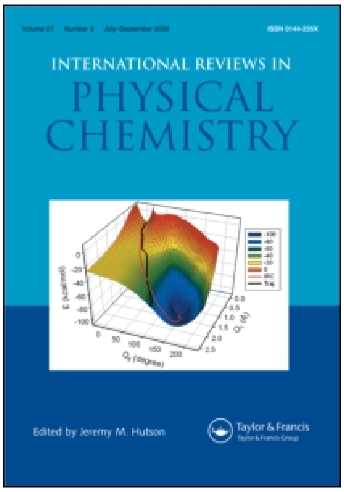

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Multireference coupled cluster method for electronic structure of molecules

Nevin Oliphant[a]; Ludwik Adamowicz[a]
[a] Department of Chemistry, University of Arizona, Tucson, Arizona, USA

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Multireference coupled cluster method for electronic structure of molecules

by NEVIN OLIPHANT and LUDWIK ADAMOWICZ
Department of Chemistry,
University of Arizona,
Tucson, Arizona 85721, USA

In this review we present a systematic derivation of the multireference coupled cluster theory based on the single reference formalism. The coupled cluster theories have recently emerged as one of the major method development activities in the electronic structure theory of atoms and molecules. Due to its size-extensive nature, using the coupled cluster method the total electronic energy of the system can be determined with the same relative accuracy as the total electronic energies of the fragments which the system separates into in the process of chemical decomposition. This feature is essential for the correct theoretical determination of dissociation energies as well as other molecular properties. One of the most difficult challenges in advancing the coupled cluster theory has been the development of the multireference coupled cluster methodology, i.e. generating a scheme which allows the reference function to incorporate more than one Slater determinant. Such development would enable a very accurate *ab initio* treatment of general categories of open-shell systems as well as the treatment of systems with stretched multiple bonds leading to a more precise determination of vibrational spectra. In this article we review our recent results in the development of a multireference coupled cluster theory. The reader will be first acquainted with the second quantization formalism, then guided through the derivation of the single reference coupled cluster theory, and finally presented with the multireference formalism. We have included several numerical examples illustrating the performance of the single reference and multireference coupled cluster methods.

1. Introduction

In recent years, the coupled cluster (CC) theories have emerged as one of the major research activities in the electronic structure theory of molecules (Čížek 1966, Čížek 1969, Paldus *et al.* 1972, Paldus and Čížek 1973, Kutzelnigg 1977, Bartlett and Purvis 1978, Pople *et al.* 1978, Bartlett and Purvis 1980, Bartlett 1981, Bartlett *et al.* 1984, Hoffman and Schaefer 1986, Scuseria and Schaefer 1988). This is due primarily to its size-extensive nature and the efficient introduction of higher categories of configuration interaction (CI) excitations. Single reference models have been shown to be highly successful for non-degenerate systems. Even in difficult quasi-degenerate situations, the single reference CC theory, including contributions from connected triple excitations clusters, provide results in agreement with the basis set limit result, i.e. full CI, to within a few kcal mol^{-1}. Consequently, the single reference CC theory very effectively includes the dynamical correlation that keeps electrons apart. However, for cases where non-dynamical correlation is important, i.e. when several configurations might be expected to make relatively equally important contributions to the exact wavefunction, the reference function should preferably include all these important configurations instead of having to depend upon the time-consuming evaluation of high-order cluster operators to introduce such quasi-degenerate effects. Hence, this spawned interest in the development of multireference (MR) CC theories (Mukherjee *et al.* 1975, 1977, 1979, Mukhopadhyay *et al.* 1979, Offerman 1976, Offerman *et al.* 1976, Monkhorst 1977, Ey 1978, Lingren 1978, Mukhopadhyay *et al.* 1979, Banerjee and Simons 1981, Jeziorski and Monkhorst 1981, Paldus 1983, Haque *et al.* 1984, Laidig and Bartlett 1984, Nakatsuji 1985, Stolarczyk and Monkhorst 1986, 1988, Laidig *et al.* 1987).

The multireference CC generalization for the open-shell molecules and bond breaking is under rapid development. There are several distinct approaches, differing not only in the methodology but also in their scope of applications. There are theories specifically designed to treat the correlation energy of the open-shell states, the category which includes bond breaking on potential energy surfaces, and there are other CC methods which are tailored to calculate energy differences between energy levels directly (Nakatsuji 1978, 1979, Paldus *et al.* 1978, Mukherjee and Mukherjee 1979, Reitz and Kutzelnigg 1979, Saute *et al.* 1979, Ghosh *et al.* 1981, 1982, Pal *et al.* 1984, Sekino and Bartlett 1984, Stolarczyk and Monkhorst 1986, 1988, Jeziorski and Paldus 1988, Meissner *et al.* 1988, Paldus *et al.* 1989, Piecuch and Paldus 1992). An essential property, which one usually insists upon for any MRCC approach to possess, is a proper linked-diagram theorem, i.e. the correct size-extensive character.

The majority of the existing MRCC methods for open-shell or quasi-degenerate states may be classified into two groups, depending upon whether they employ the valence universal wave operator and a Fock space description (Mukherjee *et al.* 1975, 1977, Offerman *et al.* 1976, Lingren 1978, Mukherjee 1979, Mukhopadhyay *et al.* 1979, Kutzelnigg 1982, Kutzelnigg and Koch 1983, Haque and Mukherjee 1984, Stolarczyk and Monkhorst 1986, 1988, Jeziorski and Paldus 1989), or a Hilbert space specific wave operator (Banerjee and Simons 1981, Jeziorski and Monkhorst 1981, Paldus 1983, Laidig and Bartlett 1984, Laidig *et al.* 1987). These methods are closely related to the multireference many-body perturbation theories (MR MBPT) (Brandow 1967, Sanders 1969, Lingren 1974, Hose and Kaldor 1979, 1981, 1982, 1984, Kaldor 1984). The first formulations of MRCC, as well as MBPT, assumed the completeness of the model space. This led to a connected expansion of the effective Hamiltonian. However, in an effective Hamiltonian method the necessity of a complete active space is almost certain to introduce intruder state problems. An attempt to drop the completeness assumption was made by Hose and Kaldor in their version of MR MBPT (Hose and Kaldor 1979, 1980, 1981, 1982, 1984). As a consequence, disconnected diagrams appeared in the Hamiltonian. In the incomplete model space version MRCC, developed later by Jeziorski and Monkhorst (1981), the disconnected terms were also observed in both the cluster operator and in the expansion of the effective Hamiltonian.

Unlike the single reference theory, there are two potential sources of size-inextensive terms in MRCC theory, i.e. the method used to construct the effective Hamiltonian and its subsequent diagonalization. The connectedness property of the cluster operator for the effective Hamiltonian is essential for the extensivity of the method. However, one must also preserve the extensive property through the diagonalization of the effective Hamiltonian within the model space. Some workers have constructed incomplete model space MRCC methods by appealing to a valence universal wave operator and Fock space description that permits cluster operators to be defined unambiguously by hierarchically solving the $N-1$ and $N+1$ electron problems, along with the N-electron problem. However, no one yet managed to formulate a general rigorous MRCC within a Hilbert space N-electron framework.

It was recently discovered (Mukhopadhyay and Mukherjee 1991) that one needs a separable wave operator to preserve the connectivity of the effective Hamiltonian, and the normalization of the wave operator, i.e. its model-space projection, must not conflict with the separability requirement. For an incomplete model space, the traditional intermediate normalization was found to be size inextensive. Several size-extensive choices of normalization of the wave operator, which have been discussed, lead generally to a rather complicated formulation of the MRCC theory.

An alternative formulation of the MRCC approach, which we have been advancing recently (Oliphant and Adamowicz 1991), avoids the complication of the previous approaches by utilizing the single reference particle–hole formalism. In this formalism the proper size-extensive character of the method, exhibits itself through the connected nature of the diagrams representing both the total energy as well as the individual contributions to the CC equations for the amplitudes. In this article we review our MRCC theory, its computational implementation and numerical results. We start with a brief introduction of the second quantization technique and its diagrammatic language, which is subsequently used to present the MRCC theory.

2. The single reference coupled cluster theory

2.1. *Second quantization*

In order to generate the algebraic expressions corresponding to the equations in coupled cluster theory, it is convenient to use diagrammatic methods. The origin of 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 (Hugenholtz 1957, Brandow 1967, Čížek 1966, Paldus and Čížek 1975, Sadlej 1989). The systematic procedure for unambiguously generating diagrams developed by Kucharski and Bartlett (Kucharski and Bartlett 1986) was used in this work.

Second quantization is a change of representation from the common coordinate representation to the occupation number representation of states. The Hartree–Fock (HF) or self consistent 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;

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

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;

$$|0\rangle = |1111111111\rangle. \tag{3}$$

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

$$|0_9^{11}\rangle = |11111111011\rangle. \tag{4}$$

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

$$a_k|n_1n_2\dots 1_kn_{k+1}\dots\rangle=(-1)^{g_k}n_k|n_1n_2\dots 0_kn_{k+1}\dots\rangle, \tag{5}$$

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 consistent way for all possible determinants resulting from spin-orbital substitutions. The n_k results from 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;

$$a_k|n_1n_2\dots 0_kn_{k+1}\dots\rangle=0. \tag{7}$$

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

$$a_k^\dagger|n_1n_2\dots 0_kn_{k+1}\dots\rangle=(-1)^{g_k}(1-n_k)|n_1n_2\dots 1_kn_{k+1}\dots\rangle. \tag{8}$$

The $(1-n_k)$ results from the fact that if a 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;

$$a_k^\dagger|n_1n_2\dots 1_kn_{k+1}\dots\rangle=0. \tag{9}$$

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);

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

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

$$[a_k,a_l]_+=a_ka_l+a_la_k=0. \tag{12}$$

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 antisymmetric with respect to the interchange of 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;

$$a_ka_k^\dagger, \tag{13}$$

with an eigenvalue equal to the one minus the occupation number of the kth spin-orbital;

$$a_ka_k^\dagger|n_1n_2\dots n_kn_{k+1}\dots\rangle=(1-n_k)|n_1n_2\dots n_kn_{k+1}\dots\rangle. \tag{14}$$

Similarly any state vector is an eigenfunction of the operator;

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

with an eigenvalue equal to the occupation number of the kth spin-orbital;

$$a_k^\dagger a_k|n_1n_2\dots n_kn_{k+1}\dots\rangle=n_k|n_1n_2\dots n_kn_{k+1}\dots\rangle. \tag{16}$$

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

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

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 Ath nucleus, and r_{ij} is the radial distance between the ith electron and the jth electron. Combining the first two terms into one electron operator h, the Hamiltonian can be written in the second quantized formalism as

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

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

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

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;

$$T_n=\left(\frac{1}{n!}\right)^2\sum_{\substack{i,j,k,\ldots,n_i\\ a,b,c,\ldots,n_a}}t_{ijk\ldots n_i}^{abc\ldots n_a}a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_k\ldots a_{n_a}^\dagger a_{n_i}. \tag{20}$$

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 wavefunction, (called amplitudes in coupled cluster theory).

2.2. *Coupled cluster theory*

The single reference coupled cluster (CC) method has been described in many places (Coester 1958, Hubbard 1957, 1958, Coester and Kümmel 1960, Sinanoglu 1962, Čížek 1966, 1969, Nesbet 1968, 1969, Paldus, Čížek and Shavitt 1972, Paldus 1977, Bartlett and Purvis 1978, 1980, Pople *et al.* 1978, Chiles and Dykstra 1981, Banerjee and Simons 1982, Purvis and Bartlett 1982, Kutzelnigg and Koch 1983, Kucharski and Bartlett 1984, 1985, Lee and Bartlett 1984, Lee *et al.* 1984, 1985, Haque and Kaldor 1985, Hoffman and Schaefer 1986, Noga and Bartlett 1987, Noga *et al.* 1987, Lee and Rice 1988, Scuseria and Schaefer 1988, Kucharski and Bartlett 1989, Oliphant and Adamowicz 1991, Piecuch and Paldus 1992). 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;

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

where the exponential operator is expanded as;

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

and the T operator is;

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

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 ts 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 (29) 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 energy;

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

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, $\langle 0_{ijkl}^{abcd}|$, etc., where;

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

$$\langle 0_{ij}^{ab}|H[1+T_1+\tfrac{1}{2}T_1^2+\tfrac{1}{3!}T_1^3+\tfrac{1}{4!}T_1^4+T_2+\tfrac{1}{2}T_2^2+T_1T_2 + \tfrac{1}{2}T_1^2T_2+T_3+T_1T_3+T_4]|0\rangle = E_{cc}\langle 0_{ij}^{ab}|T_2+\tfrac{1}{2}T_1^2|0\rangle, \quad (33)$$

$$\langle 0_{ijk}^{abc}|H[T_1+T_2+\tfrac{1}{2}T_1^2+T_3+\tfrac{1}{3!}T_1^3+T_1T_2+T_4+\tfrac{1}{4!}T_1^4+\tfrac{1}{2}T_1^2T_2+T_1T_3+\tfrac{1}{2}T_2^2 + \tfrac{1}{5!}T_1^5+\tfrac{1}{3!}T_1^3T_2+\tfrac{1}{2}T_1^2T_3+\tfrac{1}{2}T_1T_2^2+T_1T_4+T_2T_3]|0\rangle = E_{cc}\langle 0_{ijk}^{abc}|T_3+T_1T_2+\tfrac{1}{3!}T_1^3|0\rangle \quad (34)$$

$$\langle 0_{ijkl}^{abcd}|H[T_2+\tfrac{1}{2}T_1^2+T_3+\tfrac{1}{3!}T_1^3+T_1T_2+T_4+\tfrac{1}{4!}T_1^4+\tfrac{1}{2}T_1^2T_2+T_1T_3+\tfrac{1}{2}T_2^2 + \tfrac{1}{5!}T_1^5+\tfrac{1}{3!}T_1^3T_2+\tfrac{1}{2}T_1^2T_3+\tfrac{1}{2}T_1T_2^2+T_1T_4+T_2T_3+\tfrac{1}{6!}T_1^6 + \tfrac{1}{4!}T_1^4T_2+\tfrac{1}{3!}T_1^3T_3+\tfrac{1}{2}T_1^2T_4+\tfrac{1}{4}T_1^2T_2^2+T_1T_2T_3+\tfrac{1}{3!}T_2^3 + T_2T_4+\tfrac{1}{2}T_3^2]|0\rangle = E_{cc}\langle 0_{ijkl}^{abcd}|T_4+T_1T_3+\tfrac{1}{2}T_1^2T_2+\tfrac{1}{4!}T_1^4+T_1T_3|0\rangle \quad (35)$$

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).

2.3. *Coupled cluster diagrams and equations*

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

a_p becomes . (36)

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

$a_q^\dagger$ becomes . (37)

It is useful to employ the normal product form of the Hamiltonian rather than the standard form (equation 18):

As in section 2.1 of this chapter, the one and two electron parts of the Hamiltonian can be separated as;

$$H_N = H - \langle 0|H|0\rangle = F_N + V_N, \quad (38a)$$

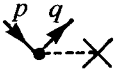
$$F_N = \sum_{p,q} f_{pq} N[a_p^\dagger a_q] \quad (38b)$$

$$V_N = \frac{1}{4}\sum_{pqrs} \langle pq\|rs\rangle N[a_p^\dagger a_r a_q a_s] \quad (38c)$$

where $N[\ldots]$ denotes the normal product (Paldus and Čizěk 1975), and

$$f_{pq} = \langle p|h|q\rangle + \sum_i \langle pi\|qi\rangle,$$

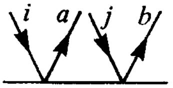
These two parts of the Hamiltonian then give rise to different diagrams. The one and two electron operators represented in second quantized formalism in equation (18) of section 2.1 are symbolized graphically as;

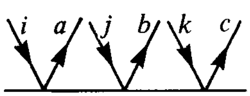
$f_{pq}N[a_q^\dagger a_p]$ becomes , (39)

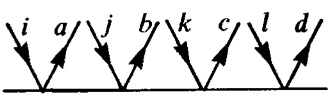
$\langle pq\|rs\rangle N[a_p^\dagger a_r a_q^\dagger a_s]$ becomes . (40)

The CC excitation operators are symbolized graphically as;

T_1 becomes , (41)

T_2 becomes , (42)

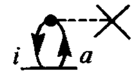
T_3 becomes , (43)

T_4 becomes . (44)

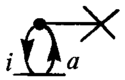
Let us consider a term from equation (30) of the last section. One of the terms from the equation is;

$$\langle 0|\sum_{p,q} f_{pq}a_q^\dagger a_p \sum_{i,a} t_i^a a_a^\dagger a_i|0\rangle. \qquad (45)$$

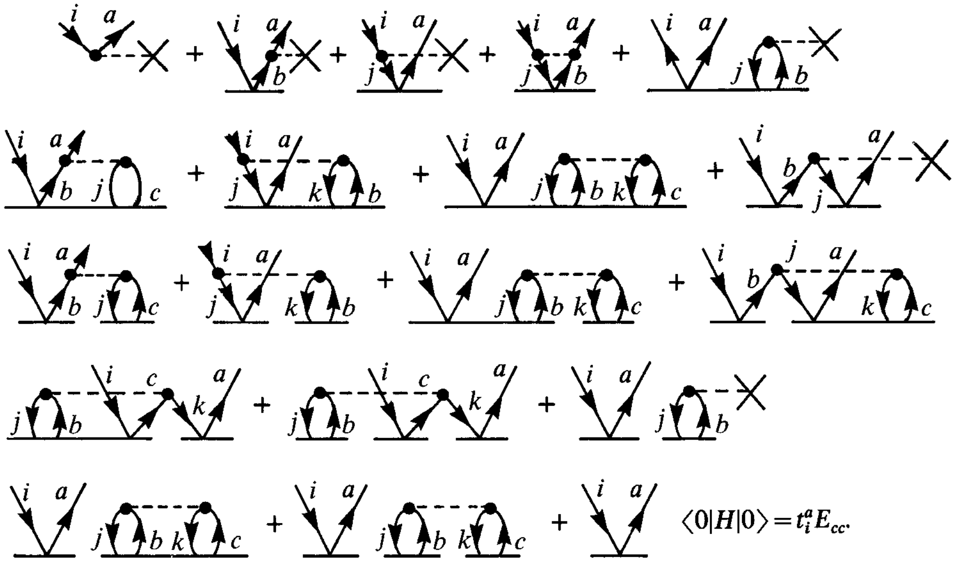
Recalling that a contraction replaces the operators involved in the contraction with its eigenvalue, contracting the second quantized operators amounts to connecting the lines of the graphical representation for these operators, (39) and (41) with the arrows pointing in the same direction. This yields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

 $= +\sum_{a,i} f_{ia}t_i^a$. (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 diagrams for coupled cluster excitation operators involved in product terms are not contracted with each other as this would produce redundant excitations. This procedure generates three diagrams for the equation which determines correlation energy, (31);

$\Delta E_{cc} =$  +  + . (47)

The singles equation, (32), generates 19 diagrams;



$\langle 0|H|0\rangle = t_i^a E_{cc}$.

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. A similar analysis of the diagrams obtained by projecting the Schrödinger equation against doubly excited determinants, (33), 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 connected singles equation which is equal to zero. This cancellation of the disconnected terms continues throughout 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;

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

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

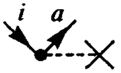
$$\begin{aligned}\langle 0_{ijk}^{abc}|H[T_2&+\tfrac{1}{2}T_2^2+T_1T_2+\tfrac{1}{2}T_1^2T_2+\tfrac{1}{3!}T_1^3T_2+\tfrac{1}{2}T_1T_2^2\\&+T_3+T_1T_3+\tfrac{1}{2}T_1^2T_3+T_2T_3+T_4+T_1T_4]|0\rangle_C=0,\end{aligned} \tag{51}$$

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

The rules for generating the algebraic code for the CC equations are (Kucharski and Bartlett 1986):

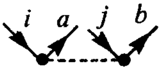
(1) Each up oriented line is labelled with an unoccupied spin-orbital label $a, b, c, d\ldots$ and each down oriented line is labelled with an occupied spin-orbital label $i, j, k, l\ldots$. The open lines are labelled in sequence from left to right.

(2) Each one-particle vertex corresponds to a one-electron integral as *⟨left, out|right, in⟩* or;



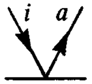
$$= f_{ai}. \qquad (53)$$

(3) Each two-particle vertex corresponds to the antisymmetrized integral *⟨left, out; right, out| |left, in; right, in⟩* or;

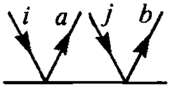


$$= \langle ab| |ij\rangle. \qquad (54)$$

(4) Cluster vertices correspond to;



$$= t_i^a,$$



$$= t_{ij}^{ab}. \qquad (55)$$

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 spinorbital 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 occupied spin-orbital labelled 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 $(1/2)^m$, 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 CC method restricted to singly and doubly excited cluster operators is called the CCSD method. The CC methods, which also include triply and triply and quadruply excited cluster operators, are called the CCSDT and CCSDTQ, methods respectively. Currently, the highest implemented level of the CC method is the CCSDTQ scheme (Oliphant and Adamowicz 1991). The complete set of diagrams and their corresponding algebraic expressions for the coupled cluster equations containing single, double, triple and quadruple excitations has been published recently (Oliphant and Adamowicz 1991).

2.4. *Solving the coupled cluster system of equations*

Our computational strategy for solving the CC equations (Oliphant and Adamowicz 1992) is similar to a previously proposed method (Purvis and Bartlett 1981). It involves first separating the coupled cluster equations into components which are linear and nonlinear with respect to the CC amplitudes;

$$\mathbf{AX} - \mathbf{B} = 0, \qquad (56)$$

where A is the matrix of coefficients for the amplitudes involved in the linear terms, $\mathbf{X}$ is a vector of coupled cluster amplitudes and $\mathbf{B}$ contains the negative of the nonlinear terms. The first approximation to the coupled cluster amplitudes is generated with the inverse of the A matrix approximated by the inverse of its diagonal elements, $\mathbf{D}^{-1}$, and multiply both sides of equation (56) by $\mathbf{D}^{-1}$;

$$\mathbf{D}^{-1}\mathbf{B}=\mathbf{X}^1. \tag{57}$$

The first approximation to the nonlinear terms can now be calculated as;

$$\mathbf{A}\mathbf{X}^1=\mathbf{B}_1. \tag{58}$$

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

$$\mathrm{Min}\,|\alpha^1\mathbf{B}_1-\mathbf{B}| \tag{59}$$

is calculated using the following expression;

$$\alpha^1=(\mathbf{B}_1\mathbf{B})/(\mathbf{B}_1\mathbf{B}_1). \tag{60}$$

Next the CC amplitudes are multiplied by the scaling factor;

$$\alpha^1\mathbf{X}^1=\mathbf{X}_1, \tag{61}$$

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

$$\mathbf{A}(\mathbf{X}_1+\mathbf{X}_2)=\mathbf{B}. \tag{62}$$

Now, an equation similar to equation (56) is used to find the correction vector;

$$\mathbf{A}\mathbf{X}_2=\mathbf{B}-\mathbf{A}\mathbf{X}_1=\mathbf{B}-\mathbf{B}_1^1=\mathbf{B}_\mathrm{D}, \tag{63}$$

and then;

$$\mathbf{X}_2=\mathbf{D}^{-1}\mathbf{B}_\mathrm{D}. \tag{64}$$

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

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

$$\mathbf{B}_1^2\mathbf{B}_1^1\alpha^1+\mathbf{B}_1^2\mathbf{B}_1^2\alpha^2=\mathbf{B}_1^2\mathbf{B}, \tag{66}$$

where

$$\mathbf{B}_1^1=\mathbf{A}\mathbf{X}_1, \tag{67}$$

$$\mathbf{B}_1^2=\mathbf{A}\mathbf{X}_2. \tag{68}$$

The above equations result from minimization of the expression $|\alpha'\mathbf{B}'+\alpha^2\mathbf{B}_1^2-\mathbf{B}|$

A linear equation solver is used at each step to find the scaling factors and the procedure is iterated until the correction vector $\mathbf{X}_n$ approaches zero.

This procedure occasionally oscillates and diverges, a more stable, albeit slower, procedure is to move some of all of the nonlinear terms in $\mathbf{B}$ to $\mathbf{B}_1$ (Oliphant and Adamowicz 1992).

The first computational implementation of the complete CCSDTQ method was presented recently (Oliphant and Adamowicz 1991). Our computer program for solving the CCSDTQ equations has been written in the most transparent form, using the spin-orbital representation of the diagrams. This has allowed direct programming of the algebraic expression corresponding to each diagram. Also all the quantities, which require storage, have been placed in the operational memory, thus eliminating 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.

2.5. *Numerical results*

Test calculations were performed for LiH and Li_2 at equilibrium and at a stretched geometry. The results are presented in table 1. For LiH a molecular orbital basis of four occupied spin-orbitals and eight virtual spin-orbitals, all of sigma symmetry were used, see table 2. 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 six occupied spin-orbitals and eight virtual spin-orbitals all with sigma symmetry were used, see table 2.

For Li_2 at equilibrium the contribution of triples is again at the μhartree level but now even at equilibrium quadruples contributes slightly 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 2, reveals that most of these also represent double excitations from a determinant that is doubly excited from the reference determinant which has become quasi-degenerate with the reference determinant as the bond was stretched. The quadruple excitation amplitudes which represent these types 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 $t_{43}^{21} = -1{\cdot}038780918$ (for the convention used for spin-orbital labels see table 1) and for Li_2 it is $t_{43}^{65} = -0{\cdot}998345227$.

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 wavefunction 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. This change can be expected to be small as long as the core electrons

Table 1. 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 2. The largest triple and quadruple coupled cluster amplitudes. For LiH, spin-orbitals 1234, (1σα, 1σβ, 2σα, 2σβ), are occupied and 12345678 (3σα, 3σβ, 4σα, 4σβ, 5σα, 5σβ, 6σα, 6σβ), are unoccupied. For Li$_2$, spin-orbitals 123456 (1σα, 1σβ, 2σα, 2σβ, 3σα, 3σβ), are occupied and 12345678 (4σα, 4σβ, 5σα, 5σβ, 6σα, 6σβ, 7σα, 7σβ), are unoccupied.

		LiH			
		3·015 a.u.			9·045 a.u.
I J K	A B C	T3	I J K	A B C	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
I J K L	A B C D	T4	I J K L	A B C D	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

		Li$_2$			
		3·015 a.u.			0·045 a.u.
I J K	A B C	T3	I J K	A B C	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
I J K L	A B C D	T4	I J K L	A B C D	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 parentheses).

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 (Adamowicz and Bartlett 1986). The FOCO set consisted of four sigma orbitals and the same Gaussian basis set as that for Lin 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) 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.

3. The multireference coupled cluster method using the single reference formalism

3.1. Theory

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 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 any of the determinants should be included.

The approximate triples method implemented and presented in this chapter, is a generalization of the multireference coupled cluster theory (Oliphant and Adamowicz 1991) with two determinants. The procedure has been recently modified (Oliphant and Adamowicz 1992) in order to accommodate more than two determinants in the reference space, as well as to make the computational implementation of the truncation scheme more tractable. In essense, the 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.

This method is not intended to approximate complete CCSDT but rather to include triple excitations in such a way as to approximate a multireference 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.

Let us consider a wavefunction which is dominated by two Slater determinants and the second determinant being a double excitation from the first;

$$|1\rangle = |0_{IJ}^{AB}\rangle. \tag{69}$$

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 referred 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 determine the reference determinants, is to perform a multiconfiguration self consistent field (MCSCF) calculation. The two most

Table 3. Single and double excitations from the second reference determinant in terms of the formal reference determinant.

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

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.

In terms of the formal reference determinant, single and double excitations from the second determinant are shown in table 3. 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 3. Since A is 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;

$$a_I^\dagger a_A a_B^\dagger a_J a_A^\dagger a_I |0\rangle = a_I^\dagger a_I a_A a_A^\dagger a_B^\dagger a_J |0\rangle = a_B^\dagger a_J |0\rangle. \tag{70}$$

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.

Let us now consider the more general case of a wavefunction which has several dominant Slater determinants, which are singly and doubly excited with respect to the formal determinant;

$$|1\rangle = |0_I^A\rangle, \qquad |1\rangle = |0_{IJ}^{AB}\rangle, \tag{71}$$

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;

$$|0_{Iij}^{Aab}\rangle, \qquad |0_{IJij}^{ABab}\rangle. \tag{72}$$

It is worth mentioning that this multideterminantal 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 invariant 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.

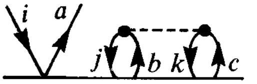
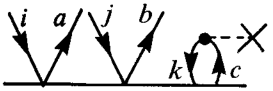
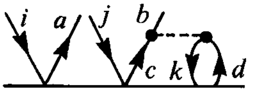
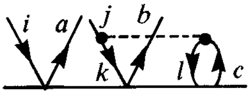
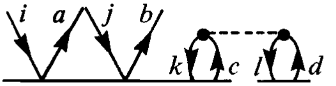
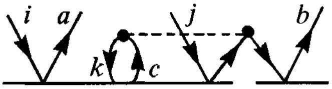
The extension to excitations from more than one determinant does not change the energy expression derived in the single reference formalism due to the fact that the Hamiltonian operator contains at most two-electron operators and the excitations from secondary determinants are in terms of higher order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

In the present stage of the implementation of our multireference coupled cluster method, all the selected quadruple excitations, which arise from double excitations of the double 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. As discussed before, 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.

Table 4. The complete set of restricted CCSDT projections. Upper case letters represent active labels and the lower case letters represent inactive labels.

Projection	Single	Double	Triple
1	$\langle 0_I^A|$	$\langle 0_{IJ}^{AB}|$	$\langle 0_{IJK}^{ABC}|$
2	$\langle 0_I^a|$	$\langle 0_{IJ}^{aB}|$	$\langle 0_{IJK}^{aBC}|$
3	$\langle 0_i^A|$	$\langle 0_{Ij}^{AB}|$	$\langle 0_{IJk}^{ABC}|$
4	$\langle 0_i^a|$	$\langle 0_{Ij}^{aB}|$	$\langle 0_{IJk}^{aBC}|$
5		$\langle 0_{IJ}^{ab}|$	$\langle 0_{IJK}^{abC}|$
6		$\langle 0_{ij}^{AB}|$	$\langle 0_{Ijk}^{ABC}|$
7		$\langle 0_{ij}^{aB}|$	$\langle 0_{Ijk}^{aBC}|$
8		$\langle 0_{Ij}^{ab}|$	$\langle 0_{IJk}^{abC}|$
9		$\langle 0_{ij}^{ab}|$	$\langle 0_{Ijk}^{abC}|$

Table 5. The set of diagrams, which have restricted summation indices in order to introduce a multireference character into a single reference CCSD method. The letter in the third column represents the index, which is restricted to active labels, and the numbers, which proceed the letter, indicate in which types of projection the index has to be restricted (see table 4). The remaining summation indices are unrestricted.

	Single excitation diagrams	
	$\langle 0_i^a \|$ projection	
	$+\frac{1}{4}\sum_{\substack{b,c\\j,k}} \langle jk\|\|bc\rangle t_{ijk}^{abc}$	24*b*; 34*j*
	Double excitation diagrams	
	$\langle 0_{ij}^{ab} \|$ projection	
	$+\sum_{\substack{c\\k}} f_{kc} t_{ijk}^{abc}$	589*c*; 679*k*
	$+\frac{1}{2}\sum_{\substack{c,d\\k}} \langle bk\|\|cd\rangle t_{ijk}^{acd}$	245789*c*; 679*k*
	$-\frac{1}{2}\sum_{\substack{c,d\\k}} \langle ak\|\|cd\rangle t_{ijk}^{bcd}$	589*c*; 679*k*
	$-\frac{1}{2}\sum_{\substack{c\\k,l}} \langle kl\|\|jc\rangle t_{ikl}^{abc}$	589*c*; 679*k*
	$+\frac{1}{2}\sum_{\substack{c\\k,l}} \langle kl\|\|ic\rangle t_{jkl}^{abc}$	589*c*; 346789*k*
	$+\sum_{\substack{c,d\\k,l}} \langle kl\|\|cd\rangle t_{ijk}^{abc} t_l^d$	589*c*; 679*k*
	$-\frac{1}{2}\sum_{\substack{c,d\\k,l}} \langle kl\|\|cd\rangle t_{ikj}^{acd} t_l^b$	245789*c*; 679*k*
	$+\frac{1}{2}\sum_{\substack{c,d\\k,l}} \langle kl\|\|cd\rangle t_{ikj}^{bcd} t_l^a$	589*c*; 679*k*
	$-\frac{1}{2}\sum_{\substack{c,d\\k,l}} \langle kl\|\|cd\rangle t_{klj}^{adb} t_i^c$	589*c*; 346789*k*
	$+\frac{1}{2}\sum_{\substack{c,d\\k,l}} \langle kl\|\|cd\rangle t_{kli}^{adb} t_j^c$	589*c*; 679*k*

In the following equations parenthesis are used to indicate the restrictions imposed on the indices of the triple excitations. These equations are;

$$\langle 0_i^a | H[1 + T_1 + \tfrac{1}{2}T_1^2 + \tfrac{1}{3!}T_1^3 + T_2 + T_1T_2 + T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix})]|0\rangle_C = 0, \tag{73}$$

$$\begin{aligned}\langle 0_{ij}^{ab} | H[1 + T_1 + \tfrac{1}{2}T_1^2 + \tfrac{1}{3!}T_1^3 + \tfrac{1}{4!}T_1^4 + T_2 + \tfrac{1}{2}T_2^2 + T_1T_2 \\ + \tfrac{1}{2}T_1^2T_2 + T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix}) + T_1T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix})]|0\rangle_C = 0,\end{aligned} \tag{74}$$

$$\begin{aligned}\langle 0_{Iij}^{Aab} | H[1 + T_1 + \tfrac{1}{2}T_1^2 + \tfrac{1}{3!}T_1^3 + \tfrac{1}{4!}T_1^4 + T_2 + \tfrac{1}{2}T_2^2 + T_1T_2 + \tfrac{1}{2}T_1^2T_2 + \tfrac{1}{3!}T_1^3T_2 \\ + \tfrac{1}{3!}T_1T_2^2 + T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix}) + T_1T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix}) + \tfrac{1}{2}T_1^2T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix}) + T_2T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix})]|0\rangle_C = 0.\end{aligned} \tag{75}$$

The complete set of restricted CCSDT projections are presented in table 4. In table 5 we show how the restrictions imposed on the triple excitation amplitudes are incorporated into the diagrams representing equations (73) and (74). For equation (75) the procedure is similar and results in a more extended set of diagrams (Oliphant and Adamowicz 1992). The multireference coupled cluster wavefunction is now given by;

$$|\psi_{\text{CCSDT}}\rangle = \exp[T_1 + T_2 + T_3(\begin{smallmatrix}Aab\\Iij\end{smallmatrix})]|0\rangle, \tag{76}$$

where the triple excitation operator is

$$T_3 = \sum_{\binom{A}{I}, \substack{i>j\\a>b}} t_{Iij}^{Aab} a_A^\dagger a_I a_a^\dagger a_i a_b^\dagger a_j. \tag{77}$$

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

3.2. *Computational implementation*

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 (75), and their corresponding sums are;

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

The capital letters represent a sum over the active labels (core or virtual) whereas the small letters represent a sum over inactive labels. 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 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.

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

$$(2) \qquad \sum_{\substack{e>F\\ l,m}} \langle lm||eF\rangle t_{lIJ}^{aeF} t_{mK}^{BC},$$

$$(3) \qquad \sum_{\substack{e>f\\ l,m}} \langle lm||ef\rangle t_{lIJ}^{Aef} t_{mk}^{BC},$$

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

$$(5) \qquad \sum_{\substack{e>F\\ l,m}} \langle lm||eF\rangle t_{lIJ}^{aeF} t_{mK}^{BC},$$

$$(6) \qquad \sum_{\substack{e>f\\ l,m}} \langle lm||ef\rangle t_{lIj}^{Aef} t_{mk}^{BC},$$

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

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

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

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;

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

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 achieve this arrangement.

3.3. *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

Table 6. Correlation energies for LiH at equilibrium† and displaced geometries for different levels of theory. The amplitudes shown in the table correspond to the secondary determinants included in MRCCSD calculations. The numbers in parentheses below CCSD and MRCCSD correlation energies represent the difference with Full CI. All energies are in atomic units.

	$R=R_e$†	$R=1·5R_e$	$R=2R_e$	$R=2·5R_e$	$R=3R_e$
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	−0·046416
$t_2^{(2)}$	±0·029169	+0·064722	±0·185693	±0·377804	±0·403532
$t_2^{(3)}$	−0·043226	−0·062463	−0·140338	−0·230839	−0·174602
MRCCSD	−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

† $R_e = 3·015$ a.u.

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 of Huzinaga's primitive Gaussians (Li(9s5p) (Dunning 1970) and H(4s) basis with a hydrogen scale factor of 1·2). The results for several internuclear separations are reported in table 6. 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 essentially 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 multiconfiguration self consistent field orbitals, which would be more appropriate for this purpose. The present multireference coupled cluster method truncated at triples (MRCCSD) did quite well at reproducing the full CI results. For all internuclear separations the MRCCSD energy is within a few hundredths 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 MRCCSD did at the equilibrium distance, $R_e = 3·015$ a.u., (30 μhartrees difference from full CI, compared to 20 μhartrees for MRCCSD). 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 than the full CI energy, compared to the MRCCSD energy which is only 10 μhartrees higher. The MRCCSD energy is consistently slightly higher than 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 (Dunning 1970) 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 7. The results at the equilibrium

Table 7. Correlation energies for BH at equilibrium† and displaced geometries for different levels of theory. The amplitude shown in the table corresponds to the secondary determinant included in MRCCSD calculations. The numbers in parenthesis below CCSD and MRCCSD correlation energies represent the difference with Full CI. All energies are in atomic units.

	$R=R_e$†	$R=2R_e$	$R=3R_e$
SCF	−25·113677	−24·986389	−24·891457
CCSD	−0·073080	0·118799	0·186280
	(+0·000912)	(+0·002772)	(+0·004172)
t_2‡	−0·055486	−0·407870	−0·862314
MRCCSD	−0·073478	−0·121015	−0·190374
	(+0·000513)	(+0·000056)	(+0·000078)
Full CI	−0·073991	−0·121071	−0·190452

† R_e = 2·329 a.u.

‡ When two additional determinants were included at equilibrium the correlation energy became −0·073738. The difference with FCI decreased to +0·000253.

Table 8. Correlation energies for H_2O at equilibrium† and displaced geometries for different levels of theory. The amplitudes shown in the table correspond to the secondary determinants included in MRCCSD calculations. The numbers in parenthesis below CCSD and MRCCSD correlation energies represent the difference with Full CI. Second set of numbers in parenthesis for the MRCCSD entry represents the difference with the CCSDT energies. All energies are in atomic units.

	$R=R_e$†	$R=2R_e$	$R=3R_e$
SCF	−76·009838	−75·803529	−75·595180
CCSD	−0·146238	0·205402	0·300732
	(+0·001790)	(+0·004068)	(+0·009334)
CCSDT†	−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
MRCCSD	−0·146929	−0·208934	−0·311256
	(+0·001099)	(+0·002058)	(−0·001190)
	(+0·000665)	(+0·000585)	(−0·001021)
Full CI†	−0·148028	−0·210990	−0·310066

† From (Noga and Bartlett 1987).

distance for CCSD and MRCCSD are comparable, and the deviation from full CI for the CCSD energy is 0·9 millihartrees while for the MRCCSD energy is 0·25 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 MRCCSD energy has fallen to 78 μhartrees. The dominant doubly excited coupled cluster amplitude at this separation is −0·86, indicating that the bond is essentially dissociated. In the case of BH MRCCSD 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 equilibrium 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 (Dunning 1970) 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 8. Four double excitations were important in this case. For all the structures considered, the MRCCSD method did substantially better than 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 multireference coupled cluster procedure for larger molecular systems.

4. Conclusions

One of the most attended frontiers of the *ab initio* Quantum Chemistry has been a development of a size extensive multireference coupled cluster methodology. The issue is far from being closed and numerous groups from all parts of the globe are active in this area of research. The goal of this effort is of a fundamental nature, and it is to correctly describe the stretching and breaking of multiple chemical bonds in a size extensive fashion. In the present review, after summarizing some of the recent developments in this area, we described the MRCC methodology, which has been under development in our group. Our approach, which is based on the single reference formalism, retains the simplicity of the orbital picture and the algebra of orbital excitation operators. The size extensivity of our method is a direct result of the connected character of the diagrams representing both the total energy and all the components of the equations for the amplitudes.

The numerical results presented here indicate that our approach may become a viable coupled cluster method for those cases, which are not adequately represented by a single reference coupled cluster wavefunction.

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