MULTIPLICITY OF MANY-BODY WAVEFUNCTIONS USING UNRESTRICTED HARTREE-FOCK REFERENCE FUNCTIONS*

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

Spin multiplicity formulae for the correlated Many Body Perturbation Theory (MBPT) and Coupled Cluster (CC) methods based upon an unrestricted Hartree Fock (UHF) reference function are presented and applied to evaluate the multiplicity in calculations of first row atoms. Spin projection in CC theory is discussed.

The exact eigenfunction of the Schrödinger equation, $\mathbf{H}\Psi = E\Psi$, is also an eigenfunction of all operators which commute with the Hamiltonian $\mathbf{H}$. Conventionally, approximate calculations of the wavefunction require the approximate wavefunctions to be eigenfunctions of these symmetry operators. Obviously, such symmetry adapted methods can greatly reduce the computational difficulty in *ab initio* calculations. However, since approximation schemes which eventually lead to the exact wavefunction will also eventually produce a wavefunction with the correct symmetry, requiring that the approximate eigenfunctions obey the symmetry relations exactly is often unnecessary. Instead, it is sometimes convenient to employ trial solutions such as unrestricted Hartree–Fock (UHF)[1] or other types of broken symmetry solutions. When such wavefunctions are used, one should calculate the values of those operators from the approximate wavefunction to assess whatever contamination from other solutions might be introduced. Such a computation is also the first step in defining projection operators that are often used to correct the broken symmetry solutions toward the exact result[2].

Since UHF based correlated methods are not spin eigenfunctions, in the following, we present a derivation of the average value of the square of the spin, $\mathbf{S} \cdot \mathbf{S}$ for the Hartree–Fock (UHF) wavefunction and a projected matrix element expression for correlated wavefunctions. The derivation employs the formalism of second quantization. The average multiplicity is determined from $\mathbf{S}^2$. Expressions for the average

multiplicity of (UHF) single determinant wavefunctions have been reported else-
where and are in common usage in several molecular structure programs[3]. We have
frequently reported multiplicities for UHF based MBPT (ref.[4]) and coupled-cluster
(CC) methods[5] using formulae for the correlated case, but we have not presented the
explicit expressions. Also, by using spin-projection methods based upon the evalua-
tion of $\mathbf{S}^2$ for CC/MBPT methods, possibly improved methods could be achieved[6,7].

Second Quantized Form of $\mathbf{S}^2$

The total spin operator, $\mathbf{S}$, of a many-electron system is a sum of one-electron
operators, $\mathbf{S}(i)$

$$\mathbf{S}(1, \ldots, N) = \sum_{i=1}^{N} \mathbf{S}(i) . \tag{1}$$

From which

$$\mathbf{S}^2 = \mathbf{S} . \mathbf{S} = \mathbf{S}_+ \mathbf{S}_- + \mathbf{S}_z^2 - \mathbf{S}_z , \tag{2}$$

where the step-up and step-down operators are defined as

$$\mathbf{S}_+ = \mathbf{S}_x + i\mathbf{S}_y \quad \text{and} \quad \mathbf{S}_- = \mathbf{S}_x - i\mathbf{S}_y .$$

Each spin orbital, $\chi_p(x)$, is composed of a spatial and spin part, $\chi_p(x) = \varphi_p(r)\,\sigma_p$,
where $\sigma_p = \alpha$ for $p = 1, \ldots, M$ and $\sigma_p = \beta$ for $p = M + 1, \ldots, 2M$. The step-up
and -down operators have the property that

$$\mathbf{S}_+\alpha = 0 \quad \mathbf{S}_+\beta = \alpha$$

$$\mathbf{S}_-\alpha = \beta \quad \mathbf{S}_-\beta = 0 \tag{3a}$$

while

$$\mathbf{S}_z\alpha = \tfrac{1}{2}\alpha \quad \mathbf{S}_z\beta = -\tfrac{1}{2}\beta . \tag{3b}$$

In this paper we choose to use a second-quantized or occupation number representa-
tion since this facilitates deriving the relevant expressions. Then, using Eq. (3) we
have for $\mathbf{S}_+$, $\mathbf{S}_-$, and $\mathbf{S}_z$,

$$\mathbf{S}_+ = \sum_{p_\alpha, q_\beta} \Delta_{pq} p_\alpha^\dagger q_\beta \tag{4a}$$

$$\mathbf{S}_- = \sum_{r_\beta, s_\alpha} \Delta_{rs} r_\beta^\dagger s_\alpha \tag{4b}$$

$$\mathbf{S}_z = \sum_{p,q} \langle p|\mathbf{S}_z|q \rangle\, p^\dagger q = \tfrac{1}{2}\sum_{p_\alpha} p_\alpha^\dagger p_\alpha - \tfrac{1}{2}\sum_{r_\beta} r_\beta^\dagger r_\beta = \tfrac{1}{2}(\mathbf{n}_\alpha - \mathbf{n}_\beta) . \tag{4c}$$

The quantity

$$\Delta_{pq} = \langle \varphi_p(r) | \varphi_q(r) \rangle , \tag{5}$$

$\Delta_{pq} = \delta_{pq}$ when p and q have the same spin, is the spatial orbital overlap. The number operators $\mathbf{n}_\alpha$ and $\mathbf{n}_\beta$ count the number of orbitals with α spin (N_α) and β spin (N_β), respectively. For any determinant, Φ, $\mathbf{n}_\alpha | \Phi \rangle = N_\alpha | \Phi \rangle$.

In the following p, q, r, s signify any spin orbitals and associated operators while a, b, c, d indicate orbitals (associated operators) unoccupied in the reference UHF determinant, $|0\rangle$ and i, j, k, l orbitals (associated operators) occupied in $|0\rangle$. Wick's theorem[8] states that any product of second-quantized operators may be written as the normal-ordered product plus all single, double, up to ... fully contracted products. Symbolically we have

$$ABC... = \{ABC...\} \; + \; \sum + \; \{\overline{ABC}...\} \quad \sum + \quad \{\overline{\overline{ABCD}...}\} \; + ... \; + \; \sum \; \{\overline{\overline{\overline{ABCD}}}...\} \; ,$$

$$\underset{\substack{single \\ contractions}}{} \qquad \underset{\substack{double \\ contractions}}{} \qquad \underset{\substack{fully\ contracted \\ terms}}{}$$

where $\{\ \}$ indicates the normal order, which places $i^\dagger$ and a on the right which exploits the fact that $i^\dagger|0\rangle = a|0\rangle = 0$. Since the only non-vanishing contractions are $\overline{i^\dagger j} = \delta_{ij}$ and $\overline{ab^\dagger} = \delta_{ab}$, we may construct the normal operator form of $\{\mathbf{S}_N^2\}$ from Eq. (2) to be

$$\{\mathbf{S}_N^2\} = \mathbf{S}^2 - \langle 0 | \mathbf{S}^2 | 0 \rangle = \sum_{a_\beta, p_\alpha, s_\alpha} \Delta_{pa} \Delta_{as} \{\mathbf{p}_\alpha^\dagger \mathbf{s}_\alpha\} \tag{6a}$$

$$- \sum_{i_\alpha, q_\beta, r_\beta} \Delta_{ir} \Delta_{qi} \{\mathbf{q}_\beta^\dagger \mathbf{r}_\beta\} \tag{6b}$$

$$+ \sum_{\substack{q_\beta, s_\alpha \\ p_\alpha, r_\beta}} \Delta_{pq} \Delta_{rs} \{\mathbf{p}_\alpha^\dagger \mathbf{q}_\beta \mathbf{r}_\beta^\dagger \mathbf{s}_\alpha\} + \{\tfrac{1}{2}(\mathbf{n}_\alpha - \mathbf{n}_\beta)\}^2 , \tag{6c}$$

$\langle 0 | \mathbf{S}^2 | 0 \rangle$ is the Fermi vacuum expectation value over the reference UHF wavefunction, $|0\rangle$. Terms $(6a)$ and $(6b)$ are derived from contraction of operators for β and α spin orbitals, respectively, and term $(6c)$ comes from no contraction.

The expectation value has the value

$$\langle 0 | \mathbf{S}^2 | 0 \rangle = \sum_{i_\alpha, a_\beta} |\Delta_{ia}|^2 + \tfrac{1}{4}(N_\alpha - N_\beta)^2 - \tfrac{1}{2}(N_\alpha - N_\beta) \tag{7a}$$

or using the resolution of the identity, $\sum_a |a\rangle \langle a| = 1 - \sum_j |j\rangle \langle j|$, Eq. $(7a)$ may be put into the more conventional form,[9]

$$\langle 0 | \mathbf{S}^2 | 0 \rangle = \tfrac{1}{2}(N_\alpha + N_\beta) + \tfrac{1}{4}(N_\alpha - N_\beta)^2 - \sum_{i_\alpha, j_\beta} |\Delta_{ij}|^2 . \tag{7b}$$

For a correlated wavefunction Φ, intermediately normalized $\langle 0|\Phi\rangle = 1$, we define

$$\langle 0|\mathbf{S}^2|\Phi\rangle = M_s(M_s + 1) \tag{8}$$

in analogy to the energy expression $\langle 0|\mathbf{H}|\Phi\rangle = E$. Then

$$2M_s + 1 = (1 + 4\langle 0|\mathbf{S}^2|\Phi\rangle)^{1/2}, \tag{9}$$

where $2M_s + 1$ is the spin multiplicity. Such an evaluation of M_s is consistent with the energy evaluation from the "transition" or projected matrix element formalism employed by CC/MBPT theory. The alternative expectation value formula $\langle\Phi|\mathbf{S}^2|\Phi\rangle/\langle\Phi|\Phi\rangle$ would suffer from the same non-terminating series that is associated with the exponential ansatz, $\Phi = \exp(\mathbf{T})|0\rangle$. The rigorous development of expectation values and properties other than the energy in CC/MBPT theory has been presented elsewhere.[10]

Using Eqs (8) and (6), and the form of the generalized Wick's theorem which only permits contractions among different normal products, we obtain

$$\langle 0|\{\mathbf{S}_N^2\}\, e^{\{\mathbf{T}\}}|0\rangle =$$

$$-\sum_{i_\beta, j_\alpha, b_\alpha} \Delta_{ji}\Delta_{ib}\mathbf{t}_{j_\alpha}^{b_\alpha} - \sum_{i_\alpha, j_\beta, b_\beta} \Delta_{ij}\Delta_{bi}\mathbf{t}_{j_\beta}^{b_\beta} \tag{10a}$$

$$-\sum_{i_\alpha, j_\beta, a_\alpha, b_\beta} \Delta_{ib}\Delta_{aj}[\mathbf{t}_{i_\alpha}^{a_\alpha}\mathbf{t}_{j_\beta}^{b_\beta} + \mathbf{t}_{i_\alpha j_\beta}^{a_\alpha b_\beta}]. \tag{10b}$$

The terms (10a) provide the single excitation contribution of α and β electrons to the projected value of $\mathbf{S}^2$, respectively, and the last term (10b) provides the contribution from double and disconnected single excitations of the α and β spin electrons.

In the following we examine the multiplicity of correlated wavefunctions such as second-order and fourth-order Many Body Perturbation Theory (MBPT) and Coupled Cluster wavefunctions together with the reference UHF wavefunction.

RESULTS AND DISCUSSION

Table I shows the calculated total energy of the first row atoms at different levels of correlation. The calculated spin multiplicity of these atoms by the method described in the previous section are summarized in Table II. There is an arbitrariness in the choice of wavefunction which represents the corresponding MBPT energies. The partial $(n - 1)$-th order wavefunction which contributes to the n-th order energy is a consistent choice in the spirit of the CC method and the present transition matrix presentation of the spin multiplicity. We illustrate the wavefunctions of this choice diagrammatically for the canonical Hartree–Fock case.[11] Detailed definition of the

antisymmetric diagrams used below for the representation of various perturbed wavefunctions may be found in ref.[11]. Multiplicity is defined as $\langle 0|\mathbf{S}^2|\Phi^{(n)}\rangle$.

The first-order wavefunction is

$$\not\phi^{(1)\cdot} \;=\; \phi^{(1)} \;=\;$$

D1
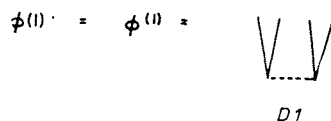
and once it is closed by a final two-electron interaction, provides the second-order energy. This is also the first approximation to the cluster amplitude in an iterative solution of the CC equations. The second-iteration wavefunction which gives the third-order energy is given in Scheme 1.

TABLE I

Total energies of first row atoms at different levels of approximation. A DZP contracted gaussian basis set is used. The values in the lower row are obtained by calculations with the core electrons uncorrelated. All entries are expressed as relative dimensionless quantities E/E_h, $E_h = 2{\cdot}6255 \,.\, 10^6 \text{ J mol}^{-1}$

Method	B	C	N	O	F
SCF	−24·52997	−37·68875	−54·39754	−74·80566	−99·39817
MBPT D(2)	−24·58017	−37·75414	−54·48091	−74·91839	−99·54714
	−24·56715	−37·74061	−54·46710	−74·90438	−99·53296
MBPT D(3)	−24·59480	−37·76936	−54·49467	−74·93167	−99·55671
	−24·58071	−37·75496	−54·48014	−74·91708	−99·54207
SDQ(4)	−24·59998	−37·77337	−54·49674	−74·93345	−99·55823
	−24·58586	−37·75897	−54·48221	−74·91886	−99·54357
SDTQ(4)	−24·60032	−37·78386	−54·49731	−74·93446	−99·55992
	−24·58616	−37·75942	−54·48275	−74·91983	−99·54523
CCD	−24·60250	−37·77473	−54·49677	−74·93342	−99·55786
	−24·58847	−37·76038	−54·48226	−74·91885	−99·54322
LCCD	−24·60694	−37·77787	−54·49874	−74·93514	−99·55920
	−24·59283	−37·76346	−54·48419	−74·92053	−99·54453
CCSD	−24·60315	−37·77529	−54·49709	−74·93390	−99·55840
	−24·58912	−37·76094	−54·48258	−74·91932	−99·54375
CCSDT-1	−24·60395	−37·77627	−54·49792	−74·93518	−99·56019
	−24·58982	−37·76186	−54·48338	−74·92056	−99·54551

$$\phi^{(2)} = \phi^{(1)} + \phi^{(2)}$$

D2   D3   D4

SCHEME 1

The diagrams *D2*, *D3*, and *D4* appear in the linear part of the first CC iteration.
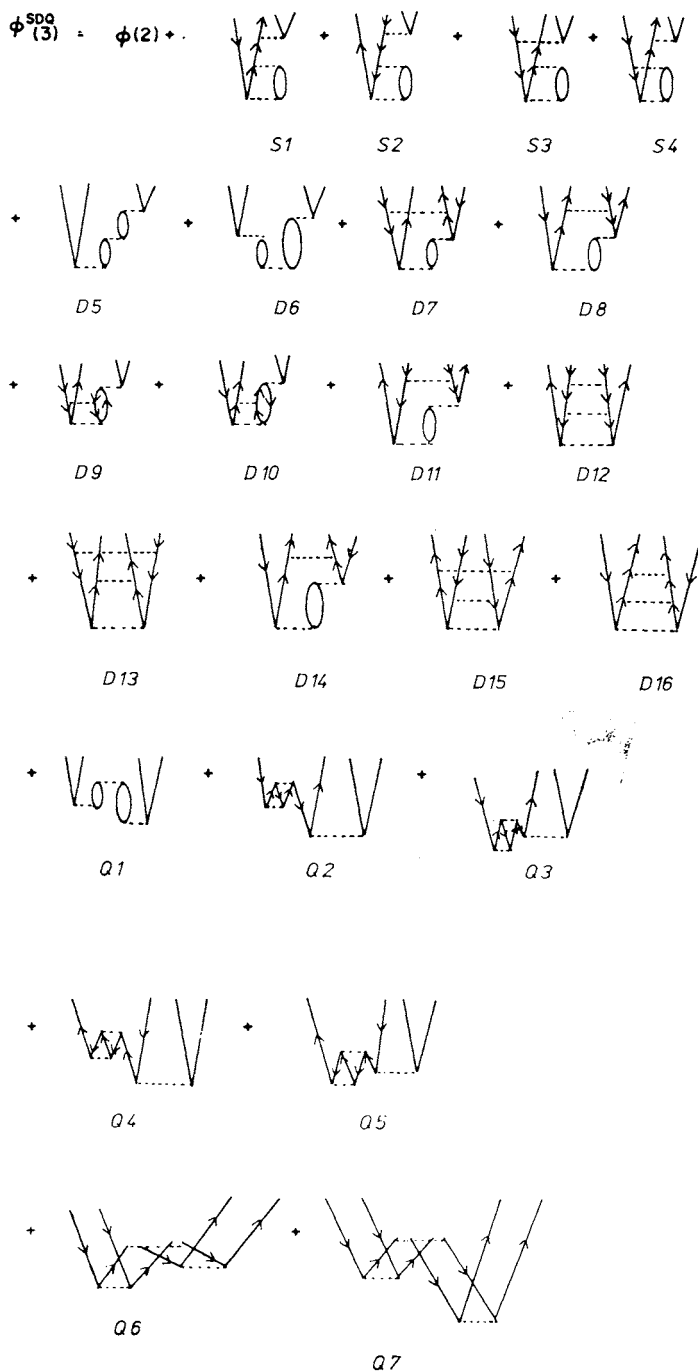
The wavefunction associated with the fourth order single, double and quadruple excitation approximation (SDQ(4)) is given in Scheme 2.

The diagrams *S1* through *S4* and *D5* through *D16* appear in the second CC linear iteration for the first time while Q diagrams appear in the first non-linear iteration. The diagrams *D5* to *D8* arise from the ring interaction in the first iteration followed by a second ring interaction in the second iteration. The diagrams *D9* and *D10* result from hole–hole $(h\text{–}h)$ and particle–particle $(p\text{–}p)$ interactions followed by a ring

TABLE II

Spin multiplicities of first row atoms computed for UHF based correlated wavefunctions. For additional details see Table I

Method	B	C	N	O	F
SCF	2·00689	3·00421	4·00268	3·00383	2·00248
MBPT D(2)	2·00358	3·00222	4·00165	3·00212	2·00114
	2·00359	3·00223	4·00165	3·00212	2·00115
MBPT D(3)	2·00224	3·00140	4·00110	3·00142	2·00073
	2·00223	3·00141	4·00110	3·00142	2·00073
SDQ(4)	2·00173	3·00108	4·00084	3·00109	2·00056
SDTQ(4)	2·00171	3·00106	4·00084	3·00107	2·00055
CCD	2·00157	3·00091	4·00065	3·00071	2·00039
	2·00156	3·00090	4·00064	3·00071	2·00039
LCCD	2·00126	3·00072	4·00051	3·00051	2·00030
	2·00126	3·00071	4·00049	3·00051	2·00030
CCSD	2·00003	3·00004	4·00005	3·00010	2·00005
	2·00002	3·00003	4·00005	3·00011	2·00006
CCSDT-1	2·00001	3·00001	4·00001	3·00003	2·00001
	2·00001	3·00001	4·00001	3·00003	2·00002

$$\phi_{(3)}^{SDQ} = \phi(2) + \ldots$$

S1   S2   S3   S4

D5   D6   D7   D8

D9   D10   D11   D12

D13   D14   D15   D16

Q1   Q2   Q3

Q4   Q5

Q6

Q7

SCHEME 2

interaction. The diagrams *D11* to *D13* are ring, *h–h* and *p–p* interactions followed by an *h–h* interaction. The diagrams *D14* to *D16* comes from ring, *h–h* and *p–p* interactions followed by a *p–p* interaction. The diagram *Q1* and pairs of diagrams *Q2–Q3*, *Q4–Q5* and *Q6–Q7*, which differ only in the time ordering of the first and second interactions, result from coupling of T_2–T_2 CC amplitudes. The CC equation accounts for all possible time orderings among the interaction lines for the various amplitudes.

SCHEME 3

The wavefunction corresponding to the full fourth-order energy, that is single, double, triple and quadruple excitation diagrams, i.e. SDTQ(4), is given in Scheme 3. Since triple excitation cluster amplitudes appear after the first iteration, the diagrams *T1* through *T16* appear in the second linear iteration which is second-order in the interaction. Because the lowest-order single cluster amplitude is already second-order

for an SCF reference, there is no disconnected contributions from T_1 in the wave-function for the fourth-order energy, but there are from T_2 which has a first-order part. It should be noted that the multiplicity thus calculated is different from the expectation value of $\mathbf{S}^2$ evaluated by the second-order MBPT wavefunction, but is more consistent with the spirit of the transition matrix formalism and CC wave-functions.

The calculated values in Tables I and II show that higher-order MBPT wave-functions such as SDTQ-MBPT(4), CCSD and CCSDT-1[5] are improved in terms of the spin multiplicity as well as the total energy. The two values correspond to results with and without correlating the core $1s$ electrons. Actually the multiplicity from CCSDT-1 indicates that the wavefunction represents almost a pure spin state. The linearized CCD fortuitously gives an energy closer to CCSDT-1 than more sophisticated methods such as CCD and CCSD, but the spin multiplicities calibrated are worse than those of the CCSD model. Thus we would expect the CCSD wave-function to be much better than the LCCD wavefunction. We also remark that the valence only correlated wavefunctions are quite accurate in terms of the spin multi-plicity, although the core electron correlation contributions to the total energy are of course important to the absolute energy value.

The contributions to the multiplicity from each term are summarized in Table III. The double excitation amplitudes contribute dominantly. However, it should be noted that the contribution from the single excitations is not negligible. The initial effect of singles makes a difference in the multiplicity between the CCD and CCSD wavefunctions, however, the contribution from disconnected singles which appears first in the fifth-order is not important for SCF reference functions. For non-Hartree--Fock spin contaminated solutions this would not be true.[12]

The UHF determinant wavefunction and determinants created by excitation from

TABLE III
Contributions from each term to the transition matrix element $\langle 0|\mathbf{S}^2|\Phi\rangle$ in the CCSD model

Types of contributions	B	C	N	O	F
$\langle 0|\mathbf{S}^2\mathbf{T}_1|0\rangle$	$-0\cdot00149$	$-0\cdot00125$	$-0\cdot00113$	$-0\cdot00088$	$-0\cdot00033$
$\langle 0|\mathbf{S}^2\,(1/2)\,\mathbf{T}_1^2|0\rangle$	$-0\cdot00000$	$-0\cdot00000$	$-0\cdot00000$	$-0\cdot00000$	$0\cdot00000$
$\langle 0|\mathbf{S}\mathbf{T}_2|0\rangle$	$-0\cdot00539$	$-0\cdot00500$	$-0\cdot00414$	$-0\cdot00471$	$-0\cdot00210$
$\langle 0|\mathbf{S}^2(\mathbf{T}_1 + (1/2)\,\mathbf{T}_1^2 + \mathbf{T}_2)|0\rangle$	$-0\cdot00688$	$-0\cdot00626$	$-0\cdot00527$	$-0\cdot00559$	$-0\cdot00243$
$\langle 0|\mathbf{S}^2(1 + \mathbf{T}_1 + (1/2)\,\mathbf{T}_1^2 + \mathbf{T}_2)|0\rangle$	$0\cdot75003$	$2\cdot00006$	$3\cdot75010$	$2\cdot00015$	$0\cdot75005$

the UHF determinant are eigenfunctions of the S_z operator as long as the number of electrons for each spin is conserved. Full configuration interaction (FCI) is the best solution in the space spanned by those determinants although the space is much larger than necessary to obtain the solution. The transition matrix calibrates the deviation of the approximate wavefunctions from the exact vector in the space. The CCSD and CCSDT-1 values indicate that the CC method corrects the approximate wavefunction in terms of the spin multiplicity as well as the energy without any condition externally imposed.

The spin operator S^2 thus formulated in normal operator form can also be used as a spin projection or annihilation operator,[6,7] $A_j \propto [S^2 - S_j(S_j + 1)]$ for some eigenvalue S_j. Use of such a projection operator provides a reasonable starting vector for a CC iteration compared to an ordinary perturbation scheme where the reference determinant would deviate considerably from the exact solution due to spin contamination. Since UHF-CC iterations slowly rotate away the spin contamination, we can accelerate the convergence by applying $A_j|0\rangle$ and truncating back to a single reference, Φ_0. This gives us a less contaminated starting point. Furthermore, since the energy is evaluated by $\langle \Phi_0|H_N e^T|\Phi_0\rangle$, left multiplication by Φ_0 eliminates further contamination introduced by $e^T|\Phi_0\rangle$. The final converged CCSD or CCSDT-1 result is unchanged by this procedure, except the convergence is accelerated. Such techniques have been used in our computer codes for sometime.[5]

However, we can obtain even less spin-contaminated results using our recently proposed open-shell spin restricted CC method.[13] In this case, we can use a restricted open-shell Hartree–Fock (ROHF) function as a reference or what we call a quasi--restricted Hartree–Fock (QRHF) function for most open-shell examples. The latter employs any set of closed-shell RHF orbitals for an open-shell case by enforcing maximum double occupancy for the high-spin determinantal form. Hence ROHF or the QRHF function is an eigenfunction of S^2. A CC calculation is then performed, just as in the UHF case, except the required computer time can be greatly reduced via fully exploiting the double occupancy of the orbitals. For such a reference for an open-shell, $\exp(T)\,\Phi_0$ will not preserve the spin-symmetry of the reference, yet by virtue of Φ_0 being an eigenfunction of S^2, projection by Φ_0 gives $E = = \langle \Phi_0|H e^T|\Phi_0\rangle$ and all spin contamination in $e^T|\Phi_0\rangle$ is removed in the *energy* evaluation. Of course, this procedure results in energies that are different than those obtained in UHF-CC, and these differences can have important consequences in cases where spin-contamination has a crucial effect as in the F–H$_2$ transition state.[14]

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