

**A critical analysis of the
“CCSD(T)” model for
the study of
electron correlation effects in
atoms and molecules¹**

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Abstract

A critical analysis of the CCSD(T) (“coupled cluster single and doubles with perturbative triples”) method is presented. This method is widely regarded as possibly the best balance between efficiency and accuracy. It includes an *a posteriori* perturbative correction to the CCSD method for terms associated with triply excited intermediate states which can support ‘chemical accuracy’. However, the CCSD method and the augmented theory CCSD(T) fails in the presence of quasidegeneracy. Recent work has shown that multireference methods give more accurate results in studies of systems in which some degree of quasidegeneracy is present. Nevertheless there is continued interest in extending the range of applicability of single reference augmented coupled cluster methods such as CCSD(T). Renormalized CCSD(T) theory, which is based on the method of moments coupled cluster theory, is claimed to be a promising approach which removes the pervasive failing of the standard CCSD(T) method but destroys its “extensivity” property.

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1 Introduction

Amongst contemporary methods for handling the electron correlation problem in molecular systems the augmented coupled cluster approximation designated CCSD(T) is seen to be one of the most popular. For example, in the *Encyclopedia of Computational Chemistry* published in 1998, Gauss writes[1]

“The popularity of CCSD(T) is certainly best explained by its excellent performance in terms of both accuracy and computational cost ...”

and furthermore

“It certainly can be stated that CCSD(T) currently represents the best compromise between accuracy and computational cost.”

These comments were made some five years ago and it would appear timely to reconsider the efficacy of the CCSD(T) approximation for present day applications.

The CCSD(T) theory is based on a coupled cluster expansion including single and double excitation terms in the cluster expansion developed with respect to a single reference function. The standard single reference CCSD expansion accounts for the dominant contributions to electron correlation energies for atomic and molecular systems which are well described by a single determinantal reference function. However, to achieve what is often termed ‘chemical accuracy’ of ~ 1 kcal/mol (1.6 *m*Hartree) the role of higher-than-pair clusters can no longer be ignored. Since higher order coupled cluster expansions, such as those designated CCSDT and CCSDTQ, are computationally prohibitive for routine applications, the CCSD(T) represents a tractable compromise in which the standard CCSD model is augmented by an *a posteriori* perturbative correction for the term associated with triple excitations. By 2000, Dunning and Peterson felt able to write[2]

“The coupled cluster method that includes all single and double excitations plus a perturbative estimate for triple excitations—CCSD(T)—provides unrivaled accuracy for a wide range of molecules (see the review by Lee and Scuseria[3], as well as the more recent papers of Dunning and co-workers[4], Martin and co-workers[5], Helgaker and co-workers[6], and Feller and co-workers[7]). For molecules well described by a Hartree-Fock wave function, the CCSD(T) method predicts bond dissociation energies, ionization potentials, and electron affinities to an accuracy of approximately ± 0.5 kcal/mol, bond lengths accurate to ± 0.0005 Å, and vibrational frequencies accurate to ± 5 cm^{-1} .”

The higher-than-pair clusters also have to be considered in situations where quasi-degeneracy effects are not negligible. This is invariably the case when bonds are stretched. The inclusion of higher-than-pair clusters is found to extend the range of applicability of the single reference methods.

However, the proper description of quasidegenerate (or degenerate) situations involving strongly interacting states of the same symmetry demands the use of a multireference formalism. In a recent paper, Abrams and Sherrill[8] studied bond-breaking reactions in BH, FH and CH₄. They compared multireference methods such as CISD[TQ]¹, SOCI² and CASPT2³ with the single reference CCSD(T) method and concluded that

“... the multireference methods including dynamical correlation (CISD[TQ], SOCI, CASPT2) all give more accurate results than the best standard single-reference method, UCCSD(T), even for these simple reactions.”

In earlier work[12] these authors had demonstrated that single reference methods are not very accurate for simple systems of this type even when the theory is developed with respect to an unrestricted Hartree-Fock reference. For the method designated UCCSD(T) (“unrestricted coupled cluster singles and doubles with perturbative triples”) differences of about 4 kcal/mol between the maximum and minimum errors along the potential energy curve.

In 1996, Paldus and his coworkers[13] demonstrated that the CCSD model fails to describe the dissociation of the ground state of the N₂ molecule. The CCSD theory developed with respect to a single determinantal restricted Hartree-Fock reference function yields a potential energy curve with a large and unphysical hump at intermediate stretched geometries. In discussing their results for the ground state of the N₂ molecule Paldus *et al*[13] write

“For $R > 4$ a.u., the configurational quasidegeneracy effects become too large, resulting in a breakdown of the closed-shell CCSD theory.”

¹CISD[TQ] is a multireference configuration interaction method including single and double excitations (MR-CISD) with respect to the reference functions. Specifically, the method includes all single and double substitutions from the reference set of all singly and doubly substituted configurations that can be formed in the active space[9][10].

²Second-order CI in which all possible singly and doubly substituted configurations are generated from every active space configuration formed by distributing the active electrons among the active orbitals.

³Complete active space second order perturbation theory method[11]

This failure of CCSD theory was found to be further aggravated when using the augmented theory CCSD(T). Paldus *et al*[13] found that

“It is interesting to observe the total failure of the CCSD(T) method as a result of the perturbative estimate of T_3 clusters. The CCSD(T) results for $R > 1.75R_e$ are completely out of order ...; the CCSD(T) energy curve monotonically decreases in this region. Remarkably enough, the CCSD curve exhibits only a hump in the same region.”

The development of multireference ‘many-body’ theories has commanded much attention over the past twenty-five years[14][15]. Multireference coupled cluster theories suffer from a number of shortcomings. In the study of entire potential energy curves or surfaces, different sets of strongly interacting states are encountered at different molecular geometries. This leads to the so-called ‘intruder state’ problem, a problem which has inhibited the development of practical multireference many-body theories until recently. Multireference Brillouin-Wigner methods for both coupled cluster expansions and perturbative treatments show considerable promise[16][17] since, by construction they avoid the problem of intruder states. Multireference coupled cluster methods, based on either the Fock space (“valence universal”)[18], [19], [20], [21] or Hilbert space (“state universal”)[22] variants of the cluster ansatz, have a high computational complexity and a consequential demand for computer resources.

In spite of this progress in the development of multireference methods there remains a continued interest in extending the range of applicability of the single reference augmented coupled cluster theory. This has led to the (complete) renormalized CCSD(T) method[23], the energy-corrected CCSD approach[24], and the reduced multireference CCSD theory[25][26]. Recent calculations[27], [28], [23], [29], [30], [31], [32], [33] have shown that these methods provide an improvement over the standard approaches not only for geometries close to equilibrium but also for highly stretched geometries.

In section 2 a brief overview of the coupled cluster theory is given. This not only serves as a reminder of the basic elements of the theory but also introduces some of the notation that will be used in following sections. Attention is turned to the central topic of this report the widely used CCSD(T) theory in section 3. This is followed, in section 4, by a discussion and the conclusions.

2 A brief overview of coupled cluster expansions

Coupled cluster theory, which was originally formulated by Coester and Kümmel [34], [35] for the description of nuclear matter, was first applied to the electron correlation problem in atoms and molecules by Čížek [36], [37]. The theory has been reviewed many times; see, for example, the articles by Paldus and Čížek [38], by Urban, Černušák, Kellö and Noga [39], by Paldus [40], [15], by Bartlett[41], by Paldus and Li[14], and the books by Hurley[42], by Čársky and Urban[43], by Lindgren and Morrison[44], by Szabo and Ostlund[45], by Wilson[46], and by Harris, Monkhorst and Freeman[47]. This section provides a brief overview of coupled cluster theory and serves to establish notation that will be employed in obtaining a practical implementation.

The exact non-relativistic wave function may be written

$$\Psi = \hat{\Omega}\Phi \tag{1}$$

where $\hat{\Omega}$ is the wave operator and Φ is some reference or model function. For simplicity, we shall restrict our attention to closed-shell systems described by a single determinant reference function. We adopt the convention that the indices i, j, k, \dots label occupied spin orbitals, a, b, c, \dots label unoccupied spin orbitals, and p, q, r, \dots label spin orbitals which can be either occupied or unoccupied. In the coupled cluster (CC) theory the wave operator is cast in the form

$$\hat{\Omega} = e^{\hat{T}} \quad (2)$$

or

$$\hat{\Omega} = \hat{1} + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \frac{1}{4!}\hat{T}^4 + \dots$$

where \hat{T} is the cluster operator which can be expanded in terms of excitation operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 \dots \quad (3)$$

with

$$\hat{T}_1 = \sum_i \sum_a t_i^a x_a^+ x_i \quad (4)$$

$$\hat{T}_2 = \left(\frac{1}{2!}\right) \sum_{i,j} \sum_{a,b} t_{ij}^{ab} x_a^+ x_i x_b^+ x_j \quad (5)$$

$$\hat{T}_3 = \left(\frac{1}{3!}\right) \sum_{i,j,k} \sum_{a,b,c} t_{ijk}^{abc} x_a^+ x_i x_b^+ x_j x_c^+ x_k \quad (6)$$

$$\hat{T}_4 = \left(\frac{1}{4!}\right) \sum_{i,j,k,l} \sum_{a,b,c,d} t_{ijkl}^{abcd} x_a^+ x_i x_b^+ x_j x_c^+ x_k x_d^+ x_l \quad (7)$$

...

The excitation operators are written in a second quantization formalism in terms of creation (x_p^+) and annihilation operators (x_p). The exponential ansatz in equation (2) is parametrized in terms of the amplitudes t_i^a , t_{ij}^{ab} , t_{ijk}^{abc} , ... These amplitudes are to be determined.

Approximate coupled cluster theories are obtained by truncating the expansion (3) for the cluster operator \hat{T} . Putting

$$\hat{T} \approx \hat{T}_2 \quad (8)$$

defines the method designated CCD, ‘‘coupled cluster doubles’’, whilst

$$\hat{T} \approx \hat{T}_1 + \hat{T}_2 \quad (9)$$

defines the CCSD approximation, ‘‘coupled cluster singles and doubles’’. The approximation

$$\hat{T} \approx \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \quad (10)$$

defines the CCSDT model, ‘‘coupled cluster singles, doubles and triples’’ whilst

$$\hat{T} \approx \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 \quad (11)$$

gives the CCSDTQ ansatz, ‘‘coupled cluster singles, doubles triples and quadruples’’. A sequence of approximate coupled cluster theories can thus be defined

which might be expected to support increasing accuracy. The practical application of these approximations rests upon the scaling of the associated algorithms with the number of orbitals, N . The CCSD algorithm is found to scale as the sixth power of the number of orbitals, N^6 . The CCSDT and CCSDTQ algorithms scales as the eighth (N^8) and tenth (N^{10}) power of the number of orbitals, respectively. As Gauss comments[1] this

“simply prohibits routine application”.

He continues

“The CCSD approach with a computational scaling of N^6 , thus has to be the basis for all applications of CC theory.”

A practical scheme to determine the cluster amplitudes $t_i^a, t_{ij}^{ab}, t_{ijk}^{abc}$, is obtained by assuming the exponential ansatz for the wave function (2), which implied the intermediate normalization condition

$$\langle \Phi | \Psi \rangle = 1, \quad (12)$$

and writing the exact Schrödinger equation

$$H_N |\Psi\rangle = \Delta E |\Psi\rangle \quad (13)$$

where is the electronic hamiltonian in N -product form

$$H_N = H - \langle H \rangle. \quad (14)$$

in which

$$\langle H \rangle = \langle \Phi | H | \Phi \rangle \equiv E_0.$$

H_N may be written

$$\begin{aligned} H_N &= \sum_p \varepsilon_p x_p^+ x_p + \sum_{p,q} f_p^q x_p^+ x_q + \frac{1}{4} \sum_{p,q,r,s} g_{pq}^{rs} x_p^+ x_q^+ x_s x_r \\ &= H_N^0 + F_N + G_N \end{aligned}$$

where the ε_p are the one-particle eigenenergies, F_N and G_N are the one- and two-body operators, respectively. F_N disappears when a canonical Hartree-Fock reference state is employed.

Multiplying equation (13) from the left by the inverse of the wave operator $\Omega^{-1} = e^{-\hat{T}}$ giving

$$e^{-\hat{T}} H_N e^{\hat{T}} |\Phi\rangle = \Delta E |\Phi\rangle. \quad (15)$$

Projecting equation (15) onto the reference configuration $|\Phi\rangle$ leads to the energy expression

$$\begin{aligned} \Delta E &= \langle \Phi | e^{-\hat{T}} H_N e^{\hat{T}} | \Phi \rangle \\ &\equiv \langle e^{-\hat{T}} H_N e^{\hat{T}} \rangle \\ &= \langle H_N e^{\hat{T}} \rangle_c \end{aligned} \quad (16)$$

where the subscript c indicated that only ‘connected’ terms are included. Assume that the N -electron space \mathcal{W} is partitioned by the excitation order k with respect to $|\Phi\rangle$, that is

$$\mathcal{W} = \bigoplus_{k=0}^N \mathcal{W}^{(k)} \quad (17)$$

with

$$\mathcal{W}^{(0)} = \{|\Phi\rangle\} \quad (18)$$

and

$$\mathcal{W}^{(k)} = \left\{ \left| \Phi_i^{(k)} \right\rangle \mid i = 1, 2, \dots, M_k \right\}. \quad (19)$$

Projecting equation (13) onto the manifold $\left\{ \left| \Phi_i^{(k)} \right\rangle \right\}$ spanning the orthogonal complement to the reference configuration $|\Phi\rangle$ gives the energy-independent coupled cluster equations

$$\left\langle \Phi_i^{(k)} \left| e^{-\hat{T}} H_N e^{\hat{T}} \right| \Phi \right\rangle = 0 \quad (20)$$

or

$$\left\langle \Phi_i^{(k)} \left| H_N e^{\hat{T}} \right| \Phi \right\rangle_c = 0 \quad (21)$$

where the subscript c again indicated that only ‘connected’ terms are included.

Explicitly, the closed shell CCSD equations which determine the energy E_{CCSD} ($\equiv \Delta E$) and the single and double amplitudes t_i^a and t_{ij}^{ab} have the form

$$\left\langle \Phi \left| H_N \left| \exp \left(\hat{T}_1 + \hat{T}_2 \right) \Phi \right\rangle_c \right\rangle = E_{\text{CCSD}}, \quad (22)$$

$$\left\langle \Phi_i^a \left| H_N \left| \exp \left(\hat{T}_1 + \hat{T}_2 \right) \Phi \right\rangle_c \right\rangle = 0, \quad \forall i, a \quad (23)$$

$$\left\langle \Phi_{ij}^{ab} \left| H_N \left| \exp \left(\hat{T}_1 + \hat{T}_2 \right) \Phi \right\rangle_c \right\rangle = 0, \quad \forall i > j, a > b, \quad (24)$$

where $\langle \Phi_i^a |$ is a state which is singly excited with respect to the reference state $|\Phi\rangle$ whilst $\langle \Phi_{ij}^{ab} |$ is a state which is doubly excited. Expanding the exponential occurring in equations (22)-(24) gives

$$\begin{aligned} \Omega_{\text{CCSD}} &= \exp \left(\hat{T}_1 + \hat{T}_2 \right) \\ &\equiv 1 + \left(\hat{T}_1 + \hat{T}_2 \right) + \frac{1}{2!} \left(\hat{T}_1 + \hat{T}_2 \right)^2 + \\ &\quad + \frac{1}{3!} \left(\hat{T}_1 + \hat{T}_2 \right)^3 + \frac{1}{4!} \left(\hat{T}_1 + \hat{T}_2 \right)^4 + \dots \end{aligned} \quad (25)$$

$$\begin{aligned} &= 1 + \left(\hat{T}_1 + \hat{T}_2 \right) + \left(\frac{1}{2} \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 \right) + \\ &\quad + \left(\frac{1}{6} \hat{T}_1^3 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{2} \hat{T}_1 \hat{T}_2^2 + \frac{1}{6} \hat{T}_2^3 \right) + \\ &\quad + \left(\frac{1}{24} \hat{T}_1^4 + \frac{1}{8} \hat{T}_1^3 \hat{T}_2 + \frac{1}{4} \hat{T}_1^2 \hat{T}_2^2 + \frac{1}{8} \hat{T}_1 \hat{T}_2^3 + \frac{1}{24} \hat{T}_2^4 \right) + \\ &\quad + \dots \end{aligned} \quad (26)$$

$$\begin{aligned} &= 1 + \hat{T}_1 + \left[\frac{1}{2} \hat{T}_1^2 + \hat{T}_2 \right] + \left[\frac{1}{6} \hat{T}_1^3 + \hat{T}_1 \hat{T}_2 \right] + \\ &\quad + \left[\frac{1}{24} \hat{T}_1^4 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 \right] + \dots \end{aligned} \quad (27)$$

where terms corresponding to single, double, triple and quadruple excitations are collected in [...] in (27). Substituting the expansion (27) in equations (22)-(24) and remembering that H_N contains operators involving no more than two electrons gives

$$\langle \Phi | H_N | \Omega_{\text{CCSD}}^{(2)} \Phi \rangle_c = E_{\text{CCSD}}, \quad (28)$$

$$\langle \Phi_i^a | H_N | \Omega_{\text{CCSD}}^{(3)} \Phi \rangle_c = 0, \quad \forall i, a \quad (29)$$

$$\langle \Phi_{ij}^{ab} | H_N | \Omega_{\text{CCSD}}^{(4)} \Phi \rangle_c = 0, \quad \forall i > j, a > b, \quad (30)$$

where the subscript c again denotes that only terms corresponding to connected diagrams are included and the components of the wave operator are written

$$\Omega_{\text{CCSD}}^{(2)} = 1 + \hat{T}_1 + \left[\frac{1}{2} \hat{T}_1^2 + \hat{T}_2 \right] \quad (31)$$

$$\Omega_{\text{CCSD}}^{(3)} = 1 + \hat{T}_1 + \left[\frac{1}{2} \hat{T}_1^2 + \hat{T}_2 \right] + \left[\frac{1}{6} \hat{T}_1^3 + \hat{T}_1 \hat{T}_2 \right] \quad (32)$$

$$\begin{aligned} \Omega_{\text{CCSD}}^{(4)} = & 1 + \hat{T}_1 + \left[\frac{1}{2} \hat{T}_1^2 + \hat{T}_2 \right] + \left[\frac{1}{6} \hat{T}_1^3 + \hat{T}_1 \hat{T}_2 \right] + \\ & + \left[\frac{1}{24} \hat{T}_1^4 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 \right]. \end{aligned} \quad (33)$$

Equations (28)-(33) are the basic equations of the CCSD approximations.

Writing in 1998, Gauss described[1] the availability of a number of “black box” codes for carrying out CCSD calculations

“The CCSD approach has been in recent years efficiently implemented in several program systems (ACES II, CADPAC, DALTON, GAUSSIAN, MOLCAS, MOLPRO, PSI, TITAN). In particular, vectorization[48], [49], exploitation of Abelian point-group symmetry[48], [50], and (partial) AO-based algorithms[51], [52], [53] have been used to accomplish this task. Calculations for molecules with up to ten nonhydrogenic atoms and more than 200 basis functions can nowadays be considered a routine matter.”

Dunning reviews[54] applications to chemical interactions, to hydrogen-bond interactions, to electrostatic interactions and dispersion interactions. He notes that the capability to perform such calculations “can be found in a number of quantum chemistry codes, including GAUSSIAN[55], CADPAC[56], GAMESS[57], MOLPRO[58], ACES[59] and DALTON[60].”

3 The CCSD(T) approximation

The first *ab initio* molecular electronic structure calculation using coupled cluster theory was reported by Paldus, Čížek and Shavitt[61] in 1972. These authors performed CPMET (“coupled pair many-electron theory” - equivalent to the CCD, “coupled cluster doubles”) calculations for the ground state of the BH₃ molecule using a minimum basis set. They showed that, whilst for tetraexcited clusters

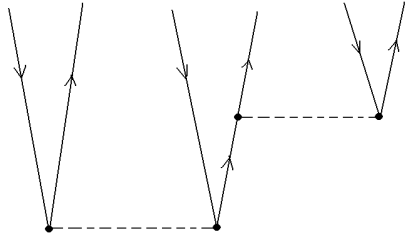


Figure 1: Second order linked diagram involving a triply excited intermediate state. [Adapted from the work of Paldus, Čížek and Shavitt [61].

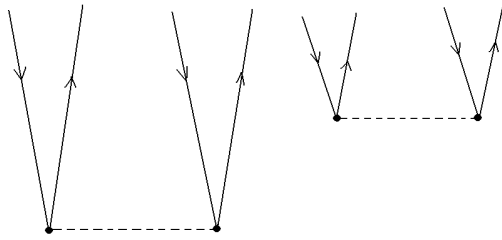


Figure 2: Second order unlinked diagram involving a quadruply excited intermediate state. [Adapted from the work of Paldus, Čížek and Shavitt [61].

the so-called unlinked clusters first contribute in second order[62] and the linked cluster terms do not occur until third order, the situation is reversed for triexcited clusters. The linked triexcited cluster first arise in second order whereas the unlinked cluster terms contribute in third order.

A typical second order diagram corresponding to a triply excited intermediate state is displayed in Figure 1. This diagram is manifestly linked. It described the creation of a doubly excited state by creating two particle-hole pairs followed by the creation of a further particle-hole pair by interaction with one of the particle lines created in the first interaction. On the other hand, the diagram shown in Figure 2, which is a second order diagram corresponding to a quadruply excited intermediate state is unlinked. It described the creation of a doubly excited state by creating two particle-hole pairs and then, without any interactions involving the original particle and hole lines, the creation of two more particle hole pairs leading to a quadruply excited intermediate state.

In third order, diagrams describing processes involving triply excited inter-

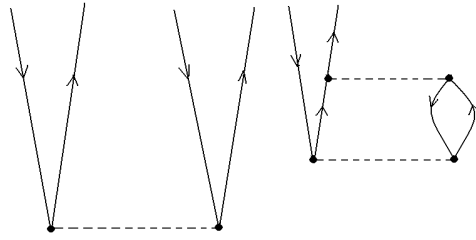


Figure 3: Third order unlinked diagram involving a triply excited intermediate state. [Adapted from the work of Paldus, Čížek and Shavitt [61].]

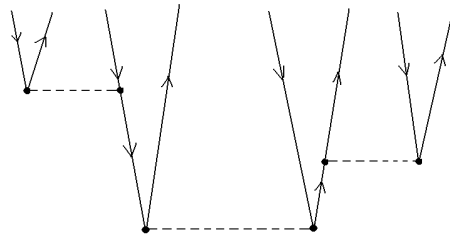


Figure 4: Third order linked diagram involving a quadruply excited intermediate state. [Adapted from the work of Paldus, Čížek and Shavitt [61].]

mediate state arise which are unlinked. An example is given in Figure 3. The left hand part of this diagram describes the creation of a doubly excited state whilst the right hand part describes the creation of a singly excited state by first creating a doubly excited state and then destroying one particle-hole pair. An example of a linked third order diagram involving a quadruply excited intermediate state is shown in Figure 4. This diagram describes the creation of a quadruple excitation beginning with a double excitation which involves the initial creation of two particle-hole pairs followed by two subsequent interactions each of which involves the creation of a particle-hole pair.

Writing in 1980, Schaefer and his coworkers open a paper[63] on “... *the importance of triply and quadruply excited electronic configurations in the water molecule*” as follows

“During the past fifteen years it has become generally accepted that for closed-shell ground state molecules with 10 or fewer electrons,

at least 90% of the electron correlation energy is included in configuration interaction treatments (CISD) involving all singly and doubly excited configurations. However, for larger systems, the importance of higher excitations of a particularly simple type, namely unlinked clusters, increases rapidly, and it has been estimated that for a molecule as small as pyrrole (36 electrons), higher than double excitations account for 20% of the correlation energy. It has also been implicitly assumed that unlinked clusters are the only type of higher excitations (triple, quadruple, ... excitations differ by three, four, ... electrons from the Hartree-Fock reference configuration) which need be considered in theoretical studies of electron correlation in molecules.”

They continue[63]

“The above view has recently been challenged by Wilson on the basis of his many-body perturbation theory (MBPT) studies of the neon atom[64] and the water molecule[65].”

In a paper entitled “*Contribution of triple substitutions to the electron correlation energy in fourth order perturbation theory*”, Krishnan, Frisch and Pople[66] write

“A general treatment of triple substitutions has been given by Wilson and Silver[67] and applied to the neon atom[64]. We have also examined the fourth-order triples energy contribution, using a somewhat different computational technique.”

They conclude

“Evidently the contributions of triple substitutions are important in accurate quantitative theories of chemical binding.”

Non-iterative *a posteriori* corrections to coupled cluster theory to account for higher order excitations employ the many-body perturbation theory expressions for a contribution of a given order substituting the fully converged amplitudes, T_1 and T_2 , for the lowest order approximations. In some instances, there may be an ambiguity in the choice of amplitude(s) to be replaced and also in the formulation employed to obtain the converged amplitudes. An analysis of the CCSD(T) model must, therefore, begin with a discussion of higher order excitations in many-body perturbation theory.

In section 3.1, fourth-order many-body perturbation theory is considered giving particular attention to the terms involving triply-excited intermediate states. Augmented coupled cluster theories are considered in section 3.2 beginning with the CCSD+T(CCSD) approximation. The CCSD(T) model takes account of certain fifth order terms in the many-body perturbation theory expansion and section 3.3 is devoted to the fifth-order energy components and a detailed analysis of those components which will later be seen to be central to the definition of the CCSD(T) model. The CCSD(T) model itself is considered in section 3.4. In section 3.5 higher order effects and augmented coupled cluster theories are briefly considered. Renormalized and completely renormalized CCSD(T) theories are considered in section 3.6.

3.1 Fourth order many-body perturbation theory

The fourth order Rayleigh-Schrödinger perturbation theory energy coefficient has the form

$$E_4 = \sum_{D_1} \sum_X \sum_{D_2} \frac{\langle \Phi | H_1 | \Phi_{D_1} \rangle \langle \Phi_{D_1} | H_1 | \Phi_X \rangle \langle \Phi_X | H_1 | \Phi_{D_2} \rangle \langle \Phi_{D_2} | H_1 | \Phi \rangle}{(E_0 - E_{D_1})(E_0 - E_X)(E_0 - E_{D_2})}$$

where Φ_{D_1} and Φ_{D_2} are states which are doubly excited with respect to the reference state Φ whilst Φ_X is a state which is singly, doubly, triply or quadruply excited with respect to Φ . E_0 is the energy corresponding to the reference state Φ ; E_{D_1} , E_X , E_{D_2} correspond to Φ_{D_1} , Φ_X , Φ_{D_2} , respectively. The fourth order energy may be written

$$E_4 = E_{4S} + E_{4D} + E_{4T} + E_{4Q}$$

each of the four terms on the right hand side being classified according to the level of excitation associated with Φ_X . The renormalization terms which arise in fourth order have been cancelled by parts of E_{4Q} . A diagrammatic analysis of these energy components shows that the fourth order energy E_4 is associated with a total of 39 Brandow diagrams for a closed-shell system described by a single determinant. 4 diagrams are associated with E_{4S} . 12 diagrams contain only doubly excited intermediate states and therefore contribute to E_{4D} . E_{4T} is the sum of contributions from 16 diagrams containing triply excited intermediate states, whilst E_{4Q} is associated with 7 energy diagrams. The energy expressions corresponding to the 16 diagrams involving triply excited intermediate states take the form

$$\begin{aligned} E_4(A_T) &= -\frac{1}{2} \sum_{ijk} \sum_{abcde} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cb | \hat{O} | ek \rangle \langle ed | \hat{O} | ij \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ij}^{de}} \\ E_4(B_T) &= -\frac{1}{2} \sum_{ijk} \sum_{abcde} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cd | \hat{O} | ej \rangle \langle eb | \hat{O} | ik \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ik}^{be}} \\ E_4(C_T) &= -\frac{1}{2} \sum_{ijklm} \sum_{abc} \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle mb | \hat{O} | kl \rangle \langle ac | \hat{O} | mj \rangle}{D_{ij}^{ab} D_{jkl}^{abc} D_{jm}^{ac}} \\ E_4(D_T) &= -\frac{1}{2} \sum_{ijklm} \sum_{abc} \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle mc | \hat{O} | kj \rangle \langle ab | \hat{O} | ml \rangle}{D_{ij}^{ab} D_{jkl}^{abc} D_{lm}^{ab}} \\ E_4(E_T) &= \sum_{ijk} \sum_{abcde} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cd | \hat{O} | ej \rangle \langle ed | \hat{O} | ik \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ik}^{de}} \\ E_4(F_T) &= \frac{1}{4} \sum_{ijk} \sum_{abcde} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cd | \hat{O} | ek \rangle \langle eb | \hat{O} | ij \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ij}^{be}} \\ E_4(G_T) &= \frac{1}{4} \sum_{ijklm} \sum_{abc} \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle mc | \hat{O} | kl \rangle \langle ab | \hat{O} | mj \rangle}{D_{ij}^{ab} D_{jkl}^{abc} D_{jm}^{ab}} \\ E_4(H_T) &= \sum_{ijklm} \sum_{abc} \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle mb | \hat{O} | kj \rangle \langle ac | \hat{O} | ml \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ij}^{de}} \end{aligned}$$

$$\begin{aligned}
E_4(I_T) &= -\frac{1}{4} \sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle lb | \hat{O} | ij \rangle \langle cd | \hat{O} | lk \rangle}{D_{ij}^{ab} D_{jkl}^{abc} D_{kl}^{cd}} \\
E_4(J_T) &= -\sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle ld | \hat{O} | ik \rangle \langle cb | \hat{O} | lj \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{jl}^{bc}} \\
E_4(K_T) &= -\sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | ic \rangle \langle ac | \hat{O} | dl \rangle \langle db | \hat{O} | kj \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{jk}^{bd}} \\
E_4(L_T) &= -\frac{1}{4} \sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ab | \hat{O} | dj \rangle \langle dc | \hat{O} | kl \rangle}{D_{ij}^{ab} D_{jkl}^{abc} D_{kl}^{cd}} \\
E_4(M_T) &= \frac{1}{2} \sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle lb | \hat{O} | ik \rangle \langle cd | \hat{O} | lj \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{ij}^{de}} \\
E_4(N_T) &= \frac{1}{2} \sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ab | \hat{O} | dl \rangle \langle dc | \hat{O} | kj \rangle}{D_{ij}^{ab} D_{jkl}^{abc} D_{jk}^{cd}} \\
E_4(O_T) &= \frac{1}{2} \sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ac | \hat{O} | dj \rangle \langle db | \hat{O} | kl \rangle}{D_{ij}^{ab} D_{jkl}^{abc} D_{kl}^{bd}} \\
E_4(P_T) &= \frac{1}{2} \sum_{ijkl} \sum_{abcd} \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle ld | \hat{O} | ij \rangle \langle cb | \hat{O} | lk \rangle}{D_{ij}^{ab} D_{ijk}^{bcd} D_{kl}^{bc}}
\end{aligned}$$

where

$$\hat{O} = \frac{I - (12)}{r_{12}}, \quad (34)$$

and r_{12} being the interelectronic distance so that

$$\begin{aligned}
\langle pq | \hat{O} | rs \rangle &= \langle pq | \frac{1}{r_{12}} | rs \rangle - \langle pq | \frac{1}{r_{12}} | sr \rangle \\
&= [pr | qs] - [ps | qr]
\end{aligned} \quad (35)$$

$$D_{ij}^{ab} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b, \quad (36)$$

is a double excitation denominator, and

$$D_{ijk}^{abc} = \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c, \quad (37)$$

where ε_p is the orbital energy for the p^{th} orbital. The direct evaluation of each of the expressions $E_4(A_T)$ - $E_4(P_T)$ involves a summation over 8 indices. Of the 16 fourth order triple excitation diagrams, 4 involve summations over 3 occupied spin orbitals and 5 unoccupied spin orbitals, 4 involve summations over 5 occupied spin orbitals and 3 unoccupied spin orbitals, and 4 involve summations over 4 occupied spin orbitals and 4 unoccupied spin orbitals. By defining the intermediates

$$f_{ijk}^{abc} = \sum_d \frac{\langle ij | \hat{O} | db \rangle \langle dk | \hat{O} | ac \rangle}{D_{ij}^{bd}}$$

and

$$g_{ijk}^{abc} = \sum_l \frac{\langle jl | \hat{O} | ba \rangle \langle ik | \hat{O} | lc \rangle}{D_{jl}^{ab}},$$

each diagrammatic term may be written in the form

$$K \sum_{ijk} \sum_{abc} \frac{\phi_{ijk}^{abc} \left\{ P(ijk) P(abc) \gamma_{ijk}^{abc} \right\}}{D_{ijk}^{abc}},$$

where ϕ_{ijk}^{abc} and γ_{ijk}^{abc} denote either an f_{ijk}^{abc} or a g_{ijk}^{abc} intermediate, K is a constant and $P(ijk)$ and $P(abc)$ are permutation operators. Specifically, the following expressions arise

$$E_4(A_T) = -\frac{1}{2} \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} f_{ijk}^{acb}}{D_{ijk}^{abc}}$$

$$E_4(B_T) = -\frac{1}{2} \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} f_{ikj}^{abc}}{D_{ijk}^{abc}}$$

$$E_4(C_T) = -\frac{1}{2} \sum_{ijk} \sum_{abc} \frac{g_{ijk}^{abc} g_{ijk}^{acb}}{D_{ijk}^{abc}}$$

$$E_4(D_T) = -\frac{1}{2} \sum_{ijk} \sum_{abc} \frac{g_{ijk}^{abc} g_{ikj}^{abc}}{D_{ijk}^{abc}}$$

$$E_4(E_T) = \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} f_{ikj}^{acb}}{D_{ijk}^{abc}}$$

$$E_4(F_T) = \frac{1}{4} \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} f_{ijk}^{abc}}{D_{ijk}^{abc}}$$

$$E_4(G_T) = \frac{1}{4} \sum_{ijk} \sum_{abc} \frac{g_{ijk}^{abc} g_{ijk}^{abc}}{D_{ijk}^{abc}}$$

$$E_4(H_T) = \sum_{ijk} \sum_{abc} \frac{g_{ijk}^{abc} g_{ikj}^{acb}}{D_{ijk}^{abc}}$$

$$E_4(I_T) = -\frac{1}{4} \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} g_{ikj}^{acb}}{D_{ijk}^{abc}}$$

$$E_4(J_T) = \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} g_{ijk}^{abc}}{D_{ijk}^{abc}}$$

$$E_4(M_T) = \frac{1}{2} \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} g_{ijk}^{acb}}{D_{ijk}^{abc}}$$

$$E_4(O_T) = \frac{1}{2} \sum_{ijk} \sum_{abc} \frac{f_{ijk}^{abc} g_{ikj}^{abc}}{D_{ijk}^{abc}}$$

$E_4(L_T)$, $E_4(K_T)$, $E_4(N_T)$, $E_4(P_T)$ are numerically equal to $E_4(I_T)$, $E_4(J_T)$, $E_4(M_T)$, $E_4(O_T)$, respectively, for real orbitals. Evaluation of the intermediates f_{ijk}^{abc} and g_{ijk}^{abc} involves a summation over a single index then determination of the individual diagrammatic terms involves a further summation over 6 indices thus forming the basis of an algorithm requiring summations over a total of 7 indices and an N^7 scaling.

The total fourth order many-body perturbation theory energy component corresponding to triply excited intermediate states may be written

$$\Delta E_t = \frac{1}{36} \sum_{ijk} \sum_{abc} D_{ijk}^{abc} |t_{ijk}^{abc}|^2 \quad (38)$$

in which the factor D_{ijk}^{abc} is given by (37) and the factor t_{ijk}^{abc} has the form where

$$t_{ijk}^{abc} = P(ijk) P(abc) \left\{ \frac{1}{D_{ijk}^{abc}} \left[\sum_e \left(\frac{1}{D_{ij}^{ae}} \langle ij | \hat{O} | ae \rangle \langle bc | \hat{O} | ek \rangle \right) - \sum_m \left(\frac{1}{D_{im}^{ae}} \langle im | \hat{O} | ab \rangle \langle mc | \hat{O} | jk \rangle \right) \right] \right\} \quad (39)$$

$P(pqr)$ is the cyclic permutation operator defined by

$$P(pqr) f(pqr) = f(pqr) + f(qrp) + f(rpq). \quad (40)$$

Goodson has shown[68] that the accuracy of fourth order many-body perturbation theory calculations can be significantly increased by using the Feenberg scaling procedure[69, 70] to repartition the hamiltonian and summing the scaled perturbation series by using quadratic Padé approximants. This approach models the known mathematical structure of the perturbation theory explicitly. Goodson[68] shows that the accuracy achieved by this approach

“is typically somewhat higher than that of CCSD(T)”

Quadratic Padé approximants were introduced by Padé in his original work[71] published in 1892. They have a functional form which allows them to describe explicitly square-root branch-point singularities (see, for example, the text by Carrier, Krook and Pearson[72]. It is only fairly recently that the mathematical properties of the quadratic Padé approximants have been studied [73], [74], [75], [76], [77]. Applications of the quadratic Padé approximants have been realized in a various areas of atomic and molecular physics[78], [79], [80], [81], [82], [83], [84], [68], [85], [86], [87], [88].

If we define three polynomials

$$P_L(\lambda) = \sum_{l=0}^L \lambda^l p_l, \quad (41)$$

$$Q_M(\lambda) = 1 + \sum_{m=1}^M \lambda^m q_m, \quad (42)$$

and

$$R_N(\lambda) = \sum_{n=0}^N \lambda^n r_n \quad (43)$$

which satisfy the equation

$$Q_M(\lambda) E^2(\lambda) - P_L(\lambda) E(\lambda) + R_N(\lambda) \sim \mathcal{O}(\lambda^{L+M+N}) \quad (44)$$

then we can solve the equation

$$Q_M(\lambda) E^2(\lambda) - P_L(\lambda) E(\lambda) + R_N(\lambda) = 0 \quad (45)$$

for $E(\lambda)$ to obtain the summation approximant

$$S_{[L/M,N]}(\lambda) = \frac{1}{2} \left[\frac{P_L(\lambda)}{Q_M(\lambda)} \pm \frac{1}{Q_M(\lambda)} \sqrt{(P_L(\lambda))^2 - 4Q_M(\lambda) R_N(\lambda)} \right] \quad (46)$$

which is termed a quadratic Padé approximant. The coefficients p_l , q_m and r_n are determined from a set of $L + M + N$ simultaneous linear equations obtained by collecting terms in (46) according to powers of λ . (46) is a multivalued approximant having two branches, which are connected by square root branch points at the roots of the discriminant polynomial

$$D_{[L/M,N]}(\lambda) = (P_L(\lambda))^2 - 4Q_M(\lambda) R_N(\lambda). \quad (47)$$

In 2000, Goodson[68] showed that the accuracy of fourth order many-body perturbation theory calculations with a Møller-Plesset zero order hamiltonian can be significantly improved by employing Feenberg scaling[69, 70] and then summing the resulting series with quadratic Padé approximants. The Feenberg scaling was carried out using the repartitioned hamiltonian

$$\mathcal{H}^{(\mu)}(\lambda) = \mu \mathcal{H}_0 + (\mathcal{H}_1 - (1 - \mu) \mathcal{H}_0) \lambda, \quad (48)$$

and the formulae

$$E_0^{(\mu)} = \mu E_0, \quad (49)$$

$$E_1^{(\mu)} = E_1 + (1 - \mu) E_0, \quad (50)$$

and

$$E_p^{(\mu)} = \frac{1}{\mu^{p-1}} \sum_{k=2}^p \binom{p-2}{k-2} (\mu-1)^{p-k} E_k, \quad p \geq 2 \quad (51)$$

relating the scaled perturbation series with the original. The quadratic Padé approximants was determined according to the scheme described above.

3.2 Augmented coupled cluster theories

In 1985, Raghavachari[89] introduced the first of the so-called augmented coupled cluster methods in which a coupled cluster expansion is supplemented by a perturbative estimate of higher order terms based on the cluster amplitudes. Specifically, Raghavachari[89] augmented the CCD model with a perturbative estimate of the energy components associated with single and with triple excitations.

In the CCSD+T(CCSD) approximation⁴ introduced by Urban et al[91], the second order MBPT amplitudes in equation (39), *i.e.*

$$\frac{1}{D_{ij}^{ae}} \langle ij | \hat{O} | ae \rangle \quad (52)$$

⁴More recently the CCSD+T(CCSD) method has been dubbed[90] CCSD[T].

and

$$\frac{1}{D_{im}^{ae}} \langle im | \hat{O} | ab \rangle \quad (53)$$

are replaced by the converged CCSD amplitudes t_{ij}^{ae} and t_{im}^{ab} . The triple excitation component of the correlation energy supported by the CCSD+T(CCSD) approximation is then given by equations (38) and (37) with t_{ijk}^{abc} defined as

$$t_{ijk}^{abc} = P(ijk) P(abc) \left\{ \frac{1}{D_{ijk}^{abc}} \left[\sum_e \left(t_{ij}^{ae} \langle bc | \hat{O} | ek \rangle \right) - \sum_m \left(t_{im}^{ab} \langle mc | \hat{O} | jk \rangle \right) \right] \right\}. \quad (54)$$

An analysis of fifth order terms led Raghavachari et al[92] to propose an augmented coupled cluster method which remedied some deficiencies of the CCSD+T(CCSD) approximation. The CCSD(T) approximation was first defined for the quadratic configuration interaction model[93] and later for the CCSD approach[92].

In 2001, Meissner and Bartlett[94] summarized the utility of the augmented CCSD methods CCSD[T] and CCSD(T) as follows

“Since the multireference methods so far have not been able to provide us with reliable, inexpensive, and wildly (*sic*) applicable computational schemes it seems that the extension of the applicability of the single-reference [coupled cluster] methods to deal more efficiently with increasing degree of quasidegeneracy is still desirable. There is no doubt that from the point of view of large scale calculations, noniterative corrections should be of primary interest since the CCSD[T] and CCSD(T) methods are usually less costly than other alternatives.”

They emphasize [94] the more limited range of applicability of the CCSD[T] theory

“Unfortunately, the CCSD[T] method which performs very well at the equilibrium geometry displays unphysical behavior at larger distances significantly overshooting the exact result. The extra term containing T_1 , included in CCSD(T), moderates this behavior, ...”

but point out[94] that

“... even this does not help much when quasidegeneracy is significant in bond breaking.”

The CCSD(T) model takes account of certain fifth order terms in the many-body perturbation theory expansion and the next section is, therefore, devoted to the fifth-order energy components in general and in particular to a detailed analysis of those components which will later be seen to be central to the definition of the CCSD(T) model.

3.3 Fifth order many-body perturbation theory

The fifth order energy may be written

$$E_5 = \sum_{D_1} \sum_{X,Y} \sum_{D_2} \{ \langle \Phi | H_1 | \Phi_{D_1} \rangle \langle \Phi_{D_1} | H_1 | \Phi_X \rangle \langle \Phi_X | H_1 | \Phi_Y \rangle \langle \Phi_Y | H_1 | \Phi_{D_2} \rangle \times \\ \times \langle \Phi_{D_2} | H_1 | \Phi \rangle \} / \{ (E_0 - E_{D_1}) (E_0 - E_X) (E_0 - E_Y) (E_0 - E_{D_2}) \} \quad (55)$$

where, as for the fourth order energy component, Φ_{D_1} and Φ_{D_2} are states which are doubly excited with respect to the reference state Φ . Φ_X and Φ_Y are states which may be singly, doubly, triply or quadruply excited with respect to Φ . E_0 is the energy corresponding to the reference state Φ ; E_{D_1} , E_X , E_Y , E_{D_2} correspond to Φ_{D_1} , Φ_X , Φ_Y , Φ_{D_2} , respectively. The total fifth order energy may be written

$$E_5 = E_{5SS} + E_{5DD} + E_{5TT} + E_{5QQ} + \\ + 2E_{5SD} + 2E_{5ST} + 2E_{5DT} + 2E_{5DQ} + \\ + 2E_{5TQ} \quad (56)$$

each of the nine terms on the right hand side being classified according to the level of excitation associated with Φ_X and Φ_Y . Factors of 2 have been included in off-diagonal terms such as E_{5SD} since $E_{5SD} = E_{5DS}$. The renormalization terms which arise in fifth order have been cancelled by parts of $2E_{5DQ}$ and $2E_{5QQ}$.

The fifth order energy diagrams for a closed shell system were first written down in 1980[95][96]. Fifth order energy diagrams can be generated from second order wave function diagrams by invoking Wigner's $2n + 1$ rule[97][98]. They have been discussed by a number of authors[99]. Explicit diagrams and corresponding algebraic expressions were given for the first time by Lyons et al[100][101] (see also [103]). There are a total of 840 energy diagrams of the Brandow or Hugenholtz form (see, for example, [?]). The numbers of energy diagrams for different levels of excitation are shown in Table 1. For example, there are a total of 16 diagrams involving single and then triply excited intermediate states, i.e. $X = 3$, $Y = 1$, together with a further 16 involving triply and then singly excited states, i.e. $X = 1$, $Y = 3$. In the tabulation of Lyons et al[101] the undirected Hugenholtz diagrams corresponding to $X = 3$, $Y = 1$ are numbered 85, 97, 103 and 106. The connectivity matrices⁵ for these diagrams are

$$H_{\text{undirected}}(85) = \begin{pmatrix} 0 & 1 & 1 & 1 & 1 \\ 1 & 0 & 3 & 0 & 0 \\ 1 & 3 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 3 \\ 1 & 0 & 0 & 3 & 0 \end{pmatrix},$$

⁵The rows and columns of the connectivity matrices for the undirected Hugenholtz diagrams label the vertices. The element i_{kl} defines the number of undirected line segments between the vertices k and l .

$$\begin{aligned}
H_{\text{undirected}}(97) &= \begin{pmatrix} 0 & 1 & 2 & 0 & 1 \\ 1 & 0 & 2 & 1 & 0 \\ 2 & 2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 3 \\ 1 & 0 & 0 & 3 & 0 \end{pmatrix}, \\
H_{\text{undirected}}(103) &= \begin{pmatrix} 0 & 1 & 2 & 1 & 0 \\ 1 & 0 & 2 & 0 & 1 \\ 2 & 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 3 \\ 0 & 1 & 0 & 3 & 0 \end{pmatrix}, \\
H_{\text{undirected}}(106) &= \begin{pmatrix} 0 & 1 & 3 & 0 & 0 \\ 1 & 0 & 1 & 1 & 1 \\ 3 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 3 \\ 0 & 1 & 0 & 3 & 0 \end{pmatrix}
\end{aligned}$$

Table 1

Number of fifth order (Brandow) energy diagrams for a closed shell system for different level of excitation^a

	S	D	T	Q
S	4	16	16	0
D	16	56	80	28
T	16	80	164	112
Q	0	28	112	112

^a Taken from reference [103].

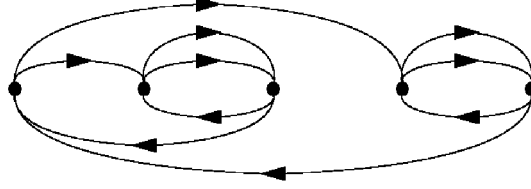
There are four directed Hugenholtz diagrams corresponding to each of these diagrams. Again using the numbering scheme of Lyons et al[101], from $H_{\text{undirected}}(85)$ we obtain the following connectivity matrices for directed Hugenholtz diagrams⁶

$$\begin{aligned}
H_{\text{directed}}(489) &= \begin{pmatrix} 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}, & H_{\text{directed}}(490) &= \begin{pmatrix} 0 & 0 & 1 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 1 & 0 & 0 & 1 & 0 \end{pmatrix}, \\
H_{\text{directed}}(491) &= \begin{pmatrix} 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 2 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}, & H_{\text{directed}}(492) &= \begin{pmatrix} 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 2 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 1 & 0 & 0 & 1 & 0 \end{pmatrix}.
\end{aligned}$$

From $H_{\text{undirected}}(97)$ we obtain the following

$$H_{\text{directed}}(569) = \begin{pmatrix} 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}, \quad H_{\text{directed}}(570) = \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 1 & 0 & 0 & 1 & 0 \end{pmatrix},$$

⁶The rows and columns of the connectivity matrices for the directed Hugenholtz diagrams label the vertices. The element i_{kl} defines the number of directed line segments between the vertices k and l .



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Figure 5: Fifth-order energy diagram contributing to the E_{5ST} energy component. (Taken from the work of Lyons *et al*[101].)

$$H_{\text{directed}}(571) = \begin{pmatrix} 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 2 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}, \quad H_{\text{directed}}(572) = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 1 & 0 & 0 & 1 & 0 \end{pmatrix},$$

whilst from $H_{\text{undirected}}(103)$ we obtain

$$H_{\text{directed}}(609) = \begin{pmatrix} 0 & 0 & 1 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 1 & 0 & 1 & 0 \end{pmatrix}, \quad H_{\text{directed}}(610) = \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix},$$

$$H_{\text{directed}}(611) = \begin{pmatrix} 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 2 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 1 & 0 & 1 & 0 \end{pmatrix}, \quad H_{\text{directed}}(612) = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}.$$

Finally, corresponding to $H_{\text{undirected}}(106)$ we have

$$H_{\text{directed}}(621) = \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}, \quad H_{\text{directed}}(622) = \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 1 & 0 & 1 & 0 \end{pmatrix},$$

$$H_{\text{directed}}(623) = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix}, \quad H_{\text{directed}}(624) = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 1 & 0 & 1 & 0 \end{pmatrix}.$$

The algebraic expressions corresponding to these 16 energy diagrams are

$$\begin{aligned}
E_{5SD}(489) &= -\frac{1}{4} \sum_{ijkl} \sum_{abcdef} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cd | \hat{O} | ik \rangle \langle bl | \hat{O} | ef \rangle \times \\
&\quad \langle ef | \hat{O} | jl \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_j^b D_{jl}^{ef} \\
E_{5SD}(490) &= +\frac{1}{4} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cd | \hat{O} | ik \rangle \langle lm | \hat{O} | je \rangle \times \\
&\quad \langle be | \hat{O} | lm \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_j^b D_{lm}^{be} \\
E_{5SD}(491) &= +\frac{1}{4} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ac | \hat{O} | kl \rangle \langle bm | \hat{O} | de \rangle \times \\
&\quad \langle de | \hat{O} | jm \rangle / D_{ij}^{ab} D_{jkl}^{abc} D_j^b D_{jm}^{de} \\
E_{5SD}(492) &= +\frac{1}{4} \sum_{ijklmn} \sum_{abcd} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ac | \hat{O} | kl \rangle \langle mn | \hat{O} | jd \rangle \times \\
&\quad \langle bd | \hat{O} | mn \rangle / D_{ij}^{ab} D_{jkl}^{abc} D_j^b D_{mn}^{bd} \\
E_{5SD}(569) &= -\frac{1}{2} \sum_{ijkl} \sum_{abcdef} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle bc | \hat{O} | ik \rangle \langle dl | \hat{O} | ef \rangle \times \\
&\quad \langle ef | \hat{O} | jl \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_j^b D_{jl}^{ef} \\
E_{5SD}(570) &= +\frac{1}{8} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cd | \hat{O} | ij \rangle \langle lm | \hat{O} | ke \rangle \times \\
&\quad \langle be | \hat{O} | lm \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_k^b D_{lm}^{be} \\
E_{5SD}(571) &= -\frac{1}{8} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ab | \hat{O} | kl \rangle \langle cm | \hat{O} | de \rangle \times \\
&\quad \langle de | \hat{O} | jm \rangle / D_{ij}^{ab} D_{jkl}^{bcd} D_j^c D_{jm}^{de} \\
E_{5SD}(572) &= -\frac{1}{2} \sum_{ijklmn} \sum_{abcd} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ac | \hat{O} | jk \rangle \langle mn | \hat{O} | ld \rangle \times \\
&\quad \langle bd | \hat{O} | mn \rangle / D_{ij}^{ab} D_{jkl}^{bcd} D_l^b D_{mn}^{bd} \\
E_{5SD}(609) &= +\frac{1}{2} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle bc | \hat{O} | ik \rangle \langle lm | \hat{O} | je \rangle \times \\
&\quad \langle de | \hat{O} | lm \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_j^d D_{lm}^{de} \\
E_{5SD}(610) &= +\frac{1}{8} \sum_{ijkl} \sum_{abcdef} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle cd | \hat{O} | ij \rangle \langle bl | \hat{O} | ef \rangle \times \\
&\quad \langle ef | \hat{O} | kl \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_k^b D_{kl}^{ef} \\
E_{5SD}(611) &= +\frac{1}{8} \sum_{ijklmn} \sum_{abcd} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ab | \hat{O} | kl \rangle \langle mn | \hat{O} | jd \rangle \times \\
&\quad \langle cd | \hat{O} | mn \rangle / D_{ij}^{ab} D_{jkl}^{abc} D_j^c D_{mn}^{cd} \\
E_{5SD}(612) &= -\frac{1}{2} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ac | \hat{O} | jk \rangle \langle bm | \hat{O} | de \rangle \times
\end{aligned}$$

$$\begin{aligned}
E_{5SD}(621) &= \frac{\langle de | \hat{O} | lm \rangle / D_{ij}^{ab} D_{jkl}^{abc} D_l^b D_{lm}^{de}}{-\frac{1}{4} \sum_{ijkl} \sum_{abcdef} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle bc | \hat{O} | ij \rangle \langle dl | \hat{O} | ef \rangle \times} \\
&\quad \langle ef | \hat{O} | kl \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_k^d D_{kl}^{ef} \\
E_{5SD}(622) &= +\frac{1}{4} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle \langle bc | \hat{O} | ij \rangle \langle lm | \hat{O} | ke \rangle \times \\
&\quad \langle de | \hat{O} | lm \rangle / D_{ij}^{ab} D_{ijk}^{bcd} D_k^d D_{lm}^{de} \\
E_{5SD}(623) &= +\frac{1}{4} \sum_{ijklm} \sum_{abcde} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ab | \hat{O} | jk \rangle \langle cm | \hat{O} | de \rangle \times \\
&\quad \langle de | \hat{O} | lm \rangle / D_{ij}^{ab} D_{jkl}^{abc} D_i^c D_{lm}^{de} \\
E_{5SD}(624) &= +\frac{1}{4} \sum_{ijklmn} \sum_{abcd} \langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle \langle ab | \hat{O} | jk \rangle \langle mn | \hat{O} | ld \rangle \times \\
&\quad \langle cd | \hat{O} | mn \rangle / D_{ij}^{ab} D_{jkl}^{abc} D_l^c D_{mn}^{cd}
\end{aligned}$$

In each of these diagrams the central interaction corresponds to an integral of the type $\langle ab | \hat{O} | ij \rangle$ where, as before the indices i and j label occupied spin orbitals whilst a and b label unoccupied spin orbitals. This interaction changes the level of excitation by two. The two integrals to the left of the central interaction integral have but one index in common. This common index may correspond either to an unoccupied spin orbital as, for example, in the expression corresponding to $E_{5SD}(489)$ for which the common index can be seen to be a , or to an occupied spin orbital as in $E_{5SD}(491)$ where the common index is i . Whatismore this common “left-hand” index occurs only in the first denominator factor (and, of course, does not arise in the central interaction integral or the two integrals to its right). The following intermediates can therefore be defined:-
(i) for $E_{5SD}(489)$

$$\sum_a \frac{\langle ij | \hat{O} | ab \rangle \langle ak | \hat{O} | cd \rangle}{D_{ij}^{ab}},$$

(ii) for $E_{5SD}(491)$

$$\sum_i \frac{\langle ij | \hat{O} | ab \rangle \langle kl | \hat{O} | ic \rangle}{D_{ij}^{ab}} \left\{ \equiv \sum_i \frac{\langle ji | \hat{O} | ba \rangle \langle kl | \hat{O} | ic \rangle}{D_{ij}^{ab}} \right\}.$$

These intermediates can be seen to be, within a factor of ± 1 , the quantities f_{ijk}^{abc} or a g_{ijk}^{abc} defined previously for the fourth order triple excitation energy component

$$f_{ijk}^{abc} = \sum_d \frac{\langle ij | \hat{O} | db \rangle \langle dk | \hat{O} | ac \rangle}{D_{ij}^{bd}}$$

and

$$g_{ijk}^{abc} = \sum_l \frac{\langle jl | \hat{O} | ba \rangle \langle ik | \hat{O} | lc \rangle}{D_{jl}^{ab}}.$$

The two integrals to the right of the central interaction integral can be seen to have three indices in common. Examination of the expressions reveals that

there are just two cases: (i) one index corresponds to an occupied spin orbital and two indices label unoccupied spin orbitals. This is the case, for example, in the expression for $E_{5SD}(489)$. (ii) one index corresponds to an unoccupied spin orbital and two indices label occupied spin orbitals. This is the case, for example, in the expression for $E_{5SD}(490)$. The common “right-hand” indices occurs only in the final denominator factor (and, of course, does not arise in the central interaction integral or the two integrals to its left). The following intermediates can, therefore, be defined:

$$f_j^b = \sum_{l,e,f} \frac{\langle bl | \hat{O} | ef \rangle \langle ef | \hat{O} | jl \rangle}{D_{jl}^{ef}}$$

and

$$g_j^b = \sum_{l,m,e} \frac{\langle lm | \hat{O} | je \rangle \langle be | \hat{O} | lm \rangle}{D_{lm}^{be}}.$$

The fifth order energy component E_{5SD} may be written in terms of the intermediates f_{ijk}^{abc} and g_{ijk}^{abc} , f_j^b and g_j^b . For example, we can write

$$E_{5SD}(489) = -\frac{1}{4} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle cd | \hat{O} | ik \rangle f_j^b / D_{ijk}^{bcd} D_j^b$$

and

$$E_{5SD}(490) = +\frac{1}{4} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle cd | \hat{O} | ik \rangle g_j^b / D_{ijk}^{bcd} D_j^b.$$

The remaining components of may be similarly written

$$\begin{aligned} E_{5SD}(491) &= +\frac{1}{4} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ac | \hat{O} | kl \rangle f_j^b / D_{jkl}^{abc} D_j^b \\ E_{5SD}(492) &= +\frac{1}{4} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ac | \hat{O} | kl \rangle g_j^b / D_{jkl}^{abc} D_j^b \\ E_{5SD}(569) &= -\frac{1}{2} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle bc | \hat{O} | ik \rangle f_j^d / D_{ijk}^{bcd} D_j^b \\ E_{5SD}(570) &= +\frac{1}{8} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle cd | \hat{O} | ij \rangle g_k^b / D_{ijk}^{bcd} D_k^b \\ E_{5SD}(571) &= -\frac{1}{8} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ab | \hat{O} | kl \rangle f_j^c / D_{jkl}^{abc} D_j^c \\ E_{5SD}(572) &= -\frac{1}{2} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ac | \hat{O} | jk \rangle g_l^b / D_{jkl}^{abc} D_l^b \\ E_{5SD}(609) &= +\frac{1}{2} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle bc | \hat{O} | ik \rangle g_j^d / D_{ijk}^{bcd} D_j^d \\ E_{5SD}(610) &= +\frac{1}{8} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle cd | \hat{O} | ij \rangle f_k^b / D_{ijk}^{bcd} D_k^b \\ E_{5SD}(611) &= +\frac{1}{8} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ab | \hat{O} | kl \rangle g_j^c / D_{jkl}^{abc} D_j^c \end{aligned}$$

$$\begin{aligned}
E_{5SD}(612) &= -\frac{1}{2} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ac | \hat{O} | jk \rangle f_l^b / D_{jkl}^{abc} D_l^b \\
E_{5SD}(621) &= -\frac{1}{4} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle bc | \hat{O} | ij \rangle f_k^d / D_{ijk}^{bcd} D_k^d \\
E_{5SD}(622) &= +\frac{1}{4} \sum_{ijk} \sum_{bcd} f_{ijk}^{cbd} \langle bc | \hat{O} | ij \rangle g_k^d / D_{ijk}^{bcd} D_k^d \\
E_{5SD}(623) &= +\frac{1}{4} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ab | \hat{O} | jk \rangle f_l^c / D_{jkl}^{abc} D_l^c \\
E_{5SD}(624) &= +\frac{1}{4} \sum_{jkl} \sum_{abc} g_{kjl}^{abc} \langle ab | \hat{O} | jk \rangle g_l^c / D_{jkl}^{abc} D_l^c
\end{aligned}$$

3.4 The CCSD(T) method

In the CCSD(T) theory, the energy correction obtained from the CCSD+T(CCSD) approximation is augmented by a fifth order term coupling single and triply excitations. The energy correction is written

$$\Delta E_t = \frac{1}{36} \sum_{ijk} \sum_{abc} D_{ijk}^{abc} t_{ijk}^{abc} (t_{ijk}^{abc} + \tilde{t}_{ijk}^{abc})$$

in which the ‘‘disconnected triple excitation amplitude’’ is defined by

$$\tilde{t}_{ijk}^{abc} = P(ijk) P(abc) \frac{1}{D_{ijk}^{abc}} t_i^a \langle bc | \hat{O} | jk \rangle$$

The justification of this *a posteriori* correction formula is only loosely based on perturbation theory and its justification warrants further examination.

Perturbative analysis of the fifth-order terms included in the CCSD(T) theory cannot provide a completely satisfactory basis for this approximation. The CCSD(T) theory was originally motivated by the requirement that contributions to the correlation energy associated with triply excited intermediate states should treat interactions with single and double excitation operators on an equal footing. In their original publication, Raghavachari *et al*[92] write

‘‘... detailed comparison of the fifth-order components ... 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 $[2E_{5ST}]$ 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.’’

They continue by giving a justification which is not based on perturbative arguments

‘‘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.”

In the *Encyclopedia of Computational Chemistry*, Gauss[1] writes

“The popularity of CCSD(T) is certainly best explained by its excellent performance in terms of both accuracy and computational cost, but a formal argument can be given to justify the (T) correction. Though single excitations first contribute in second order to the wavefunction, experience shows that their magnitude is often similar to that of the double excitations. For that reason, it might be reasonable to consider T_1 as first instead of second order. A triples correction correct to fourth order would then require inclusion of one additional fifth-order term, i.e. the one considered by CCSD(T). This argument indicates the potential numerical importance of that particular term compared to the other fifth-order contributions. Furthermore, since this fifth-order term adds a small positive contribution, it damps the overestimation of the pure fourth-order term and thus leads to improvements compared to CCSD+T(CCSD).”

In a paper entitled “*Why CCSD(T) works: a different perspective*”, Stanton[104] writes of the CCSD(T) approximation

“the terms included in this approximation cannot be intuited from a simple Hartree-Fock-based perturbative analysis.”

He continues

“In CCSD(T), two contributions are added to the CCSD energy. The first is that which is included in CCSD+T(CCSD), while the second contains contributions from fifth and higher-order terms in the conventional perturbation expansion. The additional term is nearly always positive in sign, and therefore tends to offset the characteristic overestimation of CCSD+T(CCSD). This extra contribution was first included as part of a noniterative triple excitation correction in the QCISD(T) model[93], and is a natural choice when one adopts the point of view that coupling between triply substituted determinants and the single and double excitation operators should be treated in a balanced manner. Equivalently, this term appears if one applies perturbation theory to the problem with the proviso that T_1 is treated as a first-order quantity[1], [41]. Such an even-handed approach would appear to be particularly important in difficult cases where the perturbation series is ill-behaved.”

Stanton[104] points out that

“Within the context of Hartree-Fock-based perturbation theory, however, the term involving T_1 is one of many that appear at fifth order which are not included in the CCSD treatment, but is the only one

included in CCSD(T). Numerical experimentation has demonstrated that magnitudes of the neglected fifth-order terms are comparable to and often larger than that of the one that is included[108]. So it appears that the latter is important not because of its size, but rather in its ability to provide delicate counterbalance to effects that tend to be exaggerated in CCSD+T(CCSD). Thus, it appears that there is some merit to the consistent treatment of T_1 and T_2 underlying the original formulation of the CCSD(T) method.”

Stanton[104] notes that the CCSD equations can be recast as an eigenvalue equation. Substituting the CCSD wave function

$$|\Psi_{\text{CCSD}}\rangle = \exp(T)|\Phi_0\rangle, \text{ where } T = T_1 + T_2 \quad (57)$$

in the Schrödinger equation and multiplying from the left by $\exp(-T)$ gives

$$\exp(-T)H\exp(T)|\Phi_0\rangle = \bar{H}|\Phi_0\rangle = E_{\text{CCSD}}|\Phi_0\rangle. \quad (58)$$

\bar{H} is non-Hermitian and therefore, since

$$\langle\Phi_0|\bar{H} \neq \langle\Phi_0|E_{\text{CCSD}}, \quad (59)$$

Instead we can write

$$\langle\Phi_0|\mathcal{L}\bar{H} = \langle\Phi_0|\mathcal{L}E_{\text{CCSD}} \quad (60)$$

where \mathcal{L} is the left eigenvector of \bar{H} , and we can write the energy as

$$\langle\Phi_0|\mathcal{L}\bar{H}|\Phi_0\rangle = E_{\text{CCSD}}. \quad (61)$$

The equations used to determine the cluster amplitudes may be written

$$\langle\Phi_p|\bar{H}|\Phi_0\rangle = 0, \forall p \quad (62)$$

where $\langle\Phi_p|$ is the set of determinants determined by single and double excitations. Left projection of equation (58) gives the energy expression

$$E_{\text{CCSD}} = \langle\Phi_0|\bar{H}|\Phi_0\rangle. \quad (63)$$

The matrix representation \bar{H} of has the form

$$\bar{H} = \begin{pmatrix} E_{\text{CCSD}} & \bar{H}_{0p} & \bar{H}_{0q} \\ 0 & \bar{H}_{pp} & \bar{H}_{pq} \\ \bar{H}_{q0} & \bar{H}_{qp} & \bar{H}_{qq} \end{pmatrix} \quad (64)$$

where p denotes the set of determinants obtained from $|\Phi_0\rangle$ by the promotion of one or two electrons and q represents all determinants not included in

$$\{|\Phi_g\rangle\} = \{|\Phi_0\rangle\} \cup \{|\Phi_p\rangle\} \quad (65)$$

so that

$$\{|\Phi_q\rangle\} \perp \{|\Phi_g\rangle\}. \quad (66)$$

The eigenvalues of the \bar{H} matrix in the basis

$$\{|\Phi_h\rangle\} = \{|\Phi_g\rangle\} \cup \{|\Phi_q\rangle\} \quad (67)$$

coincide with those obtained in a full configuration interaction calculation in which H is diagonalized.

In order to apply the partitioning technique due to Löwdin[105], we define the projection operators

$$\hat{P} = \sum_g |\Phi_g\rangle \langle \Phi_g| \quad (68)$$

and

$$\hat{Q} = \hat{I} - \hat{P} \quad (69)$$

We write the matrix eigenequation in the form

$$\begin{pmatrix} E_{\text{CCSD}} & \bar{H}_{0p} & \bar{H}_{0q} \\ 0 & \bar{H}_{pp} & \bar{H}_{pq} \\ \bar{H}_{q0} & \bar{H}_{qp} & \bar{H}_{qq} \end{pmatrix} \begin{pmatrix} |\Phi_0\rangle \\ |\Phi_p\rangle \\ |\Phi_q\rangle \end{pmatrix} = \mathcal{E} \begin{pmatrix} |\Phi_0\rangle \\ |\Phi_p\rangle \\ |\Phi_q\rangle \end{pmatrix} \quad (70)$$

where \mathcal{E} is the exact energy of the system under consideration. Equation (70) may be written

$$\bar{H} |\Phi\rangle = \mathcal{E} |\Phi\rangle \quad (71)$$

where

$$|\Phi\rangle = \begin{pmatrix} |\Phi_0\rangle \\ |\Phi_p\rangle \\ |\Phi_q\rangle \end{pmatrix}. \quad (72)$$

Stanton[104] employed Löwdin's technique for obtaining perturbation expansions based on a partitioning approach[105] to derive perturbative corrections to coupled cluster theory by means of a partitioning of \bar{H} . Introducing the resolution of the identity $\hat{I} = \hat{P} + \hat{Q}$ into (71) gives

$$\bar{H} (\hat{P} + \hat{Q}) |\Phi\rangle = \mathcal{E} (\hat{P} + \hat{Q}) |\Phi\rangle. \quad (73)$$

Multiplying from the left by \hat{P} yields the equation

$$\hat{P} \bar{H} (\hat{P} + \hat{Q}) |\Phi\rangle = \mathcal{E} \hat{P} |\Phi\rangle \quad (74)$$

whilst multiplying from the left by \hat{Q} gives

$$\hat{Q} \bar{H} (\hat{P} + \hat{Q}) |\Phi\rangle = \mathcal{E} \hat{Q} |\Phi\rangle \quad (75)$$

Equation (74) may be written

$$\hat{P} \bar{H} \hat{P} |\Phi\rangle + \hat{P} \bar{H} \hat{Q} |\Phi\rangle = \mathcal{E} \hat{P} |\Phi\rangle \quad (76)$$

and equation (75) as

$$\hat{Q} \bar{H} \hat{P} |\Phi\rangle + \hat{Q} \bar{H} \hat{Q} |\Phi\rangle = \mathcal{E} \hat{Q} |\Phi\rangle. \quad (77)$$

Equation (77) can be immediately rewritten as

$$\hat{Q} \bar{H} \hat{P} |\Phi\rangle = (\mathcal{E} \hat{Q} - \hat{Q} \bar{H} \hat{Q}) |\Phi\rangle \quad (78)$$

which then gives

$$\hat{Q} |\Phi\rangle = (\mathcal{E} \hat{Q} - \hat{Q} \bar{H} \hat{Q})^{-1} \hat{Q} \bar{H} \hat{P} |\Phi\rangle \quad (79)$$

Substituting the expression for $\hat{Q}|\Phi\rangle$ given in equation (79) into the second term on the left-hand side of equation (76) gives the basic equation of the partitioning approach to perturbation theory

$$\hat{P}\bar{H}\hat{P}|\Phi\rangle + \hat{P}\bar{H}\hat{Q}\left(\mathcal{E}\hat{Q} - \hat{Q}\bar{H}\hat{Q}\right)^{-1}\hat{Q}\bar{H}\hat{P}|\Phi\rangle = \mathcal{E}\hat{P}|\Phi\rangle \quad (80)$$

which can be immediately rewritten as

$$\left[\hat{P}\bar{H}\hat{P} + \hat{P}\bar{H}\hat{Q}\left(\mathcal{E}\hat{Q} - \hat{Q}\bar{H}\hat{Q}\right)^{-1}\hat{Q}\bar{H}\hat{P}\right]\hat{P}|\Phi\rangle = \mathcal{E}\hat{P}|\Phi\rangle \quad (81)$$

or

$$H_{\text{effective}}|\Phi_P\rangle = \mathcal{E}|\Phi_P\rangle \quad (82)$$

where the effective hamiltonian is given by

$$H_{\text{effective}} = \hat{P}\bar{H}\hat{P} + \hat{P}\bar{H}\hat{Q}\left(\mathcal{E}\hat{Q} - \hat{Q}\bar{H}\hat{Q}\right)^{-1}\hat{Q}\bar{H}\hat{P} \quad (83)$$

and

$$|\Phi_P\rangle = \hat{P}|\Phi\rangle \quad (84)$$

The exact eigenvalue of \bar{H} , that is \mathcal{E} , can then be written as an implicit functional

$$\langle\Phi|\mathcal{L}\hat{P}\bar{H}\hat{P}|\Phi\rangle + \langle\Phi|\mathcal{L}\hat{P}\bar{H}\hat{Q}\left(\mathcal{E}\hat{Q} - \hat{Q}\bar{H}\hat{Q}\right)^{-1}\hat{Q}\bar{H}\hat{P}|\Phi\rangle = \mathcal{E}\langle\Phi|\mathcal{L}\hat{P}|\Phi\rangle \quad (85)$$

The right- and left-hand states

$$|\Psi^{[0]}\rangle = |\Phi\rangle \quad (86)$$

$$\langle\tilde{\Psi}^{[0]}| = \langle\Phi|\mathcal{L} \quad (87)$$

are defined as the zero order wave functions. \bar{H}_{gg} is taken to be the zero order hamiltonian and the remaining terms in the matrix are classified[104] “according to the lowest nonvanishing order in correlation (with this convention, the T_1 operator is second-order and T_2 first order)”,

$$\bar{H} = \bar{H}^{[0]} + \bar{H}^{[1]} + \bar{H}^{[2]} + \dots \quad (88)$$

The application of Löwdin’s partitioning technique[105] in coupled cluster theory has also been studied recently by Head-Gordon and his coworkers [106] (see also [107]). In reference [106] these authors point out that although

“... Stanton and coworkers ... start with a perturbative expansion of \bar{H} , when deriving final working equations, they would fall back to a standard MBPT order expansion.”

Head-Gordon and his coworkers[106] propose a theory which they designate the CCSD(2) method (and the related QCCD(2) method) in which they take \bar{H} as the fundamental quantity and keep all terms through a consistent order in \bar{H} . Head-Gordon and his coworkers[106] explain that

[this brings] “several aspects of new physics into our models. The first [is] the inclusion of quadruple excitations along with and as a complement to triple excitation corrections. The second [is] the use of two-electron integrals that have been dressed by the coupled cluster correlation operator T . The other significant piece of new physics [is] the appearance of correlated “orbital energies” in the denominators of the final spin-orbital equations.”

Full details can be found in the work of Head-Gordon and his coworkers[106].

3.5 Higher order effects and augmented coupled cluster theories

In his conclusions to an article entitled “*A Road Map for the Calculation of Molecular Binding Energies*” published in 2000, Dunning[54] writes

“Inclusion of full triple excitations, the CCSDT method, in calculations of D_e for strongly bound molecules leads to slightly larger errors than does the CCSD(T) method[109], [110], [111], [112].”

He concludes therefore that

“... the excellent agreement achieved for the CCSD(T) method is partly a result of compensating errors.”

However, although the measured differences between CCSD(T) and CCSDT are

“usually just a few tenth of a kcal/mol”,

they can be larger for molecules which are poorly described by a Hartree-Fock reference function. In a study of the equilibrium atomization energies of CO, H₂O, F₂, HF, N₂ and CH₂ (¹A₁ state) using the CCSDT method, Bak *et al* [112] conclude

“The overall agreement with experiment is not improved by full relaxation of the triples, indicating some cancellation of error in the CCSD(T) model between the missing relaxation of triples and the missing contributions from connected higher excitations.”

They continue

“The missing relaxation of triples is more important than scalar relativistic effects.”

Feller [109] gauged the importance of higher order correlation effects by performing calculations using the CCSD(TQ) method on three diatomics FH, CO and N₂. He found that

“In all three cases, the experimental values of D_e were underestimated prior to consideration of higher order correlation. CCSD(TQ) decreased the theoretical values, relative to CCSD(T), thus *increasing* the deviation with respect to experiment.”

3.6 Renormalized coupled cluster methods

Potential energy curves and surfaces resulting from applications of the single reference CCSD(T) and CCSD[T] theories based on restricted Hartree-Fock function become unphysical at larger internuclear separations. The renormalized and completely renormalized coupled cluster approaches attempt to extend the range of applicability of CCSD(T) and CCSD[T] theories whilst retaining the simplicity of the single reference formalism. These approaches are based on the formalism of the method of moments of the coupled cluster equations[113], [23], [28], [118], [115], [116], [117], [118]

3.6.1 Method of moments of the coupled cluster equations

“The main idea of the [method of moments of coupled cluster] theory is that of the noniterative energy corrections which, when added to the energies obtained in the standard coupled-cluster calculations, recover the exact (full configuration interaction energy) energy. The [method of moments of coupled cluster] approximations require that a guess is provided for the electronic wave function of interest.” [118]

This method of moments of coupled cluster theory formalism allows the *renormalization* of noniterative single reference coupled cluster approximations such as CCSD[T] and CCSD(T), so that they can correctly describe entire ground state potential energy surfaces. If the energy supported by a certain coupled cluster expansion (A) is

$$E^{(A)} = \langle \Phi | \left(H e^{T^{(A)}} \right)_c | \Phi \rangle \quad (89)$$

((A) might, for example, designate the CCSD approach.), then the central idea of the method of moments of the coupled cluster (MMCC) equations is that a noniterative energy correction

$$\delta^{(A)} = \mathcal{E} - E^{(A)} \quad (90)$$

can be defined which when added to the energy $E^{(A)}$ supported by the method (A) recovers the corresponding exact energy, \mathcal{E} , i.e. the exact eigenvalue of the Schrödinger equation. An estimate of $\delta^{(A)}$ will yield

$$E_{\text{MMCC}} = E^{(A)} + \delta^{(A)}, \quad (91)$$

an estimate of \mathcal{E} . The generalized moments of the single reference coupled cluster equation is defined as follows

$$\mathcal{M}_J^{(j)}(m_A) = \left\langle \Phi_J^{(j)} \left| \left(H e^{T^{(A)}} \right)_c \right| \Phi \right\rangle, \quad (92)$$

where $\left| \Phi_J^{(j)} \right\rangle$ denotes the j -tuply excited configuration relative to $|\Phi\rangle$. The generalized moments $\mathcal{M}_J^{(j)}(m_A)$ with $j = 1, 2, \dots, m_A$ vanish. The correction $\delta^{(A)}$ is defined in terms of the moments $\mathcal{M}_J^{(j)}(m_A)$ with $j > m_A$. $\delta^{(A)}$ can be written

$$\begin{aligned} \delta^{(A)} &\equiv \mathcal{E} - E^{(A)} \\ &= \sum_{n=m_A+1}^N \sum_{j=m_A+1}^n \langle \Psi | Q_n C_{n-j}(m_A) M_j(m_A) | \Phi \rangle / \langle \Psi | e^{T^{(A)}} | \Phi \rangle \end{aligned} \quad (93)$$

where

$$C_{n-j}(m_A) = \left(e^{T^{(A)}} \right)_{n-j} \quad (94)$$

is the $(n-j)$ -body component of the wave operator $e^{T^{(A)}}$ and

$$M_j(m_A)|\Phi\rangle \equiv Q_j \left(H e^{T^{(A)}} \right)_c |\Phi\rangle. \quad (95)$$

So when $(A) = \text{CCSD}$, the generalized moments are just the equation projected onto the space of triply, quadruply, pentuply and hexuply excited configurations or

$$M_j(2)|\Phi\rangle = Q_j \left(H e^{T_1+T_2} \right)_c |\Phi\rangle, \quad j = 3, 4, 5, 6 \quad (96)$$

$$M_j(2)|\Phi\rangle = 0, \quad \text{for } j > 6 \quad (97)$$

Equation (93) is the basic equation of ground state MMCC theory. It contains two main elements *(i)* the generalized moments of the coupled cluster equations, *(ii)* the exact wave function $|\Psi\rangle$. The generalized moments of the coupled cluster equations can be easily determined once the cluster operator $T^{(A)}$ is known. In practice, some approximation to the exact wave function $|\Psi\rangle$ has to be introduced. Approximations may be obtained, for example, from limited configuration interaction calculations or from low-order many-body perturbation theory.

3.6.2 Renormalized and (completely renormalized) augmented CCSD theory: R-CCSD[T] and R-CCSD(T), CR-CCSD[T] and CR-CCSD(T)

Using low-order MBPT to obtain an approximation for $|\Psi\rangle$ leads to the so-called renormalized and completely renormalized CCSD[T] and CCSD(T) methods. Piecuch *et al* claim that

“these new approaches represent promising computational tools that remove the pervasive failing of the standard CCSD[T], CCSD(T), and CCSD(TQ_f) approximations at larger internuclear separations, whilst preserving the “black-box” character of the noniterative [single reference coupled cluster] methods.”

The standard perturbation theory correction is scaled by the inverse of the overlap between the perturbed wave function and the CCSD wave function. This destroys the extensivity of the method[28], [94]. The renormalized perturbation theory effectively divides a triples (or a triples and quadruples) excitation correction that is unphysically large at longer internuclear distances by the norm of the coupled cluster wave function, which also grows rapidly with nuclear separation.

4 Discussion and Conclusions

CCSD(T), first proposed in 1989 by Pople and his co-workers[92], is currently one of the most popular *ab initio* methods for describing electron correlation effects in molecules. This popularity rests upon the perceived accuracy of the method coupled with a computational scaling as $\mathcal{O}(n^7)$, where n is the “size” of the

problem and is usually related to the size of the basis set. Dunning and his co-workers[54], [2], [3], [4], [5], [6], [7] have performed many calibration calculations and established a broad range of applicability of the CCSD(T) method especially in conjunction with sequences of correlation consistent basis sets[119].

Today, the CCSD(T) method is available for routine applications in many quantum chemical packages, including GAUSSIAN[55], CADPAC[56], GAMESS[57], MOLPRO[58], ACES[59] and DALTON[60]. For systems which are well described by a Hartree-Fock reference function, the method can support high accuracy. However, users of the CCSD(T) method should be aware of its limitations, in particular

1. the CCSD(T) theory employs an *a posteriori* correction formula to the CCSD method which is only loosely based on perturbation theory;
2. both Stanton[104] and, more recently, Head-Gordon and his co-workers[106] have developed perturbation series with respect to a CCSD reference. Head-Gordon *et al* propose a method designated CCSD(2) which is distinct from CCSD(T);
3. there is some cancellation of error in the CCSD(T) model. For example, in calculations of molecular binding energies the CCSDT theory achieves slightly worse agreement with experiment than the CCSD(T) model;
4. the CCSD(T) model breaks down when quasidegeneracy is significant as, for example, in describing bond breaking;
5. the renormalized and (completely renormalized) augmented CCSD(T) theory suggested in recent years destroys the extensivity of the method, but extends the range of geometries that can be considered;
6. it is claimed that fourth order many-body perturbation theory can yield an accuracy that "is typically somewhat higher than that of CCSD(T)"[68] by using Feenberg scaling of the zero-order hamiltonian in conjunction with quadratic Padé approximants;
7. multireference methods are found to give more accurate results in studies of bond-breaking than the best single reference methods including CCSD(T).

There can be little doubt that the development of multireference many-body methods will eventually provide more robust framework within which to describe bond-breaking processes. Brillouin-Wigner based many-body methods[120], in particular, show significant potential in facilitating a 'black box' technology for quasidegenerate[121] and dissociative processes in molecules[122].

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