Use of cluster expansion techniques in quantum chemistry. A linear response model for calculating energy differences

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Abstract. In this paper we have reviewed the theoretical framework of the coupled-cluster (CC) based linear response model as a tool for directly calculating energy differences of spectroscopic interest like excitation energy (EE), ionisation potential (IP) or electron affinity (EA). In this model, the ground state of a many-electron system is described as in a coupled cluster theory for closed shells. The electronic ground state is supposed to interact with an external photon field of frequency w, and the poles of the linear response function as a function of w furnish with the elementary excitations of the system. Depending on the general form of the coupling term chosen, appropriate difference energies like EE, IP or EA may be generated. Pertinent derivations of the general working equations are reviewed, and specific details as well as approximations for EE, IP or EA are indicated. It is shown that the theory bears a close resemblance to the equation of motion (EOM) method but is superior to the latter in that the ground state correlation is taken to all orders and may be looked upon as essentially a variant of renormalised TDA. A perturbative analysis elucidating the underlying perturbative structure of the formulation is also given which reveals that the theory has a hybrid structure: the correlation terms are treated akin to an open shell MBPT, while the relaxation terms are treated akin to a Green function theory. A critique of the method *vis-a-vis* other CC-based approaches for difference energies forms the concluding part of our review.

Keywords. Cluster expansion techniques; linear response model; quantum chemistry; excitation energy; ionisation potential; electron affinity.

1. Introduction

One might now say with hindsight that the initial spectacular breakthrough in the theory of molecular electronic structure since the inception of quantum mechanics has mainly been due to the remarkable success of the independent particle model (IPM). With the advent of the sophisticated experimental techniques in the last decade to probe a variety of physicochemical phenomena involving excited or ionised states, it has become increasingly apparent that the IPM could fail at the outset to reproduce even qualitatively a vast body of experimental results. This has spelt a clear message to the theoreticians: there is a need to develop and apply useful correlation theories going beyond IPM and treat the energetics of the excitation and ionisation processes on a comparable and consistent level of accuracy encompassing both the ground and the excited/ionised states. A proper and balanced incorporation of correlation energy appropriate to both the ground and the excited/ionised states thus forms one of the major frontier areas of the present-day quantum chemical research (see *e.g.* Lowdin and Pullman 1983).

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While the variational approach like CI or MCSCF still remains as one of the most exploited and widely developed methods for this purpose (Shavitt 1977; Kutzelnigg 1977; Peyerimhoff 1979; Wahl and Das 1977; Jorgensen and Dalgaard 1979), it has also its limitations. With a preselected set of configurations in a truncated Hilbert space the CI wavefunction lacks the 'cluster decomposition property' ensuring the size-consistency (or separability) of the extensive quantities like energy (Primas 1965; Pople *et al* 1976; Bartlett 1981). This size-inconsistency error naturally persists in the calculation of energy differences. Moreover the CI-like approaches are 'indirect methods' for energy difference calculations in the sense that they require two separate calculations for the ground and excited/ionised states. Thus the common correlation terms for the two states which should ideally drop out on taking the energy differences are calculated redundantly. This has stimulated the search for the so-called 'direct methods' which would furnish the relevant energy differences in a one-shot process without separately calculating the energies for the respective states. In formulating these methods for many-electron systems it has transpired that the use of occupation number (or many-body) representation is much more preferable to the less compact Schrödinger representation. As the Hamiltonian H_M in occupation number representation does not explicitly involve the electron number N for the system, this opens up an immediate prospect of calculating with same H_M not only the excitation energies (EE) of a many-electron system having a specific number of electrons but also its ionisation potential (IP) or electron affinity (EA) involving a different number of electrons for the ground and the ionised states. In a direct method, one invokes a suitable 'excitation' or 'ionisation operator' which creates the appropriate excited or ionised states by acting on the ground state and posits suitable forms for these operators. The common correlation terms then automatically drop out on taking the energy differences. The occupation number representation of the relevant equations confers the flexibility of truncation for a given model in the *operator space*, rather than in the *configuration space*, and thus truncation schemes preserving size-consistency may be devised. An additional advantage of the many-body representation utilising the excitation/ionisation operators is that the calculated energy differences become progressively more accurate with increase in the number of electrons in the system.

There exist currently several direct methods for energy difference calculations. They may be divided into two broad categories: (a) perturbative methods like many-body perturbation theories (Bloch and Horowitz 1958; Brandow 1967; Kvasnicka 1977; Lindgren 1974; Johnson and Baranger 1971; Banerjee *et al* 1982a; Hose and Kaldor 1979) and (b) nonperturbative methods like Feynman-Dyson Green function theory (Linderberg and Ohrn 1971; Ohrn and Born 1981; Cizek and Paldus 1974; Csanak *et al* 1979; Oddershedde 1978; Cederbaum and Domcke 1977) and the related superoperator propagator and equation of motion (EOM) techniques (Jorgensen and Simons 1981; Rescigno *et al* 1977) and the open-shell cluster expansion techniques (Mukherjee *et al* 1975; 1977; Mukherjee 1979; Ey 1978; Lindgren 1978; Kvasnicka 1981; Westhaus and Bradford 1975; Reitz and Kutzelnigg 1979; Jeziorzki and Monkhorst 1981; Paldus *et al* 1978). Among these methods, the open-shell perturbation theories are now being increasingly used for IP and EE calculations (Kaldor 1973, 1975a, b; Hubac *et al* 1973; Kvasnicka and Hubac 1974; Yeager *et al* 1978; Lee *et al* 1980; Sheppard and Freed 1981; Yamamoto and Saika 1981; Banerjee *et al* 1982b) and it is now felt that the fully developed computational strategy will soon become competitive with the corresponding variational techniques. The Green function and the associated propa-

gator and EOM approaches have already been developed into a vast computational framework (see *e.g.* Jorgensen and Simons 1981; Ohrn and Born 1981; Resicigno *et al* 1977; Cederbaum and Domcke 1977 for extensive references).

A common shortcoming of the MBPT or the GF methods is their inability to sum up important classes of terms (or diagrams, if framed in a diagrammatic language) to all orders which might dominate in the expressions of the energy differences. Sometimes, for very special classes of terms, suitable infinite summation schemes like geometric approximations (Kelly 1969) or Padé approximations (Guest and Wilson 1979) have been invoked but there is no simple strategy for summing up general classes of diagrams to all orders. The cluster expansion techniques developed in the context of a nonperturbative framework have a decisive advantage in this respect: a cluster amplitude of the wavefunction written in a cluster expansion is a compact way of writing an infinite series of terms of a perturbative series. The cluster expansion based techniques for energy difference calculations utilising the advantages of a direct method are thus expected to obviate the limitations of the other direct methods currently in use. There is now a growing literature on this problem, but the full potentiality of this approach is yet to be explored.

We have been interested in the past decade in developing and applying the open-shell analogue of the closed shell coupled cluster (CC) method which was developed originally for treating the ground state correlation problem (see *e.g.* Kummel *et al* 1978; Bartlett 1981 for extensive references) and was eminently successful. The generalisation of the closed shell CC method to the open shell states is by no means unique or straightforward, and various authors have emphasised on the different aspects of the correlation problem which is peculiar to open shells. The formalisms developed to date can be broadly divided into two categories: (a) those which are specially designed to treat individual open-shell states *per se* and (b) those which are tailored to treat difference energies. In the first category there are the efforts of Mukherjee *et al* (1975) and Jeziorzki and Monkhorst (1981) and in the second there are the works of Mukherjee *et al* (1977); Lindgren (1978); Paldus *et al* (1978); Mukherjee and Mukherjee (1979) and Monkhorst (1977). We shall be mainly concerned in this review with the open-shell coupled cluster techniques for calculating energy differences, and in particular a coupled-cluster based linear response model which is similar in spirit to the EOM method but is a much more highly summed up version and therefore a much more convergent expansion scheme for calculating energy differences directly. The method utilises a coupled-cluster representation of the ground state and, like a direct method as EOM postulates the existence of an excitation/ionisation operator for generating the excited/ionised state from the ground state. Using time-independent many-body techniques, Mukherjee and others (Mukherjee 1979; Mukherjee and Mukherjee 1979) developed the linear response model for calculating the dynamic linear response of a correlated ground state under an external oscillatory perturbation, and sought to extract the excitation spectra of the system from the poles of the dynamic response function. This has since been generalised to incorporate IP/EA calculations (Ghosh *et al* 1981) and also both spin-conserving and spin-forbidden excitations (Ghosh *et al* 1982). Preliminary applications have produced quite encouraging results (Adnan *et al* 1980; Ghosh *et al* 1981; Adnan *et al* 1982). The method has also been rediscovered by nuclear physicists (Emrich 1981), though not in the form in which it was originally developed (Mukherjee 1979; Mukherjee and Mukherjee 1979). An analogous time-dependent formalism was also considered earlier by Monkhorst (1977).

The plan of the review is as follows. In §2 we delineate the pertinent features of the coupled-cluster based linear response theory for difference energy calculations and demonstrate that this naturally leads to a formalism very similar in spirit to a renormalised Tamm Dancoff approximation (TDA) of the EOM method. In §3 we discuss the choice of the excitation/ionisation operators as well as the cluster ansatz for the ground state and the appropriate truncation schemes. Section 4 gives a perturbative analysis of the relevant equations from the linear response theory showing its simultaneous kinship with renormalised GF theory or open-shell MBPT of the Bloch-Horowitz type and open-shell MBPT of the Brandow type. Finally, in §5 we include a brief critique of this formalism *vis-a-vis* other cluster expansion theories using a similar cluster ansatz.

2. Coupled-cluster based linear response model

2.1 *Basic methodology*

In this subsection we give a resumé of the formal developments of the CC-based linear response theory. We shall first discuss the general algebraic structure of the ultimate working equations, without explicitly specialising them for either EE or IP/EA calculations. Next we reformulate the linear response theory in a way which brings out its theoretical contents as essentially a renormalised variant of TDA.

The CC-based linear response approach invokes two successive cluster expansions on a starting uncorrelated ground state function which is chosen as the Hartree-Fock (HF) determinant ϕ_{HF}. The first cluster expansion incorporates the effect of electronic correlation in the ground state and the various cluster operators in this expansion contain n particle-n hole (np-nh) excitations out of ϕ_{HF} in a way entirely analogous to the coupled cluster theory for the closed shells (Cizek 1966, 1969). The dynamical linear response of the ground state to an external harmonic field is then calculated using the following technique: the system is assumed to interact with an external photon field where the coupling terms involve creation/destruction of a single photon of a definite frequency. The eigenstate of the composite system comprising the electronic and photon degrees of freedom ceases to contain definite number of photons. The extent of electron correlation in the electronic component of the composite system is also changed. The overall change due to the coupling is induced by the second cluster expansion operator. The cluster operators in this expansion are composite entities which create/destroy one, two, three photons and simultaneously induce various np-mh excitation out of ϕ_{HF}. The precise nature of the electronic part of the cluster operator is dictated by the nature of transition energies under study, *viz* EE, IP or EA. For EE $n = m$ and for IP/EA $n = m - 1/m + 1$, as we shall see presently. For linear response calculations it suffices to restrict the second cluster expansion to linear terms only. The associated response function then involves an expectation-value like quantity taken with respect to the electronic ground state and is proportional to the photon number of the photon field. The response function may thus be looked upon as a photon self-energy and consequently as a linear response function. When the external frequency of the photon field matches an excitation frequency corresponding to an elementary excitation (EE, IP or EA depending on the form of the coupling chosen), the linear response function becomes singular. Thus the energy differences may be calculated by

noting the zeros of the inverse of the linear response function. This is the underlying physical picture of the CC-based linear response model.

In the closed-shell CC theory (Cizek 1966, 1969), the exact ground state of a many electron system ψ_{gr} is described in terms of ϕ_{HF} and a cluster expansion operator $\exp(T)$:

$$\psi_{gr} = \exp(T)\phi_{HF}. \tag{1}$$

The associated molecular electronic Hamiltonian H_M may be written in normal order with respect to ϕ_{HF} as the vacuum as

$$H_M = E_{HF} + \sum_A \varepsilon_A N[a_A^+ a_A] + \frac{1}{2!^2} \sum_{\substack{A,B, \\ C,D}} \langle A_B|v|C_D\rangle_a N[a_A^+ a_B^+ a_D a_C], \tag{2}$$

where the spin-orbitals for representation have been taken as HF spin orbitals. From now on we shall refer to the spin-orbitals simply as orbitals for brevity.

Let us also invoke a photon field of frequency w, characterised by a Hamiltonian H_{ph}:

$$H_{ph} = wC^+C, \tag{3}$$

where C/C^+ corresponds to a destruction/creation operator of a photon of frequency w. In the absence of any interaction the Schrödinger equation for the composite system may be written as

$$[H_M + H_{ph}]\psi_{gr}\chi_{ph} = E_0\psi_{gr}\chi_{ph}, \tag{4}$$

where χ_{ph} is the photon eigenstate of H_{ph}, and E_0 is the sum of the electronic ground state energy E_{gr} and the photon energy E_{ph}. If now an interaction is switched on between the electronic and photon fields, the unperturbed state $\psi_{gr}\chi_{ph}$ will be changed to a perturbed state ψ' having no definite number of photons. The interaction Hamiltonian H_{int} may be written as (see *e.g.* Mukherjee and Mukherjee 1979)

$$H_{int} = iV_{el}[C - C^+], \tag{5}$$

where V_{el} depends on electronic operators only. The *detailed form* of V_{el} is not important for calculating the energy differences, but its *general form* (*e.g.* whether it conserves the electron number or decreases/increases by one) is dictated by our desire to calculate EE, IP or EA. The interaction will modify the nature of correlations in the electronic system and at the same time will induce photon creation/destruction. In the confines of the linear response theory, we can restrict the cluster operators inducing the change to contain creation/destruction of one photon only. Writing the perturbed state ψ' for the composite system as

$$\psi' = \exp(T)\exp(S)\phi_{HF}\chi_{HF}, \tag{6}$$

where S induces electronic excitations or detachments/attachments with consequent absorption and emission of single photons through C/C^+ operators, S in (6) may be defined as

$$S = iS_{el}[C - C^+] = S^+ + S^-, \tag{7}$$

where S_{el} corresponds to the electronic degrees of freedom S^+ and S^- correspond to the component of S involving C and C^+ respectively. The linear response function for the

electronic ground state depends on the photon frequency w through the w-dependence of the operator S coming from C/C^+ operators. The second order energy shift $\Delta E^{(2)}$ due to the function $S\phi_{HF}\chi_{ph}$ involving absorption/emission of one photon may be generally written as

$$\Delta E^{(2)}(w) = n_{ph} G(V_{el}, w) + \sum_{m \neq 0} \frac{|\langle \psi_m | V_{el} | \psi_{gr} \rangle|^2}{(E_{gr} - E_M - w)}, \tag{8}$$

where ψ_m's are excited/ionised electronic eigen-states reached through the electronic part V_{el} of H_{int}. The first term on the right side of (8) depends on the photon number n_{ph} of the photon field, and it is thus both a photon self-energy and a linear response function. From the general property of a response function in the linear response theory (Karplus and Kolker 1963; Langhoff *et al* 1972), $G(V_{el}, w)$ has poles for values of w matching an elementary excitation frequency $(E_m - E_{gr})$. If V_{el} conserves the electron number, ψ_m's are then the excited states of the electronic system (of whose ground state is ψ_{gr}), and if V_{el} destroys/creates an electron, the states ψ_m are then various cation/anion eigenstates of the parent electronic system. Thus the poles of $G(V_{el}, w)$ furnish us with EE, IP or EA depending on the specific choices of V_{el}. At any pole, $S\psi_{gr}\chi_{ph}$ is essentially a product of an appropriate excited/ionised state ψ_m and a $(N \pm 1)$-photon state $\chi_{ph\pm}$. Naturally, the quality of the state ψ_m generated depends upon the choice of S_{el} and S.

We now briefly indicate how one may arrive at the working equations for calculating the energy differences. We start out from (4), and premultiply it with $\exp(-T)$. Noting that H_{ph} does not involve electronic operators, we have, from (4):

$$[\bar{H}_M + H_{ph}] \phi_{HF}\chi_{ph} = E_0 \phi_{HF}\chi_{ph}, \tag{9}$$

where the 'dressed' Hamiltonian $\bar{H}_M$ is defined as

$$\bar{H}_M = \exp(-T) H_M \exp(T). \tag{10}$$

Projecting (9) on to the states $\phi_m^* \chi_{ph}$ where ϕ_m^*'s are the various *np-nh* excited states of ϕ_{HF}, we have

$$\langle \phi_m^* | \bar{H}_M | \phi_{HF} \rangle = 0, \quad \forall_m, \tag{11}$$

which determine the various *np-nh* cluster amplitudes of T, exactly analogous to what one obtains in closed-shell CC theory. In the coupled system in presence of the interaction the corresponding Schrödinger equation reads as

$$[H_M + H_{ph} + H_{int}] \psi' = E' \psi'. \tag{12}$$

Premultiplying (12) by $\exp(-T)$, we have

$$[\bar{H}_M + H_{ph} + \bar{H}_{int}] \exp(S)\phi_{HF}\chi_{ph} = E' \exp(S)\phi_{HF}\chi_{ph}, \tag{13}$$

where $\bar{H}_{int}$ is the transformed interaction $\exp(-T)H_{int}\exp(T)$, which can be equivalently written as

$$\bar{H}_{int} = i\bar{V}_{el}[C - C^+]. \tag{14}$$

Premultiplying (13) by $\exp(-S)$, we have

$$[\bar{\bar{H}}_M + \bar{\bar{H}}_{ph} + \bar{\bar{H}}_{int}] \phi_{HF}\chi_{ph} = E' \phi_{HF}\chi_{ph}, \tag{15}$$

where the double-bar quantities $\bar{\bar{X}}$ are the corresponding transformed operators $\bar{\bar{X}}$

induced by two successive similarity transformations:

$$\bar{X} = \exp(-S)\exp(-T)X\exp(T)\exp(S). \tag{16}$$

In the linear response theory, the expansions of all the operators $\bar{\bar{X}}$ are truncated after the terms which are linear in photon creation/destruction operators. Thus we have

$$\bar{H}_M \simeq \bar{H}_M + [\bar{H}_M, S], \tag{17}$$

$$\bar{H}_{\text{ph}} \simeq H_{\text{ph}} + [H_{\text{ph}}, S], \tag{18}$$

$$\bar{H}_{\text{int}} \simeq \bar{H}_{\text{int}}. \tag{19}$$

Projecting (15) on the states $\phi_l^* \chi_{\text{ph}}^{\mp}$ where ϕ_l^* are the states reached through V_{el}, and $\chi_{\text{ph}}^{\mp}$ are photon states with photon numbers $N - 1/N + 1$, we get

$$\langle \phi_l^* \chi_{\text{ph}}^{\mp} | [\bar{H}_M, S] + [H_{\text{ph}}, S] + \bar{H}_{\text{int}} | \phi_{\text{HF}} \chi_{\text{ph}} \rangle = 0. \tag{20}$$

Utilising the relations

$$C\chi_{\text{ph}} = (n_h)^{1/2} \chi_{\text{ph}}^{-} \tag{21a}$$

$$C^+ \chi_{\text{ph}} = (n_h + 1)^{\frac{1}{2}} \chi_{\text{ph}}^{+} \quad, \tag{21b}$$

we easily find that equation (20) is decoupled with respect to S^- and S^+ in the sense that for χ_{ph}^{-} only S^+ contributes while for χ_{ph}^{+} only S^- contributes. Thus with χ_{ph}^{-}, we have

$$\langle \phi_l^* | [\bar{H}_M, S_{\text{el}}] | \phi_{\text{HF}} \rangle - w \langle \phi_l^* | S_{\text{el}} | \phi_{\text{HF}} \rangle + \langle \phi_l^* | \bar{V}_{\text{el}} | \phi_{\text{HF}} \rangle = 0. \tag{22}$$

If we now expand S_{el} in terms of various np-nh excitations for EE, or $np - (n \pm 1)h$ for IP/EA, then we may generally write

$$S_{\text{el}} = \sum_l S_l \varphi_l^+, \tag{23}$$

where φ_l^+ are the appropriate products of np-nh operators and $S_l = S_l(w)$ are the associated cluster amplitudes. We may thus write

$$S_{\text{el}} \phi_{\text{HF}} = \sum_l S_l \phi_l^*. \tag{24}$$

Equation (22) then takes the form

$$\sum_m A_{lm} S_m(w) - w S_l(w) + V_l = 0, \tag{25}$$

where the matrix-elements A_{lm}, and V_l are defined as

$$A_{lm} = \langle \phi_l^* | [\bar{H}_M, \varphi_m^+] | \phi_{\text{HF}} \rangle, \tag{26}$$

$$V_l = \langle \phi_l^* | \bar{V}_{\text{el}} | \phi_{\text{HF}} \rangle. \tag{27}$$

Equation (25) may be written more compactly as

$$AS(w) - wS(w) + V = 0, \tag{28}$$

whence

$$S(w) = (w \cdot I - A)^{-1} V. \tag{29}$$

The part of the second order energy $\Delta E^{(2)}$ proportional to photon number n_{ph} may be written as

$$\Delta E^{(2)} = \langle \phi_{HF} \chi_{ph} | [\bar{H}_{int}, S] | \phi_{HF} \chi_{ph} \rangle, \tag{30}$$

from which it follows that $G(V_{el}, w)$ is of the form

$$G(V_{el}, w) = \mathbf{Y}(w \cdot \mathbf{1} - A)^{-1} \mathbf{V}, \tag{31}$$

from (29). Clearly, $G(V_{el}, w)$ has poles whenever the matrix $(w\mathbf{1} - A)^{-1}$ is singular, or equivalently wherever A satisfies an eigenvalue equation of the form

$$A\mathbf{X} = w\mathbf{X}, \tag{32}$$

with w as the elementary excitations (EE, IP or EA).

Equation (32) is the ultimate working equation of the cc-based linear response theory, and it was obtained in this form for EE calculations by Mukherjee and others (Mukherjee and Mukherjee 1979). For an explicit construction of the matrix A, we shall have to specify S_{el}, the nature of truncation of $\bar{H}_M$ as a multicommutator series in T and the truncation in the sum in (24). This we shall illustrate for specific cases in §§3.1 and 3.2.

2.2   *Emergence of a renormalised TDA*

A very useful new insight into the structure of (32) is obtained if we trace back its genesis through (28) to (22). Basically the energy differences are obtained as solutions of the homogeneous part of (22):

$$\langle \phi_l^* | [\bar{H}_M, S_{el}] | \phi_{HF} \rangle = w \langle \phi_l^* | S_{el} | \phi_{HF} \rangle, \tag{33}$$

with w as the relevant difference energies. This equation immediately suggests that there is an underlying commutator form of the EOM-like structure of the working equation in the linear response theory. We may naturally wonder whether we may arrive at (33) starting from a Schrödinger equation for the electronic system only. In the following we show that this is indeed the case.

Assuming that S_{el} converts the ground state ψ_{gr} to the appropriate excited or ionised states, the EOM for energy differences may be written as

$$[H_M, S_{el}] \psi_{gr} = w S_{el} \psi_{gr}. \tag{34}$$

If we now write S_{el} in terms of various *np-mh* excitation operators φ_l^+ only as has been done in (23), then the form of S_{el} corresponds to what one assumes in a generalised TDA approach (Dunning and McKoy 1967). If we now use the cc-ansatz for the ground state ψ_{gr}, then premultiplying (34) by $\exp(-T)$ and utilising (10), we have

$$[\bar{H}_M, S_{el}] \phi_{HF} = w S_{el} \phi_{HF}, \tag{35}$$

from which (33) easily follows by projecting on to the excited/ionised states ϕ_l^* reached by the components S_l of S_{el}. The emergence of (35) from EOM indicates that the ground state correlation has been incorporated into $\bar{H}_M$, so that (35) or equivalently (32) is indeed a renormalised version of *np-mh* TDA for EE, IP or EA. Equation (35) has a simpler structure if viewed as generated from (34) and it was derived in this alternative fashion by Adnan *et al* (1981) and Ghosh *et al* (1983).

3. Truncation schemes in energy difference calculation

3.1 EE *calculation*

For EE calculations, V_{el} must be an electron number conserving operator and consequently S_{el} would in general be a sum of various $np\text{-}nh$ excitation operators:

$$S_{el} = \sum_n S_n, \tag{36a}$$

with

$$S_n = \frac{1}{n!^2} \sum_{\substack{P,Q,\dots \notin \phi_{HF} \\ A,B,\dots \in \phi_{HF}}} \langle PQ \dots | S_n | AB \dots \rangle_a a_P^+ a_Q^+ \dots a_B a_A. \tag{36b}$$

This form for S_{el} for EE calculations was suggested by Mukherjee and Mukherjee 1979 who also discussed the useful approximations for singlet EE calculations. Following Cizek (1966, 1969), they truncated $\bar{H}_M$ after the quadratic power of T, and approximated T by only the 'pair correlation' cluster operator T_2. The resulting expressions for $\bar{H}_M$ have been extensively discussed by Mukherjee and coworkers who also introduced suitable diagrammatics to arrive at the expressions in a convenient manner. They chose to truncate S_{el} after the two-body term and took the operator S_{el} to be a spin-scalar type for singlet EE calculations. For triplet EE calculations, S_{el} must be chosen as a spin-vector type of operator and the resulting spin-adaptation procedures have been introduced by Ghosh *et al* (1982). Confining S_{el} to atmost two-body terms indicates that the excited states generated receive contributions from $T_2 \phi_{HF}$ and $S_2 \phi_{HF}$, showing the effect of altered correlations as a result of excitation, as also triply excited configurations simulated by a product operator of the form $T_2 S_1 \phi_{HF}$. The excited states are thus expected to be of high quality.

3.2 IP/EA *calculations*

For IP/EA calculations, V_{el} must be an electron-destroying (creating) operator, and consequently S_{el} a destroying (creating) operator:

$$S_{el}^{IP/EA} = \sum_{n=1,3,\dots} S_n^{IP/EA}, \tag{37}$$

with

$$S_n^{IP} = \frac{1}{(n-1)!} \frac{1}{n!} \sum_{\substack{P_1 P_2 \dots, P_{n-1} \notin \phi_{HF} \\ A_1, A_2, \dots, A_n \in \phi_{HF}}} \langle P_1 P_2 \cdot P_{n-1} \phi | S_n^{IP} | A_1 A_2 \dots A_n \rangle_a$$

$$[a_{P_1}^+ a_{P_2}^+ \dots a_{A_2} a_{A_1}] \tag{38a}$$

$$S_n^{EA} = \frac{1}{(n-1)!} \frac{1}{n!} \sum_{\substack{P_1, P_2, \dots P_n \notin \phi_{HF} \\ A_1, A_2, \dots A_{n-1} \in \phi_{HF}}} \langle P_1 P_2 \dots P_n | S_n^{EA} | A_1 A_2 \dots A_{n-1} \phi \rangle_a$$

$$[a_{P_1}^+ a_{P_2}^+ \dots a_{A_2} a_{A_1}] \tag{38b}$$

with ϕ symbolising a 'no-label' orbital. Ghosh *et al* (1982) gave a useful calculational scheme for IP where n is truncated after three. It is clear that S_{el}^{IP} and S_{el}^{EA} operators are related to each other through $(h\text{-}p)$ interchange, so that equations for EA can be easily generated from those of IP through $h\text{-}p$ interchanges. The ionised states for IP under the

approximations of Ghosh *et al* (1982) contain $1h$ and $2h$-$1p$ components generated by $S_1\phi_{HF}$ and $S_3\phi_{HF}$ as also $3h$-$2p$ states from the product excitations of the type $S_1 T_2 \phi_{HF}$ -. They are thus again expected to be of high quality as in EE calculations.

4. A perturbative analysis of the CC-based linear response model

In this section, we shall look into the underlying perturbative structure of the linear response theory. As may be anticipated from the pre-eminent success of the CC theory for closed shells in summing up classes of Goldstone perturbative diagrams to all orders (Cizek 1966; Kummel *et al* 1978), a similar situation is expected to prevail in the CC-based linear response theory as well. We shall presently find that such is indeed the case. The analysis will also put in proper perspective this approach *vis-a-vis* other perturbative approaches when looked at from the perturbation theoretic point of view.

Any perturbative development for EE and IP/EA calculations utilising the GF or MBPT requires specification of the appropriate unperturbed functions. The most common choice for such functions for EE calculations corresponding to the low-lying excited states are the $1p$-$1h$ determinants, and for IP/EA calculations the $1h$ and/or $1p$ states for GF. Both $1h$ and $1p$ determinants are needed if a one electron GF is used, and IP and EA are obtained in a coupled manner. For MBPT, only the $1h$ or $(1p)$ functions are needed for IP(EA) calculations. Naturally for an appropriate comparison the linear response formalism must be appropriately tailored so that the corresponding starting functions are the same as in GF or MBPT calculations.

For IP(EA) calculations, the CC-based theory starts out with $1h(1p)$ functions, and an immediate kinship with MBPT may be discerned here. Again, if one formulates a GF theory involving only one-hole functions or one-particle functions rather than the complete one electron GF then its poles which give either IP or EA only, *i.e.* IP and EA calculations may be decoupled by working with restricted kinds of GFs. Specifically, one may define hole GFs as

$$G_{AB}(T-T') = i \langle \psi_{gr} | T[a_A(T)a_B^+(T')] | \psi_{gr} \rangle \ \forall \ A, B \in \phi_{HF}, \tag{39}$$

and likewise a corresponding particle GF, whose poles provide us with IP or EA. As we shall see that the CC-based linear response model has a *hybrid structure* incorporating features of both open shell Rayleigh-Schrödinger MBPT of the Brandow type (Brandow 1967) and also of one-hole/one-particle GF. Similarly, we shall indicate that a similar situation holds true for EE calculations as well.

To facilitate our analysis, a diagrammatic analysis of the working equations would be useful. We shall show by block diagrams the structure of the working equations (32) for IP/EA and EE. As an example, figures 1(a) and 1(b) depict the equations for IP calculations. The corresponding equations for EA may be obtained by hole-particle reversal. Similarly, figures 2(a) and 2(b) show the corresponding block-structure for EE calculations. The matrices corresponding to these block-structures are also indicated in the figures. We shall now analyse the perturbative structure of these equations taking IP/EA and EE in turn.

4.1 IP/EA *calculations*

We shall specifically discuss the IP calculations only; for, the EA theory may be easily formulated from the structure for the IP theory by a simple hole-particle reversal. As $1h$
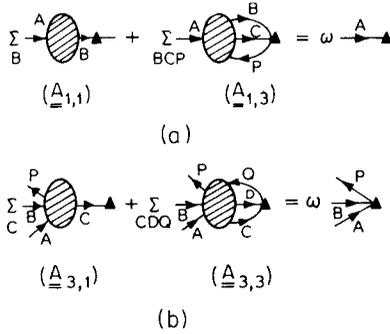
($\underline{\underline{A}}_{1,1}$)   ($\underline{\underline{A}}_{1,3}$)

(a)

($\underline{\underline{A}}_{3,1}$)   ($\underline{\underline{A}}_{3,3}$)

(b)

Figure 1. (a) and (b) depict the diagrammatics of the IP equations for shapes having one and three open lines respectively. The shaded blobs stand for the $\bar{H}_M$-vertices and lines on their left and right connect the ket and bra sides of equation (32). The filled triangles depict the S_{el}-vertices.
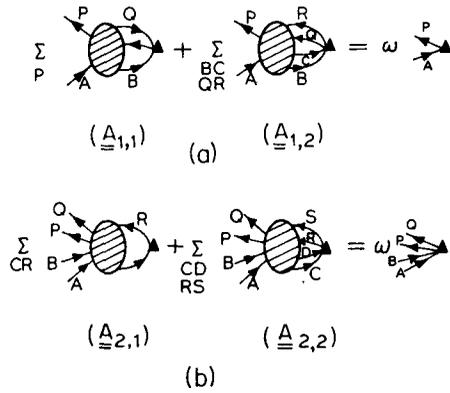

($\underline{\underline{A}}_{1,1}$)   ($\underline{\underline{A}}_{1,2}$)

(a)

($\underline{\underline{A}}_{2,1}$)   ($\underline{\underline{A}}_{2,2}$)

(b)

Figure 2. (a) and (b) depict the diagrammatics of the EE working equations from equation (32).

states are the starting functions for both hole GF and MBPT calculations, we shall have to 'fold' the effect of the S_3 components of figures 1(a) and 1(b) by partitioning technique to have an appropriate simplitude for comparison. Folding the effect of the S_3 manifold from figures 1(b) through figure (1a), we have a pseudo-eigenvalue equation of the form

$$A_{1,1}S_1 + A_{1,3}(w \cdot I - A_{3,3})^{-1}A_{3,1}S_1 = wS_1, \qquad (40)$$

with a corresponding block-structure as shown in figure 3. This looks like a Dyson equation for the hole GF because of the appearance of a w-dependent term $(w \cdot I - A_{3,3})^{-1}$. (Alternatively, (40) may be viewed as Bloch Horowitz pseudo-eigenvalue equation (Bloch and Horowitz 1958) as far as a low order perturbative analysis is concerned).

We now invoke the now well-established perturbative analysis of the closed-shell CC theory. The crux of such an analysis is that a T-diagram having a specific shape (characterised by the number of incoming and outgoing hole-particle lines) is a sum over all the Goldstone-diagrams of the same-shape. Using the concept of the generalised time ordering (GTO) (Brandow 1967, 1970), one may show (Kummel *et al* 1978), that the sets of diagrams related by GTO (*i.e.* having movable 'legs' which can be variously placed with respect to each other) may be compactly represented by a factorable diagram where a global energy denominator between the vertices is replaced in the diagram by products of local energy denominators corresponding to each 'leg'. Figure 4 shows one such factorisation for a T_2 diagram in a closed-shell CC theory. Recalling that the matrices $A_{1,1}$, $A_{1,3}$ and $A_{3,1}$ all involve the transformed Hamiltonian $\bar{H}_M$ involving a multicommutator expansion in powers of T, the associated diagrams will also involve such factorised diagrams. Specifically as the T operators can only connect an H_M vertex only from the right, a diagrammatic representation of any $\bar{H}_M$ operator having a specific shape will be represented by a sum of factorised Goldstone diagrams having the same topological structure of the $\bar{H}_M$ diagram whose factorised components will look as *downward going trees only*. As an example, the free structure of a two-body $\bar{H}_M$ vertex is depicted in figure 5.

7

Figure 3. The 'folded' form of equation (40) for IP calculations. The rectangular box cutting the lines joining the two blobs in the figure depicts the matrix-inverse $(w \cdot I - A_{3,3})^{-1}$.
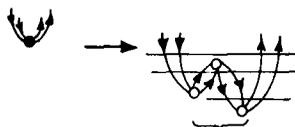

Figure 4. Generation of Goldstone diagrams admitting of GTO from the Goldstone expansion of a T_2-vertex. The lines are drawn vertically to effect an easier comparison with perturbation theory. The horizontal bar cutting the lines stands for an appropriate Goldstone energy denominator. The two-V-vertices covered by the brace are the two 'legs' admitting of GTO.
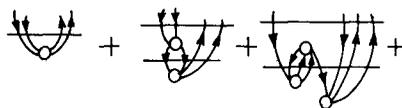
Figure 5. The generation of downward growing trees of increasing complexity from the Goldstone expansion of the T_2 vertex of figure 4.

For a perturbative analysis, we expand the series for T in each of the A matrices in terms of factorised Goldstone diagrams, and also expand out $(w \cdot I - A_{3,3})^{-1}$ in terms of $(w \cdot I - \Delta E^0)^{-1}$ involving orbital energies only and the rest ΔV $(= A_{3,3} - \Delta E^0)$ involving the two-body vertex V of Hamiltonian (equation (2)) and also the multicommutator terms involving T. Using the T_2-approximation scheme discussed in §2, the diagrams that are generated upto third order are shown in figure 6. Let us note that the matrix $A_{1,1}$ in (40) generates only the correlation terms (figures 6(a) to 6(d)) where the entry point of the hole line is below its exit point, while the w-dependent term in (40) generates the relaxation terms only. The important point to notice here is that *the correlation terms do not have any w-dependence at all*, because they are all generated by the composite H_M-T vertices which have only Rayleigh-Schrödinger energy denominators stemming from the Goldstone expansion. This part thus has the underlying perturbative structure resembling a Brandow open-shell MBPT (Brandow 1967). The energy denominators are local whenever there are components in a diagram admitting of a GTO. Moreover the denominators do not involve the labels of the lines emanating on the top of the diagram if they are not connected to the T vertices, just as is expected of a nonhermitian (unsymmetric) open shell theory as Brandow's. *The relaxations terms* (figures 6(d) to 6(g)) on the other hand, *are w-dependent* as they come out of the folding. These terms are thus analogous to the w-dependent self-energy terms of a hole GF or a Bloch-Horowitz theory. We have used single bars between successive vertices where they stand for Goldstone and double bars when they indicate w-dependent GF or Bloch-Horowitz denominators. The hybrid structure of the linear response theory is thus immediately apparent.

The above analysis raises an interesting formal problem. Viewed from a GF or Bloch-Horowitz theory, the w-independence of the correlation terms implies that the w-dependence has been expanded out, much in the same spirit as is done, for example, in Brandow's conversion of the Bloch-Horowitz series to the Rayleigh-Schrödinger series. The successive correction terms arising out of such an expansion must, therefore, have
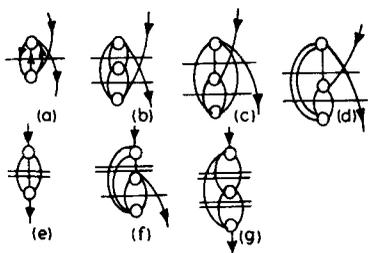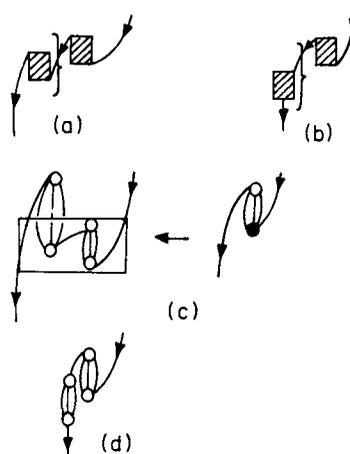
Figure 7. (a) and (b) are the 'correction terms' which should appear in (40) stemming from the conversion of the *w*-dependent terms of the correlation to *w*-independent form. (c) and (d) show two specific diagrams that are generated from the terms considered in the text. The part of the diagram (c) in the box is the part originating from the nonlinear CC equation for T_2. The parent diagram is shown on the right in (c).

Figure 6. All the diagrams for IP upto third order generated by the expansion of (40) as powers of *V*. The double bars indicate Bloch-Horowitz type of *w* dependent denominators. Note that the denominator of the bottom part of figure 6(f) is Goldstone type because it originates as a Goldstone tree from a T_2-vertex.

to be explicitly incorporated in a potentially exact theory and we show that such terms are indeed present in the linear response theory. These terms will look like insertions on basic *w*-independent correlation diagrams.

Upto the fourth order of perturbation theory we have to look for two kinds of insertions as shown in figures 7(a) and (b). Clearly, an appropriate two-body part of $\bar{H}_M$ calculated from the complete nonlinear CC theory for closed shell will automatically incorporate the component figure 7(a), as is shown explicitly in figure 7(c). The other component is not explicitly present. But one may show that if the *w*-term in $A_{1,3} (w \cdot \mathbf{1} - \Delta E^0)^{-1} A_{3,1}$ is expanded also as

$$w_\alpha \simeq \varepsilon_\alpha + \Delta f_\alpha, \tag{41}$$

corresponding to a root w_α lying closest to the unperturbed orbital energy ε_α, then the first correction generates figure 7(b). This is depicted in figure 7(d). Thus both terms are present, either explicitly or implicitly, in the linear response theory.

In the T_2-approximation, the theory is correct upto second order of perturbation theory and contains important classes of third order diagrams. The remaining third order diagrams are not all generated in this approximation, although most of them tend to cancel each other due to mutual 'antigraph' relation (Cederbaum and Domcke 1977). The pilot calculations (Ghosh *et al* 1981; Ghosh *et al* to be published) indicate that the performance of the CC-based linear response model is better than the hole GF method- indicating that the missing terms are indeed unimportant, and also that the infinite summations involving Goldstone downward trees are much more important in predicting difference energies like IP.

We conclude this subsection by indicating another peculiar formal feature of the linear response theory. Suppose we include the T_1-operators as well in our closed-shell CC calculations (this probably is energetically unimportant, but useful for bringing out the aspect of the problem we want to discuss presently). A typical diagram in the correlation term coming from T_1 may be depicted as in figure 8(a), which will contribute a third order perturbation diagram on Goldstone expansion as shown in figure 8(b). A straightforward exhaustive analysis reveals that the conjugate 'mirror image' diagram, as shown in figure 8(c) is totally absent in the theory so long as S_{el} is confined to S_1 and S_3 only. By expanding the operator space to include S_5 operators as well, as shown in figure 8(d), one may recover the conjugate diagram, as shown in figure 8(c). Thus there is an inherent asymmetry in the generation of terms upto a given order of perturbation theory in the linear response model. This stems largely from the feature that the GTO in the Goldstone expansion of T acts only downward in a CC theory.

4.2   EE calculations

A perturbative analysis involving upto the third order diagrams is extremely unwieldy because it will generate a plethora of diagrams. However, the basic features of the theory may be visualised if the effect of the S_2 block in figure 2(b) is folded in figure 2(a). A Goldstone expansion of the resulting matrices $A_{1,1}, A_{1,2}$ and $A_{2,1}$ will then yield the perturbative expansion of EE. The resultant diagrams upto second order are shown in figure 9. These are the only diagrams upto second order. For relevant comparison, either a Bloch-Horowitz theory involving $1p$-$1h$ starting functions or a p-h GF has to be invoked. For the latter, the de-excitation manifold has to be folded in. The third order and higher order diagrams obtained by factorised Goldstone expansion involving GTO are again more important than an order by order expansion, as is evidenced by the numerical performance of the method (Adnan *et al* 1980, 1982). The hybrid nature of the theory in treating the correlation and relaxation terms are again apparent, and the corresponding correction terms may also be discerned at higher orders (Ghosh *et al* to be published).
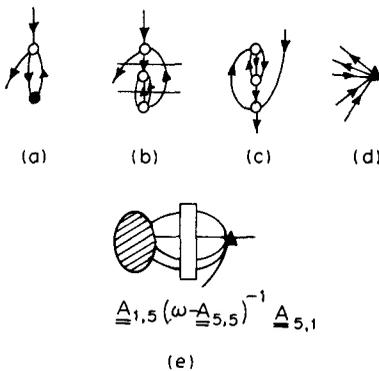

$$\underline{A}_{1,5}\left(\omega-\underline{A}_{5,5}\right)^{-1}\underline{A}_{5,1}$$

(e)

Figure 8. (a) A typical T_1 diagram contributing to (40) for IP. A third order diagram obtained from it is shown in (b). The conjugate diagram to (b) is shown in (c). (d) shows an S_5 vertex. (e) shows the block structure of the diagrams obtained by folding the effect of S_5 generating (e).
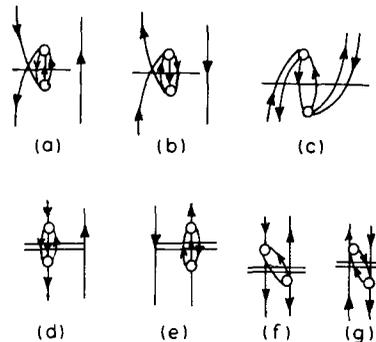

Figure 9. All the perturbation diagrams at the second order obtained from (32) for EE. (a) to (c) are the correlation terms and (d) to (g) are the relaxation terms.

5. Relationship with other cc-based theories for difference energy

In this section, we shall briefly indicate the relation of the formalism reviewed above with other cc-based approaches for treating difference energies. Elaboration of the technical difference is avoided for the sake of brevity and only the basic structural comparisons are outlined.

Monkhorst (1977) has developed a time-dependent version of the cc-theory for calculating dynamical response of a system under an external perturbation having a harmonic time variation. The evolution of the system is followed by invoking the adiabatic hypothesis. As is often acknowledged, a time-dependent evolution treated in the framework of perturbation theory involves the so-called 'secular' or divergent terms, and this needs an explicit and careful consideration of the 'phase' of the perturbed function (Langhoff *et al* 1972). Monkhorst thus had to introduce suitable phases in his perturbed wavefunction to get rid of these secular terms, which makes the development somewhat roundabout because one also needs the *ad hoc* introduction of damping factors corresponding to the adiabatic hypothesis. Monkhorst's approach and the time-independent approach discussed in this paper are like Fourier-transforms of each other as far as the basic structure is concerned—the advantages of a time-independent version being that the secular terms are naturally absent and that the relation of the theory with the renormalised TDA approach is much more transparent. Moreover, in a time-dependent approach, the identification of the excited/ionised functions as $S_{el} \exp(T)\phi_{HF}$ is not easy to visualise. The time-dependent version of the IP/EA calculations has not been developed so far to our knowledge.

Recently, Emrich (1981) has derived an EOM version for EE calculation in nuclear physics essentially along the lines of the derivation described in (34)–(35). Unfortunately Emrich missed the earlier expositions of the linear response theory (Mukherjee 1979; Mukherjee and Mukherjee 1979; Adnan *et al* 1982) and did not notice the equivalence of the linear response theory with a renormalised TDA.

Paldus *et al* (1978) developed a variational theory for difference energy calculations by starting from excited/ionised functions of the form $S_{el} \exp(T)\phi_{HF}$ similar to what is done in a linear response theory. Consequently they start from expectation value like quantities

$$\Delta E = \frac{\langle \psi_{gr}|S_{el}^+ H_M S_{el}|\psi_{gr}\rangle}{\langle \psi_{gr}|S_{el}^+ S_{el}|\psi_{gr}\rangle} - \frac{\langle \psi_{gr}|H_M|\psi_{gr}\rangle}{\langle \psi_{gr}|\psi_{gr}\rangle} \tag{42}$$

and show that the second term cancels with a component of the first term leading to

$$\Delta E = \frac{\langle \phi_{HF}|\exp(T^+)S_{el}^+ H_M S_{el} \exp(T)|\phi_{HF}\rangle_L}{\langle \phi_{HF}|\exp(T^+)S_{el}^+ S_{el} \exp(T)|\phi_{HF}\rangle_L}, \tag{43}$$

where the suffix L indicates that all the connected diagram expression for ΔE have to be taken. ΔE is thus a ratio of two polynomials involving T/T^+ unlike a simple polynomial as in a cc-based linear response theory. Variation of ΔE with respect to the cluster amplitudes of S_{el} in (43) leads to a Hermitian generalised eigenvalue problem of the Roothaan type. The linear response theory is related to Paldus approach but is nonvariational and differs from the latter in the following two important aspects that (a) the $\bar{H}_M$ in linear response theory is a terminating series while the linked quantities in (43) are nonterminating, and (b) linear response working equations are nonhermitian eigenvalue equations, while Paldus' method involves a generalised eigenvalue equation.

We believe that the linear response theory provides a viable and potentially compact method for direct calculation of energy differences like EE, IP and EA. The pilot calculations on prototypal model systems have produced quite encouraging results. The real potentiality of the approach will be revealed in more realistic applications of the theory in the *ab initio* framework, and such studies are currently being undertaken in our laboratory.

Acknowledgements

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