Theor Chim Acta (1997) 95: 97–98

Theoretica
Chimica Acta

A simple correction to final state energies of doublet radicals described by equation-of-motion coupled cluster theory in the singles and doubles approximation (Erratum)

John F. Stanton[1], **Jürgen Gauss**[2]

[1] Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry,
University of Texas at Austin, Austin, TX 78712, USA

[2] Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie, Universität Karlsruhe,
D-76128 Karlsruhe, Germany

Received September 11, 1996/Final revision received September 23, 1996/Accepted September 23, 1996

In translating Eq. (18) to the spin–orbital basis, one contribution was overlooked. Amplitudes of the l^{ab}_{ijk} and r^{ijk}_{ab} operators appearing in the energy expression (Eq. (19)) are given by

$$D^{ijk}_{ab} l^{ijk}_{ab} = P(ijk) l^{k} \langle ab \| ij \rangle - P(ijk) \sum_{e} l^{ij}_{e} \langle ab \| ek \rangle - P(ab)P(ijk) \sum_{m} l^{mk}_{a} \langle ij \| mb \rangle, \tag{1}$$

$$\begin{aligned} D^{ab}_{ijk} r^{ab}_{ijk} = {} & -P(ijk) \sum_{e} r^{e}_{ij} \langle ab \| ek \rangle - P(ab)P(ijk) \sum_{m} r^{a}_{mk} \langle ij \| mb \rangle \\ & - P(ab)P(ijk) \sum_{me} r_{m} t^{ae}_{ij} \langle mb \| ke \rangle + P(kji) \sum_{mn} r_{m} t^{ab}_{in} \langle mn \| kj \rangle \\ & - P(ijk) \sum_{m} r^{e}_{mk} \left[P(ij) \sum_{en} t^{ab}_{nj} \langle mn \| ei \rangle \right] + P(ijk)P(ab) \sum_{mef} r^{e}_{mk} t^{fb}_{ij} \langle ma \| ef \rangle \\ & + \frac{1}{2} P(ijk)P(ab) \sum_{mne} r^{a}_{mn} t^{eb}_{ij} \langle mn \| ek \rangle, \end{aligned} \tag{2}$$

where

$$D^{ab}_{ijk} = D^{ijk}_{ab} = \lambda_0 - E_0 + f_{ii} + f_{jj} + f_{kk} - f_{aa} - f_{bb}, \tag{3}$$

where E_0 is defined as the CCSD energy of the $N + 1$ electron reference state. The final term of Eq. (2) is missing from Eq. (21) in the original verison of this paper. The denominators (D) were also not included in Eqs. (20) and (21) of the original manuscript, and the corresponding seven-index denominators D^{ijkl}_{abc} and D^{abc}_{ijkl} are likewise missing from Eqs. (28) and (29). While the denominators were not neglected in the computer implementation, the missing term from Eq. (21) was not coded; the EOMIP-CCSD* energies documented in Table 1 are accordingly incorrect. Finally, in Eqs. (19) and (27), λ_0 should be replaced by $\lambda_0 - E_0$.

The table has been reproduced in full below, where the EOMIP-CCSD* values have been obtained with the corrected r^{ab}_{ijk} amplitudes. EOMIP-CCSD* final state energies listed below are uniformly more positive than the erroneous values

Table 1. Total electronic energies at the EOMIP-CCSD, EOMIP-CCSD*, UHF-CCSD and UHF-CCSD(T) levels for the two lowest electronic states of selected radicals. All calculations were performed at the geometries given in the tabular footnotes with the DZP basis set of Ref. [23]. Total energies are in hartrees; energy splittings (vertical excitation energies) in electron volts are also given in the rightmost column

HO_2[a]	X^2A''	A^2A'	Splitting
EOMIP-CCSD	− 150.597373	− 150.567336	0.817
EOMIP-CCSD*	− 150.591638	− 150.562897	0.782
UHF-CCSD	− 150.589893	− 150.563208	0.726
UHF-CCSD(T)	− 150.600054	− 150.572156	0.759
CH_3O[b]	X^2E	A^2A_1	Splitting
EOMIP-CCSD	− 114.777058	− 114.622055	4.218
EOMIP-CCSD*	− 114.770898	− 114.619553	4.118
UHF-CCSD	− 114.770867	− 114.618591	4.144
UHF-CCSD(T)	− 114.777432	− 114.625277	4.140
HCN^{+},[c]	$X^2\Pi$	$A^2\Sigma$	Splitting
EOMIP-CCSD	− 92.711025	− 92.701210	0.267
EOMIP-CCSD*	− 92.724024	− 92.701331	0.617
UHF-CCSD	− 92.723168	− 92.704110	0.519
UHF-CCSD(T)	− 92.731592	− 92.714557	0.464
CH_2O^{+},[d]	X^2B_2	A^2B_1	Splitting
EOMIP-CCSD	− 113.854249	− 113.709737	3.932
EOMIP-CCSD*	− 113.849871	− 113.711676	3.761
UHF-CCSD	− 113.849875	− 113.712988	3.725
UHF-CCSD(T)	− 113.858179	− 113.718319	3.806
N_2^{+},[e]	$X^2\Sigma_g$	$A^2\Pi_u$	Splitting
EOMIP-CCSD	− 108.739671	− 108.675096	1.757
EOMIP-CCSD*	− 108.741654	− 108.691550	1.363
UHF-CCSD	− 108.738740	− 108.689880	1.330
UHF-CCSD(T)	− 108.754336	− 108.698133	1.529

[a] r(OH) = 1.0 Å, r(OO) = 1.4 Å, θ(HOO) = 120°
[b] r(OH) = 1.0 Å, r(CO) = 1.45 Å, θ(HCO) = 110°
[c] r(CH) = 1.0 Å, r(CN) = 1.2 Å
[d] r(CH) = 1.0 Å, r(CO) = 1.2 Å, θ(HCO) = 120°
[e] r(NN) = 1.097 Å

documented in the original presentation of this research and are in generally excellent agreement with the UHF-CCSD energies. Therefore, it is not true (as stated in the original paper) that EOMIP-CCSD* energies tend to lie closer to UHF-CCSD(T) than UHF-CCSD. Nevertheless, the principal conclusions of this work:

1) excitation and final state energies calculated with EOMIP-CCSD* are more accurate and decidedly more systematic than those obtained at the EOMIP-CCSD level;
2) that inclusion of the noniterative energy correction that distinguishes the EOMIP-CCSD* and EOMIP-CCSD methods will not dominate the overall cost of calculations;

are still operative.