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Multireference coupled-cluster method using a single-reference formalism

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Oliphant, Nevin Horace, Ph.D.

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A MULTI-REFERENCE COUPLED-CLUSTER METHOD USING A SINGLE-REFERENCE FORMALISM

by

Nevin Oliphant

A Dissertation Submitted to the Faculty of the
Department of Chemistry
In Partial Fulfillment of the Requirements
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As members of the Final Examination Committee, we certify that we have read

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MULTI-REFERENCE COUPLED-CLUSTER METHOD USING A SINGLE-REFERENCE FORMALISM

ABSTRACT

The coupled-cluster (CC) equations including single, double, triple and quadruple excitations (CCSDTQ) are qraphically derived using Feynman diagrams. These equations are programmed and an iterative reduced linear equation method is used to solve these equations. A few points on the potential curves for the dissociation of some model systems with a single bond (LiH and Li_2) are calculated using CC doubles (CCD), singles and doubles (CCSD), singles, doubles and triples (CCSDT) and CCSDTQ. These calculations demonstrate the magnitude of the CC contributions arising from triple and quadruple excitation amplitudes to the stretching of a chemical bond. A multi-reference coupled-cluster singles and doubles (MRCCSD) method utilizing two reference determinants, which differ by a two electron excitation, is then proposed. One of these determinants is selected as the formal reference determinant. The proposed method is based on the single-reference coupled-cluster equations truncated after quadruples with appropriate restrictions placed on the triple and quadruple amplitudes to allow only those amplitudes which correspond to single and double excitations from the second reference determinant. The computational expense of this method is no more than twice that of singles and doubles from a single reference (CCSD). These equations are programmed and the potential curves for the dissociation of a few model systems with single bonds (LiH, BH, and H_2O) are calculated to demonstrate the correct bond dissociation properties of this method. These calculations also demonstrate how much of the CC energy contribution arising from the triple and quadruple excitation amplitudes can be attributed to single and double excitations from the second reference determinant.

I INTRODUCTION

The Hartree-Fock (HF) method[1,2] is easily the most popular independent electron model for calculating atomic and molecular electronic structure. This method is responsible for the idea of electrons occupying orbitals, or the molecular orbital picture of electrons in molecules, which most chemists refer to on a regular basis. The HF method makes the assumption that one electron moves in the average field of the other electrons and for most atoms and molecules the method provides a total electronic energy which is very close to the *exact* energy; a few examples for molecules at their equilibrium nuclear geometry, 96% for H_2, 98.9% for LiH, 99% for H_2O, and 99.5% for NH_3.[3] The *exact* energy is usually defined in quantum chemistry as the exact solution of the non-relativistic Schrödinger equation within a defined space or basis set;

$$\hat{H}\psi = E\psi \tag{1}$$

The HF method determines a set of N orthonormal orbitals such that a single determinant formed from these orbitals provides the best approximation to the ground state of the 2N-electron problem;

$$|\psi_0\rangle = |\chi_1\overline{\chi}_1\chi_2\overline{\chi}_2\cdots\chi_N\overline{\chi}_N\rangle \tag{2}$$

The 'best' spin orbitals according to the variational principle will be those that minimize the electronic energy. The HF method does however have a number of drawbacks. The biggest problem is the fact that most energies of chemical interest are of the same order as the 1% error in the HF method, for example the binding energy of LiH is approximately 1.1% of the total energy, while that of the N_2 molecule is 0.2% of the total energy.[3] Another problem with the HF method is that it does not dissociate molecules into open shell fragments correctly. Let us consider the H_2 molecule, this molecule dissociates into two neutral hydrogen atoms. The HF method restricts electrons to occupy molecular orbitals in pairs. If we use a minimal basis (one s orbital on each H atom), to form the molecular orbitals for H_2, the spatial part of the ground state wavefunction is given by;

$$\psi_{H_2}(1,2) = N(1s_{H_1} + 1s_{H_2})(1)(1s_{H_1} + 1s_{H_2})(2) \tag{3}$$

or;

$$\begin{aligned}\psi_{H_2}(1,2) &= N1s_{H_1}(1)1s_{H_1}(2) + N1s_{H_2}(1)1s_{H_2}(2) + \\ &\quad N1s_{H_1}(1)1s_{H_2}(2) + N1s_{H_2}(1)1s_{H_1}(2)\end{aligned} \tag{4}$$

where N is the normalization factor. The above wavefunction cannot be appropriate to describe the electronic state at all internuclear separations, because the ionic terms (the first and second terms) predicting that both electrons localize around one nuclei enter the expression with the same coefficient as the covalent terms (the last two terms), which describe an equal distribution of the electrons around both hydrogen nuclei. As the internuclear separation approaches infinity the first two terms in (4) should dissappear, because the probability of finding both electrons on one atom in the ground state should vanish. Thus rather than dissociating to the energy of two neutral hydrogen atoms, the HF energy continues to rise as the atoms are separated.

Correlation energy is defined as the difference between the *exact* solution to the non-relativistic Schrödinger equation and the solution to the corresponding HF problem;

$$E_{corr} = E_{exact} - E_{HF} \tag{5}$$

The term 'correlation' results from electron correlation effects or the instantaneous interaction of electrons with each other. Since electrons are charged particles, the effect of electron correlation will be to keep the electrons apart and reduce their mutual repulsion, thus, including electron correlation will lead to a lowering of energy.

In the process of forming the occupied or core orbitals for the best single determinant, the HF procedure also yields an orthonormal set of unoccupied or virtual orbitals orthogonal to the core orbitals. The simplest approach to the correlation energy problem is to consider allowing one or more of the electrons to spend 'time' in each of these previously unoccupied orbitals. This than allows the electrons to spatially avoid each other. This is an electron excitation in quantum chemical terms, and, rather then a physical process, this is simply a mathematical tool to generate excited determinants. If all possible electronically excited determinants are included in the wave function along with the HF determinant, then placing coefficients in front of the determinants and determining them variationally with respect to the energy defines the full configuration interaction (FCI) method.

$$|\psi_{FCI}\rangle = C_0|0\rangle + \sum_{\substack{i\\a}} C_i^a|0_i^a\rangle + \sum_{\substack{i,j\\a,b}} C_{ij}^{ab}|0_{ij}^{ab}\rangle + \ldots + \sum_{\substack{i,j,\ldots,n_c\\a,b,\ldots,n_v}} C_{ij\ldots n_c}^{ab\ldots n_v}|0_{ij\ldots n_c}^{ab\ldots n_v}\rangle \quad (6)$$

This is the exact answer within the basis chosen, but is not practical for large basis sets required to represent a molecule adequately. If we again consider H_2 with a minimal basis, the virtual orbital would be;

$$\phi_v = (1s_{H_1} - 1s_{H_2}) \quad (7)$$

Including all excitations involves only the double excitation, as the single excitations are not allowed by symmetry (the ground state and the doubly excited state are gerade, the singly excited states are ungerade). The FCI wavefunction is then;

$$\begin{aligned} \psi_{FCI}(1,2) &= \quad (8) \\ & C_1(1s_{H_1} + 1s_{H_2})(1)(1s_{H_1} + 1s_{H_2})(2) + \\ & C_2(1s_{H_1} - 1s_{H_2})(1)(1s_{H_1} - 1s_{H_2})(2) \end{aligned}$$

or rearranging;

$$\begin{aligned} \psi_{FCI}(1,2) &= C_A 1s_{H_1}(1)1s_{H_1}(2) + 1s_{H_2}(1)1s_{H_2}(2) + \quad (9) \\ & C_B 1s_{H_1}(1)1s_{H_2}(2) + 1s_{H_2}(1)1s_{H_1}(2) \end{aligned}$$

where;

$$\begin{aligned} C_A &= C_1 + C_2 \\ C_B &= C_1 - C_2 \end{aligned} \tag{10}$$

This wavefunction yields the exact answer within the minimal basis set. As the internuclear separation goes to infinity, the coefficient C_A, which precedes the ionic terms, becomes zero, using the variational procedure, and the molecule dissociates properly to two neutral hydrogen atoms.

In order to study problems of chemical interest, correlation must be taken into account. The FCI procedure is not practical for large scale calculations, so the most straight-forward way to deal with the problem is to truncate the FCI procedure at some point. CI including only single and double excitations (CISD), and CI including single, double, triple and quadruple excitations (CISDTQ) have become well established and are widely used in quantum chemistry.[4] The major problem with the truncated CI method is the fact that it is not size-extensive. Size-extensivity means that properties such as energy calculated by a method should scale properly with the size of the system. FCI has this property as one would expect from an exact method. Let us consider for example the energy of two non-interacting (infinitely separated) H_2 molecules calculated using the HF method. This energy would be correctly reproduced by the HF method to be twice the HF energy of a single H_2 molecule. However, the energy of the H_2 molecule calculated with CI containing only double excitations

(CID) would not be twice the CID energy of a single H_2 molecule. To obtain a correct result it would require simultaneously exciting both electrons on both molecules, which leads to a quadruple excitation. Including the product of double excitations would make CID size extensive for this example, but would not solve the problem in general.

The single-reference coupled-cluster method (CC) has been established as an accurate method[5–29] for calculating the correlation energy of chemical systems. This method is based on an exponential ansatz for the wavefunction ($\psi_{\mathrm{CC}} = e^{\mathrm{T}} \,|\, \phi_0\rangle$), where T is a cluster operator which is separated into one-electron, T_1, two-electron, $\mathrm{T}_2 \cdots$ n-electron, T_{n}, clusters with n being the number of electrons in the system.

The CC method is closely related to many-body pertubation theory (MBPT)[5,11], and can be considered to be an infinite order MBPT in certain classes of perturbation corrections (diagrams). This relationship between CC theory and MBPT was demonstrated by Hubbard.[12] A correspondance between the CC method and the configuration interaction (CI) method can be established for each level of excitation in the CI wavefunction. It can be shown that each selected CI coefficient, pertaining to a certain excitation level, corresponds to a sum of CC terms including all possible products of CC amplitudes that yield that level of excitation. The inclusion of these products of amplitudes in the CC wavefunction makes the CC method, like MBPT, exactly size-extensive.

The conceptual origin of the coupled-cluster theory of electron correlation can be traced to the correlated electron pair theories of Nesbet[13] and Sinanoglu.[14] The exponential ansatz, which defines the coupled-cluster approach, was introduced by Coester and Kummel,[6] with Ĉíẑek presenting the first explicit equations for coupled-cluster doubles (CCD).[7] Ĉíẑek also developed a diagrammatic approach to deriving algebraic expressions for general CC models. General purpose *ab-initio* programs for applying the CCD method were implemented by Bartlett et al[15] and Pople et al[16] in 1978. This was followed by the development and implementation of CC singles and doubles (CCSD) by Bartlett and Purvis.[9] At present several CC methods which approximate the effect of triple excitation amplitudes have been developed[17,18] as well as the full singles, doubles, and triples (CCSDT) method which has been implemented by Noga and Bartlett,[19] as well as Scuseria and Schaefer.[20] A method, which approximates the effect of quadruple excitation amplitudes, was also recently developed and implemented by Kucharski and Bartlett.[21] As well as the previously mentioned developments, several other quantum chemistry groups have developed and implemented CC methods of their own, including the groups of Dykstra,[22] Kaldor,[23] Kutzelnigg,[24] Monkhorst,[25] Mukherjee,[26] Nakatsuji,[27] Simons[28]and Lee and Rice.[29] In chapter 2 the development and implementation of the extension of the CC method to include the complete contribution of single, double, triple and quadruple excitation amplitudes (CCSDTQ) is discussed.[30] While large scale applications of the CCSDTQ method are not feasible at this time, the application to model systems helps to demonstrate the utility and limitations of the lower order methods (CCD, CCSD etc.).

When the system being studied is well represented by a single determinant wavefunction, which serves as the reference function, then the truncation scheme for CC is rather straight-forward. Including single and double CC amplitudes accounts for the majority of the correlation effects. The next most significant contribution comes from triple excitations and so on. When two or more determinants become necessary to describe the state of the molecule correctly, as in an open shell singlet state or in the chemical bond dissociation process, then a more complicated truncation scheme is required, the conceptually simplest of which is to systematically include higher order levels of excitations. Unfortunately this approach is not computationally tractable. An alternative to including complete levels of higher order excitations is to explicitly include those higher order excitations which are the most important. This should include single and double excitations from all determinants which are necessary to correctly describe the state being studied. This can be done either as a complicated truncation scheme or by explicitly including all the important determinants in a multi-determinant reference function.

Although single-reference CC has been well established for a number of years, the extension to multi-reference CC (MRCC) has been slow. This is in spite of extensive activity in this area.[31–39] The current approaches to MRCC usually involve the use of a complete active space (CAS) reference function and truncation of the Baker-Hausdorf expansion. While this solution to the problem is mathematically elegant, it leads to some large practical problems such as redundant amplitudes and the generation of a huge number of un-necessary (zero) amplitudes which require somewhat complicated procedures to eliminate.[36] In chapters 4 and 5 the development and implementation of a multi-reference coupled-cluster method using a single-reference formalism is discussed.[40]

II THE COUPLED-CLUSTER EQUATIONS

A. Introduction

In order to generate the algebraic expressions corresponding to the equations of the next sections, it is convenient to use diagrammatic methods. The origin of the diagrammatic techniques are attributed to Feynman and were formulated by him for use in quantum electrodynamics. Several modifications of his conventions for time independent applications have since been made.[24,27,28,29,42–44]

As was mentioned in the introduction, several groups have developed their own coupled-methods. There also exist many different, albeit similar, methods for generating diagrams, as well as several different ways of formulating the diagrams. The systematic procedure for unambiguously generating these diagrams developed by Bartlett et al[1] was used in this work.

B. Second Quantization.[41]

Second quantization is a change of representation from the common coordinate representation to the occupation number representation of states. The HF or self consistant field (SCF) method produces a set of orthonormal spin-orbitals which can be ordered and identified by a string of numbers, n_i. The numbers, n_i, identify whether a spin-orbital is occupied ($n_i = 1$) or not occupied ($n_i = 0$) in a Slater determinant. The zero order Slater determinant;

$$|0\rangle = |\chi_1\chi_2\cdots\chi_{2N}\rangle \tag{1}$$

can now be written as;

$$|0\rangle = |1_1\ 1_2\ \ldots 1_{2N}\ 0_{2N+1}\ 0_{2N+2}\ \ldots\rangle \tag{2}$$

With no loss of generality, the zeros following the last occupied spin-orbital can be omitted so that the HF determinant for a ten electron case can be written;

$$|0\rangle = |1\,1\,1\,1\,1\,1\,1\,1\,1\,1\rangle \tag{3}$$

An excitation from spin-orbital 9 to spin-orbital 11 produces the determinant;

$$|0_i^a\rangle = |1\,1\,1\,1\,1\,1\,1\,1\,0\,1\,1\rangle \tag{4}$$

Since the quantum mechanical operators, which enter the electronic hamiltonian, act on the coordinates of electrons, in order for the new notation to be of use it must be accompanied by a redefinition of the operators.

The two fundamental operators of the second quantization formalism act on the spin-orbital to change its occupation, either from zero to one or one to zero. The annihilation operator changes the occupation of a given spin-orbital from one to zero;

$$a_k \mid n_1 n_2 \ldots 1_k n_{k+1} \ldots\rangle = (-1)^{g_k} n_k \mid n_1 n_2 \ldots 0_k n_{k+1} \ldots\rangle \tag{5}$$

where;

$$g_k = \sum_{j>k} n_j \tag{6}$$

The origin of the phase factor $(-1)^g$ results from the fact that the sign of a determinant depends on the sequence of spin-orbitals. This sequence must be written in a consistant way for all possible determinants resulting from spin-orbital substitutions. The n_k results from the the fact that if an annihilation operator acts upon a spin-orbital which has an occupation number of zero, there is nothing to annihilate so the result must be zero;

$$a_k \mid n_1 n_2 \ldots 0_k n_{k+1} \ldots\rangle = 0 \tag{7}$$

The creation operator changes the occupation of a given spin-orbital from zero to one;

$$a_k^\dagger \mid n_1 n_2 \ldots 0_k n_{k+1} \ldots\rangle = (-1)^{g_k}(1 - n_k) \mid n_1 n_2 \ldots 1_k n_{k+1} \ldots\rangle \tag{8}$$

The $(1-n_k)$ results from the the fact that if an creation operator acts upon a spin-orbital, which has an occupation number of one, the spin-orbital cannot be filled again so the result must be zero;

$$a_k^\dagger \mid n_1 n_2 \ldots 1_k n_{k+1} \ldots\rangle = 0 \tag{9}$$

The creation operator is the complex conjugate of the annihilation operator and vice-versa, thus when acting upon the bra-vector their roles are reversed.

The basic algebraic properties of these operators expressed as anti-commutators follows from the definitions, (5) and (8);

$$\left[a_k^\dagger, a_l\right]_+ = a_k^\dagger a_l + a_l a_k^\dagger = \delta_{k,l} \tag{10}$$

$$\left[a_k^\dagger, a_l^\dagger\right]_+ = a_k^\dagger a_l^\dagger + a_l^\dagger a_k^\dagger = 0 \tag{11}$$

$$\left[a_k, a_l\right]_+ = a_k a_l + a_l a_k = 0 \tag{12}$$

These three relations (10),(11) and (12) describe the conditions which must be met by a wavefunction describing a many-electron system. The wavefunction must be anti-symmetric with respect to the interchange of the labels on any two electrons and the spin-orbital occupation is restricted to either 0 or 1.

One consequence of the algebraic properties is that any state vector is an eigenfunction of the operator;

$$a_k a_k^\dagger \tag{13}$$

with an eigenvalue equal to the one minus the occupation number of the k'th spin-orbital;

$$a_k a_k^\dagger \left|n_1 n_2 \ldots n_k n_{k+1} \ldots\right\rangle = (1 - n_k) \left|n_1 n_2 \ldots n_k n_{k+1} \ldots\right\rangle \tag{14}$$

Similarly any state vector is an eigenfunction of the operator;

$$a_k^\dagger a_k \tag{15}$$

with an eigenvalue equal to the the occupation number of the k'th spin-orbital;

$$a_k^\dagger a_k \left| n_1 n_2 \ldots n_k n_{k+1} \ldots \right\rangle = n_k \left| n_1 n_2 \ldots n_k n_{k+1} \ldots \right\rangle \tag{16}$$

The first operator (13), will then select only those state vectors with an occupation of zero in the k'th spin-orbital. The second operator (15), will select only those state vectors with an occupation of one in the k'th orbital.

The final concept needed from second quantization in order to construct a graphical representation, which will be useful in coupled-cluster theory, is that of a contraction. A contraction is simply the replacement of the second quantized operators, (13) and (15), with their respective eigenvalues. Two operators need not be adjacent to each other in a string of second quantized operators in order to be contracted.

The electronic non-relativistic hamiltonian, in coordinate representation, written in terms of atomic units is;

$$\hat{H} = -\sum_{i=1}^{N} \tfrac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} \frac{1}{r_{ij}} \tag{17}$$

where the indices i and j are over the N electrons, the index A is over the M nuclei, Z_A is the charge on the A'th nucleus and r_{ij} is the radial distance between the i'th electron and the j'th electron. Combining the first two terms into a one electron operator, f, this can be written in second quantized formalism as;

$$\hat{H} = \sum_{A,B} \langle A|f|B\rangle a_A^\dagger a_B + \tfrac{1}{4} \sum_{A,B,C,D} \langle AB\|CD\rangle a_A^\dagger a_B^\dagger a_D a_C \tag{18}$$

where now the summations are over the complete set of spin-orbitals. The second term is an anti-symmetric two-electron integral;

$$\langle AB\|CD\rangle = \langle AB|CD\rangle - \langle AB|DC\rangle \tag{19}$$

The hamiltonian, (18), is now an operator which acts on electronic states defined in the occupation number representation.

A general n-electron excitation operator for generating excited state vectors, (determinants), is written in second quantized form, (using coupled-cluster theory conventions) as;

$$T_n = \sum_{\substack{i,j,k,\ldots,n_i\\ a,b,c,\ldots,n_a}} t_{ijk\ldots n_i}^{abc\ldots n_a} a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_k \ldots a_{n_a}^\dagger a_{n_i} \tag{20}$$

The $i, j, k, \ldots, n_i$ refer to occupied spin-orbitals, and $a, b, c, \ldots, n_a$ refer to unoccupied spin-orbitals. The $t_{ijk\ldots n_i}^{abc\ldots n_a}$, are the constants which precede each state vector in a correlated wave function, (called amplitudes in coupled-cluster theory).

C. Coupled-cluster Theory

The single-reference coupled-cluster (CC) method has been described in many places.[5–30] This method is based on an exponential expansion of the wave operator acting on the reference determinant, $|0\rangle$, to produce the coupled-cluster wavefunction;

$$|\psi_{CC}\rangle = e^{T}\,|0\rangle \tag{21}$$

Where the exponential operator is expanded as;

$$e^{T} = 1 + T + \tfrac{1}{2}\,T^{2} + \tfrac{1}{6}\,T^{3} + \cdots \tag{22}$$

and the T operator is;

$$T = T_1 + T_2 + T_3 + T_4 + \cdots \tag{23}$$

In the language of second quantization the cluster operators are;

$$T_1 = \sum_{\substack{a\\i}} t_i^a a_a^\dagger a_i \tag{24}$$

$$T_2 = \sum_{\substack{a>b\\i>j}} t_{ij}^{ab} a_a^\dagger a_i a_b^\dagger a_j \tag{25}$$

$$T_3 = \sum_{\substack{a>b>c\\i>j>k}} t_{ijk}^{abc} a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_k \tag{26}$$

$$T_4 = \sum_{\substack{a>b>c>d\\i>j>k>l}} t_{ijkl}^{abcd} a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_k a_d^\dagger a_l \tag{27}$$

etc.

The second quantized operators produce the excited configuration determinants in the correlated wavefunction and the t's are the coefficients which determine the weight of the corresponding determinant in the wavefunction. The CC equations are derived, starting with the Schrödinger equation;

$$(H - E_{CC})|\psi_{CC}\rangle = 0 \tag{28}$$

The CC energy is determined by projecting the Schrödinger equation against the reference determinant and using the fact that the Hamiltonian operator contains at most two electron operators;

$$\langle 0|(H - E_{CC})[1 + T_1 + \tfrac{1}{2}\, T_1^2 + T_2]|0\rangle = 0 \tag{29}$$

Solving equation 9 for the energy yields;

$$E_{CC} = \langle 0|H[1 + T_1 + \tfrac{1}{2}\, T_1^2 + T_2]|0\rangle \tag{30}$$

Since the first term in the energy equation represents the zero order energy, usually the HF energy, it can be eliminated and this yields an equation for the correlation;

$$\Delta E_{CC} = \langle 0|H[T_1 + \tfrac{1}{2}\, T_1^2 + T_2]|0\rangle \tag{31}$$

The Schrödinger equation is then projected against the determinants representing all possible excited determinants for the system, beginning with single excitations, $\langle 0_i^a|$, double excitations, $\langle 0_{ij}^{ab}|$, triple excitations, $\langle 0_{ijk}^{abc}|$, , quadruple excitations, $\langle 0_{ijkl}^{abcd}|$, and so on.

$$\langle 0_i^a|H[1 + T_1 + \tfrac{1}{2}\, T_1^2 + \tfrac{1}{3!}\, T_1^3 + T_2 + T_1T_2 + T_3]|0\rangle = t_i^a E \tag{32}$$

$$\langle 0_{ij}^{ab}|H[1 + T_1 + \tfrac{1}{2}\,T_1^2 + \tfrac{1}{3!}\,T_1^3 + \tfrac{1}{4!}\,T_1^4 + T_2 + \tfrac{1}{2}\,T_2^2 + T_1T_2 + \tfrac{1}{2}\,T_1^2T_2 + T_3 + T_1T_3 + T_4]\,|0\rangle = t_{ij}^{ab}E \tag{33}$$

$$\langle 0_{ijk}^{abc}|H[T_2 + \tfrac{1}{2}\,T_2^2 + T_1T_2 + \tfrac{1}{2}\,T_1^2T_2 + \tfrac{1}{3!}\,T_1^3T_2 + \tfrac{1}{2}\,T_1T_2^2 + T_3 + T_1T_3 + \tfrac{1}{2}\,T_1^2T_3 + T_2T_3 + T_4 + T_1T_4]\,|0\rangle = t_{ijk}^{abc}E \tag{34}$$

$$\langle 0_{ijkl}^{abcd}|H[\,\tfrac{1}{2}\,T_2^2 + \tfrac{1}{2}\,T_1T_2^2 + T_3 + T_1T_3 + \tfrac{1}{2}\,T_1^2T_3 + T_2T_3 + T_4 + T_1T_4 + \tfrac{1}{2}\,T_1^2T_4 + T_2T_4 + \tfrac{1}{3!}\,T_1^3T_3 + T_1T_2T_3 + \tfrac{1}{4}\,T_1^2T_2^2 + \tfrac{1}{3!}\,T_2^3 + \tfrac{1}{2}\,T_3^2]\,|0\rangle = t_{ijkl}^{abcd}E \tag{35}$$

This provides a set of non-linear equations for determining the CC amplitudes which then lead to determination of the CC energy with the use of equation 30.

D. Coupled-cluster Diagrams

In order to transform to a diagrammatic representation of the second quantized operators, the second quantized operators are replaced by oriented lines. The annihilation operator is represented as an oriented line directed into a vertex;

a_p *becomes*

(36)

The creation operator is represented as an oriented line directed away from a vertex;

$a_q^\dagger$ *becomes*

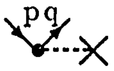
(37)

As in section B of this chapter, the one and two electron parts of the hamiltonian can be separated as;

$$H = H(p) + H(p,q) \qquad (38)$$

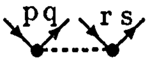
These two parts of the hamiltonian then give rise to different diagrams. The one and two electron operators represented in second quantized formalism in equation 18 of section B are symbolized graphically as;

$f_{pq} a_q^\dagger a_p$ *becomes*



(39)

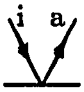
$\langle pq \| rs \rangle a_p^\dagger a_r a_q^\dagger a_s$ *becomes*



(40)

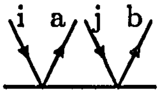
The CC excitation operators are symbolized graphically as;

T_1 *becomes*



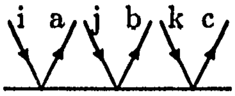
(41)

T_2 *becomes*



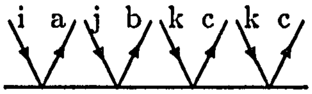
(42)

T_3 *becomes*



(43)

T_4 *becomes*



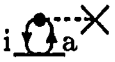
etc

(44)

Let us consider a term from equation (30) of the last section, one of the terms from the equation is;

$$\langle 0 \mid \sum_{p,q} f_{p,q} a_q^\dagger a_p \sum_{i,a} t_i^a a_a^\dagger a_i \mid 0 \rangle \tag{45}$$

Recalling that a contraction replaces the orbital counting operators with their eigenvalues, contracting the second quantized operators, amounts to connecting the lines of the graphical representation for these operators, (39) and (41) with the arrows pointing in the same direction. This yields the term;

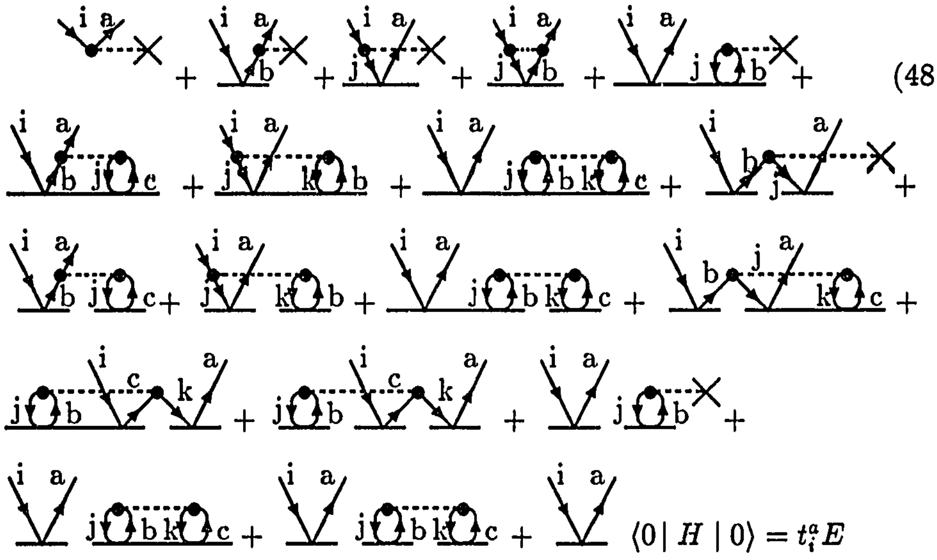


$$= \quad + \sum_{\substack{a \\ i}} f_{ia} t_i^a \tag{46}$$

This is done to each of the terms in the CC expansion. The procedure involves making the contractions in all possible ways and leaving enough open lines (unconnected lines) to generate the level of excitation of the determinant, which the Schrödinger equation is projected against for that particular equation, (in other words, by convention the contractions with the bra vector are implied). The coupled-cluster diagrams in product terms are not contracted with each other. This procedure generates three diagrams for the energy equation;

$$\Delta E \quad = \tag{47}$$

The singles equation generates 19 diagrams;



$$\langle 0 |\, H \,| 0\rangle = t_i^a E \tag{48}$$

The last four terms on the left side of the equation involve 'disconnected' terms that exactly equal the term on the right side of the equation. An similar analysis of the diagrams obtained by projecting the Schrödinger equation against a double excited determinant reveals that not only is the energy term on the right side of the equation cancelled by the disconnected terms but the remainder of the disconnected terms in the doubles equation are equal to t_{ij}^{ab} times the singles equation which is now equal to zero. This cancellation of the disconnected terms continues thoughout the orders of the coupled-cluster equations and it is this 'connected' nature of the coupled-cluster wavefunction which is responsible for its size-extensivity. Therefore only the connected terms in the equations (32) - (35) need be considered and they become;

$$\langle 0_i^a \,|\, H[1 + T_1 + \tfrac{1}{2}\, T_1^2 + \tfrac{1}{3!}\, T_1^3 + T_2 + T_1T_2 + T_3] \,|\, 0\rangle_C = 0 \tag{49}$$

$$\begin{aligned} \langle 0_{ij}^{ab} \,|\, H[1 + T_1 + \tfrac{1}{2}\, T_1^2 + \tfrac{1}{3!}\, T_1^3 + \tfrac{1}{4!}\, T_1^4 + T_2 + \tfrac{1}{2}\, T_2^2 + T_1T_2 \\ + \tfrac{1}{2}\, T_1^2T_2 + T_3 + T_1T_3 + T_4] \,|\, 0\rangle_C = 0 \end{aligned} \tag{50}$$

$$\begin{aligned} \langle 0_{ijk}^{abc} \,|\, H[T_2 + \tfrac{1}{2}\, T_2^2 + T_1T_2 + \tfrac{1}{2}\, T_1^2T_2 + \tfrac{1}{3!}\, T_1^3T_2 + \tfrac{1}{2}\, T_1T_2^2 \\ + T_3 + T_1T_3 + \tfrac{1}{2}\, T_1^2T_3 + T_2T_3 + T_4 + T_1T_4] \,|\, 0\rangle_C = 0 \end{aligned} \tag{51}$$

$$\begin{aligned} \langle 0_{ijkl}^{abcd} \,|\, H[\, \tfrac{1}{2}\, T_2^2 + \tfrac{1}{2}\, T_1T_2^2 + T_3 + T_1T_3 + \tfrac{1}{2}\, T_1^2T_3 + T_2T_3 + T_4 \\ + T_1T_4 + \tfrac{1}{2}\, T_1^2T_4 + T_2T_4 + \tfrac{1}{3!}\, T_1^3T_3 + T_1T_2T_3 \\ + \tfrac{1}{4}\, T_1^2T_2^2 + \tfrac{1}{3!}\, T_2^3 + \tfrac{1}{2}\, T_3^2] \,|\, 0\rangle_C = 0 \end{aligned} \tag{52}$$

The rules for generating the algebraic code for the CC equations are :[5]

1. Each up oriented line is labeled with an unoccupied spin-orbital label a,b,c,d... and each down oriented line is labeled with an occupied spin-orbital label i,j,k,l,... The open lines are labeled in sequence from left to right.

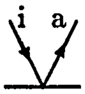
2. Each one-particle vertex corresponds to a one-electron integral as, $\langle left, out \mid right, in \rangle$ or;

$$= f_{ai} \tag{53}$$

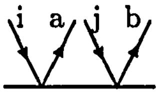
3. Each two-particle vertex corresponds to the antisymmetrized integral $\langle left, out; right, out \parallel left, in; right, in \rangle$ or;

$$= \langle ab \| ij \rangle \tag{54}$$

4. Cluster vertices correspond to;



$$= t_i^a,$$



$$= t_{ij}^{ab} \tag{55}$$

The t amplitudes are antisymmetric, $t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}$ and similarly for higher order amplitudes.

5. All orbital labels are summed over 'internal' lines, or lines that terminate below a vertex.

6. The sign of the diagram is obtained from (-1) raised to the power of the sum of the unoccupied spin-orbital labeled lines and loops. For the purpose of getting loops open lines are closed into loops.

7. The weight factor for a diagram is specified by $(\frac{1}{2})^m$, where m is the number of pairs of 'equivalent' lines. A pair of equivalent lines is defined as being two lines which begin at the same amplitude, have the same direction and end in a vertex.

8. To maintain full antisymmetry of an amplitude, the algebraic expression for a diagram should be preceded by a permutation operator permuting the open lines in all distinct ways, $\sum_P (-1)^P P$.

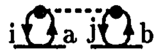
The complete complete set of diagrams and their corresponding algebraic expressions for the coupled-cluster equations containing single, double, triple and quadruple excitations are contained in Tables II1-II4.

Table II.1

A complete set of diagrams which generate the equations for energy and single excitations.

ENERGY EQUATION DIAGRAMS

$\langle 0|$ projection

1		$+\sum_{\substack{a\\i}} f_{ia}t_i^a$
2		$+\sum_{\substack{a>b\\i>j}} \langle ij \| ab\rangle t_{ij}^{ab}$
3		$+\sum_{\substack{a>b\\i>j}} \langle ij \| ab\rangle (t_i^a t_j^b - t_j^a t_i^b)$

SINGLE EXCITATION DIAGRAMS

$\langle 0_i^a|$ projection

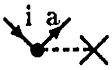
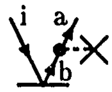
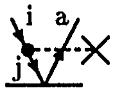
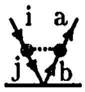
1		$+f_{ia}$
2		$+\sum_{b} f_{ab}t_i^b$
3		$-\sum_{j} f_{ji}t_j^a$
4		$-\sum_{\substack{b\\j}} \langle ja \| ib\rangle t_j^b$

Table II.1 (continued)

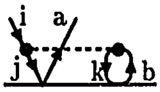
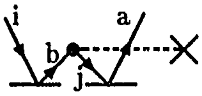
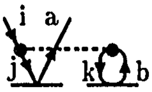
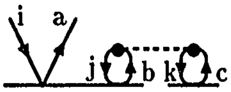
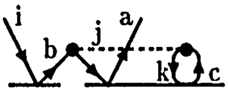
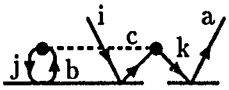
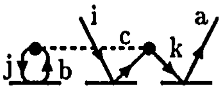
5		$+\sum_{\substack{b\\j}} f_{jb}t_{ij}^{ab}$
6		$+\frac{1}{2}\sum_{\substack{b,c\\j}}\langle aj\,\|\,bc\rangle t_{ij}^{bc}$
7		$-\frac{1}{2}\sum_{\substack{b\\j,k}}\langle jk\,\|\,ib\rangle t_{jk}^{ab}$
8		$+\frac{1}{4}\sum_{\substack{b,c\\j,k}}\langle jk\,\|\,bc\rangle t_{ijk}^{abc}$
9		$-\sum_{\substack{b\\j}} f_{jb}t_i^b t_j^a$
10		$+\sum_{\substack{b,c\\j}}\langle aj\,\|\,bc\rangle t_i^b t_j^c$
11		$-\sum_{\substack{b\\j,k}}\langle jk\,\|\,ib\rangle t_j^a t_k^b$
12		$+\sum_{\substack{b,c\\j,k}}\langle jk\,\|\,bc\rangle t_k^c t_{ij}^{ab}$
13		$-\frac{1}{2}\sum_{\substack{b,c\\j,k}}\langle jk\,\|\,bc\rangle t_i^b t_{jk}^{ac}$
14		$-\frac{1}{2}\sum_{\substack{b,c\\j,k}}\langle jk\,\|\,bc\rangle t_k^a t_{ji}^{bc}$
15		$-\sum_{\substack{b,c\\j,k}}\langle jk\,\|\,bc\rangle t_j^b t_i^c t_k^a$

Table II.2

A complete set of diagrams which generate the equations for double excitations.

DOUBLE EXCITATION DIAGRAMS

$\langle 0_{ij}^{ab}|$ projection

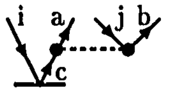
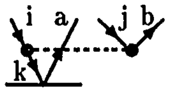
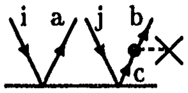
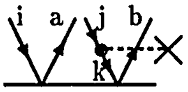
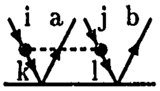
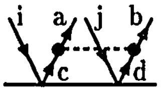
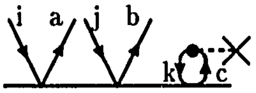
1		$+\langle ab\|ij\rangle$
2		$+\sum_{c}(-1)^{P}P(i/j)\langle cj\|ab\rangle t_{i}^{c}$
3		$-\sum_{k}(-1)^{P}P(a/b)\langle kb\|ij\rangle t_{k}^{a}$
4		$+\sum_{c}(-1)^{P}P(a/b)f_{bc}t_{ij}^{ac}$
5		$-\sum_{k}(-1)^{P}P(i/j)f_{kj}t_{ik}^{ab}$
6		$-\sum_{\substack{c\\k}}(-1)^{P}P(i/j\,\vert\,a/b)\langle kb\|jc\rangle t_{ik}^{ac}$
7		$+\frac{1}{2}\sum_{k,l}\langle kl\|ij\rangle t_{kl}^{ab}$
8		$+\frac{1}{2}\sum_{c,d}\langle ab\|cd\rangle t_{ij}^{cd}$
9		$+\sum_{\substack{c\\k}}f_{kc}t_{ijk}^{abc}$

Table II.2 (continued)

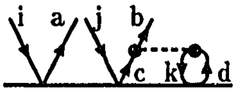
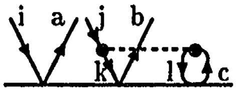
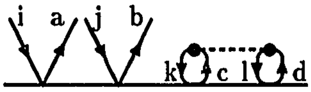
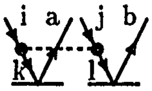
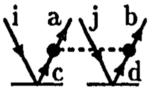
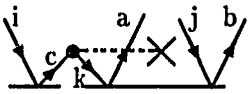
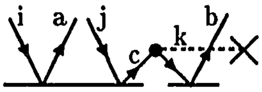
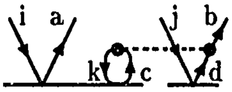
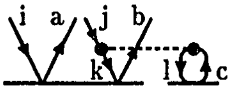
10		$+\frac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle bk\|cd\rangle t_{ijk}^{acd}$
11		$-\frac{1}{2}\sum_{\substack{c\\k,l}}(-1)^P P(i/j)\langle kl\|jc\rangle t_{ikl}^{abc}$
12		$+\frac{1}{4}\sum_{\substack{c,d\\k,l}}\langle kl\|cd\rangle t_{ijkl}^{abcd}$
13		$-\sum_{\substack{c\\k}}(-1)^P P(a/b\|i/j)\langle ak\|cj\rangle t_i^c t_k^b$
14		$+\sum_{k,l}\langle kl\|ij\rangle t_k^a t_l^b$
15		$+\sum_{c,d}\langle ab\|cd\rangle t_i^c t_j^d$
16		$-\sum_{\substack{c\\k}}(-1)^P P(i/j)f_{kc}t_{kj}^{ab}t_i^c$
17		$-\sum_{\substack{c\\k}}(-1)^P P(a/b)f_{kc}t_{ij}^{ac}t_k^b$
18		$+\sum_{\substack{c,d\\k}}(-1)^P P(a/b\|i/j)\langle kb\|cd\rangle t_{ik}^{ac}t_j^d$
19		$-\sum_{\substack{c\\k,l}}(-1)^P P(a/b\|i/j)\langle kl\|cj\rangle t_{ik}^{ac}t_l^b$
20		$-\sum_{\substack{c\\k,l}}(-1)^P P(i/j)\langle kl\|jc\rangle t_{ik}^{ab}t_l^c$

Table II.2 (continued)

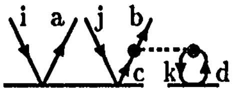
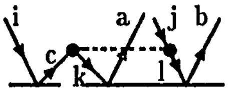
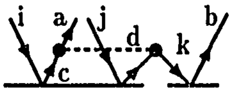
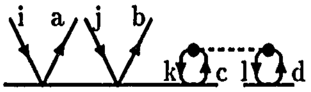
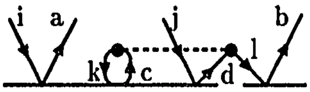
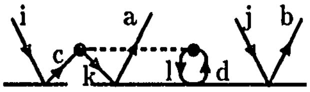
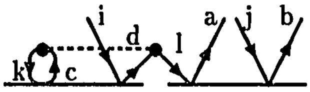
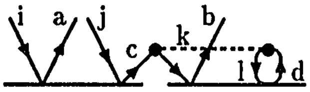
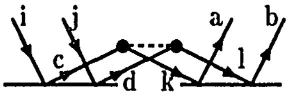
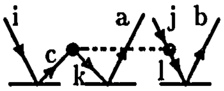
21		$+\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle bk\Vert cd\rangle t_{ij}^{ac}t_k^d$
22		$+\frac{1}{2}\sum_{\substack{c\\k,l}}(-1)^P P(i/j)\langle kl\Vert cj\rangle t_{kl}^{ab}t_i^c$
22		
23		$-\frac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle ak\Vert cd\rangle t_{ij}^{cd}t_k^b$
24		$+\sum_{\substack{c,d\\k,l}}\langle kl\Vert cd\rangle t_{ijk}^{abc}t_l^d$
25		$-\frac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^P P(a/b)\langle kl\Vert cd\rangle t_{ikj}^{acd}t_l^b$
26		$-\frac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j)\langle kl\Vert cd\rangle t_{klj}^{adb}t_i^c$
27		$-\frac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j)\langle kl\Vert cd\rangle t_{ki}^{cd}t_{lj}^{ab}$
28		$-\frac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^P P(a/b)\langle kl\Vert cd\rangle t_{ij}^{ac}t_{kl}^{bd}$
29		$+\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j)\langle kl\Vert cd\rangle t_{ik}^{ac}t_{lj}^{db}$
30		$+\frac{1}{4}\sum_{\substack{c,d\\k,l}}\langle kl\Vert cd\rangle t_{ij}^{cd}t_{kl}^{ab}$
31		$+\sum_{\substack{c\\k,l}}(-1)^P P(i/j)\langle kl\Vert cj\rangle t_i^c t_k^a t_l^b$

Table II.2 (continued)

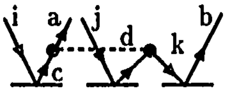
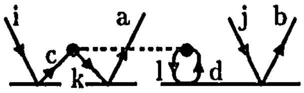
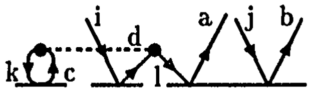
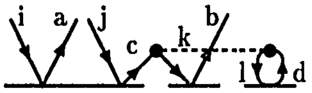
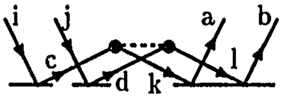
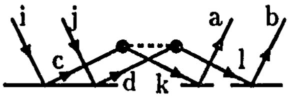
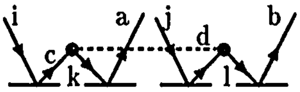
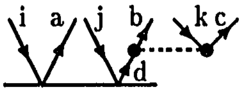
32		$-\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle ak\Vert cd\rangle t_i^c t_j^d t_k^b$
33		$-\sum_{\substack{c,d\\k,l}}(-1)^P P(a/b\vert i/j)\langle kl\Vert cd\rangle t_{lj}^{db} t_i^c t_k^a$
34		$-\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j)\langle kl\Vert cd\rangle t_{lj}^{ab} t_k^c t_i^d$
35		$-\sum_{\substack{c,d\\k,l}}(-1)^P P(a/b)\langle kl\Vert cd\rangle t_{ij}^{ac} t_k^b t_l^d$
36		$+\sum_{\substack{c,d\\k,l}}\langle kl\Vert cd\rangle t_{kl}^{ab} t_i^c t_j^d$
37		$+\sum_{\substack{c,d\\k,l}}\langle kl\Vert cd\rangle t_{ij}^{cd} t_k^a t_l^b$
38		$+\sum_{\substack{c,d\\k,l}}\langle kl\Vert cd\rangle t_i^c t_k^a t_j^d t_l^b$

Table II.3

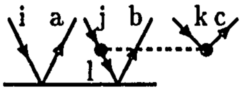
A complete set of diagrams which generate the equations for triple excitations.

TRIPLE EXCITATION DIAGRAMS

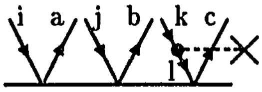
$\langle 0_{ijk}^{abc}|$ projection

1 

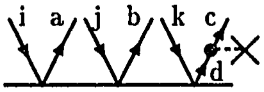
$$+\sum_{d}(-1)^P P(k/ij\,|\,a/bc)\langle bc\|dk\rangle t_{ij}^{ad}$$

2 

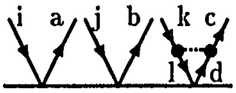
$$-\sum_{l}(-1)^P P(i/jk\,|\,ab/c)\langle lc\|jk\rangle t_{il}^{ab}$$

3 

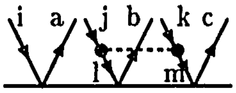
$$-\sum_{l}(-1)^P P(ij/k) f_{lk} t_{ijl}^{abc}$$

4 

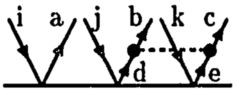
$$+\sum_{d}(-1)^P P(ab/c) f_{cd} t_{ijk}^{abd}$$

5 

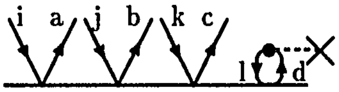
$$-\sum_{\substack{d\\l}}(-1)^P P(ab/c\,|\,ij/k)\langle lc\|kd\rangle t_{ijl}^{abd}$$

6 

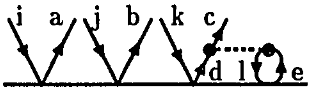
$$+\frac{1}{2}\sum_{l,m}(-1)^P P(i/jk)\langle lm\|jk\rangle t_{ilm}^{abc}$$

7 

$$+\frac{1}{2}\sum_{d,e}(-1)^P P(a/bc)\langle bc\|de\rangle t_{ijk}^{ade}$$

8 

$$+\sum_{\substack{d\\l}} f_{ld} t_{ijkl}^{abcd}$$

9 

$$+\frac{1}{2}\sum_{\substack{d,e\\l}}(-1)^P P(ab/c)\langle cl\|de\rangle t_{ijkl}^{abde}$$

Table II.3 (continued)

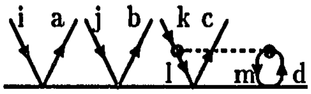
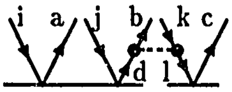
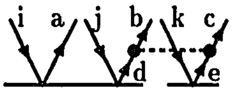
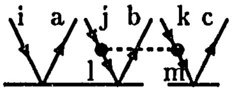
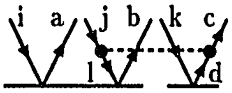
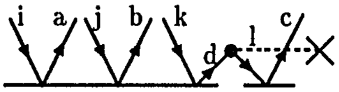
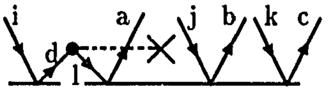
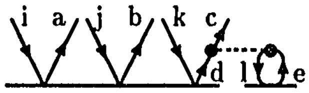
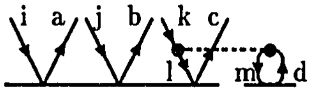
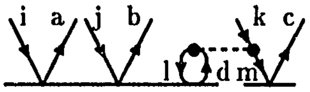
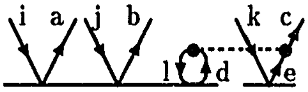
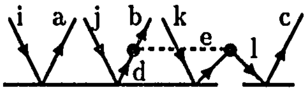
10		$-\frac{1}{2}\sum_{\substack{d\\l,m}}\langle lm\,\|\,kd\rangle t_{ijlm}^{abcd}$
11		$-\sum_{\substack{d\\l}}(-1)^P P(abc\,\|\,ij/k)\langle bl\,\|\,dk\rangle t_{ij}^{ad}t_l^c$
12		$+\sum_{d,e}(-1)^P P(a/bc\,\|\,ij/k)\langle bc\,\|\,de\rangle t_{ij}^{ad}t_k^e$
13		$+\sum_{l,m}(-1)^P P(ab/c\,\|\,i/jk)\langle lm\,\|\,jk\rangle t_{il}^{ab}t_m^c$
14		$-\sum_{\substack{d\\l}}(-1)^P P(ab/c\,\|\,ijk)\langle lc\,\|\,jd\rangle t_{il}^{ab}t_k^d$
15		$-\sum_{\substack{d\\l}}(-1)^P P(ab/c)f_{ld}t_{ijk}^{abd}t_l^c$
16		$-\sum_{\substack{d\\l}}(-1)^P P(i/jk)f_{ld}t_{ljk}^{abc}t_i^d$
17		$+\sum_{\substack{d,e\\l}}(-1)^P P(ab/c)\langle cl\,\|\,de\rangle t_{ijk}^{abd}t_l^e$
18		$-\sum_{\substack{d\\l,m}}(-1)^P P(ij/k)\langle lm\,\|\,kd\rangle t_{ijl}^{abc}t_m^d$
19		$-\sum_{\substack{d\\l,m}}(-1)^P P(ab/c\,\|\,ij/k)\langle lm\,\|\,dk\rangle t_{ijl}^{abd}t_m^c$
20		$+\sum_{\substack{d,e\\l}}(-1)^P P(ab/c\,\|\,ij/k)\langle lc\,\|\,de\rangle t_{ijl}^{abd}t_k^e$
21		$-\frac{1}{2}\sum_{\substack{d,e\\l}}(-1)^P P(abc)\langle bl\,\|\,de\rangle t_{ijk}^{ade}t_l^c$

Table II.3 (continued)

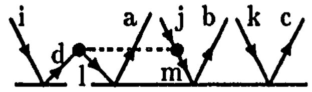
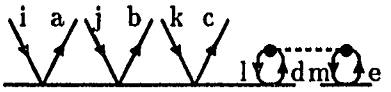
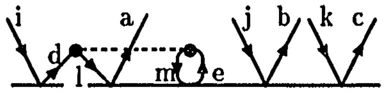
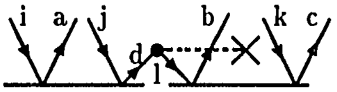
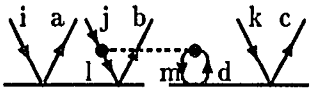
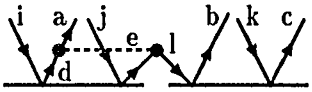
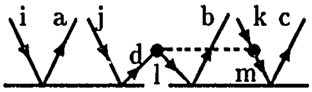
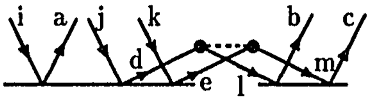
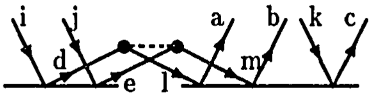
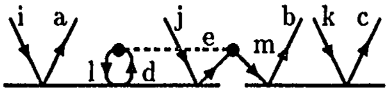
22		$+\frac{1}{2}\sum_{\substack{d\\l,m}}(-1)^P P(ijk)\langle lm \Vert dj\rangle t_{lmk}^{abc} t_i^d$
23		$+\sum_{\substack{d,e\\l,m}}\langle lm \Vert de\rangle t_{ijkl}^{abcd} t_m^e$
24		$-\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(ab/c)\langle lm \Vert de\rangle t_{ijlk}^{abde} t_m^c$
25		$-\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(i/jk)\langle lm \Vert de\rangle t_{lmjk}^{aebc} t_i^d$
26		$-\sum_{\substack{d\\l}}(-1)^P P(a/bc \vert ij/k) f_{ld} t_{ij}^{ad} t_{lk}^{bc}$
27		$-\sum_{\substack{d\\l,m}}(-1)^P P(ab/c \vert ijk)\langle lm \Vert jd\rangle t_{il}^{ab} t_{mk}^{dc}$
28		$+\sum_{\substack{d,e\\l}}(-1)^P P(abc \vert ij/k)\langle bl \Vert de\rangle t_{ij}^{ad} t_{lk}^{ec}$
29		$-\frac{1}{2}\sum_{\substack{d,e\\l}}(-1)^P P(a/bc \vert ij/k)\langle al \Vert de\rangle t_{ij}^{de} t_{lk}^{bc}$
30		$+\frac{1}{2}\sum_{\substack{d\\l,m}}(-1)^P P(a/bc \vert ij/k)\langle lm \Vert dk\rangle t_{ij}^{ad} t_{lm}^{bc}$
31		$+\frac{1}{4}\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc)\langle lm \Vert de\rangle t_{ijk}^{ade} t_{lm}^{bc}$
32		$+\frac{1}{4}\sum_{\substack{d,e\\l,m}}(-1)^P P(ij/k)\langle lm \Vert de\rangle t_{lmk}^{abc} t_{ij}^{de}$
33		$-\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc \vert ij/k)\langle lm \Vert de\rangle t_{ilj}^{ade} t_{mk}^{bc}$

Table II.3 (continued)

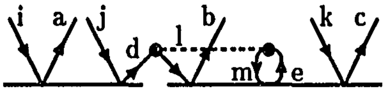
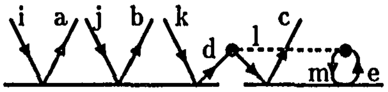
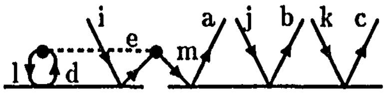
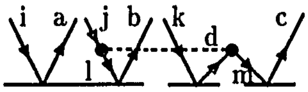
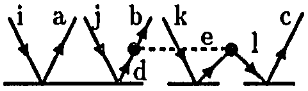
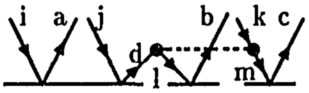
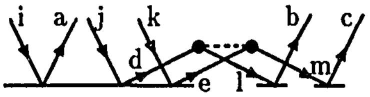
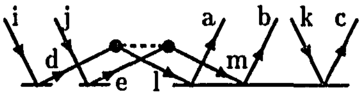
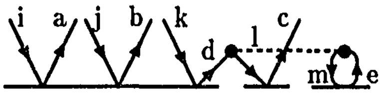
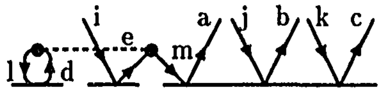
34		$-\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc\,\vert\, ij/k)\langle lm\,\Vert\, de\rangle t_{lmk}^{bec}t_{ij}^{ad}$
35		$-\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(ab/c)\langle lm\,\Vert\, de\rangle t_{ijk}^{abd}t_{lm}^{ce}$
36		$-\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(i/jk)\langle lm\,\Vert\, de\rangle t_{mjk}^{abc}t_{li}^{de}$
37		$+\sum_{\substack{d,e\\l,m}}(-1)^P P(ab/c\,\vert\, ij/k)\langle lm\,\Vert\, de\rangle t_{ijl}^{abd}t_{mk}^{ec}$
38		$+\sum_{\substack{d\\l,m}}(-1)^P P(ab/c\,\vert\, ijk)\langle lm\,\Vert\, jd\rangle t_{il}^{ab}t_k^d t_m^c$
39		$-\sum_{\substack{d,e\\l}}(-1)^P P(abc\,\vert\, ij/k)\langle bl\,\Vert\, de\rangle t_{ij}^{ad}t_k^e t_l^c$
40		$+\sum_{\substack{d\\l,m}}(-1)^P P(a/bc\,\vert\, ij/k)\langle lm\,\Vert\, dk\rangle t_{ij}^{ad}t_l^b t_m^c$
41		$-\sum_{\substack{d,e\\l}}(-1)^P P(a/bc\,\vert\, ij/k)\langle al\,\Vert\, de\rangle t_{lk}^{bc}t_i^d t_j^e$
42		$+\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc)\langle lm\,\Vert\, de\rangle t_{ijk}^{ade}t_l^b t_m^c$
43		$+\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(ij/k)\langle lm\,\Vert\, de\rangle t_{lmk}^{abc}t_i^d t_j^e$
44		$-\sum_{\substack{d,e\\l,m}}(-1)^P P(ab/c)\langle lm\,\Vert\, de\rangle t_{ijk}^{abd}t_l^c t_m^e$
45		$-\sum_{\substack{d,e\\l,m}}(-1)^P P(i/jk)\langle lm\,\Vert\, de\rangle t_{mjk}^{abc}t_l^d t_i^e$

Table II.3 (continued)

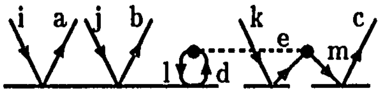
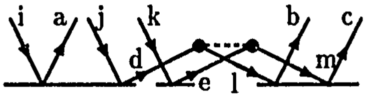
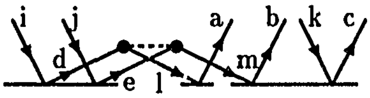
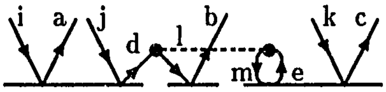
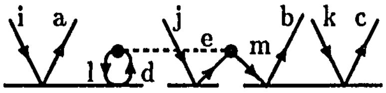
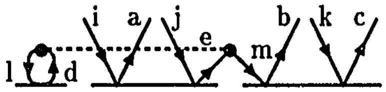
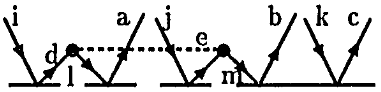
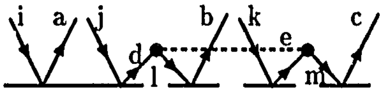
46		$-\sum_{\substack{d,e\\l,m}}(-1)^P P(ab/c\,\vert\, ij/k)\langle lm\Vert de\rangle t_{ijl}^{abd}t_k^e t_m^c$
47		$+\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc\,\vert\, ij/k)\langle lm\Vert de\rangle t_{ij}^{ad}t_{lm}^{bc}t_k^e$
48		$+\frac{1}{2}\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc\,\vert\, ij/k)\langle lm\Vert de\rangle t_{ij}^{de}t_{mk}^{bc}t_l^a$
49		$-\sum_{\substack{d,e\\l,m}}(-1)^P P(abc\,\vert\, ij/k)\langle lm\Vert de\rangle t_{ij}^{ad}t_{mk}^{ec}t_l^b$
50		$-\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc\,\vert\, ijk)\langle lm\Vert de\rangle t_{il}^{ad}t_{mk}^{bc}t_j^e$
51		$-\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc\,\vert\, ij/k)\langle lm\Vert de\rangle t_{ij}^{ae}t_{mk}^{bc}t_l^d$
52		$+\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc\,\vert\, ij/k)\langle lm\Vert de\rangle t_{mk}^{bc}t_i^d t_l^a t_j^e$
53		$+\sum_{\substack{d,e\\l,m}}(-1)^P P(a/bc\,\vert\, ij/k)\langle lm\Vert de\rangle t_{ij}^{ad}t_l^b t_k^e t_m^c$

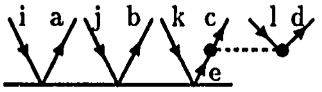
Table II.4

A complete set of diagrams which generate the equations for quadruple excitations.

QUADRUPLE EXCITATION DIAGRAMS

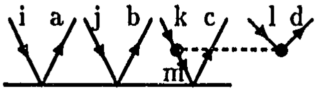
$\langle 0_{ijkl}^{abcd}|$ projection

1



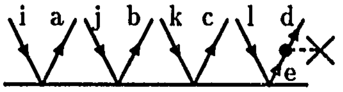
$$+\sum_{e}(-1)^{P}P(l/ijk\,|\,ab/cd)\langle cd\,\|\,el\rangle t_{ijk}^{abe}$$

2



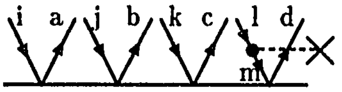
$$-\sum_{m}(-1)^{P}P(ij/kl\,|\,abc/d)\langle md\,\|\,kl\rangle t_{ijm}^{abc}$$

3



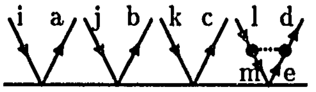
$$+\sum_{e}(-1)^{P}P(abc/d)f_{de}t_{ijkl}^{abce}$$

4



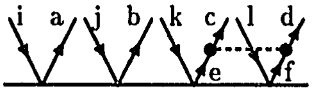
$$-\sum_{m}(-1)^{P}P(ijk/l)f_{ml}t_{ijkm}^{abcd}$$

5



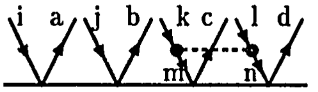
$$-\sum_{\substack{e\\m}}(-1)^{P}P(ijk/l\,|\,abc/d)\langle md\,\|\,le\rangle t_{ijkm}^{abce}$$

6



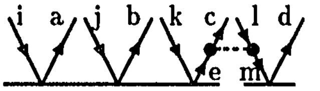
$$+\tfrac{1}{2}\sum_{e,f}(-1)^{P}P(ab/cd)\langle cd\,\|\,ef\rangle t_{ijkl}^{abef}$$

7



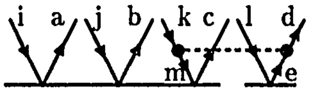
$$+\tfrac{1}{2}\sum_{m,n}(-1)^{P}P(ij/kl)\langle mn\,\|\,kl\rangle t_{ijmn}^{abcd}$$

8



$$-\sum_{\substack{e\\m}}(-1)^{P}P(ab/c/d\,|\,ijk/l)\langle cm\,\|\,el\rangle t_{ijk}^{abe}t_{m}^{d}$$

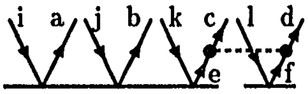
9



$$-\sum_{\substack{e\\m}}(-1)^{P}P(abc/d\,|\,ij/k/l)\langle md\,\|\,ke\rangle t_{ijm}^{abc}t_{l}^{e}$$

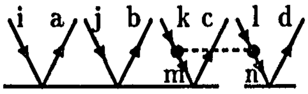
Table II.4 (continued)

10



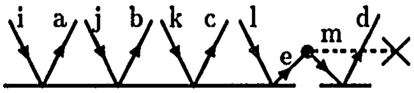
$$+\sum_{e,f}(-1)^P P(ab/cd\,|\,ijk/l)\langle cd\|ef\rangle t_{ijk}^{abe}t_l^f$$

11



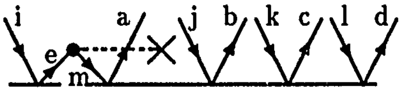
$$+\sum_{m,n}(-1)^P P(abc/d\,|\,ij/kl)\langle mn\|kl\rangle t_{ijm}^{abc}t_n^d$$

12



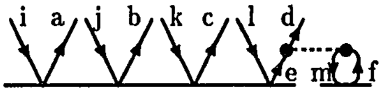
$$-\sum_{\substack{e\\m}}(-1)^P P(abc/d)f_{me}t_{ijkl}^{abce}t_m^d$$

13



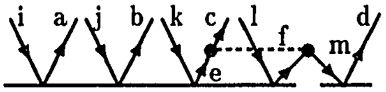
$$-\sum_{\substack{e\\m}}(-1)^P P(i/jkl)f_{me}t_{mjkl}^{abcd}t_i^e$$

14



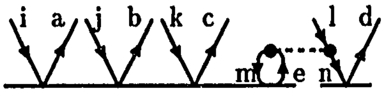
$$+\sum_{\substack{e,f\\m}}(-1)^P P(abc/d)\langle md\|ef\rangle t_{ijkl}^{abce}t_m^f$$

15

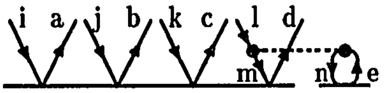


$$-\tfrac{1}{2}\sum_{\substack{e,f\\m}}(-1)^P P(ab/c/d)\langle cm\|ef\rangle t_{ijkl}^{abef}t_m^d$$

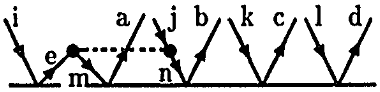
Table II.4 (continued)

16


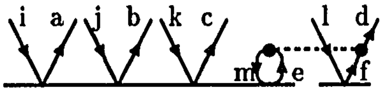
$$-\sum_{\substack{e\\m,n}}(-1)^P P(abc/d\,|\,ijk/l)\langle mn\|el\rangle t_{ijkm}^{abce}t_n^d$$

17


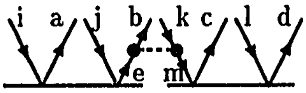
$$-\sum_{\substack{e\\m,n}}(-1)^P P(ijk/l)\langle mn\|le\rangle t_{ijkm}^{abcd}t_n^e$$

18


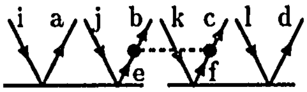
$$+\tfrac{1}{2}\sum_{\substack{e\\m,n}}(-1)^P P(i/j/kl)\langle mn\|ej\rangle t_{mnkl}^{abcd}t_i^e$$

19


$$+\sum_{\substack{e,f\\l}}(-1)^P P(abc/d\,|\,ijk/l)\langle md\|ef\rangle t_{ijkm}^{abce}t_l^f$$

20


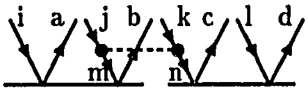
$$-\sum_{\substack{e\\m}}(-1)^P P(a/b/cd\,|\,ij/k/l)\langle bm\|ek\rangle t_{ij}^{ae}t_{ml}^{cd}$$

21


$$+\sum_{e,f}(-1)^P P(bc/ad\,|\,ij/kl)\langle bc\|ef\rangle t_{ij}^{ae}t_{kl}^{fd}$$

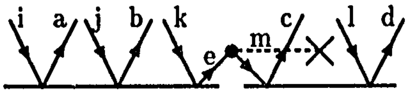
Table II.4 (continued)

22



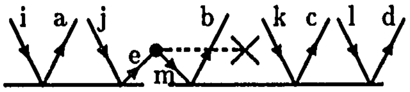
$$+\sum_{m,n}(-1)^P P(ab/cd\,|\,il/jk)\langle mn\,\|\,jk\rangle t_{im}^{ab}t_{nl}^{cd}$$

23



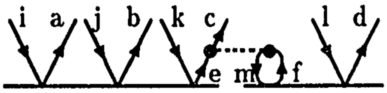
$$-\sum_{\substack{e\\m}}(-1)^P P(ab/cd\,|\,ijk/l)f_{me}t_{ijk}^{abe}t_{ml}^{cd}$$

24



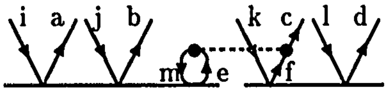
$$-\sum_{\substack{e\\m}}(-1)^P P(a/bcd\,|\,ij/kl)f_{me}t_{mkl}^{bcd}t_{ij}^{ae}$$

25



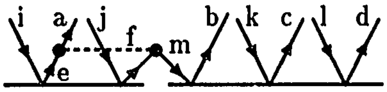
$$+\sum_{\substack{e,f\\m}}(-1)^P P(ab/c/d\,|\,ijk/l)\langle cm\,\|\,ef\rangle t_{ijk}^{abe}t_{ml}^{fd}$$

26



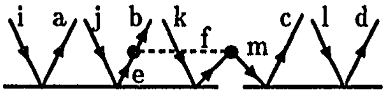
$$+\sum_{\substack{e,f\\m}}(-1)^P P(ab/c/d\,|\,ij/kl)\langle mc\,\|\,ef\rangle t_{ijm}^{abe}t_{kl}^{fd}$$

27

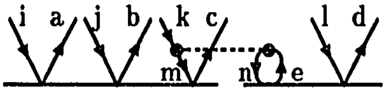


$$-\tfrac{1}{2}\sum_{\substack{e,f\\m}}(-1)^P P(a/bcd\,|\,ij/kl)\langle am\,\|\,ef\rangle t_{mkl}^{bcd}t_{ij}^{ef}$$

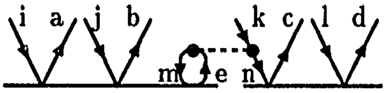
Table II.4 (continued)

28


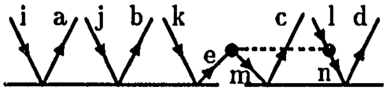
$$-\tfrac{1}{2}\sum_{\substack{e,f\\m}}(-1)^P P(a/b/cd\,|\,ijk/l)\langle bm\,\|\,ef\rangle t_{ijk}^{aef}t_{ml}^{cd}$$

29


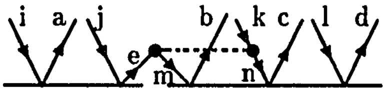
$$-\sum_{\substack{e\\m,n}}(-1)^P P(abc/d\,|\,ij/k/l)\langle mn\,\|\,ke\rangle t_{ijm}^{abc}t_{nl}^{ed}$$

30


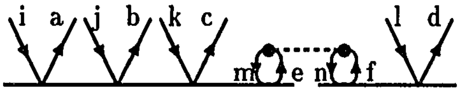
$$-\sum_{\substack{e\\m,n}}(-1)^P P(ab/cd\,|\,ij/k/l)\langle mn\,\|\,ek\rangle t_{ijm}^{abe}t_{nl}^{cd}$$

31


$$+\tfrac{1}{2}\sum_{\substack{e\\m,n}}(-1)^P P(ab/cd\,|\,ijk/l)\langle mn\,\|\,el\rangle t_{ijk}^{abe}t_{mn}^{cd}$$

32


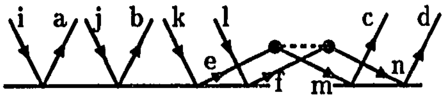
$$+\tfrac{1}{2}\sum_{\substack{e\\m,n}}(-1)^P P(a/bcd\,|\,ij/k/l)\langle mn\,\|\,ek\rangle t_{mnl}^{bcd}t_{ij}^{ae}$$

33


$$+\sum_{\substack{e,f\\m,n}}(-1)^P P(abc/d\,|\,ijk/l)\langle mn\,\|\,ef\rangle t_{ijkm}^{abce}t_{nl}^{fd}$$

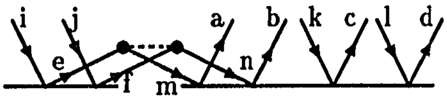
Table II.4 (continued)

34



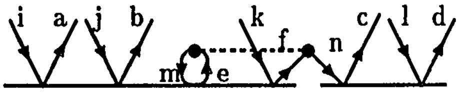
$$+\tfrac{1}{4}\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd)\langle mn\|ef\rangle t_{ijkl}^{abef}t_{mn}^{cd}$$

35



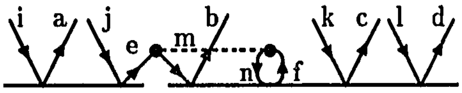
$$+\tfrac{1}{4}\sum_{\substack{e,f\\m,n}}(-1)^P P(ij/kl)\langle mn\|ef\rangle t_{mnkl}^{abcd}t_{ij}^{ef}$$

36



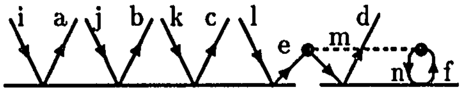
$$-\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd|ijk/l)\langle mn\|ef\rangle t_{ijmk}^{abef}t_{nl}^{cd}$$

37



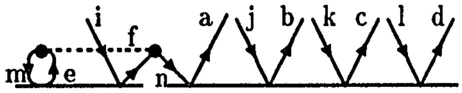
$$-\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd|ij/kl)\langle mn\|ef\rangle t_{mnkl}^{bfcd}t_{ij}^{ae}$$

38



$$-\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(abc/d)\langle mn\|ef\rangle t_{ijkl}^{abce}t_{mn}^{df}$$

39



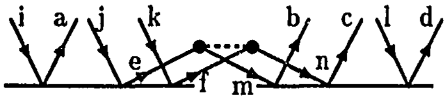
$$-\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(i/jkl)\langle mn\|ef\rangle t_{njkl}^{abcd}t_{mi}^{ef}$$

Table II.4 (continued)

40

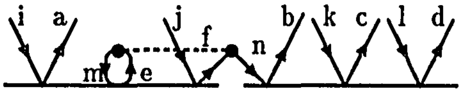
$$+\sum_{\substack{e,f\\m,n}}(-1)^P P(a/cd|ij/kl)\langle mn\|ef\rangle t_{ijm}^{abe}t_{nkl}^{fcd}$$

41



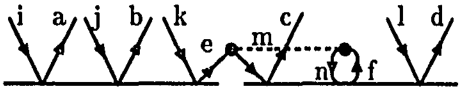
$$+\frac{1}{4}\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd|ijk/l)\langle mn\|ef\rangle t_{ijk}^{aef}t_{mnl}^{bcd}$$

42



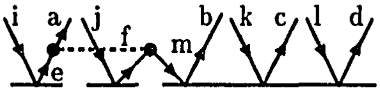
$$-\frac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd|ij/kl)\langle mn\|ef\rangle t_{imj}^{aef}t_{nkl}^{bcd}$$

43



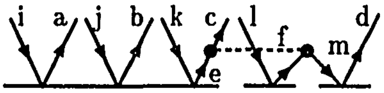
$$-\frac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd|ijk/l)\langle mn\|ef\rangle t_{ijk}^{abe}t_{mnl}^{cfd}$$

44



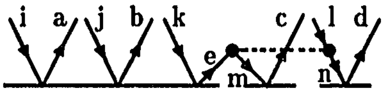
$$-\sum_{\substack{e,f\\m}}(-1)^P P(a/bcd|ij/kl)\langle am\|ef\rangle t_{mkl}^{bcd}t_i^e t_j^f$$

45

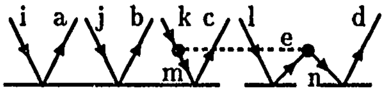


$$-\sum_{\substack{e,f\\m}}(-1)^P P(ab/c/d|ijk/l)\langle cm\|ef\rangle t_{ijk}^{abe}t_l^f t_m^d$$

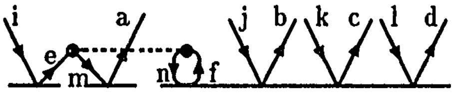
Table II.4 (continued)

46


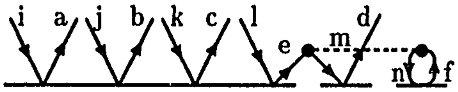
$$+\sum_{\substack{e\\m,n}}(-1)^{P}P(ab/cd\,|\,ijk/l)\langle mn\,\|\,el\rangle t_{ijk}^{abe}t_{m}^{c}t_{n}^{d}$$

47


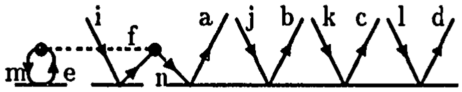
$$+\sum_{\substack{e\\m,n}}(-1)^{P}P(abc/d\,|\,ij/k/l)\langle mn\,\|\,ke\rangle t_{ijm}^{abc}t_{l}^{e}t_{n}^{d}$$

48


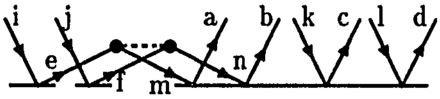
$$-\sum_{\substack{e,f\\m,n}}(-1)^{P}P(a/bcd\,|\,i/jkl)\langle mn\,\|\,ef\rangle t_{njkl}^{fbcd}t_{i}^{e}t_{m}^{a}$$

49


$$-\sum_{\substack{e,f\\m,n}}(-1)^{P}P(abc/d)\langle mn\,\|\,ef\rangle t_{ijkl}^{abce}t_{m}^{d}t_{n}^{f}$$

50


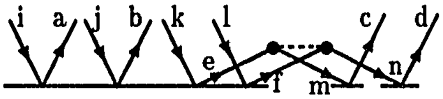
$$-\sum_{\substack{e,f\\m,n}}(-1)^{P}P(i/jkl)\langle mn\,\|\,ef\rangle t_{njkl}^{abcd}t_{m}^{e}t_{i}^{f}$$

51


$$+\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^{P}P(ij/kl)\langle mn\,\|\,ef\rangle t_{mnkl}^{abcd}t_{i}^{e}t_{j}^{f}$$

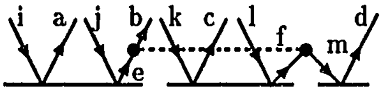
Table II.4 (continued)

52



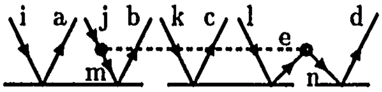
$$+\frac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd)\langle mn\|ef\rangle t_{ijkl}^{abef} t_m^c t_n^d$$

53



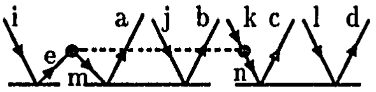
$$-\sum_{\substack{e,f\\m}}(-1)^P P(ac/b/d\,|\,ij/kl)\langle bm\|ef\rangle t_{ij}^{ae} t_{kl}^{cf} t_m^d$$

54



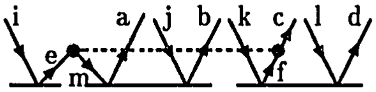
$$+\sum_{\substack{e\\m,n}}(-1)^P P(ab/c/d\,|\,i/j/kl)\langle mn\|je\rangle t_{im}^{ab} t_{kl}^{ce} t_n^d$$

55



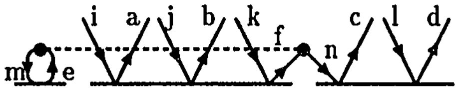
$$+\sum_{\substack{e\\m,n}}(-1)^P P(ab/cd\,|\,i/k/jl)\langle mn\|ek\rangle t_{mj}^{ab} t_{nl}^{cd} t_i^e$$

56



$$-\sum_{\substack{e,f\\m}}(-1)^P P(ab/c/d\,|\,i/j/kl)\langle mc\|ef\rangle t_{mj}^{ab} t_{kl}^{fd} t_i^e$$

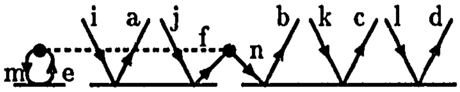
57



$$-\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd\,|\,ijk/l)\langle mn\|ef\rangle t_{ijk}^{abf} t_{nl}^{cd} t_m^e$$

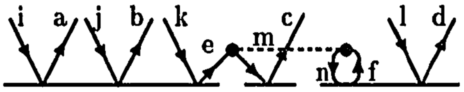
Table II.4 (continued)

58



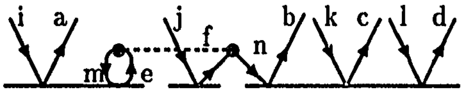
$$-\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd|ij/kl)\langle mn\|ef\rangle t_{nkl}^{bcd}t_{ij}^{af}t_m^e$$

59



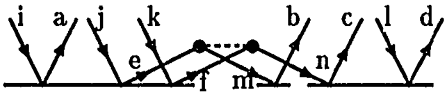
$$-\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/c/d|ijk/l)\langle mn\|ef\rangle t_{ijk}^{abe}t_{nl}^{fd}t_m^c$$

60



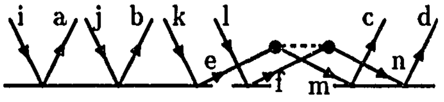
$$-\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd|i/j/kl)\langle mn\|ef\rangle t_{nkl}^{bcd}t_{im}^{ae}t_j^f$$

61



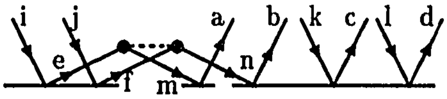
$$+\frac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(a/b/cd|ijk/l)\langle mn\|ef\rangle t_{ijk}^{aef}t_{nl}^{cd}t_m^b$$

62



$$+\frac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd|ijk/l)\langle mn\|ef\rangle t_{ijk}^{abe}t_{mn}^{cd}t_l^f$$

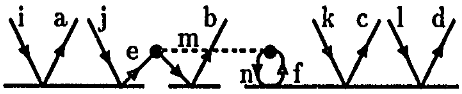
63



$$+\frac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd|ij/kl)\langle mn\|ef\rangle t_{nkl}^{bcd}t_{ij}^{ef}t_m^a$$

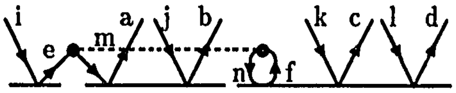
Table II.4 (continued)

64



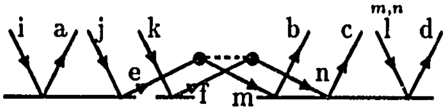
$$-\sum_{\substack{e,f\\m,n}}(-1)^P P(a/b/cd|ij/kl)\langle mn\|ef\rangle t_{nkl}^{fcd}t_{ij}^{ae}t_m^b$$

65



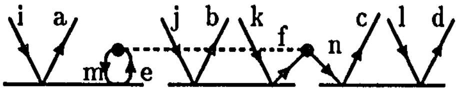
$$-\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd|i/j/kl)\langle mn\|ef\rangle t_{nkl}^{fcd}t_{mj}^{ab}t_i^e$$

66



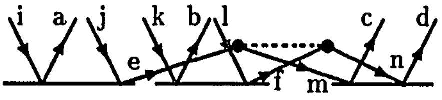
$$+\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd|ij/k/l)\langle mn\|ef\rangle t_{mnl}^{bcd}t_{ij}^{ae}t_k^f$$

67



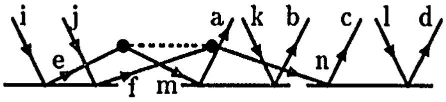
$$-\sum_{\substack{e,f\\m,n}}(-1)^P P(a/b/cd|i/jk/l)\langle mn\|ef\rangle t_{im}^{ae}t_{jk}^{bf}t_{nl}^{cd}$$

68



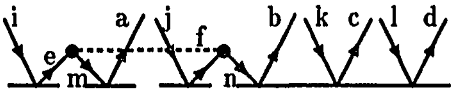
$$+\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd|ij/kl)\langle mn\|ef\rangle t_{ij}^{ae}t_{kl}^{bf}t_{mn}^{cd}$$

69

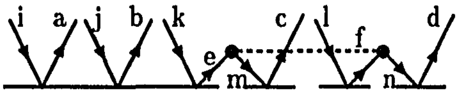


$$+\tfrac{1}{2}\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd|ij/kl)\langle mn\|ef\rangle t_{ij}^{ef}t_{mk}^{ab}t_{nl}^{cd}$$

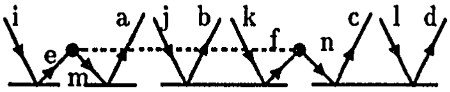
Table II.4 (continued)

70 

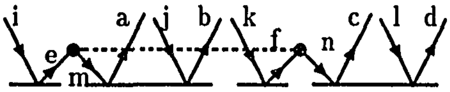
$$+\sum_{\substack{e,f\\m,n}}(-1)^P P(a/bcd\,|\,ij/kl)\langle mn\,\|\,ef\rangle t_{nkl}^{bcd}t_i^e t_m^a t_j^f$$

71 

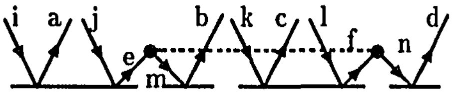
$$+\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd\,|\,ijk/l)\langle mn\,\|\,ef\rangle t_{ijk}^{abe}t_m^c t_l^f t_n^d$$

72 

$$+\sum_{\substack{e,f\\m,n}}(-1)^P P(a/b/cd\,|\,i/jk/l)\langle mn\,\|\,ef\rangle t_{jk}^{bf}t_{nl}^{cd}t_i^e t_m^a$$

73 

$$+\sum_{\substack{e,f\\m,n}}(-1)^P P(ab/cd\,|\,ik/jl)\langle mn\,\|\,ef\rangle t_{mj}^{ab}t_{nl}^{cd}t_i^e t_k^f$$

74 

$$+\sum_{\substack{e,f\\m,n}}(-1)^P P(ac/bd\,|\,ij/kl)\langle mn\,\|\,ef\rangle t_{ij}^{ae}t_{kl}^{cf}t_m^b t_n^d$$

E. Solving the Coupled-cluster System of Equations

The computational strategy for solving the CC equations, which is similar to a previously proposed method,[45] involves first separating the coupled-cluster equations into components which are linear and non-linear with respect to the CC amplitudes;

$$\underline{\underline{A}}\,\underline{X} - \underline{B} = 0 \tag{55}$$

where A is the matrix of coefficients for the amplitudes involved in the linear terms, X is a vector of coupled-cluster amplitudes and B contains the negative of the non-linear terms. The first approximation to the coupled-cluster amplitudes is to approximate the inverse of the A matrix by the inverse of its diagonal elements, D^{-1}, and multiply both sides of equation (55) by D^{-1};

$$\underline{\underline{D}}^{-1}\,\underline{B} = \underline{X}^{1} \tag{56}$$

The first approximation to the non-linear terms can now be calculated as;

$$\underline{\underline{A}}\,\underline{X_1} = \underline{B_1} \tag{57}$$

Next, the scaling factor, α, which correspondes to the minimum of the following expression;

$$Min\ |\ \alpha^{1}\underline{B_1} - \underline{B}\ | \tag{58}$$

is calculated using the following expression;

$$\alpha^{1} = (\underline{B_1}\,\underline{B})/(\underline{B_1}\,\underline{B_1}) \tag{59}$$

Next the CC amplitudes are multiplied by the scaling factor;

$$\alpha^1 \underline{X}^1 = \underline{X}_1 \tag{60}$$

and the correction vector, $\underline{X}_2$ is introduced, which satisfies the following equation;

$$\underline{\underline{A}}(\underline{X}_1 + \underline{X}_2) = \underline{B} \tag{61}$$

Now, an equation similar to equation 16 is used to find the correction vector;

$$\underline{\underline{A}}\,\underline{X}_2 = \underline{B} - \underline{\underline{A}}\,\underline{X}_1 = \underline{B} - \underline{B}_1^1 = \underline{B}_D \tag{62}$$

and then;

$$\underline{X}_2 = \underline{\underline{D}}^{-1}\,\underline{B}_D \tag{63}$$

Then $\underline{X}_2$ is orthogonalized to $\underline{X}_1$ and the following two equations are solved for the new scaling factors for the two vectors;

$$\underline{B}_1^1\,\underline{B}_1^1\alpha^1 + \underline{B}_1^1\,\underline{B}_1^2\alpha^2 = \underline{B}_1^1\,\underline{B} \tag{64}$$

$$\underline{B}_1^2\,\underline{B}_1^1\alpha^1 + \underline{B}_1^2\,\underline{B}_1^2\alpha^2 = \underline{B}_1^2\,\underline{B} \tag{65}$$

where;

$$\underline{B}_1^1 = \underline{\underline{A}}\,\underline{X}_1 \tag{66}$$

$$\underline{B}_1^2 = \underline{\underline{A}}\,\underline{X}_2 \tag{67}$$

A linear equation solver is used at each step to find the scaling factors and the procedure is iterated until the correction vector X_n approaches zero.

An example of the convergence properties of this method is presented in Table II.5. The initial guess for the amplitudes is the result of an MBPT(2) calculation. The basis set for this example is the one described in Table II.7 of the next section.

This procedure occasionally oscillates and diverges, a more stable, albeit slower, procedure is to move some or all of the non-linear terms in $\underline{B}$ to $\underline{B1}$.

The computer program for solving the CCSDTQ equations has been written in the most transparant form, using the spin-orbital representation of the diagrams. This has allowed programing the algebraic expression corresponding to each diagram in the form it appears in Table II1-II.4. Also all the quantities which require storage have been placed in the operational memory, this eliminated the need for a more complicated disk storage procedure. The Convex 240 internal memory of 1 GB made this option possible. As a result of this programming strategy the computer code is very explicit and easy to debug, an essential feature of a programming effort of this complexity.

Table II.5

Convergence behavior of the reduced linear equation method for solving the coupled-cluster equations.

	CCSD	CCSDT	CCSDTQ
Iteration	Energy	Energy	Energy
0	-0.0115232	-0.0115232	-0.0115232
1	-0.0157566	-0.0157689	-0.0157689
2	-0.0169441	-0.0169457	-0.0169456
3	-0.0175423	-0.0175513	-0.0175513
4	-0.0176170	-0.0176235	-0.0176235
5	-0.0176372	-0.0176434	-0.0176432
6	-0.0176430	-0.0176520	-0.0176519
7	-0.0176496	-0.0176608	-0.0176607
8	-0.0176498	-0.0176609	-0.0176608
9	-0.0176497	-0.0176606	-0.0176605
10	-0.0176496	-0.0176606	-0.0176606
11	-0.0176496		-0.0176606

F. The Coupled-cluster Method Including Single, Double, Triple and Quadruple Excitations; Numerical Results.

Test calculations were performed for LiH and Li_2 at equilibrium and at a stretched geometry. The results are presented in Table II.6. For LiH a molecular orbital basis of 4 occupied spin-orbitals and 8 virtual spin-orbitals, all of sigma symmetry were used, see Table II.7. At equilibrium CCSD does a very good job, with triples contributing at the μhartree level and quadruples being negligible. At the extended geometry triples contributes much more significantly and even quadruples begin to contribute slightly. CCSDTQ for LiH is equivalent to full CI and the CCSDTQ energy is in complete agreement with the full CI energy. For Li_2, a molecular orbital basis of 6 occupied spin-orbitals and 8 virtual spin-orbitals all with sigma symmetry were used, see Table II.7.

For Li_2 at equilibrium the contribution of triples is again at the μhartree level but now even at equilibrium quadruples contributes sightly and while the contribution of triples at the stretched geometry increases significantly the contribution of quadruples changes sign but remained about the same magnitude.

Examining the largest triple amplitudes for both cases, presented in Table II.7, reveals that most of these also represent double excitations from a determinant that is doubly excited from the reference determinant[40] which has become quasi-degenerate with the reference determinant as the bond was stretched. The quadruple excitation amplitudes which represent these type of excitations are capable of being represented as amplitudes of selected double excitations times this large double amplitude, however the triple excitations cannot be represented as a product of double amplitudes. For LiH this dominant double excitation is $t_{43}^{21} = -1.038780918$ (for the convention used for spin-orbital labels see Table II.6) and for Li_2 it is $t_{43}^{65} = -0.998345227$.

Linked quadruples can be thought of in a CI sense as correcting the products of amplitudes which yield a quadruple excitation level. As an example consider the quadruple excitation amplitude for LiH, t_{4321}^{4321}, this same excitation is generated by several products of amplitudes the most significant being $t_{43}^{21}t_{21}^{43}$. The first double excitation produces the quasi-degenerate determinant and the second double excitation correlates the core for this determinant. Thus for a wave-function dominated by two determinants, like the one for the LiH and Li_2 cases with stretched bonds, the dominant linked quadruple contribution provides a correction corresponding to the change in how the core correlates for the second determinant with respect to the first determinant and can be expected to be small as long as the core electrons correlate in a similar fashion for both determinants. Our results suggest that the latter is the case for both the LiH and Li_2 molecules at both the equilibrium and stretched geometries.

Table II.6

Coupled-cluster correlation energies (hartrees) for different levels of truncation

	LiH		Li_2	
	3.015 a.u.	9.045 a.u.	5.05 a.u.	40.4 a.u.
CCD	-0.0168873	-0.0724110	-0.0180015	-0.1019246
CCSD	-0.0176496	-0.1085920	-0.0181219	-0.1021333
CCSDT	-0.0176606	-0.1086567	-0.0181545	-0.1024180
CCSDTQ	-0.0176606	-0.1086573	-0.0181562	-0.1024169

Table II.7

The largest triple and quadruple coupled-cluster amplitudes. For LiH, spin-orbitals 1234, ($1\sigma\alpha, 1\sigma\beta, 2\sigma\alpha, 2\sigma\beta$), are occupied and 12345678 ($3\sigma\alpha, 3\sigma\beta$, $4\sigma\alpha, 4\sigma\beta$, $5\sigma\alpha, 5\sigma\beta$, $6\sigma\alpha, 6\sigma\beta$), are unoccupied. For Li_2, spin-orbitals 123456 ($1\sigma\alpha, 1\sigma\beta$, $2\sigma\alpha, 2\sigma\beta$, $3\sigma\alpha, 3\sigma\beta$), are occupied and 12345678 ($4\sigma\alpha, 4\sigma\beta$, $5\sigma\alpha, 5\sigma\beta$, $6\sigma\alpha, 6\sigma\beta$, $7\sigma\alpha, 7\sigma\beta$), are unoccupied.

LiH

		3.015 a.u.			9.045 a.u.
IJK	ABC	T3	IJK	ABC	T3
4 3 1	5 2 1	-0.001233208	4 3 2	4 3 2	0.006351317
4 3 2	4 2 1	0.000505260	4 3 1	3 2 1	0.001103313
4 3 2	6 4 1	0.000228419	4 2 1	6 2 1	-0.000789528
4 3 2	6 3 2	-0.000213167	4 3 2	6 5 2	-0.000483347
4 3 1	7 6 5	0.000195255	4 3 1	7 4 3	-0.000463687
IJKL	ABCD	T4	IJKL	ABCD	T4
4 3 2 1	6 3 2 1	0.000036062	4 3 2 1	6 4 3 1	-0.000135851
4 3 2 1	4 3 2 1	-0.000027332	4 3 2 1	4 3 2 1	0.000067066
4 3 2 1	6 5 2 1	-0.000013405	4 3 2 1	5 4 2 1	0.000026120
4 3 2 1	8 7 2 1	0.000009584	4 3 2 1	7 6 4 3	-0.000010013
4 3 2 1	7 6 2 1	0.000008178	4 3 2 1	8 7 2 1	0.000004352
4 3 2 1	7 5 4 2	0.000007500	4 3 2 1	8 4 3 1	-0.000003011

Table II.7 (continued)

Li_2

3.015 a.u.			9.045 a.u.		
IJK	ABC	T3	IJK	ABC	T3
5 3 2	7 6 5	0.000607571	6 5 3	6 5 3	-0.003033974
5 4 2	8 6 5	0.000607235	4 2 1	6 5 4	-0.003033885
6 5 3	6 5 3	0.000599498	6 4 1	8 6 5	0.003026553
3 2 1	6 5 3	0.000596313	6 3 1	7 6 5	0.003026538
4 3 2	6 5 2	-0.000557496	5 4 3	5 4 3	-0.002000682

IJKL	ABCD	T4	IJKL	ABCD	T4
4 3 2 1	6 5 2 1	0.000104560	6 4 3 1	5 4 2 1	0.000058998
4 3 2 1	7 6 2 1	-0.000029608	5 4 3 2	5 4 2 1	-0.000057601
6 5 4 3	8 5 2 1	0.000028668	4 3 2 1	8 5 2 1	-0.000056449
5 4 3 2	6 3 2 1	-0.000025105	6 5 4 3	8 5 2 1	-0.000054882
6 4 3 1	6 3 2 1	0.000024330	6 5 2 1	6 5 4 3	0.000018442

a) The basis set for LiH consisted of the following four contracted gaussian orbitals for the lithium atom and two for the hydrogen atom, (contraction coefficients in parenthesis).

Li:	s:	642.419 (0.00214261)	96.7985 (0.0162089)	22.0911 (0.0773156)
		6.20107 (0.245786)	1.93512 (0.470189)	0.636736 (0.345471)
	s:	2.32492 (-0.0350917)	0.632430 (-0.191233)	0.0790534 (1.08399)
	s:	0.0359620 (1.00000)		
	p_z :	0.994203 (0.155916)	0.231031 (0.607684)	0.0751386 (0.391957)
H:	s:	18.7311 (0.0334946)	2.82539 (0.234727)	0.640122 (0.813757)
	s:	0.161278 (1.00000)		

b) In the calculation on Li_2 we used first-order correlation orbitals generated using a procedure described previously.[28] The FOCO set consisted of four sigma orbitals and the same gaussian basis set as that for Li in the LiH calculation with the addition of a p_z and a d_{z^2} was used in the calculation.

p_z : 0.500000 (1.00000)
d_{z^2} : 0.500000 (1.00000)

G. The Coupled-cluster Method Truncated at Quadruples, Conclusions

At this stage of the derivation and implementation of the coupled-cluster method the contribution of this study is,

i) The complete CCSDTQ equations were diagrammatically derived and presented.

ii) The first computational implementation of the complete CCSDTQ method has been accomplished.

iii) Some numerical results on simple 'model' systems are presented.

III CONVERGING THE COUPLED-CLUSTER EQUATIONS

A. Introduction

In the next chapter a two-determinantal coupled-cluster theory which is based on a single-reference formalism.[40] will be presented. This method retains the advantages of the single-reference approach, but allows the study of inherently multi-reference cases. However, when one or more of the amplitudes becomes large, the conventional strategy for solving the single-reference coupled-cluster equations begins to show ocsillations or even diverge. In order to effectively use this method for systems which require more then one reference determinant a stabilization technique which avoids this problem is required.

In this chapter the development and implementation of a stabilization scheme is described, in which some of the terms in the single-reference coupled-cluster equation are 'quazi-linearized'. This then significantly stabilizes the reduced linear equation method which we use to solve the coupled-cluster system of equations.

B. Theory

As described in chapter 1, the coupled-cluster method utilizes an exponential expansion of the wave operator which acts on the reference determinant $|\,0\rangle$ to produce the coupled-cluster wavefunction $e^{\hat{t}}\,|\,0\rangle$. Lower case t is now being used to signify the coupled cluster operator as upper case T will be used to indicate the fortran arrays in the next section. For coupled-cluster theory including single and double excitations (CCSD) this is;

$$|\,\psi_{CCSD}\rangle = e^{\hat{t}_1+\hat{t}_2}|\,0\rangle \tag{1}$$

The symbolic form of the CCSD equations and their derivation have were presented in chapter 1. Another way of representing the CCSD system of equations is;

$$\underline{\underline{A}}\,\underline{t} + \underline{\underline{B}}\,\underline{t}^2 + \underline{\underline{C}}\,\underline{t}^3 + \underline{\underline{D}}\,\underline{t}^4 = 0 \tag{2}$$

The reduced linear equation procedure, used to solve the coupled-cluster system of equations was presented in chapter 1. In terms of the products of amplitudes, the coupled-cluster equation is divided into two parts,

$$\underline{\underline{A}}\,\underline{t} = -\underline{\underline{B}}\,\underline{t}^2 - \underline{\underline{C}}\,\underline{t}^3 - \underline{\underline{D}}\,\underline{t}^4 \tag{3}$$

Within each iteration of the procedure the terms on the right hand side of (2) are treated as a constant;

$$\underline{\underline{A}}\,\underline{t} = \underline{\underline{G}} \tag{4}$$

where;

$$\underline{\underline{G}} = -\underline{\underline{B}}\,\underline{t}^2 - \underline{\underline{C}}\,\underline{t}^3 - \underline{\underline{D}}\,\underline{t}^4 \tag{5}$$

The reduced linear equation procedure determines the coupled-cluster amplitudes as the initial guess for the amplitudes plus a series of correction vectors. Thus (4) is actaully;

$$\underline{\underline{A}}\,(\underline{t}^{(i)} + \underline{t}^{(1)} + \underline{t}^{(2)} + \ldots + \underline{t}^{(n)} = \underline{\underline{G}} \tag{6}$$

where $\underline{t}^{(i)}$ is the initial guess for the amplitude vector and the subsequent $\underline{t}^{(n)}$ are the correction vectors provided by each iteration of the procedure.

As long as the amplitudes are small the products of the amplitudes in $\underline{\underline{G}}$ are even smaller and thus the changes in these products are smaller yet. Thus, even though $\underline{\underline{G}}$ is not constant, the changes in these terms between interations are small enough to allow the linear procedure to converge quite well. However, as an amplitude gets large, it's presence in the product terms of equation (5) causes the changes in the $\underline{\underline{G}}$ vector to become large enough that it makes it difficult for the procedure to converge. It is in these cases that oscillation and possible divergence occur.

A solution to the problem was to systematically 'quasi-linearize' some of the non-linear terms on the right hand side of the equation and move them to the left hand side of the equation. If we break the quadratic term of equation (2) into its components, showing explicitly the products of the amplitudes of single and double excitations, it becomes

$$\underline{\underline{B}}\,\underline{t}^2 = \underline{\underline{B}}_{11}\,\underline{t}_1\underline{t}_1 + \underline{\underline{B}}_{12}\,\underline{t}_1\underline{t}_2 + \underline{\underline{B}}_{21}\,\underline{t}_2\underline{t}_1 + \underline{\underline{B}}_{22}\,\underline{t}_2\underline{t}_2 \tag{7}$$

This can be written as;

$$\underline{\underline{B}}\,\underline{t}^2 = \underline{\underline{B}}'_{11}\,\underline{t}_1 + \underline{\underline{B}}'_{21}\,\underline{t}_1 + \underline{\underline{B}}'_{12}\,\underline{t}_2 + \underline{\underline{B}}'_{22}\,\underline{t}_2 \tag{8}$$

Where;

$$\underline{\underline{B}}'_{11} = \underline{\underline{B}}_{11}\underline{t}_1 \tag{9}$$

$$\underline{\underline{B}}'_{21} = \underline{\underline{B}}_{21}\underline{t}_2 \tag{10}$$

$$\underline{\underline{B}}'_{12} = \underline{\underline{B}}_{12}\underline{t}_1 \tag{11}$$

$$\underline{\underline{B}}'_{22} = \underline{\underline{B}}_{22}\underline{t}_2 \tag{12}$$

The $\underline{\underline{B}}'$ matrices can now be treated as constant for each iteration and independently moved to the left side of (3). This gives us the ability to systematically remove terms from the $\underline{\underline{G}}$ vector as they become large. By doing this we prevent this vector from changing too much and thus remove the numerical instability from the procedure. As an example, moving the t_2t_2 terms to the left side yields;

$$\underline{\underline{A}}'\,\underline{t} = \underline{\underline{G}}' \tag{13}$$

where;

$$\underline{\underline{A}}' = \underline{\underline{A}} + \underline{\underline{B}}'_{22} \tag{14}$$

and;

$$\underline{\underline{G}}' = -\underline{\underline{B}}'_{11}\,\underline{t}_1 - \underline{\underline{B}}'_{21}\,\underline{t}_1 - \underline{\underline{B}}'_{12}\,\underline{t}_2 - \underline{\underline{C}}\,\underline{t}^3 - \underline{\underline{D}}\,\underline{t}^4 \tag{15}$$

Since the set of equations which determine each level of excitation in the coupled-cluster set of equations is independently equal to zero, different terms can be moved to the left hand sides of the equations corresponding to differrent levels of excitations. For example one can consider moving the $\underline{\underline{B}}'_{12}\, t_2$ and $\underline{\underline{B}}'_{22}\, t_2$ in the equations pertaining to the amplitudes of double excitations, (those are obtained by projecting the Schrödinger equation onto the doubly excited determinants), and the $\underline{\underline{B}}'_{11}\, t_1$ terms in the equations pertaining to the single excitation amplitudes.

C. Procedure

In the computational implementation of CCSD the corrections to the t_2 vectors, $t_2^{(iter)}$ obtained from each iteration are contained in the five-dimensional array UI2. Four of the indices represent the two occupied (i,j) and two unoccupied (a,b) indices of the amplitude and the fifth index represents the iteration number. As an example, let us consider the equation for determining t_{ij}^{ab} in the CCSD equation set which contains the linear term;

$$+\frac{1}{2}\sum_{k,l}\langle kl\|ij\rangle t_{kl}^{ab} \tag{16}$$

In the reduced linear equation procedure the amplitude t_{kl}^{ab} is expanded in terms of the initial guess and subsequent correction vectors;

$$t_{kl}^{ab}=\sum_{iter} t_{kl}^{ab(iter)} \tag{17}$$

Then term (17) is represented in the computational implementation as;

$$+\frac{1}{2}\sum_{iter}\sum_{k,l} F2(K,L,I,J)*UI2(K,L,A,B,ITER) \tag{18}$$

where F2(K,L,I,J) represents the two-electron integral and ITER counts the iterations. The t_2 amplitudes (term 18) are contained in the four-dimensional array T2. This array is used to calculate the non-linear terms. As an example, let us consider the equation for determining t_{ij}^{ab} in the CCSD equation set which contains the non-linear term;

$$+\frac{1}{4}\sum_{\substack{c,d\\k,l}}\langle kl\|cd\rangle t_{ij}^{cd}t_{kl}^{ab} \tag{19}$$

This term is represented in the computational implementation as;

$$+\frac{1}{4}\sum_{\substack{c,d\\k,l}} F2(K,L,C,D)*T2(I,J,C,D)*T2(K,L,A,B) \tag{20}$$

In the quasi-linearization which was implemented, the above non-linear term was considered as a linear term, consisting of a constant, which is the integral times the T2(I,J,C,D) amplitude determined in the last iteration, times the UI2(K,L,A,B,ITER) amplitude correction which is being determined in the current iteration. In order to be more precise, it should be mentioned that in the 'quasi-linearization' of term (21) both t_2 amplitudes are treated in an equivalent way, by allowing each of them to become variable while the other one is assumed constant. This leads to the following contribution of the non-linear term (20);

$$\frac{1}{4}\sum_{\substack{c,d\\k,l}} \frac{1}{2}\left[\underbrace{F2(K,L,C,D)*T2(K,L,A,B)}_{C^{CD}_{KL}(AB)}*UI2(I,J,C,D,ITER) \right. \tag{21}$$

$$\left. + \underbrace{F2(K,L,C,D)*T2(I,J,C,D)}_{C^{CD}_{KL}(IJ)}*UI2(K,L,A,B,ITER)\right]$$

The $\frac{1}{2}$ is required because in order to treat both amplitudes symmetrically the term must be counted twice. The C's are constant within each iteration. In the above form term (22) can now be moved to the part of the equation linear with respect to the coupled-cluster amplitudes. For example the second part of term (21) is combined with term (19);

$$+\frac{1}{2}\sum_{iter}\sum_{k,l}\left\{\left[F2(K,L,I,J)+\frac{1}{4}\sum_{cd}C_{KL}^{CD}(IJ)\right]*UI2(K,L,A,B,ITER)\right\} \tag{22}$$

and the first part contributes to the following term;

$$+\frac{1}{2}\sum_{iter}\sum_{c,d}\left\{\left[F2(A,B,C,D)+\frac{1}{4}\sum_{k,l}C_{KL}^{CD}(AB)\right]*UI2(I,J,C,D,ITER)\right\} \tag{23}$$

The other terms in CCSD set of equations are treated in an identical fashion. The off-diagonal t_1t_2 terms could, of course, have either or both of the amplitudes linearized independently.

D. Results

The test case used was LiH, at the internuclear distance of 9.045 a.u. At this separation which is three time the equilibrium internuclear distance of 3.015 a.u. the molecule is essentially dissociated. The basis set is given in Table III.1. The different cases studied are given in Table III.2 and the results of the convergence study are given in Table III.3. The cases differ by the terms which are 'quasi-linearized' and moved from the right hand side of the coupled-cluster equation to the left hand side and included in the A matrix. The initial guess in all cases was the t_2 amplitudes obtained from an MBPT(2) calculation.

At the internuclear separation of 9.045 a.u. the dominant t_2 amplitude is the one which represents the excitation between the two orbitals which become quasi-degenerate as the molecular bond dissociates. The converged value of this amplitude is -1.038781. This is quite large, slightly larger than the unit amplitude of the reference determinant.

One can see from Table 3, that in its original formulation with all the non-linear terms in the $\underline{B}$ vector, the method diverges rapidly. Quasi-linearizing the t_2^2 terms in the CCSD equations for double excitation amplitudes (case 2), provides enough stability for the method to converge in 37 iterations. A major improvement comes from simultaneously quasi-linearizing t_1^2 in the equations for single excitation amplitudes as well as the t_2^2 in the equation for double excitation amplitudes (case 4). This cuts the number of iterations required almost in half.

The obvious drawback to the quasi-linearization scheme is the increase in time per iteration. Since the linear terms contain an extra index to count the interation correction vectors, rather than being calculated only once per iteration, they are calculated n times per iteration, where n is the iteration number. Therefore, if the quasi-linearization of a term does not significantly improve the convergence of the calculation, then the increase in time per iteration must be considered against the reduction in the number of iterations required to achieve convergence.

Table III.1

a) The basis set for LiH consisted of the following four contracted gaussian orbitals for the lithium atom and two for the hydrogen atom, (contraction coefficients in parenthesis).

Li:	s:	642.419 (0.00214261)	96.7985 (0.0162089)	22.0911 (0.0773156)
		6.20107 (0.245786)	1.93512 (0.470189)	0.636736 (0.345471)
	s:	2.32492 (-0.0350917)	0.632430 (-0.191233)	0.0790534 (1.08399)
	s:	0.0359620 (1.00000)		
	p:	0.994203 (0.155916)	0.231031 (0.607684)	0.0751386 (0.391957)
H:	s:	18.7311 (0.0334946)	2.82539 (0.234727)	0.640122 (0.813757)
	s:	0.161278 (1.00000)		

Table III.2

Placement of the non-linear terms of the singles and doubles coupled-cluster equations for the different cases in the convergence study. A zero indicates the term is in the G matrix as with the initial formalism, a one indicates the terms has been 'quasi-linearized' and moved to the A matrix.

	Case					
	1	2	3	4	5	6
t_i^a equations[a]						
t_1^2	0	0	1	1	1	1
t_1t_2	0	0	0	0	0	1
t_{ij}^{ab} equations[b]						
t_1^2	0	0	0	0	1	0
t_1t_2	0	0	0	0	0	1
t_1t_2	0	0	0	0	0	1
t_2^2	0	1	0	1	1	1

a) Equations obtained by projecting the Schrödinger equation onto singly excited determinants $\langle {}_i^a |$.

a) Equations obtained by projecting the Schrödinger equation onto doubly excited determinants $\langle {}_{ij}^{ab} |$.

Table III.3

Convergence of the coupled-cluster equations for the six different cases studied. The initial guess for all cases was the MBPT(2) t_2 amplitudes.

	Case		
	1	2	3
1	-0.0574435	-0.0574435	-0.0574435
2	-0.0455130	-0.0489001	-0.0455130
3	-0.0591427	-0.0649951	-0.0597130
4	-0.0657546	-0.0771893	-0.0697452
5	-0.0588695	-0.0931733	-0.0667662
6	-0.0581183	-0.1006861	-0.0659064
7	-0.0550702	-0.0999628	-0.0614255
8	-0.0098079	-0.1005889	-0.0260525
9	+0.0842952	-0.1028159	+0.1353015
10	+0.1430188	-0.1059927	+0.1622724
11	+0.0188158	-0.1066463	-0.0455580
12	+0.0155439	-0.1080918	+0.0329883
13	+0.0552485	-0.1079650	+0.1066548
14	+0.0426726	-0.1080633	-0.0024183
15	+0.0304231	-0.1082260	-0.0068874
16	+0.0349017	-0.1083443	-0.0347169
17	+0.0511223	-0.1085167	-0.0316792
18	+0.0431904	-0.1085440	-0.0306369
19	+0.0485439	-0.1085418	-0.0189129
20	+0.0539394	-0.1085784	+0.0144982
21	+0.0628030	-0.1086359	-0.0005136
22	+0.0496519	-0.1087199	+0.0020676
23	+0.0433010	-0.1087110	+0.0013948
24	+0.0395649	-0.1087433	-0.0026264
25	+0.0386146	-0.1087651	-0.0022216

(continued)

Table III.3 continued

		Case	
	1	2	3
26	diverges	-0.1087857	diverges
27	·	-0.1088199	·
28	·	-0.1088362	·
29	·	-0.1088544	·
30	·	-0.1088591	·
31	·	-0.1088609	·
32	·	-0.1088620	·
33	·	-0.1088629	·
34	·	-0.1088647	·
35	·	-0.1088662	·
36	·	-0.1088660	·
37	·	-0.1088660	·
38	·	converged	·

Table III.3 (continued)

	Case 4	 5	 6
1	-0.0574435	-0.0574435	-0.0574435
2	-0.0489001	-0.0489001	-0.0504842
3	-0.0655902	-0.0658173	-0.0765271
4	-0.0838579	-0.0872831	-0.1187728
5	-0.1053388	-0.1069673	-0.0803567
6	-0.1159605	-0.1145760	-0.0866619
7	-0.1105552	-0.1098882	-0.1075589
8	-0.1084581	-0.1079838	-0.1080553
9	-0.1082772	-0.1080267	-0.1090271
10	-0.1086502	-0.1089769	-0.1090964
11	-0.1088358	-0.1086870	-0.1089146
12	-0.1088854	-0.1089218	-0.1087326
13	-0.1088903	-0.1088166	-0.1088851
14	-0.1087717	-0.1089024	-0.1088605
15	-0.1088605	-0.1088303	-0.1089014
16	-0.1088679	-0.1088899	-0.1088747
17	-0.1088680	-0.1088481	-0.1088556
18	-0.1088652	-0.1088828	-0.1088625
19	-0.1088658	-0.1088486	-0.1088682
20	-0.1088659	-0.1088850	-0.1088654
21	converged	-0.1088462	-0.1088665
22		-0.1088903	-0.1088658
23		-0.1087932	-0.1088662
24		-0.1088562	-0.1088659
25		-0.1088721	-0.1088662

(continued)

Table 3 continued

	Case 5	 6
26	-0.1088357	-0.1088661
27	-0.1088639	converged
28	-0.1088705	
29	-0.1088551	
30	-0.1088655	
31	-0.1088687	
32	-0.1088656	
33	-0.1088658	
34	-0.1088665	
35	-0.1088656	
36	-0.1088666	
37	-0.1088653	
38	-0.1088669	
39	-0.1088635	
40	-0.1088657	
41	-0.1088664	
42	-0.1088646	
43	-0.1088659	
44	-0.1088663	
45	-0.1088653	
46	-0.1088660	
47	-0.1088662	
48	-0.1088657	
49	-0.1088660	
50	-0.1088661	
51	converged	

E. Conclusion

This work demonstrates how a satisfactory convergence of the reduced linear equation procedure for solving the coupled-cluster equations can be accomplished for quasi-degenerate cases. This is an essential step towards using a coupled-cluster method based on a single-reference formalism to solve multi-reference chemical problems.

IV A Multi-reference Coupled-cluster Method Using a Single-reference Formalism

A. Introduction

The method proposed in this chapter is based on selecting the most dominant determinant in a reference function which consists of two closed-shell type configurations[37,38,40] as the 'formal' reference determinant. Single and double excitations from this reference function are included using the standard CCSD equations. The second reference determinant is included by a two electron excitation from the formal reference determinant. Single and double excitations from the second determinant are included by including only those triple and quadruple excitations from the formal reference determinant which correspond to single and double excitations from the second reference determinant.[14,15,40] This is accomplished by modifying the triple and quadruple diagrams one at a time with the appropriate restrictions. While this procedure is somewhat tedious, it allows retention of the simplicity of the single-reference CC method as well as avoiding the previously mentioned problems associated with the current MRCC approaches. Thus this chapter presents a practical method for the important case of coupled-cluster singles and doubles (CCSD) in cases requiring two reference determinants that differ by a two electron excitation.

B. Theory

In the truncated CCSDTQ approach presented in this chapter, the multi-reference character of the wavefunction is provided by extending the set of cluster operators to include triples and quadruples which are restricted to only those which correspond to single and double excitations from a second determinant that differs from the reference determinant by a two electron excitation. This will allow energy calculations which involve the stretching (dissociation) of a single chemical bond as well as certain ground and excited states which mandate a two-determinantal reference function.

Representing the second determinant as;

$$|1\rangle = |0_{IJ}^{AB}\rangle \tag{1}$$

In this presentation, the convention is that upper case letters represent the double excitation required to produce the second determinant from the formal reference determinant and lower case letters represent excitations to virtual spin-orbitals (virtual spin-orbitals are spin-orbitals which are unoccupied in both the reference determinant and the second determinant). The spin-orbitals represented by the upper case letters are special in the sense that they are not included in the sums involved in occupied or virtual spin-orbitals for triple and quadruple amplitudes, but are always specifically indicated as fixed labels. These spin-orbitals will be refered to as 'active' spin-orbitals. Since single and double amplitudes are not restricted the sums involving single and double amplitudes include the active orbitals.

The most optimal procedure to implement, is first to perform a multi-configuration self consistant field (MCSCF) calculation. The two most important determinants will be selected as 'reference' determinants for the subsequent MRCCSD calculation. One of these will be the 'formal' reference determinant and the other will be the 'second' reference determinant. The MCSCF spin-orbitals generated by this initial calculation will also be used in the MRCCSD calculation.

In terms of the formal reference determinant, single and double excitations from the second determinant are shown in Table IV.1. Since the active spin-orbitals are not included in either the set of core spin-orbitals or the set of virtual spin-orbitals, they must be specifically indicated. This leads to four types of single excitations and nine types of double excitations from the second determinant. To see how to transform the representation from the second determinant to the formal reference determinant, first represent the second determinant as $|\,0_{IJ}^{AB}\rangle$. Include the appropriate excitation, for example the first one in Table 1. Since A in occupied and I is not occupied in the second determinant, the excitation from A to I must be included, $|\,0_{IJA}^{ABI}\rangle$. Using second-quantized operators this can be represented as;

$$a_I^\dagger a_A a_B^\dagger a_J a_A^\dagger a_I \,|0\rangle = a_I^\dagger a_I a_A a_A^\dagger a_B^\dagger a_J \,|0\rangle = a_B^\dagger a_J \,|0\rangle \tag{2}$$

This yields the determinant $|\,0_J^B\rangle$, which is singly excited with respect to the formal reference determinant. Those excitations which correspond to single and double excitations from the formal reference determinant are automatically included in the full singles and doubles from the formal reference. However those excitations which correspond to triple and quadruple excitations from the formal reference determinant must be considered term by term in order to include only the desired amplitudes.

The extension to include excitations from two determinants does not change the energy expression due to the fact that the Hamiltonian operator contains at most two-electron operators. The equations which determine the CC amplitudes must now be extended to include the selected set of triples and quadruples from $|\,0\rangle$ which arise from including all single and double amplitudes from $|\,1\rangle$. In the following equations all the appropriate restrictions on triple and quadruple amplitudes are included in parenthesis. These equations define this multi-reference CC (MRCC) method.

$$\langle 0_i^a\,|H[1+T_1+\tfrac{1}{2}T_1^2+\tfrac{1}{3!}T_1^3+T_2+T_1T_2+T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})]\,|0\rangle_C=0 \quad (3)$$

$$\begin{aligned}\langle 0_{ij}^{ab}\,|H[1+T_1+\tfrac{1}{2}T_1^2+\tfrac{1}{3!}T_1^3+\tfrac{1}{4!}T_1^4+T_2+\tfrac{1}{2}T_2^2+T_1T_2+\tfrac{1}{2}T_1^2T_2+\\ T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})+T_1T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})+T_4({}^{ABab}_{IJij})]\,|0\rangle_C=0 \quad (4)\end{aligned}$$

$$\begin{aligned}\langle 0_{IJi}^{ABa}\,|H[1+T_1+\tfrac{1}{2}T_1^2+\tfrac{1}{3!}T_1^3+\tfrac{1}{4!}T_1^4+T_2+\tfrac{1}{2}T_2^2+T_1T_2+\tfrac{1}{2}T_1^2T_2+\\ \tfrac{1}{3!}T_1^3T_2+\tfrac{1}{2}T_1T_2^2+T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})+T_1T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})+\\ \tfrac{1}{2}T_1^2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})+T_2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})+\\ T_4({}^{ABab}_{IJij})+T_1T_4({}^{ABab}_{IJij})]\,|0\rangle_C=0 \quad (5)\end{aligned}$$

$$\begin{aligned}\langle 0^{ABa}_{Iij}|H[1 + T_1 + \tfrac{1}{2}\,T_1^2 + \tfrac{1}{3!}\,T_1^3 + \tfrac{1}{4!}\,T_1^4 + T_2 + \tfrac{1}{2}\,T_2^2 + T_1T_2 + \tfrac{1}{2}\,T_1^2T_2 +&\\ \tfrac{1}{3!}\,T_1^3T_2 + \tfrac{1}{2}\,T_1T_2^2 + T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + T_1T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) +&\\ \tfrac{1}{2}\,T_1^2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + T_2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) +&\\ T_4({}^{ABab}_{IJij}) + T_1T_4({}^{ABab}_{IJij})]\,|0\rangle_C = 0&\end{aligned} \tag{6}$$

$$\begin{aligned}\langle 0^{Aab}_{IJi}|H[1 + T_1 + \tfrac{1}{2}\,T_1^2 + \tfrac{1}{3!}\,T_1^3 + \tfrac{1}{4!}\,T_1^4 + T_2 + \tfrac{1}{2}\,T_2^2 + T_1T_2 + \tfrac{1}{2}\,T_1^2T_2 +&\\ \tfrac{1}{3!}\,T_1^3T_2 + \tfrac{1}{2}\,T_1T_2^2 + T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + T_1T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) +&\\ \tfrac{1}{2}\,T_1^2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + T_2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) +&\\ T_4({}^{ABab}_{IJij}) + T_1T_4({}^{ABab}_{IJij})]\,|0\rangle_C = 0&\end{aligned} \tag{7}$$

$$\begin{aligned}\langle 0^{ABab}_{IJij}|H[1 + T_1 + \tfrac{1}{2}\,T_1^2 + \tfrac{1}{3!}\,T_1^3 + \tfrac{1}{4!}\,T_1^4 + T_2 + \tfrac{1}{2}\,T_2^2 + \tfrac{1}{3!}\,T_2^3 + T_1T_2 +&\\ \tfrac{1}{2}\,T_1^2T_2 + \tfrac{1}{3!}\,T_1^3T_2 + \tfrac{1}{2}\,T_1T_2^2 + \tfrac{1}{4}\,T_1^2T_2^2 + T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) +&\\ T_1T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + \tfrac{1}{2}\,T_1^2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi})\ \tfrac{1}{3!}\,T_1^3T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) +&\\ T_2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + T_1T_2T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + T_4({}^{ABab}_{IJij}) +&\\ T_1T_4({}^{ABab}_{IJij}) + \tfrac{1}{2}\,T_1^2T_4({}^{ABab}_{IJij}) + T_2T_4({}^{ABab}_{IJij})]\,|0\rangle_C = 0&\end{aligned} \tag{8}$$

The MRCCSD wavefunction is given by the exponential expansion of the wave operator (eqns 1 and 2) where now;

$$T = T_1 + T_2 + T_3({}^{ABa}_{IJi}+{}^{ABa}_{Iij}+{}^{Aab}_{IJi}) + T_4({}^{ABab}_{IJij}) \tag{9}$$

Although a two determinantal reference function is never explicitly used in this approach, the correlated wavefunction is equivalent to;

$$|\psi_{MRCC}\rangle = e^T(|0\rangle + c_1\,|1\rangle) = e^T(|0\rangle + c_1 a_B^\dagger a_J a_A^\dagger a_I\,|0\rangle) \tag{10}$$

Where c_1 provides the correct ratio between the two determinants in the correlated wavefunction and;

$$T = T_1 + T_2 \tag{11}$$

The cluster operators T_1 and T_2 are defined as in eqns 4 and 5 of chapter 2, and amplitudes which precede identical strings of second-quantized operators resulting from operating on both determinants are combined to yield a single amplitude. How this is done can be seen by using the MRCC wavefunction in the Schrödinger equation, projecting it against the formal reference determinant and solving for the energy.

$$E_{MRCCSD} = \langle 0 | H[1 + T_1 + \tfrac{1}{2} T_1^2 + T_2](|0\rangle + c_1 a_B^\dagger a_J a_A^\dagger a_I \, |0\rangle) \tag{12}$$

The sum involved in T_2 when it acts on $|0\rangle$ includes the cluster operator;

$$t_{IJ}^{AB} a_B^\dagger a_J a_A^\dagger a_I \tag{13}$$

Adding this to the first term generated when the truncated wave operator acts on the second determinant;

$$(t_{IJ}^{AB} + c_1) a_B^\dagger a_J a_A^\dagger a_I \tag{14}$$

which can be written;

$$t_{IJ}^{AB'} a_B^\dagger a_J a_A^\dagger a_I \tag{15}$$

The prime indicates the multireference nature of the new amplitude. As a second example, when $\frac{1}{2} T_1^2$ acts on $|0\rangle$ it includes the cluster operator;

$$\tfrac{1}{2}\, t_i^a a_a^\dagger a_i t_I^A a_A^\dagger a_I \tag{16}$$

when $\frac{1}{2}\,\mathrm{T}_1^2$ acts on the second reference it includes;

$$\tfrac{1}{2}\, t_i^a a_a^\dagger a_i t_{BJI}^{JBA} a_J^\dagger a_B a_B^\dagger a_J a_A^\dagger a_I \tag{17}$$

Adding the two terms;

$$\tfrac{1}{2}\, t_i^a a_a^\dagger a_i (t_I^A + t_{BJI}^{JBA}) a_A^\dagger a_I \tag{18}$$

Which can be written;

$$\tfrac{1}{2}\, t_i^a a_a^\dagger a_i t_I^{A'} a_A^\dagger a_I \tag{19}$$

This can be done in all of the MRCC equations for all the duplicate amplitudes (or any number of constants preceding the same string of second quantized operators), thus reducing the multi-reference wavefunction to our truncated CCSDTQ wave operator acting on a single reference determinant.

An alternate derivation of our equations which better demonstrates their relationship with other MRCC methods is to begin with the generalized Bloch equation;[37,38,46,47]

$$HU = UHU \tag{20}$$

where;

$$U = \sum_\mu e^{T(\mu)} \,|\mu\rangle\langle\mu\,| \tag{21}$$

and the reference function is

$$\Phi_0 = \sum_\mu c_\mu \,|\mu\rangle \tag{22}$$

Multiply the Bloch equation from the right by the reference determinant;

$$H \sum_\mu c_\mu e^{T(\mu)} \,|\mu\rangle = \sum_\nu e^{T(\nu)} \,|\nu\rangle\langle\nu\,| H \sum_\lambda c_\lambda e^{T(\lambda)} \,|\lambda\rangle \tag{23}$$

Represent all excitations after the hamiltonian operator in terms of the formal reference;

$$He^{T*}\,|0\rangle = \sum_{\nu} e^{T(\nu)}\,|\nu\rangle\langle\nu \mid He^{T*}\,|0\rangle \tag{24}$$

where T* represents the extension to higher order excitations from the formal reference to include equivalent excitations from the secondary references. Project against all functions | G⟩ orthogonal to the formal reference;

$$\langle G \mid He^{T*}\,|0\rangle = \sum_{\nu} \langle G \mid e^{T(\nu)}\,|\nu\rangle\langle\nu \mid He^{T*}\,|0\rangle \tag{25}$$

or;

$$\langle G \mid He^{T*}\,|0\rangle = t_G\langle 0 \mid He^{T*} \mid 0\rangle + \sum_{\nu\neq 0} \langle G \mid e^{T(\nu)}\,|\nu\rangle\langle\nu \mid He^{T*}\,|0\rangle \tag{26}$$

The first term on the right cancels with the disconnected terms on the left and keeping only the connected terms, the second term is zero by virtue of the fact that it is a coefficient times another of the CC equations. This yields the single reference formalism extended to include excitations from more then one reference;

$$\langle G \mid He^{T*}\,|0\rangle = 0 \tag{27}$$

Table IV.1

Single and double excitations from the second reference determinant in terms of the formal reference determinant.

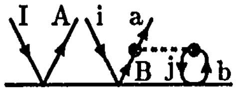
Second Determinant	Formal Reference	Type of Excitations
$\lvert 1_A^I\rangle$	$\lvert 0_J^B\rangle$	*Single*
$\lvert 1_A^a\rangle$	$\lvert 0_{IJ}^{Ba}\rangle$	*Double*
$\lvert 1_i^I\rangle$	$\lvert 0_{Ji}^{AB}\rangle$	*Double*
$\lvert 1_i^a\rangle$	$\lvert 0_{IJi}^{ABa}\rangle$	*Triple*
$\lvert 1_{AB}^{IJ}\rangle$	$\lvert 0\rangle$	*None*
$\lvert 1_{AB}^{Ia}\rangle$	$\lvert 0_J^a\rangle$	*Single*
$\lvert 1_{Ai}^{IJ}\rangle$	$\lvert 0_i^B\rangle$	*Single*
$\lvert 1_{AB}^{ab}\rangle$	$\lvert 0_{IJ}^{ab}\rangle$	*Double*
$\lvert 1_{ij}^{IJ}\rangle$	$\lvert 0_{ij}^{AB}\rangle$	*Double*
$\lvert 1_{Ai}^{Ia}\rangle$	$\lvert 0_{Ji}^{Ba}\rangle$	*Double*
$\lvert 1_{Ai}^{ab}\rangle$	$\lvert 0_{IJi}^{Bab}\rangle$	*Triple*
$\lvert 1_{ij}^{Ia}\rangle$	$\lvert 0_{Jij}^{ABa}\rangle$	*Triple*
$\lvert 1_{ij}^{ab}\rangle$	$\lvert 0_{IJij}^{ABab}\rangle$	*Quadruple*

C. Procedure

The terms from the coupled-cluster equations which determine single, double, triple and quadruple excitation amplitudes, along with the appropriate restrictions on these amplitudes to include only those terms which correspond to single and double excitations from a second reference determinant have been diagrammatically derived. This procedure generates 16 diagrams for 4 types of single projections, 161 diagrams for 9 types of double projections, 295 diagrams for 3 types of triple projections and 147 diagrams for the 1 type of quadruple projections, see Tables IV.4-IV.7.

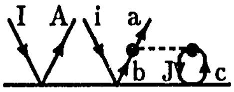
As a specific example lets consider diagram 2 from the doubles projection 6, DP6 (see Table IV.5) which contains A(B) and I(J). Since this is a triple amplitude, in order to represent a double excitation from the second determinant it must contain three upper case letters (three spin-orbitals from the excitation which generates the second reference from the first). In this case one of the labels involved in the integral which is usually summed over must be fixed. Also since active spin-orbitals are not included in the sum they must be specifically included. This gives rise to several terms, represented first in second quantized form and then followed by the corresponding diagram and term in the CC equation.

$$\langle 0^{Aa}_{Ii}|\, H(p,q) \sum_{\substack{b\\j}} t^{ABb}_{Iij} a^\dagger_A a_I a^\dagger_B a_i a^\dagger_b a_j \,|0\rangle$$

2A


$$+\sum_{\substack{b\\j}} \langle aj\,||\,Bb\rangle t^{ABb}_{Iij}$$

$$\langle 0^{Aa}_{Ii}|\, H(p,q) \sum_{b>c} t^{Abc}_{IiJ} a^\dagger_A a_I a^\dagger_b a_i a^\dagger_c a_J \,|0\rangle$$

2B


$$+\tfrac{1}{2}\sum_{b,c} \langle aJ\,||\,bc\rangle t^{Abc}_{IiJ}$$

$$-\langle 0^{aA}_{Ii}|\, H(p,q) \sum_{b} t^{aAb}_{IiJ} a^\dagger_a a_I a^\dagger_A a_i a^\dagger_b a_J \,|0\rangle$$

2D


$$-\sum_{b} \langle AJ\,||\,Ab\rangle t^{aAb}_{IiJ}$$

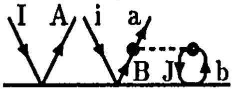
$$-\langle 0^{aA}_{Ii}|\, H(p,q) \sum_{j} t^{aAB}_{Iij} a^\dagger_a a_I a^\dagger_A a_i a^\dagger_B a_j \,|0\rangle$$

2E


$$-\sum_{j} \langle Aj\,||\,AB\rangle t^{aAB}_{Iij}$$

When the amplitude involved represents a single excitation from the second reference, two of the free labels must be fixed. This gives rise to two additional diagrams.

$$\langle 0^{Aa}_{Ii}|\, H(p,q) \sum_{b} t^{ABb}_{IiJ} a^\dagger_A a_I a^\dagger_B a_i a^\dagger_b a_J \,|0\rangle - \langle 0^{aA}_{Ii}|\, H(p,q) \sum_{b} t^{aBb}_{IiJ} a^\dagger_a a_I a^\dagger_B a_i a^\dagger_b a_J \,|0\rangle$$

2C


$$+\sum_{b} (-1)^P P(A/a) \langle aJ\,||\,Bb\rangle t^{ABb}_{IiJ}$$

$$-\langle 0^{aA}_{Ii}|\, H(p,q)\; t^{aAB}_{IiJ}\, a^{\dagger}_{a} a_{I} a^{\dagger}_{A} a_{i} a^{\dagger}_{B} a_{J}\,|0\rangle$$

2F

$$-\langle AJ\,||\,AB\rangle t^{aAB}_{IiJ}$$

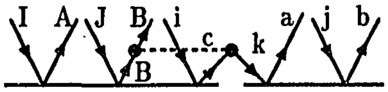
When deriving the terms containing triple and quadruple amplitudes in the equations generated by triple and quadruple projections, four additional conventions concerning permutations must be added to those of Kucharski and Bartlett.

(i) A double vertical line means no two upper case labels involved in a triple or quadruple amplitude may simultaneously be exchanged with lower case labels. This would produce a term which doesn't correspond to a single or double excitation from the second reference.

(ii) A permutation enclosed in parenthesis within the set of permutations means make all the permutations as if the enclosed permutation were not present, then make this permutation and again make all permutations with this label in place of the one it was exchanged with.

(iii) A permutation of upper case labels enclosed in parenthesis includes exchanging the label (labels) involved in the integral as well as the amplitude when necessary.

As an example of these three rules, consider diagram 25B from the quadruples projection QP1, (see Table IV.7), which contains I,J,A and B and represents a double excitation from the second reference.



$$-\sum_{\substack{c\\k}}(-1)^P P(IJi/j\,\|\,A/B/ab(A/B))\langle Bk\|Bc\rangle t_{IJi}^{ABc}t_{kj}^{ab}$$

The total number of terms generated by the permutations is 48 (see Table IV.2). Also the reader will notice that simultaneously exchanging B and another upper case letter with two lower case letters is allowed as B is involved in the integral as well as the amplitude (see diagram 11, Table IV.2). Also permutations will sometimes generate a zero amplitude by virtue of the fact that the amplitude will contain the same upper case label twice. This is necessary in order to insure that all needed permutations are included. As an example, in diagram 25B from quadruples projection QP1, in the initial diagram when A is exchanged with B the resulting amplitude is zero (t_{IJi}^{BBc}) but after B is exchanged with a, then a must be exchanged with A (see diagram 10 Table IV.3). This is of course only a notational problem arising from the desire to present the diagrams and equations in as compact a form as possible and will not present a problem in coding the program where the terms containing zero amplitudes will simply not be included.

(iv) The notation $(IJ/ij \mid * \mid Aa/Bb)$ means make only those permutations which do not decrease the number of upper case labels on either amplitude. As an example see diagram 33A in the quadruples projection QP1;

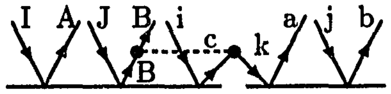
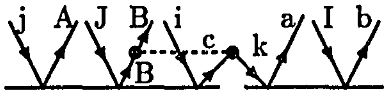
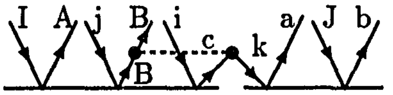
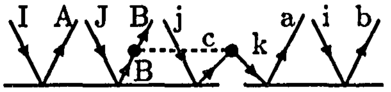
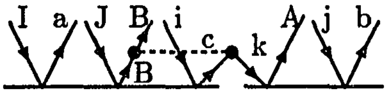
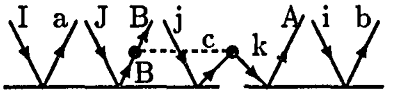
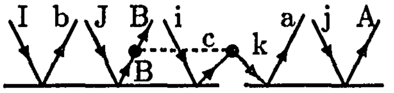
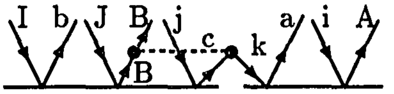
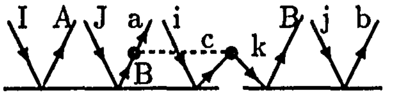
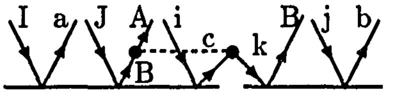
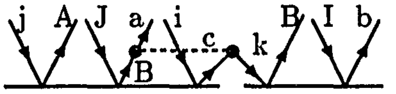
$$+\sum_{\substack{c\\k}}(-1)^{P}P(a/bB(A/B)\,|*|\,J/ij(I/J))\langle kI\|cA\rangle t_{IJk}^{Aac}t_{Iij}^{ABb}$$

The permutations involved in this diagram generates 16 terms (see Table IV.3).

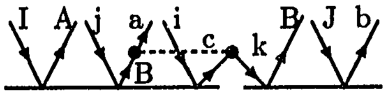
In this multi-reference scheme the CC energy should still be invariant to an internal unitary transformation among the occupied spin-orbitals, excluding however I and J. Similar invariance should hold with respect to a unitary transformation among virtual orbitals, excluding A and B.

Table IV.2

An example of all unique diagrams generated by permuting labels. The first diagram is the identity permutation.

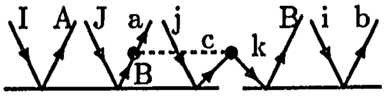
1		$-\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{IJi}^{ABc}t_{kj}^{ab}$
2		$+\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{jJi}^{ABc}t_{kI}^{ab}$
3		$+\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{Iji}^{ABc}t_{kJ}^{ab}$
4		$+\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{IJj}^{ABc}t_{ki}^{ab}$
5		$+\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{IJi}^{aBc}t_{kj}^{Ab}$
6		$-\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{IJj}^{aBc}t_{ki}^{Ab}$
7		$+\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{IJi}^{bBc}t_{kj}^{aA}$
8		$-\sum_{\substack{c\\k}}\langle Bk\Vert Bc\rangle t_{IJj}^{bBc}t_{ki}^{aA}$
9		$+\sum_{\substack{c\\k}}\langle ak\Vert Bc\rangle t_{IJi}^{ABc}t_{kj}^{Bb}$
10		$-\sum_{\substack{c\\k}}\langle Ak\Vert Bc\rangle t_{IJi}^{aBc}t_{kj}^{Bb}$
11		$-\sum_{\substack{c\\k}}\langle ak\Vert Bc\rangle t_{jJi}^{ABc}t_{kI}^{Bb}$

12



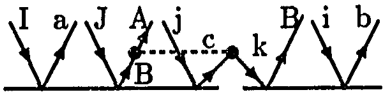
$$-\sum_{\substack{c\\k}}\langle ak\|Bc\rangle t_{Iji}^{ABc}t_{kJ}^{Bb}$$

13



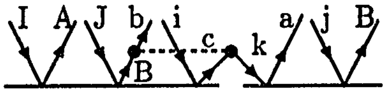
$$-\sum_{\substack{c\\k}}\langle ak\|Bc\rangle t_{IJj}^{ABc}t_{ki}^{Bb}$$

14



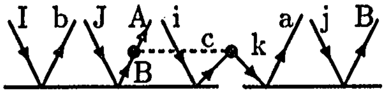
$$+\sum_{\substack{c\\k}}\langle Ak\|Bc\rangle t_{IJj}^{aBc}t_{ki}^{Bb}$$

15



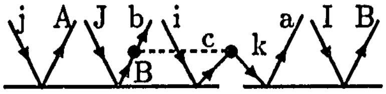
$$+\sum_{\substack{c\\k}}\langle bk\|Bc\rangle t_{IJi}^{ABc}t_{kj}^{aB}$$

16



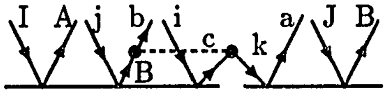
$$-\sum_{\substack{c\\k}}\langle Ak\|Bc\rangle t_{IJi}^{bBc}t_{kj}^{aB}$$

17



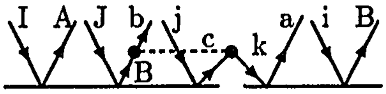
$$-\sum_{\substack{c\\k}}\langle bk\|Bc\rangle t_{jJi}^{ABc}t_{kI}^{aB}$$

18



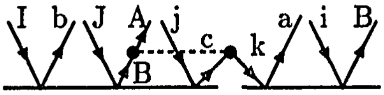
$$-\sum_{\substack{c\\k}}\langle bk\|Bc\rangle t_{Iji}^{ABc}t_{kJ}^{aB}$$

19



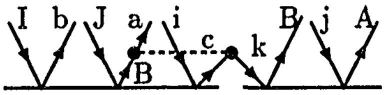
$$-\sum_{\substack{c\\k}}\langle bk\|Bc\rangle t_{IJj}^{ABc}t_{ki}^{aB}$$

20



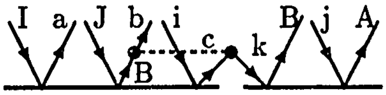
$$+\sum_{\substack{c\\k}}\langle Ak\|Bc\rangle t_{IJj}^{bBc}t_{ki}^{aB}$$

21



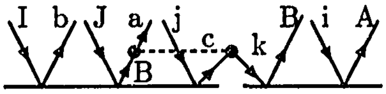
$$-\sum_{\substack{c\\k}}\langle ak\|Bc\rangle t_{IJi}^{bBc}t_{kj}^{BA}$$

22



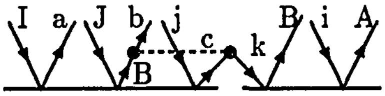
$$+\sum_{\substack{c\\k}}\langle bk\|Bc\rangle t_{IJi}^{aBc}t_{kj}^{BA}$$

23



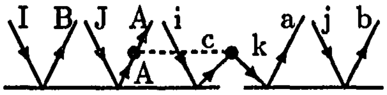
$$+\sum_{\substack{c\\k}}\langle ak\|Bc\rangle t_{IJj}^{bBc}t_{ki}^{BA}$$

24



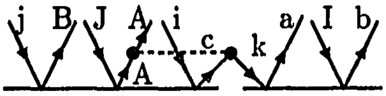
$$-\sum_{\substack{c\\k}}\langle bk\|Bc\rangle t_{IJj}^{aBc}t_{ki}^{BA}$$

25



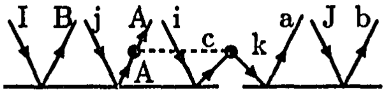
$$+\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{IJi}^{BAc}t_{kj}^{ab}$$

26



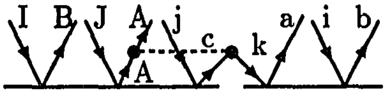
$$-\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{jJi}^{BAc}t_{kI}^{ab}$$

27



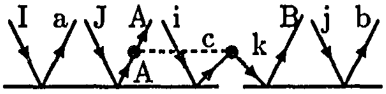
$$-\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{Iji}^{BAc}t_{kJ}^{ab}$$

28



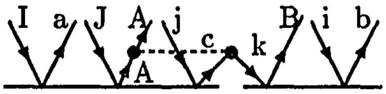
$$-\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{IJj}^{BAc}t_{ki}^{ab}$$

29



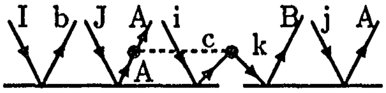
$$-\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{IJi}^{aAc}t_{kj}^{Bb}$$

30



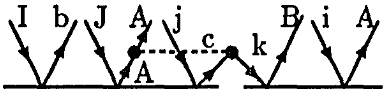
$$+\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{IJj}^{aAc}t_{ki}^{Bb}$$

31



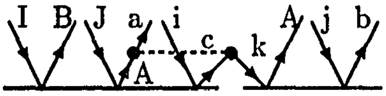
$$-\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{IJi}^{bAc}t_{kj}^{aB}$$

32



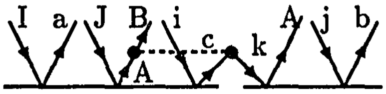
$$+\sum_{\substack{c\\k}}\langle Ak\|Ac\rangle t_{IJj}^{bAc}t_{ki}^{aB}$$

33



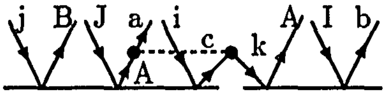
$$-\sum_{\substack{c\\k}}\langle ak\|Ac\rangle t_{IJi}^{BAc}t_{kj}^{Ab}$$

34



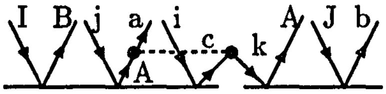
$$+\sum_{\substack{c\\k}}\langle Bk\|Ac\rangle t_{IJi}^{aAc}t_{kj}^{Ab}$$

35



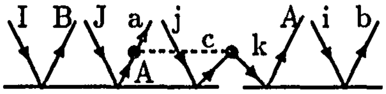
$$+\sum_{\substack{c\\k}}\langle ak\|Ac\rangle t_{jJi}^{BAc}t_{kI}^{Ab}$$

36



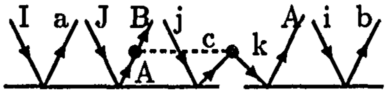
$$+\sum_{\substack{c\\k}}\langle ak\|Ac\rangle t_{Iji}^{BAc}t_{kJ}^{Ab}$$

37



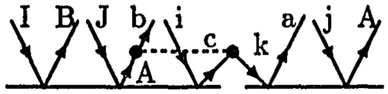
$$+\sum_{\substack{c\\k}}\langle ak\|Ac\rangle t_{IJj}^{BAc}t_{ki}^{Ab}$$

38



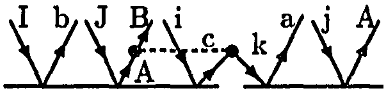
$$-\sum_{\substack{c\\k}}\langle Bk\|Ac\rangle t_{IJj}^{aAc}t_{ki}^{Ab}$$

39



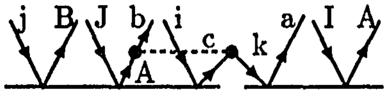
$$-\sum_{\substack{c\\k}}\langle bk\|Ac\rangle t_{IJi}^{BAc}t_{kj}^{aA}$$

40



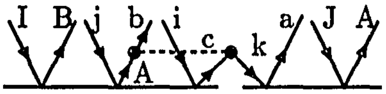
$$+\sum_{\substack{c\\k}}\langle Bk\|Ac\rangle t_{IJi}^{bAc}t_{kj}^{aA}$$

41



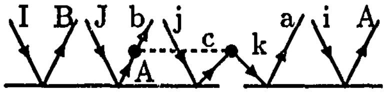
$$+\sum_{\substack{c\\k}}\langle bk\|Ac\rangle t_{jJi}^{BAc}t_{kI}^{aA}$$

42



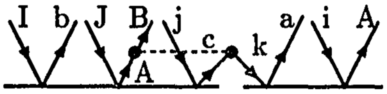
$$+\sum_{\substack{c\\k}}\langle bk\|Ac\rangle t_{Iji}^{BAc}t_{kJ}^{aA}$$

43



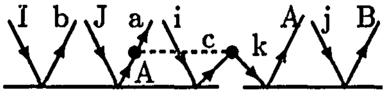
$$+\sum_{\substack{c\\k}}\langle bk\|Ac\rangle t_{IJj}^{BAc}t_{ki}^{aA}$$

44



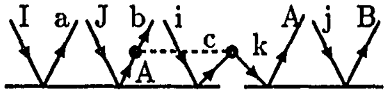
$$-\sum_{\substack{c\\k}}\langle Bk\|Ac\rangle t_{IJj}^{bAc}t_{ki}^{aA}$$

45



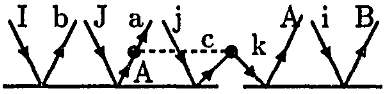
$$+\sum_{\substack{c\\k}}\langle ak\|Ac\rangle t_{IJi}^{bAc}t_{kj}^{AB}$$

46



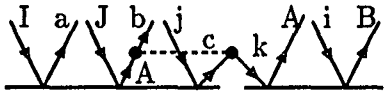
$$-\sum_{\substack{c\\k}}\langle bk\|Ac\rangle t_{IJi}^{aAc}t_{kj}^{AB}$$

47



$$-\sum_{\substack{c\\k}}\langle ak\|Ac\rangle t_{IJj}^{bAc}t_{ki}^{AB}$$

48



$$+\sum_{\substack{c\\k}}\langle bk\|Ac\rangle t_{IJj}^{aAc}t_{ki}^{AB}$$

Table IV.3

An example of all unique diagrams generated by the permutation of labels where the permutation does not decrease the number of upper-case labels on either amplitude. The first diagram is the identity permutation.

1		$+\sum_{\substack{c\\k}}\langle kI\|cA\rangle t_{IJk}^{Aac}t_{Iij}^{ABb}$
2		$-\sum_{\substack{c\\k}}\langle kI\|cA\rangle t_{IJk}^{Abc}t_{Iij}^{ABa}$
3		$+\sum_{\substack{c\\k}}\langle kI\|cA\rangle t_{Iik}^{ABc}t_{IJj}^{Aab}$
4		$+\sum_{\substack{c\\k}}\langle kI\|cA\rangle t_{Ijk}^{ABc}t_{IiJ}^{Aab}$
5		$-\sum_{\substack{c\\k}}\langle kJ\|cA\rangle t_{JIk}^{Aac}t_{Jij}^{ABb}$
6		$+\sum_{\substack{c\\k}}\langle kJ\|cA\rangle t_{JIk}^{Abc}t_{Jij}^{ABa}$
7		$-\sum_{\substack{c\\k}}\langle kJ\|cA\rangle t_{Jik}^{ABc}t_{JIj}^{Aab}$
8		$-\sum_{\substack{c\\k}}\langle kJ\|cA\rangle t_{Jjk}^{ABc}t_{JiI}^{Aab}$
9		$-\sum_{\substack{c\\k}}\langle kI\|cB\rangle t_{IJk}^{Bac}t_{Iij}^{BAb}$
10		$+\sum_{\substack{c\\k}}\langle kI\|cB\rangle t_{IJk}^{Bbc}t_{Iij}^{BAa}$
11		$-\sum_{\substack{c\\k}}\langle kI\|cB\rangle t_{Iik}^{BAc}t_{IJj}^{Bab}$

12 

$$-\sum_{\substack{c\\k}}\langle kI\|cB\rangle t_{Ijk}^{BAc}t_{IiJ}^{Bab}$$

13 

$$+\sum_{\substack{c\\k}}\langle kJ\|cB\rangle t_{JIk}^{Bac}t_{Jij}^{BAb}$$

14 

$$-\sum_{\substack{c\\k}}\langle kJ\|cB\rangle t_{JIk}^{Bbc}t_{Jij}^{BAa}$$

15 

$$+\sum_{\substack{c\\k}}\langle kJ\|cB\rangle t_{Jik}^{BAc}t_{JIj}^{Bab}$$

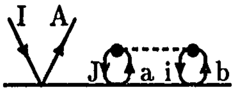
16 

$$+\sum_{\substack{c\\k}}\langle kJ\|cB\rangle t_{Jjk}^{BAc}t_{JiI}^{Bab}$$

Table IV.4

Coupled-cluster diagrams from the projection against a singly excited determinant, representing single and double excitations from a second reference determinant which is doubly excited with respect to the formal reference.

$\langle 0_I^A|$ projection (SP1)

1A		$+\frac{1}{2}\sum_{\substack{a,b\\i}}\langle Ji\|ab\rangle t_{IJi}^{Aab}$
1B		$+\frac{1}{2}\sum_{\substack{a\\i,j}}\langle ij\|Ba\rangle t_{Iij}^{ABa}$
1C		$+\sum_{\substack{a\\i}}\langle Ji\|Ba\rangle t_{IJi}^{ABa}$

$\langle 0_I^a|$ projection (SP2)

1A		$+\sum_{\substack{b\\i}}\langle Ji\|Ab\rangle t_{IJi}^{aAb}$
1B		$+\sum_{\substack{b\\i}}\langle Ji\|Bb\rangle t_{IJi}^{aBb}$
1C		$+\frac{1}{2}\sum_{i,j}\langle ij\|AB\rangle t_{Iij}^{aAB}$
1D		$+\sum_{i}\langle Ji\|AB\rangle t_{IJi}^{aAB}$

Table IV.4 (continued)

$\langle 0_i^A|$ projection (SP3)

1A		$+\sum_{\substack{a\\j}} \langle Ij \parallel Ba \rangle t_{iIj}^{ABa}$
1B		$+\sum_{\substack{a\\j}} \langle Jj \parallel Ba \rangle t_{iJj}^{ABa}$
1C		$+\frac{1}{2}\sum_{a,b} \langle IJ \parallel ab \rangle t_{iIJ}^{Aab}$
1D		$+\sum_{a} \langle IJ \parallel Ba \rangle t_{iIJ}^{ABa}$

$\langle 0_i^a|$ projection (SP4)

1A		$+\sum_{b} \langle IJ \parallel Ab \rangle t_{iIJ}^{aAb}$
1B		$+\sum_{b} \langle IJ \parallel Bb \rangle t_{iIJ}^{aBb}$
1C		$+\sum_{j} \langle Ij \parallel AB \rangle t_{iIj}^{aAB}$
1D		$+\sum_{j} \langle Jj \parallel AB \rangle t_{iJj}^{aAB}$
1E		$+\langle IJ \parallel AB \rangle t_{iIJ}^{aAB}$

Table IV.5

Coupled-cluster diagrams from the projection against a doubly excited determinant, representing single and double excitations from a second reference determinant which is doubly excited with respect to the formal reference.

$\langle 0_{IJ}^{AB}|$ projection (DP1)

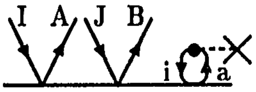
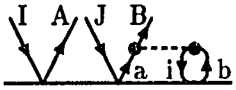
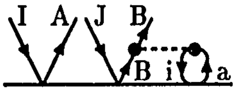
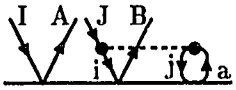
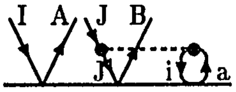
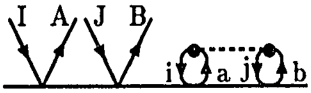
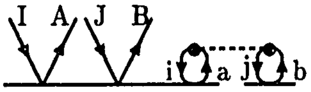
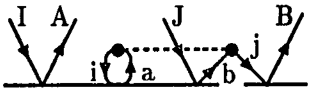
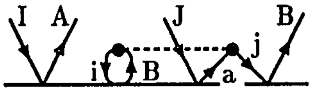
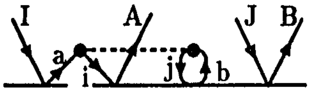
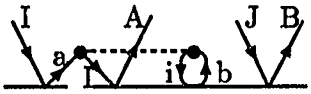
1A		$+\sum_{\substack{a\\i}} f_{ia} t_{IJi}^{ABa}$
2A		$+\frac{1}{2}\sum_{\substack{a,b\\i}}(-1)^P P(A/B)\langle Bi\|ab\rangle t_{IJi}^{Aab}$
2B		$+\sum_{\substack{a\\i}}(-1)^P P(A/B)\langle Bi\|Ba\rangle t_{IJi}^{ABa}$
3A		$-\frac{1}{2}\sum_{\substack{a\\i,j}}(-1)^P P(I/J)\langle ij\|Ja\rangle t_{Iij}^{ABa}$
3B		$-\sum_{\substack{a\\i}}(-1)^P P(I/J)\langle Ji\|Ja\rangle t_{IJi}^{ABa}$
4A		$+\frac{1}{4}\sum_{\substack{a,b\\i,j}}\langle ij\|ab\rangle t_{IJij}^{ABab}$
5A		$+\sum_{\substack{a,b\\i,j}}\langle ij\|ab\rangle t_{IJi}^{ABa} t_j^b$
6A		$-\frac{1}{2}\sum_{\substack{a,b\\i,j}}(-1)^P P(A/B)\langle ij\|ab\rangle t_{IiJ}^{Aab} t_j^B$
6B		$-\sum_{\substack{a\\i,j}}(-1)^P P(A/B)\langle ij\|Ba\rangle t_{IiJ}^{ABa} t_j^B$

Table IV.5 (continued)

7A		$-\frac{1}{2}\sum_{\substack{a,b\\i,j}}(-1)^P P(I/J)\langle ij \parallel ab\rangle t_{ijJ}^{AbB} t_I^a$
7B		$-\sum_{\substack{a,b\\i}}(-1)^P P(I/J)\langle Ii \parallel ab\rangle t_{IiJ}^{AbB} t_I^a$

$\langle 0_{IJ}^{Aa}|$ projection (DP2)

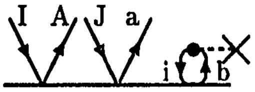
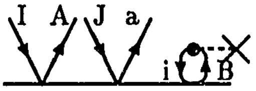
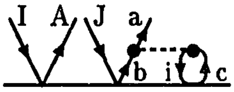
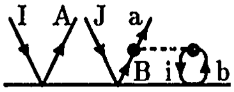
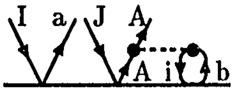
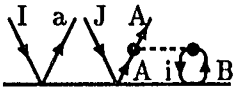
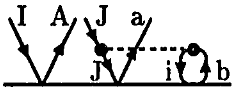
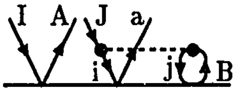
1A		$+\sum_{\substack{b\\i}} f_{ib} t_{IJi}^{Aab}$
1B		$+\sum_{i} f_{iB} t_{IJi}^{AaB}$
2A		$+\frac{1}{2}\sum_{\substack{b,c\\i}}\langle ai \parallel bc\rangle t_{IJi}^{Abc}$
2B		$+\sum_{\substack{b\\i}}(-1)^P P(A/a)\langle ai \parallel Bb\rangle t_{IJi}^{ABb}$
2C		$-\sum_{\substack{b\\i}}\langle Ai \parallel Ab\rangle t_{IJi}^{aAb}$
2D		$-\sum_{i}\langle Ai \parallel AB\rangle t_{IJi}^{aAB}$
3A		$-\sum_{\substack{b\\i}}(-1)^P P(I/J)\langle Ji \parallel Jb\rangle t_{IJi}^{Aab}$
3B		$-\frac{1}{2}\sum_{i,j}(-1)^P P(I/J)\langle ij \parallel JB\rangle t_{Iij}^{AaB}$

Table IV.5 (continued)

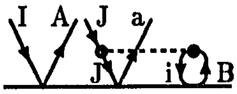
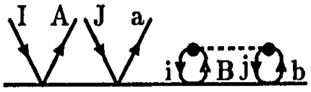
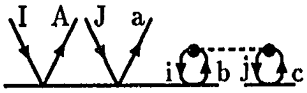
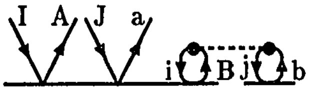
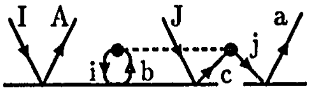
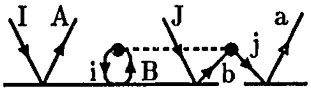
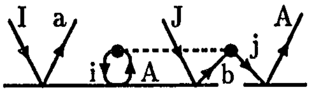
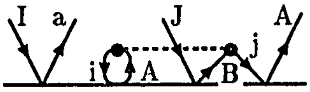
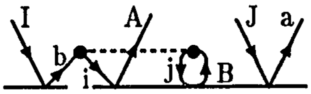
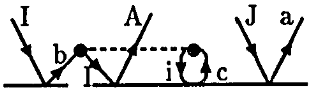
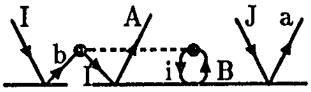
3C		$-\sum_{i}(-1)^{P}P(I/J)\langle Ji\,\Vert\,JB\rangle t_{IJi}^{AaB}$
4A		$+\frac{1}{2}\sum_{\substack{b\\i,j}}\langle ij\,\Vert\,Bb\rangle t_{IJij}^{AaBb}$
5A		$+\sum_{\substack{b,c\\i,j}}\langle ij\,\Vert\,bc\rangle t_{IJi}^{Aab}t_{j}^{c}$
5B		$+\sum_{\substack{b\\i,j}}\langle ij\,\Vert\,Bb\rangle t_{IJi}^{AaB}t_{j}^{b}$
6A		$-\frac{1}{2}\sum_{\substack{b,c\\i,j}}\langle ij\,\Vert\,bc\rangle t_{IiJ}^{Abc}t_{j}^{a}$
6B		$-\sum_{\substack{b\\i,j}}(-1)^{P}P(A/a)\langle ij\,\Vert\,Bb\rangle t_{IiJ}^{ABb}t_{j}^{a}$
6C		$+\sum_{\substack{b\\i,j}}\langle ij\,\Vert\,Ab\rangle t_{IiJ}^{aAb}t_{j}^{A}$
6D		$+\sum_{i,j}\langle ij\,\Vert\,AB\rangle t_{IiJ}^{aAB}t_{j}^{A}$
7A		$-\frac{1}{2}\sum_{\substack{b\\i,j}}(-1)^{P}P(I/J)\langle ij\,\Vert\,bB\rangle t_{ijJ}^{ABa}t_{I}^{b}$
7B		$-\sum_{\substack{b,c\\i}}(-1)^{P}P(I/J)\langle Ii\,\Vert\,bc\rangle t_{IiJ}^{Aca}t_{I}^{b}$
7C		$-\sum_{\substack{b\\i}}(-1)^{P}P(I/J)\langle Ii\,\Vert\,bB\rangle t_{IiJ}^{ABa}t_{I}^{b}$

Table IV.5 (continued)

$\langle 0_{Ii}^{AB}|$ projection (DP3)

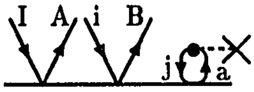
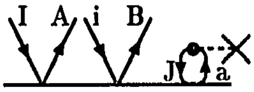
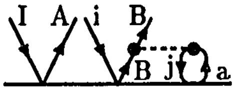
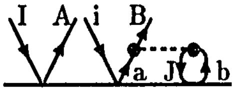
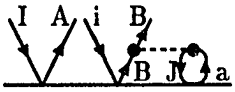
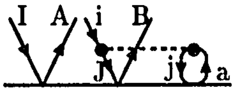
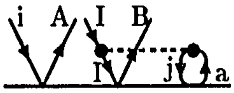
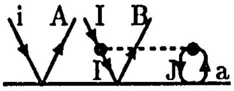
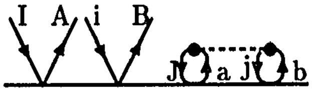
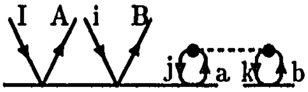
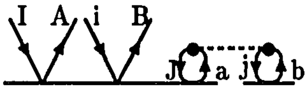
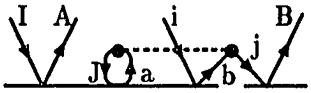
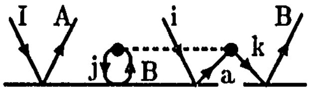
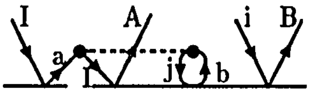
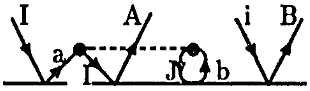
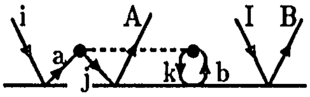
1A		$+\sum_{\substack{a\\j}} f_{ja} t_{Iij}^{ABa}$
1B		$+\sum_{a} f_{Ja} t_{IiJ}^{ABa}$
2A		$+\sum_{\substack{a\\j}}(-1)^P P(A/B)\langle Bj \parallel Ba\rangle t_{Iij}^{ABa}$
2B		$+\frac{1}{2}\sum_{a,b}(-1)^P P(A/B)\langle BJ \parallel ab\rangle t_{IiJ}^{Aab}$
2C		$+\sum_{a}(-1)^P P(A/B)\langle BJ \parallel Ba\rangle t_{IiJ}^{ABa}$
3A		$-\frac{1}{2}\sum_{\substack{a\\j,k}}\langle jk \parallel ia\rangle t_{Ijk}^{ABa}$
3B		$-\sum_{\substack{a\\j}}(-1)^P P(I/i)\langle Jj \parallel ia\rangle t_{IJj}^{ABa}$
3C		$+\sum_{\substack{a\\j}}\langle Ij \parallel Ia\rangle t_{iIj}^{ABa}$
3D		$+\sum_{a}\langle IJ \parallel Ia\rangle t_{iIJ}^{ABa}$
4A		$+\frac{1}{2}\sum_{\substack{a,b\\j}}\langle Jj \parallel ab\rangle t_{IiJj}^{ABab}$

Table IV.5 (continued)

5A		$+\sum_{\substack{a,b\\j,k}}\langle jk\Vert ab\rangle t_{Iij}^{ABa}t_k^b$
5B		$+\sum_{\substack{a,b\\j}}\langle Jj\Vert ab\rangle t_{IiJ}^{ABa}t_j^b$
6A		$-\frac{1}{2}\sum_{\substack{a,b\\j}}(-1)^P P(A/B)\langle Jj\Vert ab\rangle t_{IJi}^{Aab}t_j^B$
6B		$-\sum_{\substack{a\\j,k}}(-1)^P P(A/B)\langle jk\Vert Ba\rangle t_{Iji}^{ABa}t_k^B$
6C		$-\sum_{\substack{a\\j}}(-1)^P P(A/B)\langle Jj\Vert Ba\rangle t_{IJi}^{ABa}t_j^B$
7A		$-\sum_{\substack{a,b\\j}}(-1)^P P(I/i)\langle Jj\Vert ab\rangle t_{Jji}^{AbB}t_I^a$
7B		$-\sum_{\substack{a,b\\j}}\langle Ij\Vert ab\rangle t_{Iji}^{AbB}t_I^a$
7C		$-\sum_{a,b}\langle IJ\Vert ab\rangle t_{IJi}^{AbB}t_I^a$
7D		$+\frac{1}{2}\sum_{\substack{a,b\\j,k}}\langle jk\Vert ab\rangle t_{jkI}^{AbB}t_i^a$

$\langle 0_{IJ}^{ab}|$ projection (DP4)

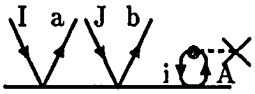
1A		$+\sum_{i} f_{iA}t_{IJi}^{abA}$

Table IV.5 (continued)

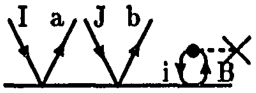
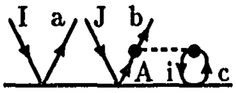
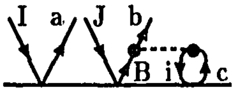
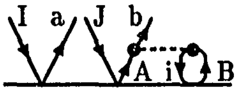
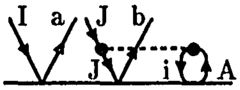
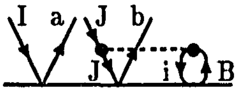
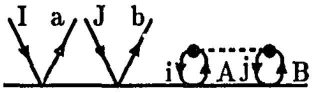
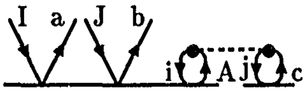
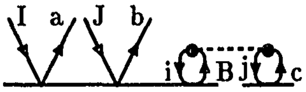
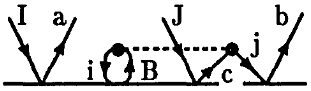
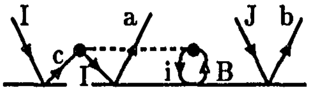
1B		$+\sum_{i} f_{iB} t_{IJi}^{abB}$
2A		$+\sum_{\substack{c\\i}}(-1)^P P(a/b)\langle bi \Vert Ac\rangle t_{IJi}^{aAc}$
2B		$+\sum_{\substack{c\\i}}(-1)^P P(a/b)\langle bi \Vert Bc\rangle t_{IJi}^{aBc}$
2C		$+\sum_{i}(-1)^P P(a/b)\langle bi \Vert AB\rangle t_{IJi}^{aAB}$
3A		$-\sum_{i}(-1)^P P(I/J)\langle Ji \Vert JA\rangle t_{IJi}^{abA}$
3B		$-\sum_{i}(-1)^P P(I/J)\langle Ji \Vert JB\rangle t_{IJi}^{abB}$
4A		$+\frac{1}{2}\sum_{i,j}\langle ij \Vert AB\rangle t_{IJij}^{abAB}$
5A		$+\sum_{\substack{c\\i,j}}\langle ij \Vert Ac\rangle t_{IJi}^{abA} t_j^c$
5B		$+\sum_{\substack{c\\i,j}}\langle ij \Vert Bc\rangle t_{IJi}^{abB} t_j^c$
6A		$-\sum_{\substack{c\\i,j}}(-1)^P P(a/b)\langle ij \Vert Ac\rangle t_{IiJ}^{aAc} t_j^b$
6B		$-\sum_{\substack{c\\i,j}}(-1)^P P(a/b)\langle ij \Vert Bc\rangle t_{IiJ}^{aBc} t_j^b$

Table IV.5 (continued)

6C		$-\sum_{i,j}(-1)^P P(a/b)\langle ij \| AB\rangle t_{IiJ}^{aAB} t_j^b$
7A		$-\sum_{\substack{c\\i}}(-1)^P P(I/J)\langle Ii \| cA\rangle t_{IiJ}^{aAb} t_I^c$
7B		$-\sum_{\substack{c\\i}}(-1)^P P(I/J)\langle Ii \| cB\rangle t_{IiJ}^{aBb} t_I^c$

$\langle 0_{ij}^{AB}|$ projection (DP5)

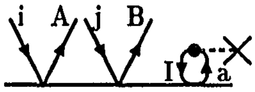
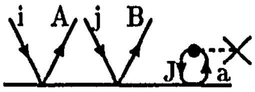
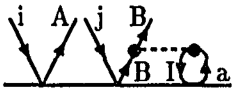
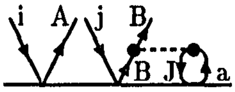
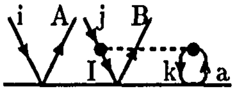
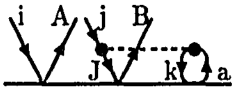
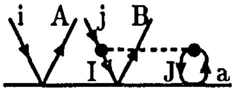
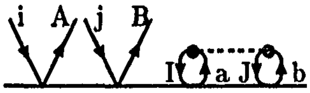
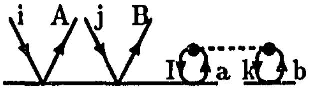
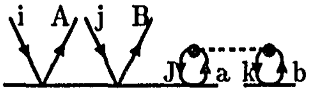
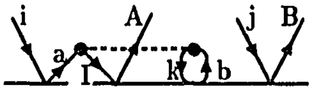
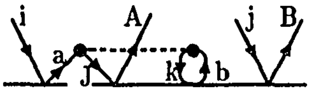
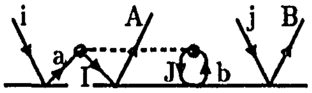
1A		$+\sum_a f_{Ia} t_{ijI}^{ABa}$
1B		$+\sum_a f_{Ja} t_{ijJ}^{ABa}$
2A		$+\sum_a(-1)^P P(A/B)\langle BI \| Ba\rangle t_{ijI}^{ABa}$
2B		$+\sum_a(-1)^P P(A/B)\langle BJ \| Ba\rangle t_{ijJ}^{ABa}$
3A		$-\sum_{\substack{a\\k}}(-1)^P P(i/j)\langle Ik \| ja\rangle t_{iIk}^{ABa}$
3B		$-\sum_{\substack{a\\k}}(-1)^P P(i/j)\langle Jk \| ja\rangle t_{iJk}^{ABa}$
3C		$-\sum_a(-1)^P P(i/j)\langle IJ \| ja\rangle t_{iIJ}^{ABa}$

Table IV.5 (continued)

4A		$+\frac{1}{2}\sum_{a,b}\langle IJ\|ab\rangle t_{ijIJ}^{ABab}$
5A		$+\sum_{\substack{a,b\\k}}\langle Ik\|ab\rangle t_{ijI}^{ABa}t_k^b$
5B		$+\sum_{\substack{a,b\\k}}\langle Jk\|ab\rangle t_{ijJ}^{ABa}t_k^b$
6A		$-\sum_{\substack{a\\k}}(-1)^P P(A/B)\langle Ik\|Ba\rangle t_{iIj}^{ABa}t_k^B$
6B		$-\sum_{\substack{a\\k}}(-1)^P P(A/B)\langle Jk\|Ba\rangle t_{iJj}^{ABa}t_k^B$
7A		$-\sum_{\substack{a,b\\k}}(-1)^P P(i/j)\langle Ik\|ab\rangle t_{Ikj}^{AbB}t_i^a$
7B		$-\sum_{\substack{a,b\\k}}(-1)^P P(i/j)\langle Jk\|ab\rangle t_{Jkj}^{AbB}t_i^a$
7C		$-\sum_{a,b}(-1)^P P(i/j)\langle IJ\|ab\rangle t_{IJj}^{AbB}t_i^a$

$\langle 0_{Ii}^{Aa}|$ projection (DP6)

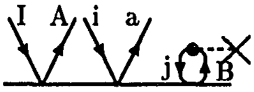
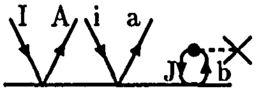
1A		$+\sum_{j} f_{jB}t_{Iij}^{AaB}$
1B		$+\sum_{b} f_{Jb}t_{IiJ}^{Aab}$

Table IV.5 (continued)

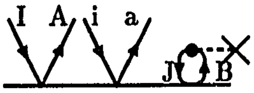
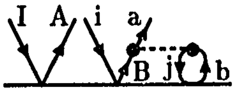
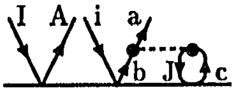
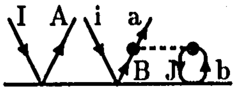
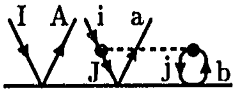
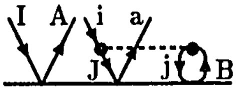
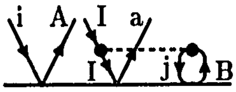
1C		$+f_{JB}t_{IiJ}^{AaB}$
2A		$+\sum_{\substack{b\\j}}\langle aj\\|Bb\rangle t_{Iij}^{ABb}$
2B		$+\frac{1}{2}\sum_{b,c}\langle aJ\\|bc\rangle t_{IiJ}^{Abc}$
2C		$+\sum_{b}(-1)^P P(A/a)\langle aJ\\|Bb\rangle t_{IiJ}^{ABb}$
2D		$-\sum_{b}\langle AJ\\|Ab\rangle t_{IiJ}^{aAb}$
2E		$-\sum_{j}\langle Aj\\|AB\rangle t_{Iij}^{aAB}$
2F		$-\langle AJ\\|AB\rangle t_{IiJ}^{aAB}$
3A		$-\sum_{\substack{b\\j}}\langle Jj\\|ib\rangle t_{IJj}^{Aab}$
3B		$-\frac{1}{2}\sum_{j,k}\langle jk\\|iB\rangle t_{Ijk}^{AaB}$
3C		$-\sum_{j}(-1)^P P(I/i)\langle Jj\\|iB\rangle t_{IJj}^{AaB}$
3D		$+\sum_{j}\langle Ij\\|IB\rangle t_{iIj}^{AaB}$

Table IV.5 (continued)

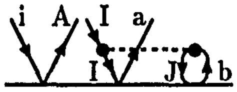
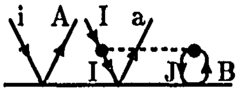
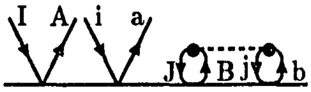
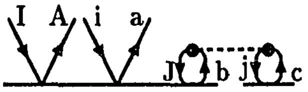
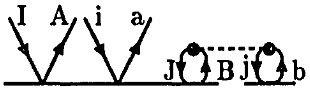
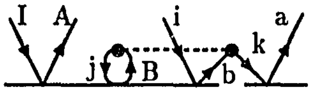
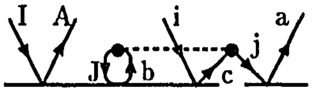
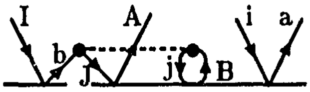
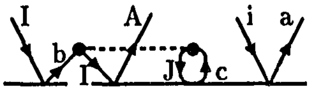
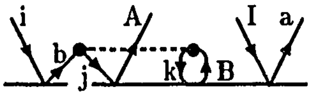
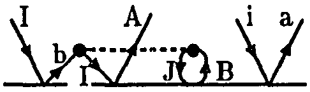
3E		$+\sum_{b}\langle IJ \Vert Ib\rangle t_{iIJ}^{Aab}$
3F		$+\langle IJ \Vert IB\rangle t_{iIJ}^{AaB}$
4A		$+\sum_{\substack{b\\ j}}\langle Jj \Vert Bb\rangle t_{IiJj}^{AaBb}$
5A		$+\sum_{\substack{b\\ j,k}}\langle jk \Vert Bb\rangle t_{Iij}^{AaB} t_{k}^{b}$
5B		$+\sum_{\substack{b,c\\ j}}\langle Jj \Vert bc\rangle t_{IiJ}^{Aab} t_{j}^{c}$
5C		$+\sum_{\substack{b\\ j}}\langle Jj \Vert Bb\rangle t_{IiJ}^{AaB} t_{j}^{b}$
6A		$-\sum_{\substack{b\\ j,k}}\langle jk \Vert Bb\rangle t_{Iji}^{ABb} t_{k}^{a}$
6B		$-\frac{1}{2}\sum_{\substack{b,c\\ j}}\langle Jj \Vert bc\rangle t_{IJi}^{Abc} t_{j}^{a}$
6C		$-\sum_{\substack{b\\ j}}(-1)^{P} P(A/a)\langle Jj \Vert Bb\rangle t_{IJi}^{ABb} t_{j}^{a}$
6D		$+\sum_{\substack{b\\ j}}\langle Jj \Vert Ab\rangle t_{IJi}^{aAb} t_{j}^{A}$
6E		$+\sum_{j,k}\langle jk \Vert AB\rangle t_{Iji}^{aAB} t_{k}^{A}$

Table IV.5 (continued)

6F		$+\sum_{j}\langle Jj \parallel AB\rangle t_{IJi}^{aAB} t_{j}^{A}$
7A		$-\sum_{\substack{b\\j}}(-1)^{P} P(I/i)\langle Jj \parallel bB\rangle t_{Jji}^{ABa} t_{I}^{b}$
7B		$-\sum_{\substack{b\\j}}\langle Ij \parallel bB\rangle t_{Iji}^{ABa} t_{I}^{b}$
7C		$-\sum_{b,c}\langle IJ \parallel bc\rangle t_{IJi}^{Aca} t_{I}^{b}$
7D		$+\sum_{\substack{b,c\\j}}\langle Jj \parallel bc\rangle t_{JjI}^{Aca} t_{i}^{b}$
7E		$+\frac{1}{2}\sum_{\substack{b\\j,k}}\langle jk \parallel bB\rangle t_{jkI}^{ABa} t_{i}^{b}$
7F		$-\sum_{b}\langle IJ \parallel bB\rangle t_{IJi}^{ABa} t_{I}^{b}$

$\langle 0_{Ii}^{ab}|$ projection (DP7)

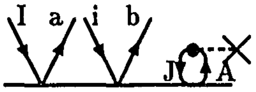
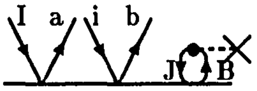
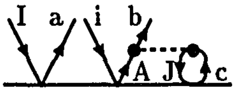
1A		$+f_{JA} t_{IiJ}^{abA}$
1B		$+f_{JB} t_{IiJ}^{abB}$
2A		$+\sum_{c}(-1)^{P} P(a/b)\langle bJ \parallel Ac\rangle t_{IiJ}^{aAc}$

Table IV.5 (continued)

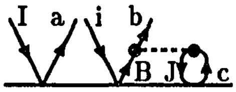
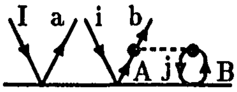
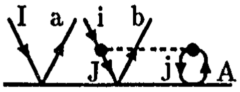
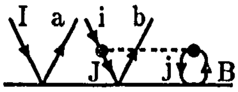
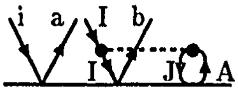
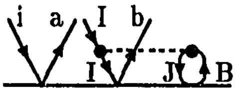
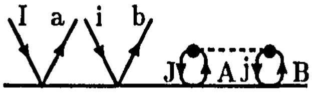
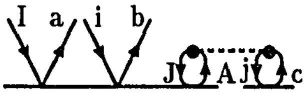
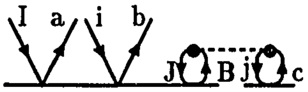
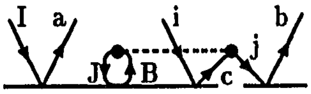
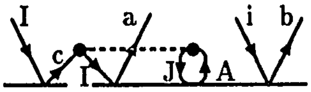
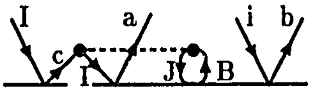
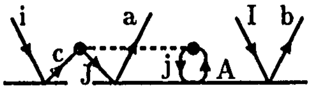
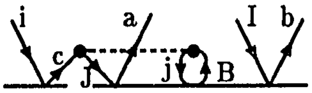
2B		$+\sum_{c}(-1)^{P}P(a/b)\langle bJ\,\|\,Bc\rangle t_{IiJ}^{aBc}$
2C		$+\sum_{j}(-1)^{P}P(a/b)\langle bj\,\|\,AB\rangle t_{Iij}^{aAB}$
2D		$+(-1)^{P}P(a/b)\langle bJ\,\|\,AB\rangle t_{IiJ}^{aAB}$
3A		$-\sum_{j}\langle Jj\,\|\,iA\rangle t_{IJj}^{abA}$
3B		$-\sum_{j}\langle Jj\,\|\,iB\rangle t_{IJj}^{abB}$
3C		$+\langle IJ\,\|\,IA\rangle t_{iIJ}^{abA}$
3D		$+\langle IJ\,\|\,IB\rangle t_{iIJ}^{abB}$
4A		$+\sum_{j}\langle Jj\,\|\,AB\rangle t_{IiJj}^{abAB}$
5A		$+\sum_{\substack{c\\j}}\langle Jj\,\|\,Ac\rangle t_{IiJ}^{abA}t_{j}^{c}$
5B		$+\sum_{\substack{c\\j}}\langle Jj\,\|\,Bc\rangle t_{IiJ}^{abB}t_{j}^{c}$
6A		$-\sum_{\substack{c\\j}}(-1)^{P}P(a/b)\langle Jj\,\|\,Ac\rangle t_{IJi}^{aAc}t_{j}^{b}$

Table IV.5 (continued)

6B		$-\sum_{\substack{c\\j}}(-1)^P P(a/b)\langle Jj\parallel Bc\rangle t_{IJi}^{aBc}t_j^b$
6C		$-\sum_{j,k}(-1)^P P(a/b)\langle jk\parallel AB\rangle t_{Iji}^{aAB}t_k^b$
6D		$-\sum_{j}(-1)^P P(a/b)\langle Jj\parallel AB\rangle t_{IJi}^{aAB}t_j^b$
7A		$-\sum_{c}\langle IJ\parallel cA\rangle t_{IJi}^{aAb}t_I^c$
7B		$-\sum_{c}\langle IJ\parallel cB\rangle t_{IJi}^{aBb}t_I^c$
7C		$+\sum_{\substack{c\\j}}\langle Jj\parallel cA\rangle t_{JjI}^{aAb}t_i^c$
7D		$+\sum_{\substack{c\\j}}\langle Jj\parallel cB\rangle t_{JjI}^{aBb}t_i^c$

$\langle 0_{ij}^{Aa}|$ projection (DP8)

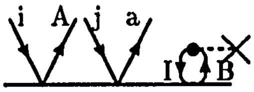
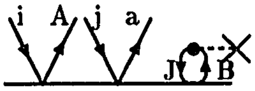
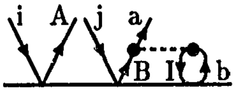
1A		$+f_{IB}t_{ijI}^{AaB}$
1B		$+f_{JB}t_{ijJ}^{AaB}$
2A		$+\sum_{b}\langle aI\parallel Bb\rangle t_{ijI}^{ABb}$

Table IV.5 (continued)

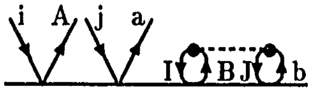
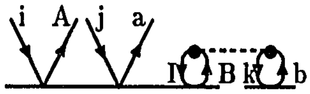
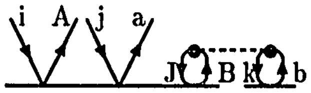
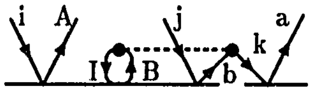
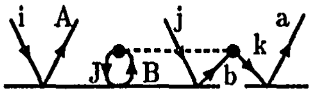
2B		$+\sum_{b}\langle aJ\,\Vert\, Bb\rangle t_{ijJ}^{ABb}$
2C		$-\langle AI\,\Vert\, AB\rangle t_{ijI}^{aAB}$
2D		$-\langle AJ\,\Vert\, AB\rangle t_{ijJ}^{aAB}$
3A		$-\sum_{k}(-1)^{P}P(i/j)\langle Ik\,\Vert\, jB\rangle t_{iIk}^{AaB}$
3B		$-\sum_{k}(-1)^{P}P(i/j)\langle Jk\,\Vert\, jB\rangle t_{iJk}^{AaB}$
3C		$-\sum_{b}(-1)^{P}P(i/j)\langle IJ\,\Vert\, jb\rangle t_{iIJ}^{Aab}$
3D		$-(-1)^{P}P(i/j)\langle IJ\,\Vert\, jB\rangle t_{iIJ}^{AaB}$
4A		$+\sum_{b}\langle IJ\,\Vert\, Bb\rangle t_{ijIJ}^{AaBb}$
5A		$+\sum_{\substack{b\\k}}\langle Ik\,\Vert\, Bb\rangle t_{ijI}^{AaB}t_{k}^{b}$
5B		$+\sum_{\substack{b\\k}}\langle Jk\,\Vert\, Bb\rangle t_{ijJ}^{AaB}t_{k}^{b}$
6A		$-\sum_{\substack{b\\k}}\langle Ik\,\Vert\, Bb\rangle t_{iIj}^{ABb}t_{k}^{a}$

Table IV.5 (continued)

6B



$$-\sum_{\substack{b\\k}}\langle Jk\,\|\,Bb\rangle t_{iJj}^{ABb}t_k^a$$

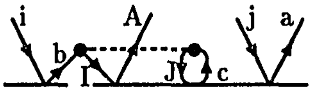
6C

$$+\sum_{k}\langle Ik\,\|\,AB\rangle t_{iIj}^{aAB}t_k^A$$

6D

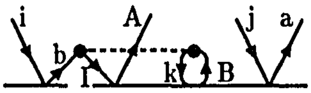
$$+\sum_{k}\langle Jk\,\|\,AB\rangle t_{iJj}^{aAB}t_k^A$$

7A



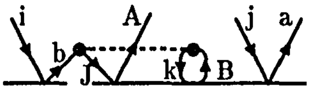
$$-\sum_{b,c}(-1)^P P(i/j)\langle IJ\,\|\,bc\rangle t_{IJj}^{Aca}t_i^b$$

7B



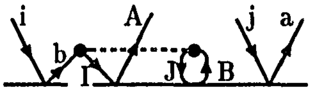
$$-\sum_{\substack{b\\k}}(-1)^P P(i/j)\langle Ik\,\|\,bB\rangle t_{Ikj}^{ABa}t_i^b$$

7C



$$-\sum_{\substack{b\\k}}(-1)^P P(i/j)\langle Jk\,\|\,bB\rangle t_{Jkj}^{ABa}t_i^b$$

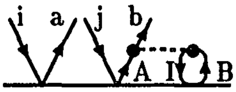
7D



$$-\sum_{b}(-1)^P P(i/j)\langle IJ\,\|\,bB\rangle t_{IJj}^{ABa}t_i^b$$

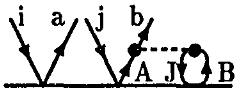
$\langle 0_{ij}^{ab}|$ projection (DP9)

2A



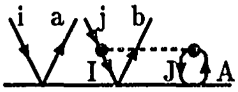
$$+\langle bI\,\|\,AB\rangle t_{ijI}^{aAB}$$

2B



$$+\langle bJ\,\|\,AB\rangle t_{ijJ}^{aAB}$$

3A



$$-(-1)^P P(i/j)\langle IJ\,\|\,jA\rangle t_{iIJ}^{abA}$$

Table IV.5 (continued)

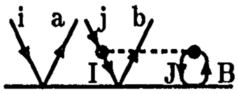
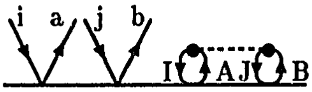
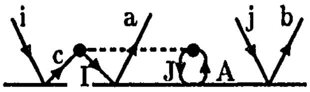
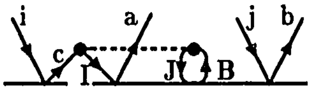
3B		$-(-1)^P P(i/j)\langle IJ \| jB\rangle t_{iIJ}^{abB}$
4A		$+\langle IJ \| AB\rangle t_{ijIJ}^{abAB}$
6A		$-\sum_{k}(-1)^P P(a/b)\langle Ik \| AB\rangle t_{iIj}^{aAB} t_k^b$
6B		$-\sum_{k}(-1)^P P(a/b)\langle Jk \| AB\rangle t_{iJj}^{aAB} t_k^b$
7A		$-\sum_{c}(-1)^P P(i/j)\langle IJ \| cA\rangle t_{IJj}^{aAb} t_i^c$
7B		$-\sum_{c}(-1)^P P(i/j)\langle IJ \| cB\rangle t_{IJj}^{aBb} t_i^c$

Table IV.6

Coupled-cluster diagrams from the projection against a triply excited determinant, representing single and double excitations from a second reference determinant which is doubly excited with respect to the formal reference.

$\langle 0^{ABa}_{IJi}|$ projection (TP1)

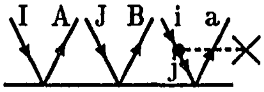
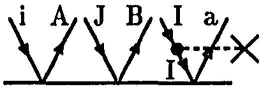
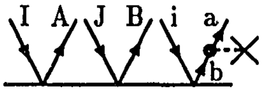
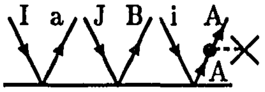
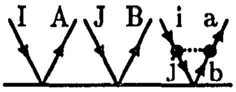
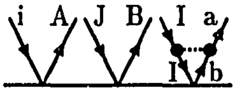
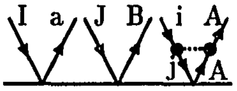
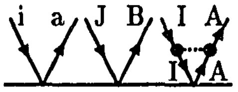
1A		$-\sum_{j}(-1)^P P(i/IJ) f_{ji} t^{ABa}_{IJj}$
1B		$+(-1)^P P(I/J) f_{II} t^{ABa}_{iJI}$
2A		$+\sum_{b}(-1)^P P(AB/a) f_{ab} t^{ABb}_{IJi}$
2B		$-(-1)^P P(A/B) f_{AA} t^{aBA}_{IJi}$
3A		$-\sum_{\substack{b\\j}}(-1)^P P(IJ/i \,\Vert\, AB/a)\langle ja \Vert ib\rangle t^{ABb}_{IJj}$
3B		$+\sum_{b}(-1)^P P(I/J \,\vert\, AB/a)\langle Ia \Vert Ib\rangle t^{ABb}_{iJI}$
3C		$+\sum_{j}(-1)^P P(IJ/i \,\vert\, A/B)\langle jA \Vert iA\rangle t^{aBA}_{IJj}$
3D		$-(-1)^P P(I/J \,\vert\, A/B)\langle IA \Vert IA\rangle t^{aBA}_{iJI}$
4A		$+\frac{1}{2}\sum_{j,k}(-1)^P P(I/J)\langle jk \Vert Ji\rangle t^{ABa}_{Ijk}$

Table IV.6 (continued)

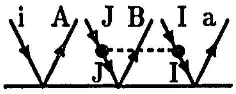
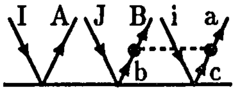
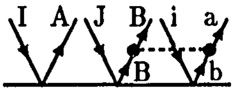
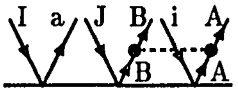
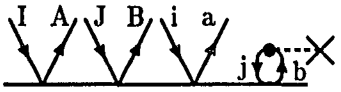
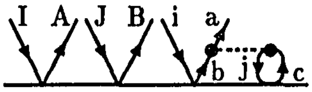
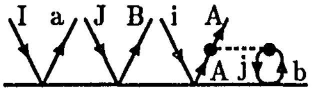
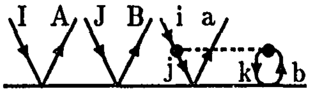
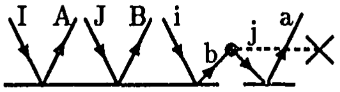
4B		$+\sum_{j}(-1)^P P(I/i(I/J))\langle Jj \Vert Ji\rangle t_{IJj}^{ABa}$
4C		$-\langle JI \Vert JI\rangle t_{iJI}^{ABa}$
5A		$+\frac{1}{2}\sum_{b,c}(-1)^P P(A/B)\langle Ba \Vert bc\rangle t_{IJi}^{Abc}$
5B		$+\sum_{b}(-1)^P P(A/a(A/B))\langle Ba \Vert Bb\rangle t_{IJi}^{ABb}$
5C		$-\langle BA \Vert BA\rangle t_{IJi}^{aBA}$
6A		$+\sum_{\substack{b\\j}} f_{jb} t_{IJij}^{ABab}$
7A		$+\frac{1}{2}\sum_{\substack{b,c\\j}}\langle aj \Vert bc\rangle t_{IJij}^{ABbc}$
7B		$-\sum_{\substack{b\\j}}(-1)^P P(A/B)\langle Aj \Vert Ab\rangle t_{IJij}^{aBAb}$
8A		$-\frac{1}{2}\sum_{\substack{b\\j,k}}\langle jk \Vert ib\rangle t_{IJjk}^{ABab}$
8B		$+\sum_{\substack{b\\j}}(-1)^P P(I/J)\langle Ij \Vert Ib\rangle t_{iJIj}^{ABab}$
9A		$-\sum_{\substack{b\\j}}(-1)^P P(AB/a) f_{jb} t_{IJi}^{ABb} t_j^a$

Table IV.6 (continued)

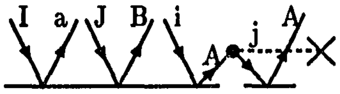
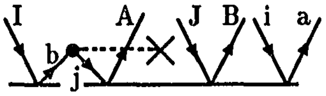
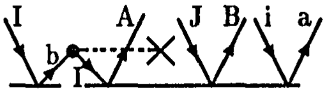
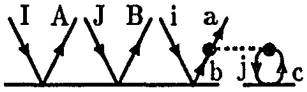
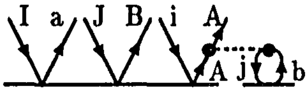
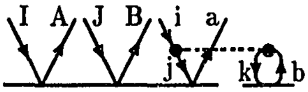
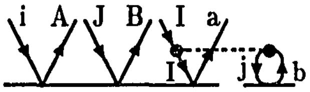
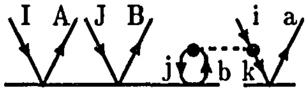
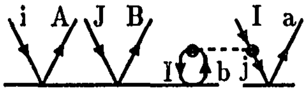
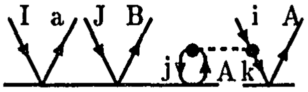
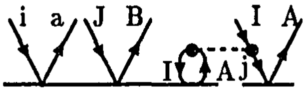
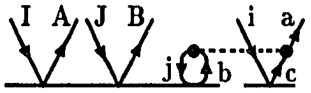
9B		$+\sum_{j}(-1)^P P(A/B) f_{jA} t_{IJi}^{aBA} t_{j}^{A}$
10A		$-\sum_{\substack{b\\j}}(-1)^P P(I/Ji) f_{jb} t_{jJi}^{ABa} t_{I}^{b}$
10B		$-\sum_{b}(-1)^P P(I/J) f_{Ib} t_{IJi}^{ABa} t_{I}^{b}$
11A		$+\sum_{\substack{b,c\\j}}(-1)^P P(AB/a) \langle aj \parallel bc\rangle t_{IJi}^{ABb} t_{j}^{c}$
11B		$-\sum_{\substack{b\\j}}(-1)^P P(A/B) \langle Aj \parallel Ab\rangle t_{IJi}^{aBA} t_{j}^{b}$
12A		$-\sum_{\substack{b\\j,k}}(-1)^P P(IJ/i) \langle jk \parallel ib\rangle t_{IJj}^{ABa} t_{k}^{b}$
12B		$+\sum_{\substack{b\\j}}(-1)^P P(I/J) \langle Ij \parallel Ib\rangle t_{iJI}^{ABa} t_{j}^{b}$
13A		$-\sum_{\substack{b\\j,k}}(-1)^P P(IJ/i \parallel AB/a) \langle jk \parallel bi\rangle t_{IJj}^{ABb} t_{k}^{a}$
13B		$+\sum_{\substack{b\\j}}(-1)^P P(I/J \mid AB/a) \langle Ij \parallel bI\rangle t_{iJI}^{ABb} t_{j}^{a}$
13C		$+\sum_{j,k}(-1)^P P(IJ/i \mid A/B) \langle jk \parallel Ai\rangle t_{IJj}^{aBA} t_{k}^{A}$
13D		$-\sum_{j}(-1)^P P(I/J \mid A/B) \langle Ij \parallel AI\rangle t_{iJI}^{aBA} t_{j}^{A}$

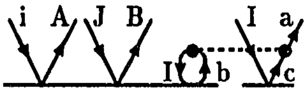
Table IV.6 (continued)

14A



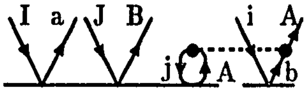
$$+\sum_{\substack{b,c\\j}}(-1)^P P(IJ/i\,\|\,AB/a)\langle ja\,\|\,bc\rangle t_{IJj}^{ABb}t_i^c$$

14B



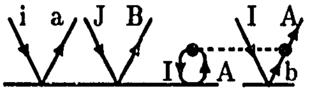
$$-\sum_{b,c}(-1)^P P(I/J\,|\,AB/a)\langle Ia\,\|\,bc\rangle t_{iJI}^{ABb}t_I^c$$

14C



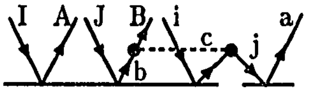
$$-\sum_{\substack{b\\j}}(-1)^P P(IJ/i\,|\,A/B)\langle jA\,\|\,Ab\rangle t_{IJj}^{aBA}t_i^b$$

14D



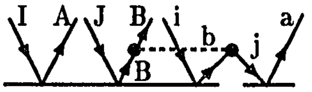
$$+\sum_{b}(-1)^P P(I/J\,|\,A/B)\langle IA\,\|\,Ab\rangle t_{iJI}^{aBA}t_I^b$$

15A



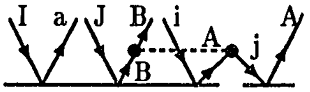
$$-\tfrac{1}{2}\sum_{\substack{b,c\\j}}(-1)^P P(B/a(A/B))\langle Bj\,\|\,bc\rangle t_{IJi}^{Abc}t_j^a$$

15B



$$-\sum_{\substack{b\\j}}(-1)^P P(AB/a(A/B))\langle Bj\,\|\,Bb\rangle t_{IJi}^{ABb}t_j^a$$

15C

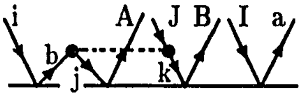


$$+\sum_{j}(-1)^P P(A/B)\langle Bj\,\|\,BA\rangle t_{IJi}^{aBA}t_j^A$$

16A

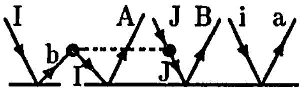
$$+\sum_{\substack{b\\j}}(-1)^P P(I/Ji(I/J))\langle jJ\,\|\,bJ\rangle t_{jJi}^{ABa}t_I^b$$

16B



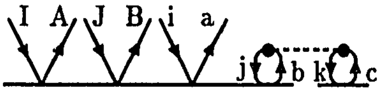
$$-\tfrac{1}{2}\sum_{\substack{b\\j,k}}(-1)^P P(i/J(I/J))\langle jk\,\|\,bJ\rangle t_{jkI}^{ABa}t_i^b$$

16C



$$+\sum_{b}(-1)^P P(I/J)\langle IJ\,\|\,bJ\rangle t_{IJi}^{ABa}t_I^b$$

17A



$$+\sum_{\substack{b,c\\j,k}}\langle jk\,\|\,bc\rangle t_{IJij}^{ABab}t_k^c$$

Table IV.6 (continued)

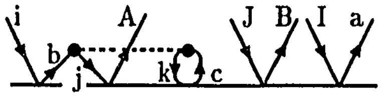
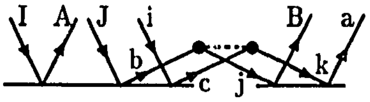
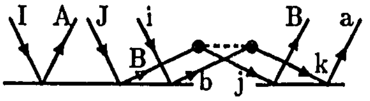
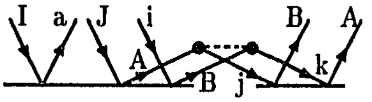
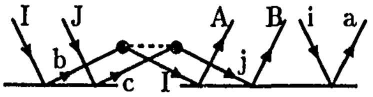
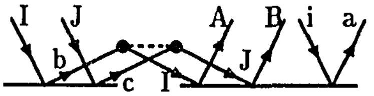
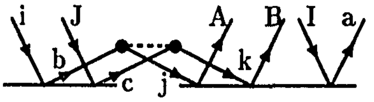
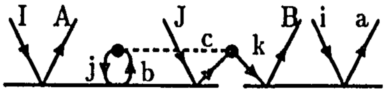
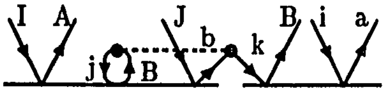
18A		$-\frac{1}{2}\sum_{\substack{b,c\\j,k}}\langle jk\Vert bc\rangle t_{IJji}^{ABbc}t_k^a$
18B		$+\sum_{\substack{b\\j,k}}(-1)^P P(A/B)\langle jk\Vert Ab\rangle t_{IJji}^{aBAb}t_k^A$
19A		$-\sum_{\substack{b,c\\j}}(-1)^P P(I/J)\langle Ij\Vert bc\rangle t_{IjJi}^{AcBa}t_I^b$
19B		$+\frac{1}{2}\sum_{\substack{b,c\\j,k}}\langle jk\Vert bc\rangle t_{jkJI}^{AcBa}t_i^b$
20A		$+\frac{1}{4}\sum_{\substack{b,c\\j,k}}(-1)^P P(A/B)\langle jk\Vert bc\rangle t_{IJi}^{Abc}t_{jk}^{Ba}$
20B		$+\frac{1}{2}\sum_{\substack{b\\j,k}}(-1)^P P(A/a(A/B))\langle jk\Vert Bb\rangle t_{IJi}^{ABb}t_{jk}^{Ba}$
20C		$-\frac{1}{2}\sum_{j,k}\langle jk\Vert AB\rangle t_{IJi}^{aAB}t_{jk}^{BA}$
21A		$+\frac{1}{2}\sum_{\substack{b,c\\j}}(-1)^P P(J/i(I/J))\langle Ij\Vert bc\rangle t_{Iji}^{ABa}t_{IJ}^{bc}$
21B		$+\frac{1}{2}\sum_{b,c}\langle IJ\Vert bc\rangle t_{IJi}^{ABa}t_{IJ}^{bc}$
21C		$-\frac{1}{4}\sum_{\substack{b,c\\j,k}}(-1)^P P(I/J)\langle jk\Vert bc\rangle t_{jkI}^{ABa}t_{iJ}^{bc}$
22A		$-\frac{1}{2}\sum_{\substack{b,c\\j,k}}(-1)^P P(A/B)\langle jk\Vert bc\rangle t_{IjJ}^{Abc}t_{ki}^{Ba}$

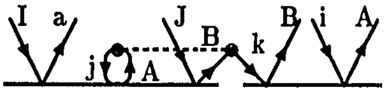
Table IV.6 (continued)

22B



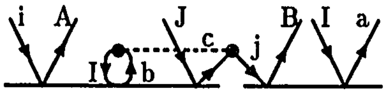
$$-\sum_{\substack{b\\j,k}}(-1)^P P(IJ/i\,\|\,A/a(A/B))\langle jk\,\|\,Bb\rangle t_{IjJ}^{ABb}t_{ki}^{Ba}$$

22C



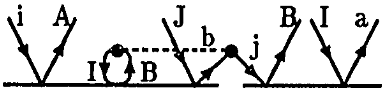
$$+\sum_{j,k}(-1)^P P(IJ/i)\langle jk\,\|\,AB\rangle t_{IjJ}^{aAB}t_{ki}^{BA}$$

22D



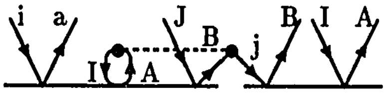
$$+\tfrac{1}{2}\sum_{\substack{b,c\\j}}(-1)^P P(A/B\,|\,(I/J))\langle Ij\,\|\,bc\rangle t_{iIJ}^{Abc}t_{jI}^{Ba}$$

22E



$$+\sum_{\substack{b\\j}}(-1)^P P(A/a(A/B)\,|\,(I/J))\langle Ij\,\|\,Bb\rangle t_{iIJ}^{ABb}t_{jI}^{Ba}$$

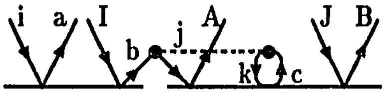
22F



$$-\sum_{j}(-1)^P P(I/J)\langle Ij\,\|\,AB\rangle t_{iIJ}^{aAB}t_{jI}^{BA}$$

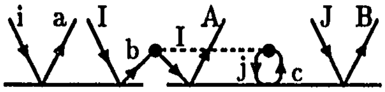
Table IV.6 (continued)

23A



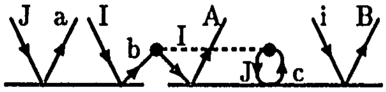
$$-\tfrac{1}{2}\sum_{\substack{b,c\\ j,k}}(-1)^P P(I/J)\langle jk\,\|\,bc\rangle t_{jkJ}^{AcB}t_{iI}^{ab}$$

23B



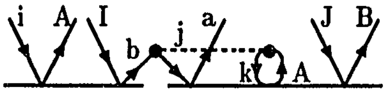
$$-\sum_{\substack{b,c\\ j}}(-1)^P P(i/J(I/J)\,\|\,a/AB)\langle Ij\,\|\,bc\rangle t_{IjJ}^{AcB}t_{iI}^{ab}$$

23C



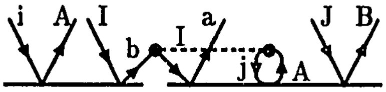
$$+\sum_{b,c}(-1)^P P(a/AB)\langle IJ\,\|\,bc\rangle t_{IJi}^{AcB}t_{JI}^{ab}$$

23D



$$+\tfrac{1}{2}\sum_{\substack{b\\ j,k}}(-1)^P P((A/B)\,|\,I/J)\langle jk\,\|\,bA\rangle t_{jkJ}^{aAB}t_{iI}^{Ab}$$

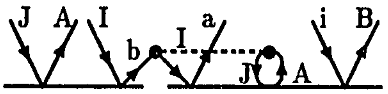
23E



$$+\sum_{\substack{b\\ j}}(-1)^P P((A/B)\,|\,i/J(I/J))\langle Ij\,\|\,bA\rangle t_{IjJ}^{aAB}t_{iI}^{Ab}$$

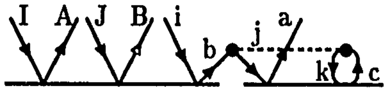
Table IV.6 (continued)

23F



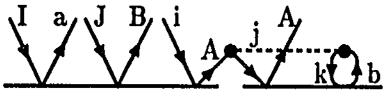
$$-\sum_{b}(-1)^P P(A/B)\langle IJ\|bA\rangle t_{IJi}^{aAB}t_{JI}^{Ab}$$

24A



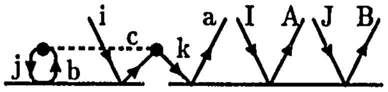
$$-\frac{1}{2}\sum_{\substack{b,c\\ j,k}}(-1)^P P(AB/a)\langle jk\|bc\rangle t_{IJi}^{ABb}t_{jk}^{ac}$$

24B



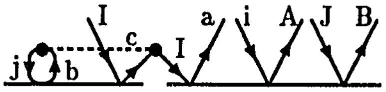
$$+\frac{1}{2}\sum_{\substack{b\\ j,k}}(-1)^P P(A/B)\langle jk\|Ab\rangle t_{IJi}^{aBA}t_{jk}^{Ab}$$

25A



$$-\frac{1}{2}\sum_{\substack{b,c\\ j,k}}(-1)^P P(i/IJ)\langle jk\|bc\rangle t_{kIJ}^{aAB}t_{ji}^{bc}$$

25B



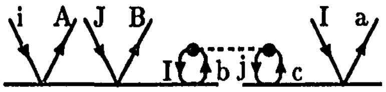
$$+\frac{1}{2}\sum_{\substack{b,c\\ j}}(-1)^P P(I/J)\langle jI\|bc\rangle t_{IiJ}^{aAB}t_{jI}^{bc}$$

Table IV.6 (continued)

26A

$$+\sum_{\substack{b,c\\j,k}}(-1)^P P(AB/a\,\|\,IJ/i)\langle jk\,\|\,bc\rangle t_{IJj}^{ABb}t_{ki}^{ca}$$

26B



$$-\sum_{\substack{b,c\\j}}(-1)^P P(AB/a\,|\,(I/J))\langle Ij\,\|\,bc\rangle t_{iJI}^{ABb}t_{jI}^{ca}$$

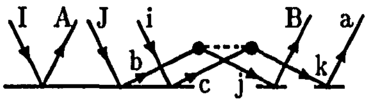
26C

$$-\sum_{\substack{b\\j,k}}(-1)^P P((A/B)\,|\,IJ/i)\langle jk\,\|\,Ab\rangle t_{IJj}^{aBA}t_{ki}^{bA}$$

26D

$$+\sum_{\substack{b\\j}}(-1)^P P((A/B)\,|\,(I/J))\langle Ij\,\|\,Ab\rangle t_{iJI}^{aBA}t_{jI}^{bA}$$

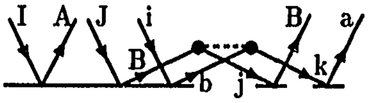
27A



$$+\tfrac{1}{2}\sum_{\substack{b,c\\j,k}}(-1)^P P(A/B)\langle jk\,\|\,bc\rangle t_{IJi}^{Abc}t_j^B t_k^a$$

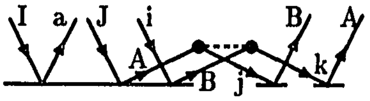
Table IV.6 (continued)

27B



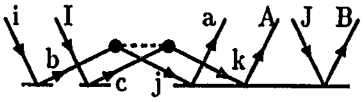
$$+\sum_{\substack{b\\j,k}}(-1)^P P(A/a(A/B))\langle jk\|Bb\rangle t_{IJi}^{ABb} t_j^B t_k^a$$

27C



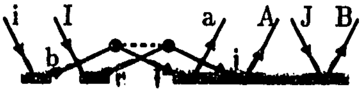
$$-\sum_{j,k}\langle jk\|AB\rangle t_{IJi}^{aAB} t_j^B t_k^A$$

28A



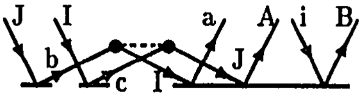
$$+\frac{1}{2}\sum_{\substack{b,c\\j,k}}(-1)^P P(I/J)\langle jk\|bc\rangle t_{jkJ}^{aAB} t_i^b t_I^c$$

28B



$$+\sum_{\substack{b,c\\j}}(-1)^P P(J/i(J/I))\langle Ij\|bc\rangle t_{IjJ}^{aAB} t_i^b t_I^c$$

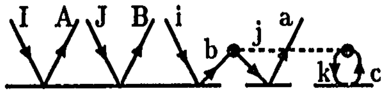
28C



$$-\sum_{b,c}\langle IJ\|bc\rangle t_{IJi}^{aAB} t_J^b t_I^c$$

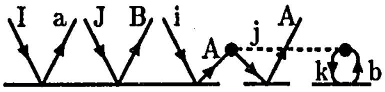
Table IV.6 (continued)

29A



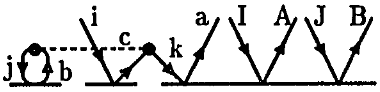
$$-\sum_{\substack{b,c\\j,k}}(-1)^P P(AB/a)\langle jk\|bc\rangle t_{IJi}^{ABb}t_j^a t_k^c$$

29B



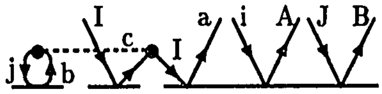
$$+\sum_{\substack{b\\j,k}}(-1)^P P(A/B)\langle jk\|Ab\rangle t_{IJi}^{aBA}t_j^A t_k^b$$

30A



$$-\sum_{\substack{b,c\\j,k}}(-1)^P P(i/IJ)\langle jk\|bc\rangle t_{kIJ}^{aAB}t_j^b t_i^c$$

30B



$$+\sum_{\substack{b,c\\j}}(-1)^P P(I/J)\langle jI\|bc\rangle t_{IiJ}^{aAB}t_j^b t_I^c$$

31A

$$-\sum_{\substack{b,c\\j,k}}(-1)^P P(AB/a\|IJ/i)\langle jk\|bc\rangle t_{IJj}^{ABb}t_i^c t_k^a$$

Table IV.6 (continued)

31B

$$+\sum_{\substack{b,c\\j}}(-1)^P P(AB/a\,|\,(I/J))\langle Ij\,\|\,bc\rangle t_{iJI}^{ABb}t_I^c t_j^a$$

31C

$$+\sum_{\substack{b\\j,k}}(-1)^P P((A/B)\,|\,IJ/i)\langle jk\,\|\,Ab\rangle t_{IJj}^{aBA}t_i^b t_k^A$$

31D

$$-\sum_{\substack{b\\j}}(-1)^P P((A/B)\,|\,(I/J))\langle Ij\,\|\,Ab\rangle t_{iJI}^{aBA}t_I^b t_j^A$$

Table IV.6 (continued)

$\langle 0_{Iij}^{ABa}|$ projection (TP2)

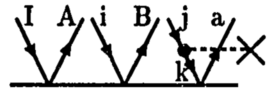
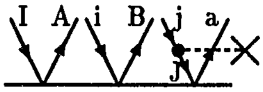
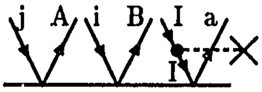
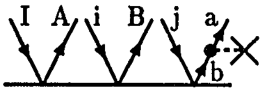
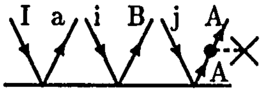
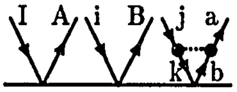
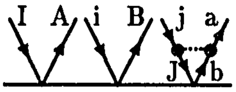
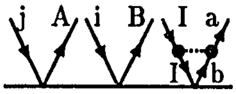
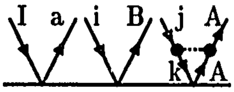
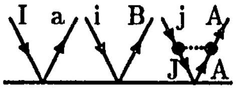
1A		$-\sum_{k}(-1)^{P}P(i/j)f_{kj}t_{Iik}^{ABa}$
1B		$-(-1)^{P}P(Ii/j)f_{Jj}t_{IiJ}^{ABa}$
1C		$+f_{II}t_{jiI}^{ABa}$
2A		$+\sum_{b}f_{ab}t_{Iij}^{ABb}$
2B		$-(-1)^{P}P(A/B)f_{AA}t_{Iij}^{aBA}$
3A		$-\sum_{\substack{b\\k}}(-1)^{P}P(i/j)\langle ka\|jb\rangle t_{Iik}^{ABb}$
3B		$-\sum_{b}(-1)^{P}P(Ii/j\|AB/a)\langle Ja\|jb\rangle t_{IiJ}^{ABb}$
3C		$+\sum_{b}\langle Ia\|Ib\rangle t_{jiI}^{ABb}$
3D		$+\sum_{k}(-1)^{P}P((A/B)\,\vert\, i/j)\langle kA\|jA\rangle t_{Iik}^{aBA}$
3E		$+(-1)^{P}P((A/B)\,\vert\, Ii/j)\langle JA\|jA\rangle t_{IiJ}^{aBA}$

Table IV.6 (continued)

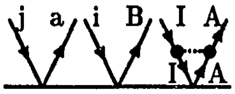
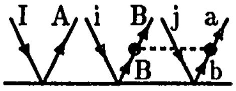
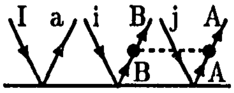
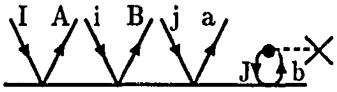
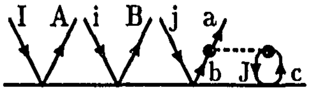
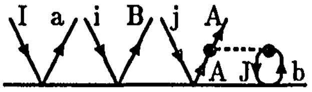
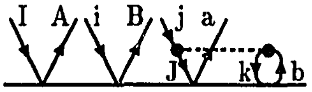
3F		$-(-1)^P P(A/B)\langle IA\|IA\rangle t_{jiI}^{aBA}$
4A		$+\frac{1}{2}\sum_{k,l}\langle kl\|ij\rangle t_{Ikl}^{ABa}$
4B		$+\sum_{k}(-1)^P P(I/ij)\langle Jk\|ij\rangle t_{IJk}^{ABa}$
4C		$-\sum_{k}(-1)^P P(i/j)\langle Ik\|Ij\rangle t_{iIk}^{ABa}$
4D		$-(-1)^P P(i/j)\langle IJ\|Ij\rangle t_{iIJ}^{ABa}$
5A		$+\sum_{b}(-1)^P P(A/B)\langle Ba\|Bb\rangle t_{Iij}^{ABb}$
5B		$-\langle BA\|BA\rangle t_{Iij}^{aBA}$
6A		$+\sum_{b} f_{Jb} t_{IijJ}^{ABab}$
7A		$+\frac{1}{2}\sum_{b,c}\langle aJ\|bc\rangle t_{IijJ}^{ABbc}$
7B		$-\sum_{b}(-1)^P P(A/B)\langle AJ\|Ab\rangle t_{IijJ}^{aBAb}$
8A		$-\sum_{\substack{b\\k}}(-1)^P P(i/j)\langle Jk\|jb\rangle t_{IiJk}^{ABab}$

Table IV.6 (continued)

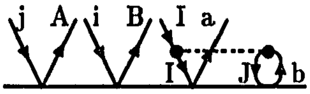
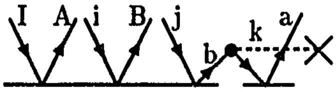
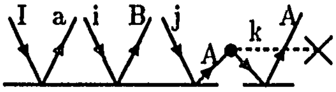
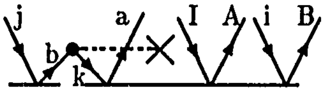
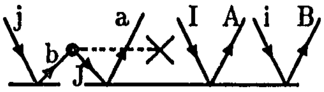
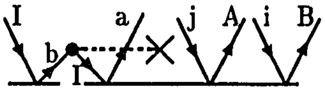
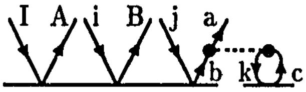
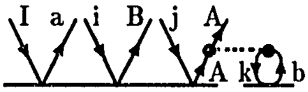
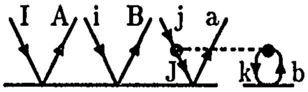
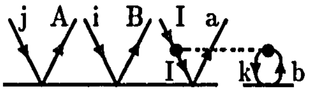
8B		$+\sum_{b}\langle IJ\,\Vert\, Ib\rangle t_{jiIJ}^{ABab}$
9A		$-\sum_{\substack{b\\k}} f_{kb}t_{Iij}^{ABb}t_{k}^{a}$
9B		$+\sum_{k}(-1)^{P}P(A/B)f_{kA}t_{Iij}^{aBA}t_{k}^{A}$
10A		$-\sum_{\substack{b\\k}}(-1)^{P}P(i/j)f_{kb}t_{kIi}^{aAB}t_{j}^{b}$
10B		$-\sum_{b}(-1)^{P}P(j/Ii)f_{Jb}t_{JIi}^{aAB}t_{j}^{b}$
10C		$+\sum_{b} f_{Ib}t_{Iji}^{aAB}t_{I}^{b}$
11A		$+\sum_{\substack{b,c\\k}}\langle ak\,\Vert\, bc\rangle t_{Iij}^{ABb}t_{k}^{c}$
11B		$-\sum_{\substack{b\\k}}(-1)^{P}P(A/B)\langle Ak\,\Vert\, Ab\rangle t_{Iij}^{aBA}t_{k}^{b}$
12A		$-\sum_{\substack{b\\k,l}}(-1)^{P}P(i/j)\langle kl\,\Vert\, jb\rangle t_{Iik}^{ABa}t_{l}^{b}$
12B		$-\sum_{\substack{b\\k}}(-1)^{P}P(j/Ii)\langle Jk\,\Vert\, jb\rangle t_{IiJ}^{ABa}t_{k}^{b}$
12C		$+\sum_{\substack{b\\k}}\langle Ik\,\Vert\, Ib\rangle t_{jiI}^{ABa}t_{k}^{b}$

Table IV.6 (continued)

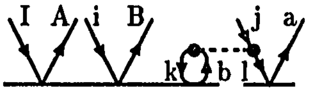
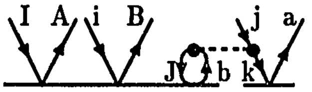
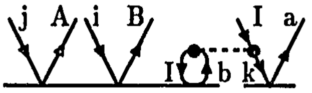
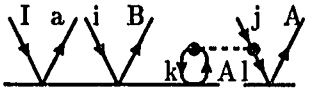
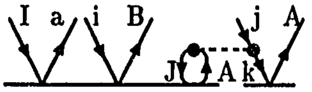
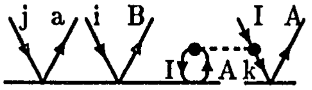
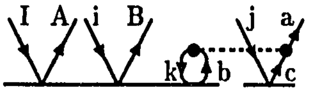
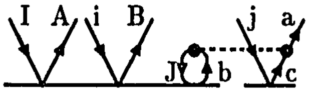
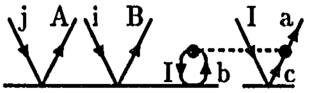
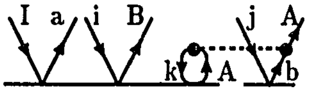
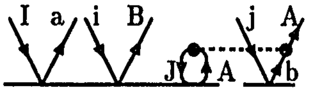
13A		$-\sum_{\substack{b\\k,l}}(-1)^P P(i/j)\langle kl\|bj\rangle t_{Iik}^{ABb}t_l^a$
13B		$-\sum_{\substack{b\\k}}(-1)^P P(j/Ii\|a/AB)\langle Jk\|bj\rangle t_{IiJ}^{ABb}t_k^a$
13C		$+\sum_{\substack{b\\k}}\langle Ik\|bI\rangle t_{jiI}^{ABb}t_k^a$
13D		$+\sum_{k,l}(-1)^P P(i/j\,\|(A/B))\langle kl\|Aj\rangle t_{Iik}^{aBA}t_l^A$
13E		$+\sum_{k}(-1)^P P(j/Ii\,\|(A/B))\langle Jk\|Aj\rangle t_{IiJ}^{aBA}t_k^A$
13F		$-\sum_{k}(-1)^P P(A/B)\langle Ik\|AI\rangle t_{jiI}^{aBA}t_k^A$
14A		$+\sum_{\substack{b,c\\k}}(-1)^P P(i/j)\langle ka\|bc\rangle t_{Iik}^{ABb}t_j^c$
14B		$+\sum_{b,c}(-1)^P P(j/Ii\|a/AB)\langle Ja\|bc\rangle t_{IiJ}^{ABb}t_j^c$
14C		$-\sum_{b,c}\langle Ia\|bc\rangle t_{jiI}^{ABb}t_I^c$
14D		$-\sum_{\substack{b\\k}}(-1)^P P(i/j\,\|(A/B))\langle kA\|Ab\rangle t_{Iik}^{aBA}t_j^b$
14E		$-\sum_{b}(-1)^P P(j/Ii\,\|(A/B))\langle JA\|Ab\rangle t_{IiJ}^{aBA}t_j^b$

Table IV.6 (continued)

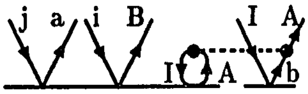
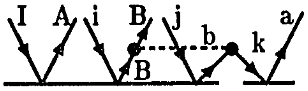
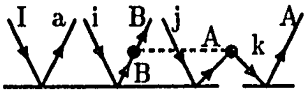
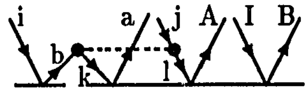
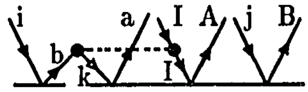
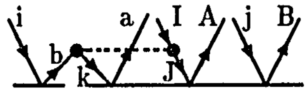
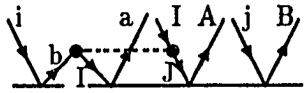
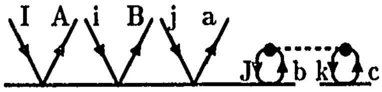
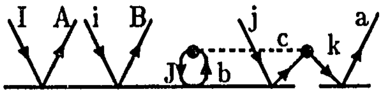
14F		$+\sum_{b}(-1)^{P}P(A/B)\langle IA\|Ab\rangle t_{jiI}^{aBA}t_{I}^{b}$
15A		$-\sum_{\substack{b\\k}}(-1)^{P}P(B/a(A/B))\langle Bk\|Bb\rangle t_{Iij}^{ABb}t_{k}^{a}$
15B		$+\sum_{k}(-1)^{P}P(A/B)\langle Bk\|BA\rangle t_{Iij}^{aBA}t_{k}^{A}$
16A		$-\frac{1}{2}\sum_{\substack{b\\k,l}}(-1)^{P}P(i/j)\langle kl\|bj\rangle t_{klI}^{aAB}t_{i}^{b}$
16B		$+\sum_{\substack{b\\k}}(-1)^{P}P(i/I/j)\langle kI\|bI\rangle t_{kIj}^{aAB}t_{i}^{b}$
16C		$+\sum_{\substack{b\\k}}(-1)^{P}P(i/I/j)\langle kJ\|bI\rangle t_{kJj}^{aAB}t_{i}^{b}$
16D		$+\sum_{b}(-1)^{P}P(i/I/j)\langle IJ\|bI\rangle t_{IJj}^{aAB}t_{i}^{b}$
17A		$+\sum_{\substack{b,c\\k}}\langle Jk\|bc\rangle t_{IijJ}^{ABab}t_{k}^{c}$
18A		$-\frac{1}{2}\sum_{\substack{b,c\\k}}\langle Jk\|bc\rangle t_{IiJj}^{ABbc}t_{k}^{a}$
18B		$+\sum_{\substack{b\\k}}(-1)^{P}P(A/B)\langle Jk\|Ab\rangle t_{IiJj}^{aBAb}t_{k}^{A}$
19A		$-\sum_{\substack{b,c\\k}}(-1)^{P}P(i/j)\langle Jk\|bc\rangle t_{JkIi}^{acAB}t_{j}^{b}$

Table IV.6 (continued)

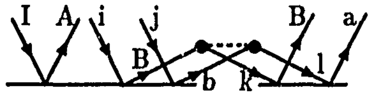
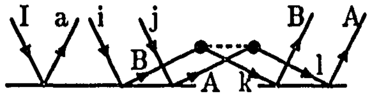
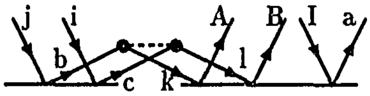
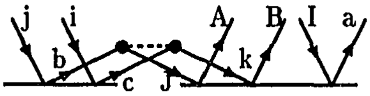
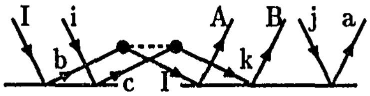
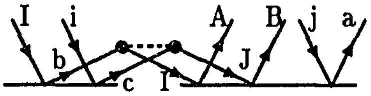
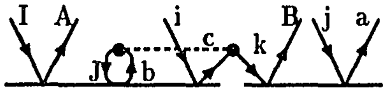
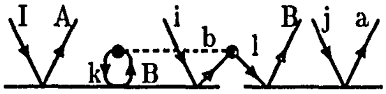
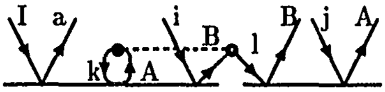
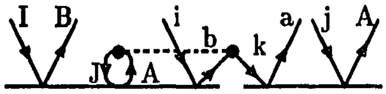
19B		$+\sum_{b,c}\langle IJ\|bc\rangle t_{IJji}^{acAB}t_I^b$
20A		$+\frac{1}{2}\sum_{\substack{b\\k,l}}(-1)^P P(A/B)\langle kl\|Bb\rangle t_{Iij}^{ABb}t_{kl}^{Ba}$
20B		$-\frac{1}{2}\sum_{k,l}\langle kl\|BA\rangle t_{Iij}^{aBA}t_{kl}^{BA}$
21A		$+\frac{1}{4}\sum_{\substack{b,c\\k,l}}\langle kl\|bc\rangle t_{klI}^{ABa}t_{ji}^{bc}$
21B		$+\frac{1}{2}\sum_{\substack{b,c\\k}}(-1)^P P(I/ij)\langle Jk\|bc\rangle t_{JkI}^{ABa}t_{ji}^{bc}$
21C		$-\frac{1}{2}\sum_{\substack{b,c\\k}}(-1)^P P(i/j)\langle Ik\|bc\rangle t_{Ikj}^{ABa}t_{Ii}^{bc}$
21D		$-\frac{1}{2}\sum_{b,c}(-1)^P P(i/j)\langle IJ\|bc\rangle t_{IJj}^{ABa}t_{Ii}^{bc}$
22A		$-\frac{1}{2}\sum_{\substack{b,c\\k}}(-1)^P P(A/B\,\|\,i/j)\langle Jk\|bc\rangle t_{IJi}^{Abc}t_{kj}^{Ba}$
22B		$-\sum_{\substack{b\\k,l}}(-1)^P P((A/B)\,\|\,i/j)\langle kl\|Bb\rangle t_{Iki}^{ABb}t_{lj}^{Ba}$
22C		$+\sum_{k,l}(-1)^P P(i/j)\langle kl\|AB\rangle t_{Iki}^{aAB}t_{lj}^{BA}$

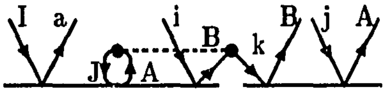
Table IV.6 (continued)

22D



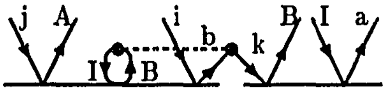
$$+\sum_{\substack{b\\k}}(-1)^P P(Ii/j\,\|\,B/a(A/B))\langle Jk\,\|\,Ab\rangle t_{IJi}^{aAb}t_{kj}^{BA}$$

22E



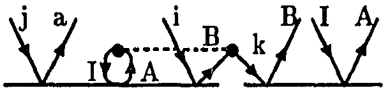
$$+\sum_{k}(-1)^P P(Ii/j)\langle Jk\,\|\,AB\rangle t_{IJi}^{aAB}t_{kj}^{BA}$$

22F



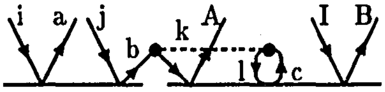
$$+\sum_{\substack{b\\k}}(-1)^P P(A/B)\langle Ik\,\|\,Bb\rangle t_{jIi}^{ABb}t_{kI}^{Ba}$$

22G



$$-\sum_{k}\langle Ik\,\|\,AB\rangle t_{jIi}^{aAB}t_{kI}^{BA}$$

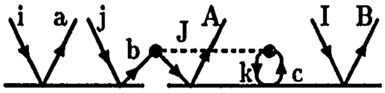
23A



$$-\tfrac{1}{2}\sum_{\substack{b,c\\k,l}}\langle kl\,\|\,bc\rangle t_{klI}^{AcB}t_{ij}^{ab}$$

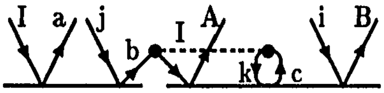
Table IV.6 (continued)

23B



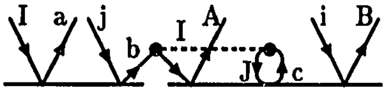
$$-\sum_{\substack{b,c\\k}}(-1)^P P(I/ij\,\|\,AB/a)\langle Jk\,\|\,bc\rangle t_{JkI}^{AcB}t_{ij}^{ab}$$

23C



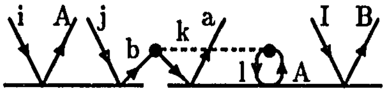
$$+\sum_{\substack{b,c\\k}}(-1)^P P(i/j)\langle Ik\,\|\,bc\rangle t_{Iki}^{AcB}t_{Ij}^{ab}$$

23D



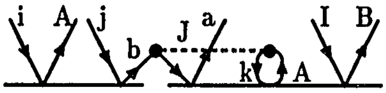
$$+\sum_{b,c}(-1)^P P(i/j\,|\,AB/a)\langle IJ\,\|\,bc\rangle t_{IJi}^{AcB}t_{Ij}^{ab}$$

23E



$$+\tfrac{1}{2}\sum_{\substack{b\\k,l}}(-1)^P P(A/B)\langle kl\,\|\,bA\rangle t_{klI}^{aAB}t_{ij}^{Ab}$$

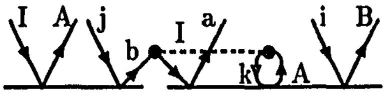
23F



$$+\sum_{\substack{b\\k}}(-1)^P P((A/B)\,|\,I/ij)\langle Jk\,\|\,bA\rangle t_{JkI}^{aAB}t_{ij}^{Ab}$$

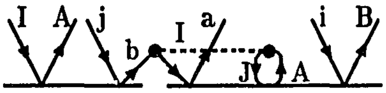
Table IV.6 (continued)

23G



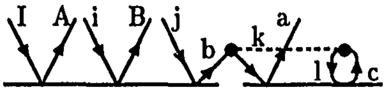
$$-\sum_{\substack{b\\k}}(-1)^P P((A/B)\,|\,i/j)\langle Ik\,\|\,bA\rangle t_{Iki}^{aAB}t_{Ij}^{Ab}$$

23H



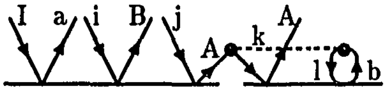
$$-\sum_{b}(-1)^P P((A/B)\,|\,i/j)\langle IJ\,\|\,bA\rangle t_{IJi}^{aAB}t_{Ij}^{Ab}$$

24A



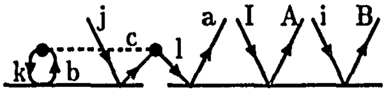
$$-\tfrac{1}{2}\sum_{\substack{b,c\\k,l}}\langle kl\,\|\,bc\rangle t_{Iij}^{ABb}t_{kl}^{ac}$$

24B



$$+\tfrac{1}{2}\sum_{\substack{b\\k,l}}(-1)^P P(A/B)\langle kl\,\|\,Ab\rangle t_{Iij}^{aBA}t_{kl}^{Ab}$$

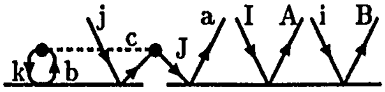
25A



$$-\tfrac{1}{2}\sum_{\substack{b,c\\k,l}}(-1)^P P(i/j)\langle kl\,\|\,bc\rangle t_{lIi}^{aAB}t_{kj}^{bc}$$

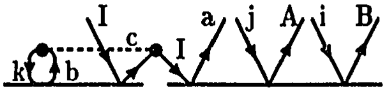
Table IV.6 (continued)

25B



$$-\tfrac{1}{2}\sum_{\substack{b,c\\k}}(-1)^P P(Ii/j)\langle kJ\|bc\rangle t_{JIi}^{aAB}t_{kj}^{bc}$$

25C

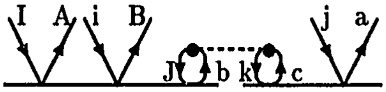


$$+\tfrac{1}{2}\sum_{\substack{b,c\\k}}\langle kI\|bc\rangle t_{Iji}^{aAB}t_{kI}^{bc}$$

26A

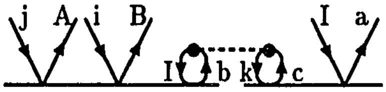
$$+\sum_{\substack{b,c\\k,l}}(-1)^P P(i/j)\langle kl\|bc\rangle t_{Iik}^{ABb}t_{lj}^{ca}$$

26B



$$+\sum_{\substack{b,c\\k}}(-1)^P P(Ii/j\|AB/a)\langle Jk\|bc\rangle t_{IiJ}^{ABb}t_{kj}^{ca}$$

26C



$$-\sum_{\substack{b,c\\k}}\langle Ik\|bc\rangle t_{jiI}^{ABb}t_{kI}^{ca}$$

Table IV.6 (continued)

26D 

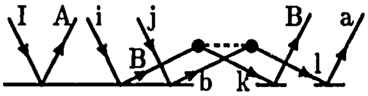
$$-\sum_{\substack{b\\k,l}}(-1)^P P(i/j\,|\,(A/B))\langle kl\,\|\,Ab\rangle t_{Iik}^{aBA}t_{lj}^{bA}$$

26E 

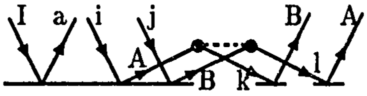
$$-\sum_{\substack{b\\k}}(-1)^P P(Ii/j\,|\,(A/B))\langle Jk\,\|\,Ab\rangle t_{IiJ}^{aBA}t_{kj}^{bA}$$

26F 

$$+\sum_{\substack{b\\k}}(-1)^P P(A/B)\langle Ik\,\|\,Ab\rangle t_{jiI}^{aBA}t_{kI}^{bA}$$

27A 

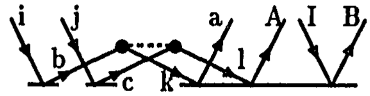
$$+\sum_{\substack{b\\k,l}}(-1)^P P(A/B)\langle kl\,\|\,Bb\rangle t_{Iij}^{ABb}t_k^B t_l^a$$

27B 

$$-\sum_{k,l}\langle kl\,\|\,AB\rangle t_{Iij}^{aAB}t_k^B t_l^A$$

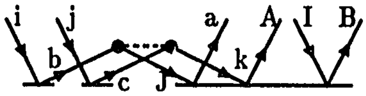
Table IV.6 (continued)

28A



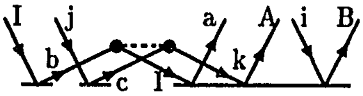
$$+\tfrac{1}{2}\sum_{\substack{b,c\\k,l}}\langle kl\,\|\,bc\rangle t_{klI}^{aAB}t_i^b t_j^c$$

28B



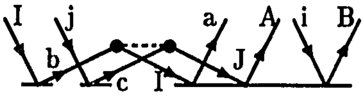
$$+\sum_{\substack{b,c\\k}}(-1)^P P(I/ij)\langle Jk\,\|\,bc\rangle t_{JkI}^{aAB}t_i^b t_j^c$$

28C



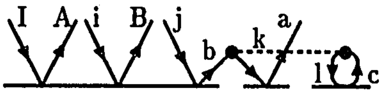
$$-\sum_{\substack{b,c\\k}}(-1)^P P(i/j)\langle Ik\,\|\,bc\rangle t_{Iki}^{aAB}t_I^b t_j^c$$

28D



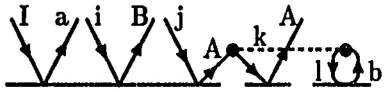
$$-\sum_{b,c}(-1)^P P(i/j)\langle IJ\,\|\,bc\rangle t_{IJi}^{aAB}t_I^b t_j^c$$

29A

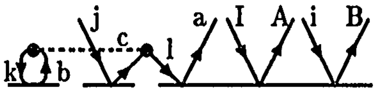


$$-\sum_{\substack{b,c\\k,l}}\langle kl\,\|\,bc\rangle t_{Iij}^{ABb}t_k^a t_l^c$$

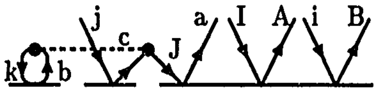
Table IV.6 (continued)

29B


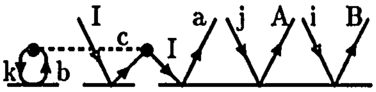
$$+\sum_{\substack{b\\k,l}}(-1)^P P(A/B)\langle kl\|Ab\rangle t_{Iij}^{aBA}t_k^A t_l^b$$

30A


$$-\sum_{\substack{b,c\\k,l}}(-1)^P P(i/j)\langle kl\|bc\rangle t_{lIi}^{aAB}t_k^b t_j^c$$

30B


$$-\sum_{\substack{b,c\\k}}(-1)^P P(j/Ii)\langle kJ\|bc\rangle t_{JIi}^{aAB}t_k^b t_j^c$$

30C


$$+\sum_{\substack{b,c\\k}}\langle kI\|bc\rangle t_{Iji}^{aAB}t_k^b t_I^c$$

31A


$$-\sum_{\substack{b,c\\k,l}}(-1)^P P(i/j)\langle kl\|bc\rangle t_{Iik}^{ABb}t_j^c t_l^a$$

Table IV.6 (continued)

31B

$$-\sum_{\substack{b,c\\k}}(-1)^P P(j/Ii\,\|\,a/AB)\langle Jk\|bc\rangle t_{IiJ}^{ABb}t_j^c t_k^a$$

31C

$$+\sum_{\substack{b,c\\k}}\langle Ik\|bc\rangle t_{jiI}^{ABb}t_I^c t_k^a$$

31D

$$+\sum_{\substack{b\\k,l}}(-1)^P P(i/j\,|\,(A/B))\langle kl\|Ab\rangle t_{Iik}^{aBA}t_j^b t_l^A$$

31E

$$+\sum_{\substack{b\\k}}(-1)^P P(j/Ii\,|\,(A/B))\langle Jk\|Ab\rangle t_{IiJ}^{aBA}t_j^b t_k^A$$

31F

$$-\sum_{\substack{b\\k}}(-1)^P P(A/B)\langle Ik\|Ab\rangle t_{jiI}^{aBA}t_I^b t_k^A$$

Table IV.6 (continued)

$\langle 0_{IJi}^{Aab}|$ projection (TP3)

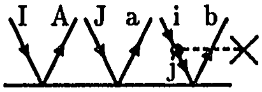
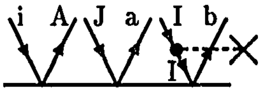
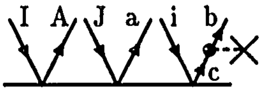
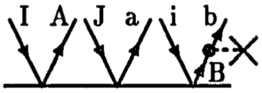
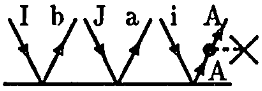
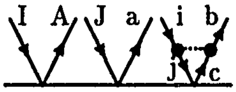
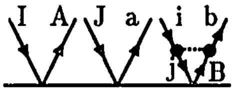
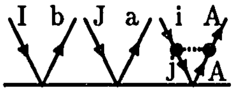
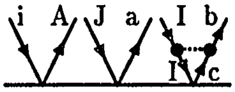
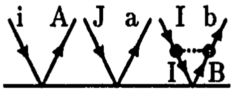
1A		$-\sum_{j} f_{ji} t_{IJj}^{Aab}$
1B		$+(-1)^{P} P(I/J) f_{II} t_{iJI}^{Aab}$
2A		$+\sum_{c}(-1)^{P} P(a/b) f_{bc} t_{IJi}^{Aac}$
2B		$+(-1)^{P} P(b/Aa) f_{bB} t_{IJi}^{AaB}$
2C		$-f_{AA} t_{IJi}^{baA}$
3A		$-\sum_{\substack{c\\j}}(-1)^{P} P(a/b)\langle jb\|ic\rangle t_{IJj}^{Aac}$
3B		$-\sum_{j}(-1)^{P} P(b/Aa\|i/IJ)\langle jb\|iB\rangle t_{IJj}^{AaB}$
3C		$+\sum_{j}\langle jA\|iA\rangle t_{IJj}^{baA}$
3D		$+\sum_{c}(-1)^{P} P(a/b\|(I/J))\langle Ib\|Ic\rangle t_{iJI}^{Aac}$
3E		$+(-1)^{P} P((I/J)\|b/Aa)\langle Ib\|IB\rangle t_{iJI}^{AaB}$

Table IV.6 (continued)

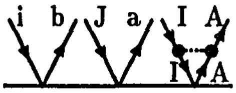
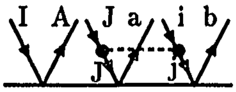
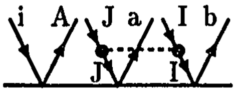
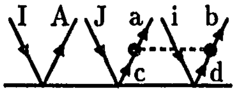
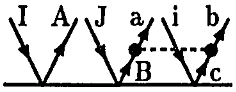
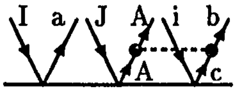
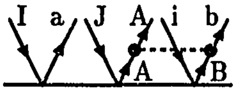
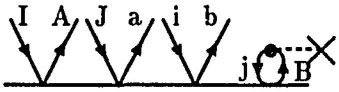
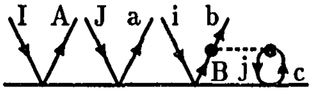
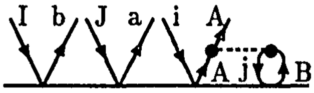
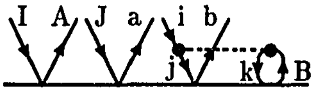
3F		$-(-1)^P P(I/J)\langle IA \| IA\rangle t_{iJI}^{baA}$
4A		$+\sum_{j}(-1)^P P(I/J)\langle Jj \| Ji\rangle t_{IJj}^{Aab}$
4B		$-\langle JI \| JI\rangle t_{iJI}^{Aab}$
5A		$+\frac{1}{2}\sum_{c,d}\langle ab \| cd\rangle t_{IJi}^{Acd}$
5B		$+\sum_{c}(-1)^P P(A/ab)\langle ab \| Bc\rangle t_{IJi}^{ABc}$
5C		$-\sum_{c}(-1)^P P(a/b)\langle Ab \| Ac\rangle t_{IJi}^{aAc}$
5D		$-(-1)^P P(a/b)\langle Ab \| AB\rangle t_{IJi}^{aAB}$
6A		$+\sum_{j} f_{jB} t_{IJij}^{AabB}$
7A		$+\sum_{\substack{c\\j}}(-1)^P P(a/b)\langle bj \| Bc\rangle t_{IJij}^{AaBc}$
7B		$-\sum_{j}\langle Aj \| AB\rangle t_{IJij}^{baAB}$
8A		$-\frac{1}{2}\sum_{j,k}\langle jk \| iB\rangle t_{IJjk}^{AabB}$

Table IV.6 (continued)

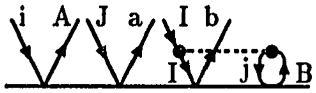
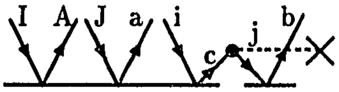
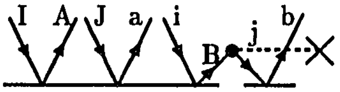
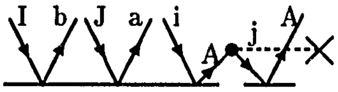
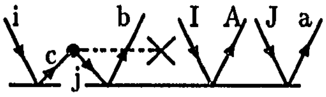
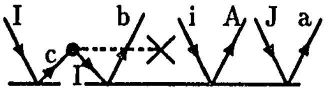
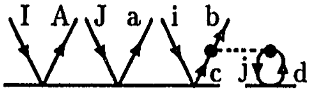
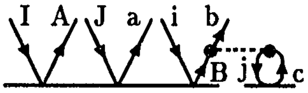
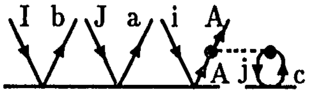
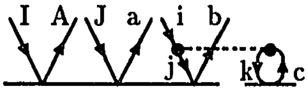
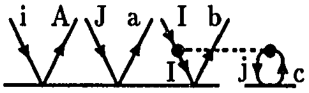
8B		$+\sum_{j}(-1)^{P}P(I/J)\langle Ij\,\|\,IB\rangle t_{iJIj}^{AabB}$
9A		$-\sum_{\substack{c\\j}}(-1)^{P}P(a/b)f_{jc}t_{IJi}^{Aac}t_{j}^{b}$
9B		$-\sum_{j}(-1)^{P}P(b/Aa)f_{jB}t_{IJi}^{AaB}t_{j}^{b}$
9C		$+\sum_{j}f_{jA}t_{IJi}^{baA}t_{j}^{A}$
10A		$-\sum_{\substack{c\\j}}f_{jc}t_{jIJ}^{bAa}t_{i}^{c}$
10B		$+\sum_{c}(-1)^{P}P(I/J)f_{Ic}t_{IiJ}^{bAa}t_{I}^{c}$
11A		$+\sum_{\substack{c,d\\j}}(-1)^{P}P(a/b)\langle bj\,\|\,cd\rangle t_{IJi}^{Aac}t_{j}^{d}$
11B		$+\sum_{\substack{c\\j}}(-1)^{P}P(b/Aa)\langle bj\,\|\,Bc\rangle t_{IJi}^{AaB}t_{j}^{c}$
11C		$-\sum_{\substack{c\\j}}\langle Aj\,\|\,Ac\rangle t_{IJi}^{baA}t_{j}^{c}$
12A		$-\sum_{\substack{c\\j,k}}\langle jk\,\|\,ic\rangle t_{IJj}^{Aab}t_{k}^{c}$
12B		$+\sum_{\substack{c\\j}}(-1)^{P}P(I/J)\langle Ij\,\|\,Ic\rangle t_{iJI}^{Aab}t_{j}^{c}$

Table IV.6 (continued)

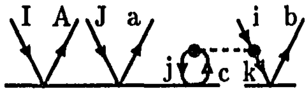
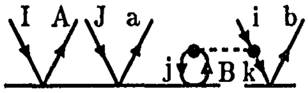
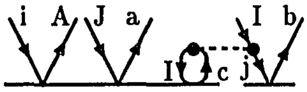
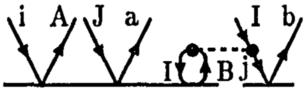
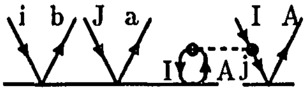
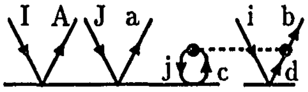
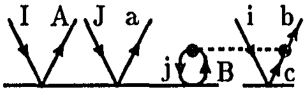
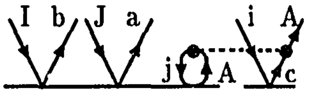
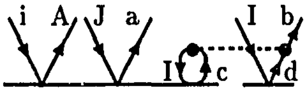
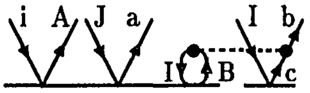
13A		$-\sum_{\substack{c\\j,k}}(-1)^P P(a/b)\langle jk\Vert ci\rangle t_{IJj}^{Aac}t_k^b$
13B		$-\sum_{j,k}(-1)^P P(b/Aa\Vert i/IJ)\langle jk\Vert Bi\rangle t_{IJj}^{AaB}t_k^b$
13C		$+\sum_{j,k}\langle jk\Vert Ai\rangle t_{IJj}^{baA}t_k^A$
13D		$+\sum_{\substack{c\\j}}(-1)^P P((I/J)\vert a/b)\langle Ij\Vert cI\rangle t_{iJI}^{Aac}t_j^b$
13E		$+\sum_{j}(-1)^P P((I/J)\vert b/Aa)\langle Ij\Vert BI\rangle t_{iJI}^{AaB}t_j^b$
13F		$-\sum_{j}(-1)^P P(I/J)\langle Ij\Vert AI\rangle t_{iJI}^{baA}t_j^A$
14A		$+\sum_{\substack{c,d\\j}}(-1)^P P(a/b)\langle jb\Vert cd\rangle t_{IJj}^{Aac}t_i^d$
14B		$+\sum_{\substack{c\\j}}(-1)^P P(b/Aa\Vert i/IJ)\langle jb\Vert Bc\rangle t_{IJj}^{AaB}t_i^c$
14C		$-\sum_{\substack{c\\j}}\langle jA\Vert Ac\rangle t_{IJj}^{baA}t_i^c$
14D		$-\sum_{c,d}(-1)^P P((I/J)\vert a/b)\langle Ib\Vert cd\rangle t_{iJI}^{Aac}t_I^d$
14E		$-\sum_{c}(-1)^P P((I/J)\vert b/Aa)\langle Ib\Vert Bc\rangle t_{iJI}^{AaB}t_I^c$

Table IV.6 (continued)

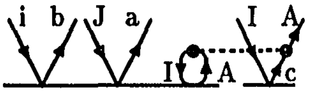
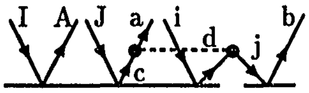
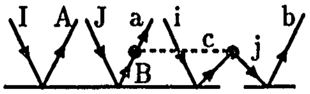
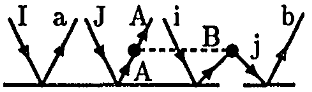
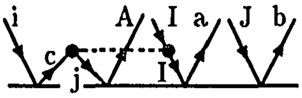
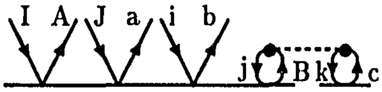
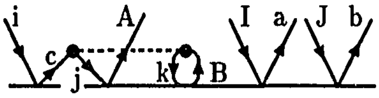
14F		$+\sum_{c}(-1)^{P}P(I/J)\langle IA\Vert Ac\rangle t_{iJI}^{baA}t_{I}^{c}$
15A		$-\frac{1}{2}\sum_{\substack{c,d\\j}}(-1)^{P}P(a/b)\langle aj\Vert cd\rangle t_{IJi}^{Acd}t_{j}^{b}$
15B		$-\sum_{\substack{c\\j}}(-1)^{P}P(A/a/b)\langle aj\Vert Bc\rangle t_{IJi}^{ABc}t_{j}^{b}$
15C		$+\sum_{\substack{c\\j}}(-1)^{P}P(A/a/b)\langle Aj\Vert Ac\rangle t_{IJi}^{aAc}t_{j}^{b}$
15D		$+\sum_{j}(-1)^{P}P(A/a/b)\langle Aj\Vert AB\rangle t_{IJi}^{aAB}t_{j}^{b}$
16A		$+\sum_{\substack{c\\j}}(-1)^{P}P(i/I(I/J))\langle jI\Vert cI\rangle t_{jIJ}^{Aab}t_{i}^{c}$
16B		$-\sum_{c}(-1)^{P}P(I/J)\langle JI\Vert cI\rangle t_{JIi}^{Aab}t_{J}^{c}$
17A		$+\sum_{\substack{c\\j,k}}\langle jk\Vert Bc\rangle t_{IJij}^{AabB}t_{k}^{c}$
18A		$-\sum_{\substack{c\\j,k}}(-1)^{P}P(a/b)\langle jk\Vert Bc\rangle t_{IJji}^{AaBc}t_{k}^{b}$
18B		$+\sum_{j,k}\langle jk\Vert AB\rangle t_{IJji}^{baAB}t_{k}^{A}$
19A		$-\frac{1}{2}\sum_{\substack{c\\j,k}}\langle jk\Vert cB\rangle t_{jkIJ}^{ABab}t_{i}^{c}$

Table IV.6 (continued)

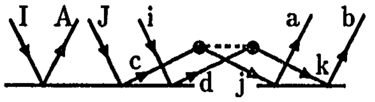
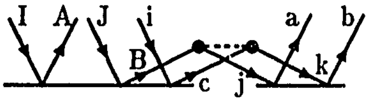
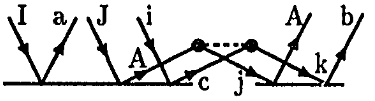
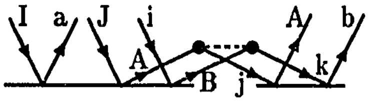
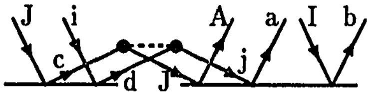
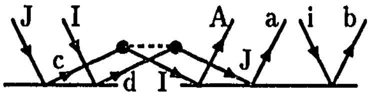
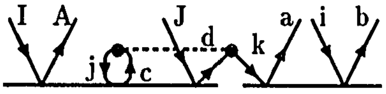
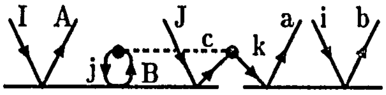
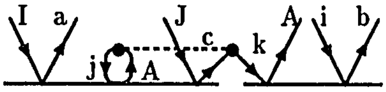
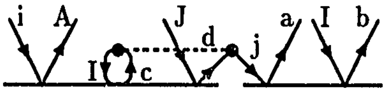
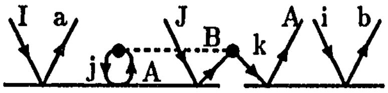
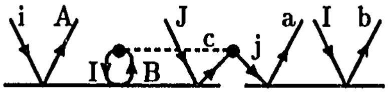
19B		$+\sum_{\substack{c\\j}}(-1)^P P(I/J)\langle Ij\Vert cB\rangle t_{IjiJ}^{ABab}t_I^c$
20A		$+\frac{1}{4}\sum_{\substack{c,d\\j,k}}\langle jk\Vert cd\rangle t_{IJi}^{Acd}t_{jk}^{ab}$
20B		$+\frac{1}{2}\sum_{\substack{c\\j,k}}(-1)^P P(A/ab)\langle jk\Vert Bc\rangle t_{IJi}^{ABc}t_{jk}^{ab}$
20C		$-\frac{1}{2}\sum_{\substack{c\\j,k}}(-1)^P P(a/b)\langle jk\Vert Ac\rangle t_{IJi}^{aAc}t_{jk}^{Ab}$
20D		$-\frac{1}{2}\sum_{j,k}(-1)^P P(a/b)\langle jk\Vert AB\rangle t_{IJi}^{aAB}t_{jk}^{Ab}$
21A		$+\frac{1}{2}\sum_{\substack{c,d\\j}}(-1)^P P(I/J)\langle Jj\Vert cd\rangle t_{JjI}^{Aab}t_{Ji}^{cd}$
21B		$-\frac{1}{2}\sum_{c,d}\langle IJ\Vert cd\rangle t_{IJi}^{Aab}t_{JI}^{cd}$
22A		$-\frac{1}{2}\sum_{\substack{c,d\\j,k}}\langle jk\Vert cd\rangle t_{IjJ}^{Acd}t_{ki}^{ab}$
22B		$-\sum_{\substack{c\\j,k}}(-1)^P P(i/IJ\Vert A/ab)\langle jk\Vert Bc\rangle t_{IjJ}^{ABc}t_{ki}^{ab}$
22C		$+\sum_{\substack{c\\j,k}}(-1)^P P(a/b)\langle jk\Vert Ac\rangle t_{IjJ}^{aAc}t_{ki}^{Ab}$
22D		$+\frac{1}{2}\sum_{\substack{c,d\\j}}(-1)^P P(I/J)\langle Ij\Vert cd\rangle t_{iIJ}^{Acd}t_{jI}^{ab}$

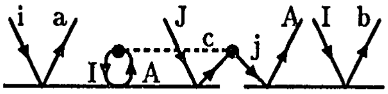
Table IV.6 (continued)

22E 

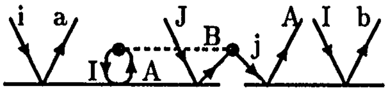
$$+\sum_{j,k}(-1)^P P(a/b|i/IJ)\langle jk\|AB\rangle t_{IjJ}^{aAB}t_{ki}^{Ab}$$

22F 

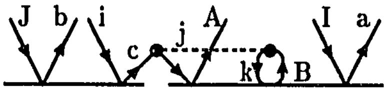
$$+\sum_{\substack{c\\j}}(-1)^P P((I/J)\,|\,A/ab)\langle Ij\|Bc\rangle t_{iIJ}^{ABc}t_{jI}^{ab}$$

22G 

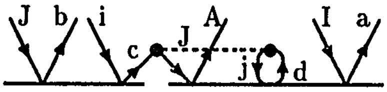
$$-\sum_{\substack{c\\j}}(-1)^P P((I/J)\,|\,a/b)\langle Ij\|Ac\rangle t_{iIJ}^{aAc}t_{jI}^{Ab}$$

22H 

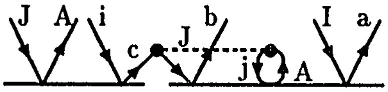
$$-\sum_{j}(-1)^P P((I/J)\,|\,a/b)\langle Ij\|AB\rangle t_{iIJ}^{aAB}t_{jI}^{Ab}$$

23A 

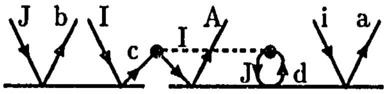
$$-\tfrac{1}{2}\sum_{\substack{c\\j,k}}(-1)^P P(I/J\,|\,a/b)\langle jk\|cB\rangle t_{jkI}^{ABa}t_{Ji}^{bc}$$

23B 

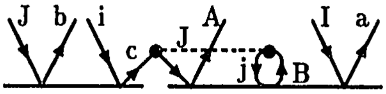
$$-\sum_{\substack{c,d\\j}}(-1)^P P((I/J)\,|\,a/b)\langle Jj\|cd\rangle t_{JjI}^{Ada}t_{Ji}^{bc}$$

23C 

$$+\sum_{\substack{c\\j}}(-1)^P P(I/J)\langle Jj\|cA\rangle t_{JjI}^{bAa}t_{Ji}^{Ac}$$

23D 

$$+\sum_{c,d}(-1)^P P(a/b)\langle IJ\|cd\rangle t_{IJi}^{Ada}t_{JI}^{bc}$$

23E 

$$-\sum_{\substack{c\\j}}(-1)^P P(I/i(I/J)\,\|\,b/Aa)\langle Jj\|cB\rangle t_{JjI}^{ABa}t_{Ji}^{bc}$$

Table IV.6 (continued)

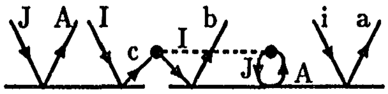
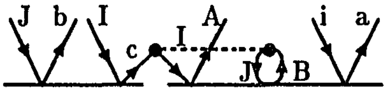
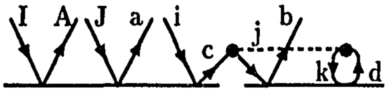
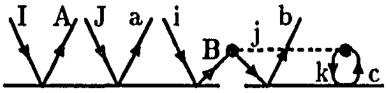
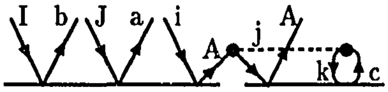
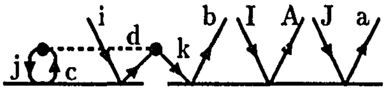
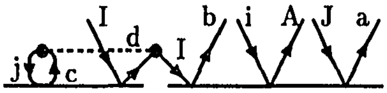
23F		$-\sum_{c}\langle IJ\,\|\,cA\rangle t_{IJi}^{bAa}t_{JI}^{Ac}$
23G		$+\sum_{c}(-1)^{P}P(b/Aa)\langle IJ\,\|\,cB\rangle t_{IJi}^{ABa}t_{JI}^{bc}$
24A		$-\frac{1}{2}\sum_{\substack{c,d\\j,k}}(-1)^{P}P(a/b)\langle jk\,\|\,cd\rangle t_{IJi}^{Aac}t_{jk}^{bd}$
24B		$-\frac{1}{2}\sum_{\substack{c\\j,k}}(-1)^{P}P(b/Aa)\langle jk\,\|\,Bc\rangle t_{IJi}^{AaB}t_{jk}^{bc}$
24C		$+\frac{1}{2}\sum_{\substack{c\\j,k}}\langle jk\,\|\,Ac\rangle t_{IJi}^{baA}t_{jk}^{Ac}$
25A		$-\frac{1}{2}\sum_{\substack{c,d\\j,k}}\langle jk\,\|\,cd\rangle t_{kIJ}^{bAa}t_{ji}^{cd}$
25B		$+\frac{1}{2}\sum_{\substack{c,d\\j}}(-1)^{P}P(I/J)\langle jI\,\|\,cd\rangle t_{IiJ}^{bAa}t_{jI}^{cd}$
26A		$+\sum_{\substack{c,d\\j,k}}(-1)^{P}P(a/b)\langle jk\,\|\,cd\rangle t_{IJj}^{Aac}t_{ki}^{db}$
26B		$+\sum_{\substack{c\\j,k}}(-1)^{P}P(b/Aa\,\|\,i/IJ)\langle jk\,\|\,Bc\rangle t_{IJj}^{AaB}t_{ki}^{cb}$
26C		$-\sum_{\substack{c\\j,k}}\langle jk\,\|\,Ac\rangle t_{IJj}^{baA}t_{ki}^{cA}$
26D		$-\sum_{\substack{c,d\\j}}(-1)^{P}P((I/J)\,|\,a/b)\langle Ij\,\|\,cd\rangle t_{iJI}^{Aac}t_{jI}^{db}$

Table IV.6 (continued)

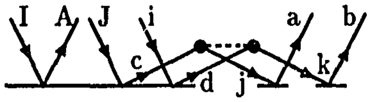
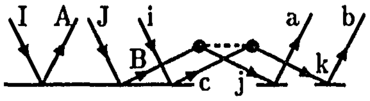
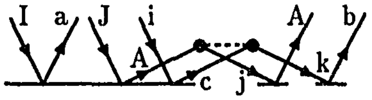
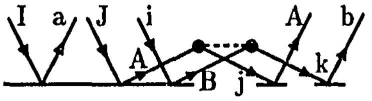
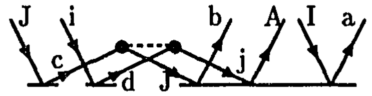
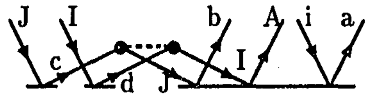
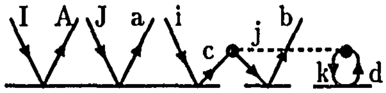
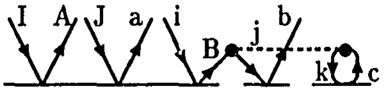
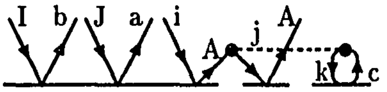
26E		$-\sum_{\substack{c\\j}}(-1)^P P((I/J)\,\vert\, b/Aa)\langle Ij \Vert Bc\rangle t_{iJI}^{AaB} t_{jI}^{cb}$
26F		$+\sum_{\substack{c\\j}}(-1)^P P(I/J)\langle Ij \Vert Ac\rangle t_{iJI}^{baA} t_{jI}^{cA}$
27A		$+\frac{1}{2}\sum_{\substack{c,d\\j,k}}\langle jk \Vert cd\rangle t_{IJi}^{Acd} t_j^a t_k^b$
27B		$+\sum_{\substack{c\\j,k}}(-1)^P P(A/ab)\langle jk \Vert Bc\rangle t_{IJi}^{ABc} t_j^a t_k^b$
27C		$-\sum_{\substack{c\\j,k}}(-1)^P P(a/b)\langle jk \Vert Ac\rangle t_{IJi}^{aAc} t_j^A t_k^b$
27D		$-\sum_{j,k}(-1)^P P(a/b)\langle jk \Vert AB\rangle t_{IJi}^{aAB} t_j^A t_k^b$
28A		$+\sum_{\substack{c,d\\j}}(-1)^P P(I/J)\langle Jj \Vert cd\rangle t_{JjI}^{bAa} t_J^c t_i^d$
28B		$-\sum_{c,d}\langle JI \Vert cd\rangle t_{JIi}^{bAa} t_J^c t_I^d$
29A		$-\sum_{\substack{c,d\\j,k}}(-1)^P P(a/b)\langle jk \Vert cd\rangle t_{IJi}^{Aac} t_j^b t_k^d$
29B		$-\sum_{\substack{c\\j,k}}(-1)^P P(b/Aa)\langle jk \Vert Bc\rangle t_{IJi}^{AaB} t_j^b t_k^c$
29C		$+\sum_{\substack{c\\j,k}}\langle jk \Vert Ac\rangle t_{IJi}^{baA} t_j^A t_k^c$

Table IV.6 (continued)

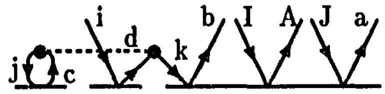
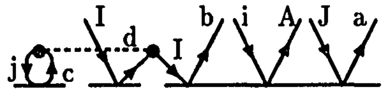
30A		$-\sum_{\substack{c,d\\j,k}}\langle jk\parallel cd\rangle t_{kIJ}^{bAa}t_j^c t_i^d$
30B		$+\sum_{\substack{c,d\\j}}(-1)^P P(I/J)\langle jI\parallel cd\rangle t_{IiJ}^{bAa}t_j^c t_I^d$
31A		$-\sum_{\substack{c,d\\j,k}}(-1)^P P(a/b)\langle jk\parallel cd\rangle t_{IJj}^{Aac}t_i^d t_k^b$
31B		$-\sum_{\substack{c\\j,k}}(-1)^P P(b/Aa\parallel i/IJ)\langle jk\parallel Bc\rangle t_{IJj}^{AaB}t_i^c t_k^b$
31C		$+\sum_{\substack{c\\j,k}}\langle jk\parallel Ac\rangle t_{IJj}^{baA}t_i^c t_k^A$
31D		$+\sum_{\substack{c,d\\j}}(-1)^P P((I/J)\mid a/b)\langle Ij\parallel cd\rangle t_{iJI}^{Aac}t_I^d t_j^b$
31E		$+\sum_{\substack{c\\j}}(-1)^P P((I/J)\mid b/Aa)\langle Ij\parallel Bc\rangle t_{iJI}^{AaB}t_I^c t_j^b$
31F		$-\sum_{\substack{c\\j}}(-1)^P P(I/J)\langle Ij\parallel Ac\rangle t_{iJI}^{baA}t_I^c t_j^A$

Table IV.7

Coupled-cluster diagrams from the projection against a quadruply excited determinant, representing single and double excitations from a second reference determinant which is doubly excited with respect to the formal reference.

$\langle 0^{ABab}_{IJij}|$ projection (QP1)

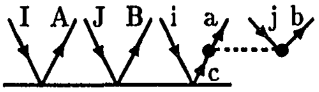
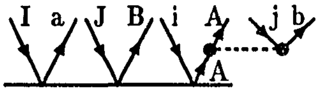
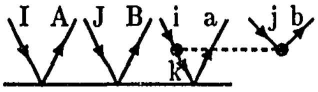
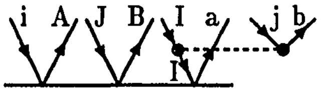
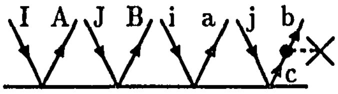
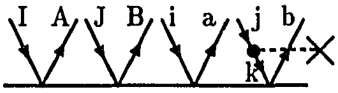
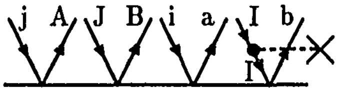
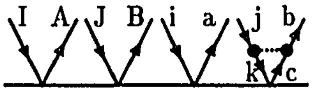
1A		$+\sum_{c}(-1)^{P}P(j/IJi\,\|\,ab/AB)\langle ab\|cj\rangle t^{ABc}_{IJi}$
1B		$-(-1)^{P}P(j/IJi\,\|\,b/aB(A/B))\langle Ab\|Aj\rangle t^{aBA}_{IJi}$
2A		$-\sum_{k}(-1)^{P}P(ij/IJ\,\|\,b/ABa)\langle kb\|ij\rangle t^{ABa}_{IJk}$
2B		$+(-1)^{P}P(j/iJ(I/J)\,\|\,b/ABa)\langle Ib\|Ij\rangle t^{ABa}_{iJI}$
3A		$+\sum_{c}(-1)^{P}P(a/b)f_{bc}t^{ABac}_{IJij}$
3B		$-(-1)^{P}P(A/B)f_{AA}t^{bBaA}_{IJij}$
4A		$-\sum_{k}(-1)^{P}P(i/j)f_{kj}t^{ABab}_{IJik}$
4B		$+(-1)^{P}P(I/J)f_{II}t^{ABab}_{jJiI}$
5A		$-\sum_{\substack{c\\k}}(-1)^{P}P(i/j\,\|\,a/b)\langle kb\|jc\rangle t^{ABac}_{IJik}$

Table IV.7 (continued)

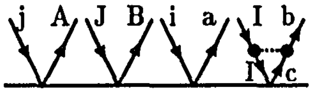
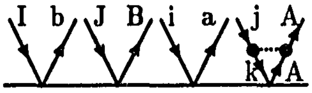
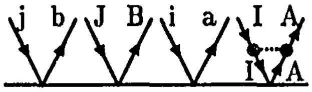
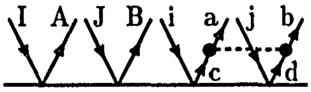
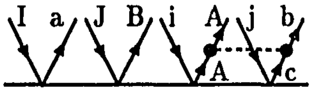
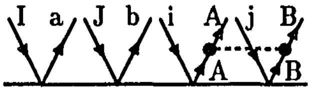
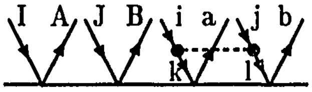
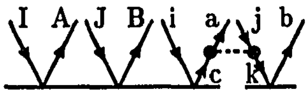
5B		$+\sum_{c}(-1)^{P}P((I/J)\,\vert\, a/b)\langle Ib\Vert Ic\rangle t_{jJiI}^{ABac}$
5C		$+\sum_{k}(-1)^{P}P(i/j\,\vert\,(A/B))\langle kA\Vert jA\rangle t_{IJik}^{bBaA}$
5D		$-(-1)^{P}P((I/J)\,\vert\,(A/B))\langle IA\Vert IA\rangle t_{jJiI}^{bBaA}$
6A		$+\frac{1}{2}\sum_{c,d}\langle ab\Vert cd\rangle t_{IJij}^{ABcd}$
6B		$-\sum_{c}(-1)^{P}P(a/b(A/B))\langle Ab\Vert Ac\rangle t_{IJij}^{aBAc}$
6C		$+\langle AB\Vert AB\rangle t_{IJij}^{abAB}$
7A		$+\frac{1}{2}\sum_{k,l}\langle kl\Vert ij\rangle t_{IJkl}^{ABab}$
7B		$-\sum_{k}(-1)^{P}P(i/j(I/J))\langle Ik\Vert Ij\rangle t_{iJIk}^{ABab}$
7C		$+\langle IJ\Vert IJ\rangle t_{ijIJ}^{ABab}$

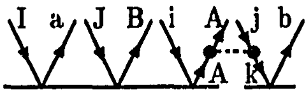
Table IV.7 (continued)

8A



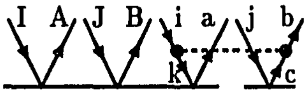
$$-\sum_{\substack{c\\k}}(-1)^P P(j/IJi\,\|\,a/b/AB)\langle ak\,\|\,cj\rangle t_{IJi}^{ABc}t_k^b$$

8B



$$+\sum_{k}(-1)^P P(j/IJi\,\|\,A/b/aB(A/B))\langle Ak\,\|\,Aj\rangle t_{IJi}^{aBA}t_k^b$$

9A

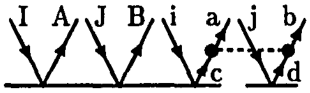


$$-\sum_{\substack{c\\k}}(-1)^P P(i/j/IJ\,\|\,b/ABa)\langle kb\,\|\,ic\rangle t_{IJk}^{ABa}t_j^c$$

9B

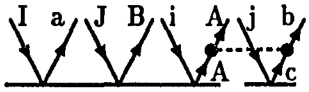
$$+\sum_{c}(-1)^P P(I/j/iJ(I/J)\,\|\,b/ABa)\langle Ib\,\|\,Ic\rangle t_{iJI}^{ABa}t_j^c$$

10A

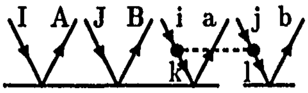


$$+\sum_{c,d}(-1)^P P(j/IJi\,\|\,ab/AB)\langle ab\,\|\,cd\rangle t_{IJi}^{ABc}t_j^d$$

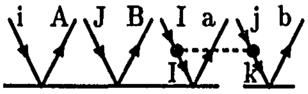
Table IV.7 (continued)

10B


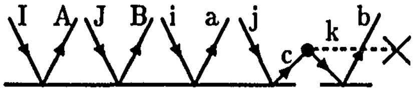
$$-\sum_{c}(-1)^{P}P(j/IJi\,\|\,b/aB(A/B))\langle Ab\|Ac\rangle t_{IJi}^{aBA}t_{j}^{c}$$

11A


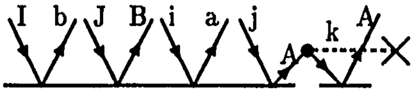
$$+\sum_{k,l}(-1)^{P}P(ij/IJ\,\|\,b/ABa)\langle kl\|ij\rangle t_{IJk}^{ABa}t_{l}^{b}$$

11B


$$-\sum_{k}(-1)^{P}P(j/iJ(I/J)\,\|\,b/ABa)\langle Ik\|Ij\rangle t_{iJI}^{ABa}t_{k}^{b}$$

12A


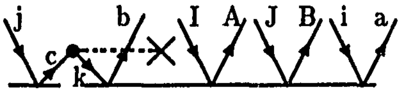
$$-\sum_{\substack{c\\k}}(-1)^{P}P(a/b)f_{kc}t_{IJij}^{ABac}t_{k}^{b}$$

12B


$$+\sum_{k}(-1)^{P}P(A/B)f_{kA}t_{IJij}^{bBaA}t_{k}^{A}$$

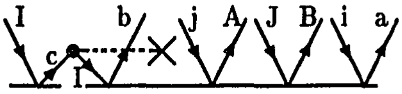
Table IV.7 (continued)

13A



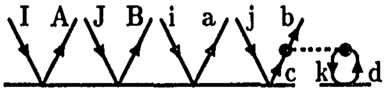
$$-\sum_{\substack{c\\k}}(-1)^P P(i/j) f_{kc} t_{kIJi}^{bABa} t_j^c$$

13B



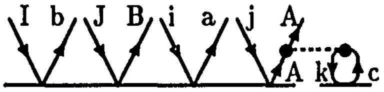
$$+\sum_{c}(-1)^P P(I/J) f_{Ic} t_{IjJi}^{bABa} t_I^c$$

14A



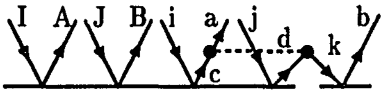
$$+\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle bk\|cd\rangle t_{IJij}^{ABac} t_k^d$$

14B



$$-\sum_{\substack{c\\k}}(-1)^P P(A/B)\langle Ak\|Ac\rangle t_{IJij}^{bBaA} t_k^c$$

15A



$$-\frac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle ak\|cd\rangle t_{IJij}^{ABcd} t_k^b$$

Table IV.7 (continued)

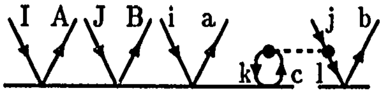
15B

$$+\sum_{\substack{c\\k}}(-1)^P P(b/Aa(A/B))\langle Ak\|Ac\rangle t_{IJij}^{aBAc}t_k^b$$

15C

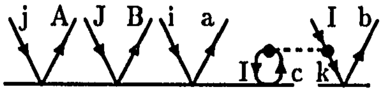
$$-\sum_{k}(-1)^P P(A/B)\langle Ak\|AB\rangle t_{IJij}^{abAB}t_k^B$$

16A



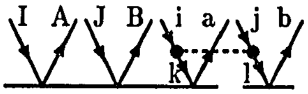
$$-\sum_{\substack{c\\k,l}}(-1)^P P(i/j\,|\,a/b)\langle kl\|cj\rangle t_{IJik}^{ABac}t_l^b$$

16B



$$+\sum_{\substack{c\\k}}(-1)^P P(I/J\,|\,a/b)\langle Ik\|cI\rangle t_{jJiI}^{ABac}t_k^b$$

11A



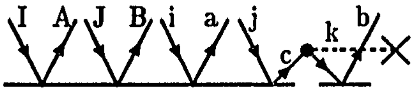
$$+\sum_{k,l}(-1)^P P(ij/IJ\|b/ABa)\langle kl\|ij\rangle t_{IJk}^{ABa}t_l^b$$

Table IV.7 (continued)

11B

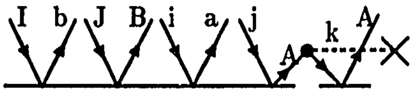
$$-\sum_{k}(-1)^{P}P(j/iJ(I/J)\,\|\,b/ABa)\langle Ik\,\|\,Ij\rangle t_{iJI}^{ABa}t_{k}^{b}$$

12A



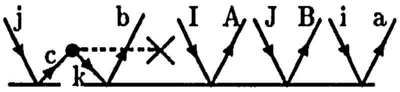
$$-\sum_{\substack{c\\k}}(-1)^{P}P(a/b)f_{kc}t_{IJij}^{ABac}t_{k}^{b}$$

12B



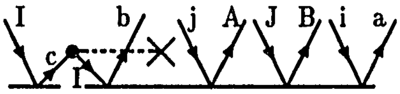
$$+\sum_{k}(-1)^{P}P(A/B)f_{kA}t_{IJij}^{bBaA}t_{k}^{A}$$

13A



$$-\sum_{\substack{c\\k}}(-1)^{P}P(i/j)f_{kc}t_{kIJi}^{bABa}t_{j}^{c}$$

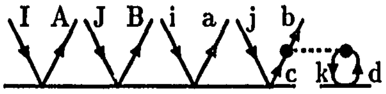
13B



$$+\sum_{c}(-1)^{P}P(I/J)f_{Ic}t_{IjJi}^{bABa}t_{I}^{c}$$

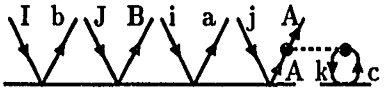
Table IV.7 (continued)

14A



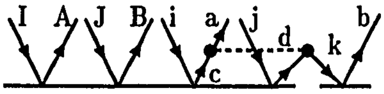
$$+\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle bk\|cd\rangle t_{IJij}^{ABac}t_k^d$$

14B



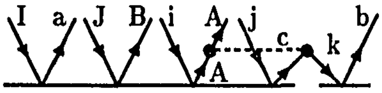
$$-\sum_{\substack{c\\k}}(-1)^P P(A/B)\langle Ak\|Ac\rangle t_{IJij}^{bBaA}t_k^c$$

15A



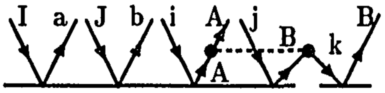
$$-\tfrac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(a/b)\langle ak\|cd\rangle t_{IJij}^{ABcd}t_k^b$$

15B



$$+\sum_{\substack{c\\k}}(-1)^P P(b/Aa(A/B))\langle Ak\|Ac\rangle t_{IJij}^{aBAc}t_k^b$$

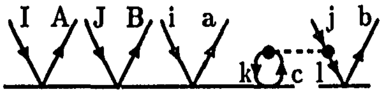
15C



$$-\sum_{k}(-1)^P P(A/B)\langle Ak\|AB\rangle t_{IJij}^{abAB}t_k^B$$

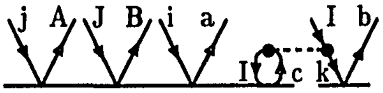
Table IV.7 (continued)

16A



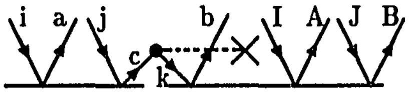
$$-\sum_{\substack{c\\k,l}}(-1)^P P(i/j\,|\,a/b)\langle kl\,\|\,cj\rangle t_{IJik}^{ABac}t_l^b$$

16B



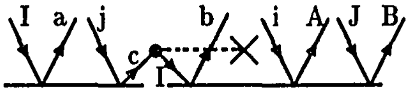
$$+\sum_{\substack{c\\k}}(-1)^P P(I/J\,|\,a/b)\langle Ik\,\|\,cI\rangle t_{jJiI}^{ABac}t_k^b$$

21A



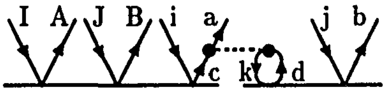
$$-\sum_{\substack{c\\k}}(-1)^P P(ij/IJ\,\|\,a/ABb)f_{kc}t_{kIJ}^{bAB}t_{ij}^{ac}$$

21B



$$+\sum_{c}(-1)^P P(j/iJ(I/J)\,\|\,a/ABb)f_{Ic}t_{IiJ}^{bAB}t_{Ij}^{ac}$$

22A



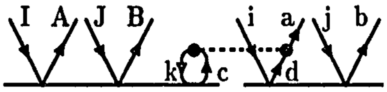
$$+\sum_{\substack{c,d\\k}}(-1)^P P(a/b/AB\,\|\,j/IJi)\langle ak\,\|\,cd\rangle t_{IJi}^{ABc}t_{kj}^{db}$$

Table IV.7 (continued)

22B

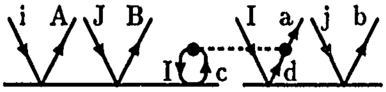
$$-\sum_{\substack{c\\k}}(-1)^P P(A/b/aB(A/B)\,\|\,j/IJi)\langle Ak\,\|\,Ac\rangle t_{IJi}^{aBA}t_{kj}^{cb}$$

23A



$$+\sum_{\substack{c,d\\k}}(-1)^P P(IJ/ij\,\|\,AB/a/b)\langle ka\,\|\,cd\rangle t_{IJk}^{ABc}t_{ij}^{db}$$

23B



$$-\sum_{c,d}(-1)^P P(iJ/j(I/J)\,\|\,AB/a/b)\langle Ia\,\|\,cd\rangle t_{iJI}^{ABc}t_{Ij}^{db}$$

23C

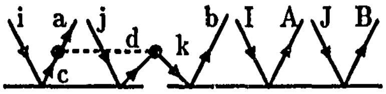
$$-\sum_{\substack{c\\k}}(-1)^P P(IJ/ij\,\|\,aB/A/b(A/B))\langle kA\,\|\,Ac\rangle t_{IJk}^{aBA}t_{ij}^{cb}$$

23D

$$+\sum_{c}(-1)^P P(iJ/j(I/J)\,\|\,aB/A/b(A/B))\langle IA\,\|\,Ac\rangle t_{iJI}^{aBA}t_{Ij}^{cb}$$

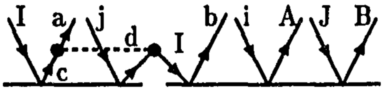
Table IV.7 (continued)

24A



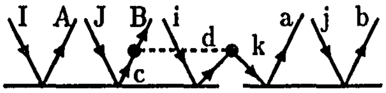
$$-\frac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(ij/IJ\,\|\,a/bAB)\langle ak\,\|\,cd\rangle t_{kIJ}^{bAB}t_{ij}^{cd}$$

24B



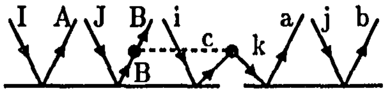
$$+\frac{1}{2}\sum_{c,d}(-1)^P P(j/iJ(I/J)\,\|\,a/bAB)\langle aI\,\|\,cd\rangle t_{IiJ}^{bAB}t_{Ij}^{cd}$$

25A



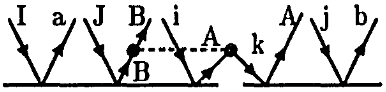
$$-\frac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(IJi/j\,|\,B/ab(A/B))\langle Bk\,\|\,cd\rangle t_{IJi}^{Acd}t_{kj}^{ab}$$

25B



$$-\sum_{\substack{c\\k}}(-1)^P P(IJi/j\,\|\,A/B/ab(A/B))\langle Bk\,\|\,Bc\rangle t_{IJi}^{ABc}t_{kj}^{ab}$$

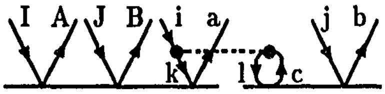
25C



$$+\sum_{k}(-1)^P P(IJi/j\,\|\,a/B/b(A/B))\langle Bk\,\|\,BA\rangle t_{IJi}^{aBA}t_{kj}^{Ab}$$

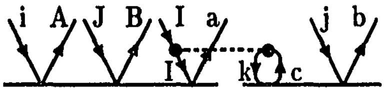
Table IV.7 (continued)

26A



$$-\sum_{\substack{c\\k,l}}(-1)^P P(IJ/i/j\,\|\,ABa/b)\langle kl\,\|\,ic\rangle t_{IJk}^{ABa}t_{lj}^{cb}$$

26B

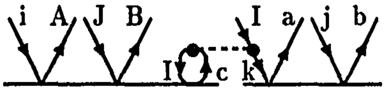


$$+\sum_{\substack{c\\k}}(-1)^P P(iJ/I/j(I/J)\,\|\,ABa/b)\langle Ik\,\|\,Ic\rangle t_{iJI}^{ABa}t_{kj}^{cb}$$

27A

$$-\sum_{\substack{c\\k,l}}(-1)^P P(IJ/i/j\,\|\,AB/ab)\langle kl\,\|\,ci\rangle t_{IJk}^{ABc}t_{lj}^{ab}$$

27B



$$+\sum_{\substack{c\\k}}(-1)^P P(iJ/I/j(I/J)\,\|\,AB/ab)\langle Ik\,\|\,cI\rangle t_{iJI}^{ABc}t_{kj}^{ab}$$

27C

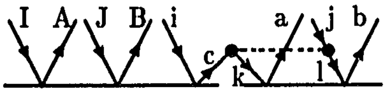
$$+\sum_{k,l}(-1)^P P(IJ/i/j\,\|\,aB/b(A/B))\langle kl\,\|\,Ai\rangle t_{IJk}^{aBA}t_{lj}^{Ab}$$

Table IV.7 (continued)

27D

$$-\sum_{k}(-1)^P P(iJ/I/j(I/J)\,\|\,aB/b(A/B))\langle Ik\,\|\,AI\rangle t_{iJI}^{aBA}t_{kj}^{Ab}$$

28A

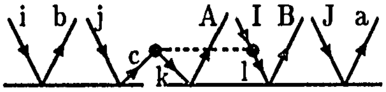


$$+\tfrac{1}{2}\sum_{\substack{c\\k,l}}(-1)^P P(IJi/j\,\|\,AB/ab)\langle kl\,\|\,cj\rangle t_{IJi}^{ABc}t_{kl}^{ab}$$

28B

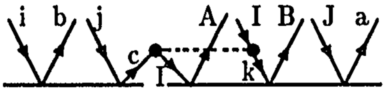
$$-\tfrac{1}{2}\sum_{k,l}(-1)^P P(IJi/j\,\|\,aB/b(A/B))\langle kl\,\|\,Aj\rangle t_{IJi}^{aBA}t_{kl}^{Ab}$$

29A



$$-\tfrac{1}{2}\sum_{\substack{c\\k,l}}(-1)^P P(ij/I(I/J)\,|\,a/b)\langle kl\,\|\,cI\rangle t_{klJ}^{ABa}t_{ij}^{bc}$$

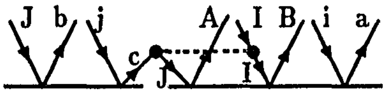
29B



$$-\sum_{\substack{c\\k}}(-1)^P P(ij/I/J(I/J)\,\|\,ABa/b)\langle Ik\,\|\,cI\rangle t_{IkJ}^{ABa}t_{ij}^{bc}$$

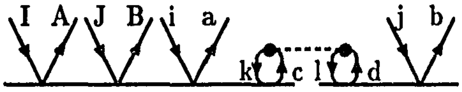
Table IV.7 (continued)

29C



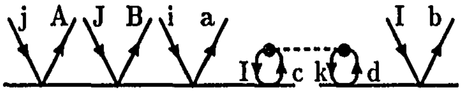
$$+\sum_{c}(-1)^{P}P(j/I/i(I/J)\,|\,ABa/b)\langle JI\|cI\rangle t_{JIi}^{ABa}t_{Jj}^{bc}$$

30A



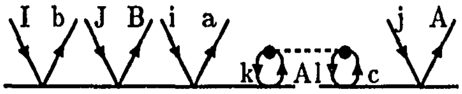
$$+\sum_{\substack{c,d\\k,l}}(-1)^{P}P(i/j\,|\,a/b)\langle kl\|cd\rangle t_{IJik}^{ABac}t_{lj}^{db}$$

30B



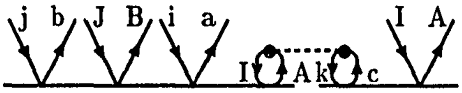
$$-\sum_{\substack{c,d\\k}}(-1)^{P}P((I/J)\,|\,a/b)\langle Ik\|cd\rangle t_{jJiI}^{ABac}t_{kI}^{db}$$

30C



$$-\sum_{\substack{c\\k,l}}(-1)^{P}P(i/j\,|\,(A/B))\langle kl\|Ac\rangle t_{IJik}^{bBaA}t_{lj}^{cA}$$

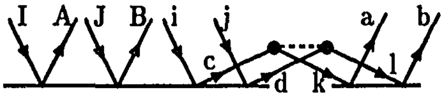
30D



$$+\sum_{\substack{c\\k}}(-1)^{P}P((I/J)\,|\,(A/B))\langle Ik\|Ac\rangle t_{jJiI}^{bBaA}t_{kI}^{cA}$$

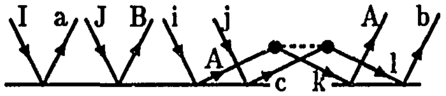
Table IV.7 (continued)

31A



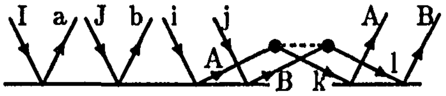
$$+\frac{1}{4}\sum_{\substack{c,d\\k,l}}\langle kl\,\|\,cd\rangle t_{IJij}^{ABcd}t_{kl}^{ab}$$

31B



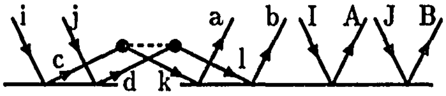
$$-\frac{1}{2}\sum_{\substack{c\\k,l}}(-1)^P P(a/b(A/B))\langle kl\,\|\,Ac\rangle t_{IJij}^{aBAc}t_{kl}^{Ab}$$

31C



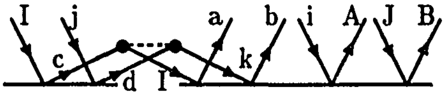
$$+\frac{1}{2}\sum_{k,l}\langle kl\,\|\,AB\rangle t_{IJij}^{abAB}t_{kl}^{AB}$$

32A



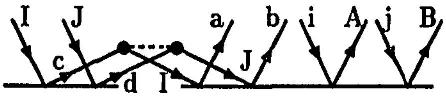
$$+\frac{1}{4}\sum_{\substack{c,d\\k,l}}\langle kl\,\|\,cd\rangle t_{klIJ}^{abAB}t_{ij}^{cd}$$

32B

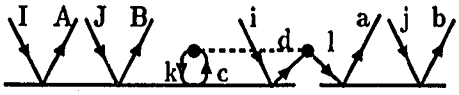


$$-\frac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(i/j(I/J))\langle Ik\|cd\rangle t_{IkiJ}^{abAB}t_{Ij}^{cd}$$

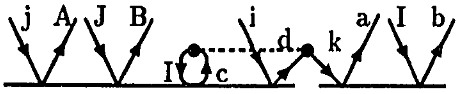
Table IV.7 (continued)

32C


$$+\tfrac{1}{2}\sum_{c,d}\langle IJ\|cd\rangle t_{IJij}^{abAB}t_{IJ}^{cd}$$

33A


$$-\tfrac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^{P}P(i/j)\langle kl\,\|\,cd\rangle t_{IJki}^{ABcd}t_{lj}^{ab}$$

33B


$$+\tfrac{1}{2}\sum_{\substack{c,d\\k}}(-1)^{P}P(I/J)\langle Ik\,\|\,cd\rangle t_{jJIi}^{ABcd}t_{kI}^{ab}$$

33C


$$+\sum_{\substack{c\\k,l}}(-1)^{P}P(i/j\,|\,a/b(A/B))\langle kl\,\|\,Ac\rangle t_{IJki}^{aBAc}t_{lj}^{Ab}$$

33D

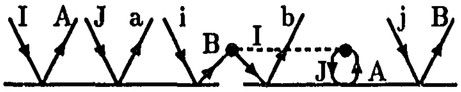

$$-\sum_{k,l}(-1)^{P}P(i/j)\langle kl\,\|\,AB\rangle t_{IJki}^{abAB}t_{lj}^{AB}$$

Table IV.7 (continued)

33E

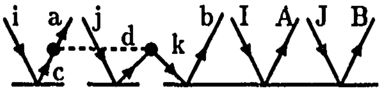
$$-\sum_{\substack{c\\k}}(-1)^P P((I/J)\,|\,a/b(A/B))\langle Ik\,\|\,Ac\rangle t_{jJIi}^{aBAc}t_{kI}^{Ab}$$

40H



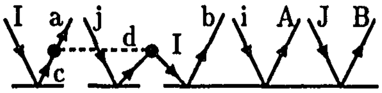
$$-(-1)^P P(a/b(A/B)\,|\,i/j)\langle IJ\,\|\,BA\rangle t_{IJi}^{AaB}t_{IJj}^{bAB}$$

41A



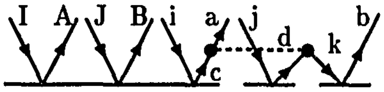
$$-\sum_{\substack{c,d\\k}}(-1)^P P(ij/IJ\,\|\,a/bAB)\langle ak\,\|\,cd\rangle t_{kIJ}^{bAB}t_i^c t_j^d$$

41B



$$+\sum_{c,d}(-1)^P P(j/iJ(I/J)\,\|\,a/bAB)\langle aI\,\|\,cd\rangle t_{IiJ}^{bAB}t_I^c t_j^d$$

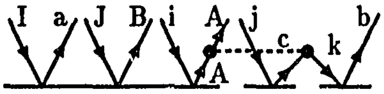
42A



$$-\sum_{\substack{c,d\\k}}(-1)^P P(a/b/AB\,\|\,IJi/j)\langle ak\,\|\,cd\rangle t_{IJi}^{ABc}t_j^d t_k^b$$

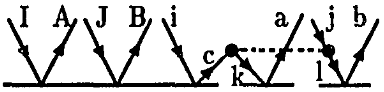
Table IV.7 (continued)

42B



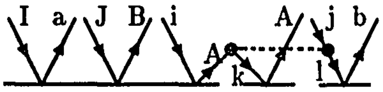
$$+\sum_{\substack{c\\k}}(-1)^P P(aB/A/b(A/B)\,\|\,IJi/j)\langle Ak\,\|\,cd\rangle t_{IJi}^{aBA}t_j^c t_k^b$$

43A



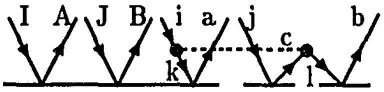
$$+\sum_{\substack{c\\k,l}}(-1)^P P(IJi/j\,\|\,AB/ab)\langle kl\,\|\,cj\rangle t_{IJi}^{ABc}t_k^a t_l^b$$

43B



$$-\sum_{k,l}(-1)^P P(IJi/j\,\|\,b/aB(A/B))\langle kl\,\|\,Aj\rangle t_{IJi}^{aBA}t_k^A t_l^b$$

44A



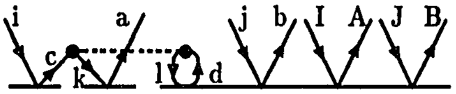
$$+\sum_{\substack{c\\k,l}}(-1)^P P(IJ/i/j\,\|\,ABa/b)\langle kl\,\|\,ic\rangle t_{IJk}^{ABa}t_j^c t_l^b$$

44B

$$-\sum_{\substack{c\\k}}(-1)^P P(iJ/I/j(I/J)\,\|\,ABa/b)\langle Ik\,\|\,Ic\rangle t_{iJI}^{ABa}t_j^c t_l^b$$

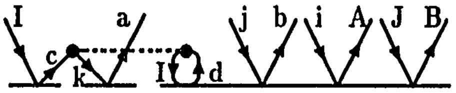
Table IV.7 (continued)

45A



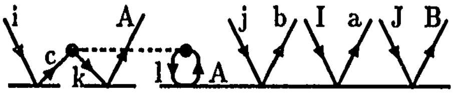
$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j\,|\,a/b)\langle kl\,\|\,cd\rangle t_{ljIJ}^{dbAB}t_i^c t_k^a$$

45B



$$+\sum_{\substack{c,d\\k}}(-1)^P P((I/J)\,|\,a/b)\langle kI\,\|\,cd\rangle t_{IjiJ}^{dbAB}t_I^c t_k^a$$

45C

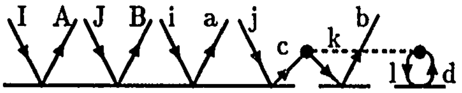


$$+\sum_{\substack{c\\k,l}}(-1)^P P(i/j\,|\,(A/B))\langle kl\,\|\,cA\rangle t_{ljIJ}^{AbaB}t_i^c t_k^A$$

45D

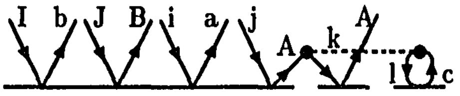
$$-\sum_{\substack{c\\k}}(-1)^P P((I/J)\,|\,(A/B))\langle kI\,\|\,cA\rangle t_{IjiJ}^{AbaB}t_I^c t_k^A$$

46A

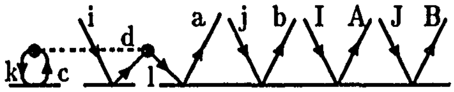


$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(a/b)\langle kl\,\|\,cd\rangle t_{IJij}^{ABac}t_k^b t_l^d$$

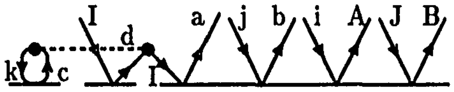
Table IV.7 (continued)

46B


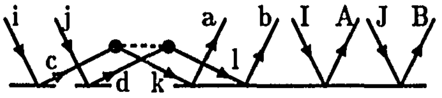
$$+\sum_{\substack{c\\k,l}}(-1)^P P(A/B)\langle kl\|Ac\rangle t_{IJij}^{bBaA}t_k^A t_l^c$$

47A


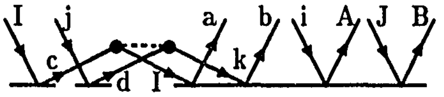
$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j)\langle kl\|cd\rangle t_{ljIJ}^{abAB}t_k^c t_i^d$$

47B


$$+\sum_{\substack{c,d\\k}}(-1)^P P(I/J)\langle kI\|cd\rangle t_{IjiJ}^{abAB}t_k^c t_I^d$$

48A


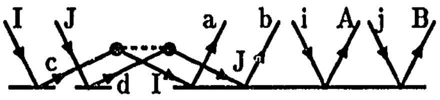
$$+\frac{1}{2}\sum_{\substack{c,d\\k,l}}\langle kl\|cd\rangle t_{klIJ}^{abAB}t_i^c t_j^d$$

48B


$$-\sum_{\substack{c,d\\k}}(-1)^P P(i/j(I/J))\langle Ik\|cd\rangle t_{IkiJ}^{abAB}t_I^c t_j^d$$

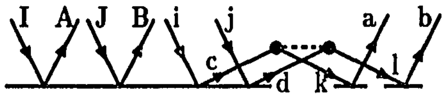
Table IV.7 (continued)

48C



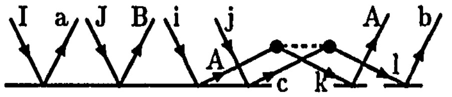
$$+\sum_{c,d}\langle IJ\|cd\rangle t_{IJij}^{abAB} t_I^c t_J^d$$

49A



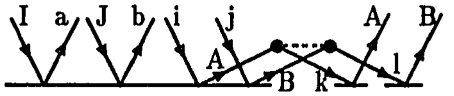
$$+\frac{1}{2}\sum_{\substack{c,d\\k,l}}\langle kl\|cd\rangle t_{IJij}^{ABcd} t_k^a t_l^b$$

49B



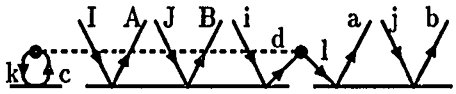
$$-\sum_{\substack{c\\k,l}}(-1)^P P(a/b(A/B))\langle kl\|Ac\rangle t_{IJij}^{aBAc} t_k^A t_l^b$$

49C



$$+\sum_{k,l}\langle kl\|AB\rangle t_{IJij}^{abAB} t_k^A t_l^B$$

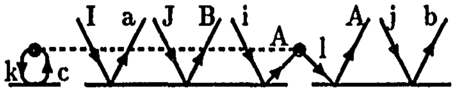
50A



$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(AB/ab\|IJi/j)\langle kl\|cd\rangle t_{IJi}^{ABd} t_{lj}^{ab} t_k^c$$

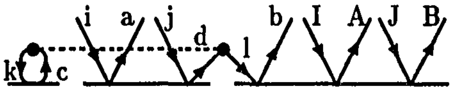
Table IV.7 (continued)

50B



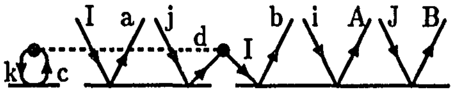
$$+\sum_{\substack{c\\k,l}}(-1)^P P(aB/b(A/B)\|IJi/j)\langle kl\|cA\rangle t_{IJi}^{aBA}t_{lj}^{Ab}t_k^c$$

51A



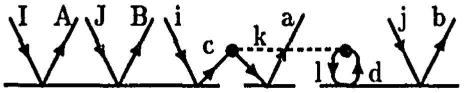
$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(bAB/a\|IJ/ij)\langle kl\|cd\rangle t_{lIJ}^{bAB}t_{ij}^{ad}t_k^c$$

51B



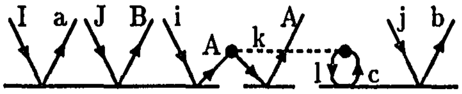
$$+\sum_{\substack{c,d\\k}}(-1)^P P(bAB/a\|iJ/j(I/J))\langle kI\|cd\rangle t_{IiJ}^{bAB}t_{Ij}^{ad}t_k^c$$

52A



$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(AB/a/b\|IJi/j)\langle kl\|cd\rangle t_{IJi}^{ABc}t_{lj}^{db}t_k^a$$

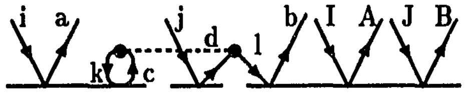
52B



$$+\sum_{\substack{c\\k,l}}(-1)^P P(aB/A/b(A/B)\|IJi/j)\langle kl\|Ac\rangle t_{IJi}^{aBA}t_{lj}^{cb}t_k^A$$

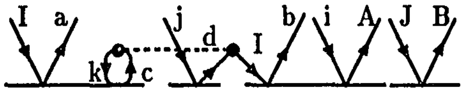
Table IV.7 (continued)

53A



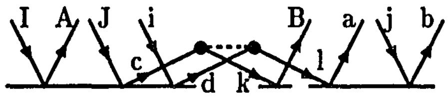
$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(bAB/a\,\|\,IJ/i/j)\langle kl\,\|\,cd\rangle t_{lIJ}^{bAB}t_{ik}^{ac}t_j^d$$

53B



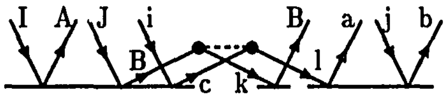
$$+\sum_{\substack{c,d\\k}}(-1)^P P(bAB/a\,\|\,iJ/I/j(I/J))\langle kI\,\|\,cd\rangle t_{IiJ}^{bAB}t_{Ik}^{ac}t_j^d$$

54A



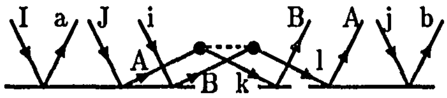
$$+\frac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j\,|\,B/ab(A/B))\langle kl\,\|\,cd\rangle t_{IJi}^{Acd}t_{lj}^{ab}t_k^B$$

54B



$$+\sum_{\substack{c\\k,l}}(-1)^P P(IJi/j\,|\,A/B/ab(A/B))\langle kl\,\|\,Bc\rangle t_{IJi}^{ABc}t_{lj}^{ab}t_k^B$$

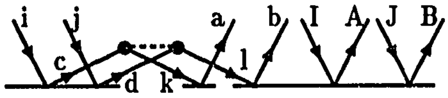
54C



$$-\sum_{k,l}(-1)^P P(IJi/j\,|\,a/B/Ab)\langle kl\,\|\,AB\rangle t_{IJi}^{aAB}t_{lj}^{Ab}t_k^B$$

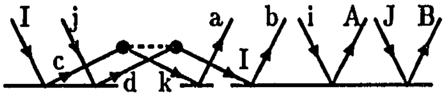
Table IV.7 (continued)

55A



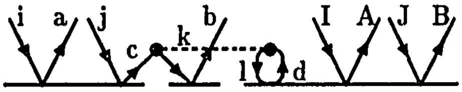
$$+\frac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^P P(bAB/a\,\|\,IJ/ij)\langle kl\,\|\,cd\rangle t_{lIJ}^{bAB}t_{ij}^{cd}t_k^a$$

55B



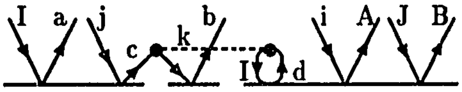
$$-\frac{1}{2}\sum_{\substack{c,d\\k}}(-1)^P P(bAB/a\,\|\,iJ/j)\langle kI\,\|\,cd\rangle t_{IiJ}^{bAB}t_{Ij}^{cd}t_k^a$$

56A



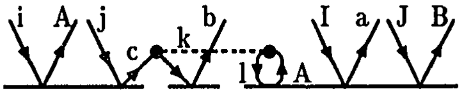
$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(IJ/ij\,\|\,a/b/AB)\langle kl\,\|\,cd\rangle t_{lIJ}^{dAB}t_{ij}^{ac}t_k^b$$

56B



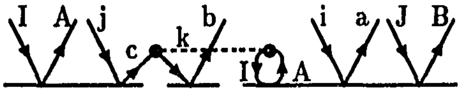
$$+\sum_{\substack{c,d\\k}}(-1)^P P(iJ/j(I/J)\,\|\,a/b/AB)\langle kI\,\|\,cd\rangle t_{IiJ}^{dAB}t_{Ij}^{ac}t_k^b$$

56C

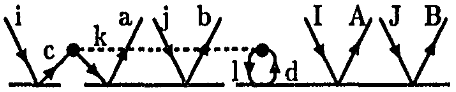


$$+\sum_{\substack{c\\k,l}}(-1)^P P(IJ/ij\,|\,A/b/aB(A/B))\langle kl\,\|\,cA\rangle t_{lIJ}^{AaB}t_{ij}^{Ac}t_k^b$$

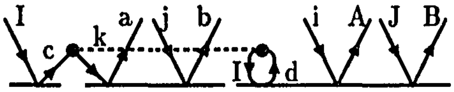
Table IV.7 (continued)

56D


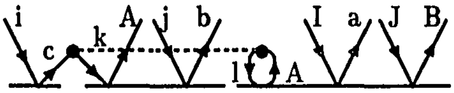
$$-\sum_{\substack{c\\k}}(-1)^P P(iJ/j(I/J)\,|\,A/b/aB(A/B))\langle kI\,\|\,cA\rangle t_{IiJ}^{AaB}t_{Ij}^{Ac}t_k^b$$

57A


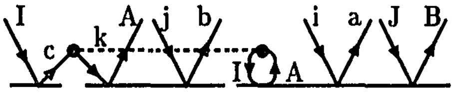
$$-\sum_{\substack{c,d\\k,l}}(-1)^P P(i/j/IJ\,\|\,ab/AB)\langle kl\,\|\,cd\rangle t_{lIJ}^{dAB}t_{kj}^{ab}t_i^c$$

57B


$$+\sum_{\substack{c,d\\k}}(-1)^P P(I/j/iJ(I/J)\,\|\,ab/AB)\langle kI\,\|\,cd\rangle t_{IiJ}^{dAB}t_{kj}^{ab}t_I^c$$

57C


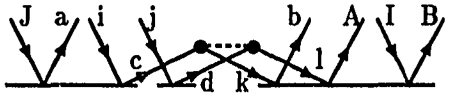
$$+\sum_{\substack{c\\k,l}}(-1)^P P(i/j/IJ\,\|\,b/aB(A/B))\langle kl\,\|\,cA\rangle t_{lIJ}^{AaB}t_{kj}^{Ab}t_i^c$$

57D


$$-\sum_{\substack{c\\k}}(-1)^P P(I/j/iJ(I/J)\,\|\,b/aB(A/B))\langle kI\,\|\,cA\rangle t_{IiJ}^{AaB}t_{kj}^{Ab}t_I^c$$

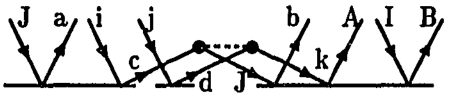
Table IV.7 (continued)

58A



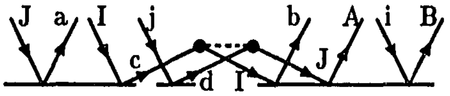
$$-\tfrac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^{P}P(Ji/j(I/J)\,|\,a/b)\langle kl\,\|\,cd\rangle t_{klI}^{bAB}t_{Ji}^{ac}t_{j}^{d}$$

58B



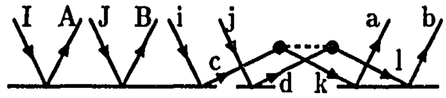
$$-\sum_{\substack{c,d\\k}}(-1)^{P}P(Ji/j/I(I/J)\,\|\,a/bAB)\langle Jk\,\|\,cd\rangle t_{JkI}^{bAB}t_{Ji}^{ac}t_{j}^{d}$$

58C



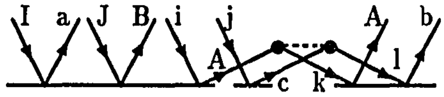
$$+\sum_{c,d}(-1)^{P}P(JI/j/i\,\|\,a/bAB)\langle IJ\,\|\,cd\rangle t_{IJi}^{bAB}t_{JI}^{ac}t_{j}^{d}$$

59A



$$+\tfrac{1}{2}\sum_{\substack{c,d\\k,l}}(-1)^{P}P(AB/ab\,\|\,IJi/j)\langle kl\,\|\,cd\rangle t_{IJi}^{ABc}t_{kl}^{ab}t_{j}^{d}$$

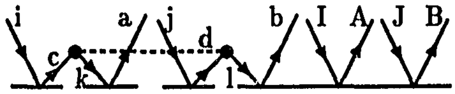
59B



$$-\tfrac{1}{2}\sum_{\substack{c\\k,l}}(-1)^{P}P(aB/b(A/B)\,\|\,IJi/j)\langle kl\,\|\,Ac\rangle t_{IJi}^{aBA}t_{kl}^{Ab}t_{j}^{c}$$

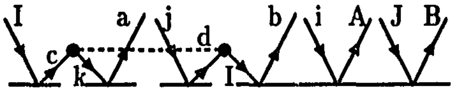
Table IV.7 (continued)

60A



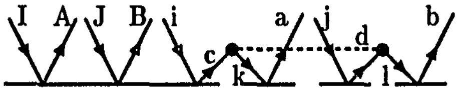
$$+\sum_{\substack{c,d\\k,l}}(-1)^P P(ij/IJ\,\|\,a/bAB)\langle kl\,\|\,cd\rangle t_{lIJ}^{bAB}t_i^c t_k^a t_j^d$$

60B



$$-\sum_{\substack{c,d\\k}}(-1)^P P(j/iJ(I/J)\,\|\,a/bAB)\langle kI\,\|\,cd\rangle t_{IiJ}^{bAB}t_I^c t_k^a t_j^d$$

61A



$$+\sum_{\substack{c,d\\k,l}}(-1)^P P(IJi/j\,\|\,AB/ab)\langle kl\,\|\,cd\rangle t_{IJi}^{ABc}t_k^a t_j^d t_l^b$$

61B

$$-\sum_{\substack{c\\k,l}}(-1)^P P(IJi/j\,\|\,aB/b(A/B))\langle kl\,\|\,Ac\rangle t_{IJi}^{aBA}t_k^A t_j^c t_l^b$$

D. Conclusion

The proposed method is applicable to the specific case of a reference with two determinants which differ by a two electron excitation. The advantages of this method are as follows. First it possesses the qualities and simplicity of single-reference CC. Second the computational expense is approximately twice that of singles and doubles from a single reference determinant. This method represents a viable, practical solution to the MRCC problem for this important case.

This method is extended to more than two reference determinants as well as to determinants which differ from the formal reference by a single electron excitation in the next chapter and some numerical results from test calculations are presented. Of course considering reference determinants which differ by more then a two electron excitation will require higher order excitations from the formal reference determinant then quadruples.

V THE IMPLEMENTATION OF A MULTI-REFERENCE METHOD USING A SINGLE-REFERENCE FORMALISM.

A. Introduction

The need for a MRCC method has been the primary reason that the full inclusion of triple excitations (CCSDT) and quadruple excitations (CCSDTQ) has been developed and implemented. However due to the enormous computational effort involved, these methods are not practical for large scale applications. Several methods, which include triples in an approximate way, have also been proposed and implemented, and since CCSDT can reproduce points on the the potential energy hypersurface for the dissociation of a single bond rather well, these approximate triples methods can also do this with some degree of success. The problem is reproducing the shape of the full configuration interaction (FCI) potential energy hypersurface correctly for the stretching of multiple bonds as well as single bonds. Essentially, in order to do this at a particular level of theory, the appropriate excitations from all significant determinants must be included. Also ideally no additional excitations from from any of the determinants should be included, otherwise the danger of intruder states will arise.

The approximate triples method implemented and presented in this chapter, is a generalization of the two-determinantal coupled-cluster theory presented in the last chapter. The procedure has been modified in order to accomodate more then two determinants in the reference space, as well as to make the computational implementation of the truncation scheme more tractable. This method is based on using a single-reference formalism and explicitly includes only those triple excitations from the 'formal' reference determinant, which correspond to single and double excitations from selected secondary reference determinants.

B. Theory

The symbolic coupled-cluster equations and their derivation have been presented in chapter II, so the details will be omitted here and later presented in the modified form, which represent our approximate triples method. This method is not intended to approximate complete CCSDT but rather to include triple excitations in such a way as to approximate a multi-reference coupled-cluster wavefunction, which includes single and double excitations from all selected determinants in addition to single and double excitations from the formal reference determinant.

It was demonstrated in chapter IV how an excitation from a second reference determinant, which is doubly excited with respect to the formal reference determinant, could be represented in terms of an excitation from the formal reference determinant. In our present formalism we utilize secondary determinants, which are singly and doubly excited with respect to the formal determinant;

$$|1\rangle = |0_I^A\rangle\,, \quad |1\rangle = |0_{IJ}^{AB}\rangle \tag{1}$$

where $|0\rangle$ is the formal reference determinant. In practice all doubly excited secondary reference determinants are selected first, and then the singly excited determinants, which correspond to all single excitations appearing in the selected doubly excited determinant, are added to the reference set. This choice of the reference determinants resembles the complete active space (CAS) approach.

Double excitations from these secondary determinants expressed in terms of excitations from the formal reference determinant, form a restricted set of single and double excitations, which are of course contained in the complete set of single and double excitations from the formal reference determinant (CCSD), along with a restricted set of triple and quadruple excitations;

$$|0^{Aab}_{Iij}\rangle\,,\quad |0^{ABab}_{IJij}\rangle \tag{2}$$

The convention is used here, that upper case letters represent the single excitation required to produce a secondary determinant from the formal reference determinant and lower case letters represent excitations to virtual spin-orbitals (virtual spin-orbitals are spin-orbitals which are un-occupied in the formal reference determinant). The spin-orbitals represented by the upper case letters are special in the sense that they represent a sum over selected secondary reference determinants, which are singly and doubly excited with respect to the 'formal' reference determinant.

The doubly excited determinants are generally the important ones in the molecular bond dissociation process. It was demonstrated in chapter IV that including single and double excitations from a second reference, which is doubly excited with respect to the formal reference, generates three types of triple excitations and one type of quadruple excitation;

$$|0^{ABa}_{IJi}\rangle \qquad |0^{Aab}_{IJi}\rangle \qquad |0^{ABa}_{Iij}\rangle \qquad |0^{ABab}_{IJij}\rangle \tag{3}$$

It is worth mentioning that this multi-determinantal approach should be invariant with respect to an internal unitary transformation among the virtual spin-orbitals, which are not occupied in any of the reference determinants, as well as with respect to an internal transformation among the spin-orbitals, which are occupied in all of the reference determinants. However the method is not in general invarient to a transformation which mixes the two sets of spin-orbitals, or to a transformation which mixes either set with the spin-orbitals which have different occupations in the reference determinants.

The extension to excitations from more then one determinant does not change the energy expression derived in the single-reference formalism due to the fact that the Hamiltonian operator contains at most two-electron operators and the excitations from secondary determinants are in terms of higher order excitations from the formal reference determinant.

In the present phase of the implementation of our multi-reference coupled-cluster method, all the selected quadruple excitations, which arise from double excitations of the doubly excited secondary reference determinants are neglected. These excitations should not be nearly as important as the triple excitations for the dissociation of a single bond. The coupled-cluster quadruple amplitudes are usually very small due to the presence of the t_2^2 terms, which accounts for most of the correlation effects represented by quadruple excitations. The equations, which determine the coupled-cluster amplitudes must now be extended to include the selected set of triples, (7). In the following equations parenthesis are used to indicate the restrictions imposed on the indices of the triple excitations. These equations are;

$$\langle 0_i^a \,|\, H[1 + T_1 + \tfrac{1}{2}\, T_1^2 + \tfrac{1}{3!}\, T_1^3 + T_2 + T_1T_2 + T_3(\tbinom{Aab}{Iij})] \,|\, 0\rangle_C = 0 \tag{4}$$

$$\begin{aligned}\langle 0_{ij}^{ab} \,|H[1 + T_1 + \tfrac{1}{2}\, T_1^2 + \tfrac{1}{3!}\, T_1^3 + \tfrac{1}{4!}\, T_1^4 + T_2 + \tfrac{1}{2}\, T_2^2 + T_1T_2 +\\ \tfrac{1}{2}\, T_1^2T_2 + T_3(\tbinom{Aab}{Iij}) + T_1T_3(\tbinom{Aab}{Iij})] \,|\, 0\rangle_C = 0\end{aligned} \tag{5}$$

$$\begin{aligned}\langle 0_{Iij}^{Aab} \,|H[1 + T_1 + \tfrac{1}{2}\, T_1^2 + \tfrac{1}{3!}\, T_1^3 + \tfrac{1}{4!}\, T_1^4 + T_2 + \tfrac{1}{2}\, T_2^2 + T_1T_2 +\\ \tfrac{1}{2}\, T_1^2T_2 + \tfrac{1}{3!}\, T_1^3T_2 + \tfrac{1}{3!}\, T_1T_2^2 + T_3(\tbinom{Aab}{Iij}) +\\ T_1T_3(\tbinom{Aab}{Iij}) + \tfrac{1}{2}\, T_1^2T_3(\tbinom{Aab}{Iij}) + T_2T_3(\tbinom{Aab}{Iij})] \,|\, 0\rangle_C = 0\end{aligned} \tag{6}$$

The multi-reference coupled-cluster wave function is now given by;

$$|\,\psi_{CCSDT}\rangle = e^{T_1 + T_2 + T_3(\binom{Aab}{Iij})}\,|\,0\rangle \tag{7}$$

where the triple excitation operator is;

$$T_3 = \sum_{\binom{A}{I},\, {i>j \atop a>b}} t_{Iij}^{Aab}\, a_A^\dagger a_I a_a^\dagger a_i a_b^\dagger a_j \tag{8}$$

The sum over $\binom{A}{I}$, indicates a sum over all selected singly excited determinants.

C. Procedure

The present procedure uses a blocked active space approach to our restrictions on the sums. The core and virtual space are both blocked into active and inactive labels. The active labels are those involved in one of the selected singly excited determinants. The labels are then arranged as inactive core, active core, active virtual and inactive virtual. Nine types of triple projections appear in equation 11, and their corresponding sums are;

$$\begin{array}{ccccccccc}
(1) & (2) & (3) & (4) & (5) & (6) & (7) & (8) & (9) \\
\langle {}^{ABC}_{IJK}| & \langle {}^{ABC}_{IJk}| & \langle {}^{aBC}_{IJK}| & \langle {}^{aBC}_{IJk}| & \langle {}^{ABC}_{Ijk}| & \langle {}^{abC}_{IJK}| & \langle {}^{aBC}_{Ijk}| & \langle {}^{abC}_{IJk}| & \langle {}^{abC}_{Ijk}| \\
\sum\limits_{\substack{I>J>K \\ A>B>C}} & \sum\limits_{\substack{I>J,k \\ A>B>C}} & \sum\limits_{\substack{I>J>K \\ a,B>C}} & \sum\limits_{\substack{I>J,k \\ a,B>C}} & \sum\limits_{\substack{I,j>k \\ A>B>C}} & \sum\limits_{\substack{I>J>K \\ a>b,C}} & \sum\limits_{\substack{I,j>k \\ a,B>C}} & \sum\limits_{\substack{i>J,k \\ a>b,C}} & \sum\limits_{\substack{I,j>k \\ a>b,C}}
\end{array}$$

The capital letters represent a sum over the active labels (core or virtual) whereas the small letters represent a sum over all labels, active and inactive. Projection number (1) represents the case where all labels are active, projections (2) and (3) represent the case with one inactive label, projections (4),(5) and (6) contain two inactive labels, projections (7) and (8) contain three inactive labels and projection (9) contains four inactive labels and one active pair. These include all possible cases as a triples projection must contain at least one active pair in order to represent a double excitation from one of the the selected secondary reference determinants. As it stands then, this procedure would select all singly and doubly excited determinants, which are contained in the active space, as reference determinants. In the computational implementation we reduce this to a set of active pairs, each pair containing an active occupied and an active unoccupied index. A series of 'if' statements is now introduced to our CCSDT code. The 'if' statements allow the procedure to continue if the projection contains an active pair (one of the singly excited determinants selected as a reference determinant). If the projection does not contain an active pair, the procedure moves to the next projection.

For each type of projection a different manipulation of the summation indices in the coupled-cluster triples equation is required. In order to be included in the coupled-cluster equation, a triple amplitude must contain at least one active core label and one active virtual label. This reduces the storage requirement for triple amplitudes from n^3v^3 to the number of pairs in the active space times n^2v^2, where n and v represent the size of the core and virtual space respectively. Projection (1) contains the entire triples equation unmodified as all indices are active. As an example of how the equation is modified for the nine projections, let us consider a single t_2t_3 term which appears in the triples equation.

$$(1) \quad \sum_{\substack{e>f \\ l,m}} \langle lm \| ef \rangle t_{lIJ}^{Aef} t_{mK}^{BC}$$

$$(2) \quad \sum_{\substack{e>f \\ l,m}} \langle lm \| ef \rangle t_{lIJ}^{Aef} t_{mk}^{BC}$$

$$(3) \quad \sum_{\substack{e>F \\ l,m}} \langle lm \| eF \rangle t_{lIJ}^{aeF} t_{mK}^{BC}$$

$$(4) \quad \sum_{\substack{e>F \\ l,m}} \langle lm \| eF \rangle t_{lIJ}^{aeF} t_{mk}^{BC}$$

$$(5) \quad \sum_{\substack{e>f \\ l,m}} \langle lm \| ef \rangle t_{lIj}^{Aef} t_{mk}^{BC}$$

$$(6) \quad \sum_{\substack{e>F \\ l,m}} \langle lm \| eF \rangle t_{lIJ}^{aeF} t_{mK}^{BC}$$

$$(7) \quad \sum_{\substack{e>F \\ l,m}} \langle lm \| eF \rangle t_{lIj}^{aeF} t_{mk}^{BC}$$

$$(8) \quad \sum_{\substack{e>F \\ l,m}} \langle lm \| eF \rangle t_{lIJ}^{aeF} t_{mk}^{bC}$$

$$(9) \quad \sum_{\substack{e>F \\ l,m}} \langle lm \| eF \rangle t_{lIj}^{aeF} t_{mk}^{bC}$$

The indices of the triple excitation amplitudes are rearranged to use two of the active labels as one index. As an example let us consider (9) from above. This is written as;

$$(9) \quad -\sum_{\substack{e>F \\ l,m}} \langle lm \| eF \rangle t(IF)_{lj}^{ae} t_{mk}^{bC}$$

where (IF) represents a single index running over all the selected active pairs. The change in sign is due to the odd number of permutations required to acheive this arrangement.

D. Results

At this point, in the implementation of the theory a series of if statements is used in the complete CCSDT equations to skip a projection if it does not contain an active pair. The same conditional requirements are used in our array of triple amplitudes by setting the amplitudes with indices, which do not include an active pair, to zero. This means that the current version of the computer program is not fully optimal, but should produce results in agreement with the theory presented in the previous section.

Our first test case is LiH. The basis set used was of double zeta quality, Dunning's contraction[48] of Huzinaga's primitive Gaussians (Li(9s5p) and H(4s) basis with a hydrogen scale factor of 1.2). The results for several internuclear separations are reported in Table V.1. Four secondary reference determinants appear significant as the bond dissociates. At the internuclear separation of 9.045 a.u the dominant double excitation amplitude was -0.95, almost equal to the unit amplitude of the formal reference determinant, indicating that the bond was essentailly dissociated. The need for as many as four secondary reference determinants, and not one as would be expected for the dissociation of a single bond, is most likely caused by the use of Hartree-Fock orbitals and not multi-configuration self consistant field orbitals, which would be more appropriate for this purpose. The present multi-reference coupled-cluster method truncated at triples

(MDCCSD) did quite well at reproducing the full CI results. For all internuclear seaparations the MDCCSD energy is within a few hundreths of a millihartree from the full CI results. On the other hand, the single-reference coupled-cluster method including single and double excitations (CCSD) reproduced the full CI energy almost as well as MDCCSD did at the equilibrium distance, $R_e = 3.015$a.u., (30 μhartrees difference from full CI, compared to 20 μhartrees for MDCCSD). However the difference between the CCSD energy and the full CI energy grew continually larger as the internuclear separation increased. This is expected since the excitations from secondary determinants, which are neglected in CCSD become more important at larger internuclear separation. At 9.045 a.u. the CCSD energy is as much as 0.4 millihartrees higher the full CI energy, compared to the MDCCSD energy which is only 10 μhartrees higher. The MDCCSD energy is consistantly slightly higher then the full CI results, indicating a very good reproduction of the shape of the full CI potential curve.

The second test case is BH. The basis set used was of double zeta quality, Dunning's contraction[48] of Huzinaga's primitive Gaussians (B(9s5p), H(4s) basis with a hydrogen scale factor of 1.2). The results for three internuclear distances, ($R_e = 2.329$a.u., $2R_e$ and $3R_e$) are presented in Table V.2. The results at the equilibrium distance for CCSD and MDCCSD are comparable, and the deviation from full CI for the CCSD energy is .9 millihartrees while for the MDCCSD energy is .25 millihartrees. Once again, as expected, the difference between the full CI energy and the CCSD energy increased as the internuclear separation increased. At three times the equilibrium internuclear separation, the difference between the CCSD energy and the full CI energy has risen to 4.2 millihartrees while the MDSSCD energy has fallen to 78 μhartrees. The dominant doubly excited coupled-cluster amplitude at this separation is -.86, indicating that the bond is essentially dissociated. In the case of BH MDCCSD did not do quite as well at reproducing the full CI potential curve, the difference with the full CI energy was quite small as the bond was stretched but a little higher at equilibrium. This was probably because there were several other double excitation coupled-cluster amplitudes corresponding to excitations from the 3σ orbital, which were significant. A subsequent calculation was done at the equilibriuim internuclear distance which included two additional reference determinants. The energy resulting from this calculation was much closer to the full CI energy. The importance of these amplitudes diminish as one of the 3σ electrons leaves with the H atom during the dissociation process. The third test case is H_2O. The basis set used was of the double zeta quality, Dunning's contraction[48] of Huzinaga's primitive Gaussians (O(9s5p) and H(4s) basis with a hydrogen scale factor of 1.2). Calculations were performed for the equilibrium structure and for the structure obtained by stretching both $O \cdots H$ bonds simultaneously. This stretching simulates the dissociation of a double bond. The results are presented in Table V.3.

Four double excitations were important in this case. For all the structures considered, the MDCCSD method did substantially better then CCSD and about equally as well as CCSDT. The agreement with CCSDT, but not as good as an agreement with full CI, indicates that probably some quadruple excitations would be important, as should be expected for stretching a double bond.

These preliminary results are quite promising and indicate that after optimization of the computer code, the method could become a practical multi-reference coupled-cluster procedure for larger molecular systems.

Table V.1

Correlation energies for LiH at equilibrium[a] and displaced geometries for different levels of theory. The amplitudes shown in the table correspond to the secondary determinants included in MDCCSD calculations. The numbers in parenthesis below CCSD and MDCCSD correlation energies represent the difference with Full CI. All energies are in atomic units.

	$R = R_e^a$	$R = 1.5R_e$	$R = 2R_e$	$R = 2.5R_e$	$R = 3R_e$
SCF	-7.981091	-7.946129	-7.897108	-7.857855	-7.828040
CCSD	-0.027558	-0.037215	-0.056351	-0.083810	-0.110686
	(+0.000030)	(+0.000062)	(+0.000156)	(+0.000229)	(+0.000396)
$t_2^{(1)}$	-0.023792	-0.069650	-0.248844	-0.629817	-0.946416
$t_2^{(2)}$	±0.029169	±0.064722	±0.185693	±0.377804	±0.403532
$t_2^{(3)}$	-0.043226	-0.062463	-0.140338	-0.230839	-0.174602
MDCCSD	-0.027568	-0.037245	-0.056472	-0.084096	-0.111072
	(+0.000020)	(+0.000032)	(+0.000035)	(+0.000014)	(+0.000010)
Full CI	-0.027588	-0.037277	-0.056507	-0.084110	-0.111082

a) $R_e = 3.015$ a.u.

Table V.2

Correlation energies for BH at equilibrium[a] and displaced geometries for different levels of theory. The amplitude shown in the table corresponds to the secondary determinant included in MDCCSD calculations. The numbers in parenthesis below CCSD and MDCCSD correlation energies represent the difference with Full CI. All energies are in atomic units.

	$\mathrm{R} = \mathrm{R}_e^a$	$R = 2R_e$	$R = 3R_e$
SCF	-25.113677	-24.986389	-24.891457
CCSD	-0.073080	0.118799	0.186280
	(+0.000912)	(+0.002772)	(+0.004172)
t_2^b	-0.055486	-0.407870	-0.862314
MDCCSD	-0.073478	-0.121015	-0.190374
	(+0.000513)	(+0.000056)	(+0.000078)
Full CI	-0.073991	-0.121071	-0.190452

a) $\mathrm{R}_e = 2.329$ a.u.

b) When two additional determinants were included at equilibrium the correlation energy became -0.073738. The difference with FCI decreased to +0.000253.

Table V.3

Correlation energies for H_2O at equilibrium[a] and displaced geometries for different levels of theory. The amplitudes shown in the table correspond to the secondary determinants included in MDCCSD calculations. The numbers in parenthesis below CCSD and MDCCSD correlation energies represent the difference with Full CI. All energies are in atomic units.

	$R = R_e^a$	$R = 2R_e$	$R = 3R_e$
SCF	-76.009838	-75.803529	-75.595180
CCSD	-0.146238	0.205402	0.300732
	(+0.001790)	(+0.004068)	(+0.009334)
CCSDT[a]	-0.147594	0.209519	0.312277
	(+0.000434)	(+0.001471)	(-0.002211)
$t_2^{(1)}$	< 0.01	-0.151375	-0.416300
$t_2^{(2)}$	< 0.01	-0.137641	-0.325476
$t_2^{(3)}$	< 0.01	-0.086370	-0.119210
$t_2^{(4)}$	< 0.01	-0.067994	-0.115207
MDCCSD	-0.146929	-0.208934	-0.311256
	(+0.001099)	(+0.002058)	(-0.001190)
	(+0.000665)	(+0.000585)	(-0.001021)
Full CI[a]	-0.148028	-0.210990	-0.310066

a) From reference 19.

E. Conclusion

This is the first development and implementation of a multi-reference coupled-cluster method based on the single-reference formalism. The results of the previous section indicate that this approach will become a viable coupled-cluster method for those cases which are not adequately represented by a single determinantal reference function. The next step in the procedure should be the inclusion of the restricted quadruple amplitudes which were neglected in the present implementation. This would facilitate a procedure applicable to the stretching of multiple bonds. The direct inclusion of quadruple amplitudes will involve solving the CCSDTQ equations for the restricted quadruple amplitudes as well as placing additional terms in the equations for doubly and triply excited amplitudes, which involve those selected quadruple amplitudes.

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