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To cite this article: A Mukhopadhyay *et al* 1979 *J. Phys. B: Atom. Mol. Phys.* **12** 1

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A non-perturbative open-shell theory for ionisation potential and excitation energies using HF ground state as the vacuum§

Atri Mukhopadhyay†, Raj Kumar Moitra† and Debashis Mukherjee‡

† Saha Institute of Nuclear Physics, Calcutta, 700 009, India

‡ Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received 30 September 1976, in final form 29 June 1978

Abstract. In this paper the authors' recently developed non-perturbative open-shell theory is adapted for 'direct' evaluation of ionisation potential and excitation energies. Separating the 'core' contribution from the 'valence' part through the use of a multiple-cluster-expansion operator, the method provides a systematic way of including various core-valence interaction and core relaxation components. HF orbitals have been used as the basis for facilitating detailed comparison of the method with perturbative and propagator techniques. It has been shown that the method encompasses all the important second-order contributions of the latter formalisms and certain other classes of diagrams in a compact manner. An application to a simple 4π electronic problem is discussed to illustrate how this method works for real systems.

1. Introduction

Many theories have recently been put forward for calculating the ionisation potential (IP) and excitation energies (EE) of atoms and molecules which successfully avoid the inadequacies of the usual configuration-interaction (CI) procedure. Among these, the propagator techniques (see, e.g. Linderberg and Öhrn 1973, Csanak *et al* 1971, Paldus and Cizek 1974) have the interesting feature that knowledge of the individual energy levels is not required and the quantities of interest emerge directly. Simultaneously, attempts have been made (Malrieu *et al* 1967, Kvasnicka and Hubac 1974) in which perturbation expansions of both the energy levels are found relative to each other. Consequently, the error sources cancel because the energy of one state comes out exactly in terms of that of the other. The difference is then obtained simply by dropping the common terms of the two energy expansions.

Based on our recent non-perturbative approach (Mukherjee *et al* 1975a, b to be referred to as I and II respectively) for open-shell systems, we propose in this paper a method for calculating the IP and EE of atoms and molecules. The basic objective of the work is to explore the extent to which our non-perturbative open-shell formalism may be looked upon as a 'direct' method for calculating the IP and EE, paralleling

§ Part of the paper presented at the National UGC Symposium on Theoretical Chemistry held in Bombay, December 1977.

the features of the propagator and perturbation approaches mentioned above. In an earlier paper (Mukherjee *et al* 1977a, to be referred to as III) we employed a *single-cluster-expansion operator* $\exp(T)$ for describing all the states of interest required to calculate the IP or EE, and it was shown that the contribution from the largest common closed-shell part of all the states vanishes when differences in energies are taken. If the ground state of the system is closed-shell, then we could choose the ground state Hartree–Fock (HF) configuration itself as the vacuum state, and then we would like to have a theory in which the energy part, common to all the states of the system, is just the exact ground state energy. This would lead to expansions for IP or EE, in which the different terms may be identified as corrections to the values of the corresponding quantities in HF theory. Furthermore, we want to decouple the calculation of core correlation from the core–valence interaction in the excited/ionised state and core relaxation effects, and this would be achieved through the use of a *product of cluster-expansion operators* for the generation of excited or ionic states. The resulting formalism is akin in spirit to the perturbative formalisms, and allows systematic inclusion of the various important interactions. The most important point is that our formalism includes in a natural way the effect of a class of important diagrams for which no well defined algebraic series can be found.

In §2 we outline the formalism as adapted for the present purpose, while for the details of diagrammatics and proof of the linked-cluster nature of the diagrams we refer to I, II and III. In §3, a 4π electronic system, the transbutadiene molecule, is considered for which we estimate the vertical ionisation potential and the π – π^* singlet and triplet excitation energies by using the formalism. Section 4 is devoted to a brief comparative study of our theory with the existing methods. In the same section, we try to classify the different contributions to the ionisation potential (IP) or excitation energies (EE) according to their representation of the orbital relaxation and pair-correlation energies. Section 5 contains the concluding remarks.

2. Theory

2.1. General considerations

We start by conveniently choosing a model space spanned by a small number of determinantal states $\phi_i(N)$ and $\phi_i(N-1)$ which are capable of describing the excited/ionised states of N -particle systems more or less satisfactorily. For the general purpose, we have to deal with open-shell problems where the zeroth-order descriptions of N and $N-1$ particle systems are given as

$$\psi_K^0(N) = \sum_i C_{Ki} \phi_i(N) \quad (1a)$$

$$\psi_K^0(N-1) = \sum_i C_{K'i} \phi_i(N-1) \quad (1b)$$

where the combining coefficients C_{Ki} and $C_{K'i}$ may not be known *a priori*. Furthermore, we have the N -electron HF determinant ϕ_{HF} in the model space, and—as mentioned before—we will choose this as our vacuum state. We shall treat the orbitals in ϕ_{HF} as holes; other orbitals will be generally termed particles. The orbitals in

ϕ_{HF} which electrons vacate in creating the determinants $\phi_i(N)$ or $\phi_i(N-1)$ we call valence holes, and the particle orbitals present in $\phi_i(N)$ will be called valence particles. We shall collectively designate these two sets simply as valence. Any determinant $\phi_i^*(N)$ or $\phi_m^*(N-1)$, which may be obtained by replacing the spin orbitals in ϕ_i 's or ϕ_{HF} by particle orbitals, or replacing hole orbitals by particle orbitals in ϕ_i , etc, belongs to a space orthogonal to the model space.

Although we shall be considering the problems of direct calculation of IP and EE side by side, we should point out here that for practical purposes we focus our attention on either IP or EE at any one time. This is, however, not obligatory and at the end of this section we shall briefly discuss an organisational scheme in which both can be handled simultaneously. The chief difference in these two approaches lies in properly selecting the cluster-expansion operators.

We now define a core-cluster-expansion operator $\exp(T_c)$, which, acting on $\phi_{\text{HF}}(N)$ converts it to the exact ground state $\psi_{\text{gr}}(N)$:

$$\psi_{\text{gr}}(N) = \exp(T_c) \phi_{\text{HF}}(N). \quad (2)$$

For excited or ionised states, we seek a multiple-cluster-expansion operator $\exp(T_c) \exp(T_v)$ (see, e.g., Mukherjee *et al* 1977b, to be referred to as IV), which transforms each function of type (1a) and (1b) to the corresponding exact states:

$$\psi_K(N) = \exp(T_c) \exp(T_v) \psi_K^0(N) \quad (3a)$$

$$\psi_{K'}(N-1) = \exp(T_c) \exp(T_v) \psi_{K'}^0(N-1). \quad (3b)$$

The functions ψ_{gr} , $\psi_K(N)$ and $\psi_{K'}(N-1)$ satisfy the respective Schrödinger equations:

$$H \psi_{\text{gr}}(N) = E_{\text{gr}} \psi_{\text{gr}}(N) \quad (4a)$$

$$H \psi_K(N) = E_K(N) \psi_K(N) \quad (4b)$$

$$H \psi_{K'}(N-1) = E_{K'}(N-1) \psi_{K'}(N-1). \quad (4c)$$

The Hamiltonian H , written out in occupation number representation, as

$$H = \sum_{A,B} \langle A|h|B \rangle X_A^\dagger X_B + \frac{1}{2!^2} \sum_{\substack{A,B \\ C,D}} \langle AB|v|CD \rangle_a X_A^\dagger X_B^\dagger X_D X_C \quad (5)$$

is the same for N - and $(N-1)$ -particle systems.

To appreciate the effect of the composite operator $\exp(T_c) \exp(T_v)$, let us look into the nature of the operators present in T_c and T_v . T_c contains excitation operators producing excitations from ϕ_{HF} to all the particle (and valence-particle) orbitals. This comes about because, according to (2), $\exp(T_c)$ correlates with the core state ϕ_{HF} quite independently of whether or not the particle orbitals are occupied in the actual excited/ionised states $\phi_i(N)/\phi_i(N-1)$. The operator T_v , on the other hand, produces excitations from valence to particle and hole to valence-particle, and also mixed types of excitation like hole to valence-particle or particle and simultaneously valence-particle to particle states. In order to incorporate the effects of core relaxation in the excited/ionised states, we have to include, in T_v operators, excitations from hole to particle in the presence of passive particle-valence orbitals present as spectators in ϕ_i . We will discuss this choice in further detail in a more appropriate place. Let us only note here that the choice of the operator $\exp(T_c) \exp(T_v)$ is perfectly general,

since on the one hand it is capable of handling all the excitations that would have to be incorporated in an exact $\psi_K(N)$ or $\psi_K(N-1)$, and on the other hand the requirement that ψ 's have to satisfy the appropriate Schrödinger equation causes the matrix elements of T_v to be adjusted accordingly. Thus the solution of the full problem proceeds in two stages: (a) calculation of T_c entering equation (2); (b) calculation of T_v entering either (3a) or (3b), with T_c now known. *Thus the core and valence problem would be decoupled*, and we might call this a 'core-valence separation' in the non-perturbative context. The concept of core-valence separation is discussed thoroughly by Brandow (1967) in the context of open-shell perturbative theory, where the perturbative analogues of diagrams akin to T_c and T_v are also succinctly discussed (see e.g. the discussion on p819 of Brandow 1967). Let us again mention here that T_v would be chosen depending on whether we want to calculate EE or IP, either separately or simultaneously.

Rewriting equations (2) and (4), we have

$$H \exp(T_c) \phi_{\text{HF}} = E_{\text{gr}} \exp(T_c) \phi_{\text{HF}} \quad (6a)$$

$$H \exp(T_c) \exp(T_v) \sum_i C_{Ki} \phi_i(N) = E_K \exp(T_c) \exp(T_v) \sum_i C_{Ki} \phi_i(N) \quad (6b)$$

$$H \exp(T_c) \exp(T_v) \sum_i C_{Ki} \phi_i(N-1) = E_{K'} \exp(T_c) \exp(T_v) \sum_i C_{Ki} \phi_i(N-1). \quad (6c)$$

Using the linked-cluster theorem for open-shells (I, II), we can now define an effective operator $U_c(H, T_c)$, such that

$$H \exp(T_c) = \exp(T_c) U_c \quad (7)$$

and we have

$$U_c \phi_{\text{HF}} = E_{\text{gr}} \phi_{\text{HF}}. \quad (8)$$

Projecting (8) to all the states orthogonal to ϕ_{HF} , we have

$$\langle \phi_l^*(N) | U_c | \phi_{\text{HF}} \rangle = 0 \quad \text{for all } l \quad (9)$$

and the solution of the set of equations (9) would yield us the matrix elements of T_c in the orbital basis.

Let us now consider equations (6b) and (6c). Using (7), we have

$$U_c \exp(T_v) \sum_i C_{Ki} \phi_i(N) = E_K \exp(T_v) \sum_i C_{Ki} \phi_i(N) \quad (10a)$$

$$U_c \exp(T_v) \sum_i C_{Ki} \phi_i(N-1) = E_{K'} \exp(T_v) \sum_i C_{Ki} \phi_i(N-1). \quad (10b)$$

According to LCT (I, II), U_c is defined entirely in terms of linked diagrams containing matrix elements of the one- and two-electron operators of the Hamiltonian and those of T_c only and, after solution of (9), may be taken as known. One useful characteristic feature of U_c is that, from (8),

$$E_{\text{gr}} = \langle \phi_{\text{HF}} | U_c | \phi_{\text{HF}} \rangle \quad (11)$$

and we may thus look upon U_c as an effective Hamiltonian in which the correlation among the core electrons has been incorporated through T_c . Equations (10a) and

(10b) may then be interpreted as valence correlation and core-valence interaction problem with 'dressed up' Hamiltonian U_c .

Let us divide U_c into E_{gr} and the rest $\bar{U}_c$:

$$U_c = E_{gr} + \bar{U}_c. \quad (12)$$

In diagrammatic language, E_{gr} consists of all the diagrams of U_c having no open lines, and $\bar{U}_c$ contains diagrams having open lines only.

We now make a 'separation' of the core part of the total energy $E_K/E_{K'}$ as

$$E_K = E_{gr} + \Delta E_K \quad (13a)$$

$$E_{K'} = E_{gr} + \Delta E_{K'}. \quad (13b)$$

Clearly, the quantities $\Delta E_K/\Delta E_{K'}$ are the EE and IP of interest to us. We can now rewrite equations (10a) and (10b) as

$$\bar{U}_c \exp(T_v) \sum_i C_{Ki} \phi_i(N) = \Delta E_K \exp(T_v) \sum_i C_{Ki} \phi_i(N) \quad (14a)$$

$$\bar{U}_c \exp(T_v) \sum_i C_{K'i} \phi_i(N-1) = \Delta E_{K'} \exp(T_v) \sum_i C_{K'i} \phi_i(N-1). \quad (14b)$$

Applying LCT once again, we have

$$\bar{U}_c \exp(T_v) = \exp(T_v) U_{c-v} \quad (15)$$

so that

$$U_{c-v} \sum_i C_{Ki} \phi_i(N) = \Delta E_K \sum_i C_{Ki} \phi_i(N) \quad (16a)$$

$$U_{c-v} \sum_i C_{K'i} \phi_i(N-1) = \Delta E_{K'} \sum_i C_{K'i} \phi_i(N-1). \quad (16b)$$

Pre-multiplying (16a) by $\phi_l^*(N)$ and (16b) by $\phi_m^*(N-1)$, we have

$$\sum_i \langle \phi_l^*(N) | U_{c-v} | \phi_i(N) \rangle C_{Ki} = 0 \quad \text{for all } l.$$

$$\sum_i \langle \phi_m^*(N-1) | U_{c-v} | \phi_i(N-1) \rangle C_{K'i} = 0 \quad \text{for all } m. \quad (17b)$$

Similarly projecting onto the model space functions $\phi_j(N)$ and $\phi_j(N-1)$, we get from (16a) and (16b),

$$\sum_i \langle \phi_j(N) | U_{c-v} | \phi_i(N) \rangle C_{Ki} = \Delta E_K C_{Kj} \quad (18a)$$

$$\sum_i \langle \phi_j(N-1) | U_{c-v} | \phi_i(N-1) \rangle C_{K'i} = \Delta E_{K'} C_{K'j}. \quad (18b)$$

Thus the combining coefficients C_{Ki} etc, left unspecified until now, form the eigenvectors of a set of matrix equations determining ΔE , and are thus linearly

independent. Thus, instead of (17a) and (17b), we may write:

$$\langle \phi_i^*(N) | U_{c-v} | \phi_l(N) \rangle = 0 \quad \text{for all } i \text{ and } l. \quad (19a)$$

$$\langle \phi_m^*(N-1) | U_{c-v} | \phi_i(N-1) \rangle = 0 \quad \text{for all } i \text{ and } m. \quad (19b)$$

Let us now note that, depending on what we really intend to calculate (EE or IP), we would solve (19a) or (19b). Each is a set of simultaneous equations in the matrix elements of T_v . Having found them, we employ them in (18a) or (18b) as the case may be, and obtain $\Delta E_K / \Delta E_{K'}$ after the diagonalisation of the matrix $\{\langle \phi_j | U_{c-v} | \phi_i \rangle\}$.

At this point, let us discuss the useful aspects concerning the choice of ϕ_{HF} as the vacuum. The orbitals chosen are Hartree-Fock orbitals, and this choice facilitates finding the corrections to Koopmans IP (Koopmans 1934) and also relates our results to those of perturbative theories. According to our earlier convention we shall label the hole states as $\alpha, \beta, \dots$, and the particle orbitals as $p, q, \dots$. Any unspecified orbital will be labelled as $A, B, \dots$. The operators $X_A^\dagger$ and X_A will now transform as

$$Y_\alpha = X_\alpha^\dagger; \quad Y_p = X_p \quad (20)$$

with

$$Y_A | \phi_{\text{HF}} \rangle = 0 \quad \text{for all } A. \quad (21)$$

The Hamiltonian, written in normal order, appears as follows

$$H = \langle \phi_{\text{HF}} | H | \phi_{\text{HF}} \rangle + F + V \quad (22a)$$

$$F = \sum_A \epsilon_A N [X_A^\dagger X_A] \quad (22b)$$

$$V = \frac{1}{2!^2} \sum_{\substack{A,B \\ C,D}} \langle AB | v | CD \rangle_a N [X_A^\dagger X_B^\dagger X_D X_C] \quad (22c)$$

where ϵ_A is the orbital energy for the orbital A .

In HF basis, the model-space configurations for the excited states are one-hole one-particle states of the type $N[Y_p^\dagger Y_\alpha^\dagger] | \phi_{\text{HF}} \rangle$, and for the ionised states, they are one-hole type $Y_\alpha^\dagger | \phi_{\text{HF}} \rangle$. For the excited states, more than one model-space function is needed to construct appropriate singlets or triplets, while for the ionised state only one will do.

So far we have made no special reference to EE or IP. In fact as mentioned earlier, we lay more stress on a scheme designed to calculate either EE or IP. Thus, in the next two sections, we discuss the details of the choice of T_v separately, first for IP and then for EE. In the last section we indicate the strategy to be followed in case we are interested in a coupled calculation of IP and EE simultaneously.

2.2. Ionisation potential

For IP, the model space includes the state ϕ_{HF} and the lowest ionised configuration $Y_\alpha^\dagger | \phi_{\text{HF}} \rangle$ or $Y_\beta^\dagger | \phi_{\text{HF}} \rangle$. Accordingly, we must choose T_v in such a manner that $\exp(T_c) \exp(T_v)$ can correlate $Y_\alpha^\dagger | \phi_{\text{HF}} \rangle$ or $Y_\beta^\dagger | \phi_{\text{HF}} \rangle$ free from unnecessary constraints.

It suffices for this purpose to include all of the following form in T_v :

$$(T_v)_p \sim \frac{1}{p!^2} \sum_{\gamma \neq \alpha, \beta} \langle \gamma r \dots | t_p^\gamma | \alpha \beta \dots \rangle_a N [Y_\gamma Y_r^\dagger \dots Y_\beta^\dagger Y_\alpha^\dagger] \quad (23a)$$

$$(T_v)_{p+1} \sim \frac{1}{(p+1)!^2} \sum \langle \gamma p q \dots | t_{p+1}^\gamma | \alpha \beta \dots \rangle_a N [Y_\gamma Y_p^\dagger Y_q^\dagger \dots Y_\beta^\dagger Y_\alpha^\dagger], \quad (23b)$$

with γ running over valence holes. It is to be noted that, by virtue of (21), (23a) and (23b) will act only on the one-hole state; the first indicates the mixed type of excitation and the second is characterised by a passive hole orbital γ acting as a spectator while α, β becomes excited to p, q . We shall call such T_v matrix elements 'reducible' matrix elements. They are thus distinguished from the scattering $\alpha \beta \dots \rightarrow p q \dots$ for the core, characterised by $\langle p q \dots | t_p^\alpha | \alpha \beta \dots \rangle_a$. Thus, say, in the expansion of $\exp(T_c) \exp(T_v) \psi_K^0(N-1)$, the weight of the configuration obtained by replacing α, β in a ϕ_i state by p, q will have contributions from both $\langle \gamma p q | t_3^\gamma | \alpha \beta \rangle_a$ and the 'irreducible' $\langle p q | t_2^\alpha | \alpha \beta \rangle_a$. The reducible part thus takes account of the change brought about in the core correlation on ionisation and evidently incorporates relaxation effects.

The effective operator U_{c-v} in equations (19b) for the ionised-state problem may be written as (I, II, IV)

$$U_{c-v} = \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{\substack{K_1, K_2 \\ K_1 + K_2 = m}} (-1)^{K_2} \sum_{R_1, \dots, R_m = T_{v_1}, \dots, T_{v_N}} [R_m \dots R_{K_1+1} (\bar{U}_c) R_1 \dots R_{K_1}]_L \quad (24)$$

In order to appreciate the structure of the matrix elements appearing in (18b) and (19b), a diagrammatic language would be very helpful. Following the usual conventions (I, II, III), we represent the Hamiltonian operators and the T_v or T_c operators by replacing α, β in a ϕ_i state by p, q will have contributions from both $\langle \gamma p q | t_3^\gamma | \alpha \beta \rangle_a$ full circles refer to H or T_c Hugenholtz vertices (Hugenholtz 1957) and full triangles refer to T_v vertices respectively.

The matrix elements of the operator U_{c-v} of the type

$$\langle \phi_m^*(N-1) | U_{c-v} | \phi_i(N-1) \rangle$$

is then just a sum of contributions coming from appropriate G blocks (I, II, III) with a composite $\bar{U}_c$ vertex and various T_v vertices. From the basic vertices F, V

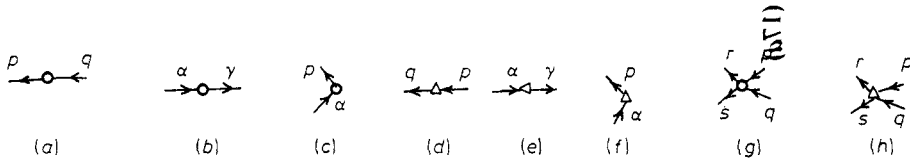


Figure 1. Typical basic F or V diagrams. Open circles represent F or V vertices.

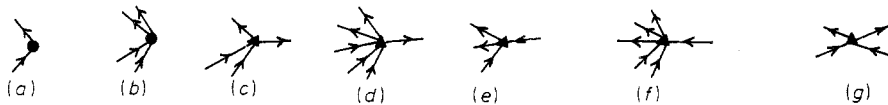


Figure 2. Basic T_c and T_v diagrams. Full circles and triangles represent T_c and T_v vertices respectively.

and T_c , composite $\bar{U}_c$ vertices may be constructed as connected diagrams joining the vertices F or V with T_c vertices. We denote the $\bar{U}_c$ vertices by open triangles. In order to write down equations (19b), we pick out the T_v diagrams one by one, and consider in each case the G block having the same shape as that of the T_v diagram considered. The sign of a diagram entering a G block and the attendant algebraic expression may be written down following the rules in I, except that now there is an additional sign $(-1)^{h_r}$, where h_r is the number of hole lines leaving the diagram from the right.

Now, let us denote the shape of a particular G block by a superscript 'a', and a particle rank of the block (i.e. number of electrons scattered) by the subscript 'p'. Depending on the shape of a particular G_p^a considered above, we encounter either of the following possibilities:

(i) The block G_p^a is an irreducible block, thus having no passive labels appearing in both ingoing and outgoing open lines. In this case, there will be as many types of equation as there are basic irreducible T_p^v diagrams, and these will all be of the form:

$$\sum B_p^a D_p^a(K_0; K_i) = 0 \quad \text{for each } a. \quad (25a)$$

K_0 and K_i are the sets of labels for outgoing and ingoing lines respectively, D_p^a is a contribution from the G block and B_p^a represents the permutation of equivalent outgoing lines and ingoing lines; the sum runs over all such permutations (I). Equivalent lines are those which lie on the same side of a G block, and which have arrows in the same sense.

(ii) The G_p^a is a reducible block containing r passive lines. In this case, the equations are of the form

$$\sum_{K=0}^r \sum B_{p-K}^a D_{p-K}^a(K_0; K_i) = 0. \quad (25b)$$

The first sum is over the G blocks having different shapes that may arise as K takes up different values between 0 and r (the latter usually represents the maximum number of holes in the ionised configuration in the model space; for the one-hole state in question, this is 1). The G block, with $K = 0$ is the reducible block G_p^a , and the superscript a refers to this. It might happen that the block with $K = r$ would look like a T_c operator (or, better, like a G block having the same shape as a T_c operator—required for getting the T_c matrix elements). In an exactly similar fashion, the matrix elements of the type $\langle \phi_j | U_{c-v} | \phi_i \rangle$ may be diagrammatically enumerated. Obviously, before constructing the G blocks for U_{c-v} , the calculations of core-excitation operators T_c have to be done in the same manner by considering the G blocks having the same shapes as the T_c , but these G blocks would consist of F , V and T_c only. To distinguish the G blocks appearing in U_{c-v} , and those appearing in $\bar{U}_c$, we draw them as big shaded triangles and shaded circles respectively. Typical G blocks considered by us for IP (and also EE) are shown in figure 3. The $\bar{U}_c$ blocks are G_1 and G_2 .

Now for the model space involving the calculations of IP in our case, we consider the state $Y_\alpha^\dagger | \phi_{HF} \rangle$, so that

$$IP = D_{10}(\alpha; \alpha) \quad (26)$$

and the diagrams entering the block G_{10} are shown in figure 5.

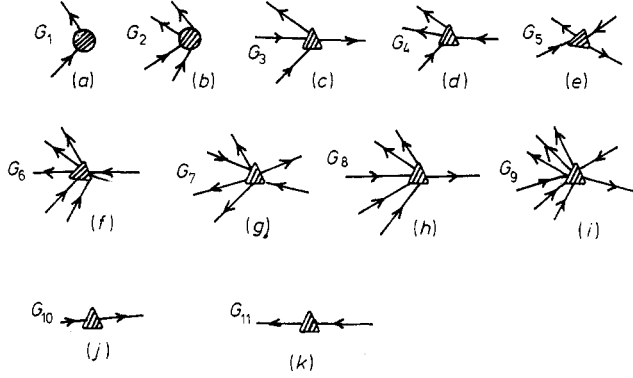


Figure 3. The G blocks. Subscript numerals are for block numberings. Shaded triangles are for G blocks determining T_v . The rest are for T_c .

2.3. Excitation energies

For EE, we must include ϕ_{HF} in the model space, and the one-hole one-particle determinantal states as $\phi_i(N)$. The operator $\exp(T_c)\exp(T_v)$ must, therefore, be able to correlate these ϕ_i free of constraints. T_v , accordingly, will have to be of the form given in (23), and also

$$T_{p+1}^v \rightarrow \frac{1}{(p+1)!^2} \sum \langle qrs \dots | t_{p+1}^v | p\alpha\beta \dots \rangle_a N[Y_q^\dagger Y_r^\dagger Y_s^\dagger \dots Y_\beta^\dagger Y_\alpha^\dagger Y_p] \quad (27a)$$

$$T_p^v \rightarrow \frac{1}{p!^2} \sum \langle \delta qrs \dots | t_p^v | \alpha\beta\gamma p \dots \rangle_a N[Y_\delta Y_q^\dagger Y_r^\dagger Y_s^\dagger \dots Y_p Y_\gamma^\dagger Y_\beta^\dagger Y_\alpha^\dagger] \quad (27b)$$

$$T_{p+1}^v \rightarrow \frac{1}{(p+1)!^2} \sum \langle pqr \dots | t_{p+1}^v | p\alpha\beta \dots \rangle_a N[Y_p^\dagger Y_q^\dagger Y_r^\dagger \dots Y_\beta^\dagger Y_\alpha^\dagger Y_p] \quad (27c)$$

The reducible operator in (27c) is introduced in order to distinguish the amplitude of scattering α, β to q, r in the one-hole one-particle states with a valence particle p . The effective operator U_{e-v} for this model space will have the same form as in (24), but the T_v operator would now contain the terms as in (23) and (27). The terms in U_{e-v} can now be enumerated and classified as in §2.2, discussed above. Essentially, these will contain the G blocks G_3 to G_{11} of figure 3. The G blocks contributing to T_c are, as usual, the blocks G_1 and G_2 . For the model space considered here, the excitation energies are given by

$$EE = D_{10}(\alpha; \alpha) + D_{11}(p; p) + D_6(p, \alpha; p, \alpha) \pm D_6(p, \alpha; \alpha, p) \quad (28)$$

where the $+/-$ sign refers to the singlet/triplet excitation energy.

2.4. A coupled scheme for calculation of IP and EE

We now discuss a scheme for the simultaneous calculation of IP and EE in the same structural framework of the present theory. The basic idea may be succinctly summarised as follows.

We start with the ϕ_{HF} as the vacuum, and determine the T_c matrix elements from (9). Next, for the ionised states, we define a multiple-cluster-expansion operator $\exp(T_c)\exp(T_v^i)$, such that

$$H \exp(T_c) \exp(T_v^i) \sum_i C_{K^i} \phi_i(N-1) = E_K \exp(T_c) \exp(T_v^i) \sum_i C_{K^i} \phi_i(N). \quad (29)$$

and finally we get

$$\langle \phi_m^*(N-1) | U_{c-v}^i | \phi_i(N-1) \rangle = 0 \quad \text{for all } m \text{ and } i, \quad (30)$$

as equations for matrix elements of T_v^i . The choice of the matrix elements of T_v^i is made following the same considerations as outlined in §2.2. U_{c-v}^i has nearly the same expression as (24), the only difference being that T_v^i rather than T_v appears in its definition. In order to correlate the excited states, we introduce an operator $\exp(T_c)\exp(T_v^i + T_v^{\text{ex}})$, where T_v^{ex} introduces excitations not covered in T_v^i as well as excitations in T_v^i , but with amplitudes containing T_v^{ex} as the operator to distinguish them from the scattering events from $\phi_i(N-1)$. The relevant equations determining T_v^{ex} have the form:

$$\langle \phi_l^*(N) | U_{c-v}^{\text{ex}} | \phi_i(N) \rangle = 0 \quad \text{for all } l \text{ and } i, \quad (31)$$

where U_{c-v}^{ex} involves an expression akin to that in (24), with $T_v^i + T_v^{\text{ex}}$ replacing T_v . In equations (31), the T_c and T_v^i matrix elements which appear will be taken as known—obtained by solving (9) and (30). Thus, determination of T_c , T_v^i and T_v^{ex} involve decoupled equations (9), (30) and (31), though the total problem of IP and EE is tangled in a way; (31) involves a knowledge of T_v^i matrix elements. If desired, a triple-cluster-expansion operator could be used for EE: $\exp(T_c)\exp(T_v^i)\exp(T_v^{\text{ex}})$, but the basic approach is more or less the same.

3. Application to the transbutadiene molecule

In order to test whether the above theory works, we have calculated the vertical ionisation potential and the first π - π^* singlet and triplet excitation energies of a 4 π electron system, the transbutadiene molecule. We first performed a HF calculation of the ground state and obtained eight spin-MO's from four MO's which we designate as (1, $\bar{1}$), (2, $\bar{2}$), (3, $\bar{3}$) and (4, $\bar{4}$) in order of increasing orbital energy. The spin-MO's having the same orbital energy are put together in the same brackets. Over this basis set, the vacuum is $A[1 \bar{1} 2 \bar{2}]$; the singly ionised configurations entering the model space for IP calculation are $A[1 \bar{1} 2]$ or $A[1 \bar{1} \bar{2}]$; the corresponding determinants for EE are $A[1 \bar{1} 2 \bar{3}]$ and $A[1 \bar{1} 3 \bar{2}]$. A in each case stands for the normalised antisymmetrisation operator. Clearly, α and $\bar{\alpha}$ in the one-hole states are 2 and $\bar{2}$ respectively, whereas p , α in (28) are 3, 2 and $\bar{p}$, $\bar{\alpha}$ are $\bar{3}$, $\bar{2}$ respectively.

Let us now consider the T_c and T_v matrix elements that enter the calculation of IP. For this, we make a list of all the three- and four-particle excited configurations that may be built out of the given basis set. For example, we have a total of two singly excited and seven doubly excited four-particle determinants which can mix with the vacuum state. For the time being, we restrict ourselves to at most doubly excited configurations. In a similar manner, we make a list of all three-particle excited configurations mixing with $A[1 \bar{1} 2]$. In writing down the corresponding T_v matrix

elements we use reducible matrix elements whenever necessary. For example, corresponding to the singly excited three-particle excited configuration $A[3\bar{1}\bar{2}]$, we use the reduced matrix element $\langle 32|t_2^y|12\rangle_a$ instead of $\langle 3|t_1^y|1\rangle_a$. As before, we consider up to doubly excited configurations. For the ionised states, this means that there are no reducible T_v matrix elements of a particle rank greater than three. It may be noted that all the T_c and T_v matrix elements together span the configurational subspace enumerated above in a completely general manner, free of unnecessary constraints, and maintain the relevant spin and spatial symmetries of the orbitals. There are altogether 19 unknowns in the IP calculation (9 T_c and 10 T_v matrix elements) and corresponding to these we have a set of 19 equations—9 containing T_c 's only and 10 containing T_v and T_c (through $\bar{U}_c$). The solution of T_c elements is thus uncoupled from that of T_v .

We confine ourselves to only those terms in $\bar{U}_c$ and U_{c-v} which are linear in T_c and T_v . To maintain this consistently, we take care that the implied product of T_c and T_v matrix elements never appears anywhere. This would be achieved if we interpret a $\bar{U}_c$ vertex as simply an F or a V vertex whenever it is connected with a T_v vertex. The system of equations (9) and (19b) would then, respectively, be of the forms

$$A^{c-c}T^c = B^c \quad (32)$$

$$A^{v-v}T^v = B^v - A^{v-c}T^c. \quad (33)$$

Solving these sets of equations in the usual manner we get the numerical values of T_c and T_v matrix elements. Having determined these, we put them in (26), and get the IP, shown in table 2.

Table 1. T matrix elements for EE.

Nature of the state correlated	No	The T matrix elements	Values
HF ground state $ \phi_{HF}\rangle$	1	$\langle 3 t_1^c 1\rangle$	0.00000
	2	$\langle 4 t_1^c 2\rangle$	-0.00252
	3	$\langle 3\ 4 t_2^z 1\ 2\rangle_a$	0.00436
	4	$\langle 3\ \bar{3} t_2^z 1\ \bar{1}\rangle_a$	-0.05514
	5	$\langle 3\ \bar{3} t_2^z 2\ \bar{2}\rangle_a$	-0.08279
	6	$\langle 3\ \bar{4} t_2^z 1\ \bar{2}\rangle_a$	0.07649
	7	$\langle 4\ \bar{3} t_2^z 1\ \bar{2}\rangle_a$	0.05675
	8	$\langle 4\ \bar{4} t_2^z 1\ \bar{1}\rangle_a$	-0.04774
	9	$\langle 4\ \bar{4} t_2^z 2\ \bar{2}\rangle_a$	-0.05788
Singly excited states $Y_3^\dagger Y_2^\dagger \phi_{HF}\rangle$ and $Y_3^\dagger Y_2^\dagger \phi_{HF}\rangle$	1	$\langle 4\ \bar{2} t_2^x 1\ \bar{1}\rangle_a$	-0.00608
	2	$\langle 3\ \bar{2} t_2^x 2\ \bar{1}\rangle_a$	0.11954
	3	$\langle 4\ \bar{4} t_2^x 1\ \bar{3}\rangle_a$	0.00548
	4	$\langle 3\ \bar{4} t_2^x 2\ \bar{3}\rangle_a$	0.10565
	5	$\langle 3\ \bar{3} t_2^x 1\ \bar{3}\rangle_a$	0.06713
	6	$\langle 4\ \bar{3} t_2^x 2\ \bar{3}\rangle_a$	0.00511
	7	$\langle 4\ \bar{2} t_2^x 1\ \bar{3}\rangle_a$	-0.19906
	8	$\langle 4\ \bar{2} t_2^x 3\ \bar{1}\rangle_a$	0.27449
	9	$\langle 4\ \bar{4}\ \bar{3} t_3^x 1\ \bar{1}\ \bar{3}\rangle_a$	-0.01282
	10	$\langle 3\ \bar{4}\ \bar{3} t_3^x 1\ 2\ \bar{3}\rangle_a$	0.01052
	11	$\langle 3\ \bar{4}\ \bar{3} t_3^x 2\ \bar{1}\ \bar{3}\rangle_a$	-0.00147

† The parameters for the calculation are taken from Cizek *et al* (1969).

Table 2. The π - π^* singlet and triplet excitation energies and vertical ionisation potential of transbutadiene in eV.

Quantities		Present results	Full CI results
Singlet	IP	11.6494	11.6830
	EE	6.5173	6.5480
Triplet	EE	3.5667	3.6858

For the excitation energies, the T_c and T_v matrix elements are built in exactly the same manner. There are once again 9 T_c matrix elements and this time 11 T_v matrix elements. In the linear approximation, the equations (9) and (19a) are again of the form (32) and (33). We have listed in table 1, the calculated values of the T_c and T_v matrix elements; the calculated EE are given in table 2.

Let us note that once equations (32) and (33) are obtained, the relevant solutions in both cases are exact within the following approximations:

- (i) linear terms in T_c and T_v are retained in $\bar{U}_c$ and U_{c-v} ;
- (ii) irreducible T_v 's are of ranks $p \leq 3$.

The solutions of the T_c and T_v matrix elements give us an idea as to which of the excited configurations will contribute significantly towards a correlated ground, ionised and excited state in the configuration mixing. It is found that most of the contributions are small thus confirming the adequacy of a linear theory. However, if one goes in for a non-linear theory, this would certainly improve on the energy value as more terms are included and, more importantly as 'unlinked cluster' type excitations (in Sinanoğlu's terminology, 1962), simulating the quadrupally excited configurations are taken into account. This is certainly needed for larger systems and more realistic calculations. But a primary linear calculation is still essential to guess which of the T_c and T_v matrix elements must be needed in the non-linear calculation. In the latter case, equations (32) and (33) would be replaced by

$$A^{c-c}T^c + D^{c-c}T^c \otimes T^c + \dots = B^c \quad (34)$$

$$\begin{aligned} A^{v-v}T^v + D^{v-v}T^c \otimes T^v + D^{v-v-c}T^c \otimes T^v \otimes T^v + \dots \\ = B^v - A^{v-c}T^c - A^{v-c-c}T^c \otimes T^c. \end{aligned} \quad (35)$$

An interesting feature of the core-valence separation discussed here is that we have automatically subtracted the correlated ground energy for the IP or EE calculation by simply dropping the closed G blocks (i.e. the G blocks having no open lines). In the definition of total ionised or excited state energy, it might then appear that an unphysical correlation correction has been introduced, namely a closed diagram in which an excitation from an already vacant hole-state to a particle is attempted. This unphysical diagram cannot contribute to the total ionised/excited state energy and must therefore be automatically compensated by a counter-diagram. This is indeed the case. We can easily verify that the unphysical core-correlation diagram shown in figure 4(a), implicitly present in the definition of the ionised/excited state is automatically cancelled by a particular term (figure 4(c)) of the U_{c-v} diagram shown in figure 4(b), if we write out the $\bar{U}_c$ vertex in figure 4(b) in full in terms of F/V and T_c vertices. For EE, all the diagrams of figure 5 contribute. In addition there are other G blocks. Of these, some typical diagrams contributing to EE are

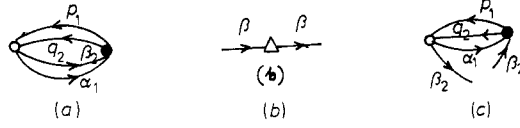


Figure 4. Cancellation of 'unphysical contributions'. Diagrams (a) and (c) cancel each other for any orbital which is vacant in one of the ionised states in the model space.

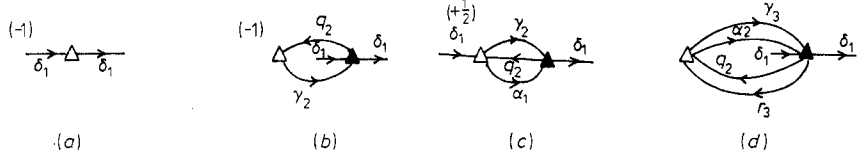


Figure 5. Diagrams contributing to IP.

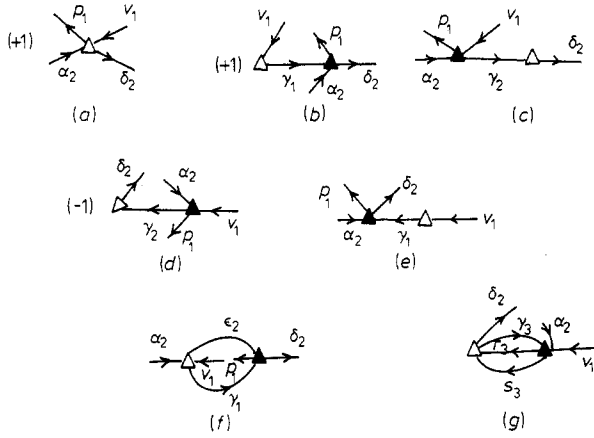


Figure 6. Some typical diagrams contributing to EE.

shown in figure 6. Some of them would be compensating diagrams correcting for the unphysical additional core-correlation energy implicitly present. There is some further partial cancellation. For example, figure 6(f) cancels part of figure 5(c).

4. Relation to perturbation theories

To see the connection of this formalism with the existing perturbative theories, we discuss an iterative method of solving the set of equations (32) and (33). To start with, we neglect the off-diagonal matrix elements of the matrices A^{c-c} , A^{v-v} etc, and find that the first approximations of T_c and T_v matrix elements are

$$T_c^o(i) \simeq B_c(i)/A^{c-c}(i, i) \quad (36a)$$

$$T_v^o(i) \simeq B_v(i)/A^{v-v}(i, i). \quad (36b)$$

Since this is tantamount to neglecting the couplings between the different T matrix elements in equations (32) and (33) we shall refer to these solutions as those in a decoupled approximation.

We find that, in this approximation, the energy values include all the important perturbation theory contributions up to second order and also up to infinite orders with regard to certain ladderings. To demonstrate this explicitly, let us first pick out the matrix element $T_v(2)$ from table 1†

$$T_v^0(2) \simeq \frac{\langle 3\bar{2}|v|2\bar{1}\rangle_a}{E(3, \bar{2}; 2, \bar{1})}. \quad (37)$$

The contribution of this to $\text{IP}^\ddagger$ is

$$E'_{\text{IP}} = \langle 3\bar{2}|v|2\bar{1}\rangle_a \langle 2\bar{1}|v|3\bar{2}\rangle_a / E(3, \bar{2}, 2, \bar{1}) \quad (38)$$

where $E(3, \bar{2}, 2, \bar{1})$ is given by

$$E(3, \bar{2}, 2, \bar{1}) = \epsilon_2 + \epsilon_{\bar{1}} - \epsilon_3 - \epsilon_{\bar{2}} + \langle 3\bar{2}|v|3\bar{2}\rangle_a - \langle 2\bar{1}|v|2\bar{1}\rangle_a \quad (39)$$

and is a shifted energy denominator of the type discussed by Epstein (1926), Nesbet (1955) and Kelly (1968). Thus, the energy given by (38) includes the effect of the hole-particle ladder $\langle 3\bar{2}|v|3\bar{2}\rangle_a$ and the hole-hole ladder $\langle 2\bar{1}|v|2\bar{1}\rangle_a$ to infinite orders. Expanding out $[\langle 3\bar{2}|v|3\bar{2}\rangle_a - \langle 2\bar{1}|v|2\bar{1}\rangle_a]$ from the denominator, the lowest-order (basic) diagram would be like

$$E''_{\text{IP}} \simeq \frac{\langle 3\bar{2}|v|2\bar{1}\rangle_a \langle 2\bar{1}|v|3\bar{2}\rangle_a}{\epsilon_2 + \epsilon_{\bar{1}} - \epsilon_3 - \epsilon_{\bar{2}}}. \quad (40)$$

This corresponds to figure 5(c) where the T vertex is replaced by a V vertex and to which the following rules apply.

- (i) Join the free ends by a fictitious broken line.
- (ii) Assign to it an orbital energy appropriate to whether it behaves as a particle line or a hole line; $-\epsilon_p$ for particle p , and ϵ_a for hole line a .
- (iii) Write down the matrix elements and energy denominator in the usual fashion.
- (iv) Assign a sign factor $(-1)^{h+l}$ where the fictitious broken line must be counted as forming a loop (l).

In this fashion, all the lowest-order contributions to IP in the decoupled approximation may be generated by replacing the T vertices in the appropriate diagram of figure 5. Diagrams thus generated are all the second-order IP diagrams of Hubac *et al* (1973) or of Paldus and Cizek (1975). These also represent the second-order irreducibles in the hole-particle formalism of Pickup and Goscinski (1973) or of Paldus and Cizek (1974).

In general, these second-order diagrams are of two types

- (i) Diagrams involving intercrossing free hole lines which will correspond always to an expression

$$\frac{1}{2} \sum_{\substack{p, q, \beta \\ \beta \neq \alpha}} \frac{\langle \alpha\beta|v|pq\rangle_a \langle pq|v|\alpha\beta\rangle_a}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q}.$$

† Refers to table 1 footnote.

‡ In IP also, the same T_v matrix element appears, but with different amplitude from that in EE .

This is the 'pair removal term' of Pickup and Goscinski (1973) and accounts for the pair correlation energies which disappear upon removal of the spin orbital α .

(ii) The other type will be the diagrams which do not contain intercrossing free hole lines; of these, many will have a passive internal hole line, and these will correspond to the expression

$$\sum_{\substack{p, \beta \\ \beta \neq \alpha}} \frac{\langle \alpha p | v | \alpha \beta \rangle_a \langle \alpha \beta | v | \alpha p \rangle_a}{\epsilon_\beta - \epsilon_p}.$$

This is the lowest-order 'orbital relaxation' part accounting for the reorganisation effects of the remaining spin orbitals following the removal of the spin orbital α . The remaining part of the diagrams in the category (ii) would correspond to an expression

$$\frac{1}{2} \sum_{\substack{\beta, \gamma, p \\ \beta, \gamma \neq \alpha}} \frac{\langle \alpha p | v | \beta \gamma \rangle_a \langle \beta \gamma | v | \alpha p \rangle_a}{\epsilon_\beta + \epsilon_\gamma - \epsilon_\alpha - \epsilon_p},$$

and corresponds to the 'pair relaxation term' which accounts for the changes in the remaining pair correlations due to reorganisation.

In an exactly similar manner, we can show that the excitation energies, calculated in the decoupled approximation of our formalism, include all the important first- and second-order contributions of perturbation expansion of the excitation energies. If we include all the T_v operators of the forms given in equations (23) and (27),

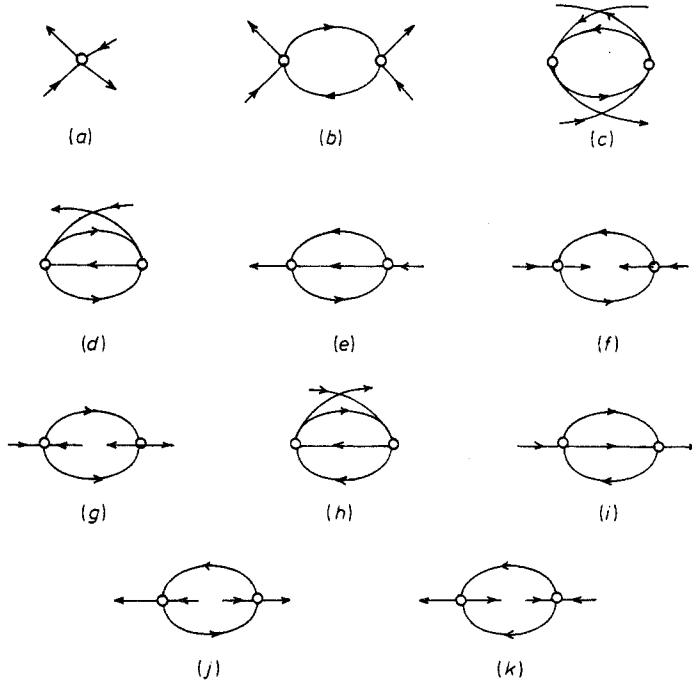


Figure 7. All second-order diagrams to IP and EE in the lowest-order decoupled approximation (equation (36)) of the formalism. Only (h) and (i) contributes to Koopmans correction.

these are as shown in figure 7. For evaluating the diagrams, the same set of rules have to be followed; the only difference is that we now have to join the free ends of the particle lines also. Figure 7(b), for example, is a second-order irreducible of Paldus and Cizek (1974) or the second-order contribution in the perturbation expansion of EE (Kvasnicka and Hubac 1974, Paldus and Cizek 1975). In a similar manner, all the second-order contributions in these formalisms may be obtained from the appropriate U_{c-v} diagrams by replacing T vertices by V vertices. The diagrams shown in figure 7 can in general be classified into two groups, one which includes the orbital-relaxation effects (namely 7(a), (b), (e) to (g), (i) and (h)) and the others which account for pair-correlation energies (namely 7(b) to (e), (h) and (i))†. Similar conclusions have also been reported by Oddershede and Jørgensen (1977a, b).

We shall now point out a further interesting feature of our formalism. If we consider the lowest-order ladder insertion obtained by taking the first power of the expanded denominator for the decoupled expression of the T_v matrix $\langle 4\ 2 | t_2^v | 3\ 1 \rangle_a$ for EE, we have a contribution

$$E'_{EE} \simeq (-1) \frac{\langle 31 | v | 42 \rangle_a \langle 42 | v | 31 \rangle_a \langle 32 | v | 32 \rangle_a}{(\epsilon_1 + \epsilon_3 - \epsilon_2 - \epsilon_4)^2} \quad (41)$$

to which corresponds to figure 8(a), where the lines with encircled arrows, namely the hole line 2 and particle line 3 appear 'folded'. The minus sign comes from this single folding of the lines coming from one pair of folded vertices. Such folded diagrams are characteristic of all perturbation expansion of energy for open shells (Brandow 1967). It is worth mentioning here that these diagrams are those which would involve 'dangerous denominators' in Paldus and Cizek (1974, 1975) formalism, as can be verified by straightening out the folds. These have been deliberately omitted by these authors. In our formalism, however, these diagrams are inherently present as 'anomalous diagrams' (I, II), originating from contracting a T_v vertex having free lines to the right with a V vertex. Transcribed into Goldstone graphology, this folded diagram plays a role akin to the so called backward RPA diagram 8(b).

Another lowest-order term—coming out of the expanded denominator of the same T_v —is

$$E''_{EE} \simeq \frac{\langle 31 | v | 42 \rangle_a \langle 41 | v | 41 \rangle_a \langle 42 | v | 31 \rangle_a}{(\epsilon_1 + \epsilon_3 - \epsilon_2 - \epsilon_4)^2} \quad (42)$$

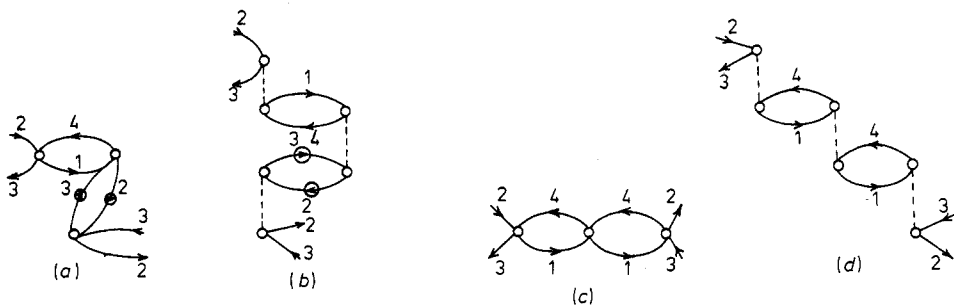


Figure 8. Higher-order EE diagrams in the decoupled approximation of this formalism. (a) is a folded diagram akin to the backward RPA Goldstone diagram (b), (c) corresponds to the forward RPA Goldstone diagram (d).

† These effects appear mixed up in the case of EE.

corresponding to diagram 8(c). One of the many possible Goldstone components of it is the diagram 8(d), which is the well known forward RPA diagram.

As we go higher up in the expanded denominators, multiply folded diagrams would automatically start appearing. Thus, in the lowest-order calculation in the decoupled approximation of our formalism, many types of interactions are present to infinite order over and above the basic second-order contributions. Looking back at the coupled equations (32) and (33), we may say that they incorporate the effect of certain classes of diagrams which, due to their not forming any well-defined series, cannot be included in a closed form in perturbation theory. In as much as two separate SCF calculations are not required here, the method enjoys all the best traits of the so-called direct methods. What is more useful, the method can be applied to open-shell problems as well.



Figure 9. 'Unlinked cluster' and 'linked cluster' type triple excitation contributions to block G_{11} .

We might briefly mention the type of diagrams one would encounter in a non-linear theory. A typical core-valence interaction diagram having a product of T_c and T_v vertices is shown in figure 9(a). This is an 'unlinked cluster type' of triple excitations coming from a $T_c T_v$ product. A linked triple excitation type of U_{c-v} diagram would have appeared in the linear theory itself if true three particle T_v involving triple excitations were included in our consideration. This would look like figure 9(b).

5. Concluding remarks

We have demonstrated that the basic strategy in choosing the T_c and T_v matrix elements used in this paper plays a crucial role in decoupling the calculation. T_c involves all excitation from ϕ_{HF} independent of the valence occupancies in $\phi_i(N)$ or $\phi_i(N-1)$, and a set of equations is solved to get the relevant matrix elements. For T_v matrix elements, one has to include all the true excitations that involve both the valence-excitation and orbital-relaxation type of T_v operators—effectively changing the overall amplitudes of T_c type excitations in the ionised/excited levels. The procedure is general and thus would lead to decoupling of the equations for T_c and T_v in a more general open-shell case.

In conclusion, we may point out that, to a given approximation which may be suggested by the system itself, the basic key of this formalism i.e. the set of diagrams comprising the G blocks, constitute a sort of 'blue print'. Although we have demonstrated the applicability of the formalism by taking a crude semi-empirical calculation in a basis set of only 8 spin MO's, it serves as a guide for other calculations involving larger basis sets. For more realistic calculations, T_c^2 terms would have to be included in the core matrix element calculations, and T_v^2 have to be included in the valence part. Such studies are currently being undertaken, and will be reported in due course.

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