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Spin-projected coupled-cluster theory with single and double excitations

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Abstract. Coupled-cluster (CC) theory including single (S) and double (D) excitations and carried out with a spin-unrestricted Hartree–Fock (UHF) reference wave function is free from $S + 1$ spin contamination as can be confirmed by an analysis of the expectation value of the spin operator, $\hat{S}^2$. Contamination by the $S + 2$ contaminant can be projected out by an approximate procedure (APCCSD) with a projection operator, $\hat{P}$, represented by the product of the spin annihilation operators $\hat{A}_{s+1}$ and $\hat{A}_{s+2}$. The computational cost of such a projection scales with $O(M^6)$ (M is the number of basis functions). The APCCSD energy obtained after annihilation of the $S + 2$ contaminant can be improved by adding triple (T) excitations in a perturbative way, thus leading to APCCSD(T) energies. For the 17 examples studied, the deviation of the UHF-CCSD(T) energies from the corresponding full configuration interaction values is reduced from 4.0 to 2.3 mhartree on the average as a result of annihilating the $S + 2$ contaminant in an approximate way. In the case of single-bond cleavage, APCSSD leads to a significant improvement of the energy in the region where the bonding electrons recouple from a closed shell to an open shell singlet electron pair.

Key words: Spin projection – Coupled-cluster theory including single and double excitations – Spin contamination

1 Introduction

Unrestricted Hartree–Fock (UHF) theory [1] is a convenient starting point for single-determinant many-body perturbation theory (MBPT) [2, 3] or coupled-cluster (CC) methods. [4–6]; however, one of the major shortcomings of the UHF method is that the wave function is not an eigenfunction of the spin operator, $\hat{S}^2$. Contaminations from higher spin states are mixed into the wave function and lead to erroneous energies that effect the shape of a potential-energy surface determined at the UHF level. Methods have been developed to project out spin contamination from higher spin states [7–16]. Frequently used are spin-projected UHF (PUHF) and spin-projected UMBPT (PMBPT) methods at second, third or fourth order [10–16].

It is a general observation that the more correlation is covered by a correlation-corrected method the less problematic is the spin-contamination problem. At the lower levels of perturbation theory, the problem of spin contamination is still imminent, so the use of spin-projected methods is necessary [10–16]. However, the more correlation corrections are added and, in particular, if infinite-order effects are covered, the more spin contamination will be reduced. This should be particularly true at the CC level of theory because this approach includes all infinite order effects for a given level of excitation, for example, CC theory including single (S) and double (D) excitations [17] covers all infinite-order effects in the space of the S and D excitations and CCSD with triple (T) excitations [18] covers all infinite-order effects in the space of S, D, and T excitations, and so on.

Schlegel [11] was the first to show that UHF-CCSD in contrast to UHF does not suffer from the $S + 1$ contaminant. This may be difficult to accept since the expectation value of $\hat{S}^2$, $\langle \hat{S}^2 \rangle_{\text{CCSD}}$, adopts relatively large values in situations where one would expect a large $S + 1$ contaminant (U description of the breaking of a single bond, singlet biradicals, etc.) We have shown recently [19] that in these cases the correct $\langle \hat{S}^2 \rangle_{\text{CCSD}}$ value [20] is no longer an appropriate diagnostic tool indicating the accuracy of the UHF-CCSD energy because its value is dominated by the response of the UHF-CCSD wave function (which does not fulfill the Hellmann–Feynman theorem) on the perturbation caused by the spin contamination introduced at the UHF level. However, if one partitions $\langle \hat{S}^2 \rangle_{\text{CCSD}}$ into an energy- and a wave-function-related part, the former adopts values

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close to 0, in line with the fact that the $S + 1$ contaminant is suppressed in the UHF-CCSD energy.

In cases where the $S + 1$ state is the only source of spin contamination at the UHF level, there is no need for spin projection at the UHF-CCSD level. Generally, there will be, however, residual contaminations from $S + 2$, etc. states even if the $S + 1$ contaminant dominates at the UHF level as, for example, when single-bond breaking or singlet biradicals have to be described. In these cases, the use of a spin-projected CC (PCC) method is desirable, which will be needed even more if UHF-CCSD is used for the description of the breaking of a multiple bond or the simultaneous breaking of two or three single bonds. Then, UHF-CCSD will suffer from spin contaminations caused by $S + 2$ or even higher states.

We present in this work theory, implementation, and application of an approximate PCCSD (APCCSD) method that makes it possible to project out the $S + 2$ contaminant in the UHF-CCSD wave function and which, therefore, can be used for a number of chemically interesting problems, avoiding in this way much more expensive methods such as multireference (MR) configuration interaction (CI) with D excitations, MRCC, or multiconfigurational self-consistent field–Møller–Plesset methods.

2 Theory for PCC methods

In the CC approach, [4–6] the energy, E_{CC}, can be expressed by Eq. (1)

$$E_{CC} = \left\langle \Phi_0 \left| \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle \ , \tag{1}$$

where Φ_0 is a reference function usually resulting from a HF calculation and the cluster operator, $\hat{T}$, in an n-electron system is given by

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots \hat{T}_n \ . \tag{2}$$

The operator $\hat{T}_m$ $(m = 1, 2, \ldots, n)$ is defined by

$$\hat{T}_m = \frac{1}{m!} \sum_{ij\ldots,ab\ldots} a_{ij\ldots}^{ab\ldots} \hat{b}_a^\dagger \hat{b}_i \hat{b}_b^\dagger \hat{b}_j \ldots \tag{3}$$

where subscripts (superscripts) $i, j, k,\ldots$ ($a, b, c,\ldots$) denote occupied (virtual) spin orbitals in the reference function, while indices $p, q, r,\ldots$ are used for general spin orbitals. The operators $\hat{b}^\dagger$ and $\hat{b}^\dagger$ are creation and annihilation operators, respectively. The amplitudes $a_{ij\ldots}^{ab\ldots}$ in Eq. (3) can be determined by solving the nonlinear equations

$$\left\langle \Phi_{ij\ldots}^{ab\ldots} \left| \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle = 0 \ . \tag{4}$$

where C indicates the limitation to connected diagram components.

One obtains from the UHF-CC description of an open-shell problem the pure spin solution by applying the projection operator $\hat{P}$ [7]:

$$\Psi_{PCC} = \hat{P} e^{\hat{T}} |\Phi_0\rangle \ , \tag{5}$$

$$\hat{P} = \prod_{k \neq s} \frac{\hat{S}^2 - k(k+1)}{s(s+1) - k(k+1)} \ . \tag{6}$$

For the PCC wave function, Ψ_{PCC}, of Eq. (5), the energy is calculated according to Eq. (7).

$$E_{PCC} = \frac{\left\langle \Phi_0 \left| \hat{H} \hat{P} e^{\hat{T}} \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \hat{P} e^{\hat{T}} \right| \Phi_0 \right\rangle} \tag{7}$$

Using the fact that $[\hat{H}, \hat{P}] = 0$, Eq. (7) can be developed according to Eqs. (8), (9), (10), and (11).

$$E_{PCC} = \frac{\left\langle \Phi_0 \left| \hat{P} \hat{H} e^{\hat{T}} \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \hat{P} e^{\hat{T}} \right| \Phi_0 \right\rangle} \tag{8}$$

$$= \frac{\left\langle \Phi_0 \left| \hat{P} \left(e^{\hat{T}} e^{-\hat{T}} \right) \hat{H} e^{\hat{T}} \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \hat{P} e^{\hat{T}} \right| \Phi_0 \right\rangle} \tag{9}$$

$$= \frac{\left\langle \Phi_0 \left| \hat{P} e^{\hat{T}} \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \hat{P} e^{\hat{T}} \right| \Phi_0 \right\rangle} \tag{10}$$

$$= \frac{\left\langle \Phi_0 \left| \hat{P} \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle + \left\langle \Phi_0 \left| \hat{P} \hat{T} \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle + \left\langle \Phi_0 \left| \hat{P} \frac{1}{2} \hat{T}^2 \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle + \cdots}{\left\langle \Phi_0 \left| \hat{P} \right| \Phi_0 \right\rangle + \left\langle \Phi_0 \left| \hat{P} \hat{T} \right| \Phi_0 \right\rangle + \left\langle \Phi_0 \left| \hat{P} \frac{1}{2} \hat{T}^2 \right| \Phi_0 \right\rangle + \cdots} \ , \tag{11}$$

where Eq. (8) was previously discussed by Schlegel [11]. To simplify Eq. (11), Eq. (12) is investigated:

$$\frac{\left\langle \Phi_0 \left| \hat{P} \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \hat{P} \right| \Phi_0 \right\rangle} = \frac{\sum_y \left\langle \Phi_0 \left| \hat{P} \right| \Phi_y \right\rangle \left\langle \Phi_y \left| \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \hat{P} \right| \Phi_0 \right\rangle} \tag{12}$$

$$= \frac{\left\langle \Phi_0 \left| \hat{P} \right| \Phi_0 \right\rangle \left\langle \Phi_0 \left| \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \hat{P} \right| \Phi_0 \right\rangle} \tag{13}$$

$$= \left\langle \Phi_0 \left| \left(\hat{H} e^{\hat{T}} \right)_C \right| \Phi_0 \right\rangle, \tag{14}$$

where the right-hand side of Eq. (12) was obtained by inserting the resolution of the identity. Equation (14) follows when considering the fact that $\langle\Phi_y|(\hat{H}e^{\hat{T}})_C|\Phi_0\rangle = 0$ for all $y = $ S, D, T,... (see Eq. 4).

Similarly, Eq. (15) can be rewritten to yield Eq. (18):

$$\frac{\left\langle\Phi_0\left|\hat{P}\hat{T}\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \cdots}{\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle + \cdots}$$

$$= \frac{\sum_y\left[\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_y\right\rangle\left\langle\Phi_y\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_y\right\rangle\left\langle\Phi_y\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \cdots\right]}{\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle + \cdots}$$

(15)

$$= \frac{\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle\left\langle\Phi_0\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle\left\langle\Phi_0\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \cdots}{\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle + \cdots}$$

(16)

$$= \frac{\left\langle\Phi_0\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle\left[\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle + \cdots\right]}{\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle + \cdots}$$

(17)

$$= \left\langle\Phi_0\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle .$$

(18)

Hence, Eq. (12) is identical to Eq. (15):

$$\frac{\left\langle\Phi_0\left|\hat{P}\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle}{\left\langle\Phi_0\left|\hat{P}\right|\Phi_0\right\rangle}$$

$$= \frac{\left\langle\Phi_0\left|\hat{P}\hat{T}\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle + \cdots}{\left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle + \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle + \cdots} .$$

(19)

By applying the identity Eq. (20),

$$\frac{f_1}{g_1} = \frac{f_2}{g_2} = \frac{f_1 + f_2}{g_1 + g_2}$$

(20)

Eq. (21) follows

$$E_{PCC} = \frac{\left\langle\Phi_0\left|\hat{P}\hat{H}e^{\hat{T}}\right|\Phi_0\right\rangle}{\left\langle\Phi_0\left|\hat{P}e^{\hat{T}}\right|\Phi_0\right\rangle} = \frac{\left\langle\Phi_0\left|\hat{P}\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle}{\left\langle\Phi_0\left|\hat{P}\right|\Phi_0\right\rangle} = E_{CC} ,$$

(21)

which simply means that there will be no spin contamination when the correct CC wave function with the full CC operator $\hat{T}$ is used.

3 Approximate PCC methods

For approximate CC wave functions using a truncated cluster operator $\hat{T}$, Eq. (21) is not fulfilled and E_{PCC} has to be calculated according to Eq. (11), which can be written according to Eq. (22).

$$E_{PCC} = \frac{A_0 + A_1 + A_2 + \cdots}{B_0 + B_1 + B_2 + \cdots}$$

(22)

$$= \frac{(A_0' + \Delta A_0) + (A_1' + \Delta A_1) + (A_2' + \Delta A_2) + \cdots}{B_0 + B_1 + B_2 + \cdots} ,$$

(23)

where

$$A_0 = \left\langle\Phi_0\left|\hat{P}\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle = A_0' + \Delta A_0 ,$$

(24)

$$A_1 = \left\langle\Phi_0\left|\hat{P}\hat{T}\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle = A_1' + \Delta A_1 ,$$

(25)

$$A_2 = \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle = A_2' + \Delta A_2 ,$$

(26)

$$A_0' = \left\langle\Phi_0\left|\hat{P}\right|\Phi_0\right\rangle\left\langle\Phi_0\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle = \left\langle\Phi_0\left|\hat{P}\right|\Phi_0\right\rangle E_{CC} ,$$

(27)

$$\Delta A_0 = \sum_y^{\text{S,D,T,Q,...}} \left\langle\Phi_0\left|\hat{P}\right|\Phi_y\right\rangle\left\langle\Phi_y\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle ,$$

(28)

$$A_1' = \left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle\left\langle\Phi_0\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle = \left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle E_{CC} ,$$

(29)

$$\Delta A_1 = \sum_y^{\text{S,D,T,Q,...}} \left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_y\right\rangle\left\langle\Phi_y\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle ,$$

(30)

$$A_2' = \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle\left\langle\Phi_0\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle$$

$$= \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle E_{CC} ,$$

(31)

$$\Delta A_2 = \sum_y^{\text{S,D,T,Q,...}} \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_y\right\rangle\left\langle\Phi_y\left|\left(\hat{H}e^{\hat{T}}\right)_C\right|\Phi_0\right\rangle ,$$

(32)

and

$$B_0 = \left\langle\Phi_0\left|\hat{P}\right|\Phi_0\right\rangle ,$$

(33)

$$B_1 = \left\langle\Phi_0\left|\hat{P}\hat{T}\right|\Phi_0\right\rangle ,$$

(34)

$$B_2 = \left\langle\Phi_0\left|\hat{P}\tfrac{1}{2}\hat{T}^2\right|\Phi_0\right\rangle .$$

(35)

The PCC energy can be expressed as the sum of two terms, one of which represents the CC energy without spin projection, while the other gives the correction term resulting from spin projection.

$$E_{PCC} = \frac{(A_0' + A_1' + A_2' + \cdots) + (\Delta A_0 + \Delta A_1 + \Delta A_2 + \cdots)}{B_0 + B_1 + B_2 + \cdots} \tag{36}$$

$$= E_{CC} + \frac{\Delta A_{0+} + \Delta A_1 + \Delta A_2 + \cdots}{B_0 + B_1 + B_2 + \cdots} \tag{37}$$

$$= E_{CC} + \Delta E_{PCC} \ , \tag{38}$$

where

$$\Delta E_{PCC} = \frac{\Delta A_0 + \Delta A_1 + \Delta A_2 + \cdots}{B_0 + B_1 + B_2 + \cdots} \ . \tag{39}$$

In the following, the CCSD approach is considered, i.e., $\hat{T} = \hat{T}_1 + \hat{T}_2$, and the question is posed how to project the $S + 2$ contaminant out of UHF-CCSD. Accordingly, the projection operator $\hat{P}$ can be approximated by the product of the annihilation operators $\hat{A}_{s+1}$ and $\hat{A}_{s+2}$.

$$\hat{P} \approx \hat{A}_{s+1}\hat{A}_{s+2}, \tag{40}$$

where the annihilation operator $\hat{A}_{s+i}$ in its general form is given by Eq. (41).

$$\hat{A}_{s+i} = \frac{\hat{S}^2 - (s+i)(s+i+1)}{\langle \hat{S}^2 \rangle_0 - (s+i)(s+i+1)}$$

$$= \frac{\{\hat{S}^2\}}{\langle \hat{S}^2 \rangle_0 - (s+i)(s+i+1)} + 1 \ , \tag{41}$$

with

$$\langle \hat{S}^2 \rangle_0 = \langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle = \langle \hat{S}^2 \rangle_{HF} \ . \tag{42}$$

In Eq. (41), $\{\hat{S}^2\}$ is the normal order form of $\hat{S}^2$ [21], i.e., $\{\hat{S}^2\} = \hat{S}^2 + \langle \hat{S}^2 \rangle_0$. If just two annihilation operators are used, Eq. (39) will reduce to Eq. (43)

$$\Delta E_{PCCSD} = \frac{\Delta A_0 + \Delta A_1}{B_0 + B_1 + B_2 + \cdots} \ , \tag{43}$$

with

$$\Delta A_0 = \sum_y^{T,Q} \langle \Phi_0 | \hat{P} | \Phi_y \rangle \langle \Phi_y | \left(\hat{H}e^{\hat{T}} \right)_C | \Phi_0 \rangle \ , \tag{44}$$

$$\Delta A_1 = \sum_y^{T} \langle \Phi_0 | \hat{P}\hat{T} | \Phi_y \rangle \langle \Phi_y | \left(\hat{H}e^{\hat{T}} \right)_C | \Phi_0 \rangle \ , \tag{45}$$

where terms ΔA_2, ΔA_3, etc. are zero for UHF-CCSD. To calculate E_{PCCSD} in Eq. (43), approximations 1 and 2, leading to spin-projected UHF-CCSD energies, APCCSD-1 and APCCSD-2, are used.

3.1 Approximation 1

This is based on approximating the spin correction by the leading term of the nominator and the denominator of Eq. (43):

$$\Delta E_{PCCSD} \approx \frac{\Delta A_0}{B_0} \ , \tag{46}$$

which implies that

$$\frac{A_0}{B_0} = \frac{A_1 + A_2 + \cdots}{B_1 + B_2 + \cdots} \tag{47}$$

and that Eq. (22) can be simplified to Eq. (48)

$$E_{APCCSD-1} = \frac{A_0 + A_1 + A_2 + \cdots}{B_0 + B_1 + B_2 + \cdots} = \frac{A_0}{B_0}$$

$$= E_{CCSD} + \frac{\Delta A_0}{B_0} \ , \tag{48}$$

which is equivalent to Eq. (46). Approximation 1 is correct for CC theory with the full cluster operator $\hat{T}$ or when the projection operator $\hat{P}$ is limited to the SD space, SDT space, etc. Alternatively, approximation 1 is also correct for UHF-CCSD in the case of just a $S + 1$ contaminant, UHF-CCSDTQ in case of just $S + 1$ and $S + 2$ contaminants, which simply means that these contaminants are totally suppressed because of infinite-order SD and SDTQ correlation effects, respectively. In all other cases, terms ΔA_0, ΔA_1, B_0, etc. of Eq. (43) have to fulfill one of three mathematical conditions to guarantee that Eq. (48) is reasonable and the APCCSD-1 energy represents a useful spin-projected CCSD energy.

– Condition 1: $\Delta A_0/B_0$, $\Delta A_1/B_1$, $\Delta A_2/B_2$ are very small:

$$\frac{A_0}{B_0} = \frac{A_0' + \Delta A_0}{B_0} \approx \frac{A_0'}{B_0} = E_{CCSD} \ , \tag{49}$$

$$\frac{A_1}{B_1} = \frac{A_1' + \Delta A_1}{B_1} \approx \frac{A_1'}{B_1} = E_{CCSD} \ . \tag{50}$$

– Condition 2: ΔA_1, B_1, B_2, ... are all negligible.
– Condition 3: The influence of ΔA_1, B_1, B_2, etc. is mutually canceled, which is equivalent to

$$\frac{\Delta A_0}{B_0} = \frac{\Delta A_1}{B_1 + B_2 + \cdots} \ . \tag{51}$$

At least one of conditions 1–3 should be fulfilled if a doublet radical or triplet biradical without any strong multireference character is described for geometries close to the equilibrium. Also, if the $S+1$ contaminant is dominant as in the case of single-bond breaking, terms ΔA_1, B_1, etc. will be relatively small. This means that in all those cases, in which UHF-CCSD provides a spincontaminated but nevertheless reasonable approximation, the APCCSD-1 method should lead to an improvement of UHF-CCSD energies. In view of the fact that the cost for calculating APCCSD-1 energies just scale with $O(M^6)$ (M is the number of basis functions, see later), this is a reasonable extension of the normal UHF-CCSD calculation.

3.2 Approximation 2

In the case that spin contamination $S + 2$ is large and dominant, the term ΔA_0 also becomes large and the term

ΔA_1 is no longer negligible. This can be seen when dissecting ΔA_0 and ΔA_1 into matrix elements:

$$A_0 \sim \langle 0|\hat{P}|\mathrm{T}\rangle\left\langle \mathrm{T}\left|\left(\hat{H}\mathrm{e}^{\hat{T}}\right)_{\mathrm{C}}\right|0\right\rangle + \langle 0|\hat{P}|\mathrm{Q}\rangle\left\langle \mathrm{Q}\left|\left(\hat{H}\mathrm{e}^{\hat{T}}\right)_{C}\right|0\right\rangle \tag{52}$$

$$A_1 \sim a_\mathrm{s}\langle 0|\hat{P}|\mathrm{Q}\rangle\left\langle \mathrm{T}\left|\left(\hat{H}\mathrm{e}^{\hat{T}}\right)_{\mathrm{C}}\right|0\right\rangle \tag{53}$$

where a_s is the amplitude of cluster operator $\hat{T}_1$ and 0, T, and Q denote reference, T, and quadruple excited functions. If the sum over all possible matrix elements covered by Eq. (52) is large, then terms in Eq. (53) cannot be neglected and Eq. (51) will not be fulfilled. In this situation, the more complete Eq. (54) has to be used, which is correct for the case that just a $S+2$ contaminant is present, which is projected out by $\hat{A}_{s+1}$ $\hat{A}_{s+2}$. However, if residual $S+3$, etc. contaminants are present, Eq. (54) will be an approximation.

$$\Delta E_{\mathrm{APCCSD-2}} = \frac{\Delta A_0 + \Delta A_1}{B_0 + B_1 + B_2 + \cdots} \tag{54}$$

APCCSD-2 is also a $O(M^6)$ method, which however is much more difficult to program since it requires the reformulation of a large number of matrix elements involving T and Q excitations in terms of intermediate arrays scaling with $O(M^6)$. Therefore, we will first develop formulas for calculating and testing the usefulness of the APCCSD-1 method before we derive in future work APCCSD-2.

4 The APCCSD-1 method

The APCCSD-1 energy is given by Eq. (55):

$$E_{\mathrm{APCCSD-1}} = E_{\mathrm{CCSD}}$$
$$+ \frac{\sum_y^{\mathrm{T,Q}} \left\langle \Phi_0|\hat{A}_{s+1}\hat{A}_{s+2}|\Phi_y\right\rangle\left\langle \Phi_y\left|\left(\hat{H}\mathrm{e}^{\hat{T}_1+\hat{T}_2}\right)_{\mathrm{C}}\right|\Phi_0\right\rangle}{\left\langle \Phi_0|\hat{A}_{s+1}\hat{A}_{s+2}|\Phi_0\right\rangle} \tag{55}$$

which by employing Eq. (42) can be expressed according to Eq. (56).

$$E_{\mathrm{APCCSD-1}} = E_{\mathrm{CCSD}}$$
$$+ \frac{\sum_y^{\mathrm{T,Q}} \left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_y\right\rangle\left\langle \Phi_y\left|\left(\hat{H}\mathrm{e}^{\hat{T}_1+\hat{T}_2}\right)_{\mathrm{C}}\right|\Phi_0\right\rangle}{\left\langle \Phi_0\left|\left[\hat{S}^2-(s+1)(s+2)\right]\left[\hat{S}^2-(s+2)(s+3)\right]\right|\Phi_0\right\rangle} \tag{56}$$

By using the expression for the normal order of $\hat{S}^2$ [21], the matrix elements $\left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_y\right\rangle$ of the numerator of Eq. (56) can be determined by Eqs. (57), (58)

$$\left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_{ijk}^{ab\bar{c}}\right\rangle = 4\sum_P (-1)^P P(i/j|a/b)S_{j\bar{c}}S_{b\bar{k}}\tilde{S}_a^i , \tag{57a}$$

$$\left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_{ijk}^{\bar{a}bc}\right\rangle = 4\sum_P (-1)^P P(\bar{i}/\bar{j}|\bar{a}/\bar{b})S_{c\bar{i}}S_{k\bar{a}}\tilde{S}_{\bar{b}}^{\bar{j}} \tag{57b}$$

$$\left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_{ij\bar{k}\bar{l}}^{ab\bar{c}\bar{d}}\right\rangle$$
$$= \sum_P (-1)^P P(i/j|\bar{k}/\bar{l}|a/b|\bar{c}/\bar{d})S_{i\bar{c}}S_{a\bar{k}}S_{j\bar{d}}S_{b\bar{l}} \tag{58}$$

where the permutation symbol $P(i/j|\bar{k}/\bar{l}|a/b|\bar{c}/\bar{d})$ means that in addition to the identity permutation, all possible products involving permutations of just i and j, $\bar{k}$ and $\bar{l}$, a and b, and $\bar{c}$ and $\bar{d}$ are allowed. The symbol $S_{p\bar{q}}$ in Eqs (57), and (58) denotes the spatial overlap between two orbitals

$$S_{p\bar{q}} = \int \phi_p\hat{S}_+\bar{\phi}_q\mathrm{d}\tau \tag{59}$$

while the quantity $\tilde{S}_a^i\left(\text{or } \tilde{S}_{\bar{b}}^{\bar{j}}\right)$ is defined by

$$\tilde{S}_a^i = \sum_{\bar{l}} S_{a\bar{l}}S_{i\bar{l}} \quad \text{or} \quad \tilde{S}_{\bar{b}}^{\bar{j}} = \sum_k S_{k\bar{b}}S_{k\bar{j}} \tag{60}$$

There are no contributions to the energy E_{APCCSD} for $\alpha\alpha\alpha$ ($\beta\beta\beta$) and $\alpha\alpha\alpha\alpha$ ($\beta\beta\beta\beta$), $\alpha\alpha\alpha\beta$ ($\beta\beta\beta\alpha$) spin cases since in the case of equal spin for orbitals p and q the spatial orbital overlap, S_{pq}, is equal to δ_{pq}.

The explicit expressions for the matrix elements $\left\langle \Phi_y\left|\left(\hat{H}\mathrm{e}^{\hat{T}_1+\hat{T}_2}\right)_{\mathrm{C}}\right|\Phi_0\right\rangle$ in the $\alpha\alpha\beta$ and $\alpha\alpha\beta\beta$ spin cases are listed in Table 1, from which one can also obtain the corresponding expressions $\left\langle \Phi_{ijk}^{\bar{a}\bar{b}c}\left|\left(\hat{H}\mathrm{e}^{\hat{T}_1+\hat{T}_2}\right)_{\mathrm{C}}\right|\Phi_0\right\rangle$ i.e., for the $\beta\beta\alpha$ spin case. The spin correction $\Delta E_{\mathrm{APCCSD-1}}$ for E_{CCSD} covers only three different types of contributions due to T and Q excitations written as

$$\Delta E_{\mathrm{APCCSD-1}} = E_{\mathrm{APCCSD-1}} - E_{\mathrm{CCSD}}$$
$$= \Delta E_{\mathrm{APCCSD-1}}(\alpha\alpha\beta) + \Delta E_{\mathrm{APCCSD-1}}(\beta\beta\alpha)$$
$$+ \Delta E_{\mathrm{APCCSD-1}}(\alpha\alpha\beta\beta) \tag{61}$$

where each energy term can be given by

$$\Delta E_{\mathrm{APCCSD-1}}(\alpha\alpha\beta)$$
$$= \frac{\sum\limits_{i<j,\bar{k},a<b,\bar{c}} \left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_{ij\bar{k}}^{ab\bar{c}}\right\rangle\left\langle \Phi_{ij\bar{k}}^{ab\bar{c}}\left|\left(\hat{H}\mathrm{e}^{\hat{T}_1+\hat{T}_2}\right)_{\mathrm{C}}\right|\Phi_0\right\rangle}{\left\langle \Phi_0\left|\left[\hat{S}^2-(s+1)(s+2)\right]\left[\hat{S}^2-(s+2)(s+3)\right]\right|\Phi_0\right\rangle} \tag{62}$$

$$\Delta E_{\mathrm{APCCSD-1}}(\beta\beta\alpha)$$
$$= \frac{\sum\limits_{\bar{i}<\bar{j},k,\bar{a}<\bar{b},c} \left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_{\bar{i}\bar{j}k}^{\bar{a}\bar{b}c}\right\rangle\left\langle \Phi_{\bar{i}\bar{j}k}^{\bar{a}\bar{b}c}\left|\left(\hat{H}\mathrm{e}^{\hat{T}_1+\hat{T}_2}\right)_{\mathrm{C}}\right|\Phi_0\right\rangle}{\left\langle \Phi_0\left|\left[\hat{S}^2-(s+1)(s+2)\right]\left[\hat{S}^2-(s+2)(s+3)\right]\right|\Phi_0\right\rangle} \tag{63}$$

$$\Delta E_{\mathrm{APCCSD-1}}(\alpha\alpha\beta\beta)=$$
$$\frac{\sum\limits_{i<j,\bar{k}<\bar{i},a<b,\bar{c}<\bar{d}} \left\langle \Phi_0|\{\hat{S}^2\}\{\hat{S}^2\}|\Phi_{ij\bar{k}\bar{l}}^{ab\bar{c}\bar{d}}\right\rangle\left\langle \Phi_{ij\bar{k}\bar{l}}^{ab\bar{c}\bar{d}}\left|\left(\hat{H}\mathrm{e}^{\hat{T}_1+\hat{T}_2}\right)_{\mathrm{C}}\right|\Phi_0\right\rangle}{\left\langle \Phi_0\left|\left[\hat{S}^2-(s+1)(s+2)\right]\left[\hat{S}^2-(s+2)(s+3)\right]\right|\Phi_0\right\rangle} \tag{64}$$

Table 1. Algebraic expression for the matrix elements $\langle\Phi_{yl}|(\hat{H}e^{\hat{T}_1+\hat{T}_2})_C|\Phi_0\rangle$ in the spin cases $\alpha\alpha\beta$ and $\alpha\alpha\beta\beta$[a]

Matrix element	Expression
$\langle\Phi^{ab\bar{c}}_{ij\bar{k}}\|(\hat{H}e^{\hat{T}_1+\hat{T}_2})_C\|\Phi_0\rangle$	$-\sum_P (-1)^P P(i/j\|a/b)\left[\sum_{\bar{d}} X(l\bar{d},b\bar{c})a^{a\bar{d}}_{jk} - \sum_l Y(\bar{l}a,\bar{k}j)a^{b\bar{c}}_{i\bar{l}}\right] + \sum_P (-1)^P P(a/b)\left[\sum_d X(\bar{k}d,\bar{c}b)a^{ad}_{ij} + \sum_l Y(la,ij)a^{b\bar{c}}_{lk}\right]$
	$+\sum_P (-1)^P P(i/j)\left[\sum_{\bar{d}} X(i\bar{d},ab)a^{d\bar{c}}_{jk} - \sum_l Y(l\bar{c},jk)a^{ab}_{i\bar{l}}\right]$
$\langle\Phi^{ab\bar{c}\bar{d}}_{ij\bar{k}\bar{l}}\|(\hat{H}e^{\hat{T}_1+\hat{T}_2})_C\|\Phi_0\rangle$	$\sum_P (-1)^P P(i/j\|\bar{k}/\bar{l}\|a/b\|\bar{c}/\bar{d})\left[-\sum_{e,\bar{f}} Z1(b\bar{c},e\bar{f})a^{e\bar{d}}_{jk}a^{a\bar{f}}_{i\bar{l}} - \sum_{m,\bar{n}} Z2(m\bar{n},\bar{j}k)a^{a\bar{d}}_{m\bar{l}}a^{b\bar{c}}_{i\bar{n}} - \sum_{m,e} Z3(\bar{m}a,\bar{k}e)a^{e\bar{d}}_{ji}a^{b\bar{c}}_{i\bar{m}}\right]$
	$+\sum_{m,\bar{e}} Z3(m\bar{d},l\bar{e})a^{a\bar{e}}_{ji}a^{b\bar{c}}_{mk} + \sum_{m,\bar{e}} Z3(\bar{m}\bar{d},\bar{k}\bar{e})a^{a\bar{e}}_{ji}a^{b\bar{c}}_{l\bar{m}} + \sum_{m,e} Z3(ma,ie)a^{e\bar{d}}_{ji}a^{b\bar{c}}_{mk}$
	$+\sum_P (-1)^P P(i/j\|\bar{k}/\bar{l}\|\bar{c}/\bar{d})\sum_{m,\bar{e}} Z3(m\bar{c},\bar{k}e)a^{e\bar{d}}_{ji}a^{ab}_{im} + \sum_P (-1)^P P(i/j\|\bar{k}/\bar{l}\|a/b)\sum_{m,\bar{e}} Z3(\bar{m}a,i\bar{e})a^{be}_{ji}a^{\bar{c}\bar{d}}_{km}$
	$-\sum_P (-1)^P P(i/j\|a/b\|\bar{c}/\bar{d})\sum_{m,\bar{e}} Z3(\bar{m}a,\bar{j}e)a^{e\bar{d}}_{ki}a^{b\bar{c}}_{l\bar{m}} + \sum_P (-1)^P P(\bar{k}/\bar{l}\|a/b\|\bar{c}/\bar{d})\sum_{m,e} Z3(m\bar{c},\bar{k}e)a^{ae}_{ij}a^{bd}_{ml}$
	$+\sum_P (-1)^P P(a/b\|\bar{c}/\bar{d})\left[\sum_{e,\bar{f}} Z1(b\bar{c},e\bar{f})a^{\bar{f}\bar{d}}_{kl}a^{ae}_{ij} + \sum_{m,n} Z2(mn,ji)a^{a\bar{d}}_{nl}a^{b\bar{c}}_{mk} + \sum_{m,n} Z2(\bar{m}\bar{n},\bar{l}k)a^{a\bar{d}}_{jn}a^{b\bar{c}}_{i\bar{m}}\right]$
	$+\sum_P (-1)^P P(i/j\|\bar{k}/\bar{l})\left[\sum_{m,\bar{n}} Z2(m\bar{n},jk)a^{\bar{c}\bar{d}}_{nl}a^{ab}_{im} - \sum_{e,f} Z1(ab,ef)a^{f\bar{d}}_{il}a^{e\bar{c}}_{jk} - \sum_{e,\bar{f}} Z1(\bar{c}\bar{d},e\bar{f})a^{b\bar{f}}_{il}a^{ae}_{jk}\right]$
	$-\sum_P (-1)^P P(\bar{k}/\bar{l}\|a/b)\sum_{m,\bar{e}} Z3(\bar{m}a,\bar{k}e)a^{be}_{ij}a^{\bar{c}\bar{d}}_{lm} - \sum_P (-1)^P P(i/j\|\bar{c}/\bar{d})\sum_{m,\bar{e}} Z3(m\bar{c},j\bar{e})a^{\bar{e}\bar{d}}_{kl}a^{ab}_{im}$

[a] The intermediate arrays X, Y, and $Z1$, $Z2$, $Z3$ are defined in Table 2

In a one-step calculation of the terms appearing in Eq. (62), the computational cost scales as $O(M^7)$ or $O(M^8)$. However, the calculation of Eq. (62) can be dissected into a sequence of several M^6 steps by introducing a set of intermediate arrays. As described in the Appendix, for example, the determination of $\Delta E_{\text{APCCSD-1}}(\alpha\alpha\beta)$ is reduced to $O(M^6)$ by using intermediate arrays $L1$–$L3$ and In, un, and vn ($n = 1,...,5$). Similarly, the matrix element $\left\langle \Phi_{ij\bar{k}l}^{ab\bar{c}\bar{d}} \left| \left(\hat{H} e^{\hat{T}_1 + \hat{T}_2} \right)_C \right| \Phi_0 \right\rangle$ is replaced by 28 intermediate arrays, such as the contractions between spatial overlap and double amplitudes and combinations of these contractions with the arrays $Z1$, $Z2$, and $Z3$ because the total cost of calculating $E_{\text{APCCSD-1}}(\alpha\alpha\beta\beta)$ is just proportional to $O(M^6)$ (see Appendix).

APCCSD calculations can be connected with a perturbative assessment of T contributions, thus leading from CCSD(T) to APCCSD(T). Both APCCSD-1 and APCCSD(T)-1 were implemented within the ab initio package COLOGNE99 [22] by programming the formulas given in the Appendix and in Tables 1 and 2. Since APCCSD calculations scale with $O(M^6)$, the calculational costs for APCCSD-1 and APCCSD(T)-1 are comparable to those of CCSD and CCSD(T) and require just the extra work of one CCSD iteration.

5 Results and discussion

APCCSD-1 and APCCSD(T)-1 energies for the F(^{2}P) atom and some doublet or triplet (bi)radicals are listed together with the corresponding $\langle \hat{S}^2 \rangle$ values in Table 3.

Also shown are results for the UHF-CCSD description of doublet/triplet (bi)radicals with stretched geometries because the simultaneous breaking of the AH bonds in these molecules leads to $S + 1$, $S + 2$, $S + 3$, etc. contaminations at the UHF level of theory. For each calculated energy its deviation from the corresponding full CI value calculated with the same basis set at the same geometry is also given as a reference for evaluating energy improvements obtained by spin projection. The relevant information on geometry and basis sets used in the calculations is given in Table 4.

As expected energy changes caused by spin projection are marginal for molecules at their equilibrium geometry, reducing the mean absolute deviation of CCSD(T) correlation energies from the corresponding FCI energies [23–26] from 0.354 to 0.242 mhartree. The energy-related expectation value, $\langle \hat{S}^2 \rangle^E$, which we identified as the appropriate diagnostic tool for the quality of the UHF-CCSD energy [19], is in all these cases close to its ideal value, in line with the fact that UHF-CCSD does not suffer from the $S + 1$ contaminant. This becomes particularly clear in the case of the UHF-CCSD description of the closed shell singlet state of CH_2, which at the UHF level strongly suffers from spin contamination by a triplet state ($\langle \hat{S}^2 \rangle_{\text{UHF}} = 0.71$, Table 3). However, at the UHF-CCSD level $\langle \hat{S}^2 \rangle_{\text{CCSD}}^E$ is 0.0016, suggesting only a small contribution from an $S + 2$ contaminant. Consequently the APCCSD energy is changed by just 0.535 mhartree and this value is positive owing to the fact that the corresponding triplet state is actually below the singlet state in this case.

The $\langle \hat{S}^2 \rangle_{\text{CCSD}}^E$ values for stretched geometries indicate the strong influence from higher spin contaminants.

Table 2. Definition of the intermediate arrays used in Table 1

Intermediate arrays[a]	Definition[b]
$X(id, bc)$	$\langle bc\|id\rangle - \sum_{m,e}\left(\langle mb\|ed\rangle a_{im}^{ce} - \langle mc\|ed\rangle a_{im}^{be}\right) + \sum_{m<n}\left(\langle mn\|id\rangle + \sum_e \langle mn\|ed\rangle a_i^e\right)\tau_{mn}^{bc}$ $+ \sum_e \langle bc\|ed\rangle a_i^e + \sum_m \left[\tilde{X}(mb, id)a_m^c - \tilde{X}(mc, id)a_m^b\right] - \sum_{m,n,e}\langle mn\|ed\rangle a_m^e a_{in}^{bc}$
$Y(la, jk)$	$\langle la\|jk\rangle + \sum_{m,e}\left(\langle ml\|ej\rangle a_{km}^{ae} - \langle ml\|ek\rangle a_{jm}^{ae}\right) + \sum_{e<f}\left(\langle la\|ef\rangle + \sum_m \langle ml\|ef\rangle a_m^a\right)\tau_{jk}^{ef}$ $+ \sum_m \langle ml\|jk\rangle a_m^a + \sum_e \left[\tilde{Y}(al, ej)a_k^e - \tilde{Y}(al, ek)a_j^e\right]$
$Z1(bc, ef)$	$\langle bc\|ef\rangle + \frac{1}{2}\sum_{m,n}\langle mn\|ef\rangle a_{mn}^{bc} - \sum_P (-1)^P P(b/c) \sum_m \left(\langle bm\|ef\rangle - \frac{1}{2}\sum_n \langle nm\|ef\rangle a_n^b\right)a_m^c$
$Z2(mn, jk)$	$\langle mn\|jk\rangle + \frac{1}{2}\sum_{e,f}\langle mn\|ef\rangle a_{jk}^{ef} + \sum_P (-1)^P P(j/k) \sum_e \left(\langle mn\|je\rangle + \frac{1}{2}\sum_f \langle mn\|fe\rangle a_j^f\right)a_k^e$
$Z3(mc, je)$	$\langle mc\|je\rangle - \sum_n \langle mn\|je\rangle a_n^c - \sum_{n,f}\langle mn\|fe\rangle a_{jn}^{fc} + \sum_f \left(\langle cm\|ef\rangle - \sum_n \langle nm\|ef\rangle a_n^c\right)a_j^f$

[a] For simplicity the arrays X, Y, and Z1, Z2, Z3 are given in a spin orbital form
[b] The arrays $\tau_{ij}^{ab}, \tilde{X}(mb, id)$ and $\tilde{Y}(al, ej)$ are given by

$$\tau_{ij}^{ab} = a_{ij}^{ab} + a_i^a a_j^b - a_i^b a_j^a$$

$$\tilde{X}(mb, id) = \langle mb\|id\rangle + \sum_e \langle mb\|ed\rangle a_i^e + \sum_{n,e}\langle mn\|ed\rangle a_{in}^{be}$$

$$\tilde{Y}(al, ej) = \langle al\|ej\rangle - \sum_m \langle ml\|ej\rangle a_m^a + \sum_{m,f}\langle ml\|ef\rangle a_{jm}^{af}$$

Table 3. Comparison of UHF-CCSD and UHF-CCSD(T) energies with APCCSD-1 and APCCSD(T)-1 energies for various radicals and biradicals[a]

System	Basis set	Geom.	$\langle \hat{S}^2 \rangle_{UHF}$	$\langle \hat{S}^2 \rangle^I_{CCSD}$	$\langle \hat{S}^2 \rangle^E_{CCSD}$	CCSD Energy	Δ_{FCI}	$\Delta E(T)$	Δ APCCSD-1	CCSD(T) Energy	Δ_{FCI}	APCCSD(T)-1 Energy	Δ_{FCI}
F atom	4s3p1d		0.7528	0.7501	0.7500	−99.544790	1.830	−0.001717	−0.000063	−99.546507	0.113	−99.546570	0.050
	4s3p2d		0.7534	0.7501	0.7500	−99.563844	2.639	−0.002533	−0.000085	−99.566377	0.106	−99.566462	0.021
	5s4p2d		0.7534	0.7502	0.7500	−99.591542	3.335	0.003183	−0.000098	−99.594725	0.152	−99.594823	0.052
CH_2 ($^1A_1$)	DZP	$1.0r_e$	0.7151	0.6415	0.0016	−39.025363	1.820	−0.001941	0.000535	−39.027303	−0.120	−39.026769	0.414
CH_2 ($^3B_1$)	DZP	$1.0r_e$	2.0151	2.0006	2.0000	−39.044170	2.090	−0.001730	−0.000148	−39.045900	0.360	−39.046048	0.212
CH_3 ($^2A_2''$)	DZP	$1.0r_e$	0.7613	0.7505	0.7500	−39.718422	2.790	−0.002290	−0.000154	−39.720712	0.500	−39.720866	0.346
		$1.5r_e$	1.0670	0.7759	0.7521	−39.474085	8.768	−0.006099	−0.001769	−39.480184	2.669	−39.481953	0.900
		$2.0r_e$	3.1536	0.8612	−1.5444	−39.283361	19.771	−0.048679	0.014138	−39.332040	−28.908	−39.317902	−14.770
NH_2 ($^2B_1$)	DZP	$1.0r_e$	0.7579	0.7504	0.7500	−55.739408	3.212	−0.002664	−0.000139	−55.742072	0.548	−55.742211	0.409
		$1.5r_e$	1.6414	0.8795	0.7329	−55.595309	9.900	−0.006072	−0.005970	−55.601381	3.828	−55.607351	−2.142
		$2.0r_e$	2.5409	1.8438	−0.6879	−55.494211	11.313	−0.003804	−0.014870	−55.498015	7.509	−55.512885	−7.361
NH_2 ($^2A_1$)	DZP	$1.0r_e$	0.7554	0.7502	0.7500	−55.685769	2.993	−0.002459	−0.000108	−55.688228	0.534	−55.688336	0.426
		$1.5r_e$	0.7782	0.7508	0.7500	−55.509945	7.669	−0.005477	−0.000228	−55.515422	2.192	−55.515650	1.964
		$2.0r_e$	1.522	0.9778	0.7171	−55.394954	20.179	−0.010138	−0.006251	−55.405092	10.041	−55.411343	3.790
SiH_2 ($^3B_1$)	DZP	$1.0r_e$	2.0054	2.0002	2.0000	−290.102248	2.303	−0.001784	−0.000095	−290.104032	0.591	−290.104127	0.424
		$1.5r_e$	2.2979	2.2071	2.0022	−289.983113	7.375	−0.005248	−0.001097	−289.988361	2.127	−289.989458	1.030
		$2.0r_e$	2.8694	2.4440	1.9633	−289.911050	14.344	−0.006173	−0.003463	−289.917223	8.171	−289.920686	4.708
Mean Absolute Deviation							7.196				4.023		2.295

[a]All energies are in hartree. Δ_{FCI} denotes energy deviations from FCI energies [23–26] and is given in mhartree as is the corresponding mean absolute deviation. $\Delta E(T)$ and $\Delta APCCSD-1$ give the energy lowering achieved by a perturbative inclusion of the T excitations at CCSD(T) and by spin projection at the APCCSD-1 level. $\langle \hat{S}^2 \rangle^I_{CCSD}$ was defined in Ref. 21 and is parallel to the correct $\langle \hat{S}^2 \rangle_{CCSD}$ value. $\langle \hat{S}^2 \rangle^E_{CCSD}$ is the energy-related part of the correct $\langle \hat{S}^2 \rangle_{CCSD}$ value [19]

Table 4. Geometries and basis sets of the electron systems investigated[a]

System	State	Symmetry	Basis set	Geometry	Reference
F	^2P		(9s6p1d) [4s3p1d] (9s6p2d) [4s3p2d] (9s6p2d) [5s3p2d]		25
CH_2 (1.0r_e)	$^1A_1$	C_{2v}	(9s5p1d/4s1p) [4s2p1d/2s1p]	$r(CH) = 1.117$ $\theta(HCH) = 102.4$	23
CH_2 (1.0r_e)	$^3B_1$	C_{2v}	(9s5p1d/4s1p) [4s2p1d/2s1p]	$r(CH) = 1.082$ $\theta(HCH) = 132.4$	23
CH_3 (1.0r_e)	$^2A_2''$	D_{2v}	(9s5p1d/4s1p) [4s2p1d/2s1p]	$r(CH) = 1.090$	24
NH_2 (1.0r_e)	$^2B_1$	C_{2v}	(9s5p1d/4s1p) [4s2p1d/2s1p]	$r(NH) = 1.024$ $\theta(HNH) = 103.4$	26
NH_2 (1.0r_e)	$^2A_1$	C_{2v}	(9s5p1d/4s1p) [4s2p1d/2s1p]	$r(NH) = 1.013$ $\theta(HNH) = 103.2$	26
SiH_2 (1.0r_e)	$^3B_1$	C_{2v}	(13s9p1d/4s1p) [6s4p1d/2s1p]	$r(SiH) = 1.466$ $\theta(HSiH) = 118.0$	26

[a]Bond distances are given in Å and angles in degree

This is confirmed by the energy lowering obtained for APCCSD-1 energies in these cases. The mean absolute deviation of UHF-CCSD energies from FCI energies is 7.196 mhartree; for UHF-CCSD(T) it is improved to 4.023 mhartree, however for APCCSD(T)-1 a mean absolute deviation of just 2.295 mhartree is obtained (values for equilibrium geometries: 2.557; 0.328; 0.261). Closer inspection reveals that improvements obtained by projecting out the $S + 2$ contaminant strongly depend on the electron configuration of the molecule in question. For example, in the $NH_2(^2B_1)$ state the single electron is in a $p\pi$ orbital and accordingly electron interactions with the σ electrons of the stretched NH bonds at $2\tau_e$ are moderate (although spin polarization between σ and π electrons is possible at the UHF-CC level). For the situation of the simultaneous stretching of two NH bonds of a closed-shell molecule, RNH_2, both the triplet and the pentuplet contaminants are present, which in the case of $NH_2(^2B_1)$ leads to quartet and sextuplet contaminants. In the case of the $NH_2(^2A_1)$ state, the single electron is in the plane of the NH bonds and, accordingly, some recoupling with the electrons of the NH bonds upon bond stretching is possible, thus leading to a lower influence of the $S + 2$, $S + 3$, etc. contaminants as in $NH_2(^2B_1)$. Improvements in relative energies achieved in the former state are significant, while in the latter state after projection the relative energy is even slightly deteriorated (the error relative to the FCI value increases from 4.4 to 4.9 kcal/mol). This is clearly a reflection of the fact that after spin projection the coefficient of a higher contaminant becomes larger as we have discussed recently [19].

The energy of FH plotted as a function of the distance r(FH) is given for UHF, UHF-CCSD, UHF-CCSD(T), APCCSD-1, and APCCSD(T)-1 in Fig. 1, while in Fig. 2 the lowering of the energy due to spin projection with the APCCSD-1 method is shown. The largest spin projection corrections are found in the region $1.4 < r$(FH) < 3.0 Å, which is exactly the region where the deviation of the energy-related part of
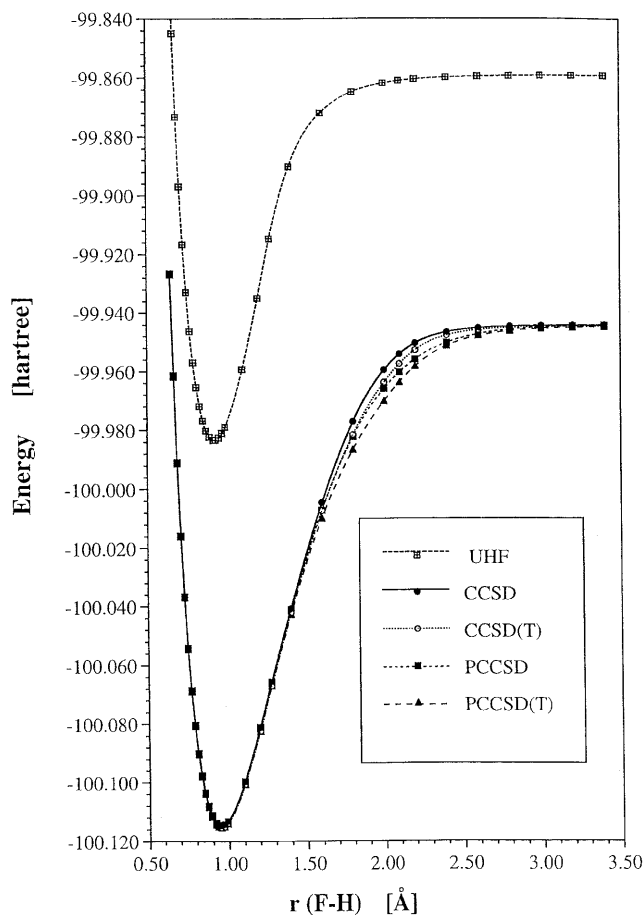

Fig. 1. The energy (in hartree) of FH shown in dependence of the distance r(F-H) in the range $0.6 < r < 3.4$ Å. *Upper curve*: UHF; *lower curves*: UHF-CCSD (*solid curve*), UHF-CCSD(T) (*dotted curve*), APCCSD-1 (*small dashes*), and APCCSD(T)-1 (*large dashes*). All calculations with the 6-31G basis set

$\langle\hat{S}^2\rangle_{CCSD}$, $\langle\hat{S}^2\rangle_{CCSD}^E$, from a value close to zero is strongest [19]. In this region, a recoupling of the electrons forming the FH bond takes place (change from a
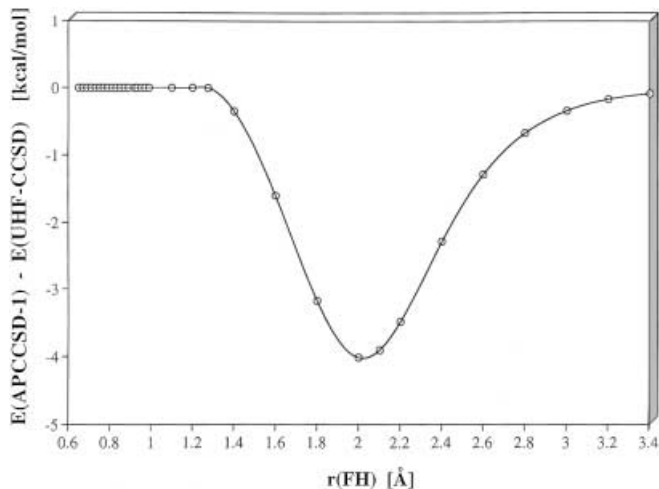
Fig. 2. Lowering of the UHF-CCSD/6-31G energy (in kcal/mol) of FH in the range $0.6 < r < 3.4$ Å due to spin-projection with the APCCSD-1 method

closed-shell singlet pair to an open-shell singlet pair), which leads to spin contamination by an $S + 2$ state. APCCSD-1 corrects in this region and leads to a potential-energy curve which is closer to the true FCI curve given by Chen and Schlegel [13].

6 Conclusions

The APCCSD-1 and APCCSD(T)-1 methods developed in this work to project out in an approximate way from the UHF-CCSD wavefunction the $S + 1$ and $S + 2$ contaminants using annihilation operators $\hat{A}_{s+1}$ and $\hat{A}_{s+2}$ offer the possibility of improving UHF-CCSD results at moderate additional cost. The methods will have their usefulness in all those cases in which the $S + 2$ contaminant plays a role but does not dominate spin contamination as in the case of high-spin, open-shell systems (doublet radicals, triplet biradicals, etc.) and many low-spin, open-shell systems, such as singlet biradicals. APCCSD-1 and APCCSD(T)-1 should also be useful when describing single-bond dissociation or transition states characterized by the breaking/forming of a single bond, while any process involving the cleavage of a multiple bond or the simultaneous breaking of more than one single bond should be better described with more complete spin-projection methods.

In view of other possibilities to circumvent or to partially avoid the spin-contamination problem in CC descriptions of open-shell systems, it is useful to coment on these methods in connection with the present work on spin-projected CC theory (for recent reviews, see Ref. [6]) The most elegant way of avoiding the spin-contamination problem is to use spin-adapted, open-shell CC methods, upon which current research is focusing [27]. However, presently there are no general programs available which can be applied to any (high- or low-spin) open-shell system in the most effective way. Clearly, one has to wait for further developments in this field.

Alternatively, one can use spin-restricted open-shell HF (ROHF) theory to set up a properly spin adapted reference for the CC calculations [28]; however, this does not imply that the correponding CC wavefunction is an eigenfunction of $\langle \hat{S}^2 \rangle$ because spin contamination can be introduced into the CC wave function by the nonlinear contributions of the cluster operators in the amplitude equations. Actually, the calculation of $\langle \hat{S}^2 \rangle$ values at the CCSD level carried out by Stanton [20] shows that the spin-contamination problem at the ROHF-CCSD level is similar to that at the UHF-CCSD level. Hence, it is still useful to invest in PCC methods, in particular in view of the fact that they, in contrast to ROHF-CC methods, do not lead to any significant increase in computational cost.

The spin-projection methods discussed in this work can be extended in several ways. On the one hand, the APCCSD-2 method is presently developed to have an appropriate tool for the description of the cleavage of double bonds as was discussed in this work. In addition, the spin-projection procedures presented in this work can be extended to include the operator $\hat{A}_{s+3}$ to annihilate beside the $S + 2$ contaminant also the $S + 3$ contaminant, which may play a role in triple-bond dissociation or the simultaneous breaking of three single bonds as observed in this work. Although inclusion of $\hat{A}_{s+3}$ complicates the projection mechanism considerably it does not raise computational cost since just disconnected pentuplet and sextuplet terms have to be considered, which can be derived from the sixth-order Møller–Plesset method developed previously [29].

Appendix

A1 Expression for $\Delta E_{APCCSD-1}(\alpha\alpha\beta)$ given in terms of intermediate arrays

$$\Delta E_{\mathrm{APCCSD}-1}(\alpha\alpha\beta)$$

$$= \frac{\sum_{i<j,\bar{k},a<b,\bar{c}} \left\langle \Phi_0 \big| \{\hat{S}^2\}\{\hat{S}^2\} \big| \Phi_{ij\bar{k}}^{ab\bar{c}} \right\rangle \left\langle \Phi_{ij\bar{k}}^{ab\bar{c}} \big| \left(\hat{H} e^{\hat{T}_1+\hat{T}_2} \right)_{\mathrm{C}} \big| \Phi_0 \right\rangle}{\left\langle \Phi_0 \big| \left[\hat{S}^2 - (s+1)(s+2) \right] \left[\hat{S}^2 - (s+2)(s+3) \right] \big| \Phi_0 \right\rangle}$$

$$(A.1)$$

The nominator of Eq. (A1) can be developed according to

$$\sum_{i<j,\bar{k},a<b,\bar{c}} \left\langle \Phi_0 \big| \{\hat{S}^2\}\{\hat{S}^2\} \big| \Phi_{ij\bar{k}}^{ab\bar{c}} \right\rangle \left\langle \Phi_{ij\bar{k}}^{ab\bar{c}} \big| \left(\hat{H} e^{\hat{T}_1+\hat{T}_2} \right)_{\mathrm{C}} \big| \Phi_0 \right\rangle$$

$$= -\sum_{ij,b\bar{d}} u1(ij,b\bar{d}) I1(ij,b\bar{d}) + \sum_{ij\bar{l}b} v1(\bar{l}j,ib) L3(j,i\bar{l},b)$$

Table A1. Definition of intermediate arrays Ln, In, un, and vn required in Eq. (A.2)

Ln	In	un	vn
$L1(i\bar{k},ab) = 4\sum_P (-1)^P P(a/b) S_{bk}\tilde{S}_a^i$	$I1(ij,b\bar{d}) = \sum_{\bar{k}a} L1(i\bar{k},ab)a_{j\bar{k}}^{a\bar{d}}$	$u1(ij,b\bar{d}) = \sum_{\bar{c}} X(i\bar{d},b\bar{c})S_{j\bar{c}}$	$v1(j,i\bar{l},b) = \sum_{\bar{k}a} L1(i\bar{k},ab)Y(\bar{l},a,\bar{k}j)$
$L2(\bar{l},b) = \sum_{i,\bar{c}} S_{i\bar{c}}a_{i\bar{l}}^{b\bar{c}}$	$I2(b,\bar{d}) = \sum_{j\bar{k},a} L1(j\bar{k},ab)a_{j\bar{k}}^{a\bar{d}}$	$u2(b,\bar{d}) = \sum_{i,\bar{c}} X(i\bar{d},b\bar{c})S_{i\bar{c}}$	$v2(\bar{l},b) = \sum_{j\bar{k},a} L1(j\bar{k},ab)Y(\bar{l}a,\bar{k}j)$
$L3(j,i\bar{l},b) = \sum_{\bar{c}} S_{j\bar{c}}a_{i\bar{l}}^{b\bar{c}}$	$I3(j\bar{k},bd) = \sum_{i,a} L1(i\bar{k},ab)a_{ij}^{ad}$	$u3(j\bar{k},bd) = \sum_{\bar{c}} X(\bar{k}d,\bar{c}b)S_{j\bar{c}}$	$v3(jl,\bar{k}b) = \sum_{i,a} L1(i\bar{k},ab)Y(la,ij)$
	$I4(\bar{k},l) = \sum_{i,a<b} L1(i\bar{k},ab)a_{il}^{ab}$	$u4(\bar{k},d) = \sum_{i,a<b} X(id,ab)L1(i\bar{k},ab)$	$v4(\bar{k},l) = \sum_{j,\bar{c}} Y(l\bar{c},j\bar{k})S_{j\bar{c}}$
	$I5(j\bar{k},il) = \sum_{a<b} L1(j\bar{k},ab)a_{il}^{ab}$	$u5(id,j\bar{k}) = \sum_{a<b} X(id,ab)L1(j\bar{k},ab)$	$v5(i,j\bar{k}l) = \sum_{\bar{c}} Y(l\bar{c},j\bar{k})S_{i\bar{c}}$

$$
\begin{aligned}
&+ \sum_{b,\bar{d}} u2(b,\bar{d})I2(b,\bar{d}) - \sum_{\bar{l},b} v2(\bar{l},b)L2(\bar{l},b) \\
&+ \sum_{j\bar{k},bd} u3(j\bar{k},bd)I3(j\bar{k},bd) + \sum_{jl,\bar{k}b} v3(jl,\bar{k}b)L3(j,l\bar{k},b) \\
&+ \sum_{\bar{k},d} u4(\bar{k},d)L2(\bar{k},d) - \sum_{\bar{k},l} v4(\bar{k},l)I4(\bar{k},l) \\
&- \sum_{id,j\bar{k}} u5(id,j\bar{k})L3(i,j\bar{k},d) + \sum_{ij\bar{k}l} v5(i,j\bar{k}l)I5(j\bar{k},il) \ .
\end{aligned}
\tag{A.2}
$$

In Eq. (A2), the intermediate arrays $L2$, $L3$, and $I1$–$I5$ correspond to contractions between spatial overlap and double amplitudes,

A2 Expression for $\Delta E_{APCCSD-1}(\alpha\alpha\beta\beta)$ given in terms of intermediate arrays

$$
\Delta E_{\text{APCCSD}-1}(\alpha\alpha\beta\beta)
$$

$$
= \frac{\displaystyle\sum_{i<j,\bar{k}<\bar{l},a<b,\bar{c}<\bar{d}} \left\langle \Phi_0 | \{\hat{S}^2\}\{\hat{S}^2\} | \Phi_{ij\bar{k}\bar{l}}^{ab\bar{c}\bar{d}} \right\rangle \left\langle \Phi_{ij\bar{k}\bar{l}}^{ab\bar{c}\bar{d}} \left| \left(\hat{H}e^{\hat{T}_1+\hat{T}_2}\right)_C \right| \Phi_0 \right\rangle}{\left\langle \Phi_0 \left| \left[\hat{S}^2 - (s+1)(s+2)\right]\left[\hat{S}^2 - (s+2)(s+3)\right] \right| \Phi_0 \right\rangle},
\tag{A.3}
$$

where

$$
\sum_{i<j,\bar{k}<\bar{l},a<b,\bar{c}<\bar{d}} \left\langle \Phi_0 | \{\hat{S}^2\}\{\hat{S}^2\} | \Phi_{ij\bar{k}\bar{l}}^{ab\bar{c}\bar{d}} \right\rangle \left\langle \Phi_{ij\bar{k}\bar{l}}^{ab\bar{c}\bar{d}} \left| \left(\hat{H}e^{\hat{T}_1+\hat{T}_2}\right)_C \right| \Phi_0 \right\rangle
$$

$$
\begin{aligned}
&= \sum_{ik,bf} w1(b\bar{f},i\bar{k})J2(\bar{k}b,if) + \sum_{j\bar{n},b\bar{d}} w2(\bar{n}j,b\bar{d})J1(j\bar{d},\bar{n}b) + \sum_{\bar{l}\bar{m},be} w3(\bar{m}e,\bar{l}b)J7(\bar{l}e,\bar{m},b) \\
&- \sum_{jm,\bar{c}e} w4(m\bar{e},j\bar{c})J8(j\bar{e},m\bar{c}) - \sum_{j\bar{m},b\bar{d}} w5(\bar{m}\bar{d},jb)J1(j\bar{d},\bar{m}b) - \sum_{m\bar{l},a\bar{c}} w6(ma,\bar{l}\bar{c})J2(\bar{l}a,m\bar{c}) \\
&+ \sum_{\bar{k}\bar{l},im} w7(m\bar{k},i\bar{l})J4(\bar{k}\bar{l},im) + \sum_{ij,\bar{k}\bar{m}} w8(\bar{m}i,\bar{k}j)J3(ij,\bar{k}\bar{m}) - \sum_{j\bar{m},b\bar{d}} w9(\bar{m}j,b\bar{d})J1(j\bar{d},\bar{m}b)
\end{aligned}
\tag{A.4}
$$

$$
\begin{aligned}
&+ \sum_{\bar{k}m,a\bar{d}} w10(m\bar{k},\bar{d}a)J2(\bar{k}a,m\bar{d}) + \sum_{ab,\bar{d}f} w11(b\bar{f},\bar{d}a)J6(ab,\bar{f}d) + \frac{1}{2}\sum_{mn,\bar{c}\bar{d}} w12(mn,\bar{c}\bar{d})J8(n\bar{d},m\bar{c}) \\
&- \frac{1}{2}\sum_{\bar{m}\bar{n},ab} w13(\bar{m}\bar{n},ab)J7(\bar{n}a,\bar{m}b) + \sum_{im,\bar{k}\bar{l}} w14(m\bar{k},i\bar{l})J4(\bar{k}\bar{l},im) + \frac{1}{2}\sum_{\bar{k}\bar{l},ef} w15(ef,\bar{k}\bar{l})J7(\bar{l}f,\bar{k}e) \\
&- \frac{1}{2}\sum_{ij,\bar{e}\bar{f}} w16(\bar{e}\bar{f},ij)J8(i\bar{f},j\bar{e}) - \sum_{\bar{l}\bar{m},be} w17(\bar{m}e,\bar{l}b)J9(\bar{l}\bar{m},be) - \sum_{im,\bar{e}\bar{d}} w18(m\bar{e},i\bar{d})J10(im,\bar{e}d) \ .
\end{aligned}
$$

while arrays un and vn ($n = 1,\ldots, 5$) cover combinations of arrays X and Y (Table 2) with the spatial overlap S_{pq} as shown in Table A1. Inspection of Table A1 reveals that calculation of the intermediate arrays in Eq. (A2) does not involve more than $O(M^6)$ computational steps.

In Eq. (A4), the intermediate arrays Im and wn ($m = 1,\ldots,10$; $n = 1,\ldots,18$) appear, which represent two different kinds of contractions of spatial overlap with double amplitudes as well as of arrays $Z1$, $Z2$, $Z3$ with integrals S_{pq} and amplitudes a_{ij}^{ab} as described in Table A2. In total, 28 intermediate arrays are used to reduce the original $\leq O(M^8)$ dependence of Eq. (35) to $O(M^6)$ steps.

Table A2. Definition of intermediate arrays Jm and wn required in Eq. (A.4)

Definition of Jm[a]	Definition of wn[a]	
$J1(\overline{ic}, \overline{ke}) = \sum_{j,\overline{d}} K1(ij, \overline{cd}) a_{jk}^{e\overline{d}}$	$w1(b\overline{f}, ik) = \sum_{\overline{c},e} Z1(b\overline{c}, ef) J1(\overline{ic}, \overline{ke})$	$w2(\overline{n}j, b\overline{d}) = \sum_{km} Z2(m\overline{n}, jk) J2(\overline{kb}, m\overline{d})$
$J2(\overline{ka}, j\overline{e}) = \sum_{l,b} K2(\overline{kl}, ab) a_{jl}^{b\overline{e}}$	$w3(\overline{me}, \overline{lb}) = \sum_{k,a} Z3(\overline{ma}, \overline{ke}) K2(\overline{kl}, ab)$	$w4(m\overline{e}, j\overline{c}) = \sum_{i,\overline{d}} Z3(\overline{md}, i\overline{e}) K1(ij, \overline{cd})$
$J3(ij, \overline{kl}) = \sum_{\overline{c}<\overline{d}} K1(ij, \overline{cd}) a_{kl}^{\overline{cd}}$	$w5(\overline{md}, jb) = \sum_{\overline{k}\overline{e}} Z3(\overline{md}, \overline{ke}) J2(\overline{kb}, j\overline{e})$	$w6(ma, \overline{lc}) = \sum_{i,e} Z3(ma, ie) J1(i\overline{c}, le)$
$J4(\overline{kl}, ij) = \sum_{a<b} K2(\overline{kl}, ab) a_{ij}^{ab}$	$w7(mk, il) = \sum_{\overline{c},e} Z3(m\overline{c}, ke) J1(i\overline{c}, le)$	$w8(\overline{m}i, kj) = \sum_{ae} Z3(\overline{ma}, i\overline{e}) J2(\overline{ka}, j\overline{e})$
$J5(\overline{cd}, ab) = \sum_{k<l} K2(\overline{kl}, ab) a_{kl}^{\overline{cd}}$	$w9(\overline{m}j, b\overline{d}) = \sum_{ae} Z3(\overline{ma}, j\overline{e}) J6(ab, \overline{ed})$	$w10(mk, \overline{d}a) = \sum_{ce} Z3(m\overline{c}, ke) J5(\overline{cd}, ae)$
$J6(ab, \overline{cd}) = \sum_{k<l} K2(\overline{kl}, ab) a_{kl}^{\overline{cd}}$	$w11(b\overline{f}, \overline{d}a) = \sum_{\overline{c},e} Z1(b\overline{c}, ef) J5(\overline{cd}, ae)$	$w12(mn, \overline{cd}) = \sum_{i<j} Z2(mn, ij) K1(ij, \overline{cd})$
$J7(le, \overline{mb}) = \sum_{i,\overline{c}} J1(\overline{ic}, le) a_{im}^{b\overline{c}}$	$w13(\overline{mn}, ab) = \sum_{k<l} Z2(\overline{mn}, \overline{kl}) K2(\overline{kl}, ab)$	$w14(m\overline{k}, il) = \sum_{j,\overline{n}} Z2(m\overline{n}, jk) J3(ij, \overline{n}\overline{l})$
$J8(j\overline{e}, m\overline{c}) = \sum_{k,b} J2(\overline{kb}, j\overline{e}) a_{mk}^{b\overline{c}}$	$w15(ef, \overline{kl}) = \sum_{a<b} Z1(ab, ef) K2(\overline{kl}, ab)$	$w16(\overline{e}f, ij) = \sum_{\overline{c}<\overline{d}} Z1(\overline{cd}, \overline{e}f) K1(ij, \overline{cd})$
$J9(\overline{lm}, be) = \sum_{i<j} J3(ij, \overline{lm}) a_{lj}^{be}$	$w17(\overline{me}, \overline{lb}) = \sum_{k,a} Z3(\overline{ma}, \overline{ke}) K2(\overline{kl}, ab)$	$w18(m\overline{e}, i\overline{d}) = \sum_{j,\overline{c}} Z3(m\overline{c}, i\overline{e}) K1(ij, \overline{cd})$
$J10(im, \overline{ed}) = \sum_{k<l} J4(\overline{kl}, im) a_{kl}^{\overline{ed}}$		

ᵃ The arrays $K1$ and $K2$ are defined by

$$K1(ij, \overline{cd}) = \sum_P (-1)^P P(i/j|\overline{c}/\overline{d}) S_{i\overline{c}} S_{j\overline{d}}$$

$$K2(\overline{kl}, ab) = \sum_P (-1)^P P(\overline{k}/\overline{l}|a/b) S_{a\overline{k}} S_{b\overline{l}}$$

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