# The full CCSDT model for molecular electronic structure

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The full coupled-cluster model (CCSDT) single, double, and triple excitation method defined by the wave function $\exp(T_1 + T_2 + T_3)|\Phi_0\rangle$ is formulated and computationally implemented for the first time. Explicit computational equations are presented. The method is applied to numerous examples including BH, FH, $C_2H_2$, CO, Ne, $F^-$, and $H_2O$ to assess its applicability to the correlation problem. Results from CCSDT agree with full CI, to an average error of less than 1 kcal/mol even for difficult bond breaking examples. A series of results for various approximate, but computationally more efficient versions of the full CCSDT model are also studied and shown to give results in excellent agreement with CCSDT. Additional comparisons with fifth-order MBPT are reported.

## I. INTRODUCTION

The coupled-cluster (CC) approach for solving the Schrödinger equation in electronic structure originates with the exponential ansatz, ($\psi_{CC} = e^T|\Phi_0\rangle$), of Coester and Kümmel.[1] $T$ is a cluster operator which is separated into one-body $T_1$, two-body $T_2$, and higher types of clusters, each of which is composed of an amplitude, and a series of excitation operators, e.g., $T_2 = \frac{1}{4}\Sigma_{i,j,a,b}\, t^{ab}_{ij}a^\dagger i b^\dagger j$.

When $T$ includes all clusters up to $T_p$ for $p$ electrons, the exact solution to the Schrödinger equation would be obtained, or the full configuration interaction (CI) (i.e., all possible excitations for $p$ electrons) in a basis set. The power of the method compared to CI rests upon the fact that for any truncation of $T$ such as $T \simeq T_2$, $\exp(T_2)|\Phi_2\rangle = [1 + T_2 + T_2^2/2 + T_2^3/3! + \cdots]|\Phi_0\rangle$ still introduces certain types of quadruple, hextuple, and higher excitations into the calculation via the "disconnected" $T_2^2/2$ and $T_2^3/3!$ terms. As long as $T_2^2/2$ is the dominant part of quadruple excitations compared to the "connected" part, $T_4$, or the other disconnected parts like $T_1T_3$, then most of the quadruple; and by analogy higher even-ordered excitation contributions are introduced into the calculation, but the quadruple excitation coefficient is only a product of the much smaller number of $T_2$ amplitudes, $t^{ab}_{ij}$. The other essential element is the size-extension property[2] which states that only *linked diagrams* remain in $\exp(T)|\Phi_0\rangle$ which guarantees correct scaling with molecular size, and for the indicative problem of separated noninteracting fragments with localized orbitals,

$$\psi_{AB} = \exp(T_{AB})|\Phi_{AB}\rangle = \exp(T_A)|\Phi_A\rangle\exp(T_B)|\Phi_B\rangle$$

$$= \psi_A\psi_B \text{ and } E^{AB}_{CC} = E^A_{CC} + E^B_{CC}.$$

The connection between CC theory and classes of an infinite-order sum of many-body perturbation theory (MBPT) correlation energy diagrams was demonstrated by Hubbard.[3] The concept of the correlation energy for a molecule being primarily composed of pair and higher cluster components was primarily popularized by Nesbet[4] and Sinanoglu,[5] although Čížek was the first person to use the exponential ansatz to write down explicit equations for the simplest practical coupled-cluster model, $\psi_{CCD} = \exp(T_2)|\Phi_0\rangle$.[6] He also developed a systematic diagrammatic procedure for deriving higher-order approximations for the cluster operator, $T$. Several semiempirical applications with the PPP and Hückel parameterization were reported by Paldus and Čížek[7(a)] Later, along with Shavitt,[7(b)] these authors reported an *ab initio* minimum basis set study of $BH_3$, an example which required only 157 distinct two-electron ($D_{3h}$, complex orbital) integrals.

The first general purpose computer codes for performing CC calculations limited to two-body clusters, CCD, were written by Bartlett and Purvis[8] and Pople *et al.*,[9] who report a number of applications in back-to-back papers in 1978. Since CCD contains the essential (disconnected) effects of quadruple and higher even-ordered excitation effects, and since these products are the dominant parts of such excitations for SCF reference functions, it was possible to obtain quite general information about the magnitude and effect of such higher excitation contributions, which generally cannot be obtained by CI correlation methods because of the excessive number of such high excitations. It was further emphasized that CC theory, as a generalization of MBPT, properly excludes the unlinked, size-inextensive terms that would remain in any but full CI. Numerically, the largest parts of higher excitation contributions are due to unlinked diagrams,[2,8,10] naturally eliminated by the exponential ansatz. The numerical importance of computations using properly size-extensive methods has now been well established,[10] with various semiempirical size-extensive corrections being proposed to routinely augment most CI applications.[11,12]

Although double-excitation clusters are clearly the dominant contributions for correlation calculations starting from a single SCF reference function, for other classes of problems it is extremely important to include the single-particle clusters, $T_1$, and their products with themselves and $T_2$.

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The full coupled-cluster single and double excitation method, $\psi_{CCSD} = \exp(T_1 + T_2)|\Phi_0\rangle$ was formulated and implemented sometime back by Purvis and Bartlett.[13] Other ways of including some single excitation effects include a transformation to Brueckner orbitals that would make $T_1 = 0$,[8] or that due to Chiles and Dykstra,[14] but CCSD is the full inclusion of all terms.

A CCSD model is crucial for the general non-Hartree–Fock case, since such an example will likely have $T_1$ amplitudes that are greater than those due to $T_2$, simply because matrix elements between an arbitrary single-determinant reference and a single excitation will not vanish as there is no Brillouin's theorem. Hence, such contributions occur in the second-order correlation energy (orders defined by $V = H - H_0$) or the same order as the first energy contribution from $T_2$. Furthermore, certain amplitudes can be quite large, perhaps even greater than unity, making it totally inappropriate to even truncate the contribution of $T_1^4/4!$ from the CCSD equations. This has enabled us to use CCSD with types of localized bond orbitals as a potential method for large molecules.[15]

For properties other than the energy, the contributions due to $\exp(T_1)$ are essential for introducing orbital relaxation, which ensures that CCSD effectively satisfies the Hellman–Feynman theorem and its higher derivatives for properties.[16] Also, we employ CCSD with other non-Hartree–Fock cases such as our recently proposed spin-eigenfunction open-shell CCSD method[17] that permits the use of CC theory without resorting to an unrestricted Hartree–Fock reference for many open-shell problems. For example, for applications to ionization potentials; we instead use the RHF orbitals of the neutral molecule subject to maximum double occupancy for each possible ion. Since such orbitals do not diagonalize the Fock operator for the ion, it is not possible to limit the calculation to just $T_2$; but, just as for properties, the required orbital relaxation is introduced for each of the possible ionized states by virtue of the coupling of $\exp(T_1)$ with $\exp(T_2)$ in the wave function.

The next important step in CC single reference theory is the CCSDT model, $\psi_{CCSDT} = \exp(T_1 + T_2 + T_3)|\Phi_0\rangle$. It is known from fourth-order MBPT that unlike the quadruple excitations, which are primarily $T_2^2/2$, (i.e., through fourth-order MBPT) that at least for SCF reference cases, the "connected" part of triple excitations, i.e., $T_3$, which also occurs first in fourth-order MBPT[18] is numerically more important than triple excitations like $T_1T_2$ or $1/3!T_1^3$, which occur in higher orders of MBPT. The work of Paldus et al.[7(b)] and Kvasnicka et al.[19] considered some effects of $T_3$ for very small basis set examples within an approximate CCSDT. For more general examples, we defined and implemented a CCSDT-1 model,[20] $\psi_{CCSDT-1} \simeq \exp(T_1 + T_2) + T_3|\Phi_0\rangle$, augmented by projecting this wave function only onto the space of single and double excitations; but using $T_2|\Phi_0\rangle$ when projecting onto the space of triple excitations (vide infra). This has a number of advantages: (1) CCSDT-1 is exact through fourth-order MBPT in the energy; (2) the wave function is exact through second-order MBPT; (3) the essential computational step which is asymptotically $\sim n_{occ}^3 n_{VIRT}^4 \sim n^7$ is the same as that in fourth-order MBPT,

and (4) it is not necessary to store any $t_{ijk}^{abc}$ amplitudes. In terms of invariance properties, just like CCD or CCSD, CCSDT-1 is invariant to transformations among just the occupied or just the virtual orbitals, since as long as entire diagrams are included (and, of course, the diagrams that arise from the off-diagonal Fock matrix elements, once such transformations destroy the canonical nature of the orbitals), the usual CC invariance properties are maintained. Several large-scale applications of CCSDT-1 have been presented.[21]

A series of higher-order CCSDT-$n$ approximations can be generated by including additional contributions of the quadratic and higher products of $T_1$ and $T_2$ onto triple excitations. This sequence of approximations has been defined by Urban et al.,[22] and recently implemented and compared with full CI by Noga, Bartlett, and Urban.[23] These models have the advantage that they are not much more time consuming than CCSDT-1 (still no worse than $\sim n^7$), but for difficult cases can provide better results.

In this paper we report for the first time, results for the full CCSDT model for electronic structure. Unlike all the previous CC approximations that include triple excitations, this model includes the contributions of $T_3$ into the $T_3$ amplitudes. This requires an $\sim n_{occ}^3 n_{VIRT}^5 \sim n^8$ step. It also requires the storage of the $t_{ijk}^{abc}$ amplitudes, making the model more demanding in terms of computer time and external storage than any of the other approximations. However, since it is the definitive coupled-cluster model with triple excitations, it provides the rigorous reference for all the other CCSDT-$n$ methods.

In the following we summarize the theory for CCSDT and discuss its computational implementation. Then we report a series of results, many of which are compared with recent full CI benchmark results,[24] to assess the accuracy of the method.

## II. THEORY

Most of the essential equations and diagrams have been presented explicitly elsewhere,[20(b),25] but to understand the hierarchy of CCSDT-$n$ approximations we need some of these expressions.

For CCSDT we are interested in

$$\psi_{CCSDT} = \exp(T_1 + T_2 + T_3)|\Phi_0\rangle, \tag{1}$$

where $\Phi_0$ is a single-determinant reference, which need not be the SCF function. In terms of spin orbitals, the cluster operators are

$$T_1 = \sum_{i,a} t_i^a a^\dagger i, \tag{2a}$$

$$T_2 = \sum_{\substack{i<j \\ a<b}} t_{ij}^{ab} a^\dagger i b^\dagger j, \tag{2b}$$

$$T_3 = \sum_{\substack{i<j<k \\ a<b<c}} t_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k. \tag{2c}$$

The indices $i,j,k...(a,b,c...)$ refer to occupied (unoccupied) spin orbitals in $\Phi_0$ and their associated creation $(a^\dagger, i^\dagger)$ and

annihilation $(a,i)$ operators. The indices $p,q,r,s,...$ represent unspecified indices and operators.

In normal product form,[6]

$$H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle$$

$$= \sum_{p,q} f_{pq} \{p^\dagger q\} + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle \{p^\dagger q^\dagger s r\}$$

$$= F_N + W_N. \tag{3}$$

The quantity $\{ABC...\}$ indicates the normal product of the creation and annihilation operators that would place all particle annihilation $(a)$ and hole annihilation $(i^\dagger)$ operators to the right of the other operators by permuting them while keeping track of the appropriate sign. Consequently, $\langle \Phi_0 | \{ABC...\} | \Phi_0 \rangle = 0$. We also define the contraction $\overline{\{AB\}}$ between two operators as $AB = \{AB\} + \overline{\{AB\}}$. This immediately tells us from the fundamental anticommunication relations, $p^\dagger q + q p^\dagger = \delta_{pq}$, that only $\overline{\{ab^\dagger\}} = \delta_{ab}$ and $\overline{\{i^\dagger j\}} = \delta_{ij}$ are nonvanishing.

Inserting the trial wave function, Eq. (1), into the Schrödinger equation, we have

$$\Delta E = E - \langle \Phi_0 | H | \Phi_0 \rangle = \langle \Phi_0 | e^{-T} H_N e^T | \Phi_0 \rangle$$

$$= \langle \Phi_0 | (H_N e^T) | \Phi_0 \rangle_C, \tag{4}$$

$$\Delta E = \langle \Phi_0 | H_N (T_2 + T_1 + T_1/2) | \Phi_0 \rangle_C.$$

The $C$ indicates that only connected diagrams need to be considered.[6,25] "Connected" and "linked" are synonomous for closed (energy) diagrams.

We can obtain the amplitudes in Eqs. (2a)–(2c) via projection of the Schrödinger equation onto the set of single $\langle \Phi_1^a |$, double $\langle \Phi_{ij}^{ab} |$, and triple excitations $\langle \Phi_{ijk}^{abc} |$, respectively, since $\langle \Phi_{ij...}^{ab...} | H_N \exp(T) | \Phi_0 \rangle_C = 0$. Here connected means a linked, open diagram that has no disconnected parts.[25]

Separating $F_N$ into a diagonal $\Sigma f_{pp} \{p^\dagger p\} = D$, and off-diagonal parts, $\sum_{p,q}^{(p \neq q)} f_{pq} \{p^\dagger q\} = F_N'$, with $V_N = F_N' + W_N$, the CCSDT amplitude equations may be put into the operator form[20,25]

$$D_1 T_1 = (F_N' + \underset{1}{[\overline{V_N T_1}]} + \underset{2}{[\overline{V_N T_2}]} + \underset{3}{[\overline{V_N T_3}]} + \underset{4}{[\overline{V_N T_1 T_2}]}$$

$$+ \underset{5}{[\overline{V_N T_1 T_2}]} + \underset{6}{[\overline{V_N T_1^2/2}]} + \underset{7}{[\overline{V_N T_1^3/3!}]}), \tag{5}$$

$$D_2 T_2 = (W_N + \underset{1}{[\overline{V_N T_2}]} + \underset{2}{[\overline{V_N T_2^2/2}]} + \underset{3}{[\overline{V_N T_3}]}$$

$$+ \underset{5}{[\overline{V_N T_1}]} + \underset{6}{[\overline{V_N T_1 T_2}]} + \underset{7}{[\overline{V_N T_1^2}]/2}$$

$$+ \underset{8}{[\overline{V_N T_1 T_3}]} + \underset{9}{[\overline{V_N T_2 T_1^2/2}]} + \underset{10}{[\overline{V_N T_1^3/3!}]}$$

$$+ \underset{11}{[\overline{V_N T_1^4/4!}]}), \tag{6}$$

$$D_3 T_3 = \underset{1}{[\overline{V_N T_2}]} + \underset{2}{[\overline{V_N T_2^2/2}]} + \underset{3}{[\overline{V_N T_3}]}$$

$$+ \underset{4}{[\overline{V_N T_1 T_2}]} + \underset{5}{[\overline{V_N T_2 T_3}]} + \underset{6}{[\overline{V_N T_1 T_3}]}$$

$$+ \underset{7}{[\overline{V_N T_2 T_1^2/2}]} + \underset{8}{[\overline{V_N T_1^2 T_1/2}]}$$

$$+ \underset{9}{[\overline{V_N T_3 T_1^2/2}]} + \underset{10}{[\overline{V_N T_2 T_1^3/3!}]}). \tag{7}$$

Once an actual configuration is specified to label the contribution to a specific amplitude in $T_n$, as $t_{ij...}^{ab...}$, the $D_n$ denominator becomes $D_n = (f_{ii} + f_{jj} + \cdots - f_{aa} - f_{bb}...)$. The form of Eqs. (5)–(7) comes from an application of the generalized Wick's theorem for normal ordered products,[26] that states that the only nonvanishing contractions are fully contracted products among the different normal product operators. Note, the cluster operators of Eq. (2) are already in normal product form. The natural truncation of Eqs. (4)–(7) to define the $T$ amplitudes and energy is simply a consequence of $H$ containing no more than two-particle operators, but the wave function always corresponds to an infinite series. The form of the coupled CCSDT equations above lends itself to an iterative, integral list directed solution; and also allows us to refer to various contributions of one type of cluster, like $T_3$, to another type, like $T_2$.

All the diagrams for the CCSDT model were presented previously,[20(b),25] including an explicit algebraic interpretation of the equation for $t_{ijk}^{abc}$. Algebraic expressions for CCSD have been given in two slightly different groupings.[13,27] The additional terms that arise from the contribution of triple excitations to the single excitation amplitude, i.e., the fourth term of Eq. (5), is $\frac{1}{4} \sum_{k,l,c,d} \langle kl || cd \rangle t_{ikl}^{acd}$ in spin-orbital form. Its initial energy contribution is fifth order in the SCF case (fourth order, otherwise). The principal contribution to the double excitation amplitude from $T_3$ arises from the fourth term of Eq. (6). This term, of which the $W_N$ part is included in CCSDT-1, has been discussed at length, previously.[20(b)] The non-Hartree–Fock part of $V_N$ gives $\sum_k f_{kc} t_{ijk}^{abc}$, which would first arise as a fourth-order energy contribution for a non-Hartree–Fock case. This term should be included in any CCSDT-1 calculation that uses non-Hartree–Fock orbitals. The remaining nonlinear $T_3$ contribution to $T_2$ is from the eighth term of Eq. (6), with value

$$\sum_{klcd} \langle kl || cd \rangle \left\{ t_k^c t_{lij}^{dab} - \frac{1}{2} (-1)^P \right.$$

$$\left. \times \sum_P [P(ab) t_k^a t_{ij}^{cdb} + P(ij) t_i^c t_{klj}^{adb}] \right\}.$$

$(-1)^P \Sigma_P P(ab)$ indicates summation with appropriate parity over the identity permutation plus the subsequent expression with indices $a$ and $b$ interchanged. This term contributes initially to the sixth-order energy in the Hartree–Fock case (fifth order otherwise). The inclusion of this contribution distinguishes CCSDT-1a from CCSDT-1b.[22]

The CCSDT-$n$ hierarchy can be summarized by what additional terms are included in Eqs. (5), (6), and (7). While CCSDT-1b includes 5.4, 6.4, and 6.8, but only 7.1,
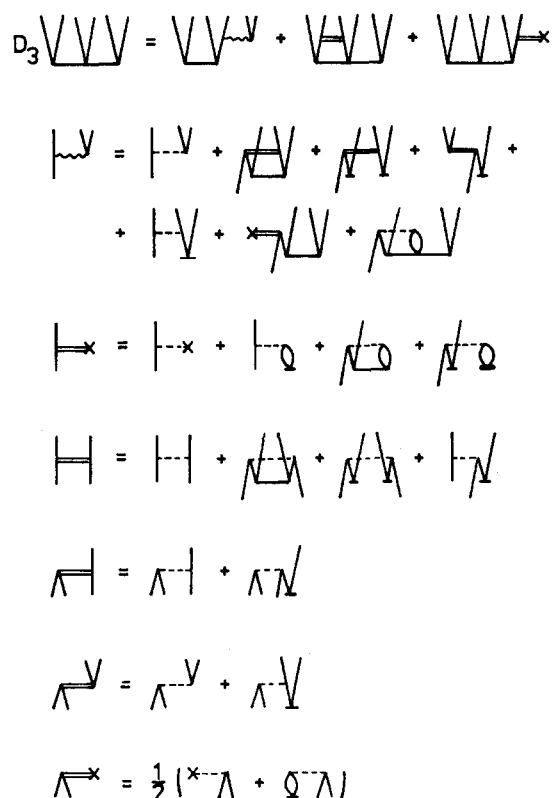
FIG. 1. All arrowless intermediate diagrams needed in the evaluation of $T_3$ amplitudes in the (full) CCSDT method. Note that by drawing arrows some diagrams of $T_2 T_1^2$ would be generated twice, but need to be taken only once. We believe that this figure is more illustrative than the large number of diagrams with arrows.

TABLE I. The spin-independent explicit formulation of the CCSDT equations for $T_3$ amplitudes.[a]

$$
\begin{aligned}
t_{ijk}^{abc} D_{ijk}^{abc} = \sum_{P_{ia,jb,kc}} & \left( \sum \chi(a,b,i,e) t_{kj}^{ce} - \sum \chi(a,m,i,j) t_{mk}^{bc} \right) \\
+ \sum_{P_{ia/jb,kc}} & \left\{ \sum \chi(a,e) t_{ijk}^{ebc} - \sum \chi(i,m) t_{mjk}^{abc} \right. \\
& + \sum \chi(j,k,m,n) t_{imn}^{abc} + \sum \chi(b,c,e,f) t_{ijk}^{aef} \\
& + \sum \chi(a,m,i,e)(2 t_{mjk}^{ebc} - t_{mjk}^{bec} - t_{mjk}^{cbe}) \\
& \left. - \sum (\chi(a,m,e,i) t_{mjk}^{ebc} + \chi(b,m,e,i) t_{mjk}^{aec} + \chi(c,m,e,i) t_{mjk}^{abe}) \right\}.
\end{aligned}
$$

[a] In Tables I and II $i,j,k...a,b,c...$ denote occupied and virtual orbitals, respectively. Summations run over all indices, unless they appear in the final expression; $P_{ia,jb,kc}$ means that summation must be performed over all 3! permutations of pairs of occupied and virtual orbitals, while $P_{ia/jb,kc}$ means that the pair $ia$ should be changed by $jb$ and $kc$. Note that there is no change of the sign, since there are always only even numbers of permutations.

CCSDT-2 also includes 7.2, which gives a fifth-order contribution to the energy, and corresponds to having all $T_2$ effects upon $T_3$. CCSDT-3 adds 7.4, 7.7, 7.8, and 7.10, i.e., all terms that do not depend upon $T_3$. We define CCSDT-4 to add the 7.3 term, which introduces the first $\sim n^8$ summation step. However, this term represents a fifth-order MBPT energy contribution just like the 7.2 term. Finally, the full CCSDT model adds in the additional nonlinear products that involve $T_3$, namely 7.5, 7.6, and 7.9.

The full CCSDT model includes all fifth-order MBPT terms except for those due to the connected four-body cluster term, $T_4$. However, the fifth-order contribution from the latter can be computed as we have shown[25] with only an $\sim n^6$ algorithm, making it potentially a small addition to the $\sim n^8$ procedure required for the 7.3 term. We have considered fifth-order MBPT and higher orders elsewhere,[28] and found some evidence that once MBPT(5) is augmented with the [2,1] Padé approximant, the model could then be comparable to the infinite-order CCSDT-$n$ methods in accuracy at least near equilibrium configurations; but, generally, not just MBPT(5) itself. By comparing results at the different CCSDT-$n$ levels, some measure of the different higher-order contributions to the energy might be assessed.

Unlike our other CCSD and CCSDT-1 programs, which have been written for the general case of different orbitals for different spins, which among other features,[17] permits the use of UHF reference functions for open shells

and certain types of bond breaking, the potentially extensive number of $t_{ijk}^{abc}$ amplitudes makes it advisable to restrict our initial CCSDT code to the closed shell, doubly occupied orbital case so that we could employ the spin-adapted form of the CCSDT equations. We choose to use the orthogonal spin-adaptation scheme of Paldus.[29] The codes are still generally applicable for the non-Hartree–Fock case, however,

The explicit spin-adapted computational equations for CCSDT-2 and CCSDT-3 have been presented elsewhere.[23] Consequently, here we do the same for the full CCSDT model, while CCSDT-4 is defined as a simplification excluding the nonlinear terms that involve $T_3$. These are shown in Tables I and II, where the indices now refer to spatial orbitals instead of spin orbitals.

As previously, we followed the established procedures[8,13,25] of using intermediate effective interactions. In Fig. 1 we show the diagrammatic representation of all necessary effective intermediates for CCSDT, while in Tables I and II there is the explicit expression for $T_3$ amplitudes, while the iterative procedure for solving the CC equations is applied.

Since computational aspects of various CCSDT-$n$ models have been discussed previously,[23] here we restrict ourselves to CCSDT-4 and (full) CCSDT. As follows directly from Table I, the inclusion of $\{V_N T_3\}$ requires computational steps over eight indices (more precisely the most time consuming step is $\sim n_{virt}^5 n_{occ}^3$ dependent). The computer time can, however, be significantly reduced both by utilizing the spatial symmetry properties of molecules (either passively[13] or explicitly,[30] and by using vector-processing computers. In addition, the implementation of the (full) CCSDT requires several steps through seven indices.

## III. NUMERICAL RESULTS AND DISCUSSION

As a first application of the CCSDT model we consider the BH molecule. (See Table III.) A full CI, DZP basis result has been previously presented at the equilibrium bond length $R_e$, and we[31] have recently computed the full CI at

TABLE II. Intermediate quantities used in Table I.[a]

$$\chi(a,b,i,e) = \langle ab\,|ie\rangle + \sum f(e,i,m,n)\tau^{ab}_{nm}$$

$$+ \sum \{(2f(b,m,e,f) - f(b,m,f,e))t^{af}_{im} - f(b,m,e,f)t^{af}_{mi} - f(a,m,f,e)t^{bf}_{mi}\}$$

$$- \sum (f(a,m,i,e)t^{b}_{m} + f(b,m,e,i)t^{a}_{m}) + \sum \langle ab\,|fe\rangle t^{f}_{i}$$

$$- \sum \langle mn|ef\rangle (2t^{abf}_{imn} - t^{abf}_{nmi} - t^{abf}_{inm}) \qquad (II.1)$$

$$\chi(a,m,i,j) = \langle am|ij\rangle + \sum f(a,m,e,f)\tau^{ef}_{ij}$$

$$- \sum \{(2f(e,j,m,n) - f(e,j,n,m))t^{ae}_{in} - f(e,j,m,n)t^{ea}_{in} - f(e,i,n,m)t^{ea}_{jn}\}$$

$$+ \sum (f(i,e,a,m)t^{e}_{j} + f(j,e,m,a)t^{e}_{i}) - \sum \langle ij|nm\rangle t^{a}_{n}$$

$$+ \sum f(m,e)t^{ae}_{ij} + \sum \langle mn|ef\rangle (2t^{aef}_{ijn} - t^{fea}_{ijn} - t^{afe}_{ijn}) \qquad (II.2)$$

$$\chi(i,m) = \langle i|f|m\rangle + \sum \langle ie||mn\rangle t^{e}_{n} + \sum \langle mn||ef\rangle \tau^{ef}_{in} \qquad (II.3)$$

$$\chi(a,e) = \langle a|f|e\rangle + \sum \langle am||ef\rangle t^{f}_{m} - \sum \langle mn||ef\rangle \tau^{af}_{mn} \qquad (II.4)$$

$$\chi(j,k,m,n) = \langle jk\,|mn\rangle + \sum \langle jk\,|ef\rangle \tau^{ef}_{mn} + \sum (\langle je|mn\rangle t^{e}_{k} + \langle ek\,|mn\rangle t^{e}_{j}) \qquad (II.5)$$

$$\chi(b,c,e,f) = \langle bc|ef\rangle + \sum \langle bc|mn\rangle \tau^{ef}_{mn} - \sum (\langle bm|ef\rangle t^{c}_{m} + \langle mc|ef\rangle t^{b}_{m}) \qquad (II.6)$$

$$\chi(a,m,e,i) = \langle am|ei\rangle - \sum \langle mn|fe\rangle \tau^{fa}_{in} - \sum \langle nm|ei\rangle t^{a}_{n} + \sum \langle am|ef\rangle t^{f}_{i} \qquad (II.7)$$

$$\chi(a,m,i,e) = \langle am|ie\rangle + \sum (\langle mn||ef\rangle t^{af}_{in} - \langle mn|ef\rangle \tau^{fa}_{in})$$

$$- \sum \langle nm|ie\rangle t^{a}_{n} + \sum \langle ae|fm\rangle t^{f}_{i} \qquad (II.8)$$

$$f(a,m,e,f) = \langle am|ef\rangle - \sum \langle nm|ef\rangle t^{a}_{n} \qquad (II.9)$$

$$f(e,i,m,n) = \langle ei|mn\rangle + \sum \langle mn|ef\rangle t^{f}_{i} \qquad (II.10)$$

$$f(a,m,i,e) = \langle am|ie\rangle + \sum \langle am|fe\rangle t^{f}_{i} \qquad (II.11)$$

$$f(a,m,e,i) = \langle am|ei\rangle + \sum \langle am|ef\rangle t^{f}_{i} \qquad (II.12)$$

$$f(i,e,a,m) = \langle ie|am\rangle - \sum \langle in|am\rangle t^{e}_{n} \qquad (II.13)$$

$$f(i,e,m,a) = \langle ie|ma\rangle - \sum \langle in|ma\rangle t^{e}_{n} \qquad (II.14)$$

$$f(m,e) = \langle m|f|e\rangle + \sum \langle mn||ef\rangle t^{f}_{n} \qquad (II.15)$$

$$\tau^{ef}_{mn} = t^{ef}_{mn} + t^{e}_{m}t^{f}_{n} \qquad (II.16)$$

[a] See Table I. For simplicity we introduced "antisymmetrized" spin independent integrals $\langle pq||rs\rangle = 2\langle pq|rs\rangle - \langle pq|sr\rangle$. In CCSDT-4 the last sums in Eq. (II.1) and (II.2) are omitted, and in Eqs. (II.3) to (II.8) only the first terms from the right-hand side remain.

$1.5R_e$ and $2.0R_e$ to have reference energies for a few points on the curve. From the first molecular MBPT results,[32] BH has been known to be a system where the correlation energy measured relative to an SCF single reference is slowly convergent, making higher-order corrections somewhat more important. Of course, once the B–H bond is stretched, the RHF reference becomes an even poorer approximation since the "nondynamical" correlation effects; i.e., those associated with quasidegenerate configurations introduced as bonds are broken, become relatively important compared to the extensive numbers of configurations that introduce the "dynamical" correlation that keeps electrons apart. This causes

TABLE III. CCSDT correlation energies for BH with DZ + P basis. (Energies in hartrees.)[a]

| | BH($R_e = 2.329$ bohr) | BH($1.5\,R_e$) | BH($2.0\,R_e$) |
|---|---|---|---|
| SCF | − 25.125 260 | − 25.062 213 | − 24.988 201 |
| CCSD | − 0.100 574 | − 0.111 119 | − 0.134 097 |
| MBPT(4) | − 0.097 306 | − 0.106 532 | − 0.125 804 |
| MBPT(5)[c] | − 0.099 841 | − 0.110 453 | − 0.133 078 |
| MBPT(5) + [2,1]Padé[c] | − 0.102 041 | − 0.113 919 | − 0.141 209 |
| CCSDT-1a | − 0.101 907 | − 0.113 155 | − 0.138 409 |
| CCSDT-1b | − 0.101 905 | − 0.113 141 | − 0.138 190 |
| CCSDT-2 | − 0.101 863 | − 0.113 096 | − 0.138 184 |
| CCSDT-3 | − 0.101 866 | − 0.113 119 | − 0.138 131 |
| CCSDT-4 | − 0.102 373 | − 0.113 884 | − 0.139 662 |
| CCSDT | − 0.102 299 | − 0.113 742 | − 0.139 112 |
| Full CI | − 0.102 355[b,c] | − 0.113 763[c] | − 0.139 132[a] |

[a] Basis set and equilibrium geometry from Ref. 24(d).
[b] Full CI at $R_e$ from Ref. 24(d).
[c] The full CI results at $1.5R_e$ and $2.0R_e$ and the MBPT(5) + [2,1] Padé results are from recent calculations in our laboratory (Ref. 31). The present $R_e$ result is converged to a precision of $2 \times 10^{-5}$, while the literature result is − 0.102 367 [Ref. 24(d)].

higher-order and higher-excitation contributions to be more significant. Full MBPT(4) differs from the full CI basis limit by 5, 7, and 13 mhartree, as a function of $R$, while any of the CC models that include some part of the triple excitations are about an order of magnitude closer, being within 0.5, 0.7, and 1.0 mhartree, respectively. The CCSDT model agrees to about four decimal places with the full CI at all $R$, with the mean error being only 0.03 mhartree. All CCSDT-$n$ models are about in equally good agreement with CCSDT, with some slight improvement at the CCSDT-4 level, since through the fifth-order energy, that method should give the same result as CCSDT.

For comparison, MBPT(5) results are also shown. The improvement over MBPT(4) is modest until augmented by the [2,1] Padé approximant. Then the agreement with full CI is quite good, but not as good as CCSDT. In particular, the finite-order MBPT(5) + [2,1] model overshoots some at 2.0 $R_e$ reflecting the comparative poorness of finite-order vs infinite-order CC models for difficult quasidegenercy problems.

The FH molecule with eight electrons correlated ($1s^2$ core is frozen) offers a different type of example as a function of $R$, although unlike BH, convergence in low-order perturbation theory is quite good. (See Table IV). However, MBPT(4) overshoots the full CI by 0.2 mhartree at $R_e$, and undershoots by 4.8 mhartree at $2R_e$. Once again at $R_e$ all the CCSDT-$n$ models provide agreement to within 0.2 mhartree, while at $1.5R_e$ the difference from full CI can be be as large as 0.7 and 1.7 mhartree at $2R_e$ where the erroneous RHF reference behavior is hard to overcome. Although the full CI is not available, we pushed the CCSDT-$n$ methods out to $3R_e$ to obtain some evidence for where RHF based CCSDT-$n$ models would fail. The simplest CCSDT-1a does appear to exceed the probable full CI value of $\sim 0.355 \pm 0.003$ by a bit, although the remaining models cluster between − 0.352 to − 0.360. This is remarkably good performance considering that MBPT(4) overshoots by $\sim 50$ mhartree. In the case of CCSDT, however, convergence was difficult at $3R_e$ due to some oscillation. The other CCSDT-$n$ models were better converged suggesting that

TABLE IV. CCSDT-$n$ correlation energies compared in full CI for HF with DZP basis at various geometries.[a]

| | $R_e$ (1.733 bohr) | $1.5R_e$ | $2.0R_e$ | $3.0R_e$ |
|---|---|---|---|---|
| SCF | − 100.047 087 | − 99.933 230 | − 99.817 571 | − 99.686 299 |
| MBPT(2) | − 0.196 078 | − 0.216 526 | − 0.239 491 | − 0.307 197 |
| CCSD | − 0.200 876 | − 0.222 066 | − 0.253 355 | − 0.335 195 |
| MBPT(4) | − 0.204 145 | − 0.226 397 | − 0.258 696 | − 0.402 989 |
| CSDT-1a | − 0.203 713 | − 0.226 676 | − 0.263 315 | − 0.36 611 |
| CCSDT-1b | − 0.203 725 | − 0.226 681 | − 0.262 972 | − 0.36 036 |
| CCSDT-2 | − 0.203 500 | − 0.226 366 | − 0.262 334 | − 0.35 818 |
| CCSDT-3 | − 0.203 492 | − 0.226 294 | − 0.261 686 | − 0.35 365 |
| CCSDT-4 | − 0.203 662 | − 0.226 643 | − 0.262 733 | − 0.35 660 |
| CCSDT | − 0.203 614 | − 0.226 479 | − 0.261 852 | − 0.35 23[c] |
| Full CI[b,d] | − 0.203 882 | − 0.227 165 | − 0.263 536 | ⋯ |

[a] Frozen core correlation energies. Basis set from Ref. 24(b).
[b] Full CI from Ref. 24(b).
[c] The energy began to oscillate during the iterative procedure.
[d] From Ref. 28, in a slightly different DZP basis whose full CI result is − 0.199 675, MBPT(5) is − 0.198 736, and the MBPT(5) + [2,1] Padé is − 0.199 142.

TABLE V. CCSDT and full CI correlation energies for $H_2O$ at equilibrium and displaced geometries using DZ and DZP bases.

| | DZ | | | DZP[c] | | |
|---|---|---|---|---|---|---|
| | $R = R_e$[a] | $R = 1.5 R_e$[b] | $R = 2.0 R_e$[b] | $R = R_e$ | $1.5 R_e$ | $2.0 R_e$ |
| SCF | − 76.009 838 | − 75.803 529 | − 75.595 180 | − 76.040 542 | − 75.800 495 | − 75.582 286 |
| CCSD | − 0.146 238 | − 0.205 402 | − 0.300 732 | − 0.211 960 | − 0.260 753 | − 0.348 579 |
| MBPT(4) | − 0.147 038 | − 0.204 865 | − 0.293 686 | − 0.215 163 | − 0.265 147 | − 0.355 123 |
| MBPT(5)[d] | − 0.147 218 | − 0.206 242 | − 0.294 019 | ··· | ··· | ··· |
| MBPT(5) + [2,1]Padé[d] | − 0.147 520 | − 0.209 026 | − 0.310 600 | ··· | ··· | ··· |
| CCSDT-1a | − 0.147 577 | − 0.209 537 | − 0.315 641 | − 0.215 486 | − 0.268 920 | − 0.372 629 |
| CCSDT-1b | − 0.147 580 | − 0.209 517 | − 0.314 160 | − 0.215 488 | − 0.268 948 | − 0.372 862 |
| CCSDT-2 | − 0.147 459 | − 0.208 938 | − 0.310 474 | − 0.215 222 | − 0.268 165 | − 0.368 968 |
| CCSDT-3 | − 0.147 450 | − 0.208 876 | − 0.309 939 | − 0.215 219 | − 0.268 114 | − 0.368 518 |
| CCSDT-4 | − 0.147 613 | − 0.209 668 | − 0.313 395 | − 0.215 624 | − 0.269 494 | − 0.374 505 |
| CCSDT | − 0.147 592 | − 0.209 470 | − 0.311 934 | − 0.215 549 | − 0.269 086 | − 0.372 154 |
| Full CI | − 0.148 028 | − 0.210 992 | − 0.310 066 | − 0.216 082 | − 0.270 911 | − 0.369 983 |

[a] Geometry and CI result from Ref. 24(e).
[b] Geometries and CI results from Ref. 24(d).
[c] Frozen core correlation energies. Basis set and full CI results from Ref. 24(b).
[d] MBPT(5) + [2,1] Padé results are from Ref. 28.

higher-order, nonlinear terms that involve $T_3$ suffer from the increasing magnitude of certain of the $T_1$ and $T_2$ amplitudes that involve the HOMO–LUMO orbitals.

For $H_2O$ we report results for both DZ and DZP bases as a function of the symmetric stretch of the two O–H bonds. (See Table V.) Since two bonds are stretched simultaneously, this is a more difficult example for an RHF single-reference based method than the BH and FH examples, as emphasized by the error in MBPT(4) at $2R_e$ being three times as great for $H_2O$ as for FH. Once again at $R_e$ the agreement of all CCSDT-$n$ models with full CI fall within 0.6 and 0.9 mhartree in the DZ and DZP bases, respectively; at $1.5R_e$, the error becomes as great as 2.7 mhartree (CCSDT-3), although CCSDT is somewhat better in both cases (1.5 and 1.8 mhartree). At $2R_e$, the inability of the simplest CCSDT-1 models to avoid exceeding the correlation energy becomes evident, although the model works better in the larger DZP basis set ( − 2.6 compared to − 5.6 mhartree). Once the $\{V_N T_2^2\}$ term is added to CCSDT-1 to define CCSDT-2 the overestimate is largely corrected, although the inclusion of $\{\widetilde{V_N T_3}\}$ in CCSDT-4 and CCSDT once again causes a small

overestimate. As is usually the case, the nonlinear terms in CC theory raise the energy while each new term linear in $T$ tends to make it lower. At $2R_e$ the full CCSDT has an error of 1.8 mhartree in the DZ basis and 2.2 mhartree for the DZP basis. This is a measure of the energy due to all higher cluster effects beginning with $T_4$. This limit of ~2 mhartree for $T_4$ should be compared with the energy difference between CCSDT and MBPT(5) which amounts to as much as ~8 mhartree at $2.0 R_e$, where such higher excitation effects are most important.

For the Ne atom we do not have any bond breaking to test the ability of RHF based CCSDT-$n$ models to describe the nondynamical correlation effects along with the dynamical correlation, so the latter can be studied somewhat as a function of basis sets. (See Table VI.) Of course, for Ne being a ten-electron system (eight correlated) like FH, the convergence is quite good, so even MBPT(4) shows relatively good agreement. However, like FH, MBPT(4) overestimates the full CI correlation energy by − 0.9, − 0.65, − 0.56 mhartree, respectively. CCSDT, however, agrees with the full CI to nearly an order of magnitude better differ-

TABLE VI. CCSDT-$n$ correlation energies compared with full CI for neon. (Energies in a.u.)[a]

| Basis | $4s2p1d$ | $6s4p1d$ | $5s3p2d$ |
|---|---|---|---|
| SCF | − 128.522 354 | − 128.543 823 | − 128.524 013 |
| MBPT(2) | − 0.174 539 | − 0.220 236 | − 0.240 859 |
| CCSD | − 0.177 966 | − 0.221 190 | − 0.241 310 |
| MBPT(4) | − 0.180 981 | − 0.224 716 | − 0.245 427 |
| CCSDT-1a | − 0.180 335 | − 0.224 161 | − 0.244 924 |
| CCSDT-1b | − 0.180 349 | − 0.224 166 | − 0.244 928 |
| CCSDT-2 | − 0.180 140 | − 0.223 896 | − 0.244 647 |
| CCSDT-3 | − 0.180 130 | − 0.223 909 | − 0.244 652 |
| CCSDT-4 | − 0.180 196 | − 0.223 974 | − 0.244 815 |
| CCSDT | − 0.180 174 | − 0.223 947 | − 0.244 788 |
| Full CI[b] | − 0.180 108 | − 0.224 065 | − 0.244 864 |

[a] Frozen core correlation energies. Basis sets as in Ref. 24(a).
[b] Full CI results from Ref. 24(a).

TABLE VII. CCSDT-$n$ correlation energies compared with full CI for fluoride.[a]

| Basis | $4s3p1d$ | $4s3p2d$ | $5s4p2d$ |
|---|---|---|---|
| SCF | − 99.442 848 | − 99.442 848 | − 99.443 696 |
| MBPT(2) | − 0.208 035 | − 0.232 449 | − 0.262 405 |
| CCSD | − 0.205 763 | − 0.229 022 | − 0.255 279 |
| MBPT(4) | − 0.215 241 | − 0.239 872 | − 0.268 392 |
| CCSDT-1a | − 0.211 601 | − 0.235 965 | − 0.264 201 |
| CCSDT-1b | − 0.211 624 | − 0.235 989 | − 0.264 223 |
| CCSDT-2 | − 0.210 724 | − 0.235 019 | − 0.263 021 |
| CCSDT-3 | − 0.210 882 | − 0.235 154 | − 0.263 192 |
| CCSDT-4 | − 0.210 323 | − 0.234 696 | − 0.262 913 |
| CCSDT | − 0.210 070 | − 0.234 353 | − 0.262 663 |
| Full CI[b] | − 0.210 493 | − 0.234 828 | − 0.262 994 |

[a] Frozen core correlation energies. Basis sets from Ref. 24(a).
[b] Full CI from Ref. 24(a).

TABLE VIII. Correlation energies for CO (DZ and DZ + P basis sets) and $C_2H_2$ (DZ + P basis set) using various CCSDT models.[a] (Energies in hartrees).

| | CO(DZ) | CO(DZ + P) | $C_2H_2$(DZ + P) |
|---|---|---|---|
| SCF | − 112.685 039 | − 112.760 093 | − 76.831 819 |
| CCSD | − 0.201 060 | − 0.295 297 | − 0.269 079 |
| MBPT(4) | − 0.215 881 | − 0.307 655 | − 0.279 914 |
| CCSDT-1a | − 0.210 553 | − 0.304 907 | − 0.280 898 |
| CCSDT-1b | − 0.210 505 | − 0.304 897 | − 0.280 902 |
| CCSDT-2 | − 0.209 183 | − 0.303 564 | − 0.279 860 |
| CCSDT-3 | − 0.209 140 | − 0.303 593 | − 0.279 862 |
| CCSDT-4 | − 0.209 487 | − 0.304 511 | − 0.281 350 |
| CCSDT | − 0.209 144 | − 0.303 981 | − 0.280 943 |

[a] Valence correlation energies. The inner shell orbitals are frozen and the corresponding virtual orbitals are dropped. Geometries and basis sets from Ref. 22.

TABLE IX. Mean error of correlation energies for CC/MBPT models that include triple excitations compared to full CI and CCSD (kcal/mol).

| | | Molecules [FH, BH, $H_2O$(DZ), $H_2O$(DZP)] | | |
|---|---|---|---|---|
| | Atoms | | | |
| Method | Ne, $F^-$ | $R_e$ | $1.5 R_e$ | $2.0 R_e$ |
| CCSD | 2.64 | 1.68 | 4.54 | 9.39 |
| MBPT(4) | 1.81 | 1.13 | 3.12 | 7.75 |
| MBPT(5)[a] | ⋯ | 0.89 | 2.53 | 6.93 |
| MBPT(5) + [2,1]Padé[a] | ⋯ | 0.28 | 0.66 | 0.82 |
| CCSD + T(CCSD) | 0.40 | 0.22 | 0.42 | 3.18 |
| CCSDT-1a | 0.40 | 0.26 | 0.71 | 1.43 |
| CCSDT-1b | 0.41 | 0.26 | 0.71 | 1.33 |
| CCSDT-2 | 0.09 | 0.36 | 0.98 | 0.56 |
| CCSDT-3 | 0.13 | 0.36 | 1.09 | 0.70 |
| CCSDT-4 | 0.06 | 0.17 | 0.53 | 1.44 |
| CCSDT | 0.15 | 0.20 | 0.64 | 0.90 |

[a] Results taken from Ref. 28 and recent computations in our laboratory. $H_2O$(DZP) is excluded, and only results for HF at $R_e$ in a different DZP basis are available (see footnote d in Table IV).

ing by only −0.06, + 0.11, + 0.08 mhartree. Once again, the linearized triple CCSDT-1 models tend to exceed the correlation energy, but only very slightly.

The convergence behavior for the isoelectronic but more diffuse $F^-$ has some important differences from Ne. (See Table VII.) Once again MBPT(4) overshoots the basis set limit correlation energy, but now by rather a large amount, − 4.7, − 5.0, and − 5.4 mhartree. Any of the CCSDT-$n$ models tend to correct this behavior, with CCSDT once again agreeing with the full CI to fractions of a mhartree for all bases (0.5, 0.5, and 0.3 mhartree).

Since triple excitations are typically more important for multiple bonded molecules, we report results for acetylene and carbon monoxide. In a DZP basis, the fourth-order triples are 11 and 12 mhartree, respectively; while in the other examples, the triples are only ∼ 1 to 3 mhartree except when bonds are stretched, where for $H_2O$ at $2R_e$ they can be as great as 12 mhartree. The triples in CO cause MBPT(4) to be significantly lower than any of the CCSDT-$n$ models that include triples iteratively. (See Table VIII.) No full CI is available for these examples, but perhaps some general features of the various CCSDT-$n$ models can be observed.

Our general rule is that linear terms lower the correlation energy while nonlinear terms act in the other direction. Typically, as in practically all examples, CCSDT-1b > CCSDT-1a since the latter adds in the nonlinear $\{V_N T_1 T_3\}$ contribution to $T_2$. Also, CCSDT-2 > CCSDT-1a,b since the $\{V_N T_2^2\}$ contribution to $T_3$ contributes positively, while the additional, but higher-order nonlinear terms arising from $T_1$ and $T_2$ that contribute to $T_3$ and are contained in the CCSDT-3 model, fail to make much difference in this example. For most cases, CCSDT-3 > CCSDT-2, attesting to the fact that the additional nonlinear $\{V_N T_1 T_2\}$, $\{V_N T_1^2 T_2\}$, $\{V_N T_2^2 T_1\}$, and $\{V_N T_1^3 T_2/3!\}$ terms definitely contribute in the opposite direction. Since CCSDT-4 < CCSDT-2, the (initially) fifth-order $\{V_N T_3\}$ negative term would appear to be greater than the fifth-order positive $\{V_N T_2^2\}$ contribution. This is particularly evident for $C_2H_2$ where CCSDT-4 is appreciably lower than CCSDT-1a, and which is one of only two such examples for any of our results. This might suggest the obvious, that when triple excitations are especially important in fourth order, they will remain

comparatively important in fifth order, as well. Yet, the triples are equally important in CO as in $C_2H_2$, and we do not find this behavior. However, for CO unlike $C_2H_2$, the MBPT(4) energy is much lower than CCSDT-4, giving a different distribution of the correlation energy. For the $H_2O$ DZP example at $2 R_e$, the fourth-order triples are also large and, at least in the DZP basis, we have the same behavior as for $C_2H_2$ with CCSDT-4 < CCSDT-1. Of course, CCSDT > CCSDT-4 because of the additional nonlinear terms that include $T_3$.

Although timings for the initial version of our CCSDT code are not entirely appropriate, since some obvious improvements have yet to be made, some indicative comparisons can be offered. For BH at $2 R_e$ with 21 functions, the MBPT(4) calculation on our FPS 164 requires 21 s, while converging CCSD to $10^{-7}$ a.u., which is comparatively slowly convergent at the stretched geometry taking 16 iterations, requires 90 s, while CCSDT-1 requires an additional 285 s. Starting from CCSDT-1 solutions, CCSDT-2 requires 316 s, and CCSDT-3, 270 s. CCSDT-4 and full CCSDT take about 1200 s. For comparison, the full CI for BH on the same machine takes about 18 000 s. For the larger $C_2H_2$ example, with 42 functions, MBPT(4) requires 167 s, CCSDT-1, 2400 s, and the full CCSDT, 9176 s. With a little additional effort at tuning the code to the FPS, we expect to gain substantially over these CCSDT timings; while explicit use of spatial symmetry would have even greater prospects for time savings.[30]

We present a summary of all the above results that can be compared to full CI in Table IX, along with our CCSD + T(CCSD) model that is much faster than any of the CCSDT-$n$ models, since it offers a noniterative inclusion of triples.[22] Although CC theory offers dramatic improvements over MBPT(4), there is really little to choose among the CCSDT-$n$ models. The full CCSDT model provides results in agreement with full CI to a mean error of less than 1 kcal/mol error at bond lengths stretched to $2 R_e$. At $R_e$ all CCSDT-$n$ results are nearly identical, while there is some

slight deterioration compared to the CCSDT reference, but only $\sim 0.5$ kcal/mol.

Also for comparison, we report a few MBPT(5) results. Low-order interations of the CCSDT equations provide all of MBPT(5) except the diagrams arising from connected $T_4$ terms. The latter, however, have been shown to be amendable to computation with only an $\sim n^6$ procedure,[25] which should require negligible computer time compared to $\sim n^8$ steps involving the contribution of $T_3$ into $T_3$. As shown and discussed more fully elsewhere,[28] MBPT(5) is not that much of an improvement over MBPT(4), except once MBPT(5) is obtained, the [2,1] Padé approximant,

$$(E_2,E_3) \begin{pmatrix} E_2 - E_3 & E_3 - E_4 \\ E_3 - E_4 & E_4 - E_5 \end{pmatrix}^{-1} \begin{pmatrix} E_2 \\ E_3 \end{pmatrix},$$

which is dependent on $E_5$ may be constructed.[34] The latter preserves the size extension of the MBPT method.[28] With this Padé extrapolation, at least for the few small basis examples shown, the results seem to be quite good as well; but in the absence of polarization functions, high-order MBPT may diverge or only converge asymptotically.[35] From MBPT(4) the [1,1] approximant may be constructed, but this offers little improvement over the MBPT(4) results themselves.[28] Typically, the $[N,N-1]$ approximants are more stable and reliable than the $[N,N]$ terms, perhaps due to the next odd order of perturbation theory always introducing the same categories of excitations as the preceding even-ordered terms, suggesting more of a geometric series dependence.

We might tend to conclude from most of these comparatively small examples that CCSDT-1a or even CCSD + T(CCSD)[33] is sufficiently close to the full CI for most purposes. However, we must recognize that for other, larger molecules where correlation is likely to be quantitatively different: i.e., transition metal systems where extensive nondynamical correlation is likely to be important; or perhaps delocalized, aromatic systems, where higher clusters may be essential; or correlation effects at transition states; plus numerous other examples that we will want to study in the future, the distinction between the full CCSDT model and its simpler approximations may become essential. Also, multireference methods offer potential improvements for examples where nondynamical correlation is particularly important.[24(b),36,37] Yet for problems that benefit from the simplicity and unambiguous use of single reference functions, the fact that CCSDT reproduces the full CI to within 1 kcal/mol for even simple systems, plus the fact that it is the most rigorous, practical single-reference correlated approach available, provides confidence in applying it to chemically interesting molecules.

## ACKNOWLEDGMENT

[1] F. Coester, Nucl. Phys. 1, 421 (1958); F. Coester and H. Kümmel, ibid. 17, 477 (1960).

[2] R. J. Bartlett, Annu. Rev. Phys. Chem. 32, 359 (1981); R. J. Bartlett, C. E. Dykstra, and J. Paldus, in Advanced Theories and Computational Approaches to the Electronic Structure of Molecules, edited by C. E. Dykstra (Reidel, Dordrecht, 1984), p. 127.

[3] J. Hubbard, Proc. R. Soc. London Ser. A 240, 539 (1957); 243, 336 (1958).

[4] R. K. Nesbet, Phys. Rev. 175, 2 (1968); Adv. Chem. Phys. 14, 1 (1969).

[5] O. Sinanoglu, J. Chem. Phys. 36, 706 (1962); Adv. Chem. Phys. 6, 35 (1964).

[6] J. Čížek, J. Chem. Phys. 45, 4256 (1966); Adv. Chem. Phys. 14, 35 (1969).

[7] (a) J. Paldus and J. Čížek, in Energy, Structure, and Reactivity, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1973); (b) J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A 5, 50 (1972).

[8] R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. 14, 561 (1978); Phys. Scr. 21, 251 (1980).

[9] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. 14, 545 (1978).

[10] R. J. Bartlett, I. Shavitt, and G. D. Purvis, J. Chem. Phys. 71, 281 (1979).

[11] S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. 8, 61 (1974).

[12] R. Ahrlichs, P. Scharf, and C. Ehrhardt, J. Chem. Phys. 82, 890 (1985).

[13] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 76, 7918 (1982).

[14] R. A. Chiles and C. E. Dykstra, J. Chem. Phys. 74, 4544 (1981).

[15] W. D. Laidig, G. D. Purvis, and R. J. Bartlett, J. Phys. Chem. 89, 2161 (1985); Int. J. Quantum Chem. Symp. 16, 561 (1982).

[16] E. A. Salter, H. Sekino, and R. J. Bartlett, J. Chem. Phys. (in press).

[17] M. Rittby and R. J. Bartlett (to be published).

[18] (a) M. J. Frisch, R. Krishnan, and J. A. Pople, Chem. Phys. Lett. 75, 66 (1980); R. Krishnan, M. J. Frisch, and J. A. Pople, J. Chem. Phys. 72, 4244 (1980); (b) M. F. Guest and S. Wilson, Chem. Phys. Lett. 73, 607 (1980); (c) R. J. Bartlett, H. Sekino, and G. D. Purvis, ibid. 98, 66 (1983); (d) M. Urban, J. Noga, and V. Kellö, Theor. Chim. Acta 62, 549 (1983); (e) V. Kvasnička, V. Laurinc, and S. Biskupic, Chem. Phys. Lett. 73, 81 (1979).

[19] (a) V. Kvasnička, Phys. Rev. A 25, 671 (1982); (b) V. Kvasnička, V. Laurinc, and S. Biskupic, Phys. Rep. 90, 159 (1982).

[20] (a) Y. S. Lee and R. J. Bartlett, J. Chem. Phys. 80, 4371 (1984); (b) Y. S. Lee, S. A. Kucharski, and R. J. Bartlett, ibid. 81, 5906 (1984); 82, 5761 (E) (1985).

[21] (a) S. J. Cole and R. J. Bartlett, Chem. Phys. Lett. 113, 271 (1985); (b) D. M. Magers, R. J. Harrison, and R. J. Bartlett, J. Chem. Phys. 84, 3284 (1986).

[22] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. 83, 4041 (1985); 85 5383 (E) (1986).

[23] J. Noga, R. J. Bartlett, and M. Urban, Chem. Phys. Lett. 134, 126 (1987).

[24] (a) C. W. Bauschlicher, Jr., S. R. Langhoff, P. R. Taylor, and H. Partridge, Chem. Phys. Lett. 126, 436 (1986); (b) C. W. Bauschlicher, Jr. and P. R. Taylor, J. Chem. Phys. 85, 2779 (1986); (c) C. W. Bauschlicher, Jr., S. R. Langhoff, P. R. Taylor, N. C. Handy, and P. J. Knowles, ibid. 85 1469 (1986); (d) R. J. Harrison and N. C. Handy, Chem. Phys. Lett. 95, 386 (1983); (e) P. Saxe, H. F. Schaefer III, and N. C. Handy, ibid. 79, 202 (1981).

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

[26] J. Paldus and J. Čížek, Adv. Quantum Chem. 9, 105 (1975).

[27] G. Fitzgerald, R. J. Harrison, and R. J. Bartlett, J. Chem. Phys. 85, 5143 (1986).

[28] W. D. Laidig, G. Fitzgerald, and R. J. Bartlett, Chem. Phys. Lett. 113, 151 (1985).

[29] (a) J. Paldus, J. Chem. Phys. 67, 303 (1977); (b) B. G. Adams and J. Paldus, Phys. Rev. A 20, 1 (1979); (c) M. Urban, V. Kellö, I. Cernusak, and J. Noga, in Methods of Computational Chemistry, Vol. I, edited by S. Wilson (Plenum, London, in press).

[30] (a) J. Noga, Comput. Phys. Commun. 29, 117 (1984); (b) P. Carsky, B. A. Hess, Jr., L. J. Schaad, M. Urban, and J. Noga, J. Chem. Phys. (submitted).

[31] S. Zarrabian and R. J. Bartlett (to be published).

[32] R. J. Bartlett and D. M. Silver, J. Chem. Phys. 62, 3258 (1975).

[33] S. J. Cole and R. J. Bartlett, J. Chem. Phys. 86, 873 (1987).

[34] R. J. Bartlett and E. J. Brandas, J. Chem. Phys. 56, 5467 (1972); 59, 2032 (1973).

[35] N. C. Handy, P. J. Knowles, and K. Somasundram, Theor. Chim. Acta 68, 87 (1985).

[36] (a) H. Lischka, R. Shepard, F. B. Brown, and I. Shavitt, Int. J. Quantum Chem. Symp. 15, 91 (1981); (b) B. Jonsson, B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, J. Chem. Phys. 74, 4566 (1981).

[37](a) D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. **30**, 1861 (1975); **33**, 955 (1977); (b) I. Lindgren, Int. J. Quantum Chem. **12**, 33 (1978); (c) B. Jeziorski and H. Monhkhorst, Phys. Rev. A **24**, 1668 (1981); (d) A. Banerjee and J. Simons, Int. J. Quantum Chem. **19**, 207 (1981); (e) J. Paldus, *New Horizons in Quantum Chemistry* (Reidel, Dordrecht, 1983), pp. 31–60; (f) W. D. Laidig and R. J. Bartlett, Chem. Phys. Lett. **104**, 424 (1984); (g) H. Baker and M. A. Robb, Mol. Phys. **50**, 20 (1983); (h) K. Tanaka and H. Terashima, Chem. Phys. Lett. **106**, 558 (1984); (i) W. D. Laidig, P. Saxe, and R. J. Bartlett, J. Chem. Phys. **86**, 887 (1987).