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M.R. Hoffmann
(Ph.D. Thesis)

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A FULL COUPLED CLUSTER SINGLES, DOUBLES AND TRIPLES
MODEL FOR THE DESCRIPTION OF
ELECTRON CORRELATION

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Ph.D. Thesis

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A Full Coupled Cluster Singles, Doubles and Triples Model
for the Description of Electron Correlation

Mark Reinhard Hoffmann

Abstract

Equations for the determination of the cluster coefficients in a full coupled cluster theory involving single, double and triple cluster operators with respect to an independent particle reference, expressible as a single determinant of spin-orbitals, are derived. The resulting wave operator is full, or untruncated, consistent with the choice of cluster operator truncation and the requirements of the connected cluster theorem. A time-independent diagrammatic approach, based on second quantization and the Wick theorem, is employed. Final equations are presented that avoid the construction of rank three intermediary tensors. The model is seen to be a computationally viable, size-extensive, high-level description of electron correlation in small polyatomic molecules.

To my Parents

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A Full Coupled Cluster Singles, Doubles and Triples Model
for the Description of Electron Correlation

1. Introduction

The computationally viable description of electron correlation for stationary state molecular systems has been the subject of considerable research in the past two decades. A recent book by Schaefer¹ gives a good historical perspective on the developments in the field of quantum chemistry. The predominant methods for the description of electron correlation have been configuration interaction (CI) and perturbation theory (PT); more recently, the variant of CI involving reoptimization of the molecular orbitals (i.e., multiconfiguration self-consistent field (MCSCF)) has received much attention.¹ As is reasonable to expect, neither CI nor PT is wholly satisfactory; a possible alternative is the use of cluster operators, in the electron excitations, to describe the correlation.

Two ongoing developments support the tenability of the coupled cluster method, an inherently complicated procedure. The first is the increasing understanding of the applicability of elegant methods from nuclear and particle physics to chemistry. The other development is the decreasing ratio of cost to operations/sec in modern high-speed computers, especially the advent of super-minicomputers.

The present work details the derivation of a full coupled cluster model, including single, double, and triple excitation operators. Second quantization and time-independent diagrams are used to facilitate the derivation; the treatment of (diagram) degeneracy and permutational symmetry is adapted from time-dependent methods. Implicit formulas are

presented in terms of products of one- and two-electron integrals, over (molecular) spin-orbitals, and cluster coefficients. Final formulas are obtained which restrict random access requirements to rank 2 modified integrals, and sequential access requirements to the rank 3 cluster coefficients.

The Coupled Cluster Method (CCM) is based on the ansatz that an exact many-particle wavefunction can be written as an exponential cluster operator acting on an independent-particle function,

$$|\psi\rangle = \exp(T)|\phi_0\rangle, \quad (1.1)$$

where

$$|\phi_0\rangle = \prod_{i=1}^N X_i^+ |\text{vac}\rangle, \quad (2)$$

$$T = T_1 + T_2 + T_3 + \dots, \quad (3)$$

and

$$T_m = \sum_{\substack{i < j < k < \dots \\ a < b < c < \dots}} t_{ijk\dots}^{abc\dots} X_a^+ X_i X_b^+ X_j X_c^+ X_k \dots; \quad (4)$$

and X_i^+ (X_i) is used to denote the creation (annihilation) of an electron in spin-orbital i . The exponential cluster expansion was introduced by Ursell and Mayer in the context of statistical mechanics; Coester and Kümmel applied the method to problems in nuclear physics in 1958-1962;² Cizek and Paldus were the first to use the method to address atomic and molecular problems.^{3,4} In the terminology of Löwdin, the cluster operator (cf. Equation (3)) is the logarithm of the wave operator.⁵

With the exponential matrix defined in the usual fashion,

$$\exp(T) = 1 + T + \frac{1}{2!} T^2 + \frac{1}{3!} T^3 + \dots; \quad (5)$$

the exact wavefunction can be written,

$$\begin{aligned}
 |\psi\rangle = & \{ (1) + (T_1) + (T_2 + \frac{1}{2!} T_1^2) + \\
 & + (T_3 + T_2 T_1 + \frac{1}{3!} T_1^3) + \\
 & + (T_4 + T_3 T_1 + \frac{1}{2!} T_2 T_1^2 + \frac{1}{2!} T_2^2 + \frac{1}{4!} T_1^4) + \\
 & + (T_5 + T_4 T_1 + T_3 T_2 + \frac{1}{2!} T_3 T_1^2 + \frac{1}{2!} T_2^2 T_1 + \frac{1}{3!} T_2 T_1^3 + \frac{1}{5!} T_1^5) + \\
 & + \dots \} |\phi_0\rangle .
 \end{aligned} \tag{6}$$

The parentheses have been included to facilitate comparison with the method of configuration interaction (CI). Defining C_i consecutively with the terms in parentheses, the exact wavefunction can be written,

$$|\psi\rangle = \{1 + C_1 + C_2 + C_3 + C_4 + C_5 + \dots\} |\phi_0\rangle . \tag{7}$$

Variational determination of the C_i coefficients in Equation (7) without truncation is referred to as "full-CI", and is the exact wavefunction subject to approximations in the operator (e.g., non-relativistic) and in the independent-particle reference (e.g., basis set limit).

Essentially all problems of chemical interest require, due to computational constraints, limiting the level of excitation used to correlate electrons. The necessary truncation is the key distinction between the coupled cluster method (CCM) and the method of configuration interaction (CI). In particular, truncations of Equation (6) are size-extensive, whereas approximations of Equation (7) are in general not.⁶ A method is said to be size-extensive if the energy of a "supermolecule" is linear in the number of non-interacting molecules included,⁶

$$E(nM) = nE(M) . \tag{8}$$

Size-extensivity can be seen to be of particular importance when a consistent description is needed over a large portion of a correlated potential energy surface.

Various approximations of Equation (6), the exact wavefunction in

the coupled cluster formalism, have been discussed in the chemical literature. In particular, Cizek's coupled-pair many-electron theory (CPMET),³ also referred to as coupled-cluster doubles (CCD) by Bartlett,⁶ has received considerable attention.^{4,7-11} In this approach, the wave operator is approximated by,

$$\exp(T) \approx 1 + T_2 + \frac{1}{2!} T_2^2 ; \quad (9)$$

the success of this rather abrupt truncation for closed-shell molecular systems is not too surprising when one considers that the dominant terms of a perturbation expansion have been included.^{4,12} The next more complete approximation to attain recognition is the extended coupled-pair many-electron theory (ECPMET) of Paldus, Cizek, and Shavitt,^{4,13,14} which includes connected single and triple excitations,

$$\exp(T) \approx 1 + T_1 + T_2 + T_3 + \frac{1}{2!} T_2^2 ; \quad (10)$$

again the terms to be included were based on a perturbation order argument.^{4,12} The contribution of connected triples was shown numerically to be not inconsequential in applications of perturbation theory.¹⁵ More recently, Purvis and Bartlett¹² reported the equations and initial implementation of a full coupled-cluster singles and doubles model (CCSD); this theory includes all terms in the first five parentheses, C_0 through C_4 , of Equation (6) except for T_3 , T_4 , and T_1T_3 . The inclusion of disconnected terms is known to enhance the numerical stability of the coupled equations.^{16,17}

In consideration of the complementary importances of connected triples and a full treatment of disconnected terms, it seems reasonable to investigate coupled cluster models which incorporate both features. This present work details the derivation of a computationally tractable full coupled-cluster singles, doubles, and triples model (CCSDT). Such a

theory includes all terms in the six parentheses given in Equation (6), except for T_4 , T_5 , and T_4T_1 . It should be noted that Kummel et. al.,¹⁸ and Lee and Bartlett,¹⁹ have undertaken similar derivations; but with emphasis on the partial inclusion of the triples cluster operator.

It is perhaps appropriate at this point to critically examine a few of the key words of coupled cluster theory. Some technical words used in discussing the coupled cluster theory have two quite different meanings, the appropriate one to be determined by the context of the occurrence. Perhaps most insidious is the word "connected". A disconnected term is the product of two or more cluster operators, e.g., T_2T_1 ; a connected term is then a single cluster operator, e.g., T_3 . However, a connected diagram is a diagram in which a line (solid, dashed, or squiggly) can be found between any two vertices (including external lines); then a disconnected diagram has an isolated part. It is this second meaning of connected which is used in Cizek's connected cluster theorem;³ but the first is which is used in the title of Purvis and Bartlett's paper,¹² "A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples". Another word used in two different ways is "complete", or "full". A complete reference is one in which all possible occupations, subject to conservation of particle number, correct description of spin statistics, and possibly spin and molecular point group symmetry restrictions, of a subset of the independent particle basis are subject to the action of the wave operator. Examples of this use of complete or full are: full CI or Complete Active Space Self-Consistent Field (CASSCF); the space of a singles and doubles excitation CI would be considered incomplete by this definition. The other usage of complete or full is to describe the

inclusion in the exponential cluster operator, or wave operator, all possible terms, connected and disconnected, subject to the restriction of connected diagrams, consistent with a given truncation of the cluster operator. This is the definition appropriate to the occurrence of "full" in the title of Purvis and Bartlett's paper.¹² A subtle, but illustrative, point: CPMET is complete, but ECPMET is not. A final word to be examined which is used in two different ways is "truncated". A cluster operator is said to be truncated when not all ranks of cluster operators up to and including T_N , where N is the total number of electrons in the system, are included. With this first usage, ECPMET and CCSDT have the same truncation, CCSD is more truncated, and CPMET is more yet. The second usage is similar but not identical to the first: a wave operator is said to be truncated when terms are neglected. Notice that the second definition of truncate is the verb form of the second definition of incomplete. Under this definition, ECPMET is quite truncated in comparison to CCSDT. We hope that this lexicographic exercise will enhance the clarity of this writing.

2. Renormalization

Both the topology of resulting diagrams and the forms of the coupled cluster equations themselves are considerably simplified by the use of operators in normal product form.^{3,8,20-22} The resulting diagrams are simplified in that certain connections, which would otherwise be legal, are eliminated, reducing the number of unique diagrams. This aspect will be discussed in Section 4, after the diagrams are introduced. The coupled cluster equations are simplified through the elimination of reference to the uncorrelated energy; this rather direct

manifestation of renormalization will be detailed in the following Section on the coupled cluster equations themselves. It is the purpose of this Section then to derive, following the general procedure of Cizek and Paldus,^{3,20} the normal product form of the Hamiltonian operator, to demonstrate how this suggests a particularly appropriate renormalized vacuum, and to examine the excitation operators with respect to normal ordering. The tensorial properties of the operators are discussed, especially the connection between rank and normal product form.

Under the Born-Oppenheimer approximation, the spin-independent, non-relativistic electronic Hamiltonian for molecular systems can be written as,

$$H = Z + V ; \quad (2.1)$$

where the first-quantized forms of the operators are,

$$Z = \sum_i z(i) , \quad (2)$$

and

$$V = \sum_{i < j} v(i,j) , \quad (3)$$

with

$$z(i) = -\frac{1}{2} \nabla_i^2 - \sum_a Q_a r_{ia}^{-1} , \quad (4)$$

and

$$v(i,j) = r_{ij}^{-1} . \quad (5)$$

In Equations (2) - (5), i and j refer to electrons, a to nuclei, r is the metric, ∇^2 the Laplacian, and Q is the (nuclear) charge. (N.B. Atomic units will be used throughout this work; e.g., $m_e = \hbar = e = 1$.) Then the second-quantized forms of the operators are given by,^{20,23-25}

$$Z = \sum_{pq} \langle p|z|q \rangle X_p^+ X_q, \quad (6)$$

and

$$V = \frac{1}{2} \sum_{pqrs} \langle pq|v|rs \rangle X_p^+ X_q^+ X_s X_r, \quad (7)$$

with,

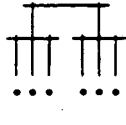
$$\langle p|z|q \rangle = \int \phi_p^*(1) z(1) \phi_q(1) d\tau_1, \quad (8)$$

and

$$\langle pq|v|rs \rangle = \int \phi_p^*(1) \phi_q^*(2) v(1,2) \phi_r(1) \phi_s(2) d\tau_1 d\tau_2; \quad (9)$$

where $p, q, r,$ and s label spin-orbitals, ϕ is the spatial representation of a spin-orbital, and integrations are over the spin and spatial coordinates of the subscripted particle.

The normal product form of the Hamiltonian operator is obtained by the use of the time-independent Wick theorem^{3,20} (also known as Wick's First Theorem²²); i.e.,

$$M_1 \dots M_{i_k} = N[M_1 \dots M_{i_k}] + \sum N[M_1 \dots M_{i_k}] \quad (10)$$


where M_i can represent either a creation or annihilation operator, and the summation extends over all possible contractions. $N[\dots]$ is used to designate the normal product of the enclosed operators: the product of operators in which all the creation operators appear to the left of all the annihilation operators, multiplied by $(-1)^P$, where p is the parity of the Fermi permutations. Similarly,

$$N[\dots \dots]$$


is the normal product with pairings.

Application of the time-independent Wick theorem to the rank 1

component of the Hamiltonian (cf. Equation (6)) gives,

$$Z = \sum_{pq} \langle p|z|q \rangle N[X_p^+ X_q] + \sum_{pq} \langle p|z|q \rangle N[\overline{X_p^+ X_q}] , \quad (11)$$

$$Z = \sum_{pq} \langle p|z|q \rangle N[X_p^+ X_q] + \sum_{pq} \langle p|z|q \rangle h(p) \delta_{pq} , \quad (12)$$

where $h(p)$ is the hole function defined by Paldus and Cizek and δ_{pq} is the Kronecker delta. We have made implicit use of the orthonormality of the spin-orbitals in obtaining Equation (12) from Equation (11). The convention we will abide by throughout this Section is that $p, q, r,$ and s extend over all spin-orbitals; $i, j, k,$ and l refer to spin-orbitals occupied in $|\Phi_0\rangle$; and $a, b, c,$ and d refer to spin-orbitals unoccupied in the reference. Then,

$$Z = \sum_{pq} \langle p|z|q \rangle N[X_p^+ X_q] + \sum_i \langle i|z|i \rangle ; \quad (13)$$

so,

$$Z = Z_1 + Z_0 , \quad (14)$$

where the subscripts refer now to the irreducible rank.

Likewise, application of the Wick theorem to the rank 2 component gives,

$$V = V_2 + V_1 + V_0 , \quad (15)$$

where,

$$V_2 = \frac{1}{2} \sum_{pqrs} \langle pq|v|rs \rangle N[X_p^+ X_q^+ X_s X_r] , \quad (16)$$

$$V_1 = \sum_{pq} \langle p|g|q \rangle N[X_p^+ X_q] , \quad (17)$$

$$V_0 = \frac{1}{2} \sum_{ij} \langle ij||ij \rangle , \quad (18)$$

and,

$$\langle p|g|q \rangle = \sum_i \langle p1||q1 \rangle , \quad (19)$$

$$\langle pq || rs \rangle = \langle pq | v | rs \rangle - \langle pq | v | sr \rangle . \quad (20)$$

Now, gathering terms of the same rank, we can write,

$$H_0 = \sum_i \langle i | z | i \rangle + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle , \quad (21)$$

$$H_1 = \sum_{pq} \{ \langle p | g | q \rangle + \langle p | z | q \rangle \} N[X_p^+ X_q] , \quad (22)$$

$$H_2 = \frac{1}{2} \sum_{pqrs} \langle pq | v | rs \rangle N[X_p^+ X_q^+ X_s X_r] . \quad (23)$$

Defining $f_{pq} = \langle p | f | q \rangle = \langle f | z + g | q \rangle$, (24)

Equation (22) may be written,

$$H_1 = \sum_{pq} f_{pq} N[X_p^+ X_q] . \quad (25)$$

Using Equation (20), the definition of the antisymmetrized two-electron integral, and the anticommutation relation of fermion annihilation operators, Equation (23) may be written,

$$H_2 = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle N[X_p^+ X_q^+ X_s X_r] . \quad (26)$$

Hence the Hamiltonian can be decomposed in terms of irreducible tensors,

$$H = H_0 + H_1 + H_2 , \quad (27)$$

i.e., written in normal product form.

Careful examination of Equation (21) reveals that H_0 is identical to the energy matrix element of the reference determinant,

$$\langle \phi_0 | H | \phi_0 \rangle = H_0 , \quad (28)$$

as given by the Slater-Condon rules.^{23,24} Hence, we are motivated to choose the reference determinant as the renormalized, or Fermi, vacuum.

The terminology of tensor operators is used extensively in this work and warrants further comment. Let us consider the action of the operator,

$$[X_r^+ X_s, \cdot] = L_r^s, \quad (29)$$

on a creation operator,

$$[X_r^+ X_s, X_u^+] = (X_r^+ X_s X_u^+ - X_u^+ X_r^+ X_s), \quad (30)$$

$$= X_r^+ (X_s X_u^+ + X_u^+ X_s), \quad (31)$$

$$= X_r^+ \delta_{su}; \quad (32)$$

where use has been made of the fermion anticommutation relations,

$$[X_p^+, X_q^+]_+ = [X_p, X_q]_+ = 0, \quad (33)$$

$$[X_p^+, X_q]_+ = \delta_{pq}. \quad (34)$$

The operator L_r^s acting on the vector field of the creation operators satisfies the transformation law for covariant vectors (e.g., tensor rank 1).²⁶ The form of the transformation operator is reasonable in light of the following two observations, though it is to be emphasized that the legitimacy of referring to the creation operators as covariant vectors resides in Equation (32). As Moshinsky noted, annihilation operators can be thought of as differentiation operators with respect to creation operators,²⁷ then similarly,

$$X_r^+ \sim \frac{\partial}{\partial X_r}, \quad (35)$$

Secondly, the commutator is the Lie product²⁶ of the operators $X_r^+ X_s$ and X_u^+ ; this choice of "multiplication" is particularly appropriate when one realizes that the $X_r^+ X_s$ are the generators of the semisimple compact Lie Group, U_n , which is associated with the infinitesimal unitary transformations of the Euclidean vector space, R_n (e.g., the space of the

creation operators).²⁷ With the above comments, the action of the transformation operator on the creation operators can formally be written in the usual form of the transformation law for covariant vectors,²⁶

$$X_r^+ = \sum_s \left(\frac{\partial X^s}{\partial X^r} \right) X_s, \quad (36)$$

where the indices on the annihilation operators have been written as superscripts in anticipation of the results of the following paragraph.

Next consider the action of the same operator, L_r^s , on the annihilation operator,

$$[X_r^+ X_s, X_u] = X_r^+ X_s X_u - X_u X_r^+ X_s, \quad (37)$$

$$= -(X_r^+ X_u + X_u X_r^+) X_s, \quad (38)$$

$$= -\delta_{ru} X_s. \quad (39)$$

So that the operator $-L_r^s$ acting on the vector field of the annihilation operators satisfies the transformation law for contravariant vectors.²⁶

Making the analogous observations as before now for the annihilation operators, the action of the transformation operator on the annihilation operators can formally be written in the usual form of the transformation law for contravariant vectors,²⁶

$$X^r = \sum_s \left(\frac{\partial X_r^+}{\partial X_s^+} \right) X^s. \quad (40)$$

The index on the annihilation operator will usually continue to be written in the conventional subscript position, except where added emphasis of the contravariant transformation property is deemed useful; in either case the same operator is intended.

A useful test on the consistency of the definition of the

transformation operator for creation operators and for annihilation operators is provided by considering the action of L_r^s on a rank 1 (in both covariant and contravariant indices) operator,

$$[X_r^+ X_s^+, X_u^+ X_v^+] = X_r^+ X_s^+ X_u^+ X_v^+ - X_u^+ X_v^+ X_r^+ X_s^+ \quad (41)$$

$$= \delta_{su} X_r^+ X_v^+ - \delta_{vr} X_u^+ X_s^+ . \quad (42)$$

For spin-orbitals, the creation and annihilation operator pair is a generator of the unitary group, so that Equation (42) can be written,

$$[e_{rs}, e_{uv}] = \delta_{su} e_{rv} - \delta_{vr} e_{us} ; \quad (43)$$

and Equation (43) is the correct equation defining the structure constants of the Lie Algebra.^{26,27}

Having established that creation and annihilation operators are rank 1 covariant and contravariant tensors, respectively, with respect to the operator $(\pm)L_r^s$, we may define an n^{th} rank boson operator as consisting of a like number of fermion creation and annihilation operators. Then the normal product of an n^{th} rank boson operator is a natural definition for the irreducible tensor.

Tensors, from the same or different fields, can be combined by outer multiplication, denoted by juxtaposing indices with order preserved on the resultant tensor.²⁶ It is possible that an index is present both in the covariant and contravariant index sets, then, with the repeated index summation convention, both are eliminated and a tensor of lower rank results. The elimination of pairs of indices is known as contraction; and outer multiplication followed by contraction is inner multiplication.²⁶ In multiplication between tensors, contractions cannot take place entirely within one normal product (i.e., generalized time-independent Wick theorem, see Section 4), hence such tensors are called irreducible.

Thus far we have only considered one (boson) vector field, namely the direct product field, $R_{n \times n}$, of creation and annihilation operators. The coefficients of the creation and annihilation operator pairs in fact also constitute vector fields; this can be shown rigorously by construction, but the result can also be inferred. Consider that the Hamiltonian and the cluster operators are index-free, or scalar operators; then the excitation operators, which form part of the said operators, must be contracted, in the sense of tensors, by the coefficients. But then we have the result that the coefficients themselves behave like tensors. This conclusion is not of immediate use, but will be important in the manipulating of the final equations (i.e., after the diagrams have contracted the excitation operators). Also, the sense of the words rank, and irreducible rank, as they have been used to describe components of the Hamiltonian is now clear: they refer to the excitation operator (or equivalently, the coefficient) part of the operator.

Finally, it should be stressed that the position of an index in a sequence is significant, since all operators (and coefficients) will eventually be written in antisymmetrized form. We can shed some light on the sign change for the transformation operator for covariant and contravariant tensors by examining the following:

$$L_r^s X_u^+ = (LX)_{r u}^s = \delta_{su} X_r^+ ; \quad (44)$$

but,

$$L_r^s X^u = (LX)_r^{su} = \delta_{ru} X^s . \quad (45)$$

In words, the transformation operator transforms a covariant vector into a covariant vector (cf. Equation (44)); but the transformation operator transforms a contravariant vector into a contravariant rank 1 tensor which is not a traditional vector. Since L_r^s is antisymmetric, the rank

1 contravariant tensor in Equation (45) can be converted into a vector by interchanging indices, which results in a minus sign. However, in cases where there is no ambiguity the covariant and contravariant indices will be collimated to make the notation more compact.

Questions concerning possible modifications to the descriptions of excited determinants and cluster operators, T_m , due to the renormalization and/or the use of normal product operators must be addressed. Excited determinants with respect to the Fermi vacuum can be written straightforwardly using creation and annihilation operators; a singly-excited determinant is given by,

$$|_i^a\rangle = X_a^+ X_i |\phi_0\rangle, \quad (46)$$

a doubly-excited determinant by,

$$|_{ij}^{ab}\rangle = X_a^+ X_i X_b^+ X_j |\phi_0\rangle, \quad (47)$$

and a triply-excited determinant by,

$$|_{ijk}^{abc}\rangle = X_a^+ X_i X_b^+ X_j X_c^+ X_k |\phi_0\rangle. \quad (48)$$

The cluster operators (cf. Equation (1.4)), like the Hamiltonian operator, are independent of the choice of vacuum level.

Application of the time-independent Wick theorem to the single-excitation operator, $X_a^+ X_i$, present in both the description of singly-excited determinants with respect to the Fermi vacuum and in the cluster operator T_1 , gives,

$$X_a^+ X_i = N[X_a^+ X_i] + N[\overline{X_a^+ X_i}], \quad (49)$$

$$X_a^+ X_i = N[X_a^+ X_i] + h(a)\delta_{ai}, \quad (50)$$

so,

$$X_a^+ X_i = N[X_a^+ X_i], \quad (51)$$

since a and i are members of disjoint sets, i.e., $i \in \{FS\}$, $a \notin \{FS\}$.

Similarly for the double-excitation operator,

$$\begin{aligned}
 X_a^+ X_i X_b^+ X_j &= N[X_a^+ X_i X_b^+ X_j] + N[\overline{X_a^+ X_i} X_b^+ X_j] + N[\overline{X_a^+ X_i} X_b X_j^+] + N[\overline{X_a^+ X_i X_b^+} X_j] + \\
 &+ N[X_a^+ \overline{X_i X_b^+}] + N[X_a^+ \overline{X_i X_b} X_j^+] + N[X_a^+ X_i \overline{X_b^+ X_j}] + \\
 &+ N[\overline{X_a^+ X_i} \overline{X_b^+ X_j}] + N[\overline{X_a^+ X_i X_b^+} X_j] + N[X_a^+ \overline{X_i X_b^+} X_j] . \quad (52)
 \end{aligned}$$

Contractions between the creation operators or the annihilation operators vanish identically because of the Fermi-Dirac statistics obeyed by electrons (cf. Equation (33)); and, as in the single-excitation operator case, contractions between creation and annihilation operators are zero, because the indices belong to disjoint sets (cf. Equation (34)); hence, Equation (52) becomes,

$$X_a^+ X_i X_b^+ X_j = N[X_a^+ X_i X_b^+ X_j] . \quad (53)$$

Further use of the anticommutation relation of fermions for orthonormal orbitals gives,

$$X_a^+ X_i X_b^+ X_j = N[X_a^+ (- X_b^+ X_i) X_j] , \quad (54)$$

$$= -N[X_a^+ X_i X_b^+ X_j] , \quad (55)$$

the Kronecker delta vanishes identically because the field operators are known to be uncontracted. Finally,

$$X_a^+ X_i X_b^+ X_j = N[X_a^+ X_b^+ X_j X_i] ; \quad (56)$$

and we are led to the interesting conclusion that the double-excitation operator, as the single excitation operator, is implicitly in normal product form. The same conclusion holds for the triple-excitation operator, with

$$X_a^+ X_i X_b^+ X_j X_c^+ X_k = N[X_a^+ X_b^+ X_c^+ X_k X_j X_i] . \quad (57)$$

3. Coupled Cluster Equations

The truncated many-particle wavefunction in the coupled cluster method is required to satisfy the Schrödinger equation,

$$H|\psi\rangle = E|\psi\rangle, \quad (3.1)$$

i.e.,
$$H \exp(T)|\phi_0\rangle = E \exp(T)|\phi_0\rangle. \quad (2)$$

The reference energy can be removed^{3,20} from the Schrödinger equation by defining

$$\Delta E = E - \langle\phi_0|H|\phi_0\rangle; \quad (3)$$

then, since H_1 and H_2 are normal product operators of greater than zero rank,

$$E = \Delta E + \langle\phi_0|H_0|\phi_0\rangle. \quad (4)$$

Recalling that H_0 is a scalar,

$$\langle\phi_0|H_0|\phi_0\rangle = H_0\langle\phi_0|\phi_0\rangle; \quad (5)$$

so, with a normalized reference,

$$E = \Delta E + H_0; \quad (6)$$

and the Schrödinger equation can be written,

$$H_N \exp(T)|\phi_0\rangle = \Delta E \exp(T)|\phi_0\rangle, \quad (7)$$

where $H_N = H_1 + H_2$.

Multiplying Equation (7) through from the left by $\exp(-T)$,

we obtain,

$$\exp(-T)H_N \exp(T)|\phi_0\rangle = \Delta E|\phi_0\rangle. \quad (8)$$

The connected cluster theorem of Cizek³ states that,

$$\exp(-T) A \exp(T) = \{A \exp(T)\}_C, \quad (9)$$

where A is any operator of the same number of creation and annihilation operators in normal product form, and the subscript C means that only connected diagrams are to be included.¹³ Then the Schrödinger equation, with no further approximation beyond the exponential ansatz,

may be written,

$$\{H_N \exp(T)\}_C |\phi_0\rangle = \Delta E |\phi_0\rangle . \quad (10)$$

Projection of Equation (10) onto the set of α -excited determinants ($\alpha = 1, 2, 3$) yields a set of coupled equations in the cluster coefficients,

$$\langle \alpha | \{H_N \exp(T)\}_C |\phi_0\rangle = \Delta E \langle \alpha | \phi_0\rangle = 0 . \quad (11)$$

Also, projection onto the reference determinant allows ΔE , and hence the correlated energy, to be calculated once the cluster coefficients are known,

$$\langle \phi_0 | \{H_N \exp(T)\}_C |\phi_0\rangle = \Delta E \langle \phi_0 | \phi_0\rangle = \Delta E . \quad (12)$$

It is clear that the necessary and sufficient number of equations in the coupled set, Equation (11), is equal to the number of unique cluster coefficients, provided that a solution exists. Since the coupled cluster equations are non-Hermitian and nonlinear, the existence of solutions and the reality of eigenvalues corresponding to solutions are not guaranteed. However, Zivkovic and Monkhorst²⁸ have recently shown, using analytic continuations of solutions to the CI problem, that for physically reasonable cases both the existence of solutions and the reality of eigenvalues is assured.

The specific equations used to determine the cluster coefficients in the CCSDT model will now be given. Projection of the Schrödinger Equation (cf. Equation (10)) onto the singly-excited space gives,

$$\langle u^\beta | \{H_N (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_3 + T_2 T_1 + \frac{1}{3!} T_1^3)\}_C |\phi_0\rangle = 0 , \quad (13)$$

$\forall u \in \{FS\}$, $\forall \beta \notin \{FS\}$; projection onto the doubly-excited space gives,

$$\begin{aligned} \langle \beta\gamma |_{uv} \{ & H_N (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_3 + T_2 T_1 + \frac{1}{3!} T_1^3 + \\ & + T_3 T_1 + \frac{1}{2} T_2^2 + \frac{1}{2} T_2 T_1^2 + \frac{1}{4!} T_1^4) \} | \phi_0 \rangle = 0 , \end{aligned} \quad (14)$$

$\forall u \langle v, u, v \rangle \in \{FS\}$, $\forall \beta \langle \gamma, \beta, \gamma \rangle \in \{FS\}$; and projection onto the triply-excited space gives,

$$\begin{aligned} \langle \beta\gamma\epsilon |_{uvw} \{ & H_N (T_1 + T_2 + \frac{1}{2} T_1^2 + T_3 + T_2 T_1 + \frac{1}{3!} T_1^3 + \\ & + T_3 T_1 + \frac{1}{2} T_2^2 + \frac{1}{2} T_2 T_1^2 + \frac{1}{4!} T_1^4 + \\ & + T_3 T_2 + \frac{1}{2} T_3 T_1^2 + \frac{1}{2} T_2^2 T_1 + \frac{1}{3!} T_2 T_1^3 + \frac{1}{5!} T_1^5) \} | \phi_0 \rangle = 0 , \end{aligned} \quad (15)$$

$\forall u \langle v \langle w, u, v, w \rangle \in \{FS\}$, $\forall \beta \langle \gamma \langle \epsilon, \beta, \gamma, \epsilon \rangle \in \{FS\}$. The correlated energy can similarly be written as,

$$\langle \phi_0 | \{ H_N (1 + T_1 + T_2 + \frac{1}{2} T_1^2) \} | \phi_0 \rangle = \Delta E . \quad (16)$$

It should be emphasized that the absence of terms in the wave operators in the above equations does not reflect further truncation (e.g., with respect to $\exp(T_1 + T_2 + T_3)$), rather it is a consequence of the triangle inequalities involving the (irreducible) ranks of the Hamiltonian, the external space operators, and the cluster operators. More specifically, a matrix element vanishes identically unless it has an overall rank of 0; from elementary vector analysis, this can only occur if the component contributions obey a triangle inequality,

$$\left| r(H_N) - \sum_i m_i \right| < \alpha < r(H_N) + \sum_i m_i , \quad (17)$$

where the m_i refer to the ranks of the individual T_m operators in a term, and α is the rank of the external space operator. The generalized time-independent Wick theorem, which will be discussed in the following Section, justifies the strict addition of the m_i 's in Equation (17).

Equations (13)-(16) reflect the triangle inequality for $\max r(H_N) = r(H_N) = 2$; of course, the potent range of the wave operator is even smaller for matrix elements involving H_1 .

As shown by Paldus, Cizek, and Shavitt,⁴ antisymmetrized (e.g., degenerate) T matrix elements,

$$\begin{aligned} t_{uvw\dots}^{\beta\gamma\epsilon\dots} &= \langle \beta\gamma\epsilon\dots | T | uvw\dots \rangle_A \\ &= \langle \beta\gamma\epsilon\dots | T | P(u|v|w|\dots)uvw\dots \rangle, \end{aligned} \quad (18)$$

are the most appropriate for use in the coupled cluster equations. The permutation operator used in Equation (18) is our adaption of the (symmetric) permutation operator of Bogoliubov and Shirkov²² used in the formal power series expansion of the scattering matrix; and will be discussed in greater detail in the following Section. The permutation operator, as used in Equation (18), represents the signed summation over all possible permutations of hole indices. With the T matrix elements as defined in Equation (18), the following specific relations hold,

$$t_{uv}^{\beta\gamma} = -t_{vu}^{\beta\gamma} = -t_{uv}^{\gamma\beta} = t_{vu}^{\gamma\beta}, \quad (19)$$

and

$$t_{uvw}^{\beta\gamma\epsilon} = -t_{vuw}^{\beta\gamma\epsilon} = t_{vwu}^{\beta\gamma\epsilon} = -t_{wvu}^{\beta\gamma\epsilon} = t_{wuv}^{\beta\gamma\epsilon} = -t_{uwx}^{\beta\gamma\epsilon} = -t_{uwx}^{\gamma\beta\epsilon}, \text{ etc.} \quad (20)$$

We have implicitly used the permutational symmetry of the T matrix elements in writing Equations (1.4), (14), and (15). In particular, the restrictions on the external indices are a direct consequence of there being only one unique T matrix element for a given set of indices.

Perhaps it is appropriate in closing this section on the coupled cluster equations to comment on the relation between perturbation theory and the coupled cluster method. The iterative scheme used to solve the coupled cluster equations can be seen as a method to simultaneously generate and evaluate diagrams of arbitrarily high order in perturbation theory.⁸ Of course, diagrams corresponding to high order connected terms (e.g., T_4 in CCSDT) will not be so generated.⁸ It is this property, generating arbitrarily high order diagrams, that makes the coupled cluster method, in principle, less subject to the issue of the "smallness" of the perturbation than perturbation theory. If one wished to speculate, it is reasonable to suppose that the coupled cluster method will prove superior to perturbation theory especially in the calculation of excited electronic states.

4. Diagrams and Rules

As was first realized by Feynman, field operators and their interactions can be represented graphically by lines and points, respectively. The evaluation of matrix elements proceeds in two steps: all topologically distinct diagrams capable of being formed from the given component diagrams are assembled and, then, the resulting diagrams are converted back to algebraic expressions using relatively straightforward rules.

The original rules and diagrams, as formulated by Feynman for quantum electrodynamics (QED), are unnecessarily general for our intended application. Rather, the time-independent formulations of Hugenholtz²⁹ and Brandow,³⁰ developed primarily for use in perturbation treatments of problems in nuclear physics, are more suitable for our

needs. Cizek and Paldus^{3,4,8,20} were the first to apply the time-independent diagrammatic approach to atomic and molecular problems, and it is their notation which we will conform to most often. A key feature of our implementation of the diagrammatic technique is the use of formal concepts used in the functional expansion of the scattering matrix in quantum electrodynamics, in a time-independent approach.

A formal similarity arises because both the scattering matrix in quantum electrodynamics and the wave operator in a full coupled cluster method (cf. Equations (1.1) and (1.4)) are exponential operators. In Bogoliubov's axiomatic formulation of the scattering matrix,²²

$$|\phi(\infty)\rangle = S(g)|\phi(-\infty)\rangle, \quad (1)$$

with

$$S(g) = 1 + \sum_{n>1} \frac{1}{n!} \int S_n(x_1, \dots, x_n) g(x_1) \dots g(x_n) dx_1 \dots dx_n, \quad (2)$$

where the x_i are coordinates of space-time and the $g(x_i)$ are functions describing the intensity of switching on the interaction. The two specific features that we adapt from Bogoliubov and Shirkov's²² formulation of Feynman's rules for use in the time-independent approach involve the use of formal permutation operators and the analysis of the symmetry factor.

We turn now to the description of the requisite component diagrams for a CCSDT theory. The basic interaction in our application of spinor electrodynamics is the absorption of an electron (or hole) and the emission of an electron (or hole), together with the absorption or emission of a photon. Solid lines will be used to represent operators of the Dirac field; since both positive and negative energy single-particle

states are admissible,^{22,25,31} the diagrammatic representation of the spinors must be directed. A left-pointed arrow will designate an electron, and a right-pointed will then denote a hole. A solid dot will be used to designate an interaction; spinor lines emerging from the dot will then correspond to electron creation operators, and spinor lines converging upon the dot will represent electron annihilation operators. The four possible relations of one spinor line and an interaction dot are shown in Figure 1.



Figure 1. Parts of diagrams representing the (a) creation of an electron, (b) annihilation of an electron, (c) annihilation of a hole, and (d) creation of a hole.

It is clear then that under the constraint of requiring one incoming line and one outgoing line that there are four versions of the basic interaction, denoted pp, ph, hp, and hh.

Different types of diagrams are used to represent non-degenerate and degenerate (i.e., antisymmetrized) operators. The time-independent non-degenerate diagrams in common usage were first suggested by Goldstone.³² In Goldstone diagrams, operators of the electromagnetic field (e.g., photons) are represented by dashed lines; the background, or averaged, electromagnetic field of the other electrons and the nuclei is represented by a small triangle. The Goldstone diagram for the hh

version of an H_1 operator (i.e., F-vertex) is given in Figure 2(a). Different versions of time-independent degenerate diagrams were suggested by Hugenholtz,²⁹ and by Brandow.³⁰ In general, Brandow diagrams appear similar to Goldstone diagrams; Hugenholtz diagrams coalesce interaction vertices separated by photons. The Brandow and Hugenholtz diagrams for F-vertices, however, are identical; the hh version is given in Figure 2(b).



Figure 2. (a) Goldstone and (b) Hugenholtz or Brandow diagrams for the hh version of an F-vertex.

Since all of the operators required in the CCSDT model are, or can be made, degenerate (cf. Sections 2 and 3), and there are most certainly fewer degenerate than non-degenerate resulting diagrams, it behooves us to use degenerate diagrams. We use Brandow's version of degenerate diagrams, mainly because the absolute phase of a degenerate diagram is indeterminate, and a (partially) non-degenerate diagram contained within the original degenerate diagram must be examined⁸ (cf. Rules 2 and 3, this Section). The direct mixed Goldstone-Brandow quasi-degenerate diagram is easily obtained from the parent Brandow diagram by replacing the squiggly line by a dashed line. Figure 3 shows the different topological representations of a hh-hh version H_2 operator (V-vertex).

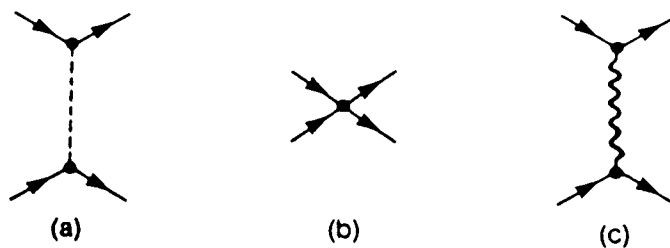


Figure 3. (a) Goldstone, (b) Hugenholtz, and (c) Brandow diagrams for hh-hh V-vertices.

Symbols for non-degenerate T operators are not needed, and no further discussion afforded them. Brandow version antisymmetrized T operators, for (irreducible) ranks one, two, and three, are shown in Figure 4.

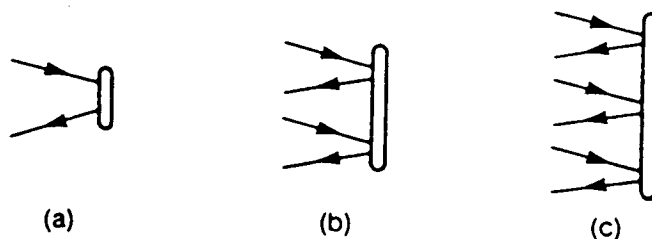


Figure 4. Brandow diagrams for (a) single, (b) double, and (c) triple antisymmetrized cluster operators.

As usual in degenerate time-independent diagrammatic methods,^{3,8,20,29,30} excited determinants are represented by external space operators rather than by pair creation/annihilation operators. Diagrammatically, an external line is a ray, whereas an internal line is

a line segment. The four possible types of rays and line segments which arise in a CCSDT method are shown in Figure 5.



Figure 5. (a) external hole line, (b) external particle line, (c) internal hole line, and (d) internal particle line.

The indexing convention we will use for the rest of the chapter is that u , v , and w will denote external holes, i and j internal holes, β , γ , and ϵ external particles (i.e., electrons), and a and b internal particles.

The component diagrams necessary for a CCSDT model have now been introduced and briefly described. We continue with a short exposition on the rules for the construction and subsequent evaluation of the resulting, or final, diagrams.

Rule 1: Juxtapose Brandow versions of all component diagrams, representing operators of the matrix element in question, to form all possible time-ordered, topologically distinct, non-vanishing, connected, canonical resulting diagrams.

The relative positions of the component diagrams can be established by considering the time-order of the operators that they represent. Hugenholtz²⁹ and Brandow³⁰ have shown the correspondence of

the order of appearance, read right to left, of operators in perturbation theory matrix elements and their time-order. Cizek and Paldus^{3,20} have extended this idea to truncated versions of coupled cluster theory. The questions which remain in our minds are whether all T operators are always "simultaneous", and whether the Hamiltonian vertex is always at a "later" time. Rather direct answers to these questions are obtained by considering the relation between commutation and time-ordering, as discussed in Bogoliubov and Shirkov's text.²² In particular, local Bose operators (i.e., field operators having the same number of fermion creation and annihilation operators) that commute have a spacelike relation (e.g., they are "simultaneous"); conversely, local Bose operators that do not commute are separated in time. It is not difficult to verify that,

$$[T_m, T_n] = 0, \quad 1 < m, n < 3, \quad (3)$$

and

$$[T_m, H] \neq 0, \quad 1 < m < 3. \quad (4)$$

So the cluster operators are seen to have a spacelike relation with each other and a timelike relation with the Hamiltonian. Then, in keeping with the choice of directions for the Dirac spinors shown in Figure 1, the topological arrangement of component diagrams is a column of cluster operators to the far right, followed by a Hamiltonian diagram to the left, followed by the external space operators on the extreme left. In agreement with the convention of Hugenholtz²⁹ (and Cizek and Paldus^{3,20}), "time flows from right to left" in our diagrams.

Component diagrams are assembled into resulting diagrams by

attaching the free ends of spinor lines. A resulting diagram with the property that a continuous line exists between each pair of interaction vertices is said to be connected. (N.B. The aforementioned line may consist of a set of Dirac spinor line segments, electromagnetic line segments, or a combination of the two.)

A large number of connected, time-ordered resulting diagrams can be eliminated from further consideration by recognizing that two of four possible types of contractions of Dirac spinor lines are vanishing.²⁰



Figure 6. Vanishing contractions of Dirac spinor lines.

The values of the two potentially non-zero joinings are given by Kronecker delta functions (i.e., for orthonormal orbitals).²⁰



Figure 7. Possibly non-vanishing contractions of Dirac spinor lines.

Additionally, consideration of connections between different T operators (cf. Figure 8(d)) can now be categorically eliminated. Of the four possible single connections between different T operators, two are identically zero "because the arrows don't match up" (cf. Figure 6). The other two possibilities, representing an annihilation operator of one T operator being contracted with a creation operator of the other T operator, give Kronecker delta contributions to the matrix element (cf.

Figure 7). However, the last two possibilities are also zero in this case, because the particle and hole index sets are disjoint. Hence, no diagrams containing connections between different T operators need be considered.

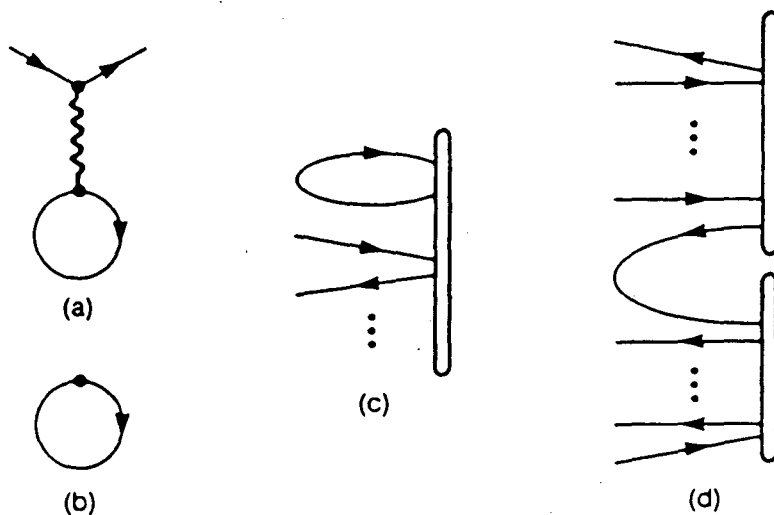


Figure 8. a) V-V, b) F-F, c) T-T, d) T-T' diagrams.

The topology of contractions is determined by the generalized time-independent Wick theorem^{20,22} and the fact that matrix elements of uncontracted operators are identically zero²⁰. The generalized time-independent Wick theorem can be written in the form,

$$\begin{aligned}
 & M_1 \dots M_{i_1} N[M_{i_1+1} \dots M_{i_2}] M_{i_2+1} \dots M_{i_3} N[M_{i_3+1} \dots M_{i_4}] \dots M_{i_k} \\
 & = N[M_1 \dots M_{i_k}] + \sum' N[M_1 \dots M_{i_k}] , \quad (5)
 \end{aligned}$$

where M_i can represent either a creation or an annihilation operator, and the prime indicates that contractions between operators originating in the same normal product are to be neglected. Since F-, V-, and T-vertices represent normal product operators (cf. Equations (2.25), (2.26), (2.51), (2.56), and (2.57)), it is clear that the diagrams shown in Figure 8(a)-(c) do not occur in the coupled cluster method.

A canonical diagram is a resulting, or final, diagram in which the external line labels conform to a specific pattern or ordering.⁸ The pattern which will be designated canonical in our diagrams has both the electron (β, γ, ϵ) and hole (u, v, w) indices progressing from top to bottom. Note that the position of an electron index relative to a hole index is in no way specified in a canonical diagram. A consequence of considering only canonical diagrams is that external lines from a common set (i.e., electron or hole) may not cross. Canonical diagrams with crossed lines from a common set are in fact topologically equivalent to a related noncanonical diagram. The noncanonical, but otherwise valid, diagrams related to a given canonical diagram by the interchange of external line indices can be generated by the action of the permutation operator on the canonical diagram, and hence will be considered at a later stage.

The final requirement for an otherwise valid resulting diagram is that it is topologically distinct from all permutations (including the identity) of all previous resulting canonical diagrams. Two diagrams are topologically distinct if there does not exist any continuous transformation (e.g., stretching, bending) converting one into the other. Heuristically, one needs to "cut and paste" in order to convert one topologically distinct diagram into another.

Rule 2: Determine the algebraic expression, up to phase and degeneracy, corresponding to each resulting canonical diagram using the following rules:

- a: Assign f_{pq} , $\langle pq || rs \rangle$, and $t_{pq\dots}^{rs\dots}$ to each F-, V-, and T-vertex, respectively, consistent with extant line indexing.
- b: Sum over each internal line.

Note that p exits an F-vertex (i.e., p represents electron creation or hole annihilation), and q enters an F-vertex (i.e., q represents electron annihilation or hole creation). Also, p and q exit V-vertices, r and s enter; but, p and q enter T-vertices, while r and s exit. Since V- and T-vertices are degenerate, the assignment of values to these vertices is determined only up to phase (cf. Equations (3.18) - (3.20)). It will expedite the establishing of the overall phase factor of the matrix element (cf. Rule 3), if antisymmetrized component matrix elements with the same ordering of indices as the corresponding direct matrix elements are used. Hence, p and r , q and s , etc., are associated, or considered participants in the same basic interaction.

The summation over internal lines is done without regard for the Pauli exclusion principle. The so-called exclusion violating (e.-v.³⁰ or EPV²⁰) terms cancel each other exactly, provided all such terms are included. The alternative, using restricted summations, would also be correct, but is unwieldy.³⁰

Rule 3: Determine the prefactor for each resulting diagram by multiplying the phase factor and the weight of the diagram:

$$\phi = \eta w . \quad (6)$$

The overall phase can be established by considering any one of the mixed Goldstone-Brandow diagrams included in a given resulting diagram. It is simplest to work with the direct mixed Goldstone-Brandow diagram, since that diagram looks like the corresponding Brandow diagram except that the degenerate V-vertex is replaced by a non-degenerate V-vertex, but with index labels intact. The phase, or sign, factor of the degenerate diagram is then equal to the phase factor of the non-degenerate diagram; i.e.,^{8,20,22,30}

$$\eta = (-1)^{\ell + h + p}, \quad (7)$$

where ℓ is the number of closed loops, h is the number of internal hole lines, and p is the parity of the permutation yielding the canonical labeling of external lines.⁸ Of course, $p = 0$ for all canonical diagrams, but this contribution to the phase must be considered in the permutation operators used to generate the noncanonical diagrams related to a given canonical resulting diagram (cf. Rule 4).

The symmetry factor, and hence the weight, is determined by an adaption of Bogoliubov and Shirkov's²² prescription for obtaining the symmetry factor in (time-dependent) quantum electrodynamics. The three contributions to the symmetry factor are:

- (1) The $n_1 \dots n_j^{\text{th}}$ term of the expansion of the wave operator contains the factor $(n_1!)^{-1} \dots (n_j!)^{-1}$. This is always compensated by the factor $(n_1!) \dots (n_j!)$, which takes into account permutation of the vertices.
- (2) The rank two Hamiltonian contains two identical creation operators and two identical annihilation operators, which introduces the factor $(2!)(2!) = 4$. This compensates the numerical factor $1/4$ associated with a V-vertex.

- (3) In case there exist c topologically equivalent variants of pairings of internal lines, they must be taken into account only once. This corresponds to the introduction of the factor $(c!)^{-1}$.

For Hamiltonians with no greater than rank 2 components, the third rule simplifies to:

- (1) Unless altered by the following rules, $c_p = c_h = c_{ph} = 1$.
- (2) If two hole lines begin at the same vertex and end at the same vertex, $c_h = 2$.
- (3) If two particle lines begin at the same vertex and end at the same vertex, $c_p = 2$.
- (4) If simultaneous interchange of the particle lines and the hole lines yields a topologically equivalent diagram and the hole and particle lines are not independently interchangeable, $c_{ph} = 2$.
- (5) The weight of the diagram is given by,

$$w = \frac{1}{c_p c_h c_{ph}} \quad (8)$$

There are two points we would like to emphasize at this time. The first is that the weight factor detailed above is in accord with the usual " $1/2$ rule" for weights in perturbation theory,^{20,29,30} and truncated coupled cluster expansions.^{3,4,8,14} The value then of the somewhat extended treatment of weight factors given in the present work is that the straightforward " $1/2$ rule" can justifiably be used in a full coupled cluster method. In particular, it was not transparent to us that the presence of the numerical factors, $(n!)^{-1}$, $n \geq 3$, in the wave operator would be exactly offset in every matrix element. It should be noted that the star product treatment developed by Cizek³ is correct and justified

for the determination of the weight factor in a full coupled cluster method; however, the procedure is a bit cumbersome when there are more than about two cluster operators.

The second point is that the use of rules originally developed for a time-dependent formalism in a time-independent diagrammatic approach is appropriate, provided that the diagrams are topologically similar, and that the rules consider only topological (e.g., not physical) aspects of the theory. The structural similarities of the (exponential) scattering matrix and the wave operator (cf. Equations (1), (2), (1.1), and (1.4)), and the physical particles and the excited (bra) determinant, have already been discussed. A subtlety is that the interaction vertices in a time-dependent formalism represent components of the Lagrangian, while the interaction vertices in a time-independent formalism represent components of the Hamiltonian. The topological equivalence is assured with the realization that the basic interaction in both versions is the entering and exiting of a spinor line together with the emission or absorption of a photon. Hence, the efficient symmetry rules set out by Bogoliubov and Shirkov²² can straightforwardly be used in a time-independent formalism.

Rule 4: Generate the algebraic expressions corresponding to the noncanonical diagrams directly from the algebraic expressions for the canonical diagrams by applying permutation operators.

The generalized time-independent Wick theorem (cf. Equation (5)) requires that all sets of contractions between operators (from different N-products) be included in the summation. The inclusion of

only canonical diagrams, as defined earlier, can be seen to represent all possible contractions between the Hamiltonian and the wave operator, but restricted contraction between the bra configuration and these combined operator products. The noncanonical diagrams then complete the set of all possible contractions between operator expressions. A noncanonical diagram is characterized by crisscrossing external lines, or equivalently (i.e., fermion operators anticommute), noncrossing external lines with permuted indices with respect to the canonical ordering.

Consider a permutation operator which generates all topologically distinct noncanonical diagrams from a given canonical diagram; essentially, this operator just relabels external lines. Since the noncanonical diagrams are structurally the same as their parent resulting diagram, the algebraic expressions for the noncanonical diagrams must be the same as the algebraic expression for the parent diagram, up to a reordering of external indices. It can be seen then that the permutation operator acting on the algebraic expression for a canonical diagram will produce algebraic expressions corresponding to noncanonical diagrams permutationally related to the parent resulting diagram.

Two properties of the permutation operator, spin statistics and topological distinctness, warrant further discussion. As pointed out by Paldus,⁸ the phase factor of a noncanonical diagram must include the contribution $(-1)^p$, where p is here the parity of the permutation yielding the canonical labeling of external lines. The origin of this term is the anticommutation of fermion field operators (cf. Equation (2.33)). So, in order for the permutation operator to generate algebraic

expressions for noncanonical diagrams with the correct overall phase, the contribution to the phase factor from the ordering of external indices must be included in the permutation operator. A second major concern is that the sum over resulting diagrams include only topologically distinct diagrams. Hence, we require that the algebraic expressions generated by the permutation operator correspond to topologically distinct noncanonical diagrams.

Since both the particle and hole labels are in general permuted, and it is often the case that the permutations are independent, it is efficacious to (always) write the permutation operator as the binary product of operators acting on the disjoint sets,

$$\begin{aligned} p(u_1, \beta_1) &= P(u_1)P'(\beta_1) , \\ &= P'(\beta_1)P(u_1) , \quad i = 1, 3 . \end{aligned} \quad (9)$$

In Equation (9), the u_1 and β_1 represent hole and particle labels, respectively, and P and P' denote single index set permutation operators. In the cases that the particle and hole permutations are dependent, the decomposition of the permutation operator into single index set permutation operators is ambiguous, i.e., two correct descriptions exist,

$$p(u_1, \beta_1) = P(u_1)P'(\beta_1) = P''(u_1)P'''(\beta_1) . \quad (10)$$

It is found that for such permutations, any correct description is adequate.

The particular form of the single index permutation operators we will use is an antisymmetrized generalization of Bogoliubov and

Shirkov's²² (symmetric) permutation operators used in the power series expansion of the scattering matrix. Vertical lines demarcate topologically distinct environments, and hence define the permutation patterns. It should be noted that a null intersection between external lines of a given index set and a topologically distinct environment is suppressed in the notation. Under the action of the permutation operator the labels in the algebraic expression lose their original significance (e.g., they become placeholders or "dummy variables"), but the ordering in the parent resulting diagram is preserved by the list of labels in the permutation operator. Hence it can be seen that the list of labels, which specifies the identity permutation, together with the placement of vertical lines completely specifies the single index set permutation operators.

There are four types of non-trivial single index set permutation operators required in a CCSDT model; i.e.,

$$P(x_1|x_2) = I - (x_1 x_2) , \quad (11)$$

$$P(x_1 x_2|x_3) = I - (x_1 x_2) - (x_2 x_3) , \quad (12)$$

$$P(x_1|x_2 x_3) = I - (x_1 x_2) - (x_1 x_3) , \quad (13)$$

and

$$\begin{aligned} P(x_1|x_2|x_3) &= I - (x_1 x_2) - (x_1 x_3) - (x_2 x_3) + \\ &\quad + (x_1 x_2)(x_2 x_3) + (x_1 x_3)(x_2 x_3) , \end{aligned} \quad (14)$$

or

$$\begin{aligned} &= I - (x_1 x_2) - (x_1 x_3) - (x_2 x_3) + \\ &\quad + (x_1 x_2 x_3) + (x_1 x_3 x_2) . \end{aligned} \quad (15)$$

In Equations (11) - (15), cyclic notation was used, with I denoting the identity permutation; and x_i representing either particles, β_i , or holes, u_i . The trivial permutation operator, $P = I$, will not be explicitly used. It should be noted that the signs are in agreement with the parities of the permutation cycles, so that the criterion of correct phase for noncanonical diagrams is implemented on the single index set permutation operator level.

Application of an appropriate single index set permutation operator on the algebraic expression corresponding to a canonical resulting diagram produces only algebraic expressions corresponding to topologically distinct noncanonical diagrams, since indices are switched between topologically nonequivalent environments. However, subsequent application of the complementary (e.g., particle/hole) single index set permutation operator may produce algebraic expressions corresponding to topologically indistinct resulting diagrams, because the action of the first operator rendered two distinct topological environments equivalent. Effectively, a specious vertical line exists in the second operator, the removal of which correctly reflects the physical situation and leads to the correct number of topologically distinct noncanonical diagrams. It is to be emphasized that the recognition of topologically distinct environments is relatively straightforward diagrammatically, and is actually a strong recommendation for a diagrammatic approach.

In summary, the rules for the construction and subsequent evaluation of diagrams corresponding to matrix elements in the CCSDT model have been given. The adaption of certain features from time-dependent diagrams, not usually found in time-independent approaches, have been seen to clarify and/or expedite time-independent diagrams.

5. Matrix Elements

The equations for the cluster coefficients and the correlated energy in a CCSDT model were given in operator form in Section 3 (cf. Equations (3.13) - (3.16)); this form is, of course, not amenable to calculations. In the present Section the time-independent techniques discussed in Section 4 are applied to evaluate the requisite matrix elements in terms of cluster coefficients and one- and two-electron integrals over the spin-orbital basis.

Table I lists all possibly non-vanishing matrix elements arising from the projection of the Schrödinger Equation onto the reference, singly-, doubly-, and triply-excited spaces. The matrix elements are assigned an ordinal number. The diagrams generated in the application of Rule 1 from the preceding Section to a given matrix element are listed on the right-hand side of the Table, below the particular matrix element. Multiple diagrams from a given matrix element are distinguished by lower case roman letters. Algebraic expressions, up to phase and symmetry, corresponding to a given diagram are evaluated using Rule 2; and designated with the letter d , and the subscript associated with the diagram. Contributions to the symmetry and phase factors are also listed, if differing from the following default values: $l = 0$, $h = 0$, $c_p = 1$, $c_h = 1$, $c_{ph} = 1$. The prefactor corresponding to a given diagram is then evaluated using Rule 3; it is symbolized by the greek letter ϕ , and the subscript of the diagram. The permutation operator generating all non-canonical diagrams related to a given diagram (cf. Rule 4) is listed, provided that either the hole or the particle permutation operator is different than the identity. The permutation operator is symbolized by the letter p , and the subscript of the diagram. Hence each diagram has

between two and four lines of text written opposite to it (e.g., left-hand side) in Table I.

The expression for a given matrix element, m , without reference to field operators is then given by,

$$[m] = \sum_{\zeta} p_{m\zeta} \phi_{m\zeta} d_{m\zeta} , \quad (5.1)$$

where the summation runs over all valid (canonical) diagrams derivable from m .

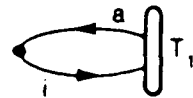
Table I. Diagrammatic evaluation of all non-vanishing matrix elements occurring in the CCSDT model. See text for explanation of symbols.

$$[1] = \langle \phi_0 | \{H_1 T_1\} \mathcal{C} | \phi_0 \rangle$$

$$d_1 = \sum_{ia} f_{ia} t_i^a$$

$$\ell = 1, h = 1$$

$$\phi_1 = 1$$

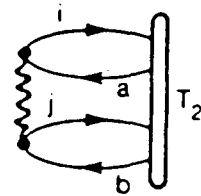


$$[2] = \langle \phi_0 | \{H_2 T_2\} \mathcal{C} | \phi_0 \rangle$$

$$d_2 = \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}$$

$$\ell = 2, h = 2, c_h = 2, c_p = 2$$

$$\phi_2 = 1/4$$



$$[3] = \langle \phi_0 | \{H_2 \frac{1}{2} T_1^2\} \mathcal{C} | \phi_0 \rangle$$

$$d_3 = \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b$$

$$\ell = 2, h = 2, c_{ph} = 2$$

$$\phi_3 = 1/2$$

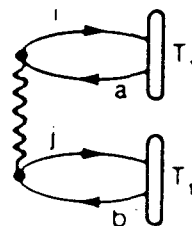
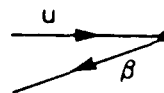


Table I (continued from previous page)

$$[4] = \langle u^\beta | \{H_1 I\} C | \phi_0 \rangle$$

$$d_4 = f_{u\beta}$$

$$\phi_4 = 1$$

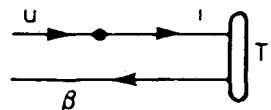


$$[5] = \langle u^\beta | \{H_1 T_1\} C | \phi_0 \rangle$$

$$d_{5a} = \sum_i f_{ui} t_i^\beta$$

$$h = 1$$

$$\phi_{5a} = -1$$



$$d_{5b} = \sum_a f_{a\beta} t_u^a$$

$$\phi_{5b} = 1$$

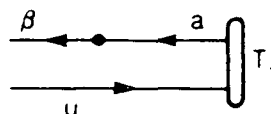


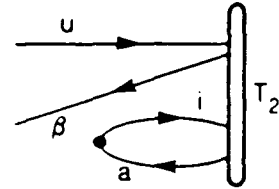
Table I (continued from previous page)

$$[6] = \langle \beta_u | \{H_1 T_2\} \mathbf{c} | \phi_0 \rangle$$

$$d_6 = \sum_{ia} f_{ia} t_{ui}^{\beta a}$$

$$l = 1, h = 1$$

$$\phi_6 = 1$$

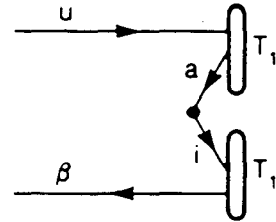


$$[7] = \langle \beta_u | \{H_1 \frac{1}{2} T_1^2\} \mathbf{c} | \phi_0 \rangle$$

$$d_7 = \sum_{ia} f_{ia} t_{u1}^{a\beta}$$

$$h = 1$$

$$\phi_7 = -1$$



$$[8] = \langle \beta_u | \{H_2 T_1\} \mathbf{c} | \phi_0 \rangle$$

$$d_8 = \sum_{ia} \langle \beta i | | a u \rangle t_1^a$$

$$h = 1$$

$$\phi_8 = -1$$

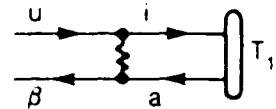


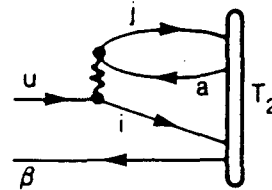
Table I (continued from previous page)

$$[9] = \langle \beta_u | \{H_2 T_2\} c | \phi_0 \rangle$$

$$d_{9a} = \sum_{ija} \langle ij || ua \rangle t_{ij}^{\beta a}$$

$$l = 1, h = 2, c_h = 2$$

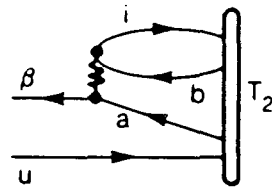
$$\phi_{9a} = -1/2$$



$$d_{9b} = \sum_{iab} \langle \beta 1 || ab \rangle t_{ui}^{ab}$$

$$l = 1, h = 1, c_p = 2$$

$$\phi_{9b} = 1/2$$



$$[10] = \langle \beta_u | \{H_2 \frac{1}{2} T_1^2\} c | \phi_0 \rangle$$

$$d_{10a} = \sum_{ija} \langle ij || ua \rangle t_i^{\beta} t_j^a$$

$$l = 1, h = 2$$

$$\phi_{10a} = -1$$

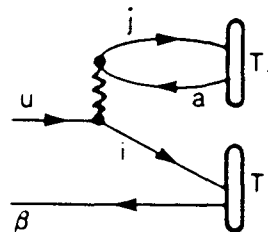
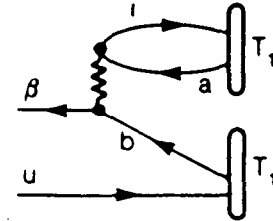


Table I (continued from previous page)

$$d_{10b} = \sum_{iab} \langle i\beta || ab \rangle t_1^a t_u^b$$

$$\ell = 1, h = 1$$

$$\phi_{10b} = 1$$

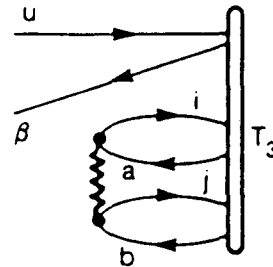


$$[11] = \langle u^\beta || \{H_2 T_3\} \mathbf{C} | \phi_0 \rangle$$

$$d_{11} = \sum_{ijab} \langle ij || ab \rangle t_{uij}^{\beta ab}$$

$$\ell = 2, h = 2, c_h = 2, c_p = 2$$

$$\phi_{11} = 1/4$$



$$[12] = \langle u^\beta || \{H_2 T_2 T_1\} \mathbf{C} | \phi_0 \rangle$$

$$d_{12a} = \sum_{ijab} \langle ij || ab \rangle t_{uij}^{\beta a} t_j^b$$

$$\ell = 2, h = 2$$

$$\phi = 1$$

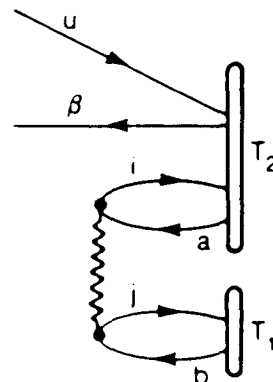
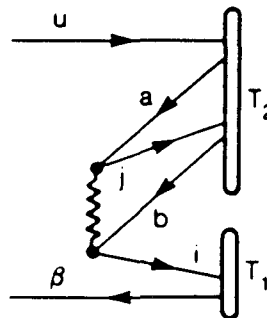


Table I (continued from previous page)

$$d_{12b} = \sum_{ijab} \langle ij || ab \rangle t_{uj}^{ab} t_i^{\beta}$$

$$h = 2, c_p = 2$$

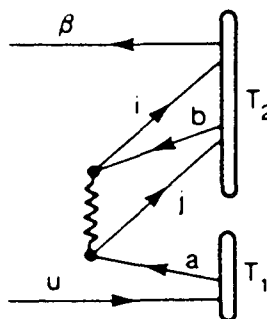
$$\phi_{12b} = 1/2$$



$$d_{12c} = \sum_{ijab} \langle ij || ba \rangle t_{ij}^{\beta b} t_u^a$$

$$h = 2, c_h = 2$$

$$\phi_{12c} = 1/2$$



$$[13] = \langle u^{\beta} | \{ H_2 \frac{1}{3!} T_1^3 \} c | \phi_0 \rangle$$

$$d_{13} = \sum_{ijab} \langle ij || ba \rangle t_{u i}^{b a} t_j^{\beta}$$

$$h = 2$$

$$\phi_{13} = 1$$

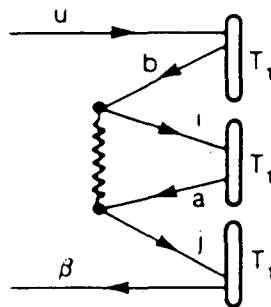


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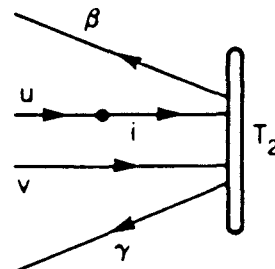
$$[14] = \langle \beta\gamma | \{H_1 T_2\}_C | \phi_0 \rangle$$

$$d_{14a} = \sum_i f_{ui} t_{iv}^{\beta\gamma}$$

$$h = 1$$

$$\phi_{14a} = -1$$

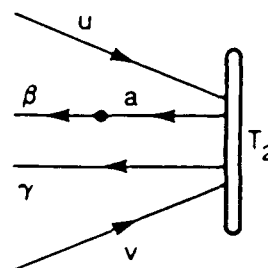
$$P_{14a} = P(u|v)$$



$$d_{14b} = \sum_a f_{a\beta} t_{uv}^{a\gamma}$$

$$\phi_{14b} = 1$$

$$P_{14b} = P(\beta|\gamma)$$



$$[15] = \langle \beta\gamma | \{H_1 T_3\}_C | \phi_0 \rangle$$

$$d_{15} = \sum_{ia} f_{ia} t_{uvi}^{\beta\gamma a}$$

$$l = 1, h = 1$$

$$\phi_{15} = 1$$

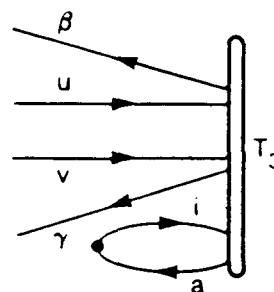


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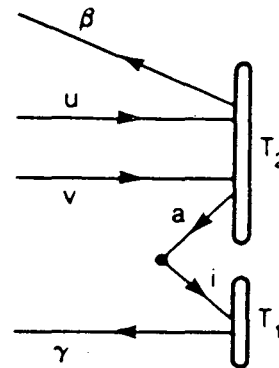
$$[16] = \langle \beta\gamma | \{H_1 T_2 T_1\}_C | \phi_0 \rangle$$

$$d_{16a} = \sum_{ia} f_{ai} t_{uv}^{\beta a \gamma} t_i$$

$$h = 1$$

$$\phi_{16a} = -1$$

$$P_{16a} = P(\beta|\gamma)$$

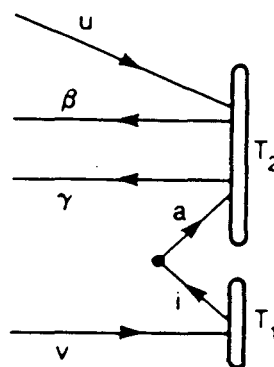


$$d_{16b} = \sum_{ia} f_{ai} t_{ui}^{\beta \gamma a} t_v$$

$$h = 1$$

$$\phi_{16b} = -1$$

$$P_{16b} = P(u|v)$$



$$[17] = \langle \beta\gamma | \{H_2 1\}_C | \phi_0 \rangle$$

$$d_{17} = \langle \beta\gamma | | uv \rangle$$

$$\phi_{17} = 1$$

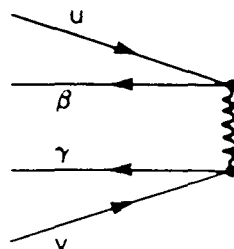


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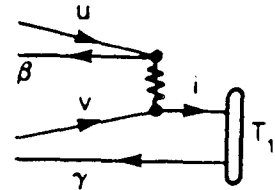
$$[18] = \langle \beta\gamma | \{H_2 T_1\}_C | \phi_0 \rangle$$

$$d_{18a} = \sum_i \langle \beta i | | uv \rangle t_i^\gamma$$

$$h = 1$$

$$\phi_{18a} = -1$$

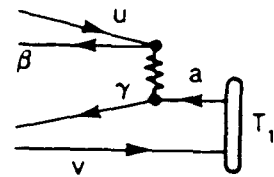
$$P_{18a} = P(\beta|\gamma)$$



$$d_{18b} = \sum_a \langle \beta\gamma | | ua \rangle t_v^a$$

$$\phi_{18b} = 1$$

$$P_{18b} = P(u|v)$$



$$[19] = \langle \beta\gamma | \{H_2 T_2\}_C | \phi_0 \rangle$$

$$d_{19a} = \sum_{ia} \langle \beta i | | au \rangle t_{iv}^{a\gamma}$$

$$h = 1$$

$$\phi_{19a} = -1$$

$$P_{19a} = P(\beta|\gamma)P(u|v)$$

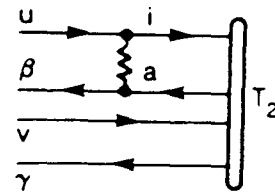
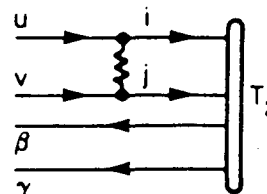


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$$d_{19b} = \sum_{1j} \langle 1j || uv \rangle t_{1j}^{\beta\gamma}$$

$$h = 2, c_h = 2$$

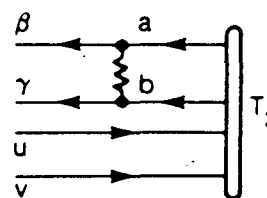
$$\phi_{19b} = 1/2$$



$$d_{19c} = \sum_{ab} \langle \beta\gamma || ab \rangle t_{uv}^{ab}$$

$$c_p = 2$$

$$\phi_{19c} = 1/2$$



$$[20] = \langle \beta\gamma || \{H_2 \frac{1}{2} T_1^2\} c | \phi_0 \rangle$$

$$d_{20a} = \sum_{1a} \langle \beta 1 || av \rangle t_u^a t_1^\gamma$$

$$h = 1$$

$$\phi_{20a} = -1$$

$$P_{20a} = P(\beta|\gamma)P(v|u)$$

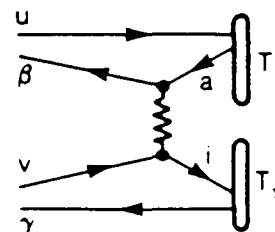
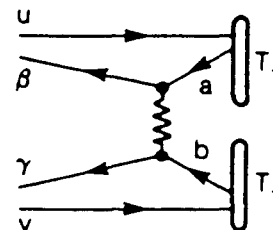


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$$d_{20b} = \sum_{ab} \langle \beta \gamma | | ab \rangle t_u^a t_v^b$$

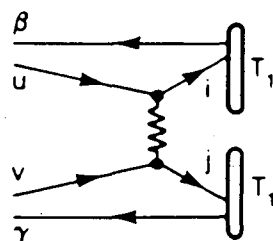
$$\phi_{20b} = 1$$



$$d_{20c} = \sum_{ij} \langle i j | | uv \rangle t_i^\beta t_j^\gamma$$

$$h = 2$$

$$\phi_{20c} = 1$$



$$[21] = \langle \beta \gamma | \{ H_2 T_3 \} c | \phi_0 \rangle$$

$$d_{21a} = \sum_{iab} \langle \gamma i | | ab \rangle t_{uv}^{\beta ab}$$

$$l = 1, h = 1, c_p = 2$$

$$\phi_{21a} = 1/2$$

$$P_{21a} = P(\gamma | \beta)$$

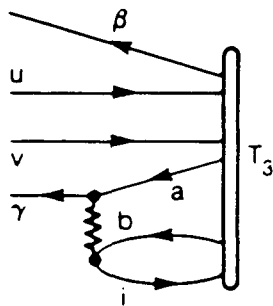


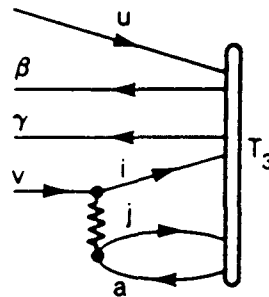
Table I (continued from previous page)

$$d_{21b} = \sum_{ija} \langle ij || va \rangle t_{uif}^{\beta\gamma a}$$

$$l = 1, h = 2, c_h = 2$$

$$\phi_{21b} = -1/2$$

$$P_{21b} = P(v|u)$$



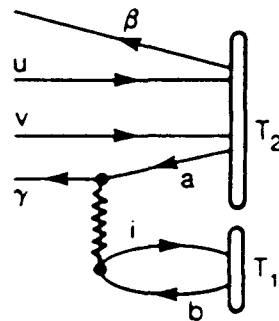
$$[22] = \langle \beta\gamma_{uv} || \{H_2 T_2 T_1\} c | \phi_0 \rangle$$

$$d_{22a} = \sum_{iab} \langle \gamma i || ab \rangle t_{uv}^{\beta a b}$$

$$l = 1, h = 1$$

$$\phi_{22a} = 1$$

$$P_{22a} = P(\gamma|\beta)$$



$$d_{22b} = \sum_{ija} \langle ij || va \rangle t_{uif}^{\beta\gamma a}$$

$$l = 1, h = 2$$

$$\phi_{22b} = -1$$

$$P_{22b} = P(v|u)$$

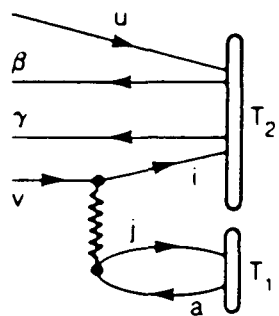


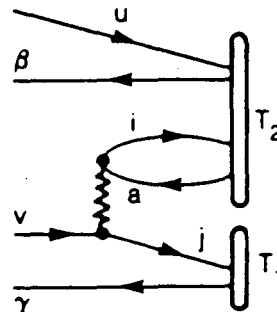
Table I (continued from previous page)

$$d_{22c} = \sum_{ija} \langle ij || av \rangle t_{ui}^{\beta a} t_j^{\gamma}$$

$$l = 1, h = 2$$

$$\phi_{22c} = -1$$

$$P_{22c} = P(\beta | \gamma) P(v | u)$$

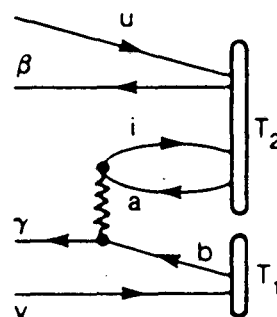


$$d_{22d} = \sum_{iab} \langle i\gamma || ab \rangle t_{ui}^{\beta a} t_v^b$$

$$l = 1, h = 1$$

$$\phi_{22d} = 1$$

$$P_{22d} = P(\gamma | \beta) P(u | v)$$



$$d_{22e} = \sum_{iab} \langle \beta i || ab \rangle t_{uv}^{ab} t_i^{\gamma}$$

$$h = 1, c_p = 2$$

$$\phi_{22e} = -1/2$$

$$P_{22e} = P(\beta | \gamma)$$

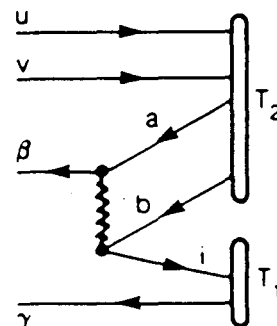


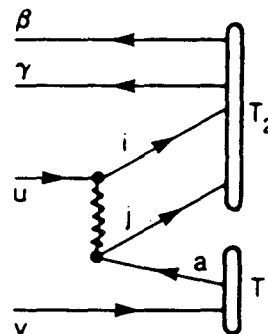
Table I (continued from previous page)

$$d_{22f} = \sum_{1ja} \langle 1j || ua \rangle t_{1j}^{\beta\gamma} t_v^a$$

$$h = 2, c_h = 2$$

$$\phi_{22f} = 1/2$$

$$\phi_{22f} = P(u|v)$$



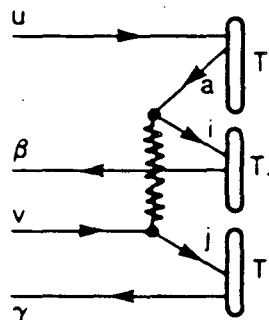
$$[23] = \langle \beta\gamma || \{H_2 \frac{1}{3!} T_1^3\} c | \phi_0 \rangle$$

$$d_{23a} = \sum_{1ja} \langle 1j || av \rangle t_u^a t_i^{\beta} t_j^{\gamma}$$

$$h = 2$$

$$\phi_{23a} = 1$$

$$P_{23a} = P(v|u)$$



$$d_{23b} = \sum_{iab} \langle 1\gamma || ab \rangle t_u^a t_i^{\beta} t_v^b$$

$$h = 1$$

$$\phi_{23b} = -1$$

$$P_{23b} = P(\gamma|\beta)$$

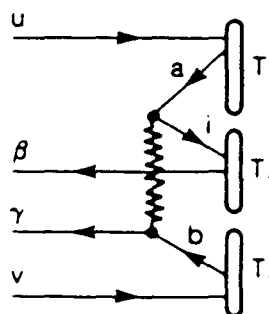


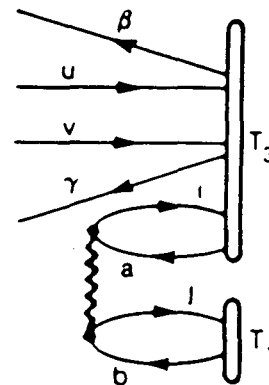
Table I (continued from previous page)

$$[24] = \langle \beta\gamma | \{H_2 T_3 T_1\} | \phi_0 \rangle$$

$$d_{24a} = \sum_{ijab} \langle ij || ab \rangle t_{uvi}^{\beta\gamma a} t_j^b$$

$$l = 2, h = 2$$

$$\phi_{24a} = 1$$

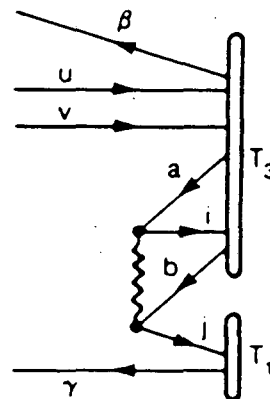


$$d_{24b} = \sum_{ijab} \langle ij || ab \rangle t_{uvi}^{\beta a b \gamma} t_j^b$$

$$h = 2, c_p = 2$$

$$\phi_{24b} = 1/2$$

$$P_{24b} = P(\beta | \gamma)$$



$$d_{24c} = \sum_{ijab} \langle ij || ab \rangle t_{uij}^{\beta\gamma a} t_v^b$$

$$h = 2, c_h = 2$$

$$\phi_{24c} = 1/2$$

$$P_{24c} = P(u | v)$$

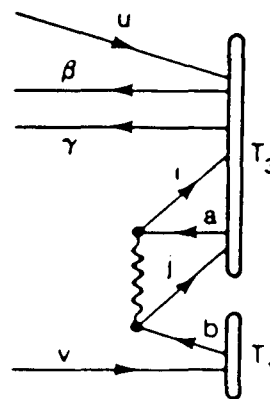


Table I (continued from previous page)

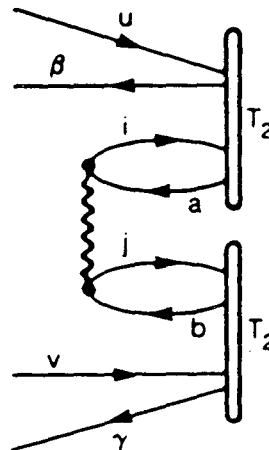
$$[25] = \langle \beta\gamma | \{H_2 \frac{1}{2}T_2^2\} c | \phi_0 \rangle$$

$$d_{25a} = \sum_{ijab} \langle ij || ab \rangle t_{ui}^{\beta a} t_{jv}^{\gamma b}$$

$$l = 2, h = 2$$

$$\phi_{25a} = 1$$

$$P_{25a} = P(\beta|\gamma)$$



$$d_{25b} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{ab} t_{ij}^{\beta\gamma}$$

$$h = 2, c_p = 2, c_h = 2$$

$$\phi_{25b} = 1/4$$

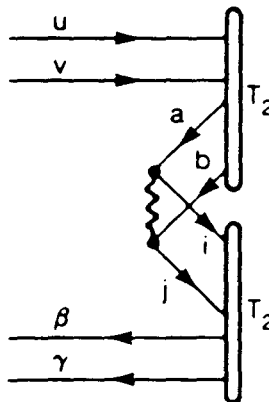


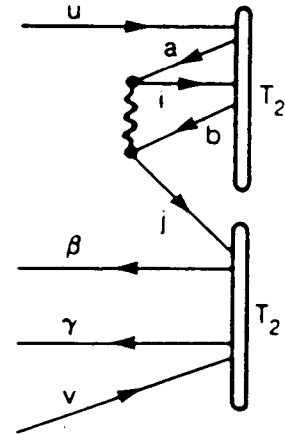
Table I (continued from previous page)

$$d_{25c} = \sum_{ijab} \langle ij || ab \rangle t_{ui}^{ab} t_{jv}^{\beta\gamma}$$

$$h = 2, c_p = 2$$

$$\phi_{25c} = 1/2$$

$$P_{25c} = P(u|v)$$



$$d_{25d} = \sum_{ijab} \langle ij || ab \rangle t_{ij}^{\beta a} t_{uv}^{b\gamma}$$

$$h = 2, c_h = 2$$

$$\phi_{25d} = 1/2$$

$$P_{25d} = P(\beta|\gamma)$$

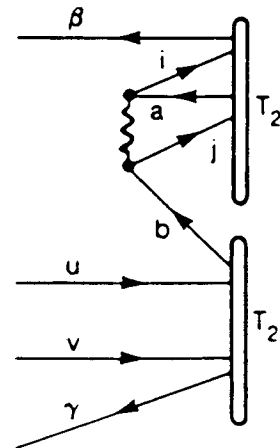


Table I (continued from previous page)

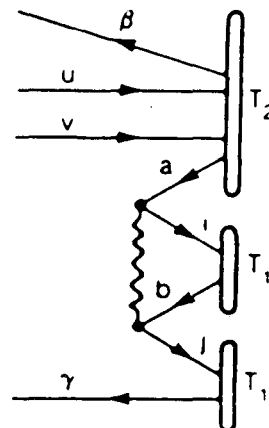
$$[26] = \langle \beta\gamma | \{H_2 \frac{1}{2}T_2 T_1^2\} C | \phi_0 \rangle$$

$$d_{26a} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{\beta a} t_{i j}^{b \gamma}$$

$$h = 2$$

$$\phi_{26a} = 1$$

$$P_{26a} = P(\beta|\gamma)$$



$$d_{26b} = \sum_{ijab} \langle ij || ab \rangle t_{ui}^{\beta \gamma} t_{j v}^{a b}$$

$$h = 2$$

$$\phi_{26b} = 1$$

$$P_{26b} = P(u|v)$$

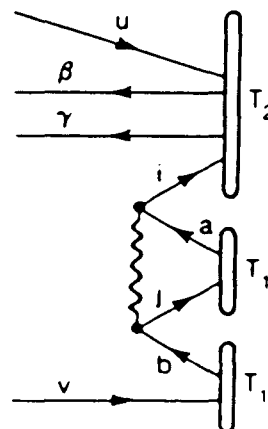


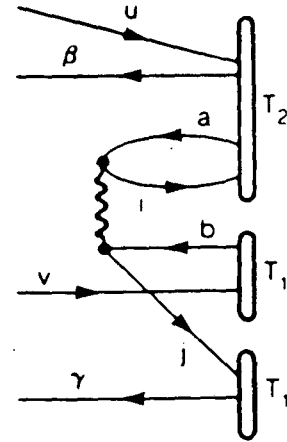
Table I (continued from previous page)

$$d_{26c} = \sum_{ijab} \langle ij || ab \rangle t_{uf}^{\beta a} t_{vj}^{\gamma b}$$

$$l = 1, h = 2$$

$$\phi_{26c} = -1$$

$$P_{26c} = P(\beta|\gamma)P(u|v)$$



$$d_{26d} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{ab} t_{ij}^{\beta\gamma}$$

$$h = 2, c_p = 2$$

$$\phi_{26d} = 1/2$$

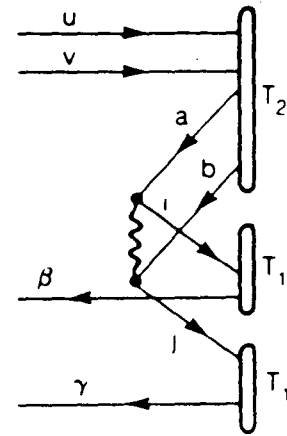
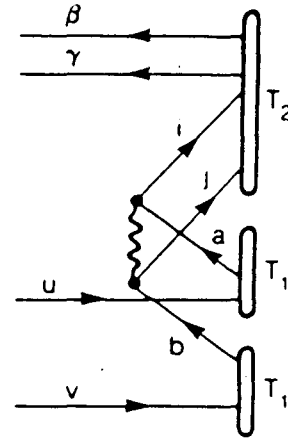


Table I (continued from previous page)

$$d_{26e} = \sum_{ijab} \langle ij || ab \rangle t_{ij}^{\beta\gamma} t_{uv}^{ab}$$

$$h = 2, c_h = 2$$

$$\phi_{26e} = 1/2$$



$$[27] = \langle \beta\gamma_{uv} || \{H_2 \frac{1}{4!} T_1^4\} c | \phi_0 \rangle$$

$$d_{27} = \sum_{ijab} \langle ij || ab \rangle t_{ui}^a t_{vj}^b t_{i1}^{\beta} t_{j1}^{\gamma}$$

$$h = 2$$

$$\phi_{27} = 1$$

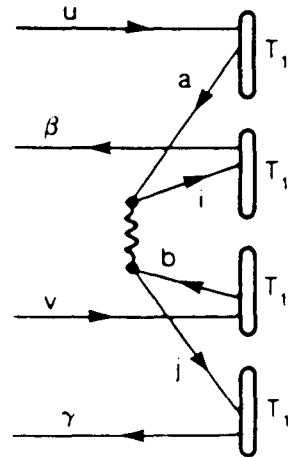


Table I (continued from previous page)

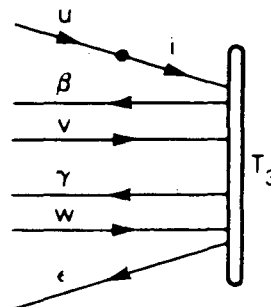
$$[28] = \langle \beta\gamma\epsilon | \{H_1 T_3\} \mathbf{c} | \phi_0 \rangle$$

$$d_{28a} = \sum_i f_{ui} t_{ivw}^{\beta\gamma\epsilon}$$

$$h = 1$$

$$\phi_{28a} = -1$$

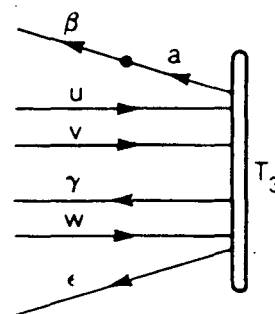
$$P_{28a} = P(u|vw)$$



$$d_{28b} = \sum_a f_{a\beta} t_{uvw}^{a\gamma\epsilon}$$

$$\phi_{28b} = 1$$

$$P_{28b} = P(\beta|\gamma\epsilon)$$



$$[29] = \langle \beta\gamma\epsilon | \{H_1 T_3 T_1\} \mathbf{c} | \phi_0 \rangle$$

$$d_{29a} = \sum_{ia} f_{ia} t_{uvw}^{\beta\gamma a \epsilon} t_i$$

$$h = 1$$

$$\phi_{29a} = -1$$

$$P_{29a} = P(\beta\gamma|\epsilon)$$

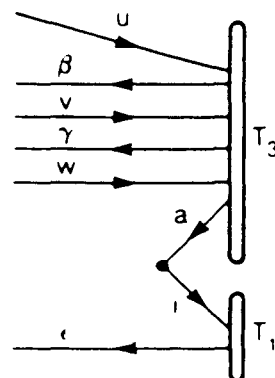


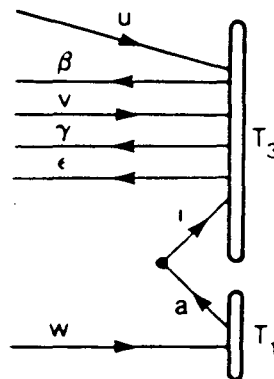
Table I (continued from previous page)

$$d_{29b} = \sum_{i_a} f_{i_a} t_{uv}^{\beta\gamma\epsilon} t_w^a$$

$$h = 1$$

$$\phi_{29b} = -1$$

$$p_{29b} = P(uv|w)$$



$$[30] = \langle \beta\gamma\epsilon |_{uvw} \{ H_1 \frac{1}{2} T_2 \} C | \phi_0 \rangle$$

$$d_{30} = \sum_{i_a} f_{i_a} t_{uv}^{\beta a} t_w^{\gamma\epsilon}$$

$$h = 1$$

$$\phi_{30} = -1$$

$$p_{30} = P(\beta|\gamma\epsilon)P(uv|w)$$

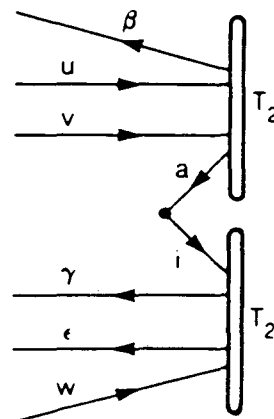


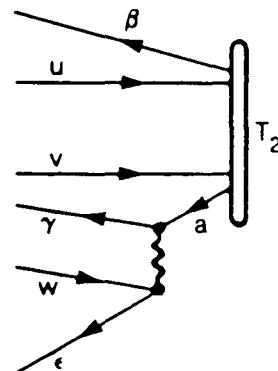
Table I (continued from previous page)

$$[31] = \langle \beta\gamma\epsilon | \{H_2 T_2\}_C | \phi_0 \rangle$$

$$d_{31a} = \sum_a \langle \gamma\epsilon | |aw\rangle t_{uv}^{\beta a}$$

$$\phi_{31a} = 1$$

$$P_{31a} = P(\gamma\epsilon|\beta)P(w|uv)$$

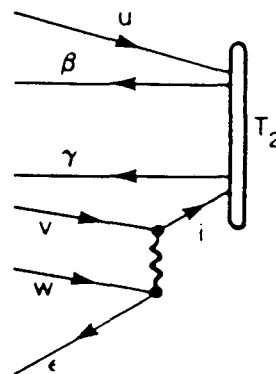


$$d_{31b} = \sum_i \langle i\epsilon | |vw\rangle t_{ui}^{\beta\gamma}$$

$$h = 1$$

$$\phi_{31b} = -1$$

$$P_{31b} = P(\epsilon|\beta\gamma)P(vw|u)$$



$$[32] = \langle \beta\gamma\epsilon | \{H_2 T_3\}_C | \phi_0 \rangle$$

$$d_{32a} = \sum_{ia} \langle \epsilon i | |aw\rangle t_{uvi}^{\beta\gamma a}$$

$$h = 1$$

$$\phi_{32a} = -1$$

$$P_{32a} = P(\epsilon|\beta\gamma)P(w|uv)$$

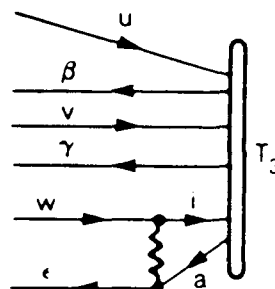


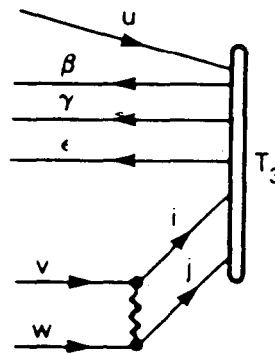
Table I (continued from previous page)

$$d_{32b} = \sum_{ij} \langle 1j || vw \rangle t_{uij}^{\beta\gamma\epsilon}$$

$$h = 2, c_h = 2$$

$$\phi_{32b} = 1/2$$

$$P_{32b} = P(vw|u)$$

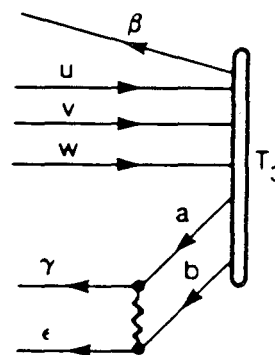


$$d_{32c} = \sum_{ab} \langle \gamma\epsilon || ab \rangle t_{uvw}^{\beta ab}$$

$$c_p = 2$$

$$\phi_{32c} = 1/2$$

$$P_{32c} = P(\gamma\epsilon|\beta)$$



$$[33] = \langle t_{uvw}^{\beta\gamma\epsilon} | \{H_2 T_2 T_1\} C | \phi_0 \rangle$$

$$d_{33a} = \sum_{ia} \langle \gamma i || aw \rangle t_{uv}^{\beta a} t_i^{\epsilon}$$

$$h = 1$$

$$\phi_{33a} = -1$$

$$P_{33a} = P(\gamma|\beta|\epsilon)P(w|uv)$$

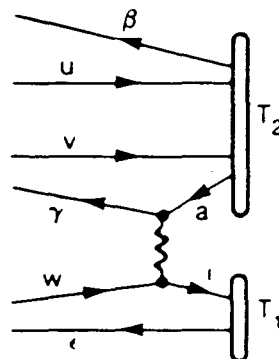


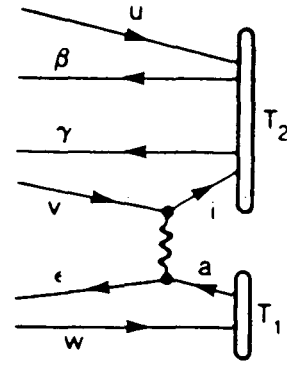
Table I (continued from previous page)

$$d_{33b} = \sum_{1a} \langle \epsilon 1 | | av \rangle t_{ui}^{\beta \gamma} t_w^a$$

$$h = 1$$

$$\phi_{33b} = -1$$

$$P_{33b} = P(\epsilon | \beta \gamma) P(v | u | w)$$

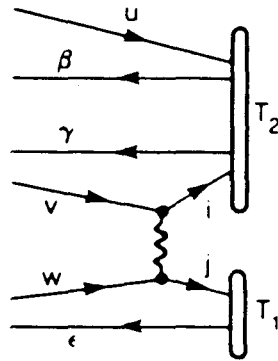


$$d_{33c} = \sum_{1j} \langle 1j | | vw \rangle t_{ui}^{\beta \gamma} t_j^{\epsilon}$$

$$h = 2$$

$$\phi_{33c} = 1$$

$$P_{33c} = P(\beta \gamma | \epsilon) P(vw | u)$$



$$d_{33d} = \sum_{ab} \langle \gamma \epsilon | | ab \rangle t_{uv}^{\beta a} t_w^b$$

$$\phi_{33d} = 1$$

$$P_{33d} = P(\gamma \epsilon | \beta) P(uv | w)$$

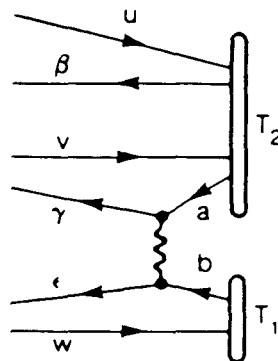


Table I (continued from previous page)

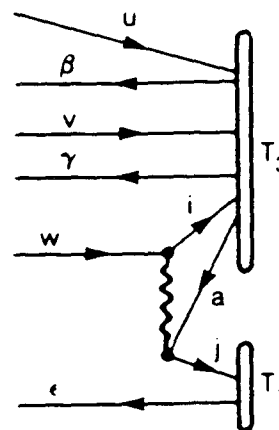
$$[34] = \langle \beta\gamma\epsilon | \{H_2 T_3 T_1\} C | \phi_0 \rangle$$

$$d_{34a} = \sum_{ija} \langle ij || wa \rangle t_{uv1}^{\beta\gamma a} t_j^\epsilon$$

$$h = 2$$

$$\phi_{34a} = 1$$

$$P_{34a} = P(\beta\gamma|\epsilon)P(w|uv)$$

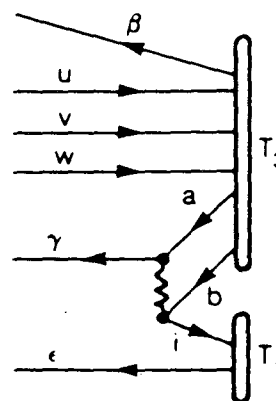


$$d_{34b} = \sum_{iab} \langle \gamma i || ab \rangle t_{uvw}^{\beta ab} t_i^\epsilon$$

$$h = 1, c_p = 2$$

$$\phi_{34b} = -1/2$$

$$P_{34b} = P(\gamma|\beta|\epsilon)$$



$$d_{34c} = \sum_{iab} \langle \epsilon i || ab \rangle t_{uv1}^{\beta\gamma a} t_w^b$$

$$h = 1$$

$$\phi_{34c} = -1$$

$$P_{34c} = P(\epsilon|\beta\gamma)P(uv|w)$$

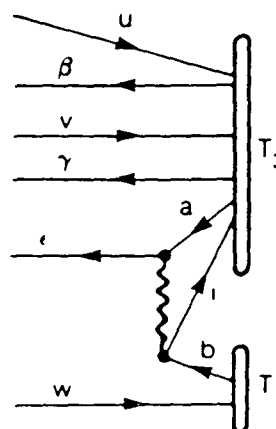


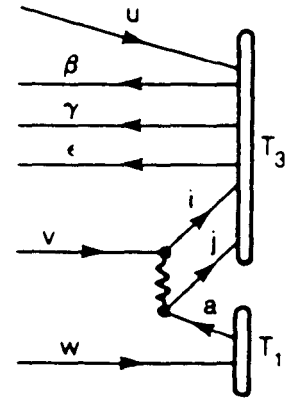
Table I (continued from previous page)

$$d_{34d} = \sum_{ija} \langle ij || va \rangle_t \begin{matrix} \beta \gamma \epsilon & a \\ u i j & w \end{matrix}$$

$$h = 2, c_h = 2$$

$$\phi_{34d} = 1/2$$

$$P_{34d} = P(v|u|w)$$

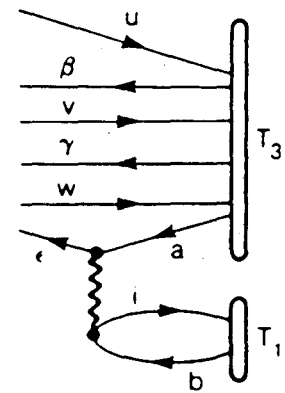


$$d_{34e} = \sum_{iab} \langle \epsilon i || ab \rangle_t \begin{matrix} \beta \gamma a & b \\ u v w & i \end{matrix}$$

$$l = 1, h = 1$$

$$\phi_{34e} = 1$$

$$P_{34e} = P(\epsilon|\beta\gamma)$$



$$d_{34f} = \sum_{ija} \langle ij || wa \rangle_t \begin{matrix} \beta \gamma \epsilon & a \\ u v i & j \end{matrix}$$

$$l = 1, h = 2$$

$$\phi_{34f} = -1$$

$$P_{34f} = P(w|uv)$$

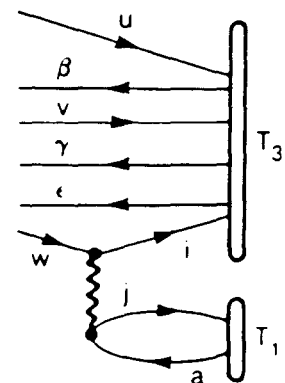


Table I (continued from previous page)

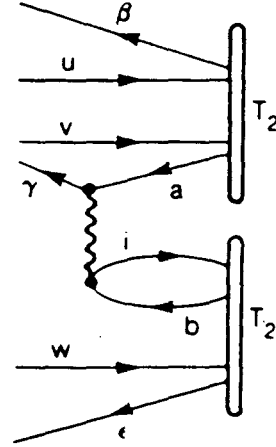
$$[35] = \langle \beta\gamma\epsilon | \{H_2 \frac{1}{2}T_2\} \mathbf{c} | \phi_0 \rangle$$

$$d_{35a} = \sum_{iab} \langle \gamma i | | ab \rangle_t \tau_{uv}^{\beta a} \tau_{iw}^{\beta \epsilon}$$

$$l = 1, h = 1$$

$$\phi_{35a} = 1$$

$$P_{35a} = P(\gamma|\beta|\epsilon)P(uv|w)$$

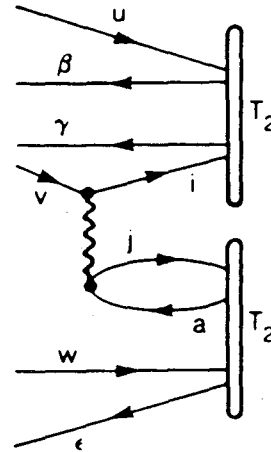


$$d_{35b} = \sum_{ija} \langle ij | | va \rangle_t \tau_{ui}^{\beta\gamma} \tau_{jw}^{a\epsilon}$$

$$l = 1, h = 2$$

$$\phi_{35b} = -1$$

$$P_{35b} = P(\beta\gamma|\epsilon)P(v|u|w)$$



$$d_{35c} = \sum_{iab} \langle \epsilon i | | ba \rangle_t \tau_{ui}^{\beta\gamma} \tau_{vw}^{a\epsilon}$$

$$h = 1, c_p = 2$$

$$\phi_{35c} = -1/2$$

$$P_{35c} = P(\epsilon|\beta\gamma)P(u|vw)$$

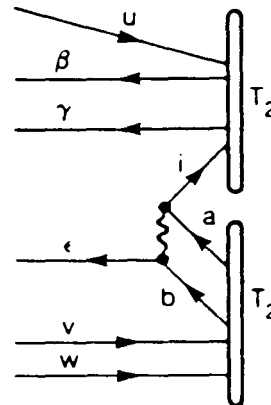


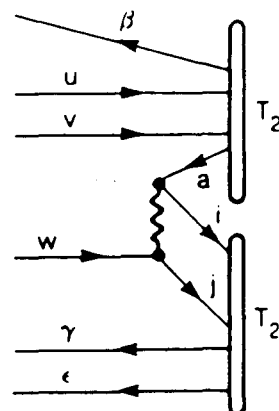
Table I (continued from previous page)

$$d_{35d} = \sum_{ija} \langle ij || aw \rangle t_{uv}^{\beta a} t_{ij}^{\gamma \epsilon}$$

$$h = 2, c_h = 2$$

$$\phi_{35d} = 1/2$$

$$P_{35d} = P(\beta | \gamma \epsilon) P(w | uv)$$



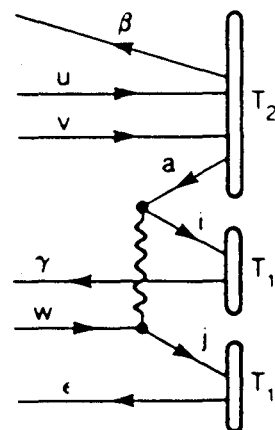
$$[36] = \langle \beta \gamma \epsilon |_{uvw} | \{ H_2 \frac{1}{2} T_2 T_1^2 \} \mathbf{C} | \phi_0 \rangle$$

$$d_{36a} = \sum_{ija} \langle ij || aw \rangle t_{uv}^{\beta a} t_i^{\gamma} t_j^{\epsilon}$$

$$h = 2$$

$$\phi_{36a} = 1$$

$$P_{36a} = P(\beta | \gamma \epsilon) P(w | uv)$$



$$d_{36b} = \sum_{ija} \langle ij || aw \rangle t_{ui}^{\beta \gamma} t_v^a t_j^{\epsilon}$$

$$h = 2$$

$$\phi_{36b} = 1$$

$$P_{36b} = P(\beta \gamma | \epsilon) P(w | u | v)$$

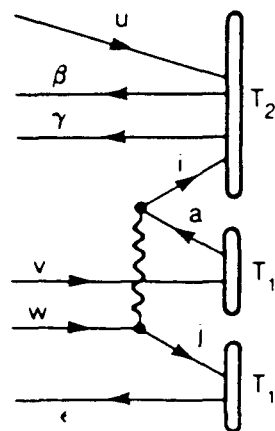


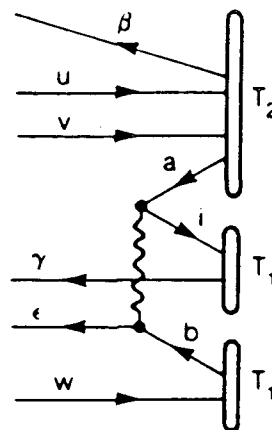
Table I (continued from previous page)

$$d_{36c} = \sum_{iab} \langle i\epsilon || ab \rangle_t \tau_{uv}^{\beta a} \tau_{i\epsilon}^{\gamma b}$$

$$h = 1$$

$$\phi_{36c} = -1$$

$$P_{36c} = P(\epsilon | \beta | \gamma) P(uv | w)$$

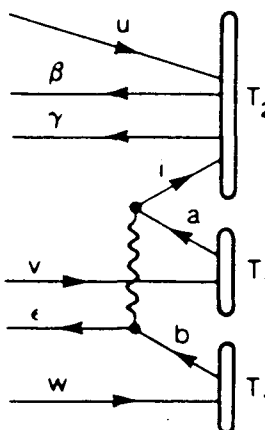


$$d_{36d} = \sum_{iab} \langle i\epsilon || ab \rangle_t \tau_{ui}^{\beta \gamma} \tau_{v\epsilon}^{a b}$$

$$h = 1$$

$$\phi_{36d} = -1$$

$$P_{36d} = P(\epsilon | \beta \gamma) P(u | vw)$$



$$[37] = \langle \beta \gamma \epsilon |_{uvw} \{ H_2 T_3 T_2 \} C | \phi_0 \rangle$$

$$d_{37a} = \sum_{ijab} \langle ij || ab \rangle_t \tau_{uvi}^{\beta ab} \tau_{jw}^{\gamma \epsilon}$$

$$h = 2, c_p = 2$$

$$\phi_{37a} = 1/2$$

$$P_{37a} = P(\beta | \gamma \epsilon) P(uv | w)$$

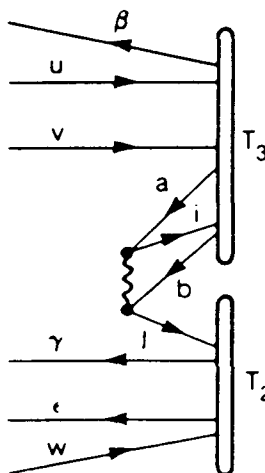


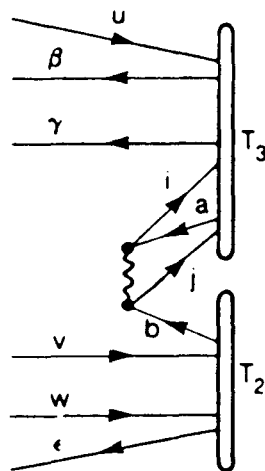
Table I (continued from previous page)

$$d_{37b} = \sum_{ijab} \langle ij || ab \rangle t_{uif}^{\beta\gamma a} t_{vw}^{\beta\epsilon}$$

$$h = 2, c_h = 2$$

$$\phi_{37b} = 1/2$$

$$P_{37b} = P(\beta\gamma|\epsilon)P(u|vw)$$

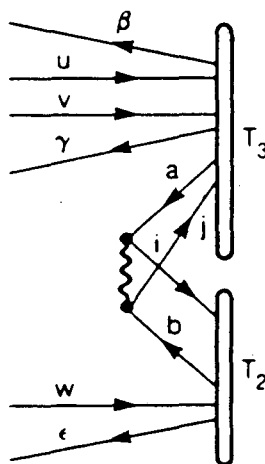


$$d_{37c} = \sum_{ijab} \langle ij || ab \rangle t_{uvj}^{\beta\gamma a} t_{iw}^{\beta\epsilon}$$

$$l = 1, h = 2$$

$$\phi_{37c} = -1$$

$$P_{37c} = P(\beta\gamma|\epsilon)P(uv|w)$$



$$d_{37d} = \sum_{ijab} \langle ij || ab \rangle t_{uif}^{\beta\gamma\epsilon} t_{vw}^{\beta\epsilon}$$

$$h = 2, c_p = 2, c_h = 2$$

$$\phi_{37d} = 1/4$$

$$P_{37d} = P(u|vw)$$

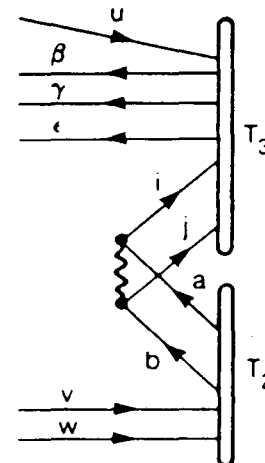


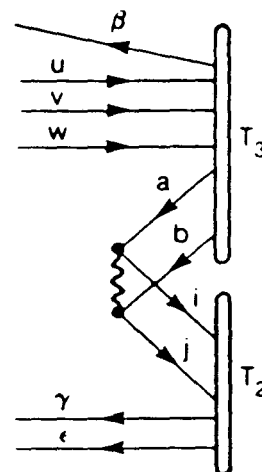
Table I (continued from previous page)

$$d_{37e} = \sum_{ijab} \langle ij || ab \rangle_t^{\beta ab, \gamma \epsilon} t_{uvw}^{\beta ab, \gamma \epsilon} t_{ij}$$

$$h = 2, c_p = 2, c_h = 2$$

$$\phi_{37e} = 1/4$$

$$p_{37e} = P(\beta | \gamma \epsilon)$$



$$d_{37f} = \sum_{ijab} \langle ij || ab \rangle_t^{\beta \gamma a, b \epsilon} t_{uvw}^{\beta \gamma a, b \epsilon} t_{ij}$$

$$h = 2, c_h = 2$$

$$\phi_{37f} = 1/2$$

$$p_{37f} = P(\beta \gamma | \epsilon)$$

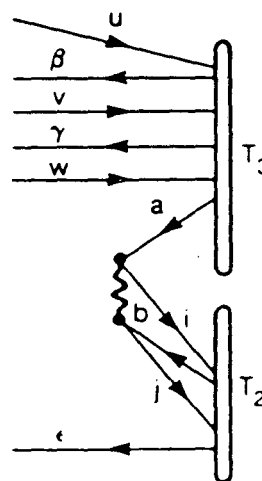


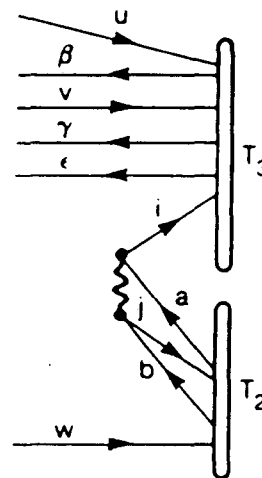
Table I (continued from previous page)

$$d_{37g} = \sum_{ijab} \langle ij || ab \rangle t_{uvi}^{\beta\gamma\epsilon} t_{jw}^{ab}$$

$$h = 2, c_p = 2$$

$$\phi_{37g} = 1/2$$

$$P_{37g} = P(uv|w)$$



$$[38] = \langle \beta\gamma\epsilon | \{H_2 \frac{1}{2} T_3 T_1^2\} C | \phi_0 \rangle$$

$$d_{38a} = \sum_{ijab} \langle ij || ab \rangle t_{uvw}^{\beta\gamma a} t_{ij}^{b\epsilon}$$

$$h = 2$$

$$\phi_{38a} = 1$$

$$P_{38a} = P(\beta\gamma|\epsilon)$$

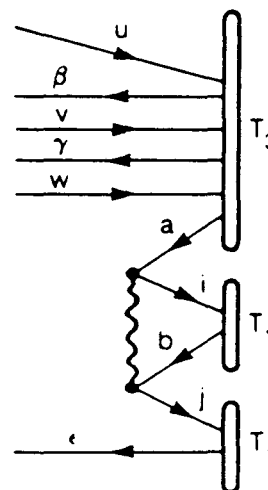


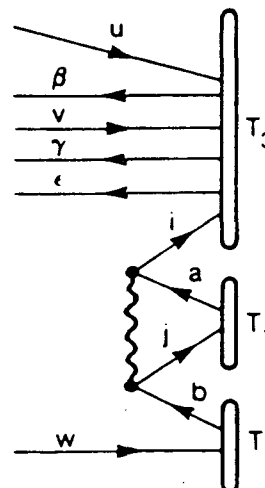
Table I (continued from previous page)

$$d_{38b} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{\beta\gamma\epsilon} t_{ij}^{ab}$$

$$h = 2$$

$$\phi_{38b} = 1$$

$$P_{38b} = P(uv|w)$$



$$d_{38c} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{\beta\gamma\epsilon} t_{ij}^{ab}$$

$$h = 2$$

$$\phi_{38c} = 1$$

$$P_{38c} = P(\beta\gamma|\epsilon)P(uv|w)$$

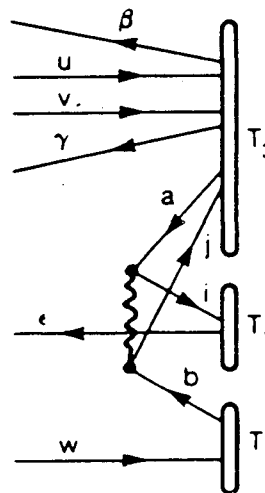


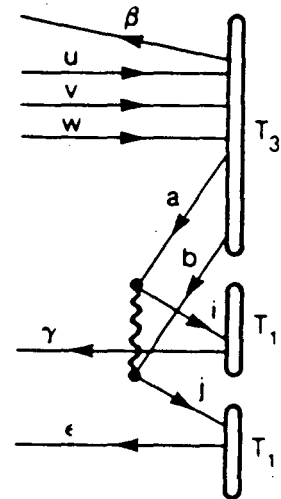
Table I (continued from previous page)

$$d_{38d} = \sum_{1jab} \langle 1j || ab \rangle_t \beta_{uvw} \gamma_{tj} \epsilon_{tj}$$

$$h = 2, c_p = -2$$

$$\phi_{38d} = 1/2$$

$$P_{38d} = P(\beta | \gamma \epsilon)$$



$$d_{38e} = \sum_{1jab} \langle 1j || ab \rangle_t \beta_{uij} \gamma_{tj} \epsilon_{tj} \frac{a}{v} \frac{b}{w}$$

$$h = 2, c_h = 2$$

$$\phi_{38e} = 1/2$$

$$P_{38e} = P(u | vw)$$

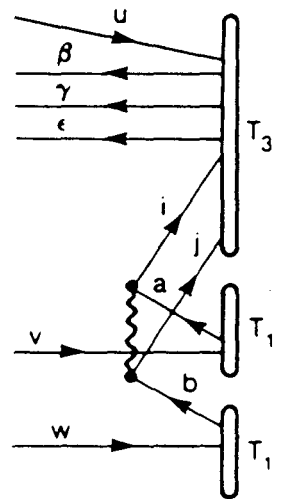


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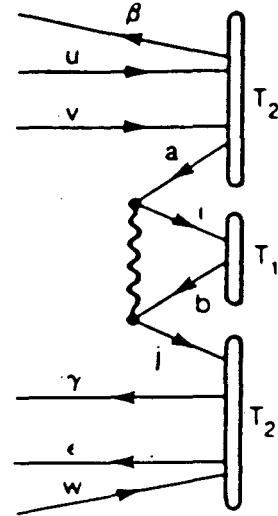
$$[39] = \langle \beta \gamma \epsilon | \{ H_2 \frac{1}{2} T_2^2 T_1 \} c | \phi_0 \rangle$$

$$d_{39a} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{\beta a} t_{i'jw}^{\beta b} \gamma \epsilon$$

$$h = 2$$

$$\phi_{39a} = 1$$

$$P_{39a} = P(\beta | \gamma \epsilon) P(uv | w)$$



$$d_{39b} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{ab} t_{i'jw}^{\beta} \gamma \epsilon$$

$$h = 2, c_p = 2$$

$$\phi_{39b} = 1/2$$

$$P_{39b} = P(\beta | \gamma \epsilon) P(uv | w)$$

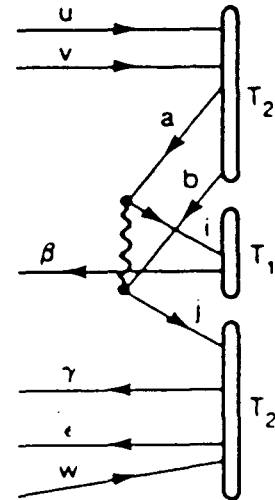


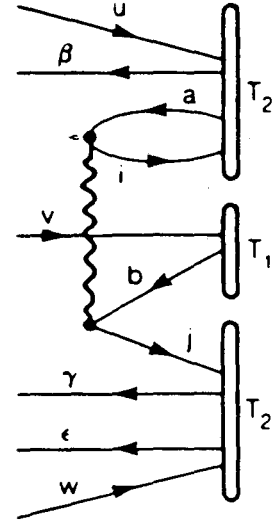
Table I (continued from previous page)

$$d_{39c} = \sum_{ijab} \langle ij || ab \rangle t_{ui}^{\beta a} t_{vj}^{b \gamma c}$$

$$l = 1, h = 2$$

$$\phi_{39c} = -1$$

$$P_{39c} = P(\beta | \gamma \epsilon) P(u | v | w)$$



$$d_{39d} = \sum_{ijab} \langle ij || ab \rangle t_{ui}^{\beta a} t_{vj}^{\gamma b \epsilon c}$$

$$l = 1, h = 2$$

$$\phi_{39d} = -1$$

$$P_{39d} = P(\beta | \gamma | \epsilon) P(u | v w)$$

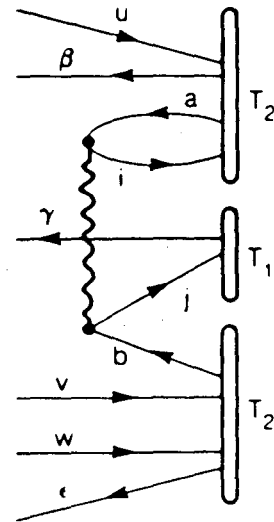


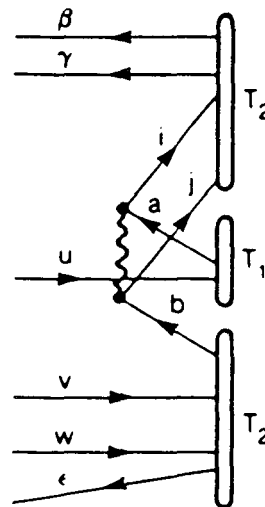
Table I (continued from previous page)

$$d_{39e} = \sum_{ijab} \langle ij || ab \rangle t_{ij}^{\beta\gamma} t_{uv}^a t_{vw}^b \epsilon$$

$$h = 2, c_h = 2$$

$$\phi_{39e} = 1/2$$

$$P_{39e} = P(\beta\gamma|\epsilon)P(u|vw)$$



$$[40] = \langle \beta\gamma\epsilon | \{H_2 \frac{1}{3!} T_2 T_1^3\} c | \phi_0 \rangle$$

$$d_{40a} = \sum_{ijab} \langle ij || ab \rangle t_{uv}^{\beta a} t_{i\gamma}^b t_{w\epsilon}^j$$

$$h = 2$$

$$\phi_{40a} = 1$$

$$P_{40a} = P(\beta|\gamma\epsilon)P(uv|w)$$

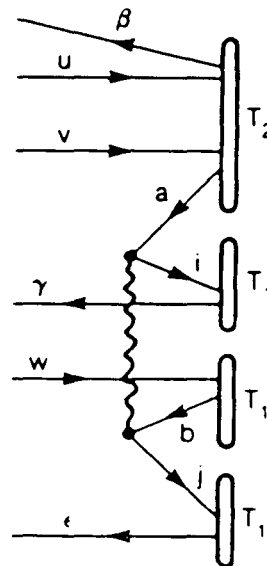


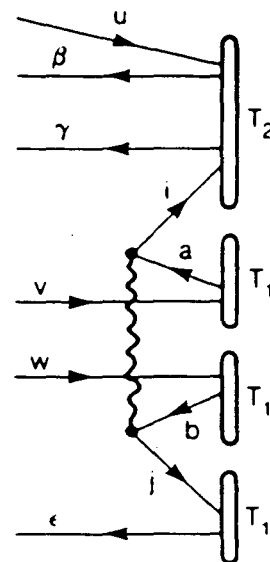
Table I (continued from previous page)

$$d_{40b} = \sum_{ijab} \langle ij || ab \rangle t_{ui}^{\beta\gamma} t_{v}^a t_w^b t_j^{\epsilon}$$

$$h = 2$$

$$\phi_{40b} = 1$$

$$p_{40b} = P(\beta\gamma|\epsilon)P(u|vw)$$



6. Final Equations

The expressions for the matrix elements obtained in the preceding Section, together with Equations (3.13) - (3.16), enable us to write implicit equations determining the cluster coefficients and the correlated energy in terms of the cluster coefficients and the one- and two-electron integrals over the spin-orbital basis. We may write Equation (3.13), the projection of the Schrödinger Equation for the CCSDT wavefunction on the singly-excited space, as,

$$0 = \sum_{m=4}^{13} [m] ; \quad (6.1)$$

likewise Equation (3.14), the projection on the doubly-excited space, can be written,

$$0 = \sum_{m=14}^{27} [m] ; \quad (2)$$

and Equation (3.15), the projection on the triply-excited space as,

$$0 = \sum_{m=28}^{40} [m] . \quad (3)$$

The equation for the correlated energy, Equation (3.16), may similarly be written as,

$$\Delta E = \sum_{m=1}^3 [m] ; \quad (4)$$

where $[m]$, the symbol for a possibly non-vanishing matrix element, is related to entries in Table I by Equation (5.1). The above equations are

however of dubious computational value: Practical random access is restricted by the size of core memory, and sequential access is limited by the size of disc storage; for small polyatomic molecules, these limits translate to $O(n^2)$ and $O(n^3)$ matrices, respectively, where n is the dimension of the binary direct product space of spin-orbitals, i.e., $n = (\text{no. of spin-orbitals})^2$. We will show that the judicious choice of the order in which cluster coefficients and integrals are combined in a multiple product results in a procedure which satisfies the above computational constraints at all stages.

Individual cluster coefficients, as well as integrals, cannot in general be freely reordered in expressions for matrix elements. In particular, the rearrangement of coefficients can be seen to correspond to a topological deformation of a diagram which alters the sequence of topologically distinct environments (cf. Rule 4); it is hardly surprising that the permutation operator, which is partially defined by the sequence, must reflect the change. To examine the specific effect of rearrangement, let $f(x_1)$ and $g(x_1)$ be arbitrary single index functions, which may however depend parametrically on other variables, and let $P(x_1|x_2)$ be the single index set permutation operator defined in Equation (4.11); then,

$$P(x_1|x_2)f(x_1)g(x_2) = f(x_1)g(x_2) - f(x_2)g(x_1) \quad (5)$$

$$= g(x_2)f(x_1) - g(x_1)f(x_2) \quad (6)$$

$$= P(x_2|x_1)g(x_2)f(x_1) \quad (7)$$

$$= P(x_2|x_1)g(x_1)f(x_2) . \quad (8)$$

Equation (8) being obtained from Equation (7) because the action of the permutation operator renders the argument index set dummy. Consider next the permutation operator $P(x_1 x_2 | x_3)$, defined in Equation (4.12), and let $h(x_1, x_2)$ be an arbitrary, antisymmetrized two index function; then,

$$\begin{aligned} P(x_1 x_2 | x_3) h(x_1, x_2) g(x_3) &= \\ &= h(x_1, x_2) g(x_3) - h(x_3, x_2) g(x_1) - h(x_1, x_3) g(x_2) \end{aligned} \quad (9)$$

$$= g(x_3) h(x_1, x_2) - g(x_1) h(x_3, x_2) - g(x_2) h(x_1, x_3) \quad (10)$$

$$= P(x_3 | x_1 x_2) g(x_1) h(x_2, x_3) . \quad (11)$$

Note that $P(x_3 | x_1 x_2)$ is the single index set permutation operator defined in Equation (4.13).

A complication arising through the switching of coefficients and the necessary corresponding switching of permutation operators is the generation of permutation operators with noncanonical index lists (e.g., if x_1, x_2, x_3 in Equation (9) represents a canonical list, then x_3, x_1, x_2 in Equation (11) certainly cannot). Hence, we must examine the symmetry properties of the permutation operators. As before let us first consider the simplest single index set permutation operator, $P(x_1 | x_2)$;

$$P(x_2 | x_1) f(x_1) g(x_2) = f(x_2) g(x_1) - f(x_1) g(x_2) \quad (12)$$

$$= -\{-f(x_2) g(x_1) + f(x_1) g(x_2)\} \quad (13)$$

$$P(x_2|x_1)f(x_1)g(x_2) = -P(x_1|x_2)f(x_1)g(x_2) ; \quad (14)$$

i.e., functionally,

$$P(x_2|x_1) = -P(x_1|x_2) . \quad (15)$$

Next, consider the permutation operator $P(x_1x_2|x_3)$. One can imagine two kinds of permutations: within a topologically distinct region, and between topologically distinct regions; we now examine the first kind,

$$\begin{aligned} P(x_2x_1|x_3)h(x_1,x_2)g(x_3) &= \\ &= h(x_2,x_1)g(x_3) - h(x_3,x_1)g(x_2) - h(x_2,x_3)g(x_1) \end{aligned} \quad (16)$$

$$= -\{-h(x_2,x_1)g(x_3) + h(x_3,x_1)g(x_2) + h(x_2,x_3)g(x_1)\} \quad (17)$$

$$= -\{h(x_1,x_2)g(x_3) - h(x_1,x_3)g(x_2) - h(x_3,x_2)g(x_1)\} \quad (18)$$

$$= -P(x_1x_2|x_3)h(x_1,x_2)g(x_3) ; \quad (19)$$

i.e., functionally,

$$P(x_2x_1|x_3) = -P(x_1x_2|x_3) . \quad (20)$$

Equation (18) was obtained from Equation (17) by use of the antisymmetry of the test function, h . Now let us consider the permutation of indices between topologically distinct regions,

$$\begin{aligned} P(x_1x_3|x_2)h(x_1,x_2)g(x_3) &= \\ &= h(x_1,x_3)g(x_2) - h(x_2,x_3)g(x_1) - h(x_1,x_2)g(x_3) \end{aligned} \quad (21)$$

$$= -\{-h(x_1,x_3)g(x_2) + h(x_2,x_3)g(x_1) + h(x_1,x_2)g(x_3)\} \quad (22)$$

$$= -\{-h(x_1, x_3)g(x_2) - h(x_3, x_2)g(x_1) + h(x_1, x_2)g(x_3)\} \quad (23)$$

$$= -P(x_1 x_2 | x_3)h(x_1, x_2)g(x_3) ; \quad (24)$$

i.e., functionally,

$$P(x_1 x_3 | x_2) = -P(x_1 x_2 | x_3) . \quad (25)$$

The symmetry properties of the permutation operator, $P(x_1 | x_2 x_3)$, need not be separately considered in light of the relation between $P(x_1 | x_2 x_3)$ and $P(x_1 x_2 | x_3)$ (cf. Equation (11)). The remaining permutation operator used in Table I but thus far not discussed in this Section is $P(x_1 | x_2 | x_3)$, defined in Equation (4.15). We now show that $P(x_1 | x_2 | x_3)$ is the composite of two single index set permutation operators already examined. In addition to f and g , let $k(x_1)$ also be an arbitrary single index function, which may depend parametrically on other variables; then,

$$P(x_1 x_2 | x_3)P(x_1 | x_2)f(x_1)g(x_2)k(x_3) = \\ = P(x_1 x_2 | x_3)\{f(x_1)g(x_2) - f(x_2)g(x_1)\}k(x_3) \quad (26)$$

$$= \{f(x_1)g(x_2) - f(x_2)g(x_1)\}k(x_3) + \\ - \{f(x_3)g(x_2) - f(x_2)g(x_3)\}k(x_1) + \\ - \{f(x_1)g(x_3) - f(x_3)g(x_1)\}k(x_2) \quad (27)$$

$$= f(x_1)g(x_2)k(x_3) - f(x_2)g(x_1)k(x_3) + \\ - f(x_3)g(x_2)k(x_1) - f(x_1)g(x_3)k(x_2) + \\ + f(x_2)g(x_3)k(x_1) + f(x_3)g(x_1)k(x_2) \quad (28)$$

$$= P(x_1|x_2|x_3)f(x_1)g(x_2)k(x_3) ; \quad (29)$$

i.e., functionally,

$$P(x_1x_2|x_3)P(x_1|x_2) = P(x_1|x_2|x_3) . \quad (30)$$

Hence the symmetry and argument exchange properties of $P(x_1|x_2|x_3)$ can be understood in terms of the already examined permutation operators $P(x_1x_2|x_3)$ and $P(x_1|x_2)$.

We have shown that though the cluster coefficients and the integrals do not in general commute, the commutation relations can be understood in terms of changes in the permutation operator. Furthermore, the symmetry properties of the permutation operators found in a CCSDT model have been characterized. The symmetry properties enable a canonical ordering of (external) indices regardless of the ordering of the cluster coefficients and integrals.

We now show that the projection of the Schrödinger Equation for the CCSDT wavefunction on the triply-excited space (cf. Equation (3)) can be written in terms of (at worst) products of unmodified rank 3 cluster coefficients and modified rank 2 integrals. Tensor notation with repeated index summation convention will be used, except of course for the permutation operator.

Consider breaking the sum in Equation (3) into eight parts, designated by Roman numerals,

$$[I] = [28a] + [29b] + [34f] + [37g] + [38b] , \quad (31)$$

$$[II] = [28b] + [29a] + [34e] + [37f] + [38a] , \quad (32)$$

$$[\text{III}] = [32a] + [34a] + [34c] + [37c] + [38c] , \quad (33)$$

$$[\text{IV}] = [32b] + [34d] + [37d] + [38e] , \quad (34)$$

$$[\text{V}] = [32c] + [34b] + [37e] + [38d] , \quad (35)$$

$$[\text{VI}] = [30] + [39a] , \quad (36)$$

$$[\text{VII}] = [31b] + [33b] + [33c] + [35b] + [36b] + [35c] + \\ + [36d] + [37a] + [39c] + [39b] + [40b] , \quad (37)$$

$$[\text{VIII}] = [31a] + [33a] + [33d] + [35a] + [36c] + [35d] + \\ + [36a] + [37b] + [39d] + [39e] + [40a] . \quad (38)$$

Let us examine each of these partial sums in turn.

$$[\text{I}] = -P(u|vw) f_{u\ i\ vw}^1 t_{i\ vw}^{\beta\gamma\epsilon} - f_a^1 P(uv|w) t_{u\ v\ i\ w}^{\beta\gamma\epsilon} t_w^a - P(u|vw) v_{u\ a}^{i\ j} t_{v\ w\ i\ j}^{\beta\gamma\epsilon} t_j^a + \\ + v_{a\ b}^{i\ j} P(uv|w) \left\{ \frac{1}{2} t_{u\ v\ i\ j}^{\beta\gamma\epsilon} t_{j\ w}^{ab} + t_{u\ v\ i\ j}^{\beta\gamma\epsilon} t_j^a t_w^b \right\} , \quad (39)$$

$$\text{where } v_{a\ b}^{i\ j} = \langle i\ j | | a\ b \rangle . \quad (40)$$

Equation (39) can be rewritten,

$$[\text{I}] = P(uv|w) t_{u\ v\ i}^{\beta\gamma\epsilon} \left\{ -f_w^i - (f t_1)_1^{i\ a} - (v t_1)_1^{i\ j\ a} + (v t_2')_2^{i\ j\ a\ b} \right\} , \quad (41)$$

$$\text{where } t_2' = \frac{1}{2} t_2 + t_1 t_1 . \quad (42)$$

The ambiguity in removing paired indices, when multiple pairs exist, can be eliminated if we adopt the convention that the first covariant summation index is implicitly paired with the first possible contravariant summation index, etc. (N.B. The cluster coefficients and the integrals are irreducible tensors of the appropriate rank (cf. Section 2) and contractions between different cluster operators also cannot occur (cf. Section 4).) It should also be noted that the ranges of the contractions are preserved by the tensor notation since covariant indices of cluster coefficients must be elements of the Fermi sea and contravariant indices cannot be elements of the Fermi sea. Then,

$$[I] = P(uv|w)t_{uv}^{\beta\gamma\epsilon}(f^{(3)})_w^i ; \quad (43)$$

where the modified one-electron integral $(f^{(3)})_w^i$ is defined,

$$(f^{(3)})_w^i = -f_w^i - (ft_1)_w^i - (vt_1)_w^i + (vt_2')_w^i . \quad (44)$$

Similarly the second partial sum,

$$\begin{aligned} [II] = & P(\beta|\gamma\epsilon)f_a^{\beta a\gamma\epsilon} - f_a^i P(\beta\gamma|\epsilon)t_{uvw}^{\beta\gamma a\epsilon} + P(\beta|\gamma\epsilon)v_{ab}^{\beta i\gamma\epsilon a} t_{i1}^b \\ & + v_{ab}^{ij} P(\beta\gamma|\epsilon) \left\{ \frac{1}{2} t_{uvw}^{\beta\gamma a} t_{ij}^{bc} + t_{uvw}^{\beta\gamma a} t_{i1}^{bj} \right\} , \quad (45) \end{aligned}$$

becomes,

$$[II] = P(\beta\gamma|\epsilon)t_{uvw}^{\beta\gamma a}(f^{(3)})_a^\epsilon , \quad (46)$$

where,

$$(f^{(3)})_a^\epsilon = f_a^\epsilon - (ft_1)_a^\epsilon + (vt_1)_a^\epsilon + (vt_2')_a^\epsilon . \quad (47)$$

The third partial sum is,

$$\begin{aligned}
 [\text{III}] = & -P(\beta|\gamma\varepsilon)P(u|vw)v_{au}^{\beta i}t_{vwi}^{\gamma\varepsilon a} + P(\beta\gamma|\varepsilon)P(u|vw)v_{ua}^{ij}t_{vwi}^{\beta\gamma a\varepsilon} + \\
 & - P(\beta|\gamma\varepsilon)P(uv|w)v_{ab}^{\beta i}t_{uvi}^{\gamma\varepsilon a}t_w^b + v_{ab}^{ij}P(\beta\gamma|\varepsilon)P(uv|w)t_{uvj}^{\beta\gamma a}t_{wi}^{\varepsilon b} + \\
 & + v_{ab}^{ij}P(\beta\gamma|\varepsilon)P(uv|w)t_{uvj}^{\beta\gamma a}t_{wi}^{\varepsilon b} ; \quad (48)
 \end{aligned}$$

and can be written,

$$[\text{III}] = P(\beta\gamma|\varepsilon)P(uv|w)t_{uvi}^{\beta\gamma a}(v^{(3)})_{aw}^{\varepsilon i} , \quad (49)$$

with the modified two-electron integral,

$$(v^{(3)})_{aw}^{\varepsilon i} = -v_{aw}^{\varepsilon i} + (vt_1)_{wa}^{i\varepsilon} - (vt_1)_{aw}^{\varepsilon i} + (vt_2)_{aw}^{i\varepsilon} + (vt_1t_1)_{aw}^{i\varepsilon} . \quad (50)$$

Note that the required inner multiplication of the three tensor product (vt_1t_1) is rank 2 at all stages;

i.e.,

$$(vt_1t_1)_{aw}^{i\varepsilon} = (vt_1)_{ab}^{i\varepsilon}t_w^b . \quad (51)$$

The fourth partial sum is,

$$\begin{aligned}
 [\text{IV}] = & \frac{1}{2}P(uv|w)v_{uv}^{ij}t_{wif}^{\beta\gamma\varepsilon} - \frac{1}{2}P(u|v|w)v_{ua}^{ij}t_{vij}^{\beta\gamma\varepsilon}t_w^a + \\
 & + \frac{1}{2}v_{ab}^{ij}P(u|vw)t_{uij}^{\beta\gamma\varepsilon}\left(\frac{1}{2}t_{vw}^{ab} + t_{vw}^{ab}\right) ; \quad (52)
 \end{aligned}$$

which gives,

$$[IV] = \frac{1}{2}P(u|vw)t_{uij}^{\beta\gamma\epsilon}(v^{(3)})_{vw}^{ij} , \quad (53)$$

with the modified two-electron integral,

$$(v^{(3)})_{vw}^{ij} = v_{vw}^{ij} + P(v|w)(vt_1)_{vw}^{ij} + (vt_2')_{vw}^{ij} . \quad (54)$$

Similarly the fifth partial sum,

$$\begin{aligned} [V] = & \frac{1}{2}P(\beta\gamma|\epsilon)v_{ab}^{\beta\gamma}t_{uvw}^{\epsilon ab} + \frac{1}{2}P(\beta|\gamma|\epsilon)v_{ab}^{\beta i}t_{uvw}^{\gamma ab}t_i^\epsilon + \\ & + \frac{1}{2}v_{ab}^{ij}P(\beta|\gamma\epsilon)t_{uvw}^{\beta ab}\left\{\frac{1}{2}t_{ij}^{\gamma\epsilon} + t_i^\gamma t_j^\epsilon\right\} , \end{aligned} \quad (55)$$

can be written as,

$$[V] = \frac{1}{2}P(\beta|\gamma\epsilon)t_{uvw}^{\beta ab}(v^{(3)})_{ab}^{\gamma\epsilon} , \quad (56)$$

with,

$$(v^{(3)})_{ab}^{\gamma\epsilon} = v_{ab}^{\gamma\epsilon} - P(\gamma|\epsilon)(vt_1)_{ab}^{\gamma\epsilon} + (vt_2')_{ab}^{\gamma\epsilon} . \quad (57)$$

The sixth partial sum is,

$$[VI] = -f_a^i P(\beta|\gamma\epsilon)P(uv|w)t_{uv}^{\beta a}t_{iw}^{\gamma\epsilon} + v_{ab}^{ij}P(\beta|\gamma\epsilon)P(uv|w)t_{uv}^{\beta a}t_i^b t_{jw}^{\gamma\epsilon} . \quad (58)$$

Though a more symmetric formulation is possible, the following suffices,

$$[VI] = P(\beta\gamma|\epsilon)P(u|vw)t_{ui}^{\beta\gamma}(v^{(3')})_{vw}^{i\epsilon} , \quad (59)$$

with,

$$(v^{(3')})_{vw}^{i\epsilon} = (ft_2)_{vw}^{i\epsilon} + (vt_1 t_2)^{\cdot i \cdot \epsilon}_{vw} . \quad (60)$$

The required inner multiplication of the three tensor product $(vt_1 t_2)$ is rank 2 or less at all stages; i.e.,

$$(vt_1 t_2)^{\cdot i \cdot \epsilon}_{vw} = (vt_1)^{\cdot i}_{a} t_{vw}^{\epsilon a} . \quad (61)$$

The seventh partial sum is,

$$\begin{aligned} [\text{VII}] = & -P(\beta|\gamma\epsilon)P(uv|w)v_{uv}^{i\beta}t_{wi}^{\gamma\epsilon} + P(\beta|\gamma\epsilon)P(u|v|w)v_{au}^{\beta i}t_{vi}^{\gamma\epsilon}{}^a + \\ & + P(\beta\gamma|\epsilon)P(uv|w)v_{uv}^{ij}t_{wi}^{\beta\gamma}t_j^\epsilon + P(\beta\gamma|\epsilon)P(u|v|w)v_{ua}^{ij}t_{vi}^{\beta\gamma}t_{jw}^{a\epsilon} + \\ & - P(\beta\gamma|\epsilon)P(u|v|w)v_{ua}^{ij}t_{vi}^{\beta\gamma}t_{w}^{a\epsilon} + P(\beta|\gamma\epsilon)P(u|vw)v_{ab}^{\beta i}t_{ui}^{\gamma\epsilon}\left\{\frac{1}{2}t_{vw}^{ab} + t_{vw}^{ab}\right\} + \\ & + \frac{1}{2}v_{ab}^{ij}P(\beta|\gamma\epsilon)P(uv|w)t_{uvi}^{\beta ab}t_{jw}^{\gamma\epsilon} - v_{ab}^{ij}P(\beta|\gamma\epsilon)P(u|v|w)t_{ui}^{\beta a}t_{vw}^{b\gamma\epsilon} + \\ & + \frac{1}{2}v_{ab}^{ij}P(\beta|\gamma\epsilon)P(uv|w)t_{uv}^{ab}t_{i}^{\beta}t_{jw}^{\gamma\epsilon} + v_{ab}^{ij}P(\beta\gamma|\epsilon)P(u|vw)t_{ui}^{\beta\gamma}t_{vw}^{a b}t_j^\epsilon ; \quad (62) \end{aligned}$$

which can be written as,

$$[\text{VII}] = P(\beta\gamma|\epsilon)P(u|vw)t_{ui}^{\beta\gamma}(v^{(3)})_{vw}^{i\epsilon} , \quad (63)$$

with,

$$\begin{aligned} (v^{(3)})_{vw}^{i\epsilon} = & -v_{vw}^{i\epsilon} - P(v|w)(vt_1)_{vw}^{\epsilon i} + (vt_1)_{vw}^{i\epsilon} + P(v|w)(vt_2)_{v \cdot w}^{i\epsilon} + \\ & + P(v|w)(vt_1 t_1)_{vw}^{\cdot i \cdot \epsilon} + (vt_2')_{vw}^{\epsilon i} - \frac{1}{2}(vt_3)_{vw}^{\cdot i \cdot \epsilon} + \end{aligned}$$

$$+ P(v|w)(vt_2t_1)^{\cdot i \epsilon}_{v \cdot w} - (vt_2' t_1)^{\cdot i \epsilon}_{vw} . \quad (64)$$

The required inner multiplications of the three tensor products (vt_2t_1) and $(vt_2' t_1)$ are rank 2 at all stages;

i.e.,

$$(vt_2t_1)^{\cdot i \epsilon}_{v \cdot w} = (vt_2)^{\cdot i \epsilon}_{av} t_w^a , \quad (65)$$

$$(vt_2' t_1)^{\cdot i \epsilon}_{vw} = (vt_2')^{ji}_{vw} t_j^\epsilon , \quad (66)$$

and construction of (vt_1t_1) was discussed in Equation (51).

Similarly the eighth partial sum,

$$\begin{aligned} [\text{VIII}] &= P(\beta\gamma|\epsilon)P(u|vw)v_{au}^{\beta\gamma}t_{vw}^{\epsilon a} + P(\beta|\gamma|\epsilon)P(u|vw)v_{au}^{\beta i}t_{vw}^{\gamma a \epsilon} + \\ &+ P(\beta\gamma|\epsilon)P(uv|w)v_{ab}^{\beta\gamma}t_{uv}^{\epsilon a}t_w^b - P(\beta|\gamma|\epsilon)P(uv|w)v_{ab}^{\beta i}t_{uv}^{\gamma a}t_{iw}^{bc} + \\ &+ P(\beta|\gamma|\epsilon)P(uv|w)v_{ab}^{\beta i}t_{uv}^{\gamma a}t_{iw}^{\epsilon b} - P(\beta|\gamma|\epsilon)P(u|vw)v_{ua}^{ij}t_{vw}^{\beta a}\left\{\frac{1}{2}t_{ij}^{\gamma \epsilon} + t_{ij}^{\gamma \epsilon}\right\} + \\ &+ \frac{1}{2}v_{ab}^{ij}P(\beta\gamma|\epsilon)P(u|vw)t_{uij}^{\beta\gamma}t_{vw}^{bc} - v_{ab}^{ij}P(\beta|\gamma|\epsilon)P(u|vw)t_{uij}^{\beta a}t_{vw}^{\gamma bc} + \\ &+ \frac{1}{2}v_{ab}^{ij}P(\beta\gamma|\epsilon)P(u|vw)t_{ij}^{\beta\gamma}t_u^a t_{vw}^{bc} + v_{ab}^{ij}P(\beta|\gamma|\epsilon)P(uv|w)t_{uv}^{\beta a}t_{iw}^{\gamma bc}t_j^\epsilon , \quad (67) \end{aligned}$$

can be written as,

$$[\text{VIII}] = P(\beta|\gamma|\epsilon)P(uv|w)t_{uv}^{\beta a}(v^{(3)})_{aw}^{\gamma \epsilon} , \quad (68)$$

with,

$$(v^{(3)})_{aw}^{\gamma \epsilon} = v_{aw}^{\gamma \epsilon} - P(\gamma|\epsilon)(vt_1)_{aw}^{\gamma \epsilon} + (vt_1)_{aw}^{\gamma \epsilon} - P(\gamma|\epsilon)(vt_2)_{aw}^{\gamma \epsilon} +$$

$$\begin{aligned}
& - P(\gamma|\epsilon)(vt_1t_1)_{a \cdot w}^{\gamma \epsilon} - (vt_2')_{wa}^{\gamma \epsilon} - \frac{1}{2}(vt_3)_{\cdot aw}^{\gamma \epsilon} + \\
& + P(\gamma|\epsilon)(vt_2t_1)_{\cdot aw}^{\gamma \epsilon} - (vt_2't_1)_{\cdot a w}^{\gamma \epsilon} .
\end{aligned} \tag{69}$$

The required inner multiplications of the three tensor products (vt_2t_1) and $(vt_2't_1)$ are rank 2 at all stages;

i.e.,

$$(vt_2t_1)_{\cdot aw}^{\gamma \epsilon} = (vt_2)_{\cdot aw}^{j\gamma} t_j^{\epsilon} , \tag{70}$$

$$(vt_2't_1)_{\cdot a w}^{\gamma \epsilon} = (vt_2')_{ba}^{\gamma \epsilon} t_w^b . \tag{71}$$

We next show that the projection of the Schrödinger Equation for the CCSDT wavefunction on the doubly-excited space can be written in terms of (at worst) products of unmodified rank 3 cluster coefficients and modified rank 2 integrals. Consider breaking the sum in Equation (2) into eight parts; the first six being,

$$[IX] = [14a] + [16b] + [22b] + [25c] + [26b] , \tag{72}$$

$$[X] = [14b] + [16a] + [22a] + [25d] + [26a] , \tag{73}$$

$$[XI] = [15] + [24a] , \tag{74}$$

$$[XII] = [25a] + [26c] , \tag{75}$$

$$[XIII] = [25b] + [26d] + [26e] + [27] , \tag{76}$$

$$\begin{aligned}
[\text{XIV}] = & [\text{17}] + [\text{18a}] + [\text{18b}] + [\text{19a}] + [\text{19b}] + [\text{20c}] + \\
& + [\text{20a}] + [\text{19c}] + [\text{20b}] + [\text{21a}] + [\text{21b}] + [\text{22c}] + \\
& + [\text{22d}] + [\text{22e}] + [\text{23b}] + [\text{22f}] + [\text{23a}] ; \quad (77)
\end{aligned}$$

the remaining two partial sums are the single diagrams [24b] and [24c]. Aside from satisfying the computational constraints, the partial summations were chosen to: 1) expose (double) cluster coefficients one index removed from the $\langle \beta\gamma |_{uv}$ component of the external space (cf. Equation (3.14)), and 2) utilize tensors already required for the triply-excited space. The first consideration facilitates the solution of the coupled cluster equations by the method of iteration (i.e., successive substitution).^{12,13} The second obviously reduces the computational effort. The appropriate forms of the above two considerations were used in the choice of partial summations for the triply-excited space, and will be used for the singly-excited space; though it should be noted that the constraints imposed by rank seriously restricted the options in the triples case.

As before, let us examine each of the partial sums in turn.

$$\begin{aligned}
[\text{IX}] = & -P(u|v)f_{uiv}^i t_{iv}^{\beta\gamma} - P(u|v)f_{aui}^i t_{iv}^{\beta\gamma a} + P(u|v)v_{ua}^{ij} t_{vj}^{\beta\gamma a} + \\
& + \frac{1}{2}v_{ab}^{ij} P(u|v)t_{uiv}^{ab} t_{jv}^{\beta\gamma} + v_{ab}^{ij} P(u|v)t_{uiv}^{\beta\gamma a} t_{jv}^a{}^b ; \quad (78)
\end{aligned}$$

which can be written,

$$[\text{IX}] = P(u|v)t_{ui}^{\beta\gamma} (f^{(2)})_v^i , \quad (79)$$

where,

$$(f^{(2)})_v^i = -f_v^i - (ft_1)_v^i - (vt_1)_v^i + (vt_2^!)^i \dots_v \quad (80)$$

Observe that the modified one-electron integral, with both indices from the Fermi sea, for the projection on the doubly-excited space, $(f^{(2)})_v^i$, is identical with the corresponding integral for the triply-excited space, $(f^{(3)})_v^i$ (cf. Equation (44)).

Now let us consider the second partial sum,

$$\begin{aligned} [X] = & P(\beta|\gamma) f_{a\,uv}^{\beta a\gamma} - P(\beta|\gamma) f_{a\,uv}^i t_{uv}^{\beta a\gamma} - P(\beta|\gamma) v_{ab}^{\beta i} t_{uv}^{\gamma a b} + \\ & + \frac{1}{2} v_{ab}^{ij} P(\beta|\gamma) t_{ij}^{\beta a} t_{uv}^{b\gamma} + v_{ab}^{ij} P(\beta|\gamma) t_{uv}^{\beta a} t_{i\,j}^{b\gamma} \quad ; \end{aligned} \quad (81)$$

which gives,

$$[X] = P(\beta|\gamma) t_{uv}^{\beta a} (f^{(2)})_a^\gamma \quad , \quad (82)$$

with,

$$(f^{(2)})_a^\gamma = f_a^\gamma - (ft_1)_a^\gamma + (vt_1)_a^\gamma + (vt_2^!)_{a..}^\gamma \quad . \quad (83)$$

As before, note that $(f^{(2)})_a^\gamma = (f^{(3)})_a^\gamma$.

The third partial sum is,

$$[XI] = f_{a\,uvi}^i t_{uv}^{\beta\gamma a} + v_{ab}^{ij} t_{uvi}^{\beta\gamma a} t_j^b \quad ; \quad (84)$$

and can be written,

$$[XI] = t_{uvi}^{\beta\gamma a} (f^{(2)})_a^i \quad , \quad (85)$$

where,

$$(f^{(2)})_a^i = f_a^i + (vt_1)_a^i \quad . \quad (86)$$

The fourth partial sum is,

$$[XII] = v_{ab}^{ij} P(\beta|\gamma) t_{ui}^{\beta a} t_{jv}^{\beta y} - v_{ab}^{ij} P(\beta|\gamma) P(u|v) t_{ui}^{\beta a} t_{v}^{\beta y} ; \quad (87)$$

or,

$$[XII] = -P(\beta|\gamma) P(u|v) (t_2')_{ui}^{ab} (v^{(2)})_{av}^{i\gamma} , \quad (88)$$

where,

$$(v^{(2)})_{av}^{i\gamma} = (vt_2)_{av}^{i\gamma} . \quad (89)$$

Similarly, the fifth partial sum,

$$[XIII] = \frac{1}{4} v_{ab}^{ij} t_{uv}^{\beta\gamma} t_{ij}^{\beta\gamma} + \frac{1}{2} v_{ab}^{ij} t_{uv}^{\beta\gamma} t_{ij}^{\beta\gamma} + \frac{1}{2} v_{ab}^{ij} t_{ij}^{\beta\gamma} t_{uv}^{\beta\gamma} + v_{ab}^{ij} t_{ui}^{\beta a} t_{v}^{\beta y} ; \quad (90)$$

can be written as,

$$[XIII] = (t_2')_{uv}^{ab} (v^{(2)})_{ab}^{\beta\gamma} , \quad (91)$$

where,

$$(v^{(2)})_{ab}^{\beta\gamma} = (vt_2)_{ab}^{\beta\gamma} . \quad (92)$$

The fourth and fifth terms, [XII] and [XIII], are anomalous in that modified cluster coefficients (e.g., rank 2) are used in the final tensor products. The particular modified cluster coefficients involved, t_2' , have already been used in several intermediate tensor products (cf. Equations (42), (54), (57), (66), and (71)).

The sixth partial sum is,

$$[XIV] = v_{uv}^{\beta\gamma} - P(\beta|\gamma) v_{uv}^{\beta i} t_i^{\beta\gamma} + P(u|v) v_{ua}^{\beta\gamma} t_v^{\beta a} - P(\beta|\gamma) P(u|v) v_{au}^{\beta i} t_{iv}^{\beta a\gamma} +$$

$$+ v_{uv}^{ij} \left\{ \frac{1}{2} t_{ij}^{\beta\gamma} + t_i^{\beta} t_j^{\beta\gamma} \right\} + P(\beta|\gamma) P(u|v) v_{au}^{\beta i} t_v^{\beta a\gamma} + v_{ab}^{\beta\gamma} \left\{ \frac{1}{2} t_{uv}^{\beta a} + t_u^{\beta a} t_v^{\beta} \right\} +$$

$$\begin{aligned}
& - \frac{1}{2}P(\beta|\gamma)v_{ab}^{\beta i}t_{uv}^{\gamma ab} + \frac{1}{2}P(u|v)v_{ua}^{ij}t_{vij}^{\beta\gamma a} + P(\beta|\gamma)P(u|v)v_{au}^{ij}t_{vij}^{\beta a\gamma} + \\
& - P(\beta|\gamma)P(u|v)v_{ab}^{\beta i}t_{uv}^{\gamma a b} - \frac{1}{2}P(\beta|\gamma)v_{ab}^{\beta i}t_{uv}^{\gamma ab}t_i^{\gamma} + P(\beta|\gamma)v_{ab}^{\beta i}t_{uv}^{\gamma a}t_v^{\gamma b} + \\
& + \frac{1}{2}P(u|v)v_{ua}^{ij}t_{ijv}^{\beta\gamma a} - P(u|v)v_{au}^{ij}t_{v i j}^{\beta a\gamma} ; \quad (93)
\end{aligned}$$

which can be rewritten as,

$$[XIV] = (v^{(2)})_{uv}^{\beta\gamma} \quad (94)$$

$$\begin{aligned}
& = v_{uv}^{\beta\gamma} - P(\beta|\gamma)(vt_1)_{uv}^{\beta\gamma} + P(u|v)(vt_1)_{uv}^{\beta\gamma} - P(\beta|\gamma)P(u|v)(vt_2)_{u\cdot v}^{\beta\gamma} + \\
& + (vt_2')_{uv}^{\beta\gamma} + P(\beta|\gamma)P(u|v)(vt_1t_1)_{uv}^{\beta\gamma} + (vt_2')_{uv}^{\beta\gamma} + \\
& - \frac{1}{2}P(\beta|\gamma)(vt_3)_{uv}^{\beta\cdot\gamma} + \frac{1}{2}P(u|v)(vt_3)_{u\cdot v}^{\beta\gamma} + \\
& + P(\beta|\gamma)P(u|v)(vt_2t_1)_{\cdot uv}^{\beta\cdot\gamma} - P(\beta|\gamma)P(u|v)(vt_2t_1)_{u\cdot v}^{\beta\gamma} + \\
& - P(\beta|\gamma)(vt_2't_1)_{\cdot uv}^{\beta\cdot\gamma} + P(u|v)(vt_2't_1)_{u\cdot v}^{\beta\gamma} . \quad (95)
\end{aligned}$$

Three tensor products were previously considered in Equations (51), (65), (66), (70), and (71).

The seventh partial sum consists of only one term which may be written,

$$[24b] = \frac{1}{2}P(\beta|\gamma)t_1^{\beta}(v^{(2)})_{uv}^{\gamma} , \quad (96)$$

with,

$$(v^{(2)})_{uv}^{\gamma} = (vt_3)_{uv}^{\gamma} . \quad (97)$$

Likewise, the eighth partial sum may be written as,

$$[24c] = \frac{1}{2}P(u|v)t_u^a(v^{(2)})_{av}^{\beta\gamma}, \quad (98)$$

with,

$$(v^{(2)})_{av}^{\beta\gamma} = (vt_3)_{a \cdot v}^{\beta\gamma}. \quad (99)$$

We next show that the projection on the singly-excited space can be written in terms of (at worst) products of unmodified rank 3 cluster coefficients and modified rank 2 integrals. Consider breaking the sum in Equation (1) into four parts,

$$[XV] = [5a] + [7] + [10a] + [12b] + [13], \quad (100)$$

$$[XVI] = [5b] + [7] + [10b] + [12c] + [13], \quad (101)$$

$$[XVII] = [4] + [6] + [8] + [9a] + [9b] + [11] + [12a], \quad (102)$$

$$[XVIII] = -[7] - [13]. \quad (103)$$

We have added to and subtracted from the sum in order to use the same modified one-electron integrals for the projection on the singly-excited space, as for the doubly- and triply-excited spaces (cf. text following Equations (80) and (83)). Let us consider each of the partial sums in turn.

$$[XV] = -f_{u1}^1 t_1^\beta - f_{a u t_1}^1 a \beta - v_{ua t_1 t_j}^{ij} \beta a - \frac{1}{2} v_{ab t_{uj} t_1}^{ij} ab \beta - v_{ab t_{u t_1} t_j}^{ij} b a \beta; \quad (104)$$

which can be written,

$$[XV] = t_i^\beta (f^{(1)})_u^i, \quad (105)$$

where,

$$(f^{(1)})_u^i = -f_u^i - (ft_1)_u^i - (vt_1)_u^i + (vt_2')_u^i. \quad (106)$$

Comparison with Equations (44) and (80) shows that the same modified one-electron integrals, with both indices from the Fermi sea, can be used for all projections;

i.e.,

$$(f')_u^i \equiv (f^{(1)})_u^i = (f^{(2)})_u^i = (f^{(3)})_u^i. \quad (107)$$

Similarly for the second partial sum,

$$[XVI] = f_{a u}^{\beta a} - f_{a u}^i t_i^{\beta a} + v_{ab}^i t_i^{\beta a} - \frac{1}{2} v_{ab}^{ij} t_{ij}^{\beta a} - v_{ab}^{ij} t_{ij}^{\beta a}; \quad (108)$$

or,

$$[XVI] = t_u^a (f^{(1)})_a^\beta, \quad (109)$$

where,

$$(f^{(1)})_a^\beta = f_a^\beta - (ft_1)_a^\beta + (vt_1)_a^\beta + (vt_2')_a^{\beta\beta}. \quad (110)$$

As before, comparison with the modified one-electron integrals for the doubly- and triply-excited spaces, Equations (47) and (83), gives,

$$(f')_a^\beta = (f^{(1)})_a^\beta = (f^{(2)})_a^\beta = (f^{(3)})_a^\beta. \quad (111)$$

The third partial sum,

$$[XVII] = f_u^\beta + f_{a u}^i t_{ui}^{\beta a} - v_{au}^i t_{ui}^{\beta a} - \frac{1}{2} v_{ua}^{ij} t_{ij}^{\beta a} + \frac{1}{2} v_{ab}^i t_{ui}^{\beta a} +$$

$$+ \frac{1}{4} v_{ab}^{ij} t_{uif}^{\beta ab} + v_{ab}^{ij} t_{uif}^{\beta a b} , \quad (112)$$

can be written as,

$$[\text{XVII}] = (f^{(1)})_u^\beta \quad (113)$$

$$= f_u^\beta - (ft_2)^\beta_u - (vt_1)^\beta_u - \frac{1}{2}(vt_2)^\beta_u + \frac{1}{2}(vt_2)^\beta_{..u} + \frac{1}{4}(vt_3)^\beta_{..u} + (vt_2 t_1)^\beta_{..u} . \quad (114)$$

The fourth partial sum, which compensates for the added terms, is

$$[\text{XVIII}] = f_{a u}^i t_{t_1}^{a \beta} + v_{ab}^{ij} t_{t_1}^b t_{t_j}^{a \beta} ; \quad (115)$$

which we can rewrite as,

$$[\text{XVIII}] = t_1^\beta (f^{(1')})_u^i , \quad (116)$$

where,

$$(f^{(1')})_u^i = (ft_1)_u^i - (vt_1 t_1)^\beta_{..u} . \quad (117)$$

Finally, the projection of the Schrödinger Equation for the CCSDT wavefunction on the reference determinant, Equation (4), may be written as,

$$\Delta E = f_{a i}^i t_1^a + \frac{1}{4} v_{ab}^{ij} t_{ij}^{ab} + \frac{1}{2} v_{ab}^{ij} t_{i j}^{a b} . \quad (118)$$

Hence the correlated energy can be expressed in terms of contractions of modified one- and two-electron integrals,

$$\Delta E = (ft_1) + \frac{1}{2}(vt_2') . \quad (119)$$

7. Discussion and Conclusions

The algebraic expressions obtained from a diagrammatic evaluation of the coupled cluster equations for a CCSDT model are resolvable into products of unmodified cluster coefficients (or trivially modified, in the case of t_2') and modified one- and two-electron integrals. At no stage of the calculation are tensors of rank greater than two required, except for the initial contraction and final expansion of the rank 3 triples cluster coefficients.

The coupled cluster equations for a CCSDT model are linear in the triples coefficients, even though the wave operator is full with respect to the logarithmic wave operator truncated at rank 3. This suggests that a single sequential pass of the triples cluster coefficients suffices for each iteration. The algorithm for the determination of the cluster coefficients would appear to be divisible into three parts: construction of the modified integrals (except (vt_3)); list-directed multiplication of the triples coefficients and the modified integrals; and, final contraction with t_1 , t_2 , and t_2' . The final forms of the coupled cluster equations derived in the preceding Section are eminently compatible with this algorithm.

A key aspect in the implementation of a full coupled cluster method is the rearrangement of the cluster equations to enable a solution by the method of iteration, or successive substitution. As discussed by Purvis and Bartlett in their paper¹² on a full coupled cluster method including single and double excitations (CCSD), a convergent solution can usually be obtained by casting the equations in a form reminiscent of perturbation theory (i.e., factor the appropriate diagonal elements of the Fock matrix). The analogous rearrangement from

implicit to iterative forms can be done for the cluster equations in the CCSDT model presented in the preceding Section.

An interesting variant iterative scheme is motivated by the near invariance of the intra-set modified one-electron integrals to external space excitation level in the cluster equations. Consider that the cluster equations for arbitrary external space rank r (>0), may be written as,

$$0 = P(u_1 \dots u_{r-1} | u_r) t_{u_1 \dots u_{r-1}}^{\beta_1 \dots \beta_r} (f')_{u_r}^i + \\ + P(\beta_1 \dots \beta_{r-1} | \beta_r) t_{u_1 \dots u_r}^{\beta_1 \dots \beta_{r-1} a} (f')_a^{\beta_r} + R_r ; \quad (7.1)$$

where P is the single index set permutation operator, R_r represents terms which are currently not of interest, f' is an intra-set modified one-electron integral; and the repeated index summation convention is used, with the appropriate modification (cf. Section 4) when an argument of the permutation operator is involved. Equation (1) may be rewritten,

$$-P(u_1 \dots u_{r-1} | u_r) t_{u_1 \dots u_r}^{\beta_1 \dots \beta_r} (f')_{u_r}^{u_r} - P(\beta_1 \dots \beta_{r-1} | \beta_r) t_{u_1 \dots u_r}^{\beta_1 \dots \beta_r} (f')_{\beta_r}^{\beta_r} \\ = P(u_1 \dots u_{r-1} | u_r) \{ t_{u_1 \dots u_{r-1}}^{\beta_1 \dots \beta_r} (f')_{u_r}^i - t_{u_1 \dots u_r}^{\beta_1 \dots \beta_r} (f')_{u_r}^{u_r} \} + \\ + P(\beta_1 \dots \beta_{r-1} | \beta_r) \{ t_{u_1 \dots u_r}^{\beta_1 \dots \beta_{r-1} a} (f')_a^{\beta_r} - t_{u_1 \dots u_r}^{\beta_1 \dots \beta_r} (f')_{\beta_r}^{\beta_r} \} + R_r . \quad (2)$$

Then consideration of the action of a permutation operator on an already antisymmetric tensor allows us to obtain,

$$\begin{aligned}
t_{u_1 \dots u_r}^{\beta_1 \dots \beta_r} &= \frac{-1}{(f')_p} \{ P(u_1 \dots u_{r-1} | u_r) t_{u_1 \dots u_{r-1}}^{\beta_1 \dots \beta_r} (f')_{u_r}^{i'} + \\
&+ P(\beta_1 \dots \beta_{r-1} | \beta_r) t_{u_1 \dots u_r}^{\beta_1 \dots \beta_{r-1} a'} (f')_{a'}^{\beta_r} + R_r \} \quad , \quad (3)
\end{aligned}$$

as iterative forms of the coupled cluster equations. In Equation (3), the index sets are given by, $p \in \{u_1, \dots, u_r, \beta_1, \dots, \beta_r\}$, $i' \in \{\bar{u}_j\} \wedge \{\overline{FS}\}$, and $a' \in \{\bar{\beta}_j\} \wedge \{\overline{FS}\}$. We have just shown that a modification to the final (implicit) equations to obtain iterative equations in a CCSDT model can be found which localizes changes to the contractions of the intra-set modified one-electron integrals and the appropriate cluster coefficients. Specifically, unrestricted sums in Equations (6.43), (6.46), (6.79), (6.82), (6.105), and (6.109), are replaced by the appropriate restricted sums. It must be emphasized that the conclusions concerning algorithm structure and required tensor ranks are equally valid for the iterative and implicit forms of the final coupled cluster equations.

The CCSDT model has been shown not to make excessive demands on either the core memory or the disc memory of modern computers, when applied to small polyatomic molecules. A complementary concern in assessing the potential usefulness of the method is the central processing unit (CPU) requirement relative to other techniques in computational chemistry. The bulwark methods, configuration interaction including all single and double excitations (CISD) and fourth order perturbation theory (PT4), have computational complexities of $O(m^6)$ and $O(m^7)$, respectively, where m is the number of orbitals. Including triples in the CI wavefunction increases the algorithm to $O(m^8)$, quadruples to $O(m^{10})$, etc. The portions of MCSCF calculations dealing

with the orbital rotations are $O(m^6)$; hence, the overall order of an MCSCF procedure is the same as the order of the corresponding configuration interaction calculation. The computational complexity of the CCSDT model, as presented in this work, is easily found to be $O(m^8)$; the CCSD model is $O(m^6)$. Since the CCSDT model includes all (connected) single, double, and triple excitations, and the dominant (connected) quadruple and quintuple excitations, it ought to be compared in reliability with CISDTQQ. Hence, the CCSDT model appears to be a computationally viable, size-extensive method for the very high-level description of electron correlation, at an only moderately high cost.

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