ON THE SIZE CONSISTENCY OF MULTIREFERENCE CEPA METHODS

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Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

The size consistency of various multireference coupled electron pair approaches (MRCEPA) is analysed. These methods include the MRCEPA0, MR averaged coupled pair functional (MR-ACPF), MR averaged quadratic coupled cluster (MR-AQCC), MR (singles and doubles) CEPA (MRDCEPA) and the recently proposed MR averaged CEPA (MR-ACEPA) methods. Test calculations on the O_2 dimer show that a correct treatment of the variationally included (VI) terms such as in the MRDCEPA and MR-ACEPA methods is necessary for obtaining nearly size-consistent results. On the other hand, the results strongly suggest that it is impossible to obtain exact size consistency with any method employing the diagonal shift formalism. The analysis also shows that the size consistency error is not significantly affected by the exclusion principle violating (EPV) terms.

Keywords: MRCEPA; MRDCEPA; Size consistency; Diagonal shift; Electron correlation; Multireference methods; Ab initio calculations; Quantum chemistry; Coupled cluster.

Over the years various extensions of single reference (SR) methods such as coupled electron pair approaches (CEPA1) or coupled pair functional (CPF)[1,2] have been developed in order to remedy the size consistency errors inherent to the multireference configuration interaction (MRCI) method. Examples are the MRCEPA0 [3], MR-ACPF [4], MR-AQCC [5], MRDCEPA [6] and the recently proposed MR-ACEPA [7] methods. In a recent attempt to formulate a multireference coupled cluster (MRCC) method[8], full configuration interaction (CI) results were used to judge their performance[6–8]. However, although these MRCEPA methods show a much better performance than MRCI with respect to approximating MRCC or full CI results, not much attention was paid to their size consistency. In this paper an analysis of the behaviour with respect to the size consistency is presented, which shows that the methods mentioned above are very different in this respect even if they yield relatively accurate representations of potential energy curves for

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some model systems in the bonding region. In this analysis the secular equations for a dimer AB are considered, where AB consists of two non-interacting monomers A and B. The size consistency is checked by studying the conditions under which these dimer secular equations are separable into the monomer secular equations.

THE MRCEPA METHOD

The MRCEPA versions discussed here may be described by the following system of equations[6,7]

$$\langle \Phi_I^{\mathrm{P}} | \hat{H} - E | \Psi \rangle = \langle \Phi_I^{\mathrm{P}} | \hat{H} - E_0 - E_{\mathrm{C}} | \Psi \rangle = 0 \tag{1a}$$

$$\langle \Phi_J^{\mathrm{Q}} | \hat{H} - E + K_J | \Psi \rangle = \langle \Phi_J^{\mathrm{Q}} | \hat{H} - E_0 - E_{\mathrm{C}} | \Psi \rangle + K_J c_J = 0 \,, \tag{1b}$$

where

$$\Psi = \sum_I c_I \Phi_I^{\mathrm{P}} + \sum_J c_J \Phi_J^{\mathrm{Q}} \tag{2}$$

and Φ_I^{P} and Φ_J^{Q} are reference (P-space) and excited (Q-space) CFs, respectively. The interacting space of the Q-space is called the R-space. The reference space is assumed to be complete, i.e., we have a complete active space (CAS) reference set. Following the CEPA philosophy the missing unlinked contributions of the R-space functions are simulated by including the diagonal shift K_J in Eq. (*1b*) in order to restore the size consistency as much as possible.

A further division of the excitations is made according to the excitation class (k,l)[6]. The excitation class of a function is defined by the number of holes k in the inactive orbital space ($0 \le k \le 2$) and by the number of particles l in the virtual orbital space ($0 \le l \le 2$).

Since Eqs (*1*) are homogeneous, the normalisation is arbitrary. For our purpose it is convenient to use intermediate normalisation, using either the projection of Ψ to the reference space or the CASSCF function as the reference function Ψ_0

$$|\Psi_0^{\mathrm{proj}}\rangle \equiv |0\rangle = \sum_{I \in \mathrm{P}} |\Phi_I^{\mathrm{P}}\rangle\langle\Phi_I^{\mathrm{P}}|\Psi\rangle = \sum_{I \in \mathrm{P}} c_I |\Phi_I^{\mathrm{P}}\rangle \quad \text{with} \quad \langle \Psi_0^{\mathrm{proj}} | \Psi_0^{\mathrm{proj}} \rangle = 1 \tag{3a}$$

or

$$|\Psi_0^{\mathrm{var}}\rangle \equiv |0\rangle = |\Psi^{\mathrm{CASSCF}}\rangle = \sum_{I \in \mathrm{P}} c_I^{\mathrm{CASSCF}} |\Phi_I^{\mathrm{P}}\rangle \quad \text{with} \quad \langle \Psi_0^{\mathrm{var}} | \Psi_0^{\mathrm{var}} \rangle = 1 \,. \tag{3b}$$

Equation (*3a*) is used for the MRCEPA0, MRDCEPA and MR-ACEPA methods, whereas Eq. (*3b*) is used for the MR-ACPF and MR-AQCC methods.

In the following, relaxation effects in the reference coefficients in the dimer calculation with respect to the monomer results are neglected. As a consequence the secular equations for the reference CFs may be combined into one equation, which is given by:

$$\langle 0|\hat{H} - E_0 - E_\mathrm{C}|\Psi\rangle = \sum_J c_J \langle 0|\hat{H}|\Phi_J^\mathrm{Q}\rangle - E_\mathrm{C} = 0 \tag{4}$$

The secular equations for the excitations Φ_J^Q are given by:

$$\langle\Phi_J^\mathrm{Q}|\hat{H} - E_0 - E_\mathrm{C} + K_J|\Psi\rangle = 0$$

or, splitting off the diagonal

$$\langle\Phi_J^\mathrm{Q}|\hat{H}|0\rangle + \sum_{J'\neq J} c_{J'}\langle\Phi_J^\mathrm{Q}|\hat{H}|\Phi_{J'}^\mathrm{Q}\rangle + c_J(\Delta E_J - E_\mathrm{C} + K_J) = 0\ , \tag{5a}$$

where

$$\Delta E_J = E_J - E_0 \tag{5b}$$

and E_0 and E_J are the energies of Ψ_0 and Φ_J^Q, respectively.

The correlation energy is divided into class contributions according to

$$E_\mathrm{C} = \sum_{k=0}^{2}\sum_{l=0}^{2} \varepsilon(k,l) \tag{6a}$$

with (Eqs (*1a*) and (*4*))

$$\varepsilon(k,l) = \sum_J c_J\langle 0|\hat{H}|\Phi_J^\mathrm{Q}(k,l)\rangle\ , \tag{6b}$$

where only those terms are included for which J corresponds to a function within class (k,l). Since the reference space is complete, there are no $\Phi_J^\mathrm{Q}(0,0)$ and $\varepsilon(0,0) = 0$.

In the following the effect of the truncation of the exponential form of the wave function[6] is represented by introducing the *topological matrices* $\mathbf{T}^{kl}$ for excitation class (k,l), defined by (Eq. (*13*) of lit.[7])

$$T_{pq}^{kl} = 1 \text{ if } k + p \leq 2 \text{ and } l + q \leq 2 \text{ and } (p > 0 \text{ or } q > 0), \text{ otherwise } T_{pq}^{kl} = 0\ , \tag{7}$$

where k and p denote numbers of holes and l and q denote numbers of particles. In the following, these matrices will be used to relate the dimer MRCEPA function to the product function $\Psi_A\Psi_B$, where Ψ_A and Ψ_B are the monomer MRCEPA functions. This product function should be rigorously size-consistent if the diagonal shifts for the dimer are additive.

The various possibilities for choosing the MRCEPA variants may be concisely represented by introducing the *shift matrices* $\mathbf{U}^{kl}$ which select the correlation energy contributions which are to be included in the diagonal shift for a class (k,l) excitation $\Phi_J^Q(k,l)$:

$$K_J(k,l) = \sum_{rs} U_{rs}^{kl} \varepsilon(r,s) \ . \tag{8}$$

The secular equation for $\Phi_J^Q(k,l)$, Eq. (*5a*), then reads

$$\langle \Phi_J^Q(k,l)|\hat{H}|0\rangle + \sum_{k'l'} \sum_{J' \neq J} c_{J'} \langle \Phi_J^Q(k,l)|\hat{H}|\Phi_{J'}^Q(k',l')\rangle +$$

$$+ c_J \left[\Delta E_J - E_C + \sum_{rs} U_{rs}^{kl} \varepsilon(r,s) \right] = 0 \ . \tag{9}$$

In the MRCEPA0, MR-ACPF and MR-AQCC approaches the shift is independent of the excitation class. In the MRCEPA0 method the shift is equal to the total correlation energy E_C, i.e. $U_{rs}^{kl} = 1$ for all k, l, r and s. In the MR-ACPF and MR-AQCC methods the exclusion principle violating (EPV) terms are avoided in an average way by using a damping factor d_n depending on the total number of correlated electrons n: $U_{rs}^{kl} = d_n$.

However, a consequence of taking the **U**-matrix elements to be independent of the indices is that part of the Q-space excitations will also contribute to the diagonal shifts. Therefore redundancies are introduced, since the Q-space correlation energy contributions to the diagonal shifts originate from excitations which do contribute to the secular equations explicitly. In the MRDCEPA and MR-ACEPA methods, these variationally included (VI) terms are excluded from contributing to the shift.

In the MRDCEPA method EPV effects are ignored, whereas in the MR-ACEPA method the EPV corrections depend on the excitation class and on the numbers of electrons in the inactive and in the active orbital spaces. The formulas used are analogous to the damping factors used in the MR-ACPF and MR-AQCC methods.

We then have (for all values of k, l, r and s)

$$\text{MRCEPA0:} \quad U_{rs}^{kl} = 1 \tag{10a}$$

$$\text{MR-ACPF:} \quad U_{rs}^{kl} = d_n^{\text{ACPF}} \tag{10b}$$

$$\text{MR-AQCC:} \quad U_{rs}^{kl} = d_n^{\text{AQCC}} \tag{10c}$$

$$\text{MRDCEPA:} \quad U_{rs}^{kl} = 1 - T_{rs}^{kl} \tag{10d}$$

$$\text{MR-ACEPA:} \quad U_{rs}^{kl} = \left(1 - T_{rs}^{kl}\right) d_{n_i,n_a}^{\text{MR-ACEPA}}(kl,rs)\,, \tag{10e}$$

where n_i and n_a are the numbers of inactive and active electrons, respectively, and $n = n_i + n_a$. The expressions for $d_{n_i,n_a}^{\text{MR-ACEPA}}(kl,rs)$ are given in Table I of lit.[7]

The use of Eq. (*10d*) or (*10e*) implies that the VI contributions are treated correctly, i.e., the redundancies are avoided by only admitting correlation energy contributions to the diagonal shift originating from excitations within the R-space.

SIZE CONSISTENCY

General Considerations

We consider two noninteracting monomers A and B. The dimer is denoted by AB. If the dimer wave function is size-consistent and localised orbitals are used, the secular equations for the dimer may be separated into the corresponding monomer equations. This will be possible if the coefficients for the dimer function may be written as products of the coefficients for the monomer functions. Therefore we start with the product $\Psi^A\Psi^B$ where Ψ^A and Ψ^B are determined by the MRCEPA equations for the subsystems A and B, respectively.

The subsystem MRCEPA functions are denoted by

$$|\Psi^A\rangle = |0^A\rangle + \sum_{klm} c_{klm}^A |klm^A\rangle \qquad |\Psi^B\rangle = |0^B\rangle + \sum_{pqn} c_{pqn}^B |pqn^B\rangle\,, \tag{11}$$

where *kl* denotes the excitation class for A, *m* is the index corresponding to an inidividual excitation on A within class (*k*,*l*), *pq* denotes the excitation class for B and *n* is the index corresponding to an individual excitation on B within class (*p*,*q*).

The product function $\Psi^A\Psi^B$ contains higher (3- and 4-fold) excitations with respect to the dimer reference set. Those functions which correspond to an excitation class (*r*,*s*) with $r > 2$ or $s > 2$ do not appear in the MRCEPA function for the dimer and therefore we project them out. The function used for investigating the separability of the MRCEPA secular equations for the dimer is then defined by

$$\Psi^{AB} = \hat{P}_a \Psi^A \Psi^B \ , \tag{12}$$

where $\hat{P}_a$ projects to the space spanned by the MRCEPA CFs for the dimer. The projection is realised by using the topological matrices $\mathbf{T}^{kl}$ as defined by Eq. (*7*)

$$\Psi^{AB} = |0^A, 0^B\rangle + \sum_{klm} c^A_{klm} |klm^A, 0^B\rangle + \sum_{pqn} c^B_{pqn} |0^A, pqn^B\rangle +$$

$$+ \sum_{kl} \sum_{pq} T^{kl}_{pq} \sum_m \sum_n c^A_{klm} c^B_{pqn} |klm^A, pqn^B\rangle \ . \tag{13}$$

In the following we will use this function in the MRCEPA secular equations for the dimer. The size consistency is then checked by verifying whether these equations are separable into the corresponding MRCEPA monomer equations.

The Secular Equation for the Reference Space

The reference space secular equation for the dimer is given by

$$\langle 0^A, 0^B | \hat{H}_A + \hat{H}_B - E_0 - E_C | \Psi^{AB} \rangle = 0 \ . \tag{14}$$

We now evaluate Eq. (*14*) by substituting Eq. (*13*).

Since a CAS reference space is also used for the dimer, the reference function $|0^A, 0^B\rangle$ satisfies the size consistency condition $E_0 = E_0^A + E_0^B$. The contribution of $|0^A, 0^B\rangle$ in Ψ^{AB} to Eq. (*14*) is thus given by

$$\langle 0^A, 0^B | \hat{H}_A + \hat{H}_B - E_0 - E_C | 0^A, 0^B \rangle = E_0^A + E_0^B - E_0 - E_C = -E_C \ . \tag{15}$$

The local excitations in Ψ^{AB} yield

$$\sum_{klm} c^{\mathrm{A}}_{klm} \langle 0^{\mathrm{A}}, 0^{\mathrm{B}} | \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}} | klm^{\mathrm{A}}, 0^{\mathrm{B}} \rangle + \sum_{pqn} c^{\mathrm{B}}_{pqn} \langle 0^{\mathrm{A}}, 0^{\mathrm{B}} | \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}} | 0^{\mathrm{A}}, pqn^{\mathrm{B}} \rangle =$$

$$= \sum_{klm} c^{\mathrm{A}}_{klm} \langle 0^{\mathrm{A}} | \hat{H}_{\mathrm{A}} | klm^{\mathrm{A}} \rangle + \sum_{pqn} c^{\mathrm{B}}_{pqn} \langle 0^{\mathrm{B}} | \hat{H}_{\mathrm{B}} | pqn^{\mathrm{B}} \rangle =$$

$$= \sum_{kl} \varepsilon^{\mathrm{A}}(k,l) + \sum_{pq} \varepsilon^{\mathrm{B}}(p,q) = E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}} \ . \qquad (16)$$

The nonlocal excitations $|klm_{\mathrm{A}}, pqn_{\mathrm{B}}\rangle$ in Eq. (*13*) involve excitations on both subsystems simultaneously and therefore they are at least doubly excited with respect to any reference CF. They involve dispersion-type excitations such as $|1,1,m^{\mathrm{A}}\rangle$ $|1,1,n^{\mathrm{B}}\rangle$ or charge-transfer excitations like $|2,0,m^{\mathrm{A}}\rangle$ $|0,2,n^{\mathrm{B}}\rangle$. All corresponding **H**-matrix elements in Eq. (*14*) only involve integrals of the kind $(i_{\mathrm{A}} j_{\mathrm{A}} / k_{\mathrm{B}} l_{\mathrm{B}})$ or $(i_{\mathrm{A}} k_{\mathrm{B}} / j_{\mathrm{A}} l_{\mathrm{B}})$ which vanish if the subsystems are far apart. Therefore the nonlocal excitations do not interact with any reference CF and, consequently, they do not contribute to Eq. (*14*)

$$\sum_{kl} \sum_{pq} T^{kl}_{pq} \sum_{m} \sum_{n} c^{\mathrm{A}}_{klm} c^{\mathrm{B}}_{pqn} \langle 0^{\mathrm{A}}, 0^{\mathrm{B}} | \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}} - E_0 - E_{\mathrm{C}} | klm^{\mathrm{A}}, pqn^{\mathrm{B}} \rangle = 0 \ . \qquad (17)$$

By combining Eqs (*15*), (*16*) and (*17*) we find

$$\langle 0^{\mathrm{A}}, 0^{\mathrm{B}} | \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}} - E_0 - E_{\mathrm{C}} | \Psi^{\mathrm{AB}} \rangle = -E_{\mathrm{C}} + E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}} = 0 \qquad (18)$$

or

$$E_{\mathrm{C}} = E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}} \ . \qquad (19)$$

This result shows that E_{C} is additive and therefore the dimer secular equation for the reference function is separable.

The Secular Equations for the Local Excitations

The next step is to evaluate the secular equations for the local excitations $|klm^{\mathrm{A}}, 0^{\mathrm{B}}\rangle$, again by substituting the explicit expression for Ψ^{AB}, Eq. (*13*). The secular equation for an excitation localised on A is given by

$$\langle klm^{\mathrm{A}}, 0^{\mathrm{B}} | \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}} - E_0 - E_{\mathrm{C}} + \sum_{rs} U^{kl}_{rs} \varepsilon(r,s) | \Psi^{\mathrm{AB}} \rangle = 0 \ . \qquad (20)$$

If the subsystems are far apart, the same reasoning as above may be used to show that all nonvanishing contributions are as follows.

Contributions from $\hat{H}_\mathrm{A}$:

$$\langle klm^\mathrm{A},0^\mathrm{B}|\hat{H}_\mathrm{A}|0^\mathrm{A},0^\mathrm{B}\rangle = \langle klm^\mathrm{A}|\hat{H}_\mathrm{A}|0^\mathrm{A}\rangle$$

$$\langle klm^\mathrm{A},0^\mathrm{B}|\hat{H}_\mathrm{A}|k'l'm'^\mathrm{A},0^\mathrm{B}\rangle = \langle klm^\mathrm{A}|\hat{H}_\mathrm{A}|k'l'm'^\mathrm{A}\rangle\ . \tag{21a}$$

Contributions from $\hat{H}_\mathrm{B}$:

$$\langle klm^\mathrm{A},0^\mathrm{B}|\hat{H}_\mathrm{B}|klm^\mathrm{A},0^\mathrm{B}\rangle = E_0^\mathrm{B}$$

$$T_{pq}^{kl}\langle klm^\mathrm{A},0^\mathrm{B}|\hat{H}_\mathrm{B}|klm^\mathrm{A},pqn^\mathrm{B}\rangle = T_{pq}^{kl}\langle 0^\mathrm{B}|\hat{H}_\mathrm{B}|pqn^\mathrm{B}\rangle\ . \tag{21b}$$

Contributions from the scalar part $-E_0 - E_\mathrm{C} + \sum_{rs} U_{rs}^{kl}\varepsilon(r,s)$:

The only contribution comes from $|klm^\mathrm{A},0^\mathrm{B}\rangle$. Since the nonlocal excitations do not contribute to the correlation energy, we have $\varepsilon(r,s) = \varepsilon^\mathrm{A}(r,s) + \varepsilon^\mathrm{B}(r,s)$. Therefore the scalar contribution may be written as

$$-E_0 - E_\mathrm{C} + \sum_{rs} U_{rs}^{kl}\varepsilon(r,s) =$$

$$-E_0^\mathrm{A} - E_\mathrm{C}^\mathrm{A} - E_0^\mathrm{B} - E_\mathrm{C}^\mathrm{B} + \sum_{rs} U_{rs}^{kl}\varepsilon^\mathrm{A}(r,s) + \sum_{rs} U_{rs}^{kl}\varepsilon^\mathrm{B}(r,s)\ . \tag{21c}$$

By combining Eqs (*20*) and (*21*) and using Eq. (*6b*) we then find

$$\langle klm^\mathrm{A}|\hat{H}_\mathrm{A}|0^\mathrm{A}\rangle + \sum_{k'l'}\sum_{m'\neq m} c_{k'l'm'}^\mathrm{A}\langle klm^\mathrm{A}|\hat{H}_\mathrm{A}|k'l'm'^\mathrm{A}\rangle +$$

$$+\, c_{klm}^\mathrm{A}\left[\Delta E_{klm}^\mathrm{A} - E_\mathrm{C}^\mathrm{A} + \sum_{rs} U_{rs}^{kl}\varepsilon^\mathrm{A}(r,s)\right] +$$

$$+\, c_{klm}^\mathrm{A}\left[-E_\mathrm{C}^\mathrm{B} + \sum_{rs}\left(U_{rs}^{kl} + T_{rs}^{kl}\right)\varepsilon^\mathrm{B}(r,s)\right] = 0\ . \tag{22}$$

Equation (*22*) is size-consistent if the following two conditions are satisfied:

1) The A-dependent part coincides with the monomer equation for $|klm^\mathrm{A}\rangle$.

2) The B-dependent part vanishes.

Effects of the VI Terms

In the MRDCEPA method the **U**- and **T**-matrices (see Eq. (*10d*)) are complementary to each other, i.e. $U_{rs}^{kl} + T_{rs}^{kl} = 1$ for all k, l, r and s. Therefore, using Eq. (*6a*), we see that the B-dependent part in Eq. (*22*) vanishes.

The A-dependent part of Eq. (*22*) is given by

$$\langle klm^{\mathrm{A}}|\hat{H}_{\mathrm{A}}|0^{\mathrm{A}}\rangle + \sum_{k'l'}\sum_{m'\neq m} c^{\mathrm{A}}_{k'l'm'}\langle klm^{\mathrm{A}}|\hat{H}_{\mathrm{A}}|k'l'm'^{\mathrm{A}}\rangle +$$

$$+c^{\mathrm{A}}_{klm}\left[\Delta E^{\mathrm{A}}_{klm} - E^{\mathrm{A}}_{\mathrm{C}} + \sum_{rs} U^{kl}_{rs}\varepsilon^{\mathrm{A}}(r,s)\right] = 0\ . \qquad (23)$$

This equation is indeed identical to the subsystem equation for $|klm^{\mathrm{A}}\rangle$ (see Eq. (*9*)). Therefore the MRDCEPA equations for the localised excitations satisfy the size consistency condition. For the MR-ACEPA method the $1 - T_{rs}^{kl}$ factor in Eq. (*10e*) also takes care of the exclusion of the VI terms. However, as discussed below, the VI-allowed contributions to the diagonal shift give rise to EPV-related size consistency errors in the MR-ACEPA method.

For the MRCEPA0, MR-ACPF and MR-AQCC methods (Eqs (*10a*)–(*10c*)), U_{rs}^{kl} does not depend on the class indices and therefore Eq. (*22*) yields a non-zero B-dependent contribution to the secular equation for $|klm^{\mathrm{A}},0^{\mathrm{B}}\rangle$, causing a deviation from size consistency.

Effects of the EPV Terms

Since the single reference (SR) ACPF and AQCC methods are not always strictly size-consistent, we first analyse the effect of the EPV diagonal shift corrections on the size consistency for the SR case.

In this case we have only (k,l) = (1,1) (single excitations) and (k,l) = (2,2) (double excitations). Assuming HF orbitals we have ε(1,1) = 0: only the double excitations contribute directly to the correlation energy. Effectively there are no VI terms and we have

$$\sum_{rs} T^{kl}_{rs}\varepsilon^{\mathrm{A}}(r,s) = T^{kl}_{11}\varepsilon^{\mathrm{B}}(1,1) + T^{kl}_{22}\varepsilon^{\mathrm{B}}(2,2) = 0\ ,$$

since ε(1,1) = 0 and $T_{22}^{kl} = 0$ for both (k,l) = (1,1) and (k,l) = (2,2). According to Eq. (*22*) the B-dependent part of the diagonal shift for a local excitation on A should always be equal to the total correlation energy on B. Therefore the EPV terms must be included in such a way that they are effectively *local* in the dimer calculation.

According to Eq. (*22*) the size consistency condition now reads

$$K^{\mathrm{AB}} = K^{\mathrm{A}} + E_{\mathrm{C}}^{\mathrm{B}} \; . \tag{24}$$

In the dimer calculation the diagonal shift is given by

$$K^{\mathrm{AB}} = d_{n_{\mathrm{A}}+n_{\mathrm{B}}}(E_{\mathrm{C}}^{\mathrm{A}} + E_{\mathrm{C}}^{\mathrm{B}}) \, ,$$

whereas for the monomer calculation for A we have

$$K^{\mathrm{A}} = d_{n_{\mathrm{A}}} E_{\mathrm{C}}^{\mathrm{A}} \; .$$

Therefore the size consistency condition, Eq. (*24*), may be written as

$$\delta K_{\mathrm{EPV}}^{\mathrm{A}} = K^{\mathrm{A}} + E_{\mathrm{C}}^{\mathrm{B}} - K^{\mathrm{AB}} = d_{n_{\mathrm{A}}} E_{\mathrm{C}}^{\mathrm{A}} + E_{\mathrm{C}}^{\mathrm{B}} - d_{n_{\mathrm{A}}+n_{\mathrm{B}}}(E_{\mathrm{C}}^{\mathrm{A}} + E_{\mathrm{C}}^{\mathrm{B}}) = 0 \; . \tag{25}$$

If this condition is not satisfied, the size consistency may be restored by adding $\delta K_{\mathrm{EPV}}^{\mathrm{A}}$ to the diagonal shift K^{AB} for a local excitation on A.

For the ACPF method the damping factor is given by

$$d_n^{\mathrm{ACPF}} = \frac{n-2}{n} \, , \tag{26}$$

where n equals the number of correlated electrons. By substituting this into Eq. (*25*) we find

$$\delta K_{\mathrm{EPV}}^{\mathrm{A}}(\mathrm{ACPF}) = \frac{n_{\mathrm{A}}-2}{n_{\mathrm{A}}} E_{\mathrm{C}}^{\mathrm{A}} + E_{\mathrm{C}}^{\mathrm{B}} - \frac{n_{\mathrm{A}}+n_{\mathrm{B}}-2}{n_{\mathrm{A}}+n_{\mathrm{B}}}(E_{\mathrm{C}}^{\mathrm{A}} + E_{\mathrm{C}}^{\mathrm{B}}) =$$

$$= 2\,\frac{n_{\mathrm{A}} E_{\mathrm{C}}^{\mathrm{B}} - n_{\mathrm{B}} E_{\mathrm{C}}^{\mathrm{A}}}{n_{\mathrm{A}}(n_{\mathrm{A}}+n_{\mathrm{B}})} \; . \tag{27}$$

From the numerator on the right-hand side of Eq. (*27*) it follows that $\delta K_{\mathrm{EPV}}^{\mathrm{A}}(\mathrm{ACPF})$ vanishes if the correlation energies are proportional to the numbers of electrons

$$\frac{E_{\mathrm{C}}^{\mathrm{A}}}{E_{\mathrm{C}}^{\mathrm{B}}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{B}}} \; . \tag{28}$$

The size consistency condition, Eq. (*25*), is satisfied if Eq. (*28*) holds. Therefore the ACPF method is strictly size-consistent for identical subsystems.

Moreover, even if the subsystems are different, Eq. (*28*) is usually almost satisfied. Therefore in practice the ACPF method is nearly size-consistent.

Although the AQCC choice

$$d_n^{\mathrm{AQCC}} = \frac{(n-2)(n-3)}{n(n-1)} \tag{29}$$

does not satisfy the size consistency condition even for identical subsystems, the error turns out to be of the same order of magnitude as for the ACPF method if the subsystems are different.

The Secular Equations for the Nonlocal Excitations

In this section the secular equations for the nonlocal excitations $|klm^{\mathrm{A}},pqn^{\mathrm{B}}\rangle$ are considered. These excitations do not contribute directly to the correlation energy. However, since they interact with the local excitations, they do affect the coefficients of the latter and therefore they may be important for the size consistency.

For the nonlocal excitations $|klm^{\mathrm{A}},pqn^{\mathrm{B}}\rangle$, where according to Eq. (*13*) the indices are such that $T_{rs}^{kl} = 1$, i.e. $k + p \le 2$ and $l + q \le 2$, we have

$$\langle klm^{\mathrm{A}}, klm^{\mathrm{B}} | \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}} - E_0 - E_{\mathrm{C}} + \sum_{rs} U_{rs}^{k+p,l+q} \varepsilon(r,s) | \Psi \rangle = 0 \,. \tag{30}$$

The non-zero contributions now correspond to those CFs in Ψ, which contain either *klm* on A or *pqn* on B or both. This yields

$$\begin{aligned} & c_{klm}^{\mathrm{A}} \langle pqn^{\mathrm{B}} | \hat{H}_{\mathrm{B}} | 0^{\mathrm{B}} \rangle + c_{klm}^{\mathrm{A}} \sum_{p'q'} T_{p'q'}^{kl} \sum_{n' \neq n} c_{p'q'n'}^{\mathrm{B}} \langle pqn^{\mathrm{B}} | \hat{H}_{\mathrm{B}} | p'q'n'^{\mathrm{B}} \rangle + \\ & + c_{pqn}^{\mathrm{B}} \langle klm^{\mathrm{A}} | \hat{H}_{\mathrm{A}} | 0^{\mathrm{A}} \rangle + c_{pqn}^{\mathrm{B}} \sum_{k'l'} T_{k'l'}^{pq} \sum_{m' \neq m} c_{k'l'm'}^{\mathrm{A}} \langle klm^{\mathrm{A}} | \hat{H}_{\mathrm{A}} | + k'l'm'^{\mathrm{A}} \rangle + \\ & + c_{klm}^{\mathrm{A}} c_{pqn}^{\mathrm{B}} \left[\Delta E_{klm}^{\mathrm{A}} + \Delta E_{pqn}^{\mathrm{B}} - E_{\mathrm{C}}^{\mathrm{A}} - E_{\mathrm{C}}^{\mathrm{B}} + \sum_{rs} U_{rs}^{k+p,l+q} \varepsilon(r,s) \right] = 0 \,. \end{aligned} \tag{31}$$

Note that in the second term in Eq. (*31*) the excitation level on B depends on the excitation level on A because of the truncation by the $T_{p'q'}^{kl}$ factor. Analogously, in the fourth term the excitation level on A depends on the excitation level on B. Since the contributions in Eq. (*31*) which are missing due to these truncations correspond to VI interactions on the monomers, they cannot be compensated by the diagonal shift mechanism.

Equation (*31*) is therefore *not* separable and therefore the MRCEPA methods discussed here are *not* rigorously size-consistent.

A METHOD FOR ESTIMATING THE SIZE CONSISTENCY ERROR

Our method may also be used to derive correction formulas for the shifts which will hopefully lead to better size consistency. Note, however, that this method only works if *localised* orbitals are used and therefore it has no general applicability. In this paper it will be used to estimate the size consistency error in the dimer calculation as defined by

$$\Delta E_{\mathrm{SC}} = E_{\mathrm{AB}} - (E_{\mathrm{A}} + E_{\mathrm{B}}) \tag{32}$$

in terms of the size consistency deviation in the diagonal shift $\delta K_{\mathrm{A,B}}$. The accuracy of our analysis is tested by comparing the total energy resulting from a dimer calculation using size-consistency-corrected shifts to the sum of the monomer energies. These results also enable us to compare various contributions to the size consistency error, such as those originating from ignoring the VI terms and those originating from the EPV corrections to the shifts.

The size consistency error is estimated by applying either uncoupled or coupled first-order perturbation theory. In the latter form the corrections to the shifts are incorporated into the diagonalisation process. In this case the coefficients are affected by the corrections to the shifts, which enables us to study the effect of relaxation of the coefficients due to the errors in the shifts.

First we consider the MRCEPA0, MR-ACPF and MR-AQCC methods. Here the U_{rs}^{kl} do not depend on the class indices. For MRCEPA0 we have Eq. (*10a*), whereas for MR-ACPF and MR-AQCC the shift depends on the number of electrons, as in Eqs (*26*) and (*29*). Using Eq. (*6a*) we then obtain for Eq. (*22*) for a local excitation on A

$$\langle klm^{\mathrm{A}} | \hat{H}_{\mathrm{A}} | 0^{\mathrm{A}} \rangle + \sum_{k'l'} \sum_{m' \neq m} c_{k'l'm'}^{\mathrm{A}} \langle klm^{\mathrm{A}} | \hat{H}_{\mathrm{A}} | k'l'm'^{\mathrm{A}} \rangle +$$

$$+ c_{klm}^{\mathrm{A}} \left[\Delta E_{klm}^{\mathrm{A}} - E_{\mathrm{C}}^{\mathrm{A}} + d_{n_{\mathrm{A}}+n_{\mathrm{B}}} E_{\mathrm{C}}^{\mathrm{A}} \right] +$$

$$+ c_{klm}^{\mathrm{A}} \left[-E_{\mathrm{C}}^{\mathrm{B}} + d_{n_{\mathrm{A}}+n_{\mathrm{B}}} E_{\mathrm{C}}^{\mathrm{B}} + \sum_{pq} T_{pq}^{kl} \varepsilon^{\mathrm{B}}(p,q) \right] = 0 \, . \tag{33}$$

For the monomer secular equation for $|klm^{\mathrm{A}}\rangle$ (see Eq. (*9*)), we now have

$$\langle klm^{\mathrm{A}}|\hat{H}_{\mathrm{A}}|0^{\mathrm{A}}\rangle + \sum_{k'l'}\sum_{m'\neq m} c^{\mathrm{A}}_{k'l'm'}\langle klm^{\mathrm{A}}|\hat{H}_{\mathrm{A}}|k'l'm'^{\mathrm{A}}\rangle +$$

$$+ c^{\mathrm{A}}_{klm}\left[\Delta E^{\mathrm{A}}_{klm} - E^{\mathrm{A}}_{\mathrm{C}} + d_{n_{\mathrm{A}}} E^{\mathrm{A}}_{\mathrm{C}}\right] = 0 \qquad (34)$$

The correction to the diagonal shift needed to restore the size consistency for the secular equations for the local excitations is obtained by taking the difference between Eqs (*34*) and (*33*)

$$\delta K^{\mathrm{A}}(k,l) = d_{n_{\mathrm{A}}} E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}} - d_{n_{\mathrm{A}}+n_{\mathrm{B}}}(E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}}) - \sum_{pq} T^{kl}_{pq}\varepsilon^{\mathrm{B}}(p,q)\,. \qquad (35)$$

The last contribution originates from the fact that the shift is taken to be independent of the excitation classes. This is the VI-related contribution. The other contributions represent the size consistency deviations implied by using Eq. (*10b*) or (*10c*) for the EPV corrections. The deviations $\delta K^{\mathrm{A}}(k,l)$ in the diagonal shifts for the local excitations are given in Table I.

For the MRDCEPA and MR-ACEPA methods, we have $\delta K^{\mathrm{VI}}_{\mathrm{A}} = 0$. For the MRDCEPA method we also have $\delta K^{\mathrm{EPV}}_{\mathrm{A}} = 0$. For the MR-ACEPA method, however, the U^{kl}_{rs} incorporate EPV damping factors (see Eq. (*10e*)). The explicit forms are derived from the data in Table I in lit.[7] and are given in the Appendix.

The first-order PT energy change due to the changes in the diagonal shifts for the local excitations is given by

$$E^{(\mathrm{I})}(\mathrm{local}) = \sum_{kl}\delta K^{\mathrm{A}}(k,l)\sum_{m}(c^{\mathrm{A}}_{klm})^2 + \sum_{pq}\delta K^{\mathrm{B}}(p,q)\sum_{n}(c^{\mathrm{B}}_{pqn})^2\,. \qquad (36)$$

TABLE I
Diagonal shift corrections related to the effects of the local excitations

Method	VI	EPV
MRCEPA0/MR-ACPF/MR-AQCC	$-\sum_{pq} T^{kl}_{pq}\varepsilon^{\mathrm{B}}(p,q)$	$d_{n_{\mathrm{A}}} E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}} - d_{n_{\mathrm{A}}+n_{\mathrm{B}}}(E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}})$
MRDCEPA	0	0
MR-ACEPA	0	see Appendix

The first-order PT energy change related to the nonlocal excitations is given by

$$E^{(\mathrm{I})}(\text{nonlocal}) = \sum_{klm} \sum_{pqn} (c^{\mathrm{A}}_{klm} c^{\mathrm{B}}_{pqn})^2 \, \delta K^{\mathrm{AB}}(k+p, l+q) \, . \qquad (37)$$

Although according to Eq. (*31*) it is impossible to obtain strict size consistency by modifying the diagonal shifts for the nonlocal excitations, an estimate may be made by assuming that the correct order of magnitude is obtained by only using the last term of the right-hand side of Eq. (*31*). If the reference function is dominant in the correlated wave function we have

$$\sum_m (c^{\mathrm{A}}_{klm})^2 << 1 \quad \text{and} \quad \sum_n (c^{\mathrm{B}}_{pqn})^2 << 1 \qquad (38)$$

The contribution to the size consistency error from the local excitations is of the second order in the coefficients, whereas the contribution from the nonlocal excitations is of the fourth order. Therefore in general the size consistency deviation in the total energy due to the nonlocal contributions may be expected to be much smaller than the contribution due to the local excitations.

RESULTS AND DISCUSSION

Test calculations were performed for a model system of two ground-state O_2 molecules at a separation of 1000 Å. For one molecule the internuclear distance R_{OO} was fixed at 1.2 Å, whereas for the other molecule two values were used: R_{OO} = 1.2 Å and R_{OO} = 1.6 Å. The calculations were performed with an adapted version of the GAMESS-UK program system[9].

For all calculations the standard DZP basis was used. For each molecule the $1\sigma_g$ and $1\sigma_u$ MOs were frozen at the RHF level. The valence MOs were determined by a CASSCF calculation including the $|(\text{core})^4(\text{inactive})^6 1\pi^2_{\mathrm{ux}} 1\pi^2_{\mathrm{uy}} 1\pi^1_{\mathrm{gx}} 1\pi^1_{\mathrm{gy}}|$ and $|(\text{core})^4(\text{inactive})^6 1\pi^1_{\mathrm{ux}} 1\pi^1_{\mathrm{uy}} 1\pi^2_{\mathrm{gx}} 1\pi^2_{\mathrm{gy}}|$ configurations, with $(\text{core})^4 = 1\sigma^2_g 1\sigma^2_u$ and $(\text{inactive})^6 = 2\sigma^2_g 2\sigma^2_u 3\sigma^2_g$. All calculations were performed within the spin-adapted formalism and the configuration sets in both the monomer and dimer calculations were obtained without imposing symmetry restrictions on the CAS reference space used for generating the single and double excitations. The dimer calculations were performed for the singlet, triplet and quintet $O_2(^3\Sigma^-_g)/O_2(^3\Sigma^-_g)$ states. The results appear to be independent of the total spin.

In the calculations with R_{OO} = 1.2 Å/R_{OO} = 1.6 Å the correlation energies of the two molecules are substantially different (E_{corr} = 0.32 hartree for R_{OO} = 1.2 Å and E_{corr} = 0.37 hartree for R_{OO} = 1.6 Å). Since the numbers of electrons in the various subshells do not change, this is a sensitive test of the behaviour of the damping-factor-type EPV correction methods for nonidentical subsystems as used in the MR-ACPF, MR-AQCC and MR-ACEPA methods (cf. Eq. (*27*) for MR-ACPF). The results are given in Tables II and III.

In Tables II and III, UPT indicates the results obtained by first-order uncoupled perturbation theory, whereas CPT corresponds to coupled PT. The corrections to the diagonal shifts are given in Table I. PT1 is obtained by using only VI type corrections, whereas for PT2 the effects of including the corrections due to EPV effects were added. For the second set of calculations (nonidentical subsystems, Table III), no convergence could be obtained for the MRCEPA0 and MR-ACPF methods. For R_{OO} = 1.6 Å the MRCEPA0 method does not even converge for the monomer.

First we compare the uncoupled and coupled PT results. The most important effect of the coupled method is shown by the MR-ACPF result in Table III. Here the dimer calculation does not converge due to intruder state problems. This means that after some iterations the energy of some excitation becomes lower than one of the important reference CFs, due to an excessively large shift for this excitation. No such problems are encoun-

Table II

Energies (hartree) and size consistency deviations ΔE_{SC} (mhartree) for O_2 (R = 1.2 Å)/O_2 (R = 1.2 Å) for various MRCEPA variants. E_{dimer} is the uncorrected MRCEPA energy for the dimer

Parameter	MRCEPA0	MR-ACPF	MR-AQCC	MRDCEPA	MR-ACEPA
A	–150.005362	–149.998138	–149.992983	–149.999653	–149.990355
2*A	–300.010724	–299.996276	–299.985966	–149.999306	–299.980710
E_{dimer}	–300.025556	–300.006900	–299.995068	–300.000133	–299.981093
ΔE_{SC}					
Uncorrected	–14.832	–10.624	–9.102	–0.827	–0.383
CPT1	–0.232	0.192	0.569	–0.827	–0.383
CPT2	–0.232	0.192	0.064	–0.827	–0.807
UPT1	–1.709	–0.495	0.101	–0.827	–0.383
UPT2	–1.709	–0.495	–0.367	–0.827	–0.753

tered with the more realistic diagonal shifts used in the other methods due to a larger damping in the MR-AQCC method and avoiding the redundancies in the MRDCEPA and MR-ACEPA methods. In the MR-ACPF/CPT calculations the diagonal shift is much smaller than in the uncorrected one, allowing the CPT calculation to converge. UPT cannot be used here, since there is no reference energy available and therefore in the following only the CPT results will be discussed in detail.

Next we assess the accuracy obtained with the assumptions and approximations used in the previous section by comparing the CPT2 results to the full size consistency deviation as given by Eq. (*32*). The full size consistency error appears to depend strongly on the method used, ranging from 18 mhartree (MR-AQCC, Table III) to 0.4 mhartree (MR-ACEPA, Table II). The full size consistency errors are much larger for the MRCEPA0, MR-ACPF and MR-AQCC methods than for MRDCEPA or MR-ACEPA. The deviations of the CPT2 results with respect to the full error amount to ca. 1 mhartree for all calculations. From this we conclude that the residual errors generated by the nonlocal excitations, together with reorganisation effects in the reference coefficients are all of the order of 1 mhartree, independently of the method used.

TABLE III
Energies (hartree) and size consistency deviations ΔE_{SC} (mhartree) for O_2 (R = 1.2 Å)/O_2 (R = 1.6 Å) for various MRCEPA variants. E_{dimer} is the uncorrected MRCEPA energy for the dimer

Parameter	MRCEPA0	MR-ACPF	MR-AQCC	MRDCEPA	MR-ACEPA
A	–150.005362	–149.998138	–149.992983	–149.999653	–149.990355
B	–	–149.934812	–149.922112	–149.939820	–149.917317
A+B	–	–299.932950	–299.915095	–299.939473	–299.907672
E_{dimer}	–	–	–299.932967	–299.940848	–299.909088
ΔE_{SC}					
Uncorrected	–	–	–17.872	–1.375	–1.416
CPT1	–	0.518	0.844	–1.375	–1.416
CPT2	–	1.136	0.743	–1.375	–1.158
UPT1	–	–	1.604	–1.375	–1.416
UPT2	–	–	1.974	–1.375	–1.162

The relative importance of the VI and EPV-induced errors now follows from a comparison of the CPT1 and CPT2 results. The data in Tables II and III clearly show that the VI-induced CPT1 corrections, where needed, are much larger than the EPV-induced changes when going from CPT1 to CPT2. The CPT2 deviations are in fact of the same order of magnitude as the residual errors, which cannot be avoided anyway. This shows that the redundancies introduced by ignoring the excitation class dependence of the diagonal shifts lead to large size consistency errors.

By incorporating the VI-induced correction terms (CPT1), much better results are obtained for all single-shift methods: MRCEPA0, MR-ACPF and MR-AQCC. The errors remaining after applying CPT1 are comparable in magnitude to the MRDCEPA or MR-ACEPA errors, where the CPT1 corrections are not needed.

CONCLUSIONS

From our results we conclude that:

1) The redundancies in the diagonal shift calculation for the MRCEPA0, MR-ACPF and MR-AQCC methods give rise to large size consistency errors, in contrast to the MRDCEPA and MR-ACEPA methods, where they are excluded from contributing to the diagonal shift.

2) The errors induced by the EPV damping factors in the MR-ACPF, MR-AQCC and MR-ACEPA methods are much smaller. In fact they are of the same magnitude as the unavoidable effects of the nonlocal excitations.

3) The exclusion of the VI terms while calculating the diagonal shifts also minimizes the intruder state problem by avoiding excessively large shifts.

APPENDIX

The damping factor $d^{\text{MR-ACEPA}}_{n_i,n_a}(kl,rs)$ in Eq. (*10e*) is taken analogous to the MR-ACPF and MR-AQCC EPV damping factors, Eqs (*26*) and (*29*); see also Table I in lit.[7] By using Eq. (*25*), $\delta K^{\mathrm{A}}_{\mathrm{EPV}} = d_{n_{\mathrm{A}}} E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}} - d_{n_{\mathrm{A}}+n_{\mathrm{B}}}(E^{\mathrm{A}}_{\mathrm{C}} + E^{\mathrm{B}}_{\mathrm{C}})$, with the class (k,l) correlation contributions $\varepsilon^{\mathrm{A}}(k,l)$ and $\varepsilon^{\mathrm{B}}(k,l)$ instead of $E^{\mathrm{A}}_{\mathrm{C}}$ and $E^{\mathrm{B}}_{\mathrm{C}}$, respectively, the corresponding shift corrections are readily derived. The results for $\delta K^{\mathrm{EPV}}_{\mathrm{A}}(k,l)$ are as follows.

n^{A}_i = # of inactive electrons on A, n^{B}_i = # of inactive electrons on B,

n^{A}_a = # of active electrons on A, n^{B}_a = # of active electrons on B

Shift for		Contribution from		
k	l	r	s	
0	l	0	s	$d^{\mathrm{AQCC}}_{n_a^{\mathrm{A}}}\varepsilon^{\mathrm{A}}(0,s)+\varepsilon^{\mathrm{B}}(0,s)-d^{\mathrm{AQCC}}_{n_a^{\mathrm{A}}+n_a^{\mathrm{B}}}[\varepsilon^{\mathrm{A}}(0,s)+\varepsilon^{\mathrm{B}}(0,s)]$
0	l	1	s	$d^{\mathrm{ACPF}}_{n_a^{\mathrm{A}}}\varepsilon^{\mathrm{A}}(1,s)+\varepsilon^{\mathrm{B}}(1,s)-d^{\mathrm{ACPF}}_{n_a^{\mathrm{A}}+n_a^{\mathrm{B}}}[\varepsilon^{\mathrm{A}}(1,s)+\varepsilon^{\mathrm{B}}(1,s)]$
0	l	2	s	0
1	l	0	s	$d^{\mathrm{ACPF}}_{n_a^{\mathrm{A}}}\varepsilon^{\mathrm{A}}(0,s)+\varepsilon^{\mathrm{B}}(0,s)-d^{\mathrm{ACPF}}_{n_a^{\mathrm{A}}+n_a^{\mathrm{B}}}[\varepsilon^{\mathrm{A}}(0,s)+\varepsilon^{\mathrm{B}}(0,s)]$
1	l	1	s	$\frac{n_i^{\mathrm{A}}-1}{n_i^{\mathrm{A}}}\frac{n_a^{\mathrm{A}}-1}{n_a^{\mathrm{A}}}\varepsilon^{\mathrm{A}}(1,s)+\varepsilon^{\mathrm{B}}(1,s)$ $-\frac{n_i^{\mathrm{A}}+n_i^{\mathrm{B}}-1}{n_i^{\mathrm{A}}+n_i^{\mathrm{B}}}\frac{n_a^{\mathrm{A}}+n_a^{\mathrm{B}}-1}{n_a^{\mathrm{A}}+n_a^{\mathrm{B}}}[\varepsilon^{\mathrm{A}}(1,s)+\varepsilon^{\mathrm{B}}(1,s)]$
1	l	2	s	$d^{\mathrm{ACPF}}_{n_i^{\mathrm{A}}}\varepsilon^{\mathrm{A}}(2,s)+\varepsilon^{\mathrm{B}}(2,s)-d^{\mathrm{ACPF}}_{n_i^{\mathrm{A}}+n_i^{\mathrm{B}}}[\varepsilon^{\mathrm{A}}(2,s)+\varepsilon^{\mathrm{B}}(2,s)]$
2	l	0	s	0
2	l	1	s	$d^{\mathrm{ACPF}}_{n_i^{\mathrm{A}}}\varepsilon^{\mathrm{A}}(1,s)+\varepsilon^{\mathrm{B}}(1,s)-d^{\mathrm{ACPF}}_{n_i^{\mathrm{A}}+n_i^{\mathrm{B}}}[\varepsilon^{\mathrm{A}}(1,s)+\varepsilon^{\mathrm{B}}(1,s)]$
2	l	2	s	$d^{\mathrm{AQCC}}_{n_i^{\mathrm{A}}}\varepsilon^{\mathrm{A}}(2,s)+\varepsilon^{\mathrm{B}}(2,s)-d^{\mathrm{AQCC}}_{n_i^{\mathrm{A}}+n_i^{\mathrm{B}}}[\varepsilon^{\mathrm{A}}(2,s)+\varepsilon^{\mathrm{B}}(2,s)]$

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