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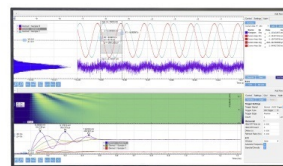
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# Spin-restricted open-shell coupled-cluster theory

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Spin-restricted CC theory is suggested as a new approach for the treatment of high-spin open-shell systems in CC theory. Spin constraints are imposed on the wave function in the sense that the projected spin eigenvalue equations are fulfilled within the (truncated) excitation space. These constraints allow a reduction in the number of independent amplitudes, thus decreasing the computational cost when implemented efficiently. The approach ensures that the spin expectation value always corresponds to the exact value, though the wave function is (for truncated CC treatments) not rigorously spin-adapted. For the specific case of high-spin doublets, detailed equations are derived for amplitudes, energy and first derivatives of the energy within the computationally most useful singles and doubles approximation. Numerical examples demonstrate the excellent performance of the spin-restricted CC approach relative to the more traditional spin-orbital based CC treatments, suggesting that it might be an attractive alternative for the treatment of high-spin open-shell systems. © 1997 American Institute of Physics. [S0021-9606(97)01845-X]

## I. INTRODUCTION

The treatment of high-spin open-shell systems is still an active topic of research in coupled-cluster (CC) theory.<sup>1</sup> Traditionally, an unrestricted Hartree–Fock (UHF) based spin-orbital CC approach (UHF-CC) has been used. Despite good results in general, two arguments can be given to show that it is not the optimal choice:

- (1) The UHF-CC wave function, like the UHF reference itself, is not an eigenfunction to  $\hat{S}^2$ ; spin contamination might therefore affect—to some degree—the quality of the results.
- (2) The computational cost of a UHF-CC treatment is about a factor of four higher than that of a corresponding closed-shell CC calculation.

Though it has been shown that spin contamination of the UHF-CC wave function is small in most cases,<sup>2–4</sup> it still appears preferable to deal with this problem explicitly, since spin contamination might be a problem in computations of spin-dependent properties and the determination of excitation energies.<sup>5</sup> The high computational costs of UHF-CC seem unnecessary, as corresponding open-shell configuration-interaction (CI) calculations can be carried out for costs similar to that for closed-shell calculations. The same should in principle be possible for CC calculations.

A first suggestion in order to deal with these issues was to use a restricted open-shell HF (ROHF) wave function instead of the UHF reference.<sup>6</sup> However, this substitution does not remedy any of the problems listed above. ROHF-CC results are still affected by spin contamination<sup>4</sup> and the computational costs are not reduced at least in a straightforward spin-orbital based implementation. As shown by Jayatilaka and Lee,<sup>7</sup> costs can be reduced by a factor of 2 through the use of so-called symmetric spin orbitals. But even then, the

computational requirements would still be larger (by a factor of 2) than for corresponding closed-shell calculations. Furthermore, the introduction of symmetric spin orbitals complicates the theory so much that no implementation based on this special choice of spin orbitals has yet been reported.

As a matter of fact, a solution to the aforementioned problems in open-shell CC theory cannot be achieved by a simple modification of the reference function. Only with an adequate modification of the cluster operator  $T$  is it possible to rectify the above mentioned problems. Therefore, rigorous spin-adapted approaches have been formulated and implemented by Janssen and Schaefer<sup>8</sup> as well as by Li and Paldus<sup>9</sup> based on a unitary group parametrization of the cluster operator. A severe disadvantage of such formulations is that the cluster operator ceases to be a pure excitation operator. As a result, contractions between different  $T$ s occur when  $\exp(T)$  is expanded in a power series. Theory and implementation are thus rather complicated.

A more pragmatic method for the treatment of high-spin cases is the so-called *partially spin-adapted* approach which has recently been advocated by Janssen *et al.*,<sup>8</sup> by Knowles *et al.*<sup>10</sup> and by Neogrády *et al.*<sup>11</sup> Significant simplifications are obtained relative to the more rigorous approaches (cf. Refs. 8 and 9) by a *partial* spin-adaptation of the cluster operator, thus ensuring that  $T$  acting on the reference state only produces states of the desired spin, while avoiding de-excitation operators. Despite encouraging numerical results and computational savings compared to the more traditional UHF- and ROHF-CC approaches, it should be noted that the partially spin-adapted approach lacks rigorous theoretical foundation. It can be shown that the method is not exact in the untruncated limit (see Sec. IV). In addition, the amount of the residual spin contamination has not yet been investigated.

In this paper we suggest a new strategy for the treatment of high-spin open-shell systems in CC theory. We demonstrate that the spin equations for the untruncated CC wave

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function can be exploited to impose constraints on the CC wave function. Thus, it is possible to formulate a rigorously spin-adapted CC scheme similar to the work of Li and Paldus<sup>9</sup> or, what we will pursue in the following, a conceptually simpler variant, the so-called *spin-restricted CC* scheme. For the latter, the CC wave function is not rigorously spin-adapted, but it can be shown that the CC expectation value always corresponds to the exact value. For the specific case of doublet states, we will derive explicit equations for energy and gradients and present numerical results.

## II. THEORY

### A. Exact coupled-cluster theory and spin

In CC theory, the wave function is given by the following exponential ansatz:

$$|\Psi\rangle = \exp(T)|0\rangle \quad (1)$$

with  $|0\rangle$  as a Slater determinant and  $T$  as the cluster operator. For the following discussion of high-spin open-shell systems, we assume that  $|0\rangle$  represents an eigenfunction for  $\hat{S}^2$ , e.g., an ROHF determinant. The cluster operator  $T$  is given as

$$T = T_1 + T_2 + \dots, \quad (2)$$

$$T_1 = \sum_i \sum_a t_i^a a^+ i, \quad (3)$$

$$T_2 = \frac{1}{4} \sum_{ij} \sum_{ab} t_{ij}^{ab} a^+ i b^+ j, \quad (4)$$

...

with the amplitudes  $t_i^a, t_{ij}^{ab}, \dots$  and the second-quantized creation and annihilation operators  $a^+, b^+, i, j, \dots$ . As usual, indices  $i, j, k, \dots$  denote occupied spin orbitals, while indices  $a, b, c, \dots$  refer to virtual spin orbitals.

Equations for energy and amplitudes are obtained by inserting the ansatz of the wave function into the Schrödinger equation. After multiplication with  $\exp(-T)$  and projection onto the reference determinant and all excited determinants  $\Phi_q$  obtained by replacing one, two, three, etc., occupied by virtual orbitals in the reference determinant, one obtains

$$E = \langle 0 | \exp(-T) H \exp(T) | 0 \rangle, \quad (5)$$

$$0 = \langle \Phi_q | \exp(-T) H \exp(T) | 0 \rangle. \quad (6)$$

The exact CC wave function obtained with the untruncated cluster operator is naturally an eigenfunction of the spin operator  $\hat{S}^2$ , i.e.,

$$\hat{S}^2 \exp(T) | 0 \rangle = s(s+1) \exp(T) | 0 \rangle, \quad (7)$$

with  $s(s+1)$  as the corresponding eigenvalue. After multiplication with  $\exp(-T)$  from the left and projection, the following equations are obtained in complete analogy to Eqn. (5) and Eqn. (6):

$$s(s+1) = \langle 0 | \exp(-T) \hat{S}^2 \exp(T) | 0 \rangle, \quad (8)$$

$$0 = \langle \Phi_q | \exp(-T) \hat{S}^2 \exp(T) | 0 \rangle. \quad (9)$$

These equations constitute a set of constraints that can be imposed on  $T$ . Though they are automatically fulfilled in the untruncated case and customarily ignored, they can be exploited to reduce the number of independent variables.

One first has to recognize that the full set of projections of the spin equation on determinants as given by Eqn. (9) contains redundancies. These can be eliminated if we do not project the spin equations on Slater determinants but rather the equivalent set of spin-adapted configurations (CSFs, configuration state functions) denoted by  $\tilde{\Phi}_p$ . The resulting equations can then be divided into two categories, namely those for which the spin of the projecting CSF corresponds to the desired spin eigenvalue  $s(s+1)$  and those for which the eigenvalue is different from  $s(s+1)$ . The CSFs in the first class will be denoted by  ${}^{s(s+1)}\tilde{\Phi}_p$ , while the others are labeled by  ${}^Q\tilde{\Phi}_p$ . In the Appendix, it is shown that it is sufficient to consider the equations

$$0 = \langle {}^Q\tilde{\Phi}_p | \exp(-T) \hat{S}^2 \exp(T) | 0 \rangle, \quad (10)$$

as the corresponding equations for  ${}^{s(s+1)}\tilde{\Phi}_p$

$$0 = \langle {}^{s(s+1)}\tilde{\Phi}_p | \exp(-T) \hat{S}^2 \exp(T) | 0 \rangle \quad (11)$$

are automatically fulfilled. This means that exploitation of the spin equations [Eqn. (9)] leaves exactly as many independent parameters undetermined as there are configurations with the desired spin  $s(s+1)$ . The number of such CSF is identical to the number of independent CI coefficients in a full CI wave function. We thus have proven that full CC and CI wave functions for high-spin open-shell systems are described by the same number of independent variables, which of course is not at all surprising.

Due to the reduced number of independent variables, the full set of equations for the amplitudes, given by Eqn. (6), contains redundancies. Those can be eliminated by considering again projections on spin-adapted configuration. Projection on configurations with spin  $s(s+1)$  then yields equations which determine the independent amplitudes, while projections of the Schrödinger equation on configurations with spin different from  $s(s+1)$  automatically vanish.

To summarize, the additional equations [Eqn. (10) and Eqn. (11)] allow certain spin properties to be imposed upon the wave function. They can be exploited to reduce the number of independent parameters and, thus, the computational cost. However, it should also be mentioned that exploitation of the spin constraints does lead to considerably more complex equations than those for the conceptually simpler spin-orbital formalism.

### B. Truncated CC schemes and spin

Approximations in CC theory are usually based on a restriction of the cluster operator to certain excitation levels. The most common choice is to restrict  $T$  to all single and double excitations

$$T \approx T_1 + T_2, \quad (12)$$

which is traditionally designated as the CC singles and doubles (CCSD) model.<sup>12</sup> The CC equations for approximate

models are obtained by projection of the Schrödinger equation on the manifold covered by the cluster operator, e.g., in case of the CCSD model by projection on all singly and double excited determinants.

Approximations like CCSD are always formulated such that the corresponding spin equations are ignored. While for the closed-shell case the CCSD wave function is automatically spin-adapted, the same is not true for open-shell systems. It appears that a straightforward truncation of  $T$  within a spin-orbital formulation is not compatible with any spin constraints on the wave function. The source of the problem is that in a truncated CC scheme projection of the CC and spin equations leads to more equations than independent variables exist.<sup>13</sup>

There are several possibilities to overcome this problem. Characteristic to all of them is that the spin equations are exploited in order to reduce the number of independent amplitudes and that only an appropriate subset of the projected Schrödinger equations is solved in order to determine the set of independent amplitudes.

In what we call *spin-restricted CC theory*, the cluster operator is truncated in the usual way, e.g., to all single and double excitations but we also require the projected spin equations Eqn. (10) and Eqn. (11) to be fulfilled in the truncated space. To obtain a matching number of amplitudes and equations, one has first to consider that the same redundancies as in the exact limit exist among the projected spin equations in the truncated case. It is sufficient to consider among the spin equations only those obtained by projection on CSFs  $\mathcal{Q}\tilde{\Phi}_p$ . In this way, the spin equations leave exactly as many parameters undetermined as there are CSFs of desired spin. Projection of the Schrödinger equation on the full truncated determinantal space (or, alternatively, on all spin-adapted CSFs) on the other hand is not feasible. In the spirit of the exact theory we, therefore, consider only projections of the Schrödinger equation on the CSFs of the desired spin ( $^{s(s+1)}\tilde{\Phi}_p$ ), as those are sufficient to determine all independent amplitudes. However, while for the exact theory, projections on  $\mathcal{Q}\tilde{\Phi}_p$  automatically vanish, the same is not true for the truncated case.

The *spin-restricted* CC theory outlined above can be summarized by the following equations:

$$0 = \langle \mathcal{Q}\tilde{\Phi}_p | \exp(-T) \hat{S}^2 \exp(T) | 0 \rangle, \quad (13)$$

$$0 = \langle ^{s(s+1)}\tilde{\Phi}_p | \exp(-T) H \exp(T) | 0 \rangle \quad (14)$$

for all  $^{s(s+1)}\tilde{\Phi}_p$  and  $\mathcal{Q}\tilde{\Phi}_p$  within the truncated excitation manifold  $\mathbf{g}$ . In our opinion, this appears to be a balanced approximation as both Schrödinger and spin equations are fulfilled within the same subspace. Moreover, improvements of both energy and spin equations are possible (up to the exact limit) by successive inclusion of additional excitations in the cluster operator.

An alternative to the spin-restricted approach would be to insist that the spin equations are satisfied within the full space rather than only in the truncated subspace. The CC wave function would be in such an approach even in the

truncated case an eigenfunction to  $\hat{S}^2$  and, thus, rigorously spin-adapted. It is therefore appropriate to term this choice in the following *spin-adapted* CC. A severe disadvantage of spin-adapted CC is, however, that the usual truncation of the cluster operator at the spin-orbital level is no longer possible, as fulfillment of the full set of spin equations requires non-vanishing amplitudes for all excitations. It is, however, possible to restrict the number of independent amplitudes to those of the number of configurations within a chosen truncated subspace with the nonvanishing values for the higher excitation amplitudes determined through the spin equations. As will be shown in a future publication, such an approach (in the high-spin open-shell case) is equivalent to those proposed by Li and Paldus<sup>9</sup> employing a unitary group parametrization of the cluster operator.

At this point, it is appropriate to present a comparison of spin-orbital, spin-restricted and spin-adapted CC treatments of high-spin open-shell systems:

(a) spin-orbital based CC schemes, e.g., ROHF-CCSD or UHF-CCSD:

- ignore spin equations, those are only fulfilled in the untruncated case
- solve Schrödinger equation within the truncated determinantal subspace
- wave function is not spin-adapted and the CC spin expectation value is different from the exact value
- improvement in energy is possible by inclusion of higher excitations in the cluster operator
- no reduction in the number of independent amplitudes and computational cost is possible

(b) spin-restricted CC scheme:

- spin equations within truncated subspace are exploited to reduce number of independent amplitudes to that of spin-adapted configurations within truncated subspace
- solve Schrödinger equation in that part of the truncated subspace that is spanned by configurations of the correct spin
- wave function is not rigorously spin adapted, but the CC spin expectation value (see section III B) is equal to the exact value
- consideration of higher excitations improves both energy and spin in the sense that the Schrödinger and spin equation are fulfilled in a larger subspace
- computational savings are possible, as the number of independent amplitudes is reduced by exploitation of the spin equations

(c) spin-adapted CC theory:

- exploit full set of spin equations
- no truncation of the cluster operator is possible at the spin-orbital level; truncations are only possible within the set of independent (spin-adapted) amplitudes obtained by exploiting the spin equations with the non-vanishing spin-orbital amplitudes for the higher excitations completely determined by the lower level excitations and the spin equations
- Schrödinger equation is solved in the truncated determinantal subspace

- wave function is rigorously spin-adapted
- consideration of higher independent excitations improves energy
- computational savings are possible due to the reduced number of independent amplitudes
- complicated theory due to the necessity to consider higher excitations in the cluster operator.

### III. SPIN-RESTRICTED CC APPROACH FOR HIGH-SPIN DOUBLET STATES WITHIN THE CCSD APPROXIMATION

In the following a detailed discussion of the spin-restricted CC theory applied in the computationally most useful singles and doubles approximation to high-spin doublet states will be presented. We first focus on energy and wave function before we briefly discuss evaluation of analytic gradients. The latter is an important prerequisite for the routine calculation of molecular properties and—in the current context—of interest for the computation of spin expectation values.

#### A. Energy and wave function

For high-spin open-shell doublet states, the reference function is given by a Slater determinant of the following type:

$$|0\rangle = t^\dagger \prod_i i^\dagger \bar{i}^\dagger |vac\rangle \quad (15)$$

with  $t$  representing the open-shell orbital (with  $\alpha$  spin),  $i$  and  $\bar{i}$  denoting  $\alpha$  and  $\beta$  occupied orbitals and  $|vac\rangle$  defining the physical vacuum state. This notation implies that the same spatial part is used for  $\alpha$  and  $\beta$  spin orbitals; consequently  $\alpha$  and  $\beta$  Fock matrices do not have a simultaneous diagonal representation.<sup>6</sup>

The CCSD wave function is then given in the usual way

$$|\Psi\rangle = \exp(T)|0\rangle \quad (16)$$

with the cluster operator  $T$  defined as in Eqn. (2) but restricted to  $T_1$  and  $T_2$ . Note that the set of occupied orbitals in our case comprises  $t$ ,  $i$  and  $\bar{i}$ , while the set of virtual orbitals consists of  $\bar{t}$ ,  $a$  and  $\bar{a}$ .

At this point, it also is necessary to introduce a set of configurations spanning the same space as the set of singly and doubly excited determinants  $\Phi_i^a$  and  $\Phi_{ij}^{ab}$ . The one given in Table I has been derived by diagonalizing the  $S^2$  matrix in this space. The pure doublet states are denoted by  ${}^D\tilde{\Phi}_p$  and they coincide with those chosen by Li and Paldus in the framework of the unitary group approach applying the first-order interacting space restriction.<sup>9,14</sup> The configurations spanning the complementary space are denoted by  ${}^Q\tilde{\Phi}_p$ . As we will see later, this choice results in a hierarchical structure of the spin equations which is convenient for the following discussion. Note that, since the determinantal space is restricted to single and double excitations, the states  ${}^Q\tilde{\Phi}_p$  corresponding to  $i, j \rightarrow a, b$  excitations are not pure spin states.<sup>15</sup>

TABLE I. Definition of the configurations in terms of the Slater determinants for a high-spin doublet state.

(a) Space of doublet states	
${}^D\tilde{\Phi}_i^a = \Phi_i^a$	
${}^D\tilde{\Phi}_i^{\bar{a}} = \Phi_i^{\bar{a}}$	
${}^D\tilde{\Phi}_{1i}^a = \frac{1}{\sqrt{2}}(\Phi_i^a + \Phi_i^{\bar{a}})$	
${}^D\tilde{\Phi}_{2i}^a = \frac{1}{\sqrt{6}}(-\Phi_i^a + \Phi_i^{\bar{a}} + 2\Phi_{ii}^{a\bar{a}})$	
${}^D\tilde{\Phi}_{1ii}^{ab} = \frac{1}{\sqrt{6}}(2\Phi_{ii}^{ab} + \Phi_{ii}^{a\bar{b}} + \Phi_{ii}^{b\bar{a}})$	
${}^D\tilde{\Phi}_{2ii}^{ab} = \frac{1}{\sqrt{2}}(\Phi_{ii}^{a\bar{b}} + \Phi_{ii}^{b\bar{a}})$	
${}^D\tilde{\Phi}_{1ij}^{ta} = \frac{1}{\sqrt{6}}(-\Phi_{ij}^{a\bar{t}} + 2\Phi_{ij}^{\bar{a}\bar{t}} + \Phi_{ji}^{a\bar{t}})$	
${}^D\tilde{\Phi}_{2ij}^{ta} = \frac{1}{\sqrt{2}}(\Phi_{ij}^{a\bar{t}} + \Phi_{ji}^{a\bar{t}})$	
${}^D\tilde{\Phi}_{1ij}^{ab} = \frac{1}{2\sqrt{3}}(2\Phi_{ij}^{ab} + \Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{b\bar{a}} + 2\Phi_{ij}^{\bar{a}\bar{b}} - \Phi_{ji}^{a\bar{b}} + \Phi_{ji}^{b\bar{a}})$	
${}^D\tilde{\Phi}_{2ij}^{ab} = \frac{1}{2}(\Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{b\bar{a}} + \Phi_{ji}^{a\bar{b}} + \Phi_{ji}^{b\bar{a}})$	
(b) Complementary space	
${}^Q\tilde{\Phi}_i^a = \frac{1}{\sqrt{3}}(\Phi_i^a - \Phi_i^{\bar{a}} + \Phi_{ii}^{a\bar{a}})$	
${}^Q\tilde{\Phi}_{ii}^{ab} = \frac{1}{\sqrt{3}}(\Phi_{ii}^{ab} - \Phi_{ii}^{a\bar{b}} + \Phi_{ii}^{b\bar{a}})$	
${}^Q\tilde{\Phi}_{ij}^{ta} = \frac{1}{\sqrt{3}}(\Phi_{ij}^{a\bar{t}} + \Phi_{ij}^{\bar{a}\bar{t}} - \Phi_{ji}^{a\bar{t}})$	
${}^Q\tilde{\Phi}_{1ij}^{ab} = \frac{1}{2}(-\Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{b\bar{a}} - \Phi_{ji}^{a\bar{b}} + \Phi_{ji}^{b\bar{a}})$	
${}^Q\tilde{\Phi}_{2ij}^{ab} = \frac{1}{2\sqrt{3}}(2\Phi_{ij}^{ab} + \Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{b\bar{a}} - 2\Phi_{ij}^{\bar{a}\bar{b}} - \Phi_{ji}^{a\bar{b}} - \Phi_{ji}^{b\bar{a}})$	
${}^Q\tilde{\Phi}_{3ij}^{ab} = \frac{1}{\sqrt{6}}(\Phi_{ij}^{ab} - \Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{b\bar{a}} + \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ji}^{a\bar{b}} - \Phi_{ji}^{b\bar{a}})$	
${}^Q\tilde{\Phi}_{4ij}^{ab} = \frac{1}{\sqrt{6}}(\Phi_{ij}^{ab} - \Phi_{ij}^{a\bar{b}} - \Phi_{ij}^{b\bar{a}} - \Phi_{ij}^{\bar{a}\bar{b}} + \Phi_{ji}^{a\bar{b}} + \Phi_{ji}^{b\bar{a}})$	

As shown in the Appendix, the spin equations only need to be projected on configurations with higher multiplicity, i.e., on  ${}^Q\tilde{\Phi}_p$  in the current case. The resulting equations are independent of the actual choice of these configurations and given as

$$t_i^a - t_i^{\bar{a}} + t_i^{\bar{t}}t_i^a + t_i^{\bar{t}}t_i^{\bar{a}} = 0, \quad (17)$$

$$t_{ij}^{ab} - t_{ij}^{a\bar{b}} + t_{ij}^{b\bar{a}} + t_i^{\bar{t}}t_{ij}^{a\bar{t}} - t_i^{\bar{t}}t_{ij}^{b\bar{t}} = 0, \quad (18)$$

$$-t_{ij}^{a\bar{t}} - t_{ij}^{\bar{a}\bar{t}} + t_{ji}^{a\bar{t}} + t_{ji}^{\bar{a}\bar{t}} - t_i^{\bar{t}}t_{ij}^{a\bar{t}} - t_i^{\bar{t}}t_{ij}^{\bar{a}\bar{t}} = 0, \quad (19)$$

$$2 t_{ij}^{ab} + P(i,j)P(a,b)(-t_{ij}^{a\bar{b}} + t_i^b t_{ij}^{a\bar{i}} + t_j^{\bar{i}} t_{ii}^{b\bar{a}} + t_j^{\bar{i}} t_{ii}^{b\bar{i}}) = 0, \quad (20)$$

$$2 t_{ij}^{a\bar{b}} + P(i,j)P(a,b)(-t_{ij}^{ab} + t_i^a t_{ij}^{b\bar{i}} + t_j^{\bar{i}} t_{ii}^{a\bar{b}} + t_j^{\bar{i}} t_{ii}^{b\bar{i}}) = 0, \quad (21)$$

$$t_{ij}^{a\bar{b}} - t_i^b t_{ij}^{a\bar{i}} + t_j^{\bar{i}} t_{ii}^{b\bar{a}} + t_j^{\bar{i}} t_{ii}^{b\bar{i}} - t_{ij}^{ab} + t_i^a t_{ij}^{b\bar{i}} - t_j^{\bar{i}} t_{ii}^{a\bar{b}} - t_j^{\bar{i}} t_{ii}^{a\bar{i}} = 0, \quad (22)$$

$$t_{ij}^{a\bar{b}} - t_i^b t_{ij}^{a\bar{i}} + t_j^{\bar{i}} t_{ii}^{b\bar{a}} + t_j^{\bar{i}} t_{ii}^{b\bar{i}} - t_{ij}^{ab} + t_i^a t_{ij}^{b\bar{i}} - t_j^{\bar{i}} t_{ii}^{a\bar{b}} - t_j^{\bar{i}} t_{ii}^{a\bar{i}} = 0 \quad (23)$$

with  $P(p,q)$  as the usual antisymmetric permutation operator. Equation (17) to Eqn. (23) impose constraints on the spin-orbital amplitudes used in Eqn. (3) and Eqn. (4) to parameterize the cluster operator  $T$  and these equations can be exploited to reduce the number of independent amplitudes. However, let us first point out the hierarchical structure of the spin equations. We find

- no constraint exists for the amplitudes  $t_i^a$  and  $t_j^{\bar{i}}$ ; the reason is that the corresponding determinants  $\Phi_i^a$  and  $\Phi_j^{\bar{i}}$  are already spin-adapted.
- There is one equation [Eqn. (17)] relating  $t_i^a$ ,  $t_j^{\bar{i}}$ , and  $t_{ij}^{a\bar{i}}$ ; this reflects the fact that the three determinants  $\Phi_i^a$ ,  $\Phi_j^{\bar{i}}$  and  $\Phi_{ij}^{a\bar{i}}$  span a space consisting of two doublet and one quartet state. Note that the corresponding equation contains a product of  $t_i^a$  and  $t_j^{\bar{i}}$ .
- There is one equation [Eqn. (18)] relating  $t_{ij}^{a\bar{b}}$ ,  $t_{ij}^{b\bar{a}}$  and  $t_{ij}^{ab}$  due to the fact that the corresponding determinantal space consists of two doublet and one quartet state. Note that products like  $t_i^a t_{ij}^{b\bar{i}}$  appear in the equation, but a unique set for those amplitudes is already determined by means of Eqn. (17).
- Similar conclusions hold for the amplitudes  $t_{ij}^{a\bar{i}}$  and  $t_{ji}^{a\bar{i}}$  and  $t_{ij}^{a\bar{b}}$ ; the corresponding equation [Eqn. (19)] contains products of  $t_i^a t_{ij}^{b\bar{i}}$ .
- Four independent equations [Eqn. (20) to Eqn. (23)] relate amplitudes  $t_{ij}^{ab}$ ,  $t_{ij}^{a\bar{b}}$  with the four possible permutations of  $t_{ij}^{a\bar{b}}$ . This agrees with the fact that the determinantal subspace spanned by the corresponding six determinants describes just two pure doublet states. Unique sets of amplitudes which appear in the product terms are already determined by the spin equations discussed before.

Using the projected spin equations, it is possible to define a set of independent variables. A straightforward choice is the use of spin-adapted combinations of the spin-orbital amplitudes. Those are obtained in the same way from spin-orbital amplitudes as the doublet CSFs from the Slater determinants. In the following, we will denote the spin-adapted

amplitudes by  $\tilde{t}$ . Our actual choice is summarized in Table II, but it is convenient for the following to introduce also a more compact notation by

$$\tilde{t}_p = \sum_q c_{pq} t_q \quad (24)$$

with  $p$  labeling the CSFs and  $q$  the spin-orbital amplitudes. It should be pointed out that the matrix  $c$  is rectangular rather than square, as we do not define spin-adapted amplitudes for higher multiplicities (unlike in case of CSFs). This means that the spin-orbital amplitudes  $t_q$  are not uniquely defined by the spin-adapted  $\tilde{t}_p$ . A unique relationship is recovered by taking into account the additional constraints given by the spin equations [Eqn. (17) to Eqn. (23)]. The resulting equations are given in Table II. We note the hierarchical structure of the equations given in Table II and that there is no need to rewrite the nonlinear contributions in terms of the spin-adapted  $\tilde{t}$ . Starting from the first equation at the top it is realized that the nonlinear contributions involve only spin-orbital amplitudes already determined by the previous equations, i.e., those in the third equation are determined by first and second equations, etc.

Equations for the amplitudes  $\tilde{t}_p$  are obtained by projecting the premultiplied Schrödinger equations on doublet CSFs  ${}^D\tilde{\Phi}_p$ :

$$\langle {}^D\tilde{\Phi}_p | \exp(-T) H \exp(T) | \Phi_0 \rangle = 0. \quad (25)$$

Note that the wave function is still most conveniently written in terms of spin-orbital amplitudes. It is therefore possible to rewrite Eqn. (25) as

$$\langle {}^D\tilde{\Phi}_p | (H \exp(T))_c | \Phi_0 \rangle = 0 \quad (26)$$

with the subscript  $c$  denoting that just the connected terms have to be considered. Rewriting the CSFs in Eqn. (26) in terms of determinants then yields

$$\sum_q c_{pq} \langle \Phi_q | (H \exp(T))_c | \Phi_0 \rangle = 0. \quad (27)$$

Equation (27) has the advantage that it can be evaluated using standard methods available from spin-orbital CC theory. It furthermore opens the possibility for a preliminary, though computationally less efficient implementation for testing purposes, as the projection of the Schrödinger equation onto the Slater determinants is easily carried out with any standard spin-orbital CC code. However, we are aware of the fact that for future routine applications of spin-restricted CCSD a more efficient implementation exploiting all advantages connected to the reduced number of independent variables is required. Here we only note that the equations can be reformulated in such a manner that the cost for a spin-restricted CCSD calculation is essentially the same as for a corresponding closed-shell calculation.<sup>16</sup>

## B. Energy derivatives

In spin-restricted CC theory, the spin-orbital amplitudes of the cluster operator fulfill two kinds of equations, namely

TABLE II. Definition of the independent (spin-adapted) amplitudes in terms of the spin-orbital amplitudes [part (a)] and expressions for the spin-orbital amplitudes in terms of the spin-adapted amplitudes [part (b)] for a high-spin doublet state.  $P(p,q)$  is the usual antisymmetrization operator.

(a) Definition of spin-adapted amplitudes in terms of spin-orbital amplitudes

$$\tilde{t}_i^a = t_i^a$$

$$\tilde{t}_i^{\bar{a}} = t_i^{\bar{a}}$$

$$\tilde{t}1_i^a = \frac{1}{\sqrt{2}}t_i^a + \frac{1}{\sqrt{2}}t_i^{\bar{a}}$$

$$\tilde{t}2_i^a = -\frac{1}{\sqrt{6}}t_i^a + \frac{1}{\sqrt{6}}t_i^{\bar{a}} + \frac{2}{\sqrt{6}}t_{i\bar{i}}^{a\bar{a}}$$

$$\tilde{t}1_{ii}^{ab} = \frac{2}{\sqrt{6}}t_{ii}^{ab} + \frac{1}{\sqrt{6}}t_{i\bar{i}}^{a\bar{b}} - \frac{1}{\sqrt{6}}t_{i\bar{i}}^{b\bar{a}}$$

$$\tilde{t}2_{ii}^{ab} = \frac{1}{\sqrt{2}}t_{i\bar{i}}^{a\bar{b}} + \frac{1}{\sqrt{2}}t_{i\bar{i}}^{b\bar{a}}$$

$$\tilde{t}1_{ij}^{ta} = \frac{2}{\sqrt{6}}t_{i\bar{j}}^{a\bar{a}} - \frac{1}{\sqrt{6}}t_{i\bar{j}}^{a\bar{t}} + \frac{1}{\sqrt{6}}t_{j\bar{i}}^{a\bar{t}}$$

$$\tilde{t}2_{ij}^{ta} = \frac{1}{\sqrt{2}}t_{i\bar{j}}^{a\bar{t}} + \frac{1}{\sqrt{2}}t_{j\bar{i}}^{a\bar{t}}$$

$$\tilde{t}1_{ij}^{ab} = \frac{1}{\sqrt{3}}t_{ij}^{ab} + \frac{1}{2\sqrt{3}}t_{i\bar{j}}^{a\bar{b}} - \frac{1}{2\sqrt{3}}t_{i\bar{j}}^{b\bar{a}} + \frac{1}{2\sqrt{3}}t_{j\bar{i}}^{b\bar{a}} - \frac{1}{2\sqrt{3}}t_{j\bar{i}}^{a\bar{b}} + \frac{1}{\sqrt{3}}t_{i\bar{j}}^{a\bar{b}}$$

$$\tilde{t}2_{ij}^{ab} = \frac{1}{2}t_{i\bar{j}}^{a\bar{b}} + \frac{1}{2}t_{i\bar{j}}^{b\bar{a}} + \frac{1}{2}t_{j\bar{i}}^{a\bar{b}} + \frac{1}{2}t_{j\bar{i}}^{b\bar{a}}$$

(b) Spin-orbital amplitudes in terms of spin-adapted amplitudes

$$t_i^a = \tilde{t}_i^a$$

$$t_i^{\bar{a}} = \tilde{t}_i^{\bar{a}}$$

$$t_{i\bar{i}}^{a\bar{a}} = \frac{\sqrt{2}}{\sqrt{3}}\tilde{t}2_i^a - \frac{1}{3}\tilde{t}_i^a t_i^{\bar{a}}$$

$$t_i^a = \frac{1}{\sqrt{2}}\tilde{t}1_i^a - \frac{1}{\sqrt{6}}\tilde{t}2_i^a - \frac{1}{3}\tilde{t}_i^a t_i^{\bar{a}}$$

$$t_i^{\bar{a}} = \frac{1}{\sqrt{2}}\tilde{t}1_i^{\bar{a}} + \frac{1}{\sqrt{6}}\tilde{t}2_i^{\bar{a}} + \frac{1}{3}\tilde{t}_i^{\bar{a}} t_i^a$$

$$t_{ij}^{ab} = \frac{\sqrt{6}}{3}\tilde{t}1_{ij}^{ab} - \frac{1}{3}P(a,b)t_i^a t_j^{\bar{a}}$$

$$t_{i\bar{j}}^{a\bar{b}} = \frac{1}{\sqrt{6}}\tilde{t}1_{ij}^{ab} + \frac{1}{\sqrt{2}}\tilde{t}2_{ii}^{ab} + \frac{1}{3}P(a,b)t_i^a t_j^{\bar{a}}$$

$$t_{i\bar{j}}^{\bar{a}a} = \frac{\sqrt{6}}{3}\tilde{t}1_{ij}^{ta} + \frac{1}{3}P(i,j)t_i^{\bar{a}} t_j^a$$

$$t_{i\bar{j}}^{a\bar{t}} = -\frac{1}{\sqrt{6}}\tilde{t}1_{ij}^{ta} + \frac{1}{\sqrt{2}}\tilde{t}2_{ij}^{ta} + \frac{1}{3}P(i,j)t_i^{\bar{a}} t_j^{\bar{t}}$$

$$t_{ij}^{ab} = \frac{1}{\sqrt{3}}\tilde{t}1_{ij}^{ab} - \frac{1}{2}P(i,j)P(a,b)(t_i^a t_j^{\bar{a}} - t_j^{\bar{a}} t_i^a + \frac{1}{3}\tilde{t}_i^a t_j^{\bar{a}})$$

$$t_{i\bar{j}}^{a\bar{b}} = \frac{1}{\sqrt{3}}\tilde{t}1_{ij}^{ab} + \frac{1}{2}P(i,j)P(a,b)(t_i^a t_j^{\bar{a}} - t_j^{\bar{a}} t_i^a - \frac{1}{3}\tilde{t}_i^a t_j^{\bar{a}})$$

$$t_{i\bar{j}}^{a\bar{b}} = \frac{\sqrt{3}}{6}\tilde{t}1_{ij}^{ab} + \frac{1}{2}\tilde{t}2_{ij}^{ab} + \frac{1}{2}(t_i^a t_j^{\bar{a}} - t_j^{\bar{a}} t_i^a + \frac{1}{3}\tilde{t}_i^a t_j^{\bar{a}}) + \frac{1}{6}(t_j^{\bar{a}} t_i^a - t_i^a t_j^{\bar{a}}) + \frac{1}{6}(t_j^{\bar{a}} t_i^{\bar{t}} - t_i^{\bar{t}} t_j^{\bar{a}}) - \frac{1}{3}\tilde{t}_i^a t_j^{\bar{a}} + \frac{1}{3}\tilde{t}_i^{\bar{a}} t_j^a$$

the projected spin equations [Eqn. (13)] and the projected Schrödinger equations [Eqn. (14)]. Derivation of a computationally efficient expression for the gradient by straightforward differentiation of the energy is more involved than for the usual CC ansatz and, therefore, we employ in the following a different approach to energy derivatives based on the use of Lagrangian multipliers. This technique has been first applied by Jørgensen and Helgaker for the derivation of gradient expressions in many-body perturbation and single-reference CC theory<sup>17</sup> and has been later successfully used in the context of multireference CC approaches.<sup>18,19</sup>

The general procedure starts with an energy functional  $F$  defined as the sum of the energy expression and of all equations for the wave function parameters multiplied by a Lagrangian multiplier (denoted in the following  $\lambda_p$ ). By construction,  $F$  is stationary with respect to the multipliers  $\lambda_p$ . It can be also made stationary with respect to the wave function parameters by requiring that the corresponding derivatives of  $F$  vanish. This additional requirement leads to a set of linear equations, the so-called  $\Lambda$  equations, which can be used to determine the actual values of the multipliers  $\lambda_p$ . A derivative expression is finally obtained by straightforward differentiation of the functional  $F$  with respect to the external perturbation

$$\frac{dE}{dx} = \frac{\partial F}{\partial x}, \quad (28)$$

where the stationarity of  $F$  with respect to wave function parameters and Lagrangian multipliers is exploited. The advantage of Eqn. (28) is that it does not involve derivatives of wave function parameters. However, the price one has to pay is that an additional, though perturbation independent set of equations for the multipliers  $\lambda_p$  has to be solved.

In case of spin-restricted CC theory, the method of Lagrangian multipliers can be used in two different ways: one can either start with spin-orbital amplitudes and consider both the projected spin [Eqn. (13)] and Schrödinger equations [Eqn. (14)] as constraints or, alternatively, one can work from the beginning with spin-adapted amplitudes as independent parameters leaving just the projected Schrödinger equations as constraints. Both approaches are equivalent, but the second appears more straightforward and is pursued in the following.

The energy functional  $F$  in spin-restricted CC theory takes then the following form:

$$F(\tilde{t}_p, \tilde{\lambda}_p) = \langle 0 | \exp(-T) H \exp(T) | 0 \rangle + \sum_{p \in \mathbf{g}} \tilde{\lambda}_p \langle {}^D \tilde{\Phi}_p | \exp(-T) H \exp(T) | 0 \rangle \quad (29)$$

with  $\tilde{t}_p$  and  $\tilde{\lambda}_p$  as independent variables. Equations for the Lagrangian multipliers  $\tilde{\lambda}_p$  are obtained through the requirement that the derivatives of  $F$  with respect to  $\tilde{t}_p$  vanish. Using the chain rule, this yields

$$0 = \frac{\partial F}{\partial \tilde{t}_p} \quad (30)$$

$$= \sum_q \frac{\partial F}{\partial t_q} \frac{dt_q}{d\tilde{t}_p}. \quad (31)$$

The first part of the right-hand side of Eqn. (31), i.e.,  $(\partial F/\partial t_q)$ , is easily evaluated using techniques from standard spin-orbital theory, while  $(\partial t_q/\partial \tilde{t}_p)$  can be obtained by differentiation of the expression of  $t_q$  as a function of  $\tilde{t}_p$ . In particular, for the specific case of high-spin doublet states the equations given in Table II can be used. The resulting equations for the multipliers  $\tilde{\lambda}_p$  are

$$0 = M1_{ij}^{ab}, \quad (32)$$

$$0 = M2_{ij}^{ab}, \quad (33)$$

$$0 = M1_{ij}^{ab} + \frac{1}{2\sqrt{6}} \sum_i (-2m_{ij}^{ab} - m_{ij}^{a\bar{b}} + m_{ij}^{b\bar{a}} - m_{ji}^{a\bar{b}} + m_{ji}^{b\bar{a}} + 2m_{ji}^{a\bar{b}}) \tilde{t}_i^a, \quad (34)$$

$$0 = M2_{ij}^{ab} + \frac{1}{2\sqrt{2}} \sum_i (-m_{ij}^{a\bar{b}} - m_{ij}^{b\bar{a}} + m_{ji}^{a\bar{b}} + m_{ji}^{b\bar{a}}) \tilde{t}_i^a, \quad (35)$$

$$0 = M1_{ij}^{at} + \frac{1}{2\sqrt{6}} \sum_b (-2m_{ij}^{ab} + m_{ij}^{a\bar{b}} + m_{ij}^{b\bar{a}} - m_{ji}^{a\bar{b}} - m_{ji}^{b\bar{a}} + 2m_{ji}^{a\bar{b}}) \tilde{t}_i^b, \quad (36)$$

$$0 = M2_{ij}^{at} + \frac{1}{2\sqrt{2}} \sum_b (m_{ij}^{a\bar{b}} - m_{ij}^{b\bar{a}} + m_{ji}^{a\bar{b}} - m_{ji}^{b\bar{a}}) \tilde{t}_i^b, \quad (37)$$

$$0 = M2_i^a + \frac{2}{3\sqrt{6}} \sum_b (-m_{ii}^{ab} + m_{ii}^{a\bar{b}} - m_{ii}^{b\bar{a}}) \tilde{t}_i^b + \frac{2}{3\sqrt{6}} \sum_j (m_{ij}^{a\bar{t}} - m_{ji}^{a\bar{t}} - m_{ij}^{a\bar{t}}) \tilde{t}_j^a + \frac{1}{3\sqrt{6}} \times \sum_{bj} (-m_{ij}^{ab} + m_{ij}^{a\bar{b}} - 2m_{ij}^{b\bar{a}} + m_{ji}^{b\bar{a}} - m_{ji}^{a\bar{b}}) \tilde{t}_i^b \tilde{t}_j^a = 0, \quad (38)$$

$$0 = M1_i^a, \quad (39)$$

$$0 = M_i^t + \frac{1}{2\sqrt{6}} \sum_{j,a>b} (-2m_{ij}^{ab} - m_{ij}^{a\bar{b}} + m_{ij}^{b\bar{a}} - m_{ji}^{a\bar{b}} + m_{ji}^{b\bar{a}} + 2m_{ji}^{a\bar{b}}) \tilde{t}_i^{ab} + \frac{1}{2\sqrt{2}} \sum_{j,a>b} (-m_{ij}^{a\bar{b}} - m_{ij}^{b\bar{a}} + m_{ji}^{a\bar{b}} + m_{ji}^{b\bar{a}}) \tilde{t}_i^{ab} + \frac{1}{3\sqrt{6}} \sum_{abj} (-m_{ij}^{ab} + m_{ij}^{a\bar{b}} - 2m_{ji}^{a\bar{b}} + m_{ji}^{b\bar{a}} - m_{ji}^{a\bar{b}}) \tilde{t}_j^b \tilde{t}_i^a + \frac{2}{3\sqrt{6}} \sum_{jb} (-m_{ij}^{b\bar{t}} + m_{ji}^{b\bar{t}} + m_{ij}^{b\bar{t}}) \tilde{t}_j^b + \frac{1}{3} \sum_a (-m_i^a + m_i^{a\bar{t}} - m_{ii}^{a\bar{t}}) \tilde{t}_i^a, \quad (40)$$

$$0 = M_i^a + \frac{1}{2\sqrt{6}} \sum_{b,i>j} (2m_{ij}^{ab} + m_{ij}^{a\bar{b}} + m_{ij}^{b\bar{a}} - m_{ji}^{a\bar{b}} - m_{ji}^{b\bar{a}} - 2m_{ji}^{a\bar{b}}) \tilde{t}_i^{bt} + \frac{1}{2\sqrt{2}} \sum_{b,i>j} (-m_{ij}^{a\bar{b}} + m_{ij}^{b\bar{a}} - m_{ji}^{a\bar{b}} + m_{ji}^{b\bar{a}}) \tilde{t}_i^{bt} + \frac{1}{3\sqrt{6}} \sum_{ijb} (-m_{ij}^{ab} + m_{ij}^{a\bar{b}} - 2m_{ji}^{a\bar{b}} + m_{ji}^{b\bar{a}} - m_{ji}^{a\bar{b}}) \tilde{t}_i^a \tilde{t}_j^b + \frac{2}{3\sqrt{6}} \sum_{bj} (m_{ij}^{ab} - m_{ij}^{a\bar{b}} + m_{ii}^{a\bar{b}}) \tilde{t}_j^b + \frac{1}{3} \sum_i (-m_i^a + m_i^{a\bar{t}} - m_{ii}^{a\bar{t}}) \tilde{t}_i^a, \quad (41)$$

with the quantities  $M_q$  and  $m_q$  defined as

$$M_q = \langle 0 | (H \exp(T))_c | \tilde{\Phi}_q \rangle + \sum_{p \in \mathbf{g}} \tilde{\lambda}_p \langle {}^D \tilde{\Phi}_p | (H \exp(T))_c | \tilde{\Phi}_q \rangle \quad (42)$$

and

$$m_q = \langle 0 | (H \exp(T))_c | \Phi_q \rangle + \sum_{p \in \mathbf{g}} \tilde{\lambda}_p \langle {}^D \tilde{\Phi}_p | (H \exp(T))_c | \Phi_q \rangle. \quad (43)$$

Note that the first part of the right-hand sides of Eqs. (32)–(41) are just the spin-adapted combination of the  $\Lambda$  equations



in spin-orbital CC theory [compare Eqn. (42)], while the other terms represent simple products of  $m_q$  with spin-adapted cluster amplitudes.

For the gradient, finally, an expression identical to that used in spin-orbital CC theory is obtained, i.e.,

$$\frac{dE}{dx} = \langle 0 | (1 + \Lambda) \exp(-T) \frac{\partial H}{\partial x} \exp(T) | 0 \rangle \quad (44)$$

with the only difference that cluster and  $\Lambda$  operator are determined by different equations. Eqn. (32) to Eqn. (44) indicate that as for energy and wave function, a preliminary implementation of spin-restricted CCSD gradients is easily possible within a spin-orbital code.

In the following, we focus on the spin expectation value  $\langle S^2 \rangle$  which is given in the context of derivative theory by<sup>4</sup>

$$\langle S^2 \rangle = s(s+1) + \langle 0 | (1 + \Lambda) \exp(-T) \hat{S}_N^2 \exp(T) | 0 \rangle \quad (45)$$

with  $\hat{S}_N^2$  as the normal-ordered spin operator. Due to fulfillment of the projected spin equations [Eqn. (9)], insertion of the resolution of identity in Eqn. (45) yields for spin-restricted CC

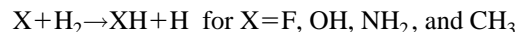
$$\begin{aligned} \langle S^2 \rangle &= s(s+1) + \sum_{p \in g} \langle 0 | (1 + \Lambda) | \Phi_p \rangle \\ &\quad \times \langle \Phi_p | \exp(-T) \hat{S}_N^2 \exp(T) | 0 \rangle \end{aligned} \quad (46)$$

$$= s(s+1). \quad (47)$$

Thus, it is seen that the expectation value of  $\langle S^2 \rangle$  always takes the exact value in spin-restricted CC theory, though the corresponding wave function is neither spin adapted nor a spin eigenfunction.

#### IV. PRELIMINARY RESULTS AND DISCUSSION

In this section, the numerical performance of the spin-restricted CCSD approach for high-spin doublet states is investigated. Table III documents energies and spin expectation values for a few selected examples. Considered are typical doublet cases such as CH(<sup>2</sup>Π), OH(<sup>2</sup>Π), CN(<sup>2</sup>Σ<sup>+</sup>), NO(<sup>2</sup>Π), CH<sub>3</sub>(<sup>2</sup>A''), NH<sub>2</sub>(<sup>2</sup>B<sub>1</sub> and <sup>2</sup>A<sub>1</sub>), as well as a few more challenging examples such as NO<sub>2</sub>(<sup>2</sup>A<sub>2</sub>), CH<sub>2</sub>N(<sup>2</sup>B<sub>2</sub>) and HCCO(<sup>2</sup>Π). Performance of spin-restricted CCSD in the calculation of chemical energy differences is investigated in Table IV, where reaction energies and activation barriers for the reaction



are reported. Calculations have been performed with a preliminary implementation of spin-restricted CCSD within a local version of the ACESII program system.<sup>20</sup>

The results reported in Table III show that the energies calculated with the spin-restricted ansatz are in all cases slightly higher than those obtained with the spin-orbital approaches. Differences are in the range of 0.0002 to 0.0065 Hartree and, therefore, might be in some cases of chemical relevance. Not surprisingly, the largest differences are found in cases where spin contamination in the spin-orbital based

TABLE III. CCSD energies (in Hartree) and expectation values of  $S^2$  calculated using different high-spin open-shell CC approaches.<sup>a</sup>

Method	Total energy	$\langle S^2 \rangle$
CH ( <sup>2</sup> Π) <sup>b</sup>		
UHF-CCSD	-38.418108	0.750165
ROHF-CCSD	-38.418017	0.750111
Spin-restricted CCSD	-38.417884	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-38.417884	0.750000
OH ( <sup>2</sup> Π) <sup>d</sup>		
UHF-CCSD	-75.644822	0.750124
ROHF-CCSD	-75.644768	0.750071
Spin-restricted CCSD	-75.644622	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-75.644621	0.750000
CN ( <sup>2</sup> Σ <sup>+</sup> ) <sup>e</sup>		
UHF-CCSD	-92.571897	0.754327
ROHF-CCSD	-92.572197	0.751453
Spin-restricted CCSD	-92.571468	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-92.571145	0.750004
NO ( <sup>2</sup> Π) <sup>f</sup>		
UHF-CCSD	-129.723209	0.750653
ROHF-CCSD	-129.722823	0.750371
Spin-restricted CCSD	-129.722343	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-129.722315	0.750001
CH <sub>3</sub> ( <sup>2</sup> A'') <sup>g</sup>		
UHF-CCSD	-39.771341	0.750260
ROHF-CCSD	-39.771278	0.750144
Spin-restricted CCSD	-39.771108	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-39.771108	0.750000
NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> ) <sup>h</sup>		
UHF-CCSD	-55.801219	0.750204
ROHF-CCSD	-55.801152	0.750122
Spin-restricted CCSD	-55.800976	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-55.800975	0.750000
NH <sub>2</sub> ( <sup>2</sup> A <sub>1</sub> ) <sup>i</sup>		
UHF-CCSD	-55.748878	0.750160
ROHF-CCSD	-55.748820	0.750100
Spin-restricted CCSD	-55.748663	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-55.748660	0.750000
NO <sub>2</sub> ( <sup>2</sup> A <sub>2</sub> ) <sup>j</sup>		
UHF-CCSD	-204.730910	0.768465
ROHF-CCSD	-204.727109	0.762368
Spin-restricted CCSD	-204.724402	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-204.724465	0.750000
CH <sub>2</sub> N ( <sup>2</sup> B <sub>2</sub> ) <sup>k</sup>		
UHF-CCSD	-93.835787	0.755786
ROHF-CCSD	-93.835872	0.751488
Spin-restricted CCSD	-93.835416	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-93.835371	0.750006
HCCO ( <sup>2</sup> Π) <sup>l</sup>		
UHF-CCSD	-151.694248	0.752818
ROHF-CCSD	-151.693525	0.751820
Spin-restricted CCSD	-151.692735	0.750000
Partially spin-adapted CCSD <sup>c</sup>	-151.692572	0.750020

<sup>a</sup>All calculations have been performed with the cc-pVTZ basis from Ref. 22.

<sup>b</sup>R(CH)=1.1199 Å.<sup>23</sup>

<sup>c</sup>Partially spin-adapted CCSD as formulated by Knowles, Hampel and Werner<sup>10</sup> and Neogrády, Urban, Hubač.<sup>11</sup>

<sup>d</sup>R(OH)=0.9697 Å.<sup>23</sup>

<sup>e</sup>R(CN)=1.1718 Å.<sup>23</sup>

<sup>f</sup>R(NO)=1.1508 Å.<sup>23</sup>

<sup>g</sup>R(CH)=1.09 Å, θ(HCH)=120°.

<sup>h</sup>R(NH)=1.024 Å, θ(HNH)=103.4°.

<sup>i</sup>R(NH)=1.00 Å, θ(HNH)=144.0°.

<sup>j</sup>R(NO)=1.29 Å, θ(ONO)=109.3°.<sup>4</sup>

<sup>k</sup>R(CN)=1.2655 Å, R(CH)=1.1010 Å, θ(HCN)=121.27°.<sup>24</sup>

<sup>l</sup>R(CC)=1.274 Å, R(CO)=1.193 Å, R(CH)=1.070 Å.<sup>25</sup>

TABLE IV. Reaction energies and activation barriers (in kcal/mol) calculated with different high-spin open-shell CCSD approaches.<sup>a</sup>

	UHF-CCSD	ROHF-CCSD	spin-restricted CCSD
(a) Reaction energies			
$F + H_2 \rightarrow FH + H$	-27.52	-27.54	-27.60
$OH + H_2 \rightarrow OH_2 + H$	-12.96	-13.00	-13.09
$NH_2 + H_2 \rightarrow NH_3 + H$	-4.24	-4.28	-4.39
$CH_3 + H_2 \rightarrow CH_4 + H$	-2.69	-2.73	-2.84
(b) Activation barriers			
$F + H_2 \rightarrow FH + H$	4.16	4.19	4.23
$OH + H_2 \rightarrow OH_2 + H$	7.78	7.87	7.96
$NH_2 + H_2 \rightarrow NH_3 + H$	11.23	11.36	11.47
$CH_3 + H_2 \rightarrow CH_4 + H$	13.08	13.18	13.27

<sup>a</sup>All calculations have been performed with the cc-pVTZ basis from Ref. 22. Geometries have been taken from Ref. 21.

results is substantial. For example, for the  $^2A_2$  state of  $NO_2$  with  $\langle S^2 \rangle$  values of 0.7685 and 0.7624 in UHF- and ROHF-CCSD calculations, the energy difference amounts to about 0.006 and 0.003 Hartree, respectively. It is tempting to consider the spin-restricted result in that particular example the more reliable, but further investigations are required before a final conclusion can be drawn.

Similar observations can be made for the reaction energies and activation barriers reported in Table IV. The deviations are generally not significant with differences of less than 0.2 to 0.3 kcal/mol in all cases. These rather small differences can be taken as strong evidence that the spin-restricted approach represents an attractive and cost-effective alternative to the spin-orbital based schemes, provided that a computationally efficient implementation will be available in the near future.

Of particular interest in the current context is a comparison of the spin-restricted approach to the so-called *partially spin-adapted* CCSD approach, which has been recently suggested as a cost-effective alternative to the spin-orbital based schemes.<sup>10,11</sup> We therefore report in Table III also energies and spin expectation values<sup>26</sup> for this high-spin open-shell CC approach. However, before a comparison of the numerical results, a brief discussion of the relationship between these two open-shell CC schemes might be warranted. As stated in the introduction, the cluster operator  $T$  generates in the partially spin-adapted approach only configurations of desired spin out of the reference determinant. This requirement on  $T$  is equivalent to a linearization of the spin-constraints imposed on the wave function within the spin-restricted scheme. The partially spin-adapted approach should therefore be considered as an approximation to the spin-restricted CC ansatz.

The consequences of the approximate incorporation of the spin constraints in the partially spin-adapted approach are that the second term on the right-hand side of Eqn. (46) does not vanish and that the spin-expectation value generally deviates from the exact result. However, as the residual spin contamination results from products of the cluster operator, it is expected to be rather small, at least when compared to spin contamination observed in spin-orbital based CC calcula-

tions. A further problem of the partially spin-adapted scheme is that in the untruncated limit the linearized spin equations do not coincide with the spin eigenvalue equations [Eqn. (9)] satisfied by the exact wave function. This means that the partially spin-adapted CC approach is—unlike the spin-restricted approach suggested in this work—not exact in the untruncated limit.

A numerical comparison of spin-restricted and partially spin-adapted CCSD is presented in Table III. It is seen that in most cases the energies differ negligibly, i.e., by less than  $2 \cdot 10^{-4}$  Hartree and that these differences are an order of magnitude smaller than those observed in comparison with the spin-orbital based schemes. The spin expectation values for the partially spin-adapted approach differ from the exact value, though again deviations are quite small. One could argue that this spin contamination appears to be unimportant. We note, however, that the largest energy difference to spin-restricted CC (and consequently to spin-orbital CC) has been found for HCCO, where the spin expectation value exhibits the largest deviation from the exact value.

## V. SUMMARY AND OUTLOOK

For the CC treatment of high-spin open-shell systems, it appears useful to take into account spin constraints derived from the spin eigenvalue equation of the exact wave function. Only then, residual spin contamination can be eliminated and the computational cost reduced to that of a corresponding closed-shell calculation. Exploitation of these constraints within the (truncated) excitation space yields what we term *spin-restricted* CC theory. Unlike a rigorously spin-adapted CC theory, this approach has the advantage that the cluster operator can still be truncated in the usual manner, i.e., at the spin-orbital level. Furthermore, spin-restricted CC theory can easily be cast in the usual spin-orbital framework of standard CC theory and, thus, has a much lower complexity than the recently suggested rigorously spin-adapted approaches. Numerical results obtained with a preliminary implementation for high-spin doublet states documents the excellent performance of this approach within the usual CCSD approximation and suggest that it might be an attractive alternative to the more traditional spin-orbital based schemes. However, it is clear that its future use depends on an efficient computational implementation of both energy and energy derivatives as well as an extension to higher multiplicity spin states. In addition, it seems mandatory to provide an efficient non-iterative treatment of triple excitations in order to go routinely beyond the CCSD level. While these aspects are mostly relevant regarding potential computational savings and do not necessarily offer new computational possibilities beyond those already available with the spin-orbital based schemes, it appears that spin-restricted CC theory has some additional promise for the treatment of excited states. There spin contamination can be in some cases a notorious problem, severely hampering the calculation of the full excitation spectra of radicals. Spin-restricted CC theory might be here a promising starting point for an

excited state treatment using, for example, the equation-of-motion ansatz with a proper description ensured by spin constraints.

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## APPENDIX

In this appendix we prove that it is sufficient to project the spin equations on configurations with spin different from the desired value  $s(s+1)$ , as projection onto configurations with the spin  $s(s+1)$  leads to equations that are automatically fulfilled. For the proof, we consider first the general set of spin equations which is required to be satisfied by the CC wave function:

$$\langle \tilde{\Phi}_p | \exp(-T) \hat{S}_N^2 \exp(T) | 0 \rangle = 0 \quad (\text{A1})$$

for all configuration  $\tilde{\Phi}_p$  and the normal-ordered spin operator  $\hat{S}_N^2$

$$\begin{aligned} \hat{S}_N^2 &= \hat{S}^2 - \langle 0 | \hat{S}^2 | 0 \rangle \\ &= \hat{S}^2 - s(s+1). \end{aligned} \quad (\text{A2})$$

We insert the resolution of identity in Eq. (A1) in between  $\exp(-T)$  and  $\hat{S}_N^2$

$$\sum_q \langle \tilde{\Phi}_p | \exp(-T) | \tilde{\Phi}_q \rangle \langle \tilde{\Phi}_q | \hat{S}_N^2 \exp(T) | 0 \rangle = 0 \quad (\text{A3})$$

and expand  $\exp(-T)$  in a power of series

$$\begin{aligned} \langle \tilde{\Phi}_p | \hat{S}_N^2 \exp(T) | 0 \rangle - \sum_q \langle \tilde{\Phi}_p | T | \tilde{\Phi}_q \rangle \langle \tilde{\Phi}_q | \hat{S}_N^2 \exp(T) | 0 \rangle \\ + \frac{1}{2} \sum_q \langle \tilde{\Phi}_p | T^2 | \tilde{\Phi}_q \rangle \langle \tilde{\Phi}_q | \hat{S}_N^2 \exp(T) | 0 \rangle - \dots = 0. \end{aligned} \quad (\text{A4})$$

Since for configurations  $\tilde{\Phi}_p$  with  $M_s = s$  the action of the normal-order spin-operator can be written as

$$\hat{S}_N^2 \tilde{\Phi}_p = \hat{S}_- \hat{S}_+ \tilde{\Phi}_p \quad \forall \tilde{\Phi}_p \text{ with } M_s = s, \quad (\text{A5})$$

the following holds for all states with spin  $s(s+1)$

$$\langle {}^{s(s+1)} \tilde{\Phi}_p | \hat{S}_N^2 = 0, \quad (\text{A6})$$

while for all other configurations

$$\langle {}^{\mathcal{Q}} \tilde{\Phi}_p | \hat{S}_N^2 \neq 0. \quad (\text{A7})$$

Furthermore, it is easy to recognize that the summation over  $q$  is actually a restricted summation, as  $T$  is a pure excitation operator. Defining the excitation rank of a configuration  $\tilde{\Phi}_p$  by

$\text{Rank}(\tilde{\Phi}_p) = \text{number of occupied } a \text{ and } \bar{a} \text{ orbitals in } \tilde{\Phi}_p$

+ number of depleted  $i$  and  $\bar{i}$  orbitals in  $\tilde{\Phi}_p$  (A8)

it is easily seen that the rank of  $\tilde{\Phi}_q$  in Eqn. (A4) must be lower than that of  $\tilde{\Phi}_p$ . Consequently, Eqn. (A4) can be rewritten as

$$\begin{aligned} 0 &= \langle \tilde{\Phi}_p | \hat{S}_N^2 \exp(T) | 0 \rangle \\ &- \sum_{q: \text{Rank}(q) \leq \text{Rank}(p)-1} \langle \tilde{\Phi}_p | T | \tilde{\Phi}_q \rangle \langle \tilde{\Phi}_q | \hat{S}_N^2 \exp(T) | 0 \rangle \\ &+ \frac{1}{2} \sum_{q: \text{Rank}(q) \leq \text{Rank}(p)-2} \langle \tilde{\Phi}_p | T^2 | \tilde{\Phi}_q \rangle \\ &\times \langle \tilde{\Phi}_q | \hat{S}_N^2 \exp(T) | 0 \rangle \\ &- \dots \end{aligned} \quad (\text{A9})$$

The hierarchical structure of the spin equations can be exploited in the following way: consider first the projection onto the reference  $\langle 0 |$

$$\langle 0 | \hat{S}_N^2 \exp(T) | 0 \rangle = 0 \quad (\text{A10})$$

which is zero by virtue of Eqn. (A6): For the projections onto configurations  $\langle \tilde{\Phi}_p |$  with rank 1, the following holds:

$$\begin{aligned} \langle \tilde{\Phi}_p | \hat{S}_N^2 \exp(T) | 0 \rangle - \langle \tilde{\Phi}_p | T | 0 \rangle \langle 0 | \hat{S}_N^2 \exp(T) | 0 \rangle \\ = 0 \quad \forall \tilde{\Phi}_p; \text{Rank}(\tilde{\Phi}_p) = 1. \end{aligned} \quad (\text{A11})$$

The last term in Eqn. (A11) vanishes because of Eqn. (A10), while the first term is zero for all configurations with spin  $s(s+1)$ . The only remaining requirement which need to be imposed on the cluster operator is therefore:

$$\langle {}^{\mathcal{Q}} \tilde{\Phi}_p | \hat{S}_N^2 \exp(T) | 0 \rangle = 0 \quad \forall \tilde{\Phi}_p; \text{Rank}(\tilde{\Phi}_p) = 1. \quad (\text{A12})$$

For configurations with rank 2, projection yields

$$\begin{aligned} \langle \tilde{\Phi}_p | \hat{S}_N^2 \exp(T) | 0 \rangle - \sum_{q: \text{Rank}(q)=1} \langle \tilde{\Phi}_p | T | \tilde{\Phi}_q \rangle \\ \times \langle \tilde{\Phi}_q | \hat{S}_N^2 \exp(T) | 0 \rangle - \langle \tilde{\Phi}_p | T | 0 \rangle \langle 0 | \hat{S}_N^2 \exp(T) | 0 \rangle \\ = 0 \quad \forall \tilde{\Phi}_p, \text{Rank}(\tilde{\Phi}_p) = 2. \end{aligned} \quad (\text{A13})$$

Second and third term vanish in Eqn. (A13) because of Eqn. (A6), Eqn. (A10) and Eqn. (A12), while the first term is 0 for all  ${}^{s(s+1)} \tilde{\Phi}_p$  with rank 2. The remaining requirement for the cluster operator therefore is

$$\langle {}^{\mathcal{Q}} \tilde{\Phi}_p | \hat{S}_N^2 \exp(T) | 0 \rangle = 0 \quad \forall \tilde{\Phi}_p; \text{Rank}(\tilde{\Phi}_p) = 2. \quad (\text{A14})$$

The procedure can recursively be repeated for all configurations with higher excitation rank. The resulting complete set of constraints for the cluster operator is then obtained to be

$$\langle {}^{\mathcal{Q}} \tilde{\Phi}_p | \hat{S}_N^2 \exp(T) | 0 \rangle = 0 \quad (\text{A15})$$

or equivalently as

$$\langle {}^{\mathcal{Q}} \tilde{\Phi}_p | \exp(-T) \hat{S}_N^2 \exp(T) | 0 \rangle = 0. \quad (\text{A16})$$

Due to the hierarchical structure of the equations, the given proof is also valid for truncated excitations spaces.

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