A new spin-restricted triple excitation correction for coupled cluster theory

Cite as: J. Chem. Phys. **107**, 7943 (1997); https://doi.org/10.1063/1.475081
Submitted: 30 June 1997 . Accepted: 14 August 1997 . Published Online: 31 August 1998

T. Daniel Crawford, Timothy J. Lee, and Henry F. Schaefer

A new spin-restricted triple excitation correction for coupled cluster theory

T. Daniel Crawford
Center for Computational Quantum Chemistry, Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556

Timothy J. Lee
NASA Ames Research Center, Moffet Field, California 94035-1000

Henry F. Schaefer III
Center for Computational Quantum Chemistry, Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556

(Received 30 June 1997; accepted 14 August 1997)

A new approach to the noniterative inclusion of the effects of connected triple excitations in the coupled cluster singles and doubles (CCSD) model is presented. The method is based on the recently developed *Z*-averaged perturbation theory, and reduces to the usual Mø ller-Plesset-based triples correction in the absence of open shells. This new correction maintains the same invariance properties as those of the CCSD energy, and requires storage of only one-third the number of two-electron integrals as more conventional corrections. The derivation and implementation of the equations are described, and the method's performance relative to more conventional triples corrections is assessed via benchmark calculations for a series of diatomic molecules. © *1997 American Institute of Physics.* [S0021-9606(97)02943-7]

I. INTRODUCTION

It was realized more than a decade ago that the effects of connected triple excitations should be included in the coupled cluster (CC) model of electron correlation[1–4] in order to obtain highly accurate predictions of molecular properties.[3–12] In particular, it has been shown[6–9,13,14] that an estimate of such excitations based on many-body perturbation theory (MBPT)[15] makes possible noniterative—and therefore relatively inexpensive—corrections to the CC singles and doubles (CCSD) energy. The first such correction to CCSD, denoted T(CCSD), was developed by Urban, Noga, Cole, and Bartlett in 1985,[13] and was designed to include a specific term which is at least fourth-order in Mø ller–Plesset perturbation theory, but which is missing in CCSD. This model was later improved by Raghavachari, Trucks, Pople, and Head-Gordon[8] who included a certain fifth-order single-excitation term to form the very popular (T) correction. The composite CCSD(T) approach, when implemented with large basis sets, provides perhaps the best balance between accuracy and affordability of any single-reference method available today for closed-shell molecules.[3,4] [See Ref. 14 for a theoretical discussion that rationalizes the success of the CCSD(T) method.]

Most of the original applications of MBPT and CC theory to high-spin open-shell systems were based on spin-unrestricted Hartree–Fock (UHF) reference wave functions. In the past several years, however, there has been considerable interest in the development and extension of these correlation methods which rely instead on spin-restricted (ROHF) determinants.[10,11,16–29] There are two motivating factors for this research. First, unlike the UHF wave function, the ROHF determinant is an eigenfunction of the $\hat{S}^2$ operator. As a result, use of the ROHF wave function as a reference may significantly reduce or even eliminate spin contamination in the correlated wave function.[30] Second, because the same spatial orbitals are used with both α and β spin functions in the ROHF determinant, there is the potential for more efficient programs which take advantage of any resulting symmetry in the correlated wave function parameters. Although the original implementation of the CCSD method by Purvis and Bartlett in 1982[31] was general enough for use with either a UHF or ROHF reference determinant, actual applications of the ROHF-CCSD method appeared in 1988 with the work of Rittby and Bartlett.[23] Unfortunately, in the standard (α,β) spin orbital basis, the exchange interactions between the open- and closed-shell electrons are not symmetric in the spin indices. As a result, the ROHF-CCSD cluster amplitudes have no more symmetry than those of the UHF-CCSD method, and, apart from limiting the number of two-electron integrals that must be stored, no improvements in computational efficiency relative to UHF-CCSD are obtained. Recently, however, Jayatilaka and Lee[32,25] have developed a new approach to the ROHF-CCSD method which utilizes the so-called symmetric spin orbital basis. In their method, the exchange interaction between open and closed shells is symmetric, and the number of independent cluster amplitudes that must be computed and stored is reduced by up to a factor of three relative to the conventional ROHF-CCSD approaches.

The extension of the ROHF-CCSD method to include the (T) correction was carried out independently by Scuseria[10] and by Gauss, Lauderdale, Stanton, Watts, and Bartlett.[11] The advantages and disadvantages of these two approaches have been discussed in detail elsewhere,[33] and we summarize the main issues here. Both corrections are based on a restricted Mø ller–Plesset perturbation theory (RMP[18] or ROHF-MBPT[19]) analysis of the ROHF-CCSD equations, but differ both in the orbitals used in the ROHF

reference determinant and in which terms are included in the final energy expression. The approach of Gauss *et al.* includes all terms from the ROHF-CCSD equations which are at least fourth-order in RMP. However, in order to maintain the same invariance properties of the ROHF-CCSD energy,[34] as well as a noniterative form for the (T) correction,[35] the RMP partitioning of the Hamiltonian requires the use of semicanonical orbitals, which are formed via diagonalization of the spin orbital Fock matrix in the occupied–occupied and virtual–virtual blocks. The rotated orbitals are of a ''different orbitals for different spins'' (DODS) type, and, as a result, the number of two-electron integrals which must be stored is increased by a factor of 3, thus making the computational requirements of Gauss *et al.*'s method the same as those of UHF-CCSD(T). Scuseria's approach,[10] on the other hand, neglects semicanonicalization of the orbitals (and therefore avoids the increased storage requirements) at the sacrifice of the rigorous invariance property in order to maintain a noniterative expression for the (T) correction. This forces an artificial orbital dependence on the correction which is not required of the ROHF or ROHF-CCSD references, and may add complications to gradient evaluation.[36,37] In addition, Scuseria's (T) correction does not include all fourth-order components of the RMP energy.

Two other triple-excitation corrections have been developed recently[38,39] which are related to the two (T) corrections described above. The first, denoted CCSD-T, was developed by Deegan and Knowles[38] as an extension to the (T) correction of Gauss *et al.*[11] and includes additional fifth-order terms while retaining the same N^7 computational scaling (where N is the the number of basis functions). Similarly to Gauss *et al.*'s approach, the -T correction also requires the use of semicanonical orbitals. The second method was developed by Neogrády and Urban as part of their work on spin-adaptation of open-shell coupled-cluster wave functions.[39] Their correction is more closely related to that of Scuseria, with the important distinctions that their approach uses spin-adapted cluster amplitudes as well as modified energy denominators, making it difficult to connect the method to an underlying perturbation theory. Like Scuseria's approach, however, Neogrády and Urban's (T) correction is not invariant to the same orbital rotations allowed for the ROHF and ROHF-CCSD wave functions.

In this work, we describe our new approach to the perturbative inclusion of connected triple excitations in the ROHF-CCSD energy. This method is based on the Z-averaged perturbation theory (ZAPT) of Lee and Jayatilaka,[21] and is referred to here as the (zT) correction. This approach is noniterative, maintains the same invariance properties as those of the ROHF-CCSD energy,[34] is complete through the fourth-order of ZAPT, and does not require a DODS canonical orbital set. In Sec. II, we describe the derivation of the method and discuss its relationship to the more conventional (T) corrections. In Sec. III, we compare the performance of the correction to the (T) approach of Gauss *et al.*[11] for a series of first-row diatomic molecules.

II. THEORY

Throughout this discussion, we will use a number of notational conventions. Spin orbitals will be indicated by lower case letters. Orbital indices p, q, r, and s will refer to general spin orbitals. The indices i, j, k, and l will refer to spin orbitals in the doubly occupied space, a, b, c, and d to spin orbitals in the ''doubly unoccupied'' space, and t, u, v, and w to spin orbitals in the singly occupied space. The upper case versions of all of the above will apply to spatial orbitals.

In ZAPT,[21] the spin orbital basis is redefined.[32] For each doubly occupied spatial orbital and each unoccupied spatial orbital, the usual α and β spin functions are used, but for the singly occupied orbitals, new spin functions,

$$\sigma^+ = \frac{1}{\sqrt{2}}(\alpha+\beta) \tag{1}$$

and

$$\sigma^- = \frac{1}{\sqrt{2}}(\alpha-\beta) \tag{2}$$

are substituted. σ^+ functions are, by convention, associated with occupied spin orbitals, and σ^- functions with unoccupied spin orbitals. This set of functions is referred to as the symmetric spin basis. In this basis the spin orbital Fock operator is represented schematically as

$$\hat{F}^{\mathrm{ZAPT}} = \begin{array}{c} \\ d_\alpha \\ d_\beta \\ s_{\sigma^+} \\ s_{\sigma^-} \\ v_\alpha \\ v_\beta \end{array} \begin{array}{c} \begin{array}{cccccc} \quad & \quad & \quad & \quad & \quad & \quad \end{array} \\ \begin{pmatrix} \hat{F}^{J_\alpha}_{I_\alpha} & \hat{F}^{J_\alpha}_{I_\beta} & \hat{F}^{I_\alpha}_{T_{\sigma^+}} & 0 & 0 & \hat{F}^{A_\beta}_{I_\alpha} \\ \hat{F}^{J_\alpha}_{I_\beta} & \hat{F}^{J_\alpha}_{I_\alpha} & \hat{F}^{I_\alpha}_{T_{\sigma^+}} & 0 & \hat{F}^{A_\beta}_{I_\alpha} & 0 \\ \hat{F}^{I_\alpha}_{T_{\sigma^+}} & \hat{F}^{I_\alpha}_{T_{\sigma^+}} & \hat{F}^{U_{\sigma^+}}_{T_{\sigma^+}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \hat{F}^{U_{\sigma^-}}_{T_{\sigma^-}} & \hat{F}^{A_\alpha}_{T_{\sigma^-}} & -\hat{F}^{A_\alpha}_{T_{\sigma^-}} \\ 0 & \hat{F}^{A_\beta}_{I_\alpha} & 0 & \hat{F}^{A_\alpha}_{T_{\sigma^-}} & \hat{F}^{B_\alpha}_{A_\alpha} & \hat{F}^{B_\beta}_{A_\alpha} \\ \hat{F}^{A_\beta}_{I_\alpha} & 0 & 0 & -\hat{F}^{A_\alpha}_{T_{\sigma^-}} & \hat{F}^{B_\beta}_{A_\alpha} & \hat{F}^{B_\alpha}_{A_\alpha} \end{pmatrix} \end{array}. \tag{3}$$

Equation (3) illustrates some of the symmetry of the Fock matrix in the symmetric spin basis, and certain elements have been set to zero due either to the ROHF convergence conditions or to the orthogonality of the component spin functions.[21] It is interesting to note that elements such as $\hat{F}^{J_\alpha}_{I_\beta}$ are not zero, in general, since the α and β spin functions are not orthogonal to the σ^+ and σ^- spin functions. For electronic states in which all open-shell electrons occupy orbitals of different symmetries, the diagonal blocks of the Fock matrix will themselves be diagonal in what has been referred to as the averaged orbital basis, defined by the operator[40]

$$\hat{F}^{\mathrm{av}} = \hat{h} + 2\hat{J}^c - \hat{K}^c + \hat{J}^o - \tfrac{1}{2}\hat{K}^o, \tag{4}$$

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 equa-

tion is exactly the same as that of the spin-integrated expressions for the doubly occupied/doubly occupied and unoccupied/unoccupied blocks of the above matrix.[32] The singly occupied/singly occupied blocks are trivially diagonal for most practical applications regardless of the spatial orbital definition, as pointed out by Lee and Jayatilaka.[21]

With the diagonal blocks of the Fock operator above taken as the ZAPT zeroth-order Hamiltonian, the various excitation operators of coupled-cluster theory may be decomposed into perturbational orders, as usual.[41] In addition, because ZAPT separates the occupied spin orbitals into doubly and singly occupied sets, and the unoccupied spin orbitals similarly, the $\hat{T}_1$ operators are also decomposed into numerous excitation classes. For example, the $\hat{T}_1$ operator is broken down into three nonzero components

$$\hat{T}_1 \rightarrow \hat{T}_i^a + \hat{T}_i^t + \hat{T}_t^a . \tag{5}$$

If further spin integration of the doubly occupied and unoccupied orbital subspaces is ignored, $\hat{T}_i^a$ first appears in the ZAPT first-order wave function, while $\hat{T}_i^t$ and $\hat{T}_t^a$ first appear in the second-order wave function.[42] The $\hat{T}_2$ operator is factored into six components,

$$\hat{T}_2 \rightarrow \hat{T}_{ij}^{ab} + \hat{T}_{ij}^{at} + \hat{T}_{ij}^{tu} + \hat{T}_{it}^{ab} + \hat{T}_{it}^{au} + \hat{T}_{tu}^{ab} , \tag{6}$$

all of which appear in the ZAPT first-order wave function. $\hat{T}_3$ is factored into ten components,

$$\hat{T}_3 \rightarrow \hat{T}_{ijk}^{abc} + \hat{T}_{ijk}^{abt} + \hat{T}_{ijk}^{atu} + \hat{T}_{ijk}^{tuv} + \hat{T}_{ijt}^{abc} + \hat{T}_{ijt}^{abu} + \hat{T}_{ijt}^{auv} + \hat{T}_{itu}^{abc} + \hat{T}_{itu}^{abv} + \hat{T}_{tuv}^{abc} , \tag{7}$$

all of which appear in the ZAPT second-order wave function.

The CCSDT operator equations[41] may be written in terms of these components, and then expressions for the ZAPT energy through fifth order (limited, of course, to triple excitations at most) may be obtained via the usual iterative procedure, just has been done for other types of many-body perturbation theory.[19,41] In addition, the usual (T) terms involving triple excitation contributions which are missing in CCSD may be identified, and explicit spin orbital equations may be derived. The primary difficulty with this approach is the factorization of each (T) component into the excitation classes above. For example, the first-order double excitation contribution to the second-order triple excitations is factored appropriately into a total of 42 separate contributions. Because of the large number of terms which arise naturally upon factorization of the cluster operators above, we have found it convenient to carry out these derivations both diagrammatically and algebraically. The diagrams necessary for ZAPT and the symmetric spin–orbital CCSD are modified versions of the conventional diagrams used in coupled-cluster theory,[41,43] and are complicated by the fact that there are two types of hole lines and two types of particle lines. The algebraic analysis was carried out using our own computer program for the explicit evaluation of the second-quantized equations via Wick's theorem using the symbolic manipulator, MATHEMATICA.[44] The algorithm and syntax used within this program is described explicitly in Ref. 45.

In the conventional ROHF-CCSD(T) methods, there are three components of the energy correction:[35] $E_T^{[4]}$, $E_{DT}^{[4]}$, and $E_{ST}^{[4]}$, where the notation, $[n]$ indicates that the energy contribution is complete through the nth order of the appropriate perturbation theory. The first of these is simply the triple excitation contribution from the fourth-order RMP energy. The second is the fourth-order energy correction from double excitation/triple excitation products. This term is zero in pure Møller–Plesset-based (T) corrections,[8] such as those applicable to closed-shell systems or to open-shell systems with UHF reference wave functions. The third term is the fourth-order energy correction arising from single excitation/triple excitation products. In the pure Møller–Plesset-based (T) corrections, this terms is properly designated as $E_{ST}^{[5]}$ because single excitations do not appear until the second-order wave function as a consequence of Brillouin's theorem. Because all three terms are at least fourth order in RMP, the ROHF-CCSD(T) approach of Gauss *et al.* is identical to an RMP-based CCSD+T(CCSD).[35] It is important to note that the complete triples correction is computed using the converged CCSD $\hat{T}_1$ and $\hat{T}_2$ amplitudes rather than the finite-order amplitudes.[14]

In the (zT) approach, the general structure of the correction is the same as that of the (T) approach. Because all double excitation classes appear in first order in ZAPT (without spin factorization of the doubly occupied and unoccupied orbital subspaces), and all triple excitation classes in second order, the $E_T^{[4]}$ and $E_{DT}^{[4]}$ terms retain the same order as in the ROHF-CCSD(T) approach. However, because single excitations are separated into first- and second-order components, the single–triple product term, E_{ST} contains both fourth- and fifth-order ZAPT contributions.[46] We therefore refer to this term here as $E_{ST}^{[4,5]}$. The equations for each of the triple excitation amplitudes are given in the Appendix, along with the explicit equations for the energy contributions.

Since the (zT) equations require no ROHF orbital rotation which breaks spin restriction, it is not necessary to deal with more than a single set of two-electron integrals. This represents a significant improvement in disk storage requirements relative to the ROHF-CCSD(T) method of Gauss *et al.*[11] In addition, because the underlying ZAPT is invariant to the same orbital rotations allowed for the ROHF reference wave function, the (zT) energy is invariant as well, unlike the ROHF-CCSD(T) method of Scuseria.[10] Furthermore, the computational cost of the correction is also improved relative to the methods of both Gauss *et al.* and Scuseria, since the ''closed-shell'' portion of the correction [i.e., the leading terms in Eqs. (A3), (A13), (A14), and (A15)], may be spin-factored into fewer components than the corresponding expressions in the conventional approaches.

We have implemented the (zT) equations given in the Appendix in a developmental computer program. In an attempt to minimize errors, the equations were programmed using a modified MATHEMATICA-generated C-language code. This program was tested using the following technique. A

separate code was written which, if provided with semicanonical orbitals in the standard (α,β) spin orbital basis, would compute the ROHF-CCSD(T) energy of Gauss *et al.* This test program used a spin orbital formulation and was therefore necessarily independent of any orbital-subspace or spin factorization. Because the (zT) equations may be viewed simply as an orbital subspace factorization of the purely spin orbital (T) equations (subject to the constraint that only symmetric spin functions are used), both the (zT) program and the spin orbital (T) program will give the (zT) energy correction if provided with the average spatial orbitals for which ZAPT is canonical. For a number of small molecules, with varying numbers of open-shell electrons and basis sets, the two codes were found to produce identical results. In addition, each individual $\hat{T}_3$ contribution from Eq. (7) was tested by restricting the loops in the (T) program to specific orbital subsets. It should be noted that our implementation does not require storage of any triple-excitation amplitudes.

The most efficient implementation of the (zT) method would require a reformulation of the ROHF-CCSD equations in the symmetric spin orbital basis, as Jayatilaka and Lee have advocated.[25,47] However, this is not absolutely necessary. It is possible to add the (zT) correction to currently existing ROHF-CCSD programs, and, therefore to take advantage of their improved efficiency relative to the conventional (T) corrections. As pointed out by Jayatilaka and Lee,[25] the ROHF-CCSD equations will converge to the same result, regardless of the orbital basis chosen, though the energies computed at each iteration will differ between the two methods. Therefore, if the average orbitals defined above were used in an existing code, the converged singles and doubles amplitudes (denoted here by s_i^a and s_{ij}^{ab}, respectively) may then be transformed into the symmetric spin orbital basis using the following equations:

$$t_{I_\alpha}^{A_\alpha}=\frac{1}{2}[s_{I_\alpha}^{A_\alpha}+s_{I_\beta}^{A_\beta}] \tag{8}$$

$$t_{I_\alpha}^{A_\beta}=\frac{1}{2}[s_{I_\alpha}^{A_\alpha}-s_{I_\beta}^{A_\beta}] \tag{9}$$

$$t_{I_\alpha}^{T_{\sigma^-}}=\frac{1}{\sqrt{2}}s_{I_\beta}^{T_\beta}, \tag{10}$$

$$t_{T_{\sigma^+}}^{A_\alpha}=\frac{1}{\sqrt{2}}s_{T_\alpha}^{A_\alpha}, \tag{11}$$

$$t_{I_\alpha J_\beta}^{A_\alpha B_\beta}=\frac{1}{4}[s_{I_\alpha J_\alpha}^{A_\alpha B_\alpha}+s_{I_\beta J_\beta}^{A_\beta B_\beta}+s_{I_\alpha J_\beta}^{A_\alpha B_\beta}+s_{I_\beta J_\alpha}^{A_\beta B_\alpha}+s_{J_\alpha I_\beta}^{A_\alpha B_\beta}+s_{J_\beta I_\alpha}^{A_\beta B_\alpha}], \tag{12}$$

$$t_{I_\alpha J_\alpha}^{A_\beta B_\beta}=\frac{1}{4}[s_{I_\alpha J_\alpha}^{A_\alpha B_\alpha}+s_{I_\beta J_\beta}^{A_\beta B_\beta}-s_{I_\alpha J_\beta}^{A_\alpha B_\beta}-s_{I_\beta J_\alpha}^{A_\beta B_\alpha}+s_{J_\alpha I_\beta}^{A_\alpha B_\beta}+s_{J_\beta I_\alpha}^{A_\beta B_\alpha}], \tag{13}$$

$$t_{I_\alpha J_\alpha}^{A_\alpha B_\alpha}=\frac{1}{4}[s_{I_\alpha J_\alpha}^{A_\alpha B_\alpha}+s_{I_\beta J_\beta}^{A_\beta B_\beta}+s_{I_\alpha J_\beta}^{A_\alpha B_\beta}+s_{I_\beta J_\alpha}^{A_\beta B_\alpha}-s_{J_\alpha I_\beta}^{A_\alpha B_\beta}-s_{J_\beta I_\alpha}^{A_\beta B_\alpha}], \tag{14}$$

$$t_{I_\alpha J_\beta}^{A_\alpha B_\alpha}=\frac{1}{4}[s_{I_\alpha J_\alpha}^{A_\alpha B_\alpha}-s_{I_\beta J_\beta}^{A_\beta B_\beta}-s_{I_\alpha J_\beta}^{A_\alpha B_\beta}+s_{I_\beta J_\alpha}^{A_\beta B_\alpha}-s_{J_\alpha I_\beta}^{A_\alpha B_\beta}+s_{J_\beta I_\alpha}^{A_\beta B_\alpha}], \tag{15}$$

$$t_{I_\alpha J_\alpha}^{A_\beta B_\alpha}=\frac{1}{4}[s_{I_\alpha J_\alpha}^{A_\alpha B_\alpha}-s_{I_\beta J_\beta}^{A_\beta B_\beta}+s_{I_\alpha J_\beta}^{A_\alpha B_\beta}-s_{I_\beta J_\alpha}^{A_\beta B_\alpha}-s_{J_\alpha I_\beta}^{A_\alpha B_\beta}+s_{J_\beta I_\alpha}^{A_\beta B_\alpha}], \tag{16}$$

$$t_{I_\beta J_\beta}^{T_{\sigma^-}U_{\sigma^-}}=\frac{1}{2}s_{I_\beta J_\beta}^{T_\beta U_\beta}, \tag{17}$$

$$t_{T_{\sigma^+}U_{\sigma^+}}^{A_\alpha B_\alpha}=\frac{1}{2}s_{T_\alpha U_\alpha}^{A_\alpha B_\alpha}, \tag{18}$$

$$t_{T_{\sigma^+}J_\beta}^{A_\alpha U_{\sigma^-}}=\frac{1}{2}s_{T_\alpha J_\beta}^{A_\alpha U_\beta}, \tag{19}$$

$$t_{I_\alpha J_\beta}^{A_\alpha T_{\sigma^-}}=\frac{1}{\sqrt{8}}[-s_{I_\beta J_\beta}^{A_\beta T_\beta}-s_{I_\alpha J_\beta}^{A_\alpha T_\beta}-s_{J_\alpha I_\beta}^{A_\alpha T_\beta}], \tag{20}$$

$$t_{I_\alpha J_\alpha}^{A_\alpha T_{\sigma^-}}=\frac{1}{\sqrt{8}}[s_{I_\beta J_\beta}^{A_\beta T_\beta}+s_{I_\alpha J_\beta}^{A_\alpha T_\beta}-s_{J_\alpha I_\beta}^{A_\alpha T_\beta}], \tag{21}$$

$$t_{I_\alpha J_\alpha}^{A_\beta T_{\sigma^-}}=\frac{1}{\sqrt{8}}[-s_{I_\beta J_\beta}^{A_\beta T_\beta}+s_{I_\alpha J_\beta}^{A_\alpha T_\beta}-s_{J_\alpha I_\beta}^{A_\alpha T_\beta}], \tag{22}$$

$$t_{T_{\sigma^+}J_\beta}^{A_\alpha B_\beta}=\frac{1}{\sqrt{8}}[s_{T_\alpha J_\alpha}^{A_\alpha B_\alpha}+s_{T_\alpha J_\beta}^{A_\alpha B_\beta}+s_{T_\alpha J_\beta}^{B_\alpha A_\beta}], \tag{23}$$

$$t_{T_{\sigma^+}J_\beta}^{A_\alpha B_\alpha}=\frac{1}{\sqrt{8}}[s_{T_\alpha J_\alpha}^{A_\alpha B_\alpha}-s_{T_\alpha J_\beta}^{A_\alpha B_\beta}+s_{T_\alpha J_\beta}^{B_\alpha A_\beta}], \tag{24}$$

$$t_{T_{\sigma^+}J_\alpha}^{A_\alpha B_\alpha}=\frac{1}{\sqrt{8}}[s_{T_\alpha J_\alpha}^{A_\alpha B_\alpha}+s_{T_\alpha J_\beta}^{A_\alpha B_\beta}-s_{T_\alpha J_\beta}^{B_\alpha A_\beta}]. \tag{25}$$

These new amplitudes may then be used in a properly spin-factored implementation of the (zT) equations given in the Appendix to obtain the (zT) correction to the ROHF-CCSD energy.

III. TEST CALCULATIONS

In order to make direct comparisons between the performance of the new (zT) correction and that of more conventional approaches, we have calculated a number of spectroscopic constants for a series of diatomic molecules using both the (zT) correction and the (T) correction of Gauss *et al.*[11] For these comparisons, a double-zeta basis, including polarization functions (DZP) was used. This basis consisted of the standard Huzinaga–Dunning[48,49] set of contracted Gaussian functions with one additional set of higher-angular-

TABLE I. Equilibrium bond lengths, r_e in Å, harmonic vibrational frequencies, ω_e in cm^{-1}, and anharmonic constants, $\omega_e x_e$ in cm^{-1}, as determined at the CCSD(zT) and CCSD(T) (Ref. 11) levels of theory with a DZP basis set.

	r_e		ω_e		$\omega_e x_e$	
	CCSD(zT)	CCSD(T)	CCSD(zT)	CCSD(T)	CCSD(zT)	CCSD(T)
C_2 $\tilde{a}\,^3\Pi_u$	1.33676	1.33697	1617.8	1616.5	11.319	11.338
C_2 $\tilde{b}\,^3\Sigma_g^-$	1.39389	1.39403	1445.3	1444.3	10.936	10.970
C_2^- $\tilde{X}\,^2\Sigma_g^+$	1.29518	1.29519	1747.6	1747.6	11.390	11.408
CF $\tilde{X}\,^2\Pi$	1.29961	1.29966	1282.9	1282.7	10.572	10.576
CH $\tilde{X}\,^2\Pi$	1.13447	1.13447	2845.4	2845.4	64.925	65.936
CN $\tilde{X}\,^2\Sigma^+$	1.19786	1.19790	2026.9	2025.8	13.034	13.103
NH $\tilde{X}\,^3\Sigma^-$	1.05220	1.05222	3242.3	3242.0	81.209	82.234
NO $\tilde{X}\,^2\Pi$	1.18023	1.18020	1866.7	1867.5	13.916	13.846
O_2 $\tilde{X}\,^3\Sigma_g^-$	1.23473	1.23502	1565.7	1563.2	11.273	11.312
O_2^+ $\tilde{a}\,^4\Pi_u$	1.40555	1.40617	1020.2	1017.1	10.607	10.695
OH $\tilde{X}\,^2\Pi$	0.98155	0.98155	3734.2	3734.1	89.981	89.795

momentum polarization functions on each atom. The contraction scheme for this basis was (9s5p/4s2p) for all first row atoms and (4s/2s) for hydrogen. The exponents used for the polarization functions in this basis were: $\alpha_p(\mathrm{H})=0.75$, $\alpha_d(\mathrm{C})=0.75$, $\alpha_d(\mathrm{N})=0.8$, $\alpha_d(\mathrm{O})=0.85$, and $\alpha_d(\mathrm{F})=1.0$. Pure angular momentum functions were used for all d-type orbitals. The new (zT) correction was implemented within the PSI[50] suite of programs. ROHF-CCSD(T) energies were computed using the ACESII[51] program system. The $1s$-like molecular orbital for each first-row atom was held doubly occupied and the corresponding virtual molecular orbital was deleted in the correlated calculations. Bond lengths were optimized until the residual internal coordinate gradient was less than $10^{-6}\ E_h/a_0$. Molecular constants were obtained via higher-order central difference formulae based on displacements of ± 0.005 Å and ± 0.01 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 $\hat{T}_1$ and $\hat{T}_2$ 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}.

The computed equilibrium bond lengths, r_e, harmonic vibrational frequencies, ω_e, and anharmonic constants, $\omega_e x_e$, are given in Table I. It is clear that very few differences exist between the results obtained by the two methods. For example, bond lengths compare to within 0.001 Å, and harmonic vibrational frequencies to within 3 cm^{-1}. All other results differ only neglibly. The largest difference occurs for the $\tilde{a}\,^4\Pi$ state of the oxygen cation. In nearly all cases, the (zT) results are nominally closer to experiment[52] than the (T) values. However, it is not clear that this behavior would continue for larger basis sets. It is in any case certain that, in spite of the fact that it is computationally less intensive, the (zT) method performs at least as well as the (T) method for the systems examined here.

IV. CONCLUSIONS

We have constructed a new noniterative correction, denoted (zT), for the effects of connected triple excitations in the ROHF-CCSD energy, based on ZAPT. The correction reduces to the usual Møller–Plesset-based (T) correction for closed-shell systems. This approach retains the energy invariance to orbital rotations[34] present in the ROHF and ROHF-CCSD energies, but requires storage of only one-third the number of two-electron integrals needed by other triples corrections.[11,35] We have also shown that for a series of first-row diatomic molecules in low-lying high-spin open-shell electronic states, the (zT) correction performs at least as well as the usual (T) correction. In the future, we plan to develop analytic energy gradients for this method so that it may be applied routinely in high-level *ab initio* calculations of molecular properties.

ACKNOWLEDGMENTS

This research was sponsored by the National Science Foundation under Grant Number CHE-9527468. The authors would like to thank Professor John F. Stanton, Dr. Dylan Jayatilaka and Dr. C. Brian Kellogg for helpful discussions.

APPENDIX: WORKING EQUATIONS

The indices i, j, k, and l will refer to spin orbitals in the doubly occupied space, a, b, c, and d to spin orbitals in the ''doubly unoccupied'' space, and t, u, v, and w to spin orbitals in the singly occupied space. The upper case versions of all of the above will apply to spatial orbitals. The spin functions indicated here have been descibed in Sec. II. Two-electron integrals are given in antisymmetrized Dirac notation, and summation is implied over repeated indices. The D_{ijk}^{abc} are the usual energy denominators based on diagonal Fock matrix elements. The two-element and three-element permutation operators are defined by their action on functions $g(pq)$ and $g(pqr)$, respectively, as

$$P(pq)g(pq) \equiv g(pq) - g(qp) \tag{A1}$$

and

$$P(p/qr)g(pqr) \equiv g(pqr) - g(qpr) - g(rqp). \tag{A2}$$

Triple excitation equations

$$\begin{aligned} D_{ijk}^{abc} t_{ijk}^{abc} = &- P(k/ij)P(a/bc) t_{ij}^{ad} \langle kd \| bc \rangle - P(i/jk)P(c/ab) t_{il}^{ab} \langle jk \| lc \rangle - P(k/ij)P(a/bc) t_{ij}^{aW_{\sigma^-}} \langle kW_{\sigma^-} \| bc \rangle \\ &- P(c/ab)P(i/jk) t_{iW_{\sigma^+}}^{ab} \langle jk \| W_{\sigma^+} c \rangle - P(i/jk)P(c/ab) t_{iW_{\sigma^+}}^{ab} \langle jk \| W_{\sigma^+} c \rangle, \end{aligned} \tag{A3}$$

$$\begin{aligned} D_{ijk}^{abT_{\sigma^-}} t_{ijk}^{abT_{\sigma^-}} = &- P(ab)P(k/ij) t_{ij}^{ac} \langle kc \| bT_{\sigma^-} \rangle - P(i/jk) t_{il}^{ab} \langle jk \| lT_{\sigma^-} \rangle - P(k/ij)P(ab) t_{ij}^{aU_{\sigma^-}} \langle kU_{\sigma^-} \| bT_{\sigma^-} \rangle \\ &+ P(k/ij) t_{ij}^{cT_{\sigma^-}} \langle kc \| ab \rangle + P(i/jk)P(ab) t_{il}^{aT_{\sigma^-}} \langle jk \| lb \rangle - P(k/ij) t_{ij}^{T_{\sigma^-}U_{\sigma^-}} \langle kU_{\sigma^-} \| ab \rangle \\ &- P(i/jk) t_{iW_{\sigma^+}}^{ab} \langle jk \| W_{\sigma^+} T_{\sigma^-} \rangle + P(i/jk)P(ab) t_{iW_{\sigma^+}}^{aT_{\sigma^-}} \langle jk \| W_{\sigma^+} b \rangle, \end{aligned} \tag{A4}$$

$$\begin{aligned} D_{ijk}^{aT_{\sigma^-}U_{\sigma^-}} t_{ijk}^{aT_{\sigma^-}U_{\sigma^-}} = &- P(k/ij) t_{ij}^{ab} \langle kb \| T_{\sigma^-}U_{\sigma^-} \rangle - P(k/ij) t_{ij}^{aV_{\sigma^-}} \langle kV_{\sigma^-} \| T_{\sigma^-}U_{\sigma^-} \rangle - P(k/ij)P(T_{\sigma^-}U_{\sigma^-}) t_{ij}^{bT_{\sigma^-}} \langle kb \| aU_{\sigma^-} \rangle \\ &- P(i/jk)P(T_{\sigma^-}U_{\sigma^-}) t_{il}^{aT_{\sigma^-}} \langle jk \| lU_{\sigma^-} \rangle + P(k/ij)P(T_{\sigma^-}U_{\sigma^-}) t_{ij}^{T_{\sigma^-}V_{\sigma^-}} \langle kV_{\sigma^-} \| aU_{\sigma^-} \rangle \\ &- P(i/jk) t_{il}^{T_{\sigma^-}U_{\sigma^-}} \langle jk \| la \rangle - P(i/jk)P(T_{\sigma^-}U_{\sigma^-}) t_{iW_{\sigma^+}}^{aT_{\sigma^-}} \langle jk \| W_{\sigma^+}U_{\sigma^-} \rangle, \end{aligned} \tag{A5}$$

$$\begin{aligned} D_{ijk}^{T_{\sigma^-}U_{\sigma^-}V_{\sigma^-}} t_{ijk}^{T_{\sigma^-}U_{\sigma^-}V_{\sigma^-}} = &+ P(T_{\sigma^-}/U_{\sigma^-}V_{\sigma^-})P(k/ij) t_{ij}^{dT_{\sigma^-}} \langle kd \| U_{\sigma^-}V_{\sigma^-} \rangle \\ &- P(k/ij)P(T_{\sigma^-}/U_{\sigma^-}V_{\sigma^-}) t_{ij}^{T_{\sigma^-}W_{\sigma^-}} \langle kW_{\sigma^-} \| U_{\sigma^-}V_{\sigma^-} \rangle \\ &- P(i/jk)P(V_{\sigma^-}/T_{\sigma^-}U_{\sigma^-}) t_{il}^{T_{\sigma^-}U_{\sigma^-}} \langle jk \| lV_{\sigma^-} \rangle, \end{aligned} \tag{A6}$$

$$\begin{aligned} D_{ijT_{\sigma^+}}^{abc} t_{ijT_{\sigma^+}}^{abc} = &- P(c/ab)P(ij) t_{ik}^{ab} \langle jT_{\sigma^+} \| kc \rangle - P(a/bc) t_{ij}^{ad} \langle T_{\sigma^+} d \| bc \rangle - P(a/bc) t_{ij}^{aW_{\sigma^-}} \langle T_{\sigma^+} W_{\sigma^-} \| bc \rangle \\ &+ P(ij)P(a/bc) t_{iT_{\sigma^+}}^{ad} \langle jd \| bc \rangle + P(c/ab) t_{kT_{\sigma^+}}^{ab} \langle ij \| kc \rangle - P(c/ab)P(ij) t_{iU_{\sigma^+}}^{ab} \langle jT_{\sigma^+} \| U_{\sigma^+} c \rangle \\ &+ P(ij)P(a/bc) t_{iT_{\sigma^+}}^{aW_{\sigma^-}} \langle jW_{\sigma^-} \| bc \rangle - P(c/ab) t_{T_{\sigma^+}U_{\sigma^+}}^{ab} \langle ij \| U_{\sigma^+} c \rangle, \end{aligned} \tag{A7}$$

$$\begin{aligned} D_{ijT_{\sigma^+}}^{abU_{\sigma^-}} t_{ijT_{\sigma^+}}^{abU_{\sigma^-}} = &- P(ab) t_{ij}^{ac} \langle T_{\sigma^+} c \| bU_{\sigma^-} \rangle - P(ij) t_{ik}^{ab} \langle jT_{\sigma^+} \| kU_{\sigma^-} \rangle + t_{ij}^{cU_{\sigma^-}} \langle T_{\sigma^+} c \| ab \rangle - P(ab) t_{ij}^{aV_{\sigma^-}} \langle T_{\sigma^+} V_{\sigma^-} \| bU_{\sigma^-} \rangle \\ &+ P(ij)P(ab) t_{ik}^{aU_{\sigma^-}} \langle jT_{\sigma^+} \| kb \rangle - P(ij) t_{iT_{\sigma^+}}^{cU_{\sigma^-}} \langle jc \| ab \rangle + P(ij)P(ab) t_{iT_{\sigma^+}}^{aV_{\sigma^-}} \langle jV_{\sigma^-} \| bU_{\sigma^-} \rangle \\ &+ P(ij)P(ab) t_{iV_{\sigma^+}}^{aU_{\sigma^-}} \langle jT_{\sigma^+} \| V_{\sigma^+} b \rangle - P(ab) t_{kT_{\sigma^+}}^{aU_{\sigma^-}} \langle ij \| kb \rangle - t_{ij}^{U_{\sigma^-}V_{\sigma^-}} \langle T_{\sigma^+} V_{\sigma^-} \| ab \rangle \\ &+ P(ij)P(ab) t_{iT_{\sigma^+}}^{ac} \langle jc \| bU_{\sigma^-} \rangle - P(ij) t_{iV_{\sigma^+}}^{ab} \langle jT_{\sigma^+} \| V_{\sigma^+}U_{\sigma^-} \rangle + t_{kT_{\sigma^+}}^{ab} \langle ij \| kU_{\sigma^-} \rangle - t_{T_{\sigma^+}V_{\sigma^+}}^{ab} \langle ij \| V_{\sigma^+}U_{\sigma^-} \rangle, \end{aligned} \tag{A8}$$

$$\begin{aligned} D_{ijV_{\sigma^+}}^{aT_{\sigma^-}U_{\sigma^-}} t_{ijV_{\sigma^+}}^{aT_{\sigma^-}U_{\sigma^-}} = &- P(T_{\sigma^-}U_{\sigma^-}) t_{ij}^{bT_{\sigma^-}} \langle V_{\sigma^+} b \| aU_{\sigma^-} \rangle - P(ij)P(T_{\sigma^-}U_{\sigma^-}) t_{ik}^{aT_{\sigma^-}} \langle jV_{\sigma^+} \| .kU_{\sigma^-} \rangle \\ &+ P(T_{\sigma^-}U_{\sigma^-}) t_{ij}^{T_{\sigma^-}W_{\sigma^-}} \langle V_{\sigma^+}W_{\sigma^-} \| aU_{\sigma^-} \rangle - P(ij) t_{ik}^{T_{\sigma^-}U_{\sigma^-}} \langle jV_{\sigma^+} \| ka \rangle + P(ij) t_{iV_{\sigma^+}}^{ab} \langle jb \| T_{\sigma^-}U_{\sigma^-} \rangle \\ &+ P(T_{\sigma^-}U_{\sigma^-}) t_{kV_{\sigma^+}}^{aT_{\sigma^-}} \langle ij \| kU_{\sigma^-} \rangle - P(ij)P(T_{\sigma^-}U_{\sigma^-}) t_{iW_{\sigma^+}}^{aT_{\sigma^-}} \langle jV_{\sigma^+} \| W_{\sigma^+}U_{\sigma^-} \rangle \\ &+ P(ij)P(T_{\sigma^-}U_{\sigma^-}) t_{iV_{\sigma^+}}^{bT_{\sigma^-}} \langle jb \| aU_{\sigma^-} \rangle + P(ij) t_{iV_{\sigma^+}}^{aW_{\sigma^-}} \langle jW_{\sigma^-} \| T_{\sigma^-}U_{\sigma^-} \rangle, \end{aligned} \tag{A9}$$

$$\begin{aligned} D_{iT_{\sigma^+}U_{\sigma^+}}^{abc} t_{iT_{\sigma^+}U_{\sigma^+}}^{abc} = &- P(c/ab) t_{ij}^{ab} \langle jc \| T_{\sigma^+}U_{\sigma^+} \rangle - P(c/ab)P(T_{\sigma^+}U_{\sigma^+}) t_{jT_{\sigma^+}}^{ab} \langle iU_{\sigma^+} \| jc \rangle - P(c/ab) t_{iV_{\sigma^+}}^{ab} \langle T_{\sigma^+}U_{\sigma^+} \| V_{\sigma^+} c \rangle \\ &- P(c/ab)P(T_{\sigma^+}U_{\sigma^+}) t_{iT_{\sigma^+}}^{ad} \langle U_{\sigma^+} d \| bc \rangle - P(T_{\sigma^+}U_{\sigma^+})P(a/bc) t_{iT_{\sigma^+}}^{aW_{\sigma^-}} \langle U_{\sigma^+} W_{\sigma^-} \| bc \rangle \\ &- P(a/bc) t_{T_{\sigma^+}U_{\sigma^+}}^{ad} \langle id \| bc \rangle + P(c/ab)P(T_{\sigma^+}U_{\sigma^+}) t_{T_{\sigma^+}V_{\sigma^+}}^{ab} \langle iU_{\sigma^+} \| V_{\sigma^+} c \rangle, \end{aligned} \tag{A10}$$

$$D^{abV_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}} t^{abV_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}} = +P(ab)t^{aV_{\sigma^-}}_{ij}\langle jb\|T_{\sigma^+}U_{\sigma^+}\rangle - P(T_{\sigma^+}U_{\sigma^+})t^{ab}_{jT_{\sigma^+}}\langle iU_{\sigma^+}\|jV_{\sigma^-}\rangle - P(ab)P(T_{\sigma^+}U_{\sigma^+})t^{ac}_{iT_{\sigma^+}}$$
$$\times\langle U_{\sigma^+}c\|bV_{\sigma^-}\rangle + P(ab)P(T_{\sigma^+}U_{\sigma^+})t^{aV_{\sigma^-}}_{jT_{\sigma^+}}\langle iU_{\sigma^+}\|jb\rangle + P(ab)t^{aV_{\sigma^-}}_{iW_{\sigma^+}}\langle T_{\sigma^+}U_{\sigma^+}\|W_{\sigma^+}b\rangle$$
$$+P(T_{\sigma^+}U_{\sigma^+})t^{cV_{\sigma^-}}_{iT_{\sigma^+}}\langle U_{\sigma^+}c\|ab\rangle - P(ab)P(T_{\sigma^+}U_{\sigma^+})t^{aW_{\sigma^-}}_{iT_{\sigma^+}}\langle U_{\sigma^+}W_{\sigma^-}\|bV_{\sigma^-}\rangle$$
$$+P(T_{\sigma^+}U_{\sigma^+})t^{ab}_{T_{\sigma^+}W_{\sigma^+}}\langle iU_{\sigma^+}\|W_{\sigma^+}V_{\sigma^-}\rangle - P(ab)t^{ac}_{T_{\sigma^+}U_{\sigma^+}}\langle ic\|bV_{\sigma^-}\rangle, \tag{A11}$$

$$D^{abc}_{T_{\sigma^+}U_{\sigma^+}V_{\sigma^+}} t^{abc}_{T_{\sigma^+}U_{\sigma^+}V_{\sigma^+}} = +P(T_{\sigma^+}/U_{\sigma^+}V_{\sigma^+})P(c/ab)t^{ab}_{iT_{\sigma^+}}\langle ic\|U_{\sigma^+}V_{\sigma^+}\rangle - P(V_{\sigma^+}/T_{\sigma^+}U_{\sigma^+})P(a/bc)t^{ad}_{T_{\sigma^+}U_{\sigma^+}}\langle V_{\sigma^+}d\|bc\rangle$$
$$-P(c/ab)P(T_{\sigma^+}/U_{\sigma^+}V_{\sigma^+})t^{ab}_{T_{\sigma^+}W_{\sigma^+}}\langle U_{\sigma^+}V_{\sigma^+}\|W_{\sigma^+}c\rangle. \tag{A12}$$

Fourth-order triple excitation contributions

$$E^{[4]}_T = \tfrac{1}{36}(t^{abc}_{ijk})^2 D^{abc}_{ijk} + \tfrac{1}{12}(t^{abT_{\sigma^-}}_{ijk})^2 D^{abT_{\sigma^-}}_{ijk} + \tfrac{1}{12}(t^{aT_{\sigma^-}U_{\sigma^-}}_{ijk})^2 D^{aT_{\sigma^-}U_{\sigma^-}}_{ijk} + \tfrac{1}{36}(t^{T_{\sigma^-}U_{\sigma^-}V_{\sigma^-}}_{ijk})^2 D^{T_{\sigma^-}U_{\sigma^-}V_{\sigma^-}}_{ijk} + \tfrac{1}{12}(t^{abc}_{ijT_{\sigma^+}})^2 D^{abc}_{ijT_{\sigma^+}}$$
$$+ \tfrac{1}{4}(t^{abU_{\sigma^-}}_{ijT_{\sigma^+}})^2 D^{abU_{\sigma^-}}_{ijT_{\sigma^+}} + \tfrac{1}{4}(t^{aT_{\sigma^-}U_{\sigma^-}}_{ijV_{\sigma^+}})^2 D^{aT_{\sigma^-}U_{\sigma^-}}_{ijV_{\sigma^+}} + \tfrac{1}{12}(t^{abc}_{iT_{\sigma^+}U_{\sigma^+}})^2 D^{abc}_{iT_{\sigma^+}U_{\sigma^+}} + \tfrac{1}{4}(t^{abV_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}})^2 D^{abV_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}}$$
$$+ \tfrac{1}{4}(t^{aV_{\sigma^-}W_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}})^2 D^{aV_{\sigma^-}W_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}} + \tfrac{1}{36}(t^{abc}_{T_{\sigma^+}U_{\sigma^+}V_{\sigma^+}})^2 D^{abc}_{T_{\sigma^+}U_{\sigma^+}V_{\sigma^+}}. \tag{A13}$$

Single excitation/triple excitation contributions

$$E^{[4,5]}_{ST} = \tfrac{1}{4}t^a_i t^{abc}_{ijk}\langle jk\|bc\rangle + \tfrac{1}{2}t^a_i t^{abT_{\sigma^-}}_{ijk}\langle jk\|bT_{\sigma^-}\rangle + \tfrac{1}{4}t^{T_{\sigma^-}}_i t^{abT_{\sigma^-}}_{ijk}\langle jk\|ab\rangle + \tfrac{1}{4}t^a_i t^{aT_{\sigma^-}U_{\sigma^-}}_{ijk}\langle jk\|T_{\sigma^-}U_{\sigma^-}\rangle$$
$$+ \tfrac{1}{2}t^{T_{\sigma^-}}_i t^{aT_{\sigma^-}U_{\sigma^-}}_{ijk}\langle jk\|aU_{\sigma^-}\rangle + \tfrac{1}{4}t^{T_{\sigma^-}}_i t^{T_{\sigma^-}U_{\sigma^-}V_{\sigma^-}}_{ijk}\langle jk\|U_{\sigma^-}V_{\sigma^-}\rangle + \tfrac{1}{2}t^a_i t^{abc}_{ijT_{\sigma^+}}\langle jT_{\sigma^+}\|bc\rangle + \tfrac{1}{4}t^a_{T_{\sigma^+}}t^{abc}_{ijT_{\sigma^+}}\langle ij\|bc\rangle$$
$$+ t^a_i t^{abU_{\sigma^-}}_{ijT_{\sigma^+}}\langle jT_{\sigma^+}\|bU_{\sigma^-}\rangle + \tfrac{1}{2}t^{U_{\sigma^-}}_i t^{abU_{\sigma^-}}_{ijT_{\sigma^+}}\langle jT_{\sigma^+}\|ab\rangle + \tfrac{1}{2}t^a_{T_{\sigma^+}}t^{abU_{\sigma^-}}_{ijT_{\sigma^+}}\langle ij\|bU_{\sigma^-}\rangle + t^{T_{\sigma^-}}_i t^{aT_{\sigma^-}U_{\sigma^-}}_{ijV_{\sigma^+}}\langle jV_{\sigma^+}\|aU_{\sigma^-}\rangle$$
$$+ \tfrac{1}{4}t^a_{V_{\sigma^+}}t^{aT_{\sigma^-}U_{\sigma^-}}_{ijV_{\sigma^+}}\langle ij\|T_{\sigma^-}U_{\sigma^-}\rangle + \tfrac{1}{4}t^a_i t^{abc}_{iT_{\sigma^+}U_{\sigma^+}}\langle T_{\sigma^+}U_{\sigma^+}\|bc\rangle + \tfrac{1}{2}t^a_{T_{\sigma^+}}t^{abc}_{iT_{\sigma^+}U_{\sigma^+}}\langle iU_{\sigma^+}\|bc\rangle$$
$$+ \tfrac{1}{4}t^{V_{\sigma^-}}_i t^{abV_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}}\langle T_{\sigma^+}U_{\sigma^+}\|ab\rangle + t^a_{T_{\sigma^+}}t^{abV_{\sigma^-}}_{iT_{\sigma^+}U_{\sigma^+}}\langle iU_{\sigma^+}\|bV_{\sigma^-}\rangle + \tfrac{1}{4}t^a_{T_{\sigma^+}}t^{abc}_{T_{\sigma^+}U_{\sigma^+}V_{\sigma^+}}\langle U_{\sigma^+}V_{\sigma^+}\|bc\rangle. \tag{A14}$$

Double excitation/triple excitation contributions

$$E^{[4]}_{DT} = \tfrac{1}{4}f^a_i t^{bc}_{jk}t^{abc}_{ijk} + \tfrac{1}{2}f^a_i t^{bT_{\sigma^-}}_{jk}t^{abT_{\sigma^-}}_{ijk} + \tfrac{1}{4}f^a_i t^{T_{\sigma^-}U_{\sigma^-}}_{jk}t^{aT_{\sigma^-}U_{\sigma^-}}_{ijk} + \tfrac{1}{2}f^a_i t^{bc}_{jT_{\sigma^+}}t^{abc}_{ijT_{\sigma^+}} + f^a_i t^{bU_{\sigma^-}}_{jT_{\sigma^+}}t^{abU_{\sigma^-}}_{ijT_{\sigma^+}} + \tfrac{1}{4}f^a_i t^{bc}_{T_{\sigma^+}U_{\sigma^+}}t^{abc}_{iT_{\sigma^+}U_{\sigma^+}}. \tag{A15}$$

[1] J. Čížek, J. Chem. Phys. **45**, 4256 (1966).
[2] R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989).
[3] T. J. Lee and G. E. Scuseria, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S. R. Langhoff (Kluwer Academic, Dordrecht, 1995), pp. 47–108.
[4] R. J. Bartlett, in *Modern Electronic Structure Theory*, No. 2 in Advanced Series in Physical Chemistry, edited by D. R. Yarkony (World Scientific, Singapore, 1995), Chap. 16, p. 1047.
[5] R. J. Bartlett, H. Sekino, and G. D. Purvis, Chem. Phys. Lett. **98**, 66 (1983).
[6] Y. S. Lee, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **81**, 5906 (1984).
[7] J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).
[8] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[9] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990); **167**, 609(E) (1990).
[10] G. E. Scuseria, Chem. Phys. Lett. **176**, 27 (1991).
[11] J. Gauss, W. J. Lauderdale, J. F. Stanton, J. D. Watts, and R. J. Bartlett, Chem. Phys. Lett. **182**, 207 (1991).
[12] J. R. Thomas, B. J. DeLeeuw, G. Vacek, T. D. Crawford, Y. Yamaguchi, and H. F. Schaefer, J. Chem. Phys. **99**, 403 (1993).
[13] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).
[14] J. F. Stanton, Chem. Phys. Lett. (in press).
[15] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).
[16] I. Hubač and P. Čársky, Phys. Rev. A **22**, 2392 (1980).
[17] R. D. Amos, J. S. Andrews, N. C. Handy, and P. J. Knowles, Chem. Phys. Lett. **185**, 256 (1991).
[18] P. J. Knowles, J. S. Andrews, R. D. Amos, N. C. Handy, and J. A. Pople, Chem. Phys. Lett. **186**, 130 (1991).
[19] W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, Chem. Phys. Lett. **187**, 21 (1991).
[20] C. M. Murray and E. R. Davidson, Chem. Phys. Lett. **187**, 451 (1991).
[21] T. J. Lee and D. Jayatilaka, Chem. Phys. Lett. **201**, 1 (1993).
[22] P. M. Kozlowski and E. R. Davidson, Chem. Phys. Lett. **226**, 440 (1994).
[23] M. Rittby and R. J. Bartlett, J. Phys. Chem. **92**, 3033 (1988).
[24] C. L. Janssen and H. F. Schaefer, Theor. Chim. Acta **79**, 1 (1991).
[25] D. Jayatilaka and T. J. Lee, J. Chem. Phys. **98**, 9734 (1993).
[26] P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993).
[27] P. Neogrády, M. Urban, and I. Hubač, J. Chem. Phys. **100**, 3706 (1994).
[28] X. Li and J. Paldus, J. Chem. Phys. **101**, 8812 (1994).
[29] P. G. Szalay and J. Gauss, J. Chem. Phys. (to be published).
[30] It has been shown that for a number of ROHF-based perturbation theories, spin contamination is often eliminated for lower-order energies, and sig-

nificantly reduced for higher-order energies. ROHF-CCSD energies have been shown to be completely spin projected, as well, though the spin contamination which still exists in the wavefunction can indirectly affect the energy; that is, the ROHF-CCSD energy will differ from that obtained from a completely spin-adapted approach. However, Stanton (Ref. 53) has questioned the significance of this difference for ground state properties.

[31] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[32] D. Jayatilaka and T. J. Lee, Chem. Phys. Lett. **199**, 211 (1992).

[33] T. D. Crawford and H. F. Schaefer, J. Chem. Phys. **104**, 6259 (1996).

[34] T. D. Crawford, H. F. Schaefer, and T. J. Lee, J. Chem. Phys. **105**, 1060 (1996).

[35] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).

[36] D. Jayatilaka and N. C. Handy, Int. J. Quantum Chem. **42**, 445 (1992).

[37] T. J. Lee, S. C. Racine, J. E. Rice, and A. P. Rendell, Mol. Phys. **85**, 561 (1995).

[38] M. J. O. Deegan and P. J. Knowles, Chem. Phys. Lett. **227**, 321 (1994).

[39] P. Neogrády and M. Urban, Int. J. Quantum Chem. **55**, 187 (1995).

[40] F. W. Bobrowicz and W. A. Goddard, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer (Plenum, New York, 1977), Chap. 4, p. 79.

[41] S. A. Kucharski and R. J. Bartlett, Adv. Quantum Chem. **18**, 281 (1986).

[42] As has been pointed out (Ref. 21) taking into account spin integration leads to the conclusion that single excitations do not appear in the first-order wave function since the first-order $t_{I_\alpha}^{A_\alpha}$ amplitudes are zero and the first-order $t_{I_\alpha}^{A_\beta}$ amplitudes are classified as double excitations due to interacting space arguments. This type of analysis for the higher-excitation amplitudes leads to similar conclusions and is discussed in Ref. 54.

[43] F. E. Harris, H. J. Monkhorst, and D. L. Freeman, *Algebraic and Diagrammatic Methods in Many-Fermion Theory* (Oxford University Press, New York, 1992).

[44] S. Wolfram, *Mathematica: A System for Doing Mathematics by Computer*, 2nd ed. (Addison-Wesley, Reading, Massachusetts, 1991).

[45] T. D. Crawford, Ph.D. thesis, University of Georgia, 1996.

[46] If those single excitation contributions involving the open-shell orbitals were removed from E_{ST}, then a ZAPT-based CCSD+T(CCSD) method (cf. Ref. 13) would result.

[47] D. Jayatilaka (unpublished notes).

[48] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[49] T. H. Dunning, J. Chem. Phys. **53**, 2823 (1970).

[50] C. L. Janssen, E. T. Seidl, G. E. Scuseria, T. P. Hamilton, Y. Yamaguchi, R. B. Remington, Y. Xie, G. Vacek, C. D. Sherrill, T. D. Crawford, J. T. Fermann, W. D. Allen, B. R. Brooks, G. B. Fitzgerald, D. J. Fox, J. F. Gaw, N. C. Handy, W. D. Laidig, T. J. Lee, R. M. Pitzer, J. E. Rice, P. Saxe, A. C. Scheiner, and H. F. Schaefer, PSI 2.0.8 (PSITECH, Inc., Watkinsville, GA, 1995). This program is generally available for a handling fee of $100.

[51] J. F. Stanton, J. Gauss, W. J. Lauderdale, J. D. Watts, and R. J. Bartlett, ACES II, The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor, the ABACUS integral derivative program written by T. U. Helgaker, H. J. Aa. Jensen, P. Jørgensen and P. R. Taylor, and the PROPS property evaluation integral code of P. R. Taylor.

[52] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[53] J. F. Stanton, J. Chem. Phys. **101**, 371 (1994).

[54] T. J. Lee, A. P. Rendell, K. G. Dyall, and D. Jayatilaka, J. Chem. Phys. **100**, 7400 (1994).