Erratum: "Coupled cluster theory for high spin, open shell reference wave functions" [J. Chem. Phys. 99, 5219 (1993)]

Peter J. Knowles, Claudia Hampel, and Hans-Joachim Werner

ERRATA

Erratum: "Coupled cluster theory for high spin, open shell reference wave functions" [J. Chem. Phys. 99, 5219 (1993)]

Peter J. Knowles
School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

Claudia Hampel and Hans-Joachim Werner
Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D–70569 Stuttgart, Germany

Equation (63) of Ref. 1 is incomplete for the diagonal "semi-internal" configurations Φ_{it}^{at}. For the semi-internal configurations the contravariant functions defined in Eq. (61) take the explicit form

$$\Phi_{ti}^{au} = \frac{1}{3}[\tilde{e}_{at}\bar{e}_{ui} + \delta_{tu}\tfrac{1}{2}(\bar{e}_{ai} - \tilde{e}_{ai})]|0\rangle, \tag{1}$$

which leads to

$$\mathcal{V}_{au}^{ti} = \frac{1}{3}V_{au}^{ti} + \frac{1}{6}\delta_{tu}(\bar{V}_a^j - \tilde{V}_a^j). \tag{2}$$

The second term, which contributes only for $t=u$, was overlooked when deriving Eq. (63). A similar term should be added to Eq. (58). This means that the Schrödinger equation was projected with some functions that were not spin eigenfunctions. This has no effect if the wave function Ψ is a spin eigenfunction, as is the case for configuration interaction with single and double excitations (CISD). However, since the partially spin adapted coupled-cluster wave function based on spin-restricted orbitals (RHF-RCCSD) is spin adapted only in the linear terms, a small error results.

The contravariant functions Φ_{ti}^{at} in Eq. (1) are not biorthogonal to the covariant functions defined by the operators in Eq. (48) of Ref. 1. More suitable contravariant functions, which fulfill the orthogonality condition, are

$$\bar{\Phi}_{ti}^{au} = \left[\tilde{e}_{at}\bar{e}_{ui} + \delta_{tu}\frac{1}{m+2}\left(\bar{e}_{ai} - \tilde{e}_{ai} - \sum_v \tilde{e}_{av}\bar{e}_{vi}\right)\right]|0\rangle, \tag{3}$$

where m is the number of open-shell orbitals. Using these configurations one obtains

$$\langle\bar{\Phi}_{ti}^{au}|\hat{T}|0\rangle = T_{au}^{ti} \tag{4}$$

and

$$\mathcal{V}_{au}^{ti} = V_{au}^{ti} + \delta_{tu}\frac{1}{m+2}\left[\bar{V}_a^j - \tilde{V}_a^j - \sum_v V_{av}^{vi}\right]. \tag{5}$$

Employing Eq. (2) or (5) yields the same solution, but by using Eq. (5) convergence is improved for states with triplet or higher spin multiplicity. The effect of the additional terms is very small, typically of the order of 0.01–0.1 mhartree. In all cases we have tested so far, the energy difference between

TABLE I. A comparison of RHF-RCCSD and RHF-UCCSD spectroscopic constants for some diatomic molecules.[a]

| Molecule | | | | | |
Method	$E(r_e)$	r_e/Å	B_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}
CN($X\,^2\Sigma^+$)					
RHF-UCCSD	−92.564 364 4	1.1646	1.924	2146.6	12.3
RHF-RCCSD	−92.563 315 1	1.1641	1.925	2148.3	12.4
RHF-RCCSD (Ref. 1)	−92.563 160 5	1.1641	1.925	2148.2	12.5
NO($X\,^2\Pi$)					
RHF-UCCSD	−129.724 331 9	1.1439	1.726	1986.5	12.9
RHF-RCCSD	−129.723 793 6	1.1435	1.727	1991.0	12.8
RHF-RCCSD (Ref. 1)	−129.723 729 5	1.1435	1.727	1991.9	12.7
O$_2$($X\,^3\Sigma_g^-$)					
RHF-UCCSD	−150.141 733 5	1.1970	1.471	1677.7	10.2
RHF-RCCSD	−150.140 732 7	1.1964	1.473	1680.8	10.2
RHF-RCCSD (Ref. 1)	−150.140 618 1	1.1965	1.473	1680.2	10.2

[a]Basis cc-pVQZ (Ref. 4), but with highest angular momentum functions omitted ($5s4p3d2f/4s3p2d$); small deviations from RHF-UCCSD values in Table I of Ref. 1 can be attributed to the stricter convergence thresholds used here.

RHF-UCCSD (i.e., spin-restricted orbitals with unrestricted coupled-cluster amplitudes) and RHF-RCCSD is reduced.

The resulting partially spin adapted RCCSD method still differs from the ones described in Refs. 2 and 3 by the inclusion of the ''disconnected'' terms

$$\Delta \widetilde{V}^{pq} = \widetilde{v}^p \widetilde{t}^{q\dagger} + \widetilde{t}^p \widetilde{v}^{q\dagger} - \widetilde{v}^q \widetilde{t}^{p\dagger} - \widetilde{t}^q \widetilde{v}^{p\dagger}, \tag{6}$$

$$\Delta \bar{V}^{pq} = \bar{v}^p \bar{t}^{q\dagger} + \bar{t}^p \bar{v}^{q\dagger} - \bar{v}^q \bar{t}^{p\dagger} - \bar{t}^q \bar{v}^{p\dagger}, \tag{7}$$

$$\Delta V^{pq} = \widetilde{v}^p \bar{t}^{q\dagger} + \widetilde{t}^p \bar{v}^{q\dagger} \tag{8}$$

in the residuals $\widetilde{V}^{pq}$, $\bar{V}^{pq}$, and V^{pq}, respectively. These terms vanish in the case of RHF-UCCSD, but give small contributions for RCCSD, since in this case the individual $\widetilde{v}^p$ and $\bar{v}^p$ do not become zero for the converged solution. The appearance of these terms is not erroneous but is a consequence of the fact that we have not multiplied the Schrödinger equation from the left by $\exp(-\hat{T})$ before projection [cf. Eqs. (4)–(6) of Ref. 1]. For consistency with other programs we now recommend the removal of these terms as well, which typically cause energy changes of only a few microhartree.

Table I shows some results which can be compared with Table I of Ref. 1. The largest energy change is found for CN (0.15 mhartree). The change in the spectroscopic constants, however, is very small, and is almost within the error bounds of the polynomial fit of the potential energy curve. Similar results are obtained for the other molecules shown in Table I of Ref. 1. The corrected RHF-RCCSD method is identical to the partially spin adapted CCSD methods of Refs. 2 and 3.

[1] P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993).
[2] P. Neogrády, M. Urban, and I. Hubač, J. Chem. Phys. **100**, 3706 (1994).
[3] P. G. Szalay and J. Gauss, J. Chem. Phys. **107**, 9028 (1997).
[4] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).