

TOWARDS A FULL CCSDT MODEL FOR ELECTRON CORRELATION. CCSDT-*n* MODELS[☆]Jozef NOGA¹, Rodney J. BARTLETT²*Quantum Theory Project, University of Florida, Gainesville, FL 32611, USA*

and

Miroslav URBAN

Department of Physical Chemistry, Comenius University, Mlynská dolina, 84215 Bratislava, Czechoslovakia

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The first numerical results using two extended coupled cluster models that include triple excitations, CCSDT-2 and CCSDT-3, are reported and compared to full CI for several systems. These methods are shown to be superior to CCSDT-1 when the reference function is poor, such as in bond breaking cases. The errors compared to full CI vary from 0.1 to 1.2 kcal/mol.

1. Introduction

Undoubtedly, during the last decade the coupled cluster (CC) method [1–8] has proven to be a very powerful approach for the calculation of the electron correlation energy. This is largely due to two attractive features: correct scaling with molecular size (i.e. size extensivity) and the convenient inclusion of many effects of higher excitations. The method is based upon the exponential ansatz of Coester and Kümmel [1] in which the exact wavefunction is given by the action of an exponential excitation operator $\exp(T)$ onto a reference wavefunction,

$$|\Psi\rangle = \exp(T)|\Phi\rangle, \quad (1)$$

where T is a sum of all possible l -fold excitation operators,

$$T_l = \sum t_{ijk\dots}^{abc\dots} a^+i b^+j c^+k \dots \quad (2)$$

In practice, so far only one-, two- and three-particle excitation operators have been considered in T [7–13]. Despite this, many higher excitation effects are included in the wavefunction expansion due to the so-called “disconnected” but “linked” diagram clusters appearing in the expansion of $\exp(T)$ as products of various T_l . According to the level of excitation operator chosen, one arrives at the hierarchy of CC methods. When $T = T_2$, we obtain CCD [2–4]; for $T = T_1 + T_2$, CCSD [9]; and various CCSDT- n models ($T = T_1 + T_2 + T_3$) which differ in the degree of evaluation of the T_3 amplitudes [10–12]. Using the intermediate normalization, the energy and matrix elements of the operator T can be obtained by projecting the Schrödinger equation onto the reference determinant and excited substituted determinants, respectively,

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¹ Permanent address: Institute of Inorganic Chemistry, Slovak Academy of Sciences, 84236 Bratislava, Czechoslovakia.

² Guggenheim Fellow. To whom correspondence should be addressed.

$$\Delta E = \langle \Phi | (H_N \exp(T)) | \Phi \rangle_C, \quad (3)$$

$$\langle \Phi_{ijk\dots}^{abc\dots} | (H_N \exp(T)) | \Phi \rangle_C = 0, \quad (4)$$

where H_N is the normal product form of the Hamiltonian and C means that only connected diagrams have to be included in accordance with the connected and linked diagram theorems.

The general scheme for obtaining the explicit form of the CC equations was proposed twenty years ago by Čížek [2], and the first ab initio calculations for a small molecular system BH_3 , with a minimal basis set, were performed by Paldus et al. [13], including some considerations of T_1 and T_3 contributions. However, a minimum basis set is incapable of providing very meaningful estimates of the magnitude of the importance of different cluster operators. Large scale general purpose computer programs for the original Čížek's CPMET (i.e. CCD) method were initially implemented by Bartlett and Purvis [4] and by Pople et al. [14]. The first computations of potential energy surfaces were reported by Bartlett et al. [15], and Purvis and Bartlett [16]. These CC codes permit the use of different orbitals for different spins, allowing the use of UHF functions for open-shell and bond-breaking problems.

The system of coupled equations derived from eq. (4), which we solve iteratively in an integral driven form, uses either Padé approximants [17], the reduced linear equation method [18], or a Newton–Raphson method [3] to accelerate the convergence. Another computational approach, termed the coefficient matrix procedure and restricted to closed shells, has been applied to the CCD equations by Chiles and Dykstra [19]. In addition, the use of molecular symmetry can drastically improve the computational efficiency [20,21] for cases of high symmetry.

From ref. [12], but particularly after fourth-order MBPT results had appeared, it was apparent that the effect of other connected T operators besides T_2 were far from negligible, even for small molecular systems [6,7]. The CCD model was first extended so that the single excitation operator T_1 was included exactly. This CCSD method was programmed for large scale computations by Purvis and Bartlett [9]. The proper inclusion of the T_1 operator permits the use of non-Hartree–Fock reference functions of wide variety [22]. CCSD also accounts for disconnected triples ($T_1 T_2$ and $T_1^3/3!$), quadruples ($T_1^4/4!$ and $T_2 T_1^2/2$), and other higher excitations like $T_1 T_2^2/2$, etc., but it is known from the order-by-order perturbation analysis of MBPT that for Hartree–Fock reference cases the connected triple excitations generated by T_3 are of greater importance. This is in contrast to the case of quadruple excitations, where “disconnected” $T_2^2/2!$ terms constitute the dominant (i.e. fourth-order) contributions [13]. The importance of connected triples has since been confirmed by numerous applications [23–27]. Thus the next logical and required step in the improvement of the single-reference CC method is the inclusion of the “connected” triple excitation operator into T .

The inclusion of triple excitations is not a simple task, however, since the CCSDT equations contain summations over as many as eight indices (i.e. $\approx n_{\text{occ}}^3 n_{\text{virt}}^5$) which cannot be reduced further without approximation. At present, it is clear that such calculations would become prohibitive for larger molecular systems. Fortunately, the dominant part of the T_3 amplitudes arises from the lowest-order contribution due to T_2 clusters. If we define $H_N = H_N^0 + V_N$, then $D_3 T_3 = \{\overline{V_N T_2}\}$, where D_3 is the triple excitation denominator and $\{\overline{V_N T_2}\}$ indicates fully contracted products among the normal ordered operators [11]. In turn, we evaluate a new contribution to T_2 via $D_2 T_2 = \{\overline{V_N T_3}\}$ and iterate with all other terms to convergence. The non-Hartree–Fock case requires that off-diagonal Fock matrix elements be retained in V_N as well. Such a calculation contains two steps involving summations through seven indices, and avoids any need to store any t_{ijk}^{abc} amplitudes, which is another important simplification. The implementation of the method to include this dominant part of T_3 (CCSDT-1a) was accomplished by Lee, Kucharski and Bartlett [10,11]. It is correct through fourth order in the MBPT energy and second order in the MBPT wavefunction.

Results for several examples show that CCSDT-1a is an excellent approximation to full CI (at least for small systems) when it is applied at equilibrium geometries. Slightly poorer results are obtained for stretched geometries [28] when using a restricted Hartree–Fock reference function that is separating incorrectly. In the previous paper

of this series [12], hereafter referred to as I, we proposed further improvements of the existing CC models which are only slightly more expensive than the CCSDT-1a, but account for many contributions to T_3 amplitudes which come from disconnected clusters. They may be important particularly when the pertinent system is not at the minimum of the potential energy surface, in calculations with localized orbitals [22], or other demanding examples. CCSDT-1b introduces contributions of $T_1 T_3$ to the T_2 amplitudes in addition to all terms in CCSDT-1a, while the CCSDT-2 and CCSDT-3 equations have never been previously evaluated.

In the present paper we report the first results with the CCSDT-2 and CCSDT-3 models defined in I. In contrast to CCSDT-1, in these extended models in the calculation of the T_3 amplitudes, $\exp(T)$ is approximated by the full exponentials, $\exp(T_2)$ and $\exp(T_1 + T_2)$, respectively. This still preserves the main attractive feature of the CCSDT-1 method, namely that the $\approx n_{\text{occ}}^3 n_{\text{virt}}^3$ T_3 amplitudes need not be stored from iteration to iteration, but introduces many extensive non-linear effects on T_3 of which $T_2^2/2$ might be expected to be the most important.

Note that as long as entire linked diagrams are evaluated, any such approximate contribution of T_3 is size-extensive. Furthermore, as long as the off-diagonal Fock matrix elements are introduced, any linked diagram approximation to the CC equation is invariant to transformations among just occupied or unoccupied orbitals, just as the full CCSDT equations would be.

2. CCSDT-2 and CCSDT-3 methods – the practical implementation

The complete CCSDT equations for the T_3 amplitudes were given in ref. [11] in a form in which there was a one-to-one correspondence between the formulae and diagrams. Their practical implementation requires reorganization of these basic formulae following established procedures previously used in the CCD and CCSD [4,5,9] cases, by defining the use of effective intermediate interactions. For the spin free formulation, the CCSDT-2 intermediates are the same as used by Kvasnička et al. [5]. In fig. 1 is presented the diagrammatic formulation of the CCSDT-3 equations for the T_3 amplitudes, which is rather simple. This corresponds to the following explicit equations:

$$t_{ijk}^{abc} D_{ijk}^{abc} = \sum (-1)^p P(a/bc|k/ij) \chi(b, c, e, k) t_{ij}^{ae} - \sum (-1)^p P(c/ab|i/jk) \chi(m, c, j, k) t_{im}^{ab}, \quad (5)$$

$$\begin{aligned} \chi(b, c, e, k) = & \langle bc \| ek \rangle + \frac{1}{2} \sum f(e, k, m, n) (t_{mn}^{bc} + t_m^b t_n^c - t_n^b t_m^c) \\ & + \sum [f(b, m, e, f) t_{km}^{cf} - f(c, m, e, f) t_{km}^{bf}] \\ & - \sum [f(e, k, m, c) t_m^b - f(e, k, m, b) t_m^c] + \sum \langle bc \| ef \rangle t_k^f, \end{aligned} \quad (6)$$

$$\begin{aligned} \chi(m, c, j, k) = & \langle mc \| jk \rangle + \sum f(m, e) t_{jk}^{ec} + \frac{1}{2} \sum f(c, m, e, f) (t_{jk}^{ef} + t_j^e t_k^f - t_k^e t_j^f) \\ & + \sum [f(e, j, n, m) t_{kn}^{ce} - f(e, k, n, m) t_{jn}^{ce}] \\ & + \sum [f(m, c, e, k) t_j^e - f(m, c, e, j) t_k^e] - \sum \langle jk \| mn \rangle t_n^c, \end{aligned} \quad (7)$$

$$f(m, e) = \langle m | f | e \rangle + \sum \langle mn \| ef \rangle t_n^f, \quad (8)$$

$$f(e, k, m, n) = \langle ek \| mn \rangle + \sum \langle ef \| mn \rangle t_k^f, \quad (9)$$

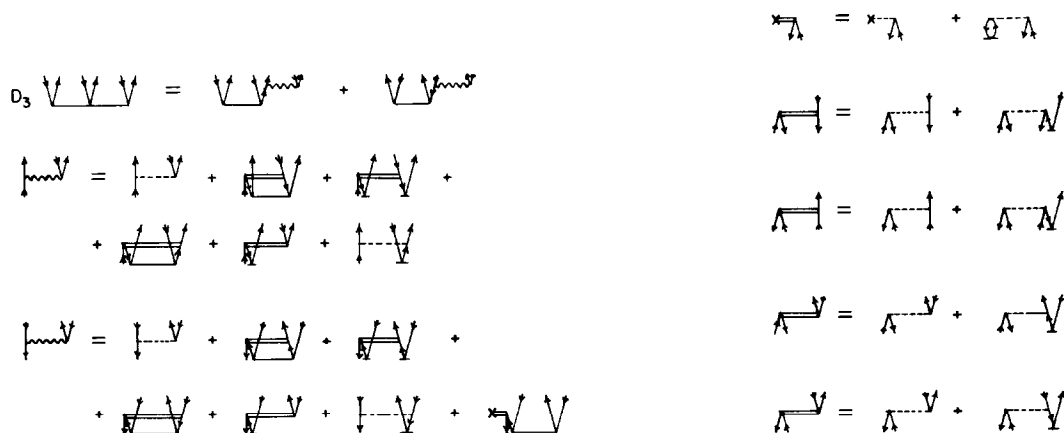


Fig. 1. Antisymmetrized effective interaction diagrams contributing to the T_3 amplitudes in CCSDT-3.

$$f(b, m, e, f) = \langle bm \| ef \rangle - \sum \langle nm \| ef \rangle t_n^b, \quad (10)$$

$$f(e, k, m, c) = \langle ek \| mc \rangle + \sum \langle ef \| mc \rangle t_k^f, \quad (11)$$

$$f(m, c, e, k) = \langle mc \| ek \rangle - \sum \langle mn \| ek \rangle t_n^c. \quad (12)$$

All summations are understood to be over common hole “ m, n ” or particle “ e, f ” indices that do not appear on the left of the expression. The inclusion of the t_i^a contributions distinguishes CCSDT-3 from CCSDT-2. In eq. (5) $P(a/bc|k/\#)$ means that the summation is performed over all nine permutations which correspond to interchanging a with b and c , and k with i and j [11]. p is the parity of the permutation, and D_{ijk}^{abc} is the usual Møller–Plesset D_3 denominator, $\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c$.

3. Results and discussion

Here we have extended most of the calculations from I. Results are given in tables 1–3. For comparison we

Table 1
CCSDT correlation energies (in hartree) compared with MBPT and full CI for BH, HF (DZ + P bases) and NH₃ (DZ basis) a)

| | BH | HF b) | NH ₃ b) |
|--------------|------------|-------------|--------------------|
| SCF | –25.125260 | –100.048009 | –56.165931 |
| SDTQ-MBPT(4) | –0.097306 | –0.200120 | –0.124761 |
| CCSDT-1a | –0.101907 | –0.199518 | –0.126235 |
| CCSDT-1b | –0.101905 | –0.199531 | –0.126231 |
| CCSDT-2 | –0.101863 | –0.199322 | –0.126113 |
| CCSDT-3 | –0.101866 | –0.199312 | –0.126111 |
| full CI c) | –0.102367 | –0.199675 | –0.126681 |

a) Geometries from ref. [29].

b) Valence correlation energy. The inner shell orbital is frozen and the corresponding virtual orbital is dropped.

c) CI results from ref. [29].

Table 2

CCSDT, MBPT(4), and full CI correlation energies (in hartree) for H₂O at equilibrium and displaced geometries in a DZ basis

| | $R = R_e$ a) | $R = 1.5 R_e$ b) | $R = 2.0 R_e$ b) |
|--------------|--------------|------------------|------------------|
| SCF | -76.009838 | -75.803529 | -75.595180 |
| SDTQ-MBPT(4) | -0.147038 | -0.204865 | -0.293686 |
| CCSDT-1a | -0.147577 | -0.209537 | -0.315641 |
| CCSDT-1b | -0.147580 | -0.209517 | -0.314160 |
| CCSDT-2 | -0.147459 | -0.208938 | -0.310474 |
| CCSDT-3 | -0.147450 | -0.208876 | -0.309939 |
| full CI | -0.148028 | -0.210992 | -0.310066 |

a) Geometry and CI result from ref. [29]. b) Geometries and CI results from ref. [30].

show as well some previous results with MBPT(4) and the CCSDT-1a and CCSDT-1b methods. In table 1 we present results for the BH, HF, and NH₃ molecular systems at equilibrium geometries containing only single bonds. For all three systems excellent agreement with full CI was already achieved at both CCSDT-1 levels.

In BH in particular, slow convergence of perturbation theory due to the quasidegeneracy of the σ and π orbitals in BH leaves the discrepancy of ≈ 5 mhartree between MBPT(4) and CCSDT-1 models. FH, on the other hand, behaves entirely differently, with MBPT(4) exceeding the full CI. As one might expect, the contribution of disconnected clusters to the T_3 amplitudes is positive, but rather negligible. This equally applies to H₂O at equilibrium geometry, as seen in table 2. Much larger, no longer negligible effects are observed when the two OH bonds are stretched, since the RHF reference function is less appropriate. Despite the fact that the agreement between the full CI and CCSDT-2 and CCSDT-3 for H₂O at $R = R_e$ and $R = 1.5 R_e$ is slightly worse than with CCSDT-1, the geometry dependence of the difference between full CI and CCSDT-2 and CCSDT-3 is significantly more stable. This feature is emphasized especially for $R = 2.0 R_e$, where CCSDT-1 significantly overshoots the full CI. The much better agreement of CCSDT-2 and CCSDT-3 is a very encouraging result, since it demonstrates the further applicability of the one-reference approach even for quasidegenerate bond breaking cases. Obviously, once one is close enough to the full CI, as seems to be the case in these examples, the poorness of the single-reference function becomes irrelevant. Hence, in many cases, CCSDT- n diminishes the need for multireference CC approaches [31]. The relative simplicity of the single determinantal approach, and its potential applicability to classes of problems such as in the solid state, where multireference approaches are not feasible, recommend its continued extension to obtain efficient algorithms.

In the full CCSDT model one should expect a negative contribution of the connected T_3 clusters to T_3 amplitudes, though in the exact CCSDT we also have other disconnected clusters containing T_3 which contribute, and they may have an opposite effect. To learn about these effects the full CCSDT results would be very useful [32]. However, algorithms to include T_3 contributions into T_3 would appear to depend upon the simultaneous storage of two lists of $\approx n_{\text{occ}}^3 n_{\text{virt}}^3 T_3$ amplitudes, placing a more severe demand on external storage.

In table 3 DZP results for molecules with triple bonds at equilibrium geometries are shown. In contrast to single-bonded systems, here we observe a relatively much larger effect of $T_2^2/2$ clusters on T_3 amplitudes. In the CC development, such disconnected clusters are responsible for approximately 0.5% of the total correlation energy versus 0.1% in single-bonded molecules (note that $T_2^2/2$ has a much greater effect if compared in terms of CI quadruple excitations since such terms are also responsible for the elimination of unlinked diagrams [15]). The absolute value of these contributions may also be of chemical significance for highly accurate predictions of molecular energies and properties.

A larger set of calculations for various types of systems for which the comparison with full CI is available will be discussed in our forthcoming paper [32], which also reports the full CCSDT results.

To conclude, let us draw attention to the difference between CCSDT-2 and CCSDT-3. In all cases shown in this

Table 3
CCSDT and MBPT(4) correlation energies (in hartree) of CO (DZ and DZ + P basis sets) and C₂H₂ (DZ + P basis set) ^{a)}

| | CO(DZ) | CO(DZ + P) | C ₂ H ₂ (DZ + P) |
|--------------|-------------|-------------|--|
| SCF | -112.685039 | -112.760093 | -76.831819 |
| SDTQ-MBPT(4) | -0.215881 | -0.307655 | -0.279914 |
| CCSDT-1a | -0.210553 | -0.304907 | -0.280898 |
| CCSDT-1b | -0.210505 | -0.304897 | -0.280902 |
| CCSDT-2 | -0.209183 | -0.303564 | -0.279860 |
| CCSDT-3 | -0.209140 | -0.303593 | -0.279862 |

^{a)} Valence correlation energies. The inner shell orbitals are frozen and the corresponding virtual orbitals are dropped. Geometries and basis sets from ref. [12].

paper (except, perhaps for H₂O at $R = 2.0 R_e$) we may observe a practically negligible contribution from other than $T_2^2/2$ clusters. One can, however, easily see from eqs. (5)–(12) that the additional cost in performing CCSDT-2 calculations when the disconnected clusters with T_2 are included is negligible in comparison with the most time consuming steps. The CCSDT-3 method is more precise from the theoretical point of view, but numerically would be expected to be more accurate only when T_1 amplitudes are large, such as in non-Hartree–Fock cases [22].

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