A comparison of two approaches to perturbation triple excitation corrections to the coupled-cluster singles and doubles method for high-spin open-shell systems

T. Daniel Crawford, and Henry F. Schaefer

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A comparison of two approaches to perturbation triple excitation corrections to the coupled-cluster singles and doubles method for high-spin open-shell systems

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An analysis of molecular properties is presented for several first-row diatomic molecules as determined at the CCSD(T) level of theory. In particular, a comparison of spectroscopic constants predicted by the ROHF-CCSD(T) methods of Scuseria vs Gauss et al. is given. Accurate determination of the values of equilibrium bond lengths, dissociation energies, harmonic vibrational frequencies, anharmonic constants, vibration–rotation coupling constants, and centrifugal distortion constants show only small differences between the two methods. In particular, we show that the average absolute differences between the two methods for the equilibrium bond length, harmonic vibrational frequency, and the dissociation energy are 0.000 09 Å, 0.8 cm⁻¹ and 0.1 kcal/mol, respectively. © 1996 American Institute of Physics.

I. INTRODUCTION

In the past 15 years, coupled-cluster methods have proven to be exceptionally valuable for the theoretical prediction of molecular properties. While the coupled-cluster singles and doubles method (CCSD) (Ref. 4) provides high levels of accuracy for many systems, it was shown in the last decade[5–11] that effects of triple excitations must be included in order to properly reproduce the results of benchmark full configuration interaction (CI) studies. In particular, the CCSD method including a perturbational estimate of triple excitations, first done by Urban et al.14 and then improved by a single excitation addition, known as CCSD(T), is able to accurately determine properties for most chemical systems.[15,10,16–20]

For low-lying states of high-spin open-shell molecules adequately described by a single restricted determinant, there are currently two predominate extensions of the spin-restricted open-shell Hartree–Fock–Fock reference CCSD (ROHF-CCSD) method of Rittby and Bartlett, both of which are referred to as CCSD(T). The first of these was introduced by Scuseria as a spin-dependent implementation of the formulation for closed-shell systems. The second was proposed by Gauss, Lauderdale, Stanton, Watts, and Bartlett as an extension of their related techniques to non-Hartree–Fock reference wave functions and to regain the invariance properties of CCSD. Both approaches are based on a ROHF many-body perturbation theory analysis (ROHF-MBPT) (Refs. 24, 25) [also known as restricted Möller–Plesset (RMP) theory][26] of the spin–orbital CCSD equations, and the two methods are therefore closely related. The differences only occur in fourth- and higher-order perturbation theory, and, as partly shown numerically by Watts et al., are not expected to be large for most high-spin ROHF-based CCSD(T) applications. For more general non-HF cases, however, this will not necessarily be the case. While there has been some discussion of the theoretical differences between these techniques, no explicit quantitative examination and comparison of the molecular properties predicted by the two approaches has been demonstrated. It should also be noted that another approach to the perturbational inclusion of triple excitations (known as CCSD-T) has been recently introduced in the literature, and has been shown to produce promising results.

This research examines results obtained with the two methods by comparing predicted molecular properties for a series of diatomic systems. In particular, for ten diatomic molecules in ground and excited states, values of the equilibrium bond length, rₑ, dissociation energy, Dₑ, harmonic vibrational frequency, ωₑ, anharmonic constant, ωₑxₑ, vibration–rotation coupling constant, αₑ, and the centrifugal distortion constant, Dₑ, are compared.

II. THEORETICAL DISTINCTIONS BETWEEN THE METHODS

Following the presentation of Watts et al., the general ROHF-MBPT-based (T) correction to the CCSD energy is given by

\[ E_{r} = E_{r}^{(4)} + E_{ST}^{(5)} + E_{DF}^{(4)} \]

\[ = \frac{1}{36} \sum_{abc} t^{abc} D^{abc} t^{abc} + \frac{1}{4} \sum_{abc} t^{abc} (bc) f^{abc} + \frac{1}{4} \sum_{abc} t^{abc} f_{j}^{abc}, \]

where the \( T_{3} \) amplitudes are determined from

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*Department of Defense Graduate Fellow; Fritz London Graduate Fellow.*

\[ D_{ijk}^{abc} = D_{ijk}^{abc} \left[ t(c)^{abc} + t(d)^{abc} \right] - P(ijk) \sum_m (1 - \delta_{im}) f_{im}^{abc} + P(ab) \]
\[ \times \sum_e (1 - \delta_{ae}) f_{ae}^{bce}. \]  
(2)

The connected triples amplitudes are obtained by
\[ D_{ijk}^{abc} t(c)^{abc} = P(ijk) P(ab)c \]
\[ \times \left[ \sum_q t_{ij}^{bc}(bc||ei) - \sum_m t_{im}^{bc}(jk||ma) \right] \]  
(3)
and the disconnected triples amplitudes by
\[ D_{ijk}^{abc} t(d)^{abc} = P(ijk) P(ab)c \]
\[ \times \left[ \sum_q t_{ij}^{bc}(bc||jk) + f_{id}^{bce} \right]. \]  
(4)

In these equations, the usual conventions that \( i, j, k, l, \ldots \)
\((a, b, c, d, \ldots)\) represent spin–orbitals occupied (unoccupied)
in the reference wave function are preserved. \( p, q, r, s, \ldots \) represent
general spin–orbitals. \( f_{pq} \) is the \( pq \)th element of the spin–
orbital Fock matrix,
\[ f_{pq} = h_{pq} + \sum_m \langle pm|qm \rangle \]  
(5)
and the \( D_{ijk}^{abc} \) prefactors are the usual energy denominators
based on diagonal Fock matrix elements. The permutation operators
are defined by their action on a function, \( g(pqr) \), as
\[ P(pqr)g(pqr) = g(pqr) - g(qpr) - g(rqp). \]  
(6)

These equations are general in that they may be applied with
any single determinant reference wave function. The perturbational
analysis by which these equations are constructed depends specifically
on the ROHF-MBPT partitioning of the Hamiltonian.24–26 This analysis
has been presented before9,30 and will be omitted here.

These equations may be implemented in a straightforward manner
by iterating Eq. (2) to determine the \( T_3 \) amplitudes, and then simply
inserting these into Eq. (1). However, this approach is an iterative \( \approx N^2 \)
procedure (where \( N \) is the number of spin–orbitals) and would require
storage of the intermediate \( T_3 \) amplitudes, both of which are undesirable.

The \( \text{CCSD(T)} \) correction presented by Scuseria17 [hereafter
referred to as “(T)-A”] does not implement these equations exactly.
First, the fourth-order doubles-triples term, \( E_{DD}^{[4]} \) is dropped. (With
a Hartree–Fock reference, i.e., RHF or UHF, this term is zero.) Second,
the last two terms on the right-hand side in Eq. (2) (which are also zero with a canonical
Hartree–Fock reference) are dropped, thus providing a
non-iterative equation for the \( T_3 \) amplitudes. This approach
maintains spin-restriction on the reference molecular orbitals,
and thus offers certain simplifications when these equations
are spin-factorized and implemented on the computer. However, it has been pointed out18,27 that this approach does
not provide an energy which is invariant to unitary transformations of occupied or virtual orbitals among themselves.
(For a discussion of energy invariance in single-reference
many-body perturbation theory, as well as perturbation-based corrections, see Ref. 40.) One consequence of this is
that the energy is dependent on the particular definition of
ROHF orbitals used. That is, since ROHF orbitals are defined
only to within rotations which mix the doubly-occupied, singly-occupied, and unoccupied spaces (and not
within each)31–33 (T)-A does not provide a unique definition
of the CCSD(T) energy alone. Additionally, a lack of such
invariance properties can make construction of orbital response
corrections to analytic gradients more complicated.34 However, if a single definition of ROHF orbitals
is maintained at all molecular geometries, a continuous
potential energy surface can be constructed with this method.

The particular ROHF orbital definition used by (T)-A is
based on an averaged Fock operator, defined within the
doubly-occupied, singly-occupied, and unoccupied orbital
subspaces. This operator is defined in terms of spatial orbitals as
\[ \hat{F}^{av} = \hat{h} + \hat{J}^c - \hat{K}^c + \hat{J}^a - \frac{1}{2} \hat{K}^a, \]  
(7)
where \( \hat{h} \) is the usual one-electron Hamiltonian, \( \hat{J}^c \) and \( \hat{K}^c \) are
the Coulomb and exchange operators, respectively, including
only the closed-shell orbitals, and \( \hat{J}^a \) and \( \hat{K}^a \) are these operators
including only the singly-occupied orbitals. This operator
was used in configuration interaction and coupled pair
functional calculations in order to help simplify construction
of analytic gradients.35,36 In addition, this operator has recently
found use in open-shell perturbation theory.37–40

The \( \text{CCSD(T)} \) correction presented by Gauss et al.18 [hereafter
referred to as “(T)-B”] implements the above equations exactly. However, a noniterative procedure for
the solution of Eq. (2) is obtained by the use of semicanonical
orbitals (i.e., those orbitals with which the spin–orbital Fock matrix is diagonal in the occupied/occupied and virtual/
virtual subspaces). As a result, the last two terms on the
right-hand side of Eq. (2) are zero. One drawback to this
approach is that spin-restriction on the molecular orbitals
is destroyed, and therefore some computational simplifications
are lost. An important advantage is that the energy is invariant
to all rotations of molecular spin–orbitals which are allowed
for the reference determinant.

III. COMPARISON OF THE METHODS

In order to make quantitative comparisons between the
three \( \text{CCSD(T)} \) methods, we have examined selected
properties of the following diatomic systems, \( ^3\Pi_u \) \( C_2 \), \( ^3\Sigma_g^- \) \( C_2 \), \( ^3\Sigma_g^+ \) \( C_2 \), \( ^3\Pi \) \( CF \), \( ^3\Pi \) \( CH \), \( ^3\Sigma_g^+ \) \( CN \), \( ^3\Sigma_g^- \) \( NH \), \( ^3\Pi \) \( NO \), \( ^3\Sigma_g^- \) \( O_2 \), \( ^3\Pi \) \( SO_2 \), and \( ^3\Pi \) \( OH \). The properties of interest include
the equilibrium bond length, \( r_e \), dissociation energy, \( D_e \), harmonic vibrational frequency, \( \omega_e \), anharmonic constant,
\( \omega_e x_e \), vibration-rotation coupling constant, \( \alpha_e \), and
the centrifugal distortion constant, \( D_e \).

Two basis sets were used in this research. The smaller
is a double-zeta plus polarization (DZP) basis, consisting of the
standard Huzinaga–Dunning\textsuperscript{41,42} set of contracted Gaussian functions with one additional set of higher-angular-momentum polarization functions on each atom. The contraction scheme for this basis is (9s5p4d3f/4s3p2d) for all first row atoms and (4s2p) for hydrogen. The exponents used for the polarization functions in this basis are $\alpha_p(\text{H}) = 0.75$, $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{N}) = 0.8$, $\alpha_d(\text{O}) = 0.85$, and $\alpha_d(\text{F}) = 1.0$.

Pure angular momentum functions are used for all $d$-type orbitals. The larger basis is a triple-zeta plus double polarization plus one additional set of higher angular momentum functions on each atom (TZ2P+f). This basis consists of the standard Huzinaga–Dunning\textsuperscript{41,43} set of contracted Gaussian functions with the contraction scheme (10s6p5s3p) for all first-row atoms and (5s3p) on hydrogen. In addition two sets of $d$-type functions are added to the first-row atoms and two sets of $p$-type functions to hydrogen, with the following polarization exponents: $\alpha_p(\text{H}) = 1.5, 0.375$, $\alpha_d(\text{C}) = 1.5, 0.375$, $\alpha_d(\text{N}) = 1.6, 0.4$, $\alpha_d(\text{O}) = 1.7, 0.425$, and $\alpha_d(\text{F}) = 2.0, 0.5$. Finally, one additional set of $f$-type functions is added to each first-row atom and one set of $d$-type functions to hydrogen, with the following polarization exponents: $\alpha_d(\text{H}) = 1.0$, $\alpha_d(\text{C}) = 0.8$, $\alpha_d(\text{N}) = 1.0$, $\alpha_d(\text{O}) = 1.4$, $\alpha_d(\text{F}) = 1.85$. Pure angular momentum functions are used for all $d$- and $f$-type orbitals.

CCSD(T) energies were computed using the psi (Ref. 44) and ACESII (Ref. 45) program systems. Bond lengths were optimized until the residual internal coordinate gradient was less than $10^{-3} E_b/\lambda_0$. Molecular constants were obtained via higher-order central difference formulas based on displacements of $\pm 0.005 \, \text{Å}$ and $\pm 0.01 \, \text{Å}$ from the equilibrium geometries. SCF reference wave functions computed using the psi program package were converged until the rms of the density matrix elements of successive iterations was less than $10^{-11}$ while those computed with the ACESII program package were converged until the largest change in a single element of the density was less than $10^{-11}$. Additionally, CCSD wave functions computed with psi were converged until the rms of the $T_1$ and $T_2$ amplitude vectors of successive iterations was less than $10^{-11}$, while those computed with ACESII were converged until the largest change in a single amplitude was less than $10^{-11}$.

Harmonic vibrational frequencies were obtained using the equation

$$\omega_c = 5.308 \times 10^{-11} \sqrt{\frac{f_{rr}}{\mu}},$$

where $\omega_c$ is given in cm$^{-1}$, the quadratic force constant, $f_{rr}$, in mdy/Å$^2$, and the reduced mass, $\mu$, in kg. Vibration-rotation coupling constants were obtained from

$$\alpha_v = -\frac{6B_c^2}{\omega_c} \left( 1 + 1.050 \times 52 \times 10^{-3} \frac{\omega_c f_{rrr}}{\sqrt{B_c^2 f_{rr}^2}} \right),$$

where $\alpha_v$ and the rotational constant, $B_c$, are given in cm$^{-1}$ and the cubic force constant, $f_{rrr}$, in mdy/Å$^3$. Anharmonic constants were obtained using the equation\textsuperscript{46}

$$\omega_{ex} = 1.241 \times 55 \times 10^{-6} \left( \frac{\omega_c}{f_{rr}} \right)^2 \left( \frac{5f_{rrr}^2}{3f_{rr}^2} - f_{rrrr} \right),$$

where $\omega_{ex}$ is given in cm$^{-1}$ and the quartic force constant, $f_{rrrr}$, in mdy/Å$^3$. Finally, centrifugal distortion constants were obtained using the equation

$$\overline{D}_c = \frac{4B_c^3}{\omega_c^2},$$

where $\overline{D}_c$ is given in cm$^{-1}$.

### IV. RESULTS AND DISCUSSION

The values for the equilibrium bond length, dissociation energy, harmonic vibrational frequency, anharmonic constants, vibration-rotation coupling constants, and centrifugal distortion constants for each method and basis set as well as the experimental results\textsuperscript{47} are given in Tables I–VI, respect-

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**TABLE I. Equilibrium bond lengths ($r_e$) in Å, as determined at the CCSD(T) level of theory with DZP and TZ2P+f basis sets.** Method A is that of Scuseria (Ref. 17) while method B is that of Gauss et al. (Ref. 18).

Experimental results are taken from Huber and Herzberg (Ref. 47).

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**TABLE II. Dissociation energies ($D_c$) in kcal/mol, as determined at the CCSD(T) level of theory with DZP and TZ2P+f basis sets.** Method A is that of Scuseria (Ref. 17) while method B is that of Gauss et al. (Ref. 18).

Experimental results are taken from Huber and Herzberg (Ref. 47).
TABLE III. Harmonic vibrational frequencies (ων) in cm⁻¹, as determined at the CCSD(T) level of theory with DZP and TZ2P+f basis sets. Method A is that of Scuseria (Ref. 17) while method B is that of Gauss et al. (Ref. 18). Experimental results are from Huber and Herzberg (Ref. 47).

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Average absolute error 21.1 21.7 6.6 6.4

Note: ³π²⁺ is the average frequency of the two spin–orbit coupled states.

TABLE IV. Anharmonic constants (ωνxν) in cm⁻¹, as determined at the CCSD(T) level of theory with DZP and TZ2P+f basis sets. Method A is that of Scuseria (Ref. 17) while method B is that of Gauss et al. (Ref. 18). Experimental results are taken from Huber and Herzberg (Ref. 47).

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Average absolute error 1.41 1.38 1.28 0.87

Note: ³π²⁺ is the average constant of the two spin–orbit coupled states.

TABLE V. Vibration-rotation coupling constants (αν) in cm⁻¹, as determined at the CCSD(T) level of theory with DZP and TZ2P+f basis sets. Method A is that of Scuseria (Ref. 17) while method B is that of Gauss et al. (Ref. 18). Experimental results are taken from Huber and Herzberg (Ref. 47).

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<td>CF X²Π</td>
<td>0.0175</td>
<td>0.0175</td>
<td>0.0183</td>
<td>0.0183</td>
<td>0.0184  ⁴</td>
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<tr>
<td>CH X²Π</td>
<td>0.5288</td>
<td>0.5287</td>
<td>0.5534</td>
<td>0.5504</td>
<td>0.534  ⁴</td>
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<tr>
<td>CN X²Σ⁺</td>
<td>0.0165</td>
<td>0.0165</td>
<td>0.0174</td>
<td>0.0174</td>
<td>0.0174  ⁴</td>
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<tr>
<td>NH X²Σ⁺</td>
<td>0.6561</td>
<td>0.6559</td>
<td>0.6658</td>
<td>0.6656</td>
<td>0.6490  ⁴</td>
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<td></td>
</tr>
<tr>
<td>NO X²Π</td>
<td>0.0166</td>
<td>0.0165</td>
<td>0.0174</td>
<td>0.0174</td>
<td>0.0177  ⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ 3Σ⁺ ³Π²⁺</td>
<td>0.0149</td>
<td>0.0149</td>
<td>0.0150</td>
<td>0.0151</td>
<td>0.0159  ⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ 3Σ⁺ ³Π²⁻</td>
<td>0.0154</td>
<td>0.0154</td>
<td>0.0147</td>
<td>0.0147</td>
<td>0.0158  ⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH X²Π</td>
<td>0.7272</td>
<td>0.7271</td>
<td>0.7294</td>
<td>0.7293</td>
<td>0.7242  ⁴</td>
<td></td>
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</tr>
</tbody>
</table>

Average absolute error 0.0021 0.0020 0.0040 0.0037

Note: ³π²⁺ is the average constant of the two spin–orbit coupled states.

monic vibrational frequencies (Table III) is also small (only 0.8 cm⁻¹). For this second-order property, both methods reproduce the experimental results quite well. The largest difference is just around 16 cm⁻¹ for O₂ 3ΠΠ⁺.

For anharmonic constants, shown in Table IV, the differences between the two methods usually lie around 0.1 cm⁻¹. However, certain cases show much larger differences. CH X²Π, in particular, has a difference of almost 4 cm⁻¹, with (T)-B lying closer to experiment. The reason for this discrepancy seems to reside in the E(^F^)(DT) term, which is missing in (T)-A. In most cases, this term is at least an order of magnitude smaller than the E(^F^)(DT) component, 27 which itself is usually at least an order of magnitude smaller than E(^F^)(DT).

Table VII gives the values of each component of the triples correction for both (T)-A and (T)-B for each molecule with
the TZ2P+f basis set. Clearly, both methods have very similar values for $E^{(4)}_T$ and $E^{(5)}_T$, indicating that the most important difference lies in the $E^{(4)}_{DT}$ component of the energy in (T)-B. For CH $X^2\Sigma^+$, the $E^{(4)}_{DT}$ term is nearly equal in magnitude to $E^{(5)}_T$, but of opposite sign. It should be noted, however, that both methods fare less well relative to experiment for this system as well. For almost all other cases $E^{(5)}_T$ and $E^{(4)}_{DT}$ differ more drastically. An exception is $O_2 X^3\Sigma^-$, where $E^{(4)}_{DT}$ is actually larger than $E^{(5)}_T$, but has the same sign. It seems that in those cases where the occupied/virtual block of the Fock matrix, $f_{ia}$, is large such that $E^{(4)}_{DT}$ is large relative to $E^{(5)}_T$, and of opposite sign, the two methods differ in higher-order properties such as anharmonic constants. Such cases may sometimes arise when the Brillouin condition is strongly violated by the ROHF solution.48

Vibration-rotation coupling constants (shown in Table V) on the other hand, show very few differences between the two methods, with most cases agreeing to within 0.0001 cm$^{-1}$. Again, the largest difference for this third-order property is seen for CH $X^2\Sigma^+$ (0.0030 cm$^{-1}$). This again seems to be due to the relatively large magnitude of $E^{(4)}_{DT}$. It is interesting to note that for vibration-rotation coupling constants, both methods differ from experiment more with the larger basis set than the smaller. Finally, centrifugal distortion constants show only slight differences between the two approaches, with most values within 0.01×10$^{-6}$ cm$^{-1}$ of each other.

V. CONCLUSIONS

We have quantitatively investigated the differences in predicted molecular properties for the two most widely used implementations of the ROHF-CCSD(T) method for high-spin open-shell systems.17,18 These two approaches may be viewed as based on the same underlying perturbation theory (ROHF-MBPT), but differ in the terms retained in the final implementation. We have shown that the two methods provide nearly identical molecular properties for the diatomic systems investigated here. The only significant difference between the two methods seems to be in higher-order properties such as anharmonic constants. Even for these, these differences only seem to arise when the magnitude of the fourth-order component, $E^{(4)}_{DT}$, rivals that of $E^{(5)}_T$, and is of opposite sign. Such cases may arise when the ROHF and UHF solutions differ significantly—sometimes indicating significant spin contamination of the latter. However, for the lower-order properties, such as equilibrium geometries, dissociation energies, and harmonic vibrational frequencies, the two methods differ negligibly. The method of Scuseria17 has some computational advantages over that of Gauss et al.18 since the former does not require transformation of the molecular orbital set into semicanonical orbitals. On the other hand, the latter is more theoretically justified, in that it provides energies which are invariant to orbital rotations in the occupied or virtual subspaces (similar to ROHF-CCSD itself), hence providing computational advantages in the construction of analytic gradients. Our future work will focus on the construction of a new (T) correction (based on a different form of single-reference open-shell perturbation theory), which maintains spin-restriction of the reference molecular orbitals and which retains the same invariance properties as ROHF-CCSD.

ACKNOWLEDGMENTS

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TABLE VII. $E^{(4)}_T$, $E^{(5)}_T$, and $E^{(4)}_{DT}$ components (in $E_h$) of the two CCSD(T) corrections considered here with a TZ2P+f basis. Method A is that of Scuseria (Ref. 17) while method B is that of Gauss et al. (Ref. 18).

<table>
<thead>
<tr>
<th></th>
<th>$E^{(4)}_T$</th>
<th>$E^{(5)}_T$</th>
<th>$E^{(4)}_{DT}$</th>
<th>$E^{(5)}_{DT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$\ddot{\alpha}$ $\Pi_u$</td>
<td>-0.018 996 1</td>
<td>0.000 779 0</td>
<td>-0.018 989 6</td>
<td>0.000 777 0</td>
</tr>
<tr>
<td>C$\ddot{\beta}$ $\Sigma^+$</td>
<td>-0.010 789 0</td>
<td>0.000 159 8</td>
<td>-0.010 835 4</td>
<td>0.000 160 4</td>
</tr>
<tr>
<td>C$\ddot{\gamma}$ $\Sigma^+$</td>
<td>-0.023 925 1</td>
<td>0.001 228 5</td>
<td>-0.023 837 3</td>
<td>0.001 217 3</td>
</tr>
<tr>
<td>CF $X^2\Pi$</td>
<td>-0.014 286 4</td>
<td>0.001 434 9</td>
<td>-0.014 289 7</td>
<td>0.001 438 5</td>
</tr>
<tr>
<td>CH $X^2\Pi$</td>
<td>-0.003 504 5</td>
<td>0.000 184 8</td>
<td>-0.003 508 5</td>
<td>0.000 181 0</td>
</tr>
<tr>
<td>CN $X^2\Sigma^+$</td>
<td>-0.023 922 9</td>
<td>0.003 705 0</td>
<td>-0.023 912 4</td>
<td>0.003 717 6</td>
</tr>
<tr>
<td>NH $X^1\Sigma^+$</td>
<td>-0.004 029 1</td>
<td>0.001 016 3</td>
<td>-0.004 037 2</td>
<td>0.001 015 6</td>
</tr>
<tr>
<td>NO $X^2\Pi$</td>
<td>-0.020 627 9</td>
<td>0.001 616 8</td>
<td>-0.020 550 8</td>
<td>0.001 603 8</td>
</tr>
<tr>
<td>$O_2 X^3\Sigma^-$</td>
<td>-0.018 823 0</td>
<td>-0.000 075 8</td>
<td>-0.018 738 7</td>
<td>-0.000 077 7</td>
</tr>
<tr>
<td>$O_2^+ a^4\Pi_u$</td>
<td>-0.016 577 6</td>
<td>0.000 217 1</td>
<td>-0.016 548 8</td>
<td>0.000 213 1</td>
</tr>
<tr>
<td>OH $X^2\Pi$</td>
<td>-0.005 347 6</td>
<td>0.000 141 6</td>
<td>-0.005 351 6</td>
<td>0.000 142 0</td>
</tr>
</tbody>
</table>

It should be noted that Ref. 27 contains a minor typographical error, namely a transposition of $T_2$ amplitude indices, which is corrected here in Eq. (3).


48. Such cases are those in which the UHF and ROHF solutions are very different from one another, often due to significant spin-contamination of the UHF wave function.