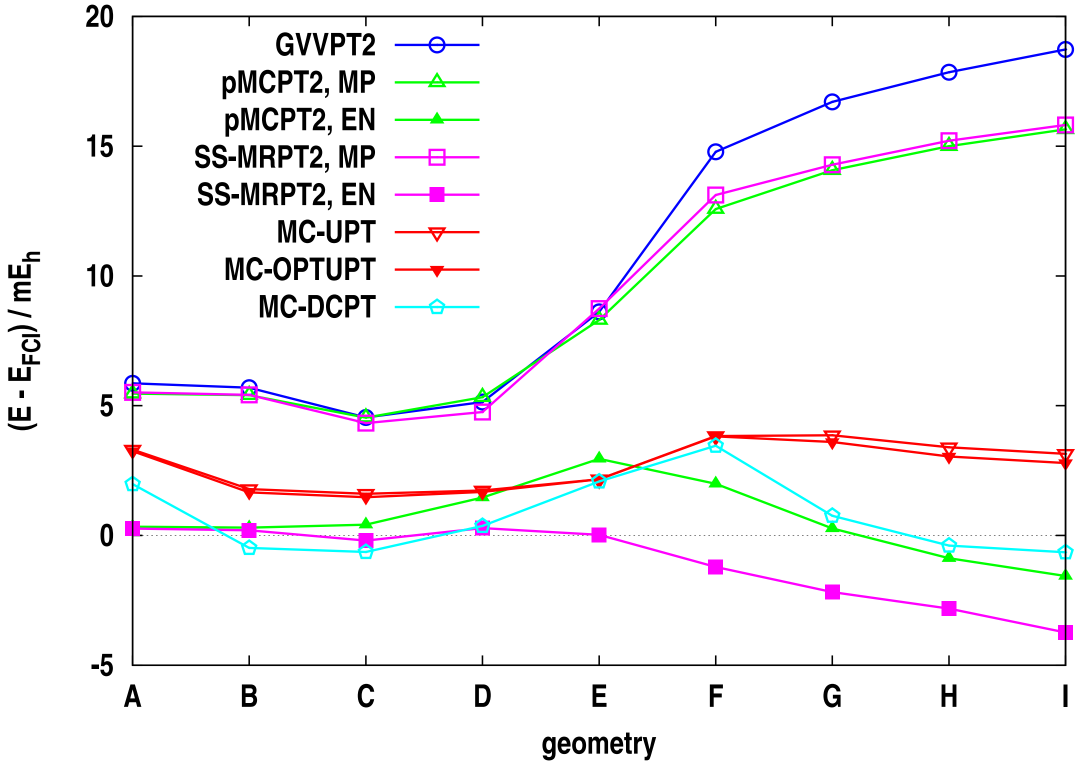
Figure 1: Total energy (in Hartrees) and energy errors with respect to full CI (in milli-Hartrees) of the H_2O molecule as both O-H bonds are elongated. Reference function is an APSG function[46] with two basis functions on each OH bond. The $\angle$(HOH) angle is fixed at 104.0^o. Dunning's DZP basis set is applied[47].

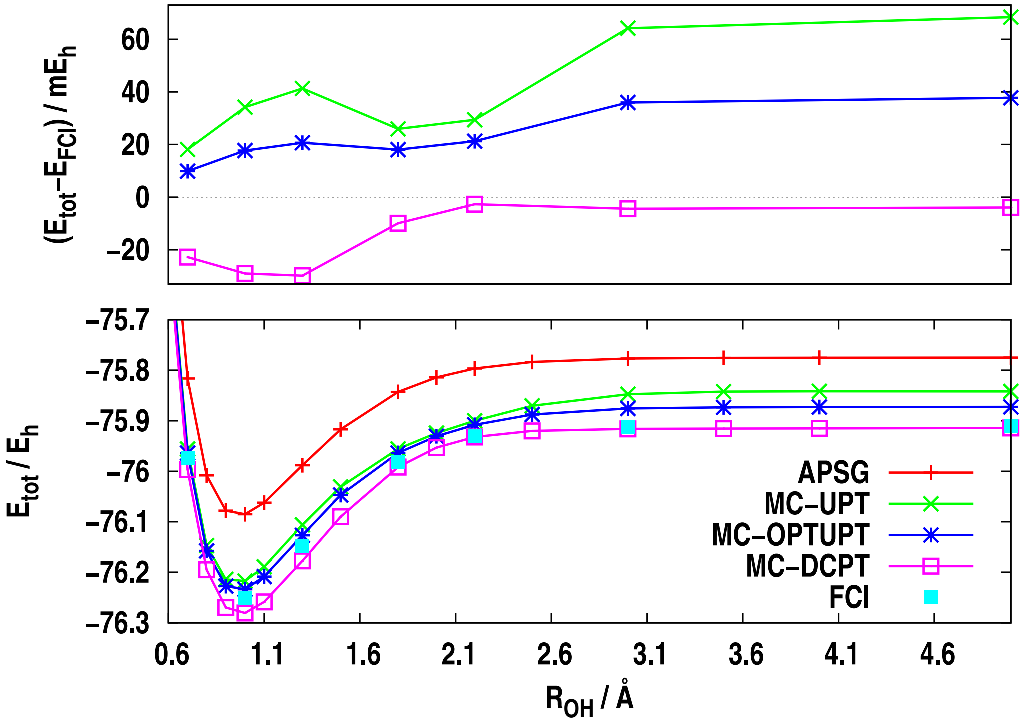
Figure 2: Energy errors of MR function based correction schemes with respect to FCI for the ground state of the BeH_2 system. Dunning's DZ set[47] is taken for the hydrogen atoms. For beryllium the basis of Purvis et al.[53] is used with the p function decontracted, leaving the most compact primitive (exponent 5.693880) alone and contracting the remaining two into a second p function (exponents 1.555630, 0.171855 and coefficients 0.144045, 0.949692 respectively). Illustration of the geometry points A, B, C, D, E, F, G, H, I is shown in Figure 3. Reference function is CAS(4,4). Data plotted for GVVPT2 are taken from Ref.[34]. Data for SS-MRPT have been recomputed applying a Tikhonov-damping of $\omega = 0.003$[68].

Figure 3: Geometry points A, B, C, D, E, F, G, H, I of the BeH_2 system[53]. Coordinates of the hydrogen atoms in atomic units are $(0, \pm 2.54, 0)$, $(0, \pm 2.08, 1.0)$, $(0, \pm 1.62, 2.0)$, $(0, \pm 1.39, 2.5)$, $(0, \pm 1.275, 2.75)$, $(0, \pm 1.16, 3.0)$ $(0, \pm 0.93, 3.5)$, $(0, \pm 0.70, 4.0)$, $(0, \pm 0.70, 6.0)$ respectively at points A, B, C, D, E, F, G, H, I. The beryllium lies in the origin of the coordinate system.



20
15
10
5
0
-5
$(E - E_{FCI}) / mE_h$
A
B
C
D
E
F
G
H
I
geometry
GVVPT2
pMCPT2, MP
pMCPT2, EN
SS-MRPT2, MP
SS-MRPT2, EN
MC-UPT
MC-OPTUPT
MC-DCPT

Figure 1



$(E_{tot}-E_{FCI})$ / mE_h
60
40
20
0
-20
E_{tot} / E_h
-75.7
-75.8
-75.9
-76
-76.1
-76.2
-76.3
APSG
MC-UPT
MC-OPTUPT
MC-DCPT
FCI
0.6
1.1
1.6
2.1
2.6
3.1
3.6
4.1
4.6
R_{OH} / Å

Figure 2

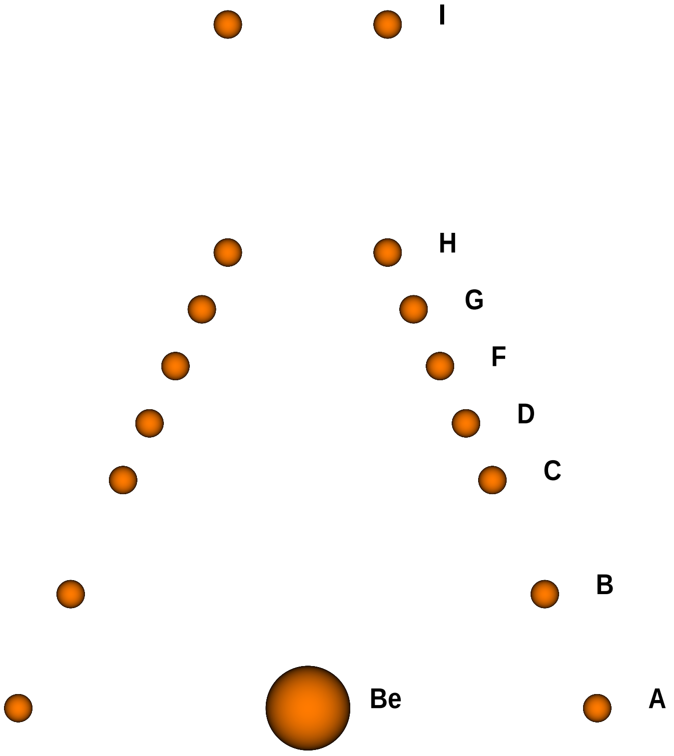


Figure 3

METHOD	TOTAL ENERGY, $\mathbf{E}_h$		ENERGY ERROR, $\mathbf{mE}_h$		INCONSISTENCY
	monomer	**dimer**	**monomer**	**dimer**	$\mathbf{mE}_h$
APSG	-75.997192	-151.994385	180.73	361.45	0.00
MC-DCPT	-76.225048	-152.429526	-47.13	-73.69	20.57
MC-UPT	-76.148885	-152.286306	29.03	69.53	11.46
MC-OPTUPT	-76.169387	-152.326606	8.53	29.23	12.17
pMCPT2	-76.180899	-152.354078	-2.98	1.76	7.72
uMCPT2	-76.200857	-152.401716	-22.94	-45.88	0.00
FCI	-76.177919	-152.355837			0.00

Table 1: Total energies and energy errors for a single H_2O molecule (monomer) and two noninteracting H_2O molecules (dimer). Reference function is an APSG function[46] with two basis functions on each OH bond. Dunning's pVTZ basis is applied[48], geometry is specified by R(OH)= 1.3 Å and $\angle$(HOH)=104.0^o. Energy error is computed as $E - E_{\mathrm{FCI}}$, size-inconsistency is defined as $E_{\mathrm{dimer}} - 2E_{\mathrm{monomer}}$. Of the two MCPT2 variants 'p' denotes the original, projected formulation[50] while 'u' refers to the size-consistent or unprojected theory[52]. Both MCPT2 calculations adopted the Davidson-Kapuy partitioning, see also[51].

METHOD	TOTAL ENERGY, $\mathbf{E}_h$		ENERGY ERROR, $\mathbf{mE}_h$		INCONSISTENCY
	monomer	**dimer**	**monomer**	**dimer**	$\mathbf{mE}_h$
CAS	-76.006585	-152.013171	171.33	342.67	0.00
MC-DCPT	-76.215323	-152.413085	-37.40	-57.25	17.56
MC-UPT	-76.166995	-152.321409	10.92	34.43	12.58
MC-OPTUPT	-76.177052	-152.341862	0.87	13.98	12.24
pMCPT2	-76.178325	-152.349997	-0.41	5.84	6.65
uMCPT2	-76.193558	-152.387117	-15.64	-31.28	0.00
MRMP	-76.166583	-152.337050	11.34	18.79	-3.88
NEVPT2 SC	-76.179660	-152.359319	-1.74	-3.48	0.00
NEVPT2 PC	-76.180133	-152.360266	-2.21	-4.43	0.00
FCI	-76.177919	-152.355837			0.00

Table 2: Total energies and energy errors for a single H_2O molecule (monomer) and two noninteracting H_2O molecules (dimer). Reference function is a CAS(4,4) for the monomer while it is CAS(8,8) for the dimer. No level shift was applied when computing the MRMP[3,4] correction. Acronym 'SC' refers to the strongly contracted version of NEVPT2, 'PC' denotes the partially contracted theory[14,49]. For other particulars see Table 1.

METHOD	TOTAL ENERGY, $\mathbf{E}_h$		ENERGY ERROR, $\mathbf{mE}_h$		S-T SPLITTING
	triplet	**singlet**	**triplet**	**singlet**	$\mathbf{mE}_h$
CAS(6,6)	-38.962086	-38.940324	69.28	68.35	21.76
uMCPT2	-39.019682	-38.995787	11.68	12.89	23.90
MC-DCPT	-39.033611	-39.008972	-2.25	-0.29	24.64
MC-UPT	-39.026355	-39.003201	5.01	5.48	23.15
MC-OPTUPT	-39.027129	-39.003732	4.24	4.95	23.40
FCI	-39.031365	-39.008678			22.69

Table 3: Energy errors ($E - E_{\mathrm{FCI}}$) and singlet-triplet splittings ($E_{\mathrm{singlet}} - E_{\mathrm{triplet}}$) of the CH_2 molecule in the polarized VDZ basis of Dunning and Hay[55]. Zero-order reference function is obtained by a CAS(6,6) calculation. Geometry is R(CH)= 1.0780 Å , ∠(HCH)= 132.9^o for the triplet state and R(CH)= 1.1086 Å , ∠(HCH)= 102.0^o for the singlet state. The size-consistent or unprojected version of MCPT2 was computed in the IPEA partitioning[69].

METHOD	TOTAL ENERGY		T-Q SPACING	
	$E(^5\Sigma_u^-)$	$E(^3\Sigma_u^-)$	$E(^3\Sigma_u^-) - E(^5\Sigma_u^-)$	
	$\mathbf{E}_h$		$\mathbf{mE}_h$	**eV**
CAS(9,6)	-1519.4611	-1519.4612	-0.11	-0.003
MC-UPT	-1519.8445	-1519.8442	0.34	0.009
MC-OPTUPT	-1519.8849	-1519.8828	2.07	0.056
MRMP	-1519.9640	-1519.9573	6.71	0.183
NEVPT2 SC	-1519.9283	-1519.9241	4.20	0.114
NEVPT2 PC	-1519.9295	-1519.9221	7.39	0.201

Table 4: Total energies and energy spacing of the lowest $^5\Sigma_u^-$ and $^3\Sigma_u^-$ levels of the Sc_2 molecule in the TZVP+G(3df,2p) basis set[63]. Reference function is obtained by a CAS(9,6) calculation. Small terms in the determinantal expansion of the reference were discarded (coefficient absolute value below $6.5 \cdot 10^{-4}$ for the $^5\Sigma_u^-$ and below $5.8 \cdot 10^{-4}$ for the $^3\Sigma_u^-$ state). This does not affect the CAS energy in the digits tabulated. In all MRPT calculations the first twelve occupied orbitals were kept frozen. Geometry is R(ScSc)= 2.65 Å for both states.