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Many-body Perturbation Theory for Open-shell Systems. Expansion through Fourth-order

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All of the diagrams which arise in the many-body perturbation theory of open-shell systems using a restricted Hartree–Fock reference function are given through fourth-order in the energy. New effects which arise in fourth-order are discussed.

Key words: Many-body perturbation theory – Electron correlation – Open-shell systems.

1. Introduction

Many-body perturbation theory has been shown to form a simple yet accurate approach to the correlation problem in atoms and molecules [1–4]. For closed-shell systems calculations taken through third-order in the energy yield an accuracy comparable with that attained by other techniques currently used in quantum chemistry. The basis set truncation error is usually more significant than the error arising from the truncation of the perturbation series at third-order. However, studies of closed-shell systems [5, 6] have demonstrated that the fourth-order terms are often "chemically significant", having a magnitude greater than 1 millihartree. Third-order many-body perturbation theory calculations for open-shell systems using a restricted Hartree–Fock formalism [7, 8] have been shown to exhibit similar features to closed-shell studies. It is probable that, although the basis set truncation error is dominant, fourth-order terms will be "chemically significant" in open-shell calculations.

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In this paper the fourth-order diagrams which arise in open-shell calculations using a restricted Hartree–Fock reference function are given in full. We have used a method of permutational analysis in order to obtain this set of diagrams. A complete set of fourth-order diagrams for closed shell systems has been given previously [5]. In the present paper we shall only give the additional diagrams which arise when a restricted Hartree–Fock reference function is employed. The diagrammatic conventions employed are described in detail in Ref. [3] where the rules for obtaining the algebraic expression corresponding to each of the diagrams are given in detail.

The diagrammatic many-body perturbation theory for open-shell systems is outlined in the following section. The fourth-order diagrams are discussed in detail in Sect. 3. This is followed by some concluding remarks.

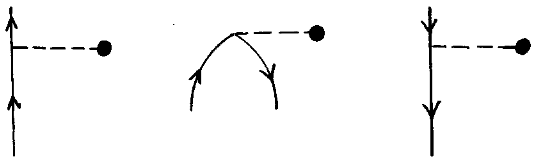
2. Diagrammatic Many-body Perturbation Theory for Open-shell Systems

Hubač and Čársky [7] have given a detailed discussion of the many-body perturbation theory for open-shell systems using a restricted Hartree–Fock reference function. We shall follow much of the notation of these authors in the present work.

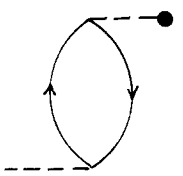
The restricted Hartree–Fock operator, f_R, can be written in the form

$$f_R = f + U$$

where f is the Hartree–Fock operator given in Eq. (3) of Ref. [7] and U is a one-electron operator which depends on the particular electronic configuration under consideration. Hubač and Čársky [7] give the definition of U. When a diagrammatic perturbation expansion for the correlation energy of an open-shell system is made the one-electron operator U leads to diagrams with insertions of the type shown in Fig. 1. A complete set of diagrams of this type through third-order using the diagrammatic conventions of Refs. [3, 5] has been given in [3].



Type A



Type B

Fig. 1. One-electron insertions

Since the electronic hamiltonian is hermitian, its energy eigenvalue is real. The sum of all terms of a given order in the perturbative energy expansion is also real. However, the energies corresponding to individual diagrams are not necessarily real if complex one-electron functions are used. In this case, a diagram is always accompanied by its complex conjugate to give a sum that is real. This situation arises in fourth-order. Diagrammatically, the process of complex conjugation can be accomplished by (1) rotating the diagram by 180° about an axis parallel to the interaction lines, and (2) changing the direction of all the arrows. This relation between diagrams will be expressed in the following manner

$$X = c(Y).$$

Diagram X is the complex conjugate of diagram Y. If $X = c(X)$ then the diagram is equal to its complex conjugate and is therefore real. If not, the final diagram will be identical to some other diagram, which is equal to the complex conjugate of the original diagram. If real orbitals are used, each diagram is real even if its complex conjugate diagram has a different appearance. Complex conjugation relations between diagrams significantly reduce the number of algebraic expressions which have to be considered in order to evaluate the energy through a given order.

A further reduction in the number of algebraic expressions required to evaluate the energy to a given order can be obtained if the time-reversal symmetry of the diagrams is exploited. The time-reversal operation will be represented as follows

$$X = t(Y).$$

If diagram Y is rotated by 180° about an axis parallel to the interaction lines diagram X is obtained. This changes all hole lines into particle lines and vice versa. It suffices to present only one of the expressions for two diagrams which are related by time-reversal since the other is obtained by interchanging hole and particle index designations, reordering the numerator factors, and changing the sign of each denominator factor. It should be noted that two diagrams which are related by time-reversal are not equal; they are distinct and must be separately evaluated. Nevertheless, this symmetry property can be exploited in computer programs [9].

In this paper, we shall use the following notation for integrals:
(a) matrix elements of the one-electron operator U will be denoted by

$$U_{pq} = \langle \phi_p | U | \phi_q \rangle$$

where ϕ denotes a one-electron state function;
(b) antisymmetrized two-electron integrals will be written:

$$I_{pqrs} = \int dr_1 \int dr_2\, \phi_p^*(r_1)\phi_q^*(r_2) r_{12}^{-1} (\phi_r(r_1)\phi_s(r_2) - \phi_s(r_1)\phi_r(r_2))$$

where r_{12} is the electron-electron separation.

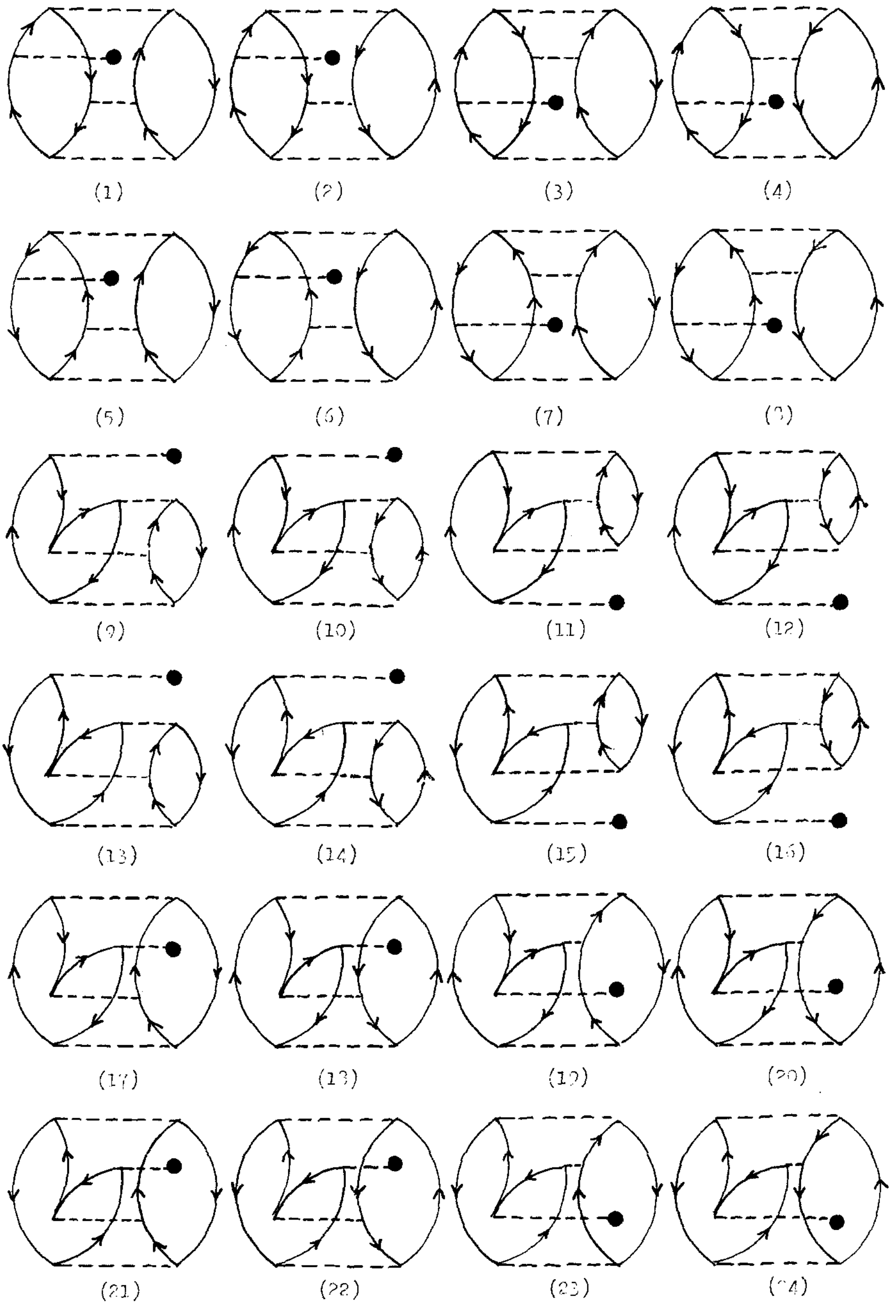


Fig. 2. Fourth-order energy diagrams which involve a single one-electron insertion of type *A*

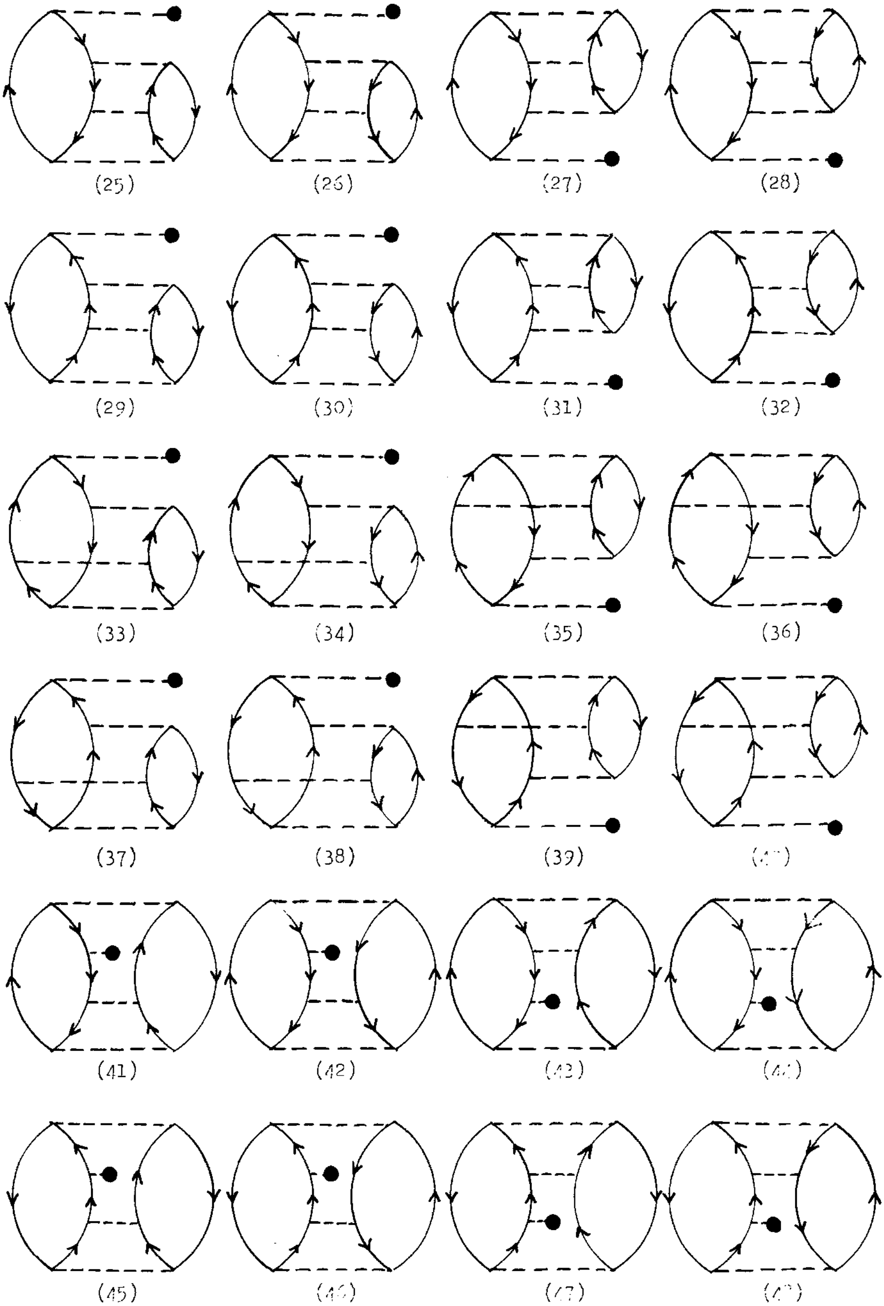

(25) (26) (27) (28)
(29) (30) (31) (32)
(33) (34) (35) (36)
(37) (38) (39) (40)
(41) (42) (43) (44)
(45) (46) (47) (48)

Fig. 2. (*cont.*)

The denominator factors which arise in the perturbation expressions for the energy may be written in terms of the one-electron orbital energies, e_p, as

$$D_{ijk\ldots abc\ldots} = e_i + e_j + e_k + \cdots - e_a - e_b - e_c - \cdots.$$

3. Fourth-order Energy Diagrams

In fourth-order of the perturbation expansion for the electronic energy, diagrams can arise which involve a single one-electron insertion, two, three or four one-electron insertions. Fourth-order diagrams which involve no one-electron insertions at all are fully discussed elsewhere [5]. It is useful to classify the fourth-order diagrams according to the number of one-electron insertions. The diagrams can be further classified according to the type of insertion designated by A and B in Fig. 1.

There are 48 diagrams which contain a single one-electron insertion of type A. These diagrams are shown in Fig. 2. The first eight diagrams involve only doubly-excited intermediate states whereas diagrams (9) to (16) involve singly-, doubly- and triply-excited states. Diagrams (17) to (24) involve doubly- and triply-excited states, diagrams (25) to (40) involve singly- and doubly-excited intermediate states, and diagrams (41) to (48) involve only doubly-excited states. The first diagram shown in Fig. 2 corresponds to the following algebraic expression

$$-\sum_{ijk}\sum_{abcd}\frac{I_{ijab}I_{kbic}U_{ad}I_{dckj}}{D_{ijab}D_{jkac}D_{jkcd}}.$$

Similar expressions for the remaining diagrams in Fig. 2 can be obtained using the standard rules [3, 5].

In Fig. 3 the remaining 24 diagrams which arise in fourth-order and which involve a single one-electron insertion of type B are displayed. The first 8 diagrams involve singly- and doubly-excited intermediate states whereas the remaining diagrams in Fig. 3 involve a triply-excited intermediate state together with a singly-excited and/or doubly-excited states. The first diagram in Fig. 3 gives rise to the following algebraic expression

$$-\frac{1}{2}\sum_{ijkl}\sum_{abc}\frac{I_{ijab}I_{kbij}I_{alkc}U_{cl}}{D_{ijab}D_{ka}D_{lc}}$$

whereas diagram (9), the first to involve a triply-excited intermediate state, leads to the following expression

$$-\frac{1}{2}\sum_{ijkl}\sum_{abc}\frac{I_{ijab}I_{klic}I_{abkj}U_{cl}}{D_{ijab}D_{ijkabc}D_{lc}}.$$

The remaining expressions arising from the diagrams in Fig. 3 can be readily obtained by applying the standard rules [3, 5].

There are 70 diagrams which involve two one-electron insertions: 58 of these contain insertions of type A and the remainder insertions of type B. These

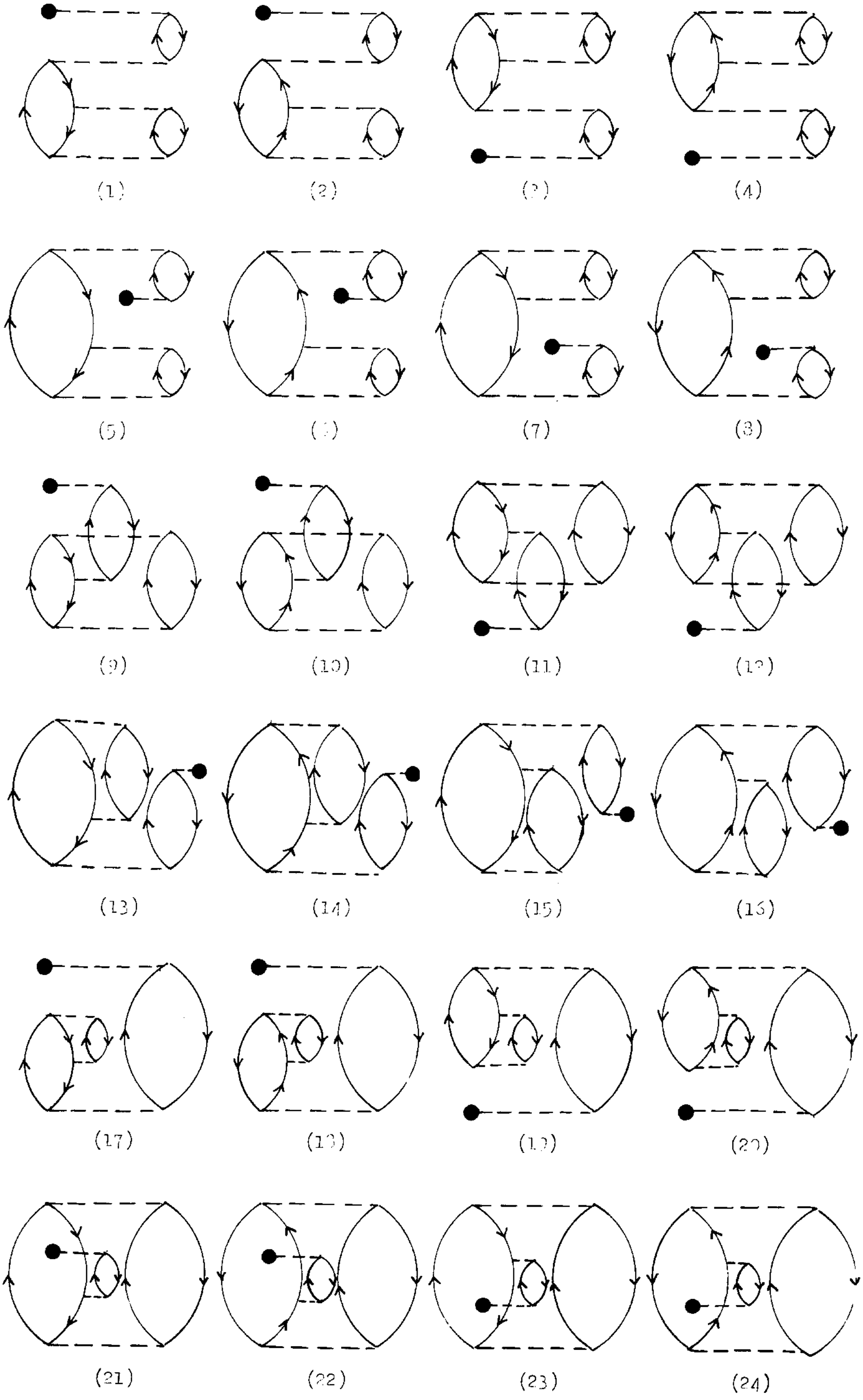


Fig. 3. Fourth-order energy diagrams which involve a single one-electron insertion of type *B*

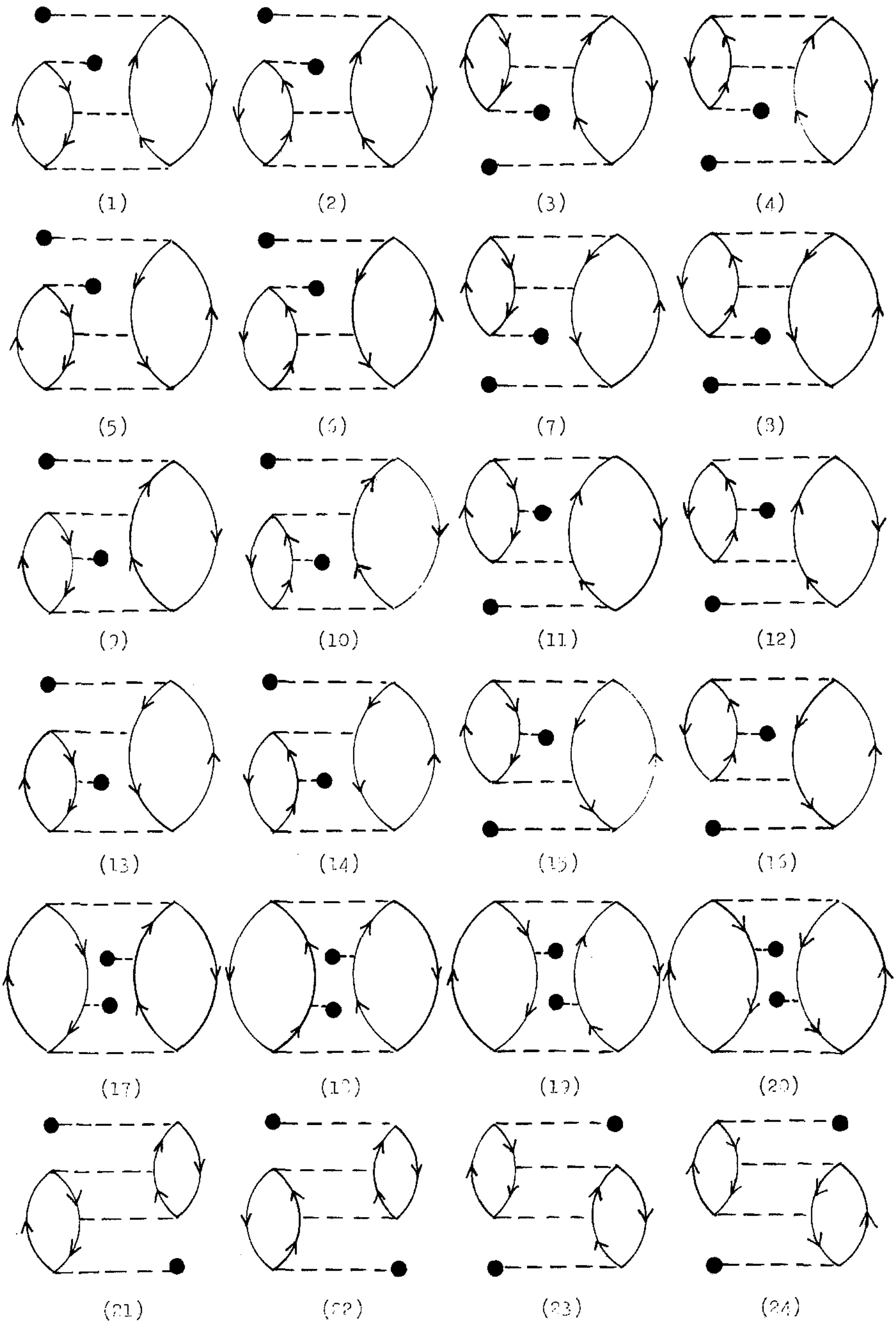


Fig. 4. Fourth-order energy diagrams which involve two one-electron insertions of type *A*

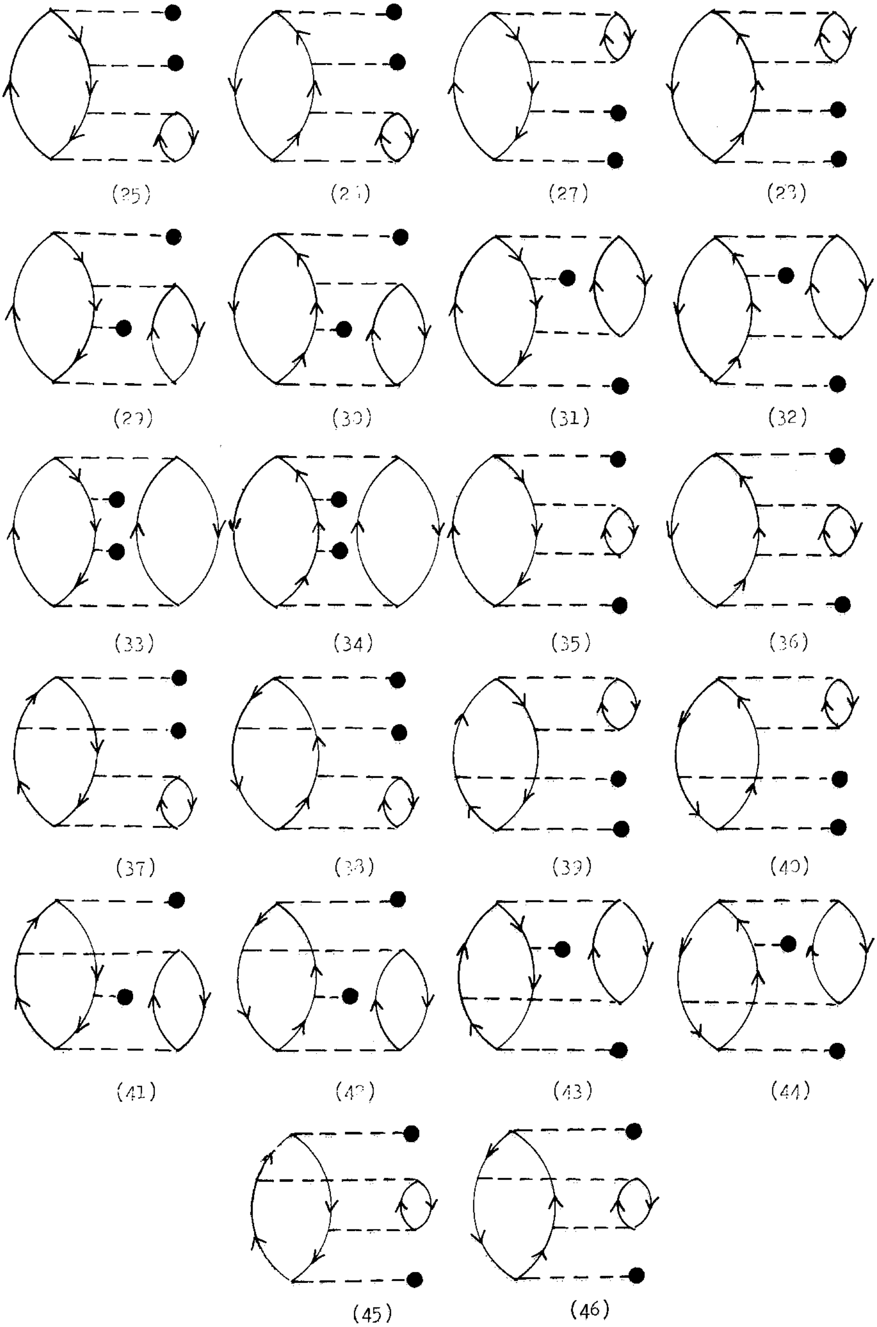
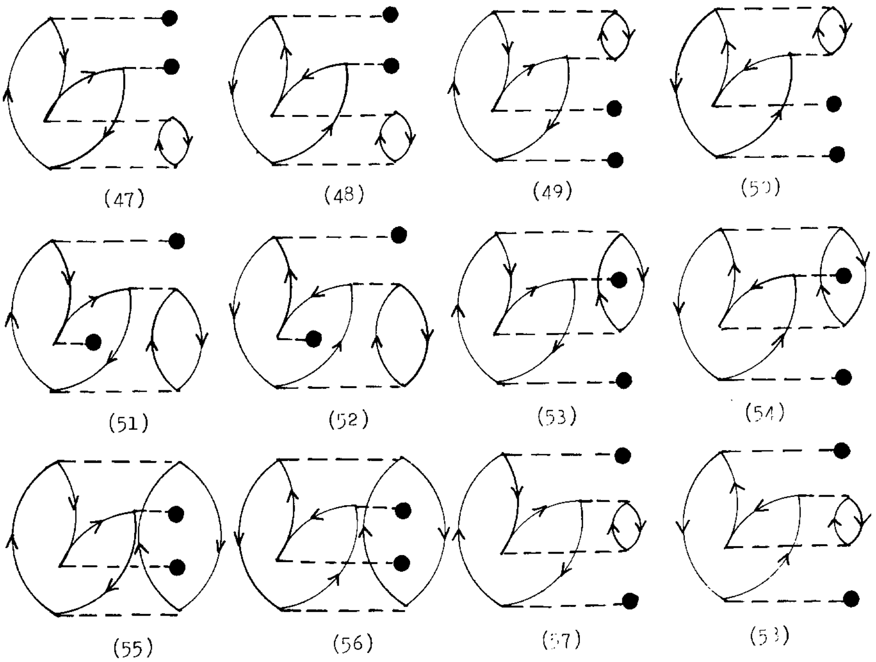


Fig. 4. (*cont.*)



(47) (48) (49) (50)

(51) (52) (53) (54)

(55) (56) (57) (58)

Fig. 4. (*cont.*)

diagrams are shown in Figs. 4 and 5, respectively. The first 50 diagrams shown in Fig. 4 involve only singly-excited and doubly-excited intermediate states; diagrams (17) to (20) involve doubly-excited states only. The last eight diagrams given in Fig. 4 involve triply-excited intermediate states as well as singly- and/or doubly-excited states. It should be noted that whereas the diagrams which involve a single one-electron insertion give rise to expressions which contain a summation over seven indices, the diagrams which involve two one-electron insertions give rise to expressions which contain a summation over six indices. For example, the expression corresponding to the first diagram shown in Fig. 4 is

$$-\sum_{ijk}\sum_{abc}\frac{I_{ijab}I_{kbic}U_{ak}U_{cj}}{D_{ijab}D_{jkac}D_{jc}}.$$

The twelve diagrams which contain two one-electron insertions of type B are displayed in Fig. 5. Typical expressions corresponding to these diagrams are:

(1) diagram (5) which involves singly-, doubly- and triply-excited intermediate states

$$+\sum_{ijk}\sum_{abc}\frac{I_{ijab}U_{kc}I_{cbkj}U_{ai}}{D_{ijab}D_{ijkabc}D_{ia}}.$$

(2) diagram (9) which involves doubly- and triply-excited intermediate states

$$+\sum_{ijk}\sum_{abc}\frac{I_{ijab}U_{kc}U_{ai}I_{cbkj}}{D_{ijab}D_{ijkabc}D_{jkbc}}.$$

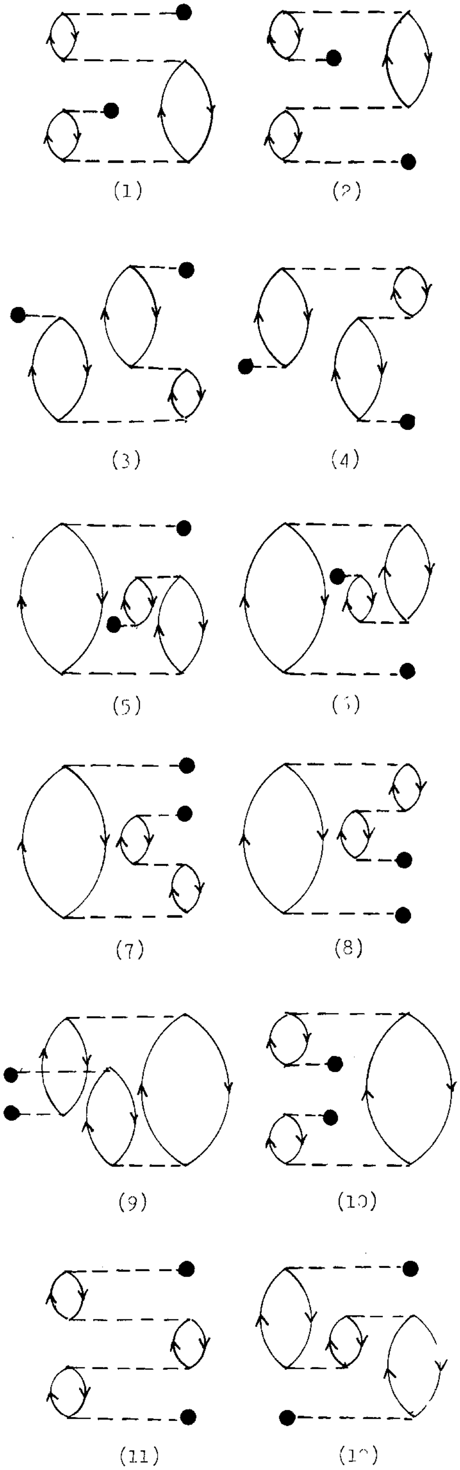


Fig. 5. Fourth-order energy diagrams which involve two one-electron insertions of type B

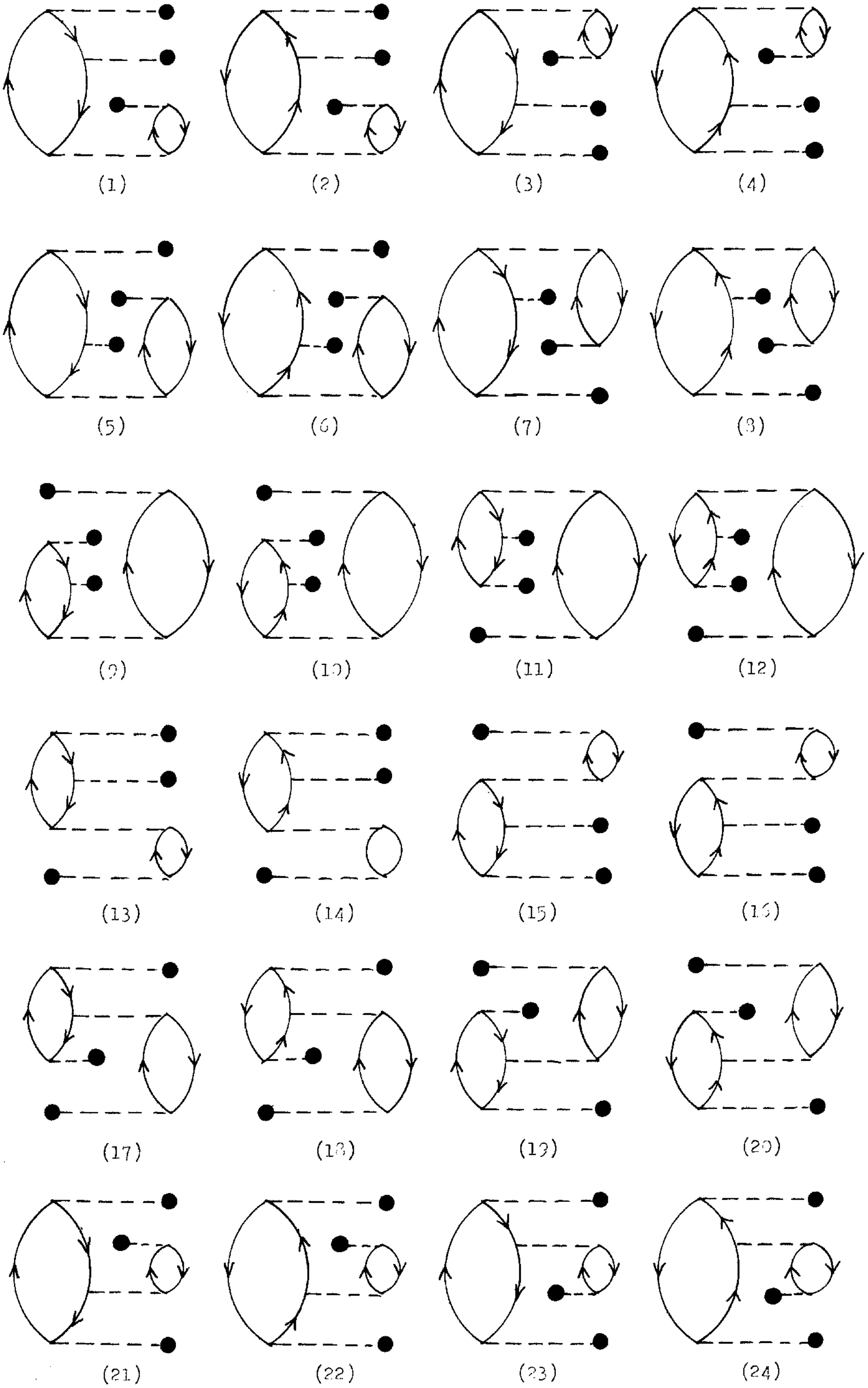


Fig. 6. Fourth-order energy diagrams which involve three one-electron insertions

(3) diagram (11) which involves only singly-excited states

$$+\sum_{ijk}\sum_{abc}\frac{U_{ia}I_{ajib}I_{kbcj}U_{ck}}{D_{ia}D_{jb}D_{kc}}.$$

The 24 diagrams which contain three one-electron insertions are given in Fig. 6. Each of these diagrams contain two insertions of type A and one insertion of type B. The diagrams shown in Fig. 6 involve only singly- and doubly-excited intermediate states. The first diagram corresponds to the algebraic expression

$$-\sum_{ijk}\sum_{ab}\frac{I_{ijab}U_{bj}U_{ki}U_{ak}}{D_{ijab}D_{ia}D_{ka}}.$$

Expressions corresponding to the remaining diagrams may be obtained by application of the standard rules [3, 5]. Each of the expressions contains a summation over five indices.

The final set of diagrams, shown in Fig. 7, involve four one-electron insertions. We give the algebraic expression corresponding to the first

$$+\sum_{ijk}\sum_{a}\frac{U_{ia}U_{ji}U_{kj}U_{ak}}{D_{ia}D_{ja}D_{ka}}$$

and the fifth of these

$$-\sum_{ij}\sum_{ab}\frac{U_{ia}U_{jb}U_{bi}U_{aj}}{D_{ia}D_{ijab}D_{ja}}$$

as typical examples. Each expression involve a summation over four indices.

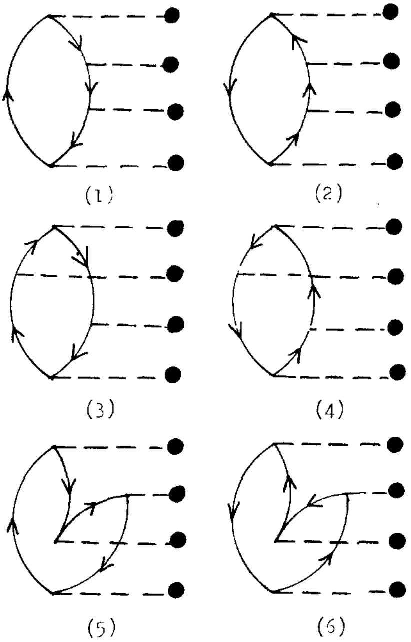


Fig. 7. Fourth-order energy diagrams which involve four one-electron insertions

Table 1. Characteristics of fourth-order energy diagrams which involve a single one-electron insertion of type *A*

D	(pqr)	n_h	n_p	$n_h\ (equ)$	$n_p\ (equ)$	$t(D)$	$c(d)$
(1)	(222)	3	4	0	0	(8)	(3)
(2)	(222)	4	3	2	0	(7)	(4)
(3)	(222)	3	4	0	0	(6)	(1)
(4)	(222)	4	3	2	0	(5)	(2)
(5)	(222)	3	4	0	2	(4)	(7)
(6)	(222)	4	3	0	0	(3)	(8)
(7)	(222)	3	4	0	2	(2)	(5)
(8)	(222)	4	3	0	0	(1)	(6)
(9)	(231)	3	4	1	1	(16)	(11)
(10)	(231)	4	3	0	0	(15)	(12)
(11)	(132)	3	4	1	1	(14)	(9)
(12)	(132)	4	3	0	0	(13)	(10)
(13)	(231)	3	4	0	0	(12)	(15)
(14)	(231)	4	3	1	1	(11)	(16)
(15)	(132)	3	4	0	0	(10)	(13)
(16)	(132)	4	3	1	1	(9)	(14)
(17)	(232)	3	4	0	0	(24)	(19)
(18)	(232)	4	3	1	1	(23)	(20)
(19)	(232)	3	4	0	0	(22)	(17)
(20)	(232)	4	3	1	1	(21)	(18)
(21)	(232)	3	4	1	1	(20)	(23)
(22)	(232)	4	3	0	0	(19)	(24)
(23)	(232)	3	4	1	1	(18)	(21)
(24)	(232)	4	3	0	0	(17)	(22)
(25)	(221)	4	3	0	0	(32)	(27)
(26)	(221)	5	2	2	0	(31)	(27)
(27)	(122)	4	3	0	0	(30)	(25)
(28)	(122)	5	2	2	0	(29)	(26)
(29)	(221)	2	5	0	2	(28)	(31)
(30)	(221)	3	4	0	0	(27)	(32)
(31)	(122)	2	5	0	2	(26)	(29)
(32)	(122)	3	4	0	0	(25)	(30)
(33)	(221)	3	4	1	1	(40)	(35)
(34)	(221)	4	3	0	0	(39)	(36)
(35)	(122)	3	4	1	1	(38)	(33)
(36)	(122)	4	3	0	0	(37)	(34)
(37)	(221)	3	4	0	0	(36)	(39)
(38)	(221)	4	3	1	1	(35)	(40)
(39)	(122)	3	4	0	0	(34)	(37)
(40)	(122)	4	3	1	1	(33)	(38)
(41)	(222)	4	3	0	0	(43)	(43)
(42)	(222)	5	2	1	1	(47)	(44)
(43)	(222)	4	3	0	0	(46)	(41)
(44)	(222)	5	2	1	1	(45)	(42)
(45)	(222)	2	5	1	1	(44)	(47)
(46)	(222)	3	4	0	0	(43)	(48)
(47)	(222)	2	5	1	1	(42)	(45)
(48)	(222)	3	4	0	0	(41)	(46)

In Tables 1–6, a summary of the properties of the diagrams given in Figs. 2–7 is given. In each of these Tables the following quantities are given:

(1) (pqr) denotes the levels of excitation which are present in the diagram D. Diagram (1) of Fig. 2 involves only doubly-excited intermediate states whereas diagram (1) of Fig. 5 involves one doubly-excited state and two singly-excited intermediate states.

(2) n_h and n_p are the number of hole lines and number of particle lines, respectively, in each of the diagrams. $n_h(equ)$ and $n_p(equ)$ are the number of equivalent pairs of hole lines and equivalent pairs of particle lines, respectively, in the diagram D.

(3) $t(D)$ is the diagram which is related by time-reversal symmetry to diagram D. $c(D)$ is the diagram related to diagram D by complex conjugation; D and $c(D)$ give equal contributions to the energy of real orbitals are employed and only one of them actually has to be evaluated. As noted in the previous section time-reversal symmetry and complex conjugation relations significantly reduce the number of algebraic expressions which have to be written down.

Table 2. Characteristics of fourth-order energy diagrams which involve a single one-electron insertion of type B

D	(pqr)	n_h	n_p	$n_h\,(equ)$	$n_p\,(equ)$	$t(D)$	$c(D)$
(1)	(211)	4	3	1	0	(4)	(3)
(2)	(211)	3	4	0	1	(3)	(4)
(3)	(112)	4	3	1	0	(2)	(1)
(4)	(112)	3	4	0	1	(1)	(2)
(5)	(212)	4	3	1	0	(8)	(7)
(6)	(212)	3	4	0	1	(7)	(8)
(7)	(212)	4	3	1	0	(6)	(5)
(8)	(212)	3	4	0	1	(5)	(6)
(9)	(231)	4	3	0	1	(12)	(11)
(10)	(231)	3	4	1	0	(11)	(12)
(11)	(132)	4	3	0	1	(10)	(9)
(12)	(132)	3	4	1	0	(9)	(10)
(13)	(232)	4	3	1	0	(16)	(15)
(14)	(232)	3	4	0	1	(15)	(16)
(15)	(232)	4	3	1	0	(14)	(13)
(16)	(232)	3	4	0	1	(13)	(14)
(17)	(231)	4	3	1	0	(20)	(19)
(18)	(231)	3	4	0	1	(19)	(20)
(19)	(132)	4	3	1	0	(18)	(17)
(20)	(132)	3	4	0	1	(17)	(18)
(21)	(232)	4	3	0	1	(24)	(23)
(22)	(232)	3	4	1	0	(23)	(24)
(23)	(232)	4	3	0	1	(22)	(21)
(24)	(232)	3	4	1	0	(21)	(22)

Table 3. Characteristics of fourth-order energy diagrams which involve two one-electron insertions of type *A*

D	(*pqr*)	n_h	n_p	n_h (*equ*)	n_p(*equ*)	*t*(*D*)	*c*(*D*)
(1)	(221)	3	3	0	0	(8)	(3)
(2)	(221)	2	4	0	1	(7)	(4)
(3)	(122)	3	3	0	0	(6)	(1)
(4)	(122)	2	4	0	1	(5)	(2)
(5)	(221)	4	2	1	0	(4)	(7)
(6)	(221)	3	3	0	0	(3)	(8)
(7)	(122)	4	2	1	0	(2)	(5)
(8)	(122)	3	3	0	0	(1)	(6)
(9)	(221)	3	3	0	1	(16)	(11)
(10)	(221)	2	4	0	0	(15)	(12)
(11)	(122)	3	3	0	1	(14)	(9)
(12)	(122)	2	4	0	0	(13)	(10)
(13)	(221)	4	2	0	0	(12)	(15)
(14)	(221)	3	3	1	0	(11)	(16)
(15)	(122)	4	2	0	0	(10)	(13)
(16)	(122)	3	3	1	0	(9)	(14)
(17)	(222)	3	3	0	0	(17)	(19)
(18)	(222)	2	4	1	0	(20)	(18)
(19)	(222)	3	3	0	0	(19)	(17)
(20)	(222)	4	2	0	1	(18)	(20)
(21)	(121)	3	3	0	0	(21)	(23)
(22)	(121)	2	4	0	1	(24)	(22)
(23)	(121)	3	3	0	0	(23)	(21)
(24)	(121)	4	2	1	0	(22)	(24)
(25)	(211)	4	2	0	0	(28)	(27)
(26)	(211)	2	4	0	1	(27)	(28)
(27)	(112)	4	2	1	0	(26)	(25)
(28)	(112)	2	4	0	1	(25)	(26)
(29)	(221)	4	2	0	0	(32)	(31)
(30)	(221)	2	4	0	0	(31)	(32)
(31)	(122)	4	2	0	0	(30)	(29)
(32)	(122)	2	4	0	0	(29)	(30)
(33)	(222)	4	2	0	1	(34)	(33)
(34)	(222)	2	4	1	0	(33)	(34)
(35)	(121)	4	2	1	0	(36)	(35)
(36)	(121)	2	4	0	1	(35)	(36)
(37)	(211)	3	3	1	0	(40)	(39)
(38)	(211)	3	3	0	1	(39)	(40)
(39)	(112)	3	3	1	0	(38)	(37)
(40)	(112)	3	3	0	1	(37)	(38)
(41)	(221)	3	3	0	1	(44)	(43)
(42)	(221)	3	3	1	0	(43)	(44)
(43)	(122)	3	3	0	1	(42)	(41)
(44)	(122)	3	3	1	0	(41)	(42)
(45)	(121)	3	3	1	0	(46)	(45)
(46)	(121)	3	3	0	1	(45)	(46)
(47)	(221)	3	3	0	0	(50)	(49)
(48)	(221)	3	3	0	0	(49)	(50)
(49)	(122)	3	3	0	0	(48)	(47)

Table 3. (*cont.*)

D	(pqr)	n_h	n_p	$n_h\ (equ)$	$n_p(equ)$	$t(D)$	$c(D)$
(50)	(122)	3	3	0	0	(47)	(48)
(51)	(231)	3	3	1	0	(54)	(53)
(52)	(231)	3	3	0	1	(53)	(54)
(53)	(132)	3	3	1	0	(52)	(51)
(54)	(132)	3	3	0	1	(51)	(52)
(55)	(232)	3	3	0	1	(56)	(55)
(56)	(232)	3	3	1	0	(55)	(56)
(57)	(131)	3	3	0	1	(58)	(57)
(58)	(131)	3	3	1	0	(57)	(58)

4. Concluding Remarks

There are 209 principal Goldstone diagrams in fourth-order when open-shell systems are treated in zero-order by the restricted Hartree–Fock approximation. The restricted Hartree–Fock approach is preferable to the unrestricted Hartree–Fock method [10] for obtaining a zero-order wave function since the former approach ensures that the wave function is an eigenfunction of S^2, where S is the operator associated with the total spin. 39 of these 211 diagrams contain no one-electron insertions and also arise in the closed-shell case [5]. The remaining 172 diagrams, all of which contain one-electron insertions, are given in Figs. 2–7 of the present paper. 72 of these diagrams contain a single one-electron insertion and give rise to 7 other Goldstone diagrams related by exchange of electrons. 70 diagrams contain two one-electron insertions and give rise to 3 other Goldstone diagrams by electron exchange. The 24 diagrams which contain three one-electron insertions each lead to one other Goldstone diagram. Finally, there are 6 Goldstone diagrams which have four one-electron insertions.

Table 4. Characteristics of fourth-order energy diagrams which involve two one-electron insertions of type B

D	(pqr)	n_h	n_p	$n_h\ (equ)$	$n_p(equ)$	$t(D)$	$c(D)$
(1)	(211)	3	3	0	0	(2)	(2)
(2)	(112)	3	3	0	0	(1)	(1)
(3)	(221)	3	3	0	0	(4)	(4)
(4)	(122)	3	3	0	0	(3)	(3)
(5)	(231)	3	3	0	0	(6)	(6)
(6)	(132)	3	3	0	0	(5)	(5)
(7)	(221)	3	3	0	0	(8)	(8)
(8)	(122)	3	3	0	0	(7)	(7)
(9)	(232)	3	3	0	0	(9)	(9)
(10)	(212)	3	3	0	0	(10)	(10)
(11)	(111)	3	3	0	0	(11)	(11)
(12)	(131)	3	3	0	0	(12)	(12)

Table 5. Characteristics of fourth-order energy diagrams which involve three one-electron insertions

D	(pqr)	n_h	n_p	$n_h\,(equ)$	$n_p(equ)$	$t(D)$	$c(D)$
(1)	(211)	3	2	0	0	(4)	(3)
(2)	(211)	2	3	0	0	(3)	(4)
(3)	(112)	3	2	0	0	(2)	(1)
(4)	(112)	2	3	0	0	(1)	(2)
(5)	(221)	3	2	0	0	(8)	(7)
(6)	(221)	2	3	0	0	(7)	(8)
(7)	(122)	3	2	0	0	(6)	(5)
(8)	(122)	2	3	0	0	(5)	(6)
(9)	(221)	3	2	0	0	(12)	(11)
(10)	(221)	2	3	0	0	(11)	(12)
(11)	(122)	3	2	0	0	(10)	(9)
(12)	(122)	2	3	0	0	(9)	(10)
(13)	(111)	3	2	0	0	(16)	(15)
(14)	(111)	2	3	0	0	(15)	(16)
(15)	(111)	3	2	0	0	(14)	(13)
(16)	(111)	2	3	0	0	(13)	(14)
(17)	(121)	3	2	0	0	(20)	(19)
(18)	(121)	2	3	0	0	(19)	(20)
(19)	(121)	3	2	0	0	(18)	(17)
(20)	(121)	3	2	0	0	(17)	(18)
(21)	(121)	3	2	0	0	(24)	(23)
(22)	(121)	2	3	0	0	(23)	(24)
(23)	(121)	3	2	0	0	(22)	(21)
(24)	(121)	2	3	0	0	(21)	(22)

Time reversal symmetry and complex conjugation symmetry can be used to relate some of the diagrams. For example, in Fig. 7, diagrams (1) and (2) are related by time reversal while diagrams (3) and (4) are related by complex conjugation.

When a restricted Hartree–Fock reference function is used in a many-body perturbation theory treatment of open-shell systems only 16 principal Goldstone diagrams arise through third-order in the energy. Such calculations are, therefore, open to a relatively simple interpretation. The addition of the fourth-order term

Table 6. Characteristics of fourth-order energy diagrams which involve four one-electron insertions

D	(pqr)	n_h	n_p	$n_h\,(equ)$	$n_p(equ)$	$t(D)$	$c(D)$
(1)	(111)	3	1	0	0	(2)	(1)
(2)	(111)	1	3	0	0	(1)	(2)
(3)	(111)	2	2	0	0	(3)	(4)
(4)	(111)	2	2	0	0	(4)	(3)
(5)	(121)	2	2	0	0	(6)	(5)
(6)	(121)	2	2	0	0	(5)	(6)

complicates the situation considerably. Third-order calculations for open-shell systems using a restricted Hartree–Fock reference function [7, 8] have been shown to exhibit similar features to closed-shell studies [1, 3, 4]. For closed-shell systems fourth-order terms, including those involving triply-excited and quadruply-excited intermediate states, have been shown to be of some importance [3, 6]. If fourth-order terms are also important in studies of open-shell systems, then it is important that all diagrams through a given order be included in their entirety [5].

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