

A FIFTH-ORDER PERTURBATION COMPARISON OF ELECTRON CORRELATION THEORIES

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Electron correlation theories such as configuration interaction (CI), coupled-cluster theory (CC), and quadratic configuration interaction (QCI) are assessed by means of a Møller–Plesset perturbation expansion of the correlation energy up to fifth order. The computational efficiencies and relative merits of the different techniques are outlined. A new augmented version of coupled-cluster theory, denoted as CCSD(T), is proposed to remedy some of the deficiencies of previous augmented coupled-cluster models.

1. Introduction

There are several existing theoretical methods for treating the electron correlation problem starting from a Hartree–Fock (HF) single determinantal wavefunction (for a general introduction to Hartree–Fock-based methods, see ref. [1]). One of the most commonly used techniques is Møller–Plesset (MP) (or many-body) perturbation theory [2–7] which is often carried out to fourth order. Among the non-perturbative methods are configuration interaction [8–10] (CI), the coupled-cluster (CC) method [11–23], and the recently introduced quadratic configuration interaction (QCI) technique [24,25]. These all are iterative techniques which include at least some terms up to infinite order in perturbation theory. In addition, there are several augmented techniques [19,24,26] which contain an iterative procedure followed by a non-iterative treatment of the effects of high excitations.

In this paper, we compare the different correlation methods by means of a perturbation expansion of the correlation energy up to fifth order. This gives an indication of the type of effects which are neglected in the approximate schemes. Our algebraic treatment and partitioning of the terms in fifth-order per-

turbation theory is different from and complementary to the diagrammatic treatment carried out previously by Kucharski and Bartlett [7]. Only the summary of our results is given in this brief report and fuller details of our formulation including numerical comparisons will be discussed in a future publication [27].

An important aspect of any correlation scheme is the computational dependence, which determines the range of applicability of the method to interesting chemical problems. In this paper, we focus attention on the computational aspects of all the methods, distinguishing clearly between iterative and non-iterative requirements. In this context, the augmented QCI or CC treatments probably represent the best compromise between accuracy and applicability. However, our fifth-order analysis reveals a deficiency in the currently available augmented CC method [19]. We propose a new augmented method (labelled CCSD(T)) in this paper to remedy this deficiency, and report some interesting results on the asymmetric stretching frequency of ozone [28,29].

2. Correlation schemes considered

In this section, we give a brief summary of the methods considered in this paper and present the defining equations. This enables the different schemes to be compared to each other in section 3. The CI method [8] is generally performed in the configuration space of all single and double substitutions (CSID) from the HF determinant. The CISD projection equations can be written as

$$\langle \Psi_0 | H | T_2 \Psi_0 \rangle = E_{\text{corr}}, \quad (1)$$

$$\langle \Psi_i^a | \bar{H} | (T_1 + T_2) \Psi_0 \rangle = a_i^a E_{\text{corr}}, \quad (2)$$

$$\langle \Psi_{ij}^{ab} | \bar{H} | (1 + T_1 + T_2) \Psi_0 \rangle = a_{ij}^{ab} E_{\text{corr}}, \quad (3)$$

where Ψ_0 is the starting HF determinant, E_{corr} is the correlation energy, $\bar{H} = H - E_{\text{HF}}$, E_{HF} is the Hartree-Fock energy and T_1, T_2, \dots are operators which generate linear combinations of all single, double, ... substitutions ($\Psi_i^a, \Psi_{ij}^{ab}, \dots$) involving unknown coefficients $a_i^a, a_{ij}^{ab}, \dots$. As is well known [9,10], the CISD method is not size-consistent (i.e. the energy is not additive for infinitely separated systems) and an approximate size-consistency correction (Davidson correction) [10] is usually applied to the final energy.

The quadratic configuration interaction method [24] including all single and double substitutions (QCISD) is *exactly* size-consistent. The projection equations defining the QCISD method are

$$\langle \Psi_0 | H | T_2 \Psi_0 \rangle = E_{\text{corr}}, \quad (4)$$

$$\langle \Psi_i^a | \bar{H} | (T_1 + T_2 + T_1 T_2) \Psi_0 \rangle = a_i^a E_{\text{corr}}, \quad (5)$$

$$\langle \Psi_{ij}^{ab} | \bar{H} | (1 + T_1 + T_2 + \frac{1}{2} T_2^2) \Psi_0 \rangle = a_{ij}^{ab} E_{\text{corr}}. \quad (6)$$

The additional quadratic terms introduced, $T_1 T_2$ in (5) and $\frac{1}{2} T_2^2$ in (6) are responsible for restoring size-consistency to the QCISD equations.

In order to obtain quantitative accuracy, the augmented QCISD(T) procedure was also proposed [24] where the effects of triple substitutions were *evaluated once* using the *converged* amplitudes,

$\Delta E_T(\text{QCISD})$

$$= \left(2 \sum_s^S + \sum_s^D \right) \sum_t^T \sum_u^D (E_0 - E_t)^{-1} a_s V_{st} V_{tu} a_u, \quad (7)$$

where V denotes the perturbation operator. It should be noted that the triples correction formula in (7)

has contributions resulting from the interaction with *both single and double substitutions*. Previous works by Raghavachari [26] and by Urban et al. [19] have included similar corrections to coupled-cluster methods but based only on the converged doubles amplitudes.

Coupled-cluster theory [11,12] starts with an exponential form of the wavefunction $\Psi = e^T \Psi_0$ where $T = T_1 + T_2 + \dots$ and the projection equations for the CCSD method [17] can be written as

$$\langle \Psi_0 | H | (T_2 + \frac{1}{2} T_1^2) \Psi_0 \rangle = E_{\text{corr}}, \quad (8)$$

$$\langle \Psi_i^a | \bar{H} | (T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{6} T_1^3) \Psi_0 \rangle = a_i^a E_{\text{corr}}, \quad (9)$$

$$\langle \Psi_{ij}^{ab} | \bar{H} | (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{6} T_1^3 + \frac{1}{2} T_2^2 + \frac{1}{2} T_2 T_1^2 + \frac{1}{24} T_1^4) \Psi_0 \rangle = (a_{ij}^{ab} + a_i^a a_j^b - a_i^b a_j^a) E_{\text{corr}}. \quad (10)$$

In addition to the CCSD method, the equations for the full CCSDT scheme ($\Psi = e^T \Psi_0$ where $T = T_1 + T_2 + T_3$) have been implemented first by Noga and Bartlett [21] and more recently by Scuseria and Schaefer [23]. Several approximate *iterative* treatments denoted by CCSDT- n ($n = 1, 2, 3, \dots$) have also been proposed by Bartlett and coworkers [18-20] to simplify the equations to be solved. In addition, a non-iterative treatment of triples leading to the augmented method CCSD+T(CCSD) has been proposed by Urban et al. [19],

$$T(\text{CCSD}) = \sum_s^D \sum_t^T \sum_u^D (E_0 - E_t)^{-1} a_s V_{st} V_{tu} a_u \quad (11)$$

using the converged CCSD doubles amplitudes.

3. Fifth-order perturbation expansion

In Møller-Plesset theory [2], electron correlation is treated as a perturbation on the Hartree-Fock problem. The correlation terms at different orders can be considered as arising from single, double, triple, quadruple, ... substitutions from the HF determinant. The second and third orders contain contributions from only double substitutions and, as a consequence, all commonly used iterative techniques are correct to third order. The fourth- and

fifth-order correlation energy contributions can be conveniently partitioned as follows:

$$E^4 = E_S^4 + E_D^4 + E_T^4 + E_Q^4, \quad (12)$$

$$E^5 = E_{SS}^5 + E_{DD}^5 + E_{TT}^5 + E_{QQ}^5 + 2E_{SD}^5 + 2E_{ST}^5 + 2E_{DT}^5 + 2E_{DQ}^5 + 2E_{TQ}^5, \quad (13)$$

where S, D, T and Q refer to single, double, triple, and quadruple substitutions. In these expressions, the renormalization terms which occur in fourth and fifth orders have already been cancelled by parts of E_Q^4 , $2E_{DQ}^5$ and E_{QQ}^5 . Note that we have included factors of two in off-diagonal terms such as E_{SD}^5 , since there are really two equal parts E_{SD}^5 and E_{DS}^5 .

4. Computational efficiencies and relative merits

In this section, we summarize a comparison of the fifth-order terms as well as the computational requirements of each of the methods which we have discussed in this paper. In particular, we consider in detail those methods which are correct to fourth order either directly or in an augmented form. For example, it is known that the QCISD and CCSD procedures are correct to fourth order in the SDQ space [14,24] and, hence, any of the augmented or iterative QCI or CC procedures containing triples are fully correct to fourth order. The CISD method itself is not listed since it contains only the SD terms in all orders and contains no TQ terms. The other correlation techniques not considered in this paper such

as CEPA [30] or CPF [31] methods do not obtain the fourth-order TQ contributions correctly.

In table 1, we summarize the fifth-order expansions of different correlated treatments. In the first column, we have also included the computational requirements of the methods in increasing order of complexity. In this context, it is important to distinguish between the iterative and non-iterative computational requirements in methods where there is a one-off evaluation at the convergence of an iterative scheme. In addition, the fifth-order terms have been arranged in such a manner so as to motivate a perturbative consideration of the effects of higher substitutions. Thus, the terms E_{SS}^5 , $2E_{SD}^5$, and E_{DD}^5 are arranged together as a unit, the terms $2E_{ST}^5$, $2E_{DT}^5$, and $2E_{DQ}^5$ which are linear in T or Q as the next unit, and finally E_{TT}^5 , $2E_{TQ}^5$, and E_{QQ}^5 which are all quadratic in T and Q as the last unit. This partitioning is useful in considering T and Q as a perturbation to SD-based methods.

First, we consider the QCISD and CCSD methods. If n is the number of occupied orbitals and N is the number of virtual orbitals, the leading order terms ($\mathcal{O}(n^2N^4) + \mathcal{O}(n^3N^3)$) are identical for the two methods [22] and larger than that of the CISD method. However, the number of $\mathcal{O}(n^2N^3)$ terms which have to be evaluated increases progressively as we go from CISD to QCISD to CCSD. In addition, each of these methods require an iterative treatment for their solution which introduces a multiplicative factor of n_{iter} where n_{iter} is the number of iterations required for a converged solution.

The triples contributions introduce another order

Table 1
Comparison of correlation techniques in fifth order ^{a)}

Cost	Method	SS	2SD	DD	2ST	2DT	2DT	TT	2TQ	QQ
iterative N^6	QCISD	✓	✓	✓			✓			×
	CCSD	✓	✓	✓	1/2		✓		×	×
iterative N^6 + one N^7	CCSD+T(CCSD)	✓	✓	✓	1/2	✓	✓		×	×
	QCISD(T)	✓	✓	✓	✓	✓	✓			×
	CCSD(T)	✓	✓	✓	✓	✓	✓		×	×
iterative N^7	CCSDT-1	✓	✓	✓	✓	✓	✓		×	×
	CCSDT-2, 3	✓	✓	✓	✓	✓	✓		1/2	×
iterative N^8	CCSDT	✓	✓	✓	✓	✓	✓	✓	1/2	×

^{a)} ✓ indicates that the term is included fully. × indicates that the term is included only partially. 1/2 indicates that only half this term is included correctly.

of complexity but are usually necessary for quantitative accuracy [5,6]. The schemes QCISD(T) and CCSD+T(CCSD) introduce the triples in a non-iterative manner and thus the $\mathcal{O}(n^3N^4)$ term needs to be evaluated only once. The result is a method which is still practical and can be applied to reasonably large problems where such effects may be important.

The approximate CCSDT- n models all include triples contributions in an iterative manner including at least the linear terms. Therefore, all these methods require an $\mathcal{O}(n^3N^4)$ computation to be performed in each of n_{iter} iterations. This may limit the applicability of such methods in the case of larger molecules.

The complete CCSDT calculation which requires the evaluation of the TT interactions requires $\mathcal{O}(n^3N^5)$ computational steps in each iteration. Thus such a scheme is applicable to only the smallest problems of practical interest. It should be noted that the CISDT method, though not discussed in this paper, also requires $\mathcal{O}(n^3N^5)$ computational steps in each iteration resulting from the calculation of the TT interactions.

Thus, we conclude that the most widely applicable of the available size-consistent schemes which require inclusion of triple substitutions are QCISD(T) and CCSD+T(CCSD). Both methods are fully correct to fourth order and differ only slightly in fifth order. However, detailed comparison of the fifth-order components from table I shows that the QCISD(T) methods fully includes all terms *linear* in T and Q whereas the CCSD+T(CCSD) method includes only half of the contributions of the $2E_{ST}^5$ term. This is due to the fact that in the CCSD+T(CCSD) method the triples correction arises only from D whereas the QCISD(T) method includes such corrections from both S and D. This may cause an imbalance in the relative contributions of the different terms in the CCSD+T(CCSD) method in cases where the correlation effects are large.

This conclusion can also be considered in a non-perturbative manner. The basic philosophy of the QCISD and CCSD methods is to treat singles and doubles on an equal footing by considering them iteratively. Thus, calculating a triples correction from both of them as in the QCISD(T) method is quite logical and consistent with the basic iterative schemes. The fifth-order discrepancy noted for the

CCSD+T(CCSD) scheme is then the lowest-order realization of deficiencies which are present in all higher orders.

5. A new augmented coupled-cluster technique

In this section, we consider the performance of the QCISD(T) and CCSD+T(CCSD) schemes in more detail and suggest an improved augmented coupled-cluster technique. We illustrate the differences between these methods by considering the asymmetric stretching frequency of ozone which is well known to be particularly sensitive to the correlation effects included in the calculation [28,29]. Using a polarized double-zeta basis set [28], the basic QCISD and CCSD methods obtain values for this frequency [28,29] which are within 15% of experiment though the errors have opposite signs. However, after adding the triples correction, the QCISD(T) method obtains a value [29] of 934 cm^{-1} which is still in fairly good agreement with experiment (1089 cm^{-1}) [32] whereas the CCSD+T(CCSD) method yields an *imaginary* frequency [28] ($128i$ indicating an asymmetric geometry). It is clear that the T(CCSD) method is overestimating the importance of triples to the frequency.

In order to investigate the origin of this effect, we obtained the structure and asymmetric stretching frequency of ozone using an augmented QCISD method where a triples correction similar to the T(CCSD) scheme was used. This again yielded an imaginary frequency, indicating that the error in the CCSD+T(CCSD) method results from the use of an inappropriate triples correction.

This suggests a significantly improved augmented CCSD technique can be obtained by using a triples formula which results from the interaction with both singles and doubles, i.e. somewhat analogous to that used in the QCISD(T) method. We suggest a new augmented technique, termed CCSD(T), using the triples correction formula

$$\Delta E_T(\text{CCSD}) = \left(\sum_s^S + \sum_s^D \right) \sum_t^T \sum_u^D (E_0 - E_t)^{-1} a_s V_{st} V_{tu} a_u. \quad (14)$$

It may be noted that (14) differs from the triples formula (7) used in the QCISD(T) method by a factor of two in the singles term. This is due to the fact that the QCISD and CCSD procedures are themselves somewhat different and the CCSD method already contains half of the $2E_{ST}^5$ terms as evident from table 1.

The CCSD(T) procedure is now very similar to the QCISD(T) scheme. Evaluation of the asymmetric vibrational frequency of ozone with the CCSD(T) method yields a value of 977 cm^{-1} , in fairly good agreement with the experimental value of 1089 cm^{-1} and comparable to the QCISD(T) value of 933 cm^{-1} . We expect both the QCISD(T) and CCSD(T) schemes to be useful for studying electron correlation effects in molecules.

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