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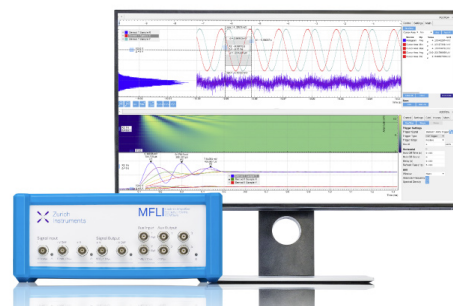
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A comparison of two approaches to perturbation triple excitation corrections to the coupled-cluster singles and doubles method for high-spin open-shell systems

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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. [S0021-9606(96)01416-5]

I. INTRODUCTION

In the past 15 years, coupled-cluster methods¹⁻³ 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 decade⁵⁻¹¹ that effects of triple excitations must be included in order to properly reproduce the results of benchmark full configuration interaction (CI) studies.^{12,13} In particular, it has been demonstrated that 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),^{8,9} 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 reference CCSD (ROHF-CCSD) method of Rittby and Bartlett,²¹ both of which are referred to as CCSD(T).^{17,18} The first of these was introduced by Scuseria¹⁷ as a spin-dependent implementation of the formulation for closed-shell systems. The second was proposed by Gauss, Lauderdale, Stanton, Watts, and Bartlett¹⁸ as an extension of their related techniques²² to non-Hartree-Fock reference wave functions and to regain the invariance properties of CCSD.²³ Both approaches are based on a ROHF many-body perturbation theory analysis (ROHF-MBPT) (Refs. 24, 25) [also known as restricted Møller-Plesset (RMP) theory²⁶] 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.*²⁷ 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,^{18,27} 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.²⁸

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, r_e , dissociation energy, D_e , harmonic vibrational frequency, ω_e , anharmonic constant, $\omega_e x_e$, vibration-rotation coupling constant, α_e , and the centrifugal distortion constant, \bar{D}_e , are compared.

II. THEORETICAL DISTINCTIONS BETWEEN THE METHODS

Following the presentation of Watts *et al.*,²⁷ the general ROHF-MBPT-based (T) correction to the CCSD energy is given by

$$\begin{aligned} E_{(T)} &= E_T^{(4)} + E_{ST}^{(5)} + E_{DT}^{(4)} \\ &= \frac{1}{36} \sum_{abcijk} t_{ijk}^{abc} D_{ijk}^{abc} t_{ijk}^{abc} + \frac{1}{4} \sum_{abcijk} t_i^a \langle bc || jk \rangle t_{ijk}^{abc} \\ &\quad + \frac{1}{4} \sum_{abcijk} t_{ij}^{ab} f_{kc} t_{ijk}^{abc}, \end{aligned} \quad (1)$$

where the T_3 amplitudes are determined from

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$$D_{ijk}^{abc} t_{ijk}^{abc} = D_{ijk}^{abc} [t(c)_{ijk}^{abc} + t(d)_{ijk}^{abc}] - P(i/jk) \sum_m (1 - \delta_{im}) f_{im} t_{jkm}^{abc} + P(a/bc) \times \sum_e (1 - \delta_{ae}) f_{ae} t_{ijk}^{bce}. \quad (2)$$

The connected triples amplitudes are obtained by²⁹

$$D_{ijk}^{abc} t(c)_{ijk}^{abc} = P(i/jk) P(a/bc) \times \left[\sum_e t_{jk}^{ae} \langle bc || ei \rangle - \sum_m t_{im}^{bc} \langle jk || ma \rangle \right] \quad (3)$$

and the disconnected triples amplitudes by

$$D_{ijk}^{abc} t(d)_{ijk}^{abc} = P(i/jk) P(a/bc) [t_i^a \langle bc || jk \rangle + f_{ia} t_{jk}^{bc}]. \quad (4)$$

In these equations, the usual conventions that i, j, k, l, \dots (a, b, c, d, \dots) represent spin-orbitals occupied (unoccupied) in the reference wave function are preserved. p, q, r, s, \dots represent general spin-orbitals. f_{pq} is the p qth element of the spin-orbital Fock matrix,

$$f_{pq} = h_{pq} + \sum_m \langle pm || qm \rangle \quad (5)$$

and the $D_{ijk \dots}^{abc \dots}$ 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

$$P(p/qr)g(pqr) \equiv g(pqr) - g(qpr) - g(rqp). \quad (6)$$

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 before^{9,30} 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 $\approx N^7$ 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 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, $E_{DT}^{(4)}$ 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-factored and implemented on the computer. However, it has been pointed out^{18,27} 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 contributions 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 as³¹

$$\hat{F}^{\text{av}} = \hat{h} + 2\hat{J}^c - \hat{K}^c + \hat{J}^o - \frac{1}{2}\hat{K}^o, \quad (7)$$

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}^o and \hat{K}^o 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 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 two CCSD(T) methods, we have examined selected properties of the following diatomic systems, $\tilde{a}^3\Pi_u C_2$, $\tilde{b}^3\Sigma_g^- C_2$, $\tilde{X}^2\Sigma_g^+ C_2^-$, $\tilde{X}^2\Pi CF$, $\tilde{X}^2\Pi CH$, $\tilde{X}^2\Sigma^+ CN$, $\tilde{X}^3\Sigma^- NH$, $\tilde{X}^2\Pi NO$, $\tilde{X}^3\Sigma_g^- O_2$, $\tilde{a}^4\Pi_u O_2^+$, and $\tilde{X}^2\Pi OH$. The properties of interest include the equilibrium bond length, r_e , dissociation energy, D_e , harmonic vibrational frequency, ω_e , anharmonic constant, $\omega_e x_e$, vibration-rotation coupling constant, α_e , and the centrifugal distortion constant, \tilde{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^{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 (9s5p/4s2p) for all first row atoms and (4s/2s) 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^{41,43} set of contracted Gaussian functions with the contraction scheme (10s6p/5s3p) for all first-row atoms and (5s/3s) 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: $\alpha_d(\text{H})=1.0$, $\alpha_f(\text{C})=0.8$, $\alpha_f(\text{N})=1.0$, $\alpha_f(\text{O})=1.4$, $\alpha_f(\text{F})=1.85$. 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 $10^{-8} E_h/a_0$. Molecular constants were obtained via higher-order central difference formulas based on displacements of $\pm 0.005 \text{ \AA}$ and $\pm 0.01 \text{ \AA}$ 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

$$\omega_e = 5.308\,837\,5 \times 10^{-11} \sqrt{\frac{f_{rr}}{\mu}}, \quad (8)$$

where ω_e is given in cm^{-1} , the quadratic force constant, f_{rr} , in mdyn/\AA , and the reduced mass, μ , in kg. Vibration-rotation coupling constants were obtained from⁴⁶

$$\alpha_e = \left(\frac{-6B_e^2}{\omega_e} \right) \left(1 + 1.050\,52 \times 10^{-3} \frac{\omega_e f_{rrr}}{\sqrt{B_e f_{rr}^3}} \right), \quad (9)$$

where α_e and the rotational constant, B_e , are given in cm^{-1} and the cubic force constant, f_{rrr} , in mdyn/\AA^2 . Anharmonic constants were obtained using the equation⁴⁶

TABLE I. Equilibrium bond lengths (r_e) in \AA , 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).

	DZP		TZ2P+f		Expt
	(T)-A	(T)-B	(T)-A	(T)-B	
$\text{C}_2 \tilde{a}^3\Pi_u$	1.335 35	1.335 58	1.315 00	1.315 22	1.311 9
$\text{C}_2 \tilde{b}^3\Sigma_g^-$	1.392 51	1.392 51	1.371 59	1.371 61	1.369 2
$\text{C}_2^- \tilde{X}^2\Sigma_g^+$	1.293 68	1.293 85	1.272 07	1.272 22	1.268 2
CF $\tilde{X}^2\Pi$	1.298 30	1.298 32	1.277 66	1.277 70	1.271 8
CH $\tilde{X}^2\Pi$	1.133 34	1.133 33	1.117 67	1.117 66	1.119 9
CN $\tilde{X}^2\Sigma^+$	1.196 84	1.196 94	1.175 39	1.175 47	1.171 8
NH $\tilde{X}^3\Sigma^-$	1.051 24	1.051 21	1.037 32	1.037 30	1.036 2
NO $\tilde{X}^2\Pi$	1.179 52	1.179 47	1.155 55	1.155 52	1.150 77
$\text{O}_2 \tilde{X}^3\Sigma_g^-$	1.233 95	1.234 28	1.212 58	1.212 86	1.207 52
$\text{O}_2^+ \tilde{a}^4\Pi_u$	1.405 09	1.405 29	1.383 69	1.383 84	1.381 3
OH $\tilde{X}^2\Pi$	0.980 86	0.980 85	0.970 22	0.970 20	0.969 66
Average absolute error	0.022 04	0.022 13	0.003 18	0.003 26	...

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

where $\omega_e x_e$ is given in cm^{-1} and the quartic force constant, f_{rrrr} , in mdyn/\AA^3 . Finally, centrifugal distortion constants were obtained using the equation

$$\bar{D}_e = \left(\frac{4B_e^3}{\omega_e^2} \right), \quad (11)$$

where \bar{D}_e 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 results⁴⁷ are given in Tables I–VI, respec-

TABLE II. Dissociation energies (D_e) 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).

	DZP		TZ2P+f		Expt
	(T)-A	(T)-B	(T)-A	(T)-B	
$\text{C}_2 \tilde{a}^3\Pi_u$	129.1	129.1	138.3	138.4	143.8
$\text{C}_2 \tilde{b}^3\Sigma_g^-$	111.0	111.0	121.7	121.8	127.5
$\text{C}_2^- \tilde{X}^2\Sigma_g^+$	179.6	179.6	189.0	189.0	198.1
CF $\tilde{X}^2\Pi$	119.7	119.7	127.2	127.2	132.6
CH $\tilde{X}^2\Pi$	77.9	77.9	81.8	81.8	83.9
CN $\tilde{X}^2\Sigma^+$	157.8	157.8	172.5	172.5	181.9
NH $\tilde{X}^3\Sigma^-$	74.1	74.1	79.7	79.7	84.7
NO $\tilde{X}^2\Pi$	127.6	127.6	143.0	142.9	152.5
$\text{O}_2 \tilde{X}^3\Sigma_g^-$	102.2	102.4	112.8	112.9	120.2
$\text{O}_2^+ \tilde{a}^4\Pi_u$	45.9	46.0	55.3	55.4	62.1
OH $\tilde{X}^2\Pi$	97.7	97.7	103.9	103.9	106.6
Average absolute error	15.6	15.6	6.3	6.2	...

TABLE III. Harmonic vibrational frequencies (ω_e) 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).

	DZP		TZ2P+f		Expt
	(T)-A	(T)-B	(T)-A	(T)-B	
$\text{C}_2 \tilde{a}^{-3}\Pi_u$	1622.2	1620.6	1643.2	1641.6	1641.4
$\text{C}_2 \tilde{b}^{-3}\Sigma_g^-$	1448.2	1448.2	1471.4	1471.2	1470.4
$\text{C}_2^- \tilde{X}^{-2}\Sigma_g^+$	1753.0	1751.8	1784.3	1783.1	1781.0
$\text{CF} \tilde{X}^{-2}\Pi$	1287.0	1286.9	1297.0	1296.7	1308.1
$\text{CH} \tilde{X}^{-2}\Pi$	2851.7	2851.9	2865.8	2866.0	2858.5
$\text{CN} \tilde{X}^{-2}\Sigma^+$	2032.3	2030.2	2066.4	2064.7	2068.6
$\text{NH} \tilde{X}^{-3}\Sigma^-$	3247.7	3248.1	3267.3	3267.5	3282.2
$\text{NO} \tilde{X}^{-2}\Pi$	1870.1	1871.2	1893.2	1893.9	1904.1 ^a
$\text{O}_2 \tilde{X}^{-3}\Sigma_g^-$	1568.3	1566.0	1581.4	1579.4	1580.2
$\text{O}_2^+ \tilde{a}^{-4}\Pi_u$	1018.6	1018.0	1052.0	1051.5	1035.7
$\text{OH} \tilde{X}^{-2}\Pi$	3739.2	3739.4	3740.1	3740.3	3737.8
Average absolute error	21.1	21.7	6.6	6.4	...

^aAverage frequency of the two spin-orbit coupled states.

tively. It is obvious from examination of these tables that only minor differences exist between the two methods for all of the properties considered in this work.

In particular, the average absolute difference in the equilibrium bond length, as seen in Table I, is 0.000 09 Å, with neither method consistently giving longer or shorter bonds than the other. Both methods fare well relative to the experimental results; all bond lengths are reproduced to around 0.01 Å, with an average absolute error of about 0.003 Å at the TZ2P+f level. Dissociation energies (Table II) are also nearly identical between the two methods, with an average absolute difference of 0.1 kcal/mol. The methods reproduce the experimental results with reasonable accuracy with the larger basis set, though differences of up to nearly 10 kcal/mol are found ($\text{NO} \tilde{X}^{-2}\Pi$). These are most likely due to basis set deficiencies. The average absolute difference in har-

TABLE IV. Anharmonic constants ($\omega_e x_e$) 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).

	DZP		TZ2P+f		Expt
	(T)-A	(T)-B	(T)-A	(T)-B	
$\text{C}_2 \tilde{a}^{-3}\Pi_u$	11.336	11.348	11.393	11.484	11.67
$\text{C}_2 \tilde{b}^{-3}\Sigma_g^-$	10.992	10.998	11.265	11.274	11.1
$\text{C}_2^- \tilde{X}^{-2}\Sigma_g^+$	11.395	11.411	11.526	11.548	11.58
$\text{CF} \tilde{X}^{-2}\Pi$	10.669	10.656	10.800	10.970	11.10
$\text{CH} \tilde{X}^{-2}\Pi$	66.235	66.273	72.379	68.453	63.0
$\text{CN} \tilde{X}^{-2}\Sigma^+$	12.976	13.090	13.461	13.145	13.087
$\text{NH} \tilde{X}^{-3}\Sigma^-$	82.665	82.617	79.460	79.468	78.3
$\text{NO} \tilde{X}^{-2}\Pi$	13.751	13.868	13.751	13.597	14.088 ^a
$\text{O}_2 \tilde{X}^{-3}\Sigma_g^-$	11.359	11.372	10.909	10.923	11.98
$\text{O}_2^+ \tilde{a}^{-4}\Pi_u$	10.735	10.708	9.719	9.873	10.39
$\text{OH} \tilde{X}^{-2}\Pi$	90.265	90.244	85.177	85.168	84.881
Average absolute error	1.41	1.38	1.28	0.87	...

^aAverage constant of the two spin-orbit coupled states.

TABLE V. Vibration-rotation coupling constants (α_e) 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).

	DZP		TZ2P+f		Expt
	(T)-A	(T)-B	(T)-A	(T)-B	
$\text{C}_2 \tilde{a}^{-3}\Pi_u$	0.0156	0.0156	0.0164	0.0164	0.0166
$\text{C}_2 \tilde{b}^{-3}\Sigma_g^-$	0.0155	0.0155	0.0163	0.0163	0.0163
$\text{C}_2^- \tilde{X}^{-2}\Sigma_g^+$	0.0156	0.0156	0.0164	0.0164	0.0167
$\text{CF} \tilde{X}^{-2}\Pi$	0.0175	0.0175	0.0183	0.0183	0.0184
$\text{CH} \tilde{X}^{-2}\Pi$	0.5288	0.5287	0.5534	0.5504	0.534
$\text{CN} \tilde{X}^{-2}\Sigma^+$	0.0165	0.0165	0.0174	0.0174	0.0174
$\text{NH} \tilde{X}^{-3}\Sigma^-$	0.6561	0.6559	0.6658	0.6656	0.6490
$\text{NO} \tilde{X}^{-2}\Pi$	0.0166	0.0165	0.0174	0.0174	0.0177 ^a
$\text{O}_2 \tilde{X}^{-3}\Sigma_g^-$	0.0149	0.0149	0.0150	0.0151	0.0159
$\text{O}_2^+ \tilde{a}^{-4}\Pi_u$	0.0154	0.0154	0.0147	0.0147	0.0158
$\text{OH} \tilde{X}^{-2}\Pi$	0.7272	0.7271	0.7294	0.7293	0.7242
Average absolute error	0.0021	0.0020	0.0040	0.0037	...

^aAverage 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 $\text{O}_2^+ \tilde{a}^{-4}\Pi_u$.

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. $\text{CH} \tilde{X}^{-2}\Pi$, 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 $E_{DT}^{(4)}$ term, which is missing in (T)-A. In most cases, this term is at least an order of magnitude smaller than the $E_{ST}^{(5)}$ component,²⁷ which itself is usually at least an order of magnitude smaller than $E_T^{(4)}$. Table VII gives the values of each component of the triples correction for both (T)-A and (T)-B for each molecule with

TABLE VI. Centrifugal distortion constants (\bar{D}_e) in 10^{-6}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).

	DZP		TZ2P+f		Expt
	(T)-A	(T)-B	(T)-A	(T)-B	
$\text{C}_2 \tilde{a}^{-3}\Pi_u$	5.95	5.95	6.35	6.36	6.44
$\text{C}_2 \tilde{b}^{-3}\Sigma_g^-$	5.80	5.80	6.15	6.16	6.22
$\text{C}_2^- \tilde{X}^{-2}\Sigma_g^+$	6.16	6.16	6.58	6.58	6.9
$\text{CF} \tilde{X}^{-2}\Pi$	6.07	6.07	6.58	6.58	6.5
$\text{CH} \tilde{X}^{-2}\Pi$	1383.5	1383.4	1489.3	1489.2	1450.0
$\text{CN} \tilde{X}^{-2}\Sigma^+$	5.85	5.86	6.31	6.31	6.40
$\text{NH} \tilde{X}^{-3}\Sigma^-$	1619.9	1619.7	1733.8	1733.7	1709.7
$\text{NO} \tilde{X}^{-2}\Pi$	4.89	4.88	5.39	5.39	N/A
$\text{O}_2 \tilde{X}^{-3}\Sigma_g^-$	4.31	4.32	4.71	4.72	4.839
$\text{O}_2^+ \tilde{a}^{-4}\Pi_u$	4.69	4.69	4.82	4.82	4.88
$\text{OH} \tilde{X}^{-2}\Pi$	1806.0	1805.9	1927.2	1927.1	1938
Average absolute error	14.96	14.98	6.33	6.31	...

TABLE VII. $E_T^{(4)}$, $E_{ST}^{(5)}$, and $E_{DT}^{(4)}$ 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).

	(T)-A		(T)-B		
	$E_T^{(4)}$	$E_{ST}^{(5)}$	$E_T^{(4)}$	$E_{ST}^{(5)}$	$E_{DT}^{(4)}$
$C_2 \tilde{a}^3\Pi_u$	-0.018 996 1	0.000 779 0	-0.018 989 6	0.000 777 0	-0.000 127 4
$C_2 \tilde{b}^3\Sigma_g^-$	-0.010 789 0	0.000 159 8	-0.010 835 4	0.000 160 4	-0.000 018 5
$C_2 \tilde{X}^2\Sigma_g^+$	-0.023 925 1	0.001 228 5	-0.023 837 3	0.001 217 3	-0.000 130 3
CF $\tilde{X}^2\Pi$	-0.014 285 4	0.001 434 9	-0.014 289 7	0.001 438 5	-0.000 015 1
CH $\tilde{X}^2\Pi$	-0.003 504 5	0.000 018 4	-0.003 508 5	0.000 018 1	-0.000 015 1
CN $\tilde{X}^2\Sigma^+$	-0.023 922 9	0.003 705 0	-0.023 912 4	0.003 717 6	-0.000 031 1
NH $\tilde{X}^3\Sigma^-$	-0.004 029 1	0.000 016 3	-0.004 037 2	0.000 015 6	-0.000 009 2
NO $\tilde{X}^2\Pi$	-0.020 627 9	0.001 616 8	-0.020 550 8	0.001 603 8	-0.000 083 3
$O_2 \tilde{X}^3\Sigma_g^-$	-0.018 823 0	-0.000 075 8	-0.018 738 7	-0.000 077 7	-0.000 302 6
$O_2^+ \tilde{a}^4\Pi_u$	-0.016 577 6	0.000 217 1	-0.016 548 8	0.000 213 1	-0.000 143 9
OH $\tilde{X}^2\Pi$	-0.005 347 6	0.000 141 6	-0.005 351 6	0.000 142 0	-0.000 000 5

the TZ2P+f basis set. Clearly, both methods have very similar values for $E_T^{(4)}$ and $E_{ST}^{(5)}$, indicating that the most important difference lies in the $E_{DT}^{(4)}$ component of the energy in (T)-B. For CH $\tilde{X}^2\Pi$, the $E_{DT}^{(4)}$ term is nearly equal in magnitude to $E_{ST}^{(5)}$, 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 $E_{ST}^{(5)}$ and $E_{DT}^{(4)}$ differ more drastically. An exception is $O_2 \tilde{X}^3\Sigma_g^-$, where $E_{DT}^{(4)}$ is actually larger than $E_{ST}^{(5)}$, 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 $E_{DT}^{(4)}$ is large relative to $E_{ST}^{(5)}$, 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 $\tilde{X}^2\Pi$ (0.0030 cm^{-1}). This again seems to be due the relatively large magnitude of $E_{DT}^{(4)}$. 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 $0.01 \times 10^{-6} \text{ cm}^{-1}$ 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 be-

tween 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, $E_{DT}^{(4)}$ rivals that of $E_{ST}^{(5)}$, 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.

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