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On the hierarchy equations of the wave-operator for open-shell systems

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Abstract. Starting with the open-shell analogue of the Gell Mann-Low theorem of many-body perturbation theory, a non-perturbative linear operator equation is derived for the linked part of the wave-operator W for open-shell systems. It is shown that, for a proper treatment of the linked nature of the wave-operator, a separation into its connected and disconnected components has to be made, and this leads to a hierarchy of equations for the various connected components. It is proved that the set of equations can be cast into a form equivalent to the non-perturbative equations of the wave-operator recently derived by Mukherjee and others in a coupled-cluster or exp(T) type formalism if a consistent use is made of a 'core-valence separability' condition introduced earlier. A comparison of the coupled-cluster representation of W with the perturbative representation reveals that various alternative forms of W in the coupled-cluster representation are possible and these reflect alternative ways of realising the core-valence expansion of the wave-operator. In particular it is emphasised how the use of Mandelstam block-ordering simplifies the coupled-cluster theories to a considerable extent and a comparison is made with coupled-cluster methods for open-shells put forward very recently by Ey and Lindgren. Finally, it is shown how difference energies of interest may be derived in a compact manner using the Mandelstam block-ordering of the wave-operator.

Keywords. Many-body theory; non-perturbative open-shell theory; atoms; molecules.

1. Introduction

The present paper—the first in a series—is mainly concerned with the relation between non-perturbative and perturbative treatments of the linked part of the wave-operator W in many-electron open-shell systems. Unlike that in the closed-shell context, the relation between the perturbative and non-perturbative theories in open-shells has not been completely explored (see, e.g., the comments by Brandow 1975, 1977) and the present work may be taken to serve as a preliminary study in that direction. The paper is organised as follows. In § 2, we develop a linear operator equation for the linked part of the operator W starting with the open-shell analogue of the Gell Mann-Low theorem of the open-shell perturbative theories, and show that, for a proper treatment of the linked-nature of the terms, a separation into its connected and disconnected components have to be made. The operator equation is non-perturbative, but is derived in a perturbative manner. In § 3, we show that using the linked cluster theorem derived in connection with the non-perturbative open-shell theory (Mukherjee *et al* 1975 a,b) and a generalisation of the concept of core-valence separation (Brandow 1967; Mukherjee *et al* 1977a; Mukhopadhyay *et al*

1978; Ey 1978), we may convert the linear operator equation for W into hierarchy of equations for the connected parts of W and show that this set is equivalent to the non-perturbative equations recently derived by us (Mukherjee *et al* 1975 a,b). In § 4, we compare the algebraic structure of the linked part of W with the corresponding open-shell perturbative expression and show that various alternative avenues exist for realising the wave-operator in the non-perturbative theory. It is shown that these various alternatives correspond to different ways of expressing the core-valence interaction in the non-perturbative expansion of the wave-function for the system. In particular, the relative efficacies of two alternative expansions—the Baker-Hausdorff multicommutator expansion and the other a Mandelstam block-ordered operator product representation—are compared, and the relation between the present work and the very recent theories of Ey and Lindgren (Ey 1978; Lindgren; to be published) is investigated. We came to know about these studies after the first draft of our paper was completed. In § 5 we shall outline a theory dealing with difference energies of interest—like transition energy and ionisation potential—using the Mandelstam-ordered product representation of the wave-operator.

2. The open-shell analogue of the Gell Mann-Low theorem and derivation of an operator equation in W

We start with the hamiltonian H, and partition it as follows:

$$H = H_0 + V \tag{1}$$

with $$H_0 \psi_i^0 = E_i^0 \psi_i^0 \tag{2}$$

The functions ψ_i^0 are either exactly degenerate or nearly so, and may be said to span a model space characterised by the model-space projector P:

$$P = \sum_i |\psi_i^0\rangle \langle\psi_i^0| . \tag{3}$$

In what follows, the formal manipulations are considerably simplified if we assume an exact degeneracy of the model-space functions ψ_i^0, and put all the unperturbed energies simply as E^0. Removal of degeneracy may be effected later by using the technique advocated by Brandow (1967).

We classify all the spin-orbitals into core (hole), valence and particle orbitals in the usual manner (Mukherjee *et al* 1975 a,b, 1977 a,b,c), and designate them as $(\alpha, \beta, \ldots)$, $(\bar{p}, \bar{q}, \ldots)$, and $(p, q, \ldots)$ respectively. The exact eigenfunctions ψ_K of H, corresponding to the exact energies E^K, are then expressed as the action of the wave-operator W (Moller 1945) on a linear combination of the model space functions; W induces excitations from core to valence/particle and valence-to-particle levels and thus superposes ' excited ' functions on to the model-space components ψ_i^0.

In recent years, several studies have appeared where a compact expression of W was derived for open-shells using many-body perturbation theories (Brandow 1967; Sanders 1969; Oberlechner *et al* 1970; Johnson and Baranger 1971; Kuo *et al* 1971;

Kvasnicka 1974; Lindgren 1974). Although the approach to the problem and the emphasis given to various aspects differ rather considerably from one author to the other, all derive a form of W containing linked terms only, and all show that a linked cluster theorem is valid for open-shell systems as well. The relationship between these theories is far from trivial, and this has been explored in recent studies by Klein (1974) and Brandow (1975). For our purpose, it is useful to start with the Gell Mann-Low factorisation theorem for the open-shell case which leads to an operator equation for the linked part of the wave-operator. In so far as we shall exploit only the algebraic factorisation implied by the open-shell Gell Mann-Low theorem, several alternative perturbative approaches deriving the theorem in a time-dependent formalism using different time-bases (Morita 1963; Kuo *et al* 1971; Oberlechner *et al* 1970) would imply for us essentially the same thing. The pertinent point for us is the following factorisation,

$$W\psi_i^0 = \sum_j [W_{\mathrm{FL}} \mid \psi_j^0\rangle] \langle\psi_j \mid W \mid \psi_i^0\rangle \tag{4}$$

where W_{FL} has no singular energy denominators. W_{FL} is a collection of all operators which in diagrammatic parlance consists of all the excitations from core-to-valence/particle, valence-to-particle and mixed core-valence-to-particle/valence levels, excluding the ones containing vacuum fluctuations (i.e. pure core-correlation diagrams) and also the diagrams with a disconnected pure valence-valence scattering components. Furthermore, if any two vertices of the interaction V are connected by valence-lines only in such a way that a vanishing energy denominator is implied then the lines would appear as ' folded ' through suitable juggling of the interaction vertices (Brandow 1967; Oberlechner *et al* 1970; Kuo *et al* 1971). (There are other subtle features which we shall discuss later). W_{FL} is thus an acronym for ' folded linked ' expansion of W. Let us emphasise here that various terms of W_{FL} may be disconnected, and thus the term ' linked ' merely qualifies that diagrams do not contain vacuum fluctuations and valence-valence scattering components.

It may be shown (Brandow 1967; Kuo *et al* 1971; Oberlechner *et al* 1970) that the exact energies E^K may be obtained from solution of a model-space secular equation

$$\sum_j \langle\psi_i^0 \mid HW_{\mathrm{FL}} \mid \psi_j^0\rangle\, b_{jk} = E^K b_{ik}. \tag{5}$$

The combining coefficients b_{ik} may be shown to be such that the functions ψ_K, defined through

$$\psi_K = \sum_i \psi_i^0\, b_{ik}, \tag{6}$$

have the significance that they are projections to the model space of the exact eigenfunctions of H having respective eigenvalues E^K. The quantity HW_{FL} would consist of all connected diagrams having various valence lines as the only ingoing and outgoing lines. A completely closed part of HW_{FL} would give the exact energy of

the core, and is constant for all the states. The rest is the valence energy and the core-valence interaction. We may call HW_{FL} as an effective hamiltonian H_{eff}.

Let us now try to convert W_{FL} into a series expansion in V, using the line of reasoning one follows to derive an algebraic-cum-diagrammatic representation of W for closed-shells (Goldstone 1957). Noting the fact that (1) various vertices of V in W_{FL} may in general be connected (excluding vacuum fluctuation and valence-valence scattering components) and (2) the vertices would be joined by folded lines when the ' stretched ' diagram would entail a vanishing energy denominator, we may write W_{FL} as

$$W_{\mathrm{FL}} = \sum_{n=0}^{\infty} \left[\left(\frac{QV}{E^0 - H_0} \right)^n \right]_{\mathrm{FL}} \tag{7}$$

where Q is defined through (3), and

$$\left[\left(\frac{QV}{E^0 - H_0} \right)^n \right]_{\mathrm{FL}}$$

is the nth order term in the expansion of W_{FL} with a rule of joining of the vertices as dictated by the properties (1) and (2) of W_{FL} noted above.

Now we shall show that by using a rather simple manipulation of (7), we may derive an operator equation in W_{FL}. Writing W_{FL} as

$$W_{\mathrm{FL}} = 1 + \sum_{p=1}^{\infty} W_{\mathrm{FL}}^{(p)} = 1 + \omega \tag{8}$$

where $W_{\mathrm{FL}}^{(p)}$ is the p-body part of W_{FL}, we have

$$\omega = \sum_{n=1}^{\infty} \left[\left(\frac{QV}{E^0 - H_0} \right)^n \right]_{\mathrm{FL}} \tag{9}$$

A typical term of ω would have the following characteristics: the diagrammatic structure would be such that it would have two kinds of blocks—one in which there are ingoing valence lines and the core lines, if any, appear only in a subdiagram connected with another having ingoing valence lines, and another kind of block having core-excitations only. This structure of ω would be useful later when we compare the perturbative and non-perturbative theories.

If we now dissect each term in ω diagrammatically in such a way that the lines joining the extreme left vertex V to the rest are severed, and call the rest as ω', then symbolically we may write

$$\left[\left(\frac{QV}{E^0 - H_0} \right) \omega' \right]_{\mathrm{FL}} = W. \tag{10}$$

The dissection procedure is really using Wick's theorem backwards—i.e. writing a normal product of operators with all possible contractions into a product of two disjoint terms. Let us note that the mode of joining $[QV/(E^0-H_0)]$ and w' in (10) must then follow the same restrictions in joining as are there in W_{FL}. From the mode of construction w' *must consist of linked terms only*, and it follows from (10) that

$$\omega = \frac{QV}{E^0-H_0} + \left\{\left(\frac{QV}{E^0-H_0}\right)\sum_{n=1}^{\infty}\left[\left(\frac{QV}{E^0-H_0}\right)^n\right]_{FL}\right\}_{FL} \tag{11a}$$

or,
$$\omega = \frac{QV}{E^0-H_0} + \left[\left(\frac{QV}{E^0-H_0}\right)\omega\right]_{FL} \tag{11b}$$

The equation for W_{FL} then takes the form

$$W_{FL} = 1 + \left[\left(\frac{QV}{E^0-H_0}\right)W_{FL}\right]. \tag{12}$$

Let us first observe that, although (12) is derived from a perturbative expansion of W_{FL}, the equation is basically non-perturbative as the infinite sum in V has been explicitly summed up in (12). One might thus imagine that (12) must in some way be related to non-perturbative theories which do not use the expansion (7). However this analysis is rather involved which may not be apparent from the rather deceptive simplicity of (12). The difficulty arises because we lump together in a $W_{FL}^{(p)}$ all the diagrams with p incoming and outgoing lines, and are not explicitly keeping track of whether the diagrams are all connected or disconnected. As a result, when we join the lines of V with W_{FL} in

$$\left[\left(\frac{QV}{E^0-H_0}\right)W_{FL}\right],$$

we would no longer be sure that we are not introducing vacuum fluctuations or valence-valence scattering diagrams. This is best illustrated in figure 1, where we join V with a $W_{FL}^{(4)}$ to get a two-body term. Now $W_{FL}^{(4)}$ consists of both connected and disconnected diagrams, and a blanket diagram as in figure 1a does not tell us whether it is really a linked term like that in figure 1b, or an unlinked term

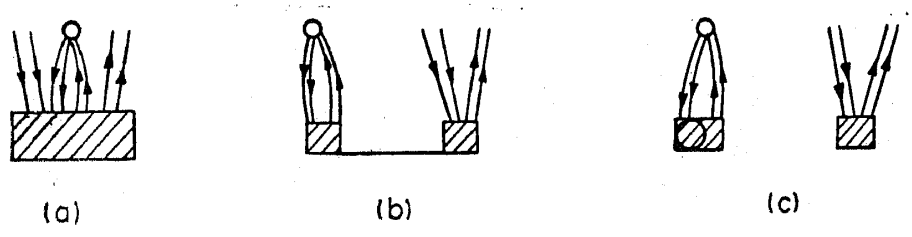

Figure 1. (a) A blanket four body term of W_{FL}. (b) A linked four body term of W_{FL}. (c) An unlinked counterpart.

as in figure 1c. Consequently, from the block structure alone, we cannot extract only the linked diagrams of the block shown in figure 1b, and put it as a component of $W_{FL}^{(2)}$. This clearly shows that for a proper treatment of (12) in general, one must separate the connected and disconnected parts of W_{FL} and thus keep away from introducing spurious diagrams in the process of joining $[QV/(E^0-H_0)$ with W_{FL}. An Ursell-Mayer type or coupled-cluster representation of W_{FL} would have the advantage of explicitly keeping track of the connected and disconnected components and we make use of this to convert (12) into a more tractable expression.

3. Coupled-cluster representation of W_{FL} and hierarchy equations for $W_{FL}^{(p)}$

Let us now exploit the observation that all the terms of W_{FL} contain connected and disconnected components inducing transitions from core-to-valence/particle, valence-to-particle and mixed core-valence-to-particle-valence transitions without vacuum fluctuations and valence-valence transitions. Clearly, a p-body operator $W_{FL}^{(p)}$ would be of the form

$$W_{FL}^{(p)} \sim \sum_i \prod_{pi} W_{FLC}^{(pi)} \tag{13}$$

where each $W_{FLC}^{(pi)}$ is the connected part of the pi-body operator of W_{FL}, and only those pi-body operators appear in the product which make it a real p-body operator. Thus, $W_{FL}^{(p)}$ would consist of $W_{FLC}^{(p)}$ and a product of lower rank $W_{FLC}^{(pi)}$'s. The Coester-Kummel ansatz of representing the wave-operator as an exponential (Coester 1958; Coester and Kummel 1960) satisfies the form (13) for each $W_{FL}^{(p)}$, and this we try to exploit.

Equation (5) implies that there is a constant energy ' shift ' in each E^K representing the exact energy of the ' core ' as it would have in the absence of ' valence ' electrons. If we call this E_c, then the diagrams for this would be the closed-shell type Goldstone diagrams and the calculation of E_c should be uncoupled from the calculation of the rest of the energy. We have shown that such a core-valence separation may be effected in a coupled-cluster non-perturbative theory if we write W_{FL} as (Mukherjee *et al* 1977a; Mukhopadhyay *et al* 1978)

$$W_{FL} = \exp(T_c)\exp(T_v) \tag{14}$$

T_C contains excitation operators inducing excitations from the core to all the valence and particle levels, quite regardless of whether some of the valence levels

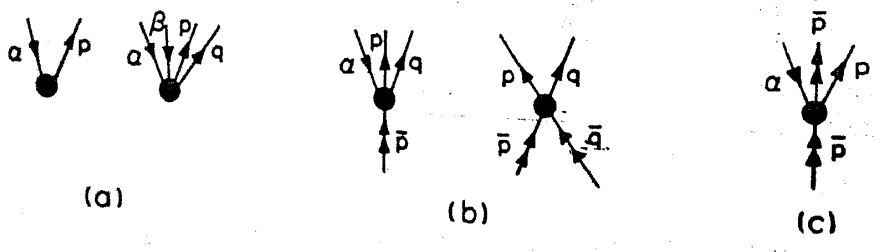

Figure 2. (a) T_c vertices. (b) T_v vertices. (c) T_v vertex with a passive $\bar{p} \to \bar{p}$ scattering.

would ultimately be occupied in the actual system. T_V contains excitations from the valence to particles and mixed excitations like hole-valence to particle/valence-particles. In order to incorporate the effect of core-relaxation effect, we have to include in T_V excitation from holes to valence/particle in the presence of 'passive' valence levels present as spectator (for details, see e.g. Mukherjee *et al* 1977a, 1977b; Mukhopadhyay *et al* 1978). The essential point for us is the observation that T_V always contains incoming valence-lines. A set of typical T_C and T_V vertices is shown in figure 2.

In what follows we shall somewhat change the notations of our earlier non-perturbative papers to make the ensuing derivations more transparent and the terminology more uniform. We define a 'connected term' (called a linked term in our earlier work) like $\{T^n\ HT^m\}_C$ as a collection of connected diagrams containing $nT(T_C$ or $T_V)$ vertices to the left of H, m T vertices to its right. The connection follows a rule that we start out from H and begin connecting the H vertex with T vertices on its immediate left or right and move out systematically connecting the next neighbours and proceed without skipping any intermediate T during the process. Using this notation, we would rewrite (12) in a compact fashion. Using the representation (14), we have

$$\exp(T_C)\exp(T_V) = 1 + \left[\left(\frac{QV}{E^0-H_0}\right)\exp(T_C)\exp(T_V)\right]_{FL} \tag{15}$$

Let us now analyse the quantity

$$\left[\left(\frac{QV}{E^0-H_0}\right)\exp(T_C)\exp(T_V)\right]_{FL}.$$

This consists of two kinds of blocks. The first contains products of the following two sets of diagrams. (a) A set containing all the connected diagrams containing the V-vertex and a string of T_C and T_V vertices such that the lines connecting the T vertex joined to the V-vertex are not folded. In the string, the T_C's appear next to V, and next there would be T_V's. By the very mode of construction the T_C-vertices cannot be mutually connected, but T_V-vertices can be so. This is somewhat awkward but this can be circumvented as discussed later. (b) Another set containing products of T_C and T_V operators with all possible contractions forming a cluster. We introduce diagrammatic representations as shown in figures

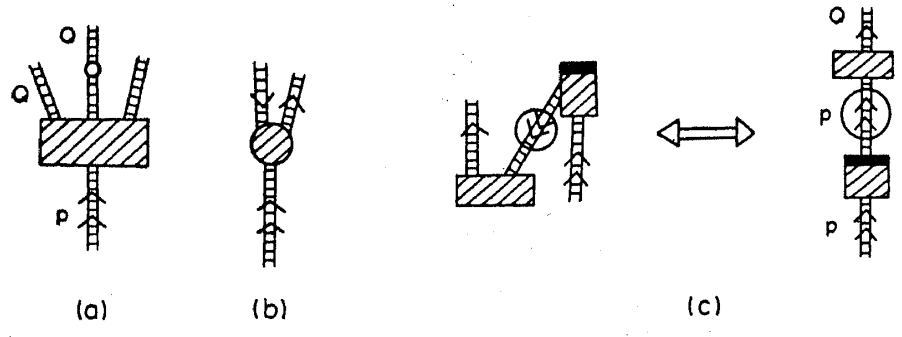

Figure 3. The various blocks appearing in (15). (see text for details)

3a and 3b for these two sets. The double arrowed double line entering the shaded block from below signifying the string of T_c and T_v vertices in figure 3a are a collection of valence lines. The vertex V and the block are joined by valence/particle/hole lines in all possible ways. (The block may even be empty with respect to T). The outgoing lines are not all valence lines. The ladder-like double lines, emanating from the top of the block and joining V and the block, are a collection of all possible allowed sets of valence/particle/hole lines. *In case the open-lines emanating from the block are absent, the lines joining V and the block cannot be all valence.* There may not be valence lines entering the block from the bottom at all. This occurs when there is no T_v vertex present in the string of T-vertices connected to V. The set (b) is designated by the diagram of figure 3b. They are the collection of connected as well as disconnected clusters of T_c and T_v operators. The set of ingoing and outgoing bunches of hole, valence and particle lines are shown as in the figure.

Now we consider the second kind of block. This consists again of two kinds of sets of diagrams. (a) A set containing all the connected diagrams having two strings of T-operators joined to V. One string contains the V and a set of T-operators which is connected to the other string containing T_v-operators only through 'folded' valence lines. The 'folded string' when 'stretched' is such that from the perturbation theoretic standpoint it would have implied a vanishing denominator. Let us note that it is not necessary that the vertex V itself has to be joined by the folded lines to the string of T_v-vertices; rather the whole connected cluster of V and T_c and T_v would be joined by folded lines emanating from anywhere in the cluster. A typical diagram where V itself does not have folded lines is shown in figure 4. This subtle feature is a reflection of what is called 'reduction of projected core excitation' (Brandow 1967). This indicates that the block would have the general structure as in figure 3c. The shaded block with blackened top indicates the connected cluster of V, T_c and T_v. The stretched form shows that in the perturbative interpretation a possible energy denominator in the position of the encircled part would have been vanishing. There would be an added (—1) sign factor arising from the folding operation (Brandow 1967). *The block which is folded cannot be empty*, though the other block may contain only the V vertex. Moreover, from the string structure it is clear that the folded block cannot contain T_c vertices. (b) The other set is of the same type as shown in figure 3b.

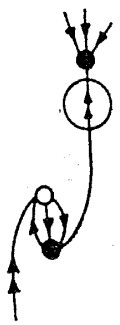

Figure 4. A term of figure 3(c) having a T_c and a T_v vertex joined by folded line (see text).

Using the above considerations, we can now write (15) as follows:

$$\exp(T_c)\exp(T_v) = 1 + QN\Big[\sum_{m,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\{VT_c^m T_v^n\}_c^{QP}\exp(T_c)\exp(T_v)\Big]$$

$$- QN\Big[\sum_{m,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\sum_{l=1}^{\infty}\frac{1}{e!}\{T_v^l\{VT_c^m T_v^n\}_c^{PP}\}_c^{QP}\exp(T_c)\exp(T_v)\Big], \tag{16}$$

where $\{\ \}_c^{QP}$ stands for connected terms implying $Q \leftarrow P$ scattering and $\{\ \}_c^{PP}$ implies valence-valence scattering. The sum over l in (16) starts from unity, showing that the block folded in 3(c) is not empty. The symbol $N[\ ]$ stands for normal ordering.

Now we use the concept of core-valence separation and introduce the generalisation thereof—to be henceforth called ' sub-system embedding condition '. This concept is inherently present in the many-body perturbative theories (Brandow 1967) but needs a careful treatment and explanation in the context of the non-perturbative theory. The concept implies that the total system energy for an N_v valence problem consists of contributions from various p-body parts of H_{eff}:

$$H_{eff} = \sum_{p=0}^{N_v} H_{eff}^{(p)} \tag{17}$$

with the added feature that the energies of any sub-system containing $N_{v'} < N_v$ valence electrons would merely come from the corresponding terms:

$$H_{eff} \text{ for } N_{v'} \text{ valence problem} \Longrightarrow \sum_{p=0}^{N_{v'}} H_{eff}^{(p)} \tag{18}$$

There is thus an ' anfbau principle ' for building up the N_v valence problem from the core problem by successive addition of valence electrons. The $p=0$ contribution signifies the total core energy. We shall now show that (16) may be simplified still further.

Premultiplying (16) with $Q(E^0-H_0)$, post multiplying by P, and using the commutativity of Q with H_0, we have

$$Q(E^0-H_0)\exp(T_c)\exp(T_v)P = QN\Big[\sum_{m,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\{VT_c^m T_v^n\}_c^{QP}$$

$$\times \exp(T_c)\exp(T_v)\Big]P - QN\Big[\sum_{m,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\sum_{l=1}^{\infty}\frac{1}{l!}$$

$$\times \{T_v^l\{VT_c^m T_v^n\}_c^{PP}\}_c^{QP}\exp(T_c)\exp(T_v)\Big]P. \tag{19}$$

Let us now note that the E^0 and H_0 terms of the left side of (19) may also be absorbed respectively with the second and first terms of the right side with proper

signs if we use Wick's theorem on each of the term of the left side and write $E^0 \exp(T_c) \exp(T_v) P$ as $\exp(T_c) \exp(T_v) H_0 P$:

$$0 = QN\Big[\sum_{m,n=0}^{\infty} \frac{1}{m!}\frac{1}{n!} \{H T_c^m T_v^n\}_c^{QP} \exp(T_c) \exp(T_v)\Big] P$$

$$- QN\Big[\sum_{m,n=0}^{\infty} \frac{1}{m!}\frac{1}{n!} \sum_{l=1}^{\infty} \frac{1}{l!} \{T_v^l \{H T_c^m T_v^n\}_c^{PP}\}_c^{QP}$$

$$\times \exp(T_c) \exp(T_v)\Big] P. \tag{20}$$

Let us now consider the core problem. The core-energy would be contributed by $H_{\text{eff}}^{(0)}$ only coming from the core part of W_{FL}. Hence only the terms containing T_c only would contribute non-trivially if we take in the Q space excited determinants obtained by lifting electrons from the core-to-valence particles and P space to be the core function only. Further $\exp(T_v)$ acting on the core gives zero, so that we have

$$0 = QN\Big[\sum_{m=0}^{\infty} \{H T_c^m\}_c^{QP} \exp(T_c)\Big] P, \tag{21}$$

for the core-problem. Now using the linked cluster theorem derived previously (Mukherjee *et al* 1975a, b) and noting the fact that T_c has no lines to the right, we find

$$QN\Big[\sum_{m=0}^{\infty} \frac{1}{m!} \{H T_c^m\}_c^{QP}\Big] P = 0. \tag{22}$$

This is thus an equation for the core containing connected diagrams only.

For the one-valence problem, we choose the one-valence functions in the P space and the set of $(N_c + 1)$-excited determinants for the Q space. The non-trivial contribution in (20) would then come from the 1-valence parts of

$$\{H T_c^m T_v^n\}_c^{QP}, \quad \{T_v^l \{H T_c^m T_v^n\}_c^{PP}\}_c^{QP},$$

and the corresponding zero-valence part. Using an additional superscript to indicate valence-rank of these operators, we have

$$QN\Big[\sum_{m,n=0}^{\infty} \frac{1}{m!}\frac{1}{n!} (\{H T_c^m T_v^n\}_c^{QP})^{(1)} \exp(T_c) \exp(T_v)\Big] P$$

$$- QN\Big[\sum_{m,n=0}^{\infty} \frac{1}{m!}\frac{1}{n!} \sum_{l=1}^{\infty} \frac{1}{l!} (\{T_v^l \{H T_c^m T_v^n\}_c^{PP}\}_c^{QP})^{(1)}$$

$$\times \exp(T_c) \exp(T_v)\Big] P$$

$$+ QN\Big[\sum_{m=0}^{\infty}\frac{1}{m!}\,(\{H\,T_c^m\}_c^{QP})^{(0)}\exp(T_c)\exp(T_v)\Big]P = 0. \tag{23}$$

Clearly the valence rank here refers to incoming valence lines in the operators of $\{\ \}_c^{QP}$.

Now, due to core-valence separation, the last term in (23) is zero from (22). For the rest of the terms in (23), $\exp(T_c)\exp(T_v)$ may be trivially factored out because except the unit term of its expansion, the rest increases the number of incoming valence line from more than one and they are trivially zero (there are not more than one valence electron to be destroyed from the P space). Thus, we have

$$QN\Big[\sum_{m,\,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\,(\{H\,T_c^m\,T_v^n\}_c^{QP})^{(1)}\Big]P$$

$$- QN\Big[\sum_{m,\,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\sum_{l=1}^{\infty}\frac{1}{l!}\,(\{T_v^l\,\{H\,T_c^m\,T_v^n\}_c^{PP}\}_c^{PQ})^{(1)}\Big]P = 0, \tag{24}$$

for the one-valence problem.

For the two-valence problem the one-valence and zero-valence problem are likewise embedded, and we have thus quite generally,

$$QN\Big[\sum_{m,\,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\,(\{H\,T_c^m\,T_v^n\}_c^{QP})^{(p)}\Big]P$$

$$- QN\Big[\sum_{m,\,n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}\sum_{l=1}^{\infty}\frac{1}{l!}\,(\{T_v^l\,\{H\,T_c^m\,T_v^n\}_c^{PP}\}_c^{QP})^{(p)}\Big]P = 0 \tag{25}$$

for the p-valence problem. The set of equations (25) for $p = 0$ to N_v are equivalent to the perturbative expansion for W_{FL} as they are derived from (7), but contain only the connected terms. This has been possible through a clear book-keeping of the connected and disconnected parts of W_{FL}. Our task now is to show that they are entirely equivalent to the non-perturbative equations derived through the use of linked cluster theorem in our earlier work (Mukherjee *et al* 1975a, b; 1977a, 1978).

The non-perturbative theory using core-valence separation was derived in the following manner. For the core problem, we solved a set of equations

$$\langle\psi_{l*}^{N_c}\,|\,H_c\,|\,\psi_{\text{core}}\rangle = 0 \quad \text{for all } l, \tag{26}$$

where H_c is given by (Mukherjee *et al* 1977a)

$$H_c = \sum_{m=0}^{\infty}\frac{1}{m!}\{H\,T_c^m\}_c. \tag{27}$$

But only the $(\{\ \}_c^{QP})^{(0)}$ term of H_c would however contribute in a non-trivial manner, and hence we have

$$\langle \psi_{l*}^{N_c} \mid \sum_{m=0}^{\infty} \frac{1}{m!} (\{H T_c^m\}_c^{QP})^{(0)} \mid \psi_{\text{core}} \rangle = 0. \tag{28}$$

This is clearly equivalent to the equation (22) obtained from the perturbative development, and shows that the core-problem is equivalent in the non-perturbative and the perturbative theories.

For the N_v-valence problem, we solved a set of equations

$$\langle \psi_{l*}^{N_v} \mid H_{c-v} \mid \psi_{i0}^{N_v} \rangle = 0 \text{ for all } l \text{ and } i. \tag{29}$$

The operator H_{c-v} is given by

$$H_{c-v} = \sum_{l,n=0}^{\infty} (-1)^l \frac{1}{l!} \frac{1}{n!} \{T_v^l H_c T_v^n\}_c. \tag{30}$$

The non-trivial contribution of (30) to (20) would come from

$$\langle \psi_{l*}^{N_v} \mid \sum_{l,n=0}^{\infty} (-1)^l \frac{1}{l!} \frac{1}{n!} \sum_{p=0}^{N_v} (\{T_v^l H_c T_v^n\}_c^{QP})^{(p)} \mid \psi_{i0}^{N_v} \rangle = 0. \tag{31}$$

Of this, the $p = 0$ body contribution is zero from (28); ($p = 0$ body contribution cannot come from terms containing T_v). If we assume now the 'subsystem embedding condition' in the same spirit as in the perturbative theory (Mukherjee *et al* 1975c, 1977a, b; Mukhopadhyay *et al* 1978; particularly the last article demonstrates this concept in a separate section, though it is not mentioned by this name), then we have to assume that the corresponding (N_v-1)-valence problem has also a similar set of equations,

$$\langle \psi_{l*}^{N_v} \mid H_{c-v} \mid \psi_{i0}^{N_v-1} \rangle = 0, \tag{32}$$

whence it follows that

$$\langle \psi_{l*}^{N_v} \mid \sum_{l,n=0}^{\infty} (-1)^l \frac{1}{l!} \frac{1}{n!} (\{T_v^l H_c T_v^n\}_c^{QP})^{(N_v)} \mid \psi_{i0}^{N_v} \rangle = 0. \tag{33}$$

By considering the successive hierarchy of other (N_v-2), (N_v-3), problem, we can generally say that

$$QN \Big[\sum_{l,n=0}^{\infty} (-1)^l \frac{1}{l!} \frac{1}{n!} (\{T_v^l H_c T_v^n\}_c^{QP})^{(p)} \Big] P = 0 \text{ for all } p=0, N_v. \tag{34}$$

Thus, the corresponding non-perturbative equation derived by the use of linked cluster theorem has the structure as implied by (34) for the p-valence problem, and unlike the core problem, has no immediate resemblance to (25) obtained from perturbation theory. We shall now show in two steps that they are equivalent.

In the first step, we shall demonstrate that (25) follows as an identity from the non-perturbative development, and in the second step, we shall use this identity to convert (34) to (25)! (The demonstration of the equivalence of the identity with (25) shows that a purely non-perturbative derivation of the equivalence of (34) with (25) has been possible).

For the N_v-valence state with energy E^K, we define the Schrödinger equation as

$$H W_{FL} \bar{\psi}_K^{N_v} = E^K W_{FL} \bar{\psi}_K^{N_v}, \tag{35}$$

where $\bar{\psi}_K^{N_v}$ is written as a linear combination

$$\bar{\psi}_K^{N_v} = \sum_i \psi_{i^0}^{N_v} C_{iK} \tag{36}$$

Using (14), we have

$$H \exp(T_c) \exp(T_v) \bar{\psi}_K^{N_v} = E^K \exp(T_c) \exp(T_v) \bar{\psi}_K^{N_v} \tag{37}$$

Using the definition of H_c (Mukherjee *et al* 1977a) we have

$$H_c \exp(T_v) \bar{\psi}_K^{N_v} = E^K \exp(T_v) \bar{\psi}_K^{N_v}. \tag{38}$$

After a second use of the linked-cluster theorem, we have

$$H_{c-v} \bar{\psi}_K^{N_v} = E^K \bar{\psi}_K^{N_v}. \tag{39}$$

Multiplying by the model space left eigenvector $\langle \tilde{\bar{\psi}}_K^{N_v} |$, we have

$$E^K = \langle \tilde{\bar{\psi}}_K^{N_v} | H_{c-v} | \bar{\psi}_K^{N_v} \rangle, \tag{40a}$$

or, equivalently,

$$E^K = \langle \tilde{\bar{\psi}}_K^{N_v} | \sum_{m=0}^{\infty} \frac{1}{m!} \{H_c T_v^m\}_c^{PP} | \bar{\psi}_K^{N_v} \rangle. \tag{40b}$$

In (40b), there are no T_v-operators to the left of H_c, because then the total term $\{\ \}_c$ cannot remain in the P space (T_v has free particle hole lines to its left which would annihilate $\langle \bar{\psi}_K^{N_v} |$ if T_v sits on the left of H_c).

The left and right model space eigenvectors are biorthogonal, satisfying the completeness relation

$$\sum_{K \in P} | \bar{\psi}_K^{N_v} \rangle \langle \tilde{\bar{\psi}}_K^{N_v} | = \mathbf{1}_{PP}, \tag{41}$$

where $\mathbf{1}_{PP}$ is the unit operator in the model space. Moreover

$$\langle \tilde{\bar{\psi}}_L^{N_v} \mid H_{c-v} \mid \bar{\psi}_K^{N_v} \rangle = E^K \delta_{KL}. \tag{42}$$

From (29), we have further

$$\langle \psi_{l^*}^{N_v} \mid H_{c-v} \mid \bar{\psi}_K^{N_v} \rangle = 0. \tag{43}$$

Then, projecting (38) on to $\langle \psi_{l^*}^{N_v} \mid$, and using the definition of E^K from (40a), we have

$$\langle \psi_{l^*}^{N_v} \mid H_c \exp(T_v) \mid \bar{\psi}_K^{N_v} \rangle = \langle \psi_{l^*}^{N_v} \mid \exp(T_v) \mid \tilde{\bar{\psi}}_K^{N_v} \rangle \langle \tilde{\bar{\psi}}_K^{N_v} \mid H_{c-v} \mid \bar{\psi}_K^{N_v} \rangle \tag{44}$$

Using (29) and (42), we deduce

$$\begin{aligned} &\langle \psi_{l^*}^{N_v} \mid H_c \exp(T_v) \mid \bar{\psi}_K^{N_v} \rangle \\ &= \langle \psi_{l^*}^{N_v} \mid \exp(T_v) \sum_{n=0}^{\infty} \frac{1}{n!} \{H_c T_v^n\}_c^{PP} \mid \bar{\psi}_K^{N_v} \rangle \end{aligned} \tag{45}$$

Using Wick's theorem, we have

$$\begin{aligned} &\langle \psi_{l^*}^{N_v} \mid N\Big[\sum_{n=0}^{\infty} \frac{1}{n!} \{H_c T_v^n\}_c^{QP} \exp(T_v)\Big] \mid \bar{\psi}_K^{N_v} \rangle \\ &= \langle \psi_{l^*}^{N_v} \mid N\Big[\exp(T_v) \sum_{l=1}^{\infty} \frac{1}{l!} \sum_{n=0}^{\infty} \frac{1}{n!} \{T_v^l \{H_c T_v^n\}_c^{PP}\}_c^{QP}\Big] \mid \bar{\psi}_K^{N_v} \rangle. \end{aligned} \tag{46}$$

Using the core-valence separation and the subsystem embedding condition in the same way as was done in deriving (25) from (20) we have

$$\begin{aligned} &QN\Big[\sum_{n=0}^{\infty} \frac{1}{n!} (\{H_c T_v^n\}_c^{QP})^{(p)}\Big] P \\ &= QN\Big[\sum_{l=1}^{\infty} \frac{1}{l!} \sum_{n=0}^{\infty} \frac{1}{n!} (\{T_v^l \{H_c T_v^n\}_c^{PP}\}_c^{QP})^{(p)}\Big] P. \end{aligned} \tag{47}$$

Using (27), we have

$$\begin{aligned} &QN\Big[\sum_{m,n=0}^{\infty} \frac{1}{m!} \frac{1}{n!} (\{H T_c^m T_v^n\}_c^{QP})^{(p)}\Big] P \\ &= QN\Big[\sum_{m,n=0}^{\infty} \frac{1}{m!} \frac{1}{n!} \sum_{l=1}^{\infty} \frac{1}{l!} (\{T_v^l \{H T_c^m T_v^n\}_c^{PP}\}_c^{QP})^{(p)}\Big] P, \end{aligned} \tag{48}$$

showing that (25) is implied by the non-perturbative theory as a consequence of the core-valence separation and the subsystem embedding conditions.

Now, we manipulate (34) as follows:

$$0 = QN\Big[\sum_{l,n=0}^{\infty}(-1)^l\,\frac{1}{l!}\,\frac{1}{n!}\,(\{T_V{}^l\,H_C\,T_V{}^n\}_C^{QP})^{(p)}\Big]P$$

$$= QN\Big[\sum_{l,n=0}^{\infty}(-1)^l\,\frac{1}{l!}\,\frac{1}{n!}(\{T_V{}^l\,\{H_C\,T_V{}^n\}_C^{QP}\}_C^{QP})^{(p)}$$

$$+\,(\{T_V{}^l\,\{H_C\,T_V{}^n\}_C^{PP}\}_C^{QP})^{(p)}\Big]P. \tag{49}$$

We now use (47) for each q-body component of $\{H_C\,T_V{}^n\}_C^{QP}$, and thus find

$$\text{R.H.S. of (49)} = QN\Big[\sum_{n=0}^{\infty}\frac{1}{n!}\,(\{H_C\,T_V{}^n\}_C^{QP})^{(p)}\Big]P$$

$$+\,QN\Big[\sum_{l=1}^{\infty}\frac{(-1)^l}{l!}\sum_{n=0}^{\infty}\frac{1}{n!}\,(\{T_V{}^l\,\{H_C\,T_V{}^n\}_C^{PP}\}_C^{QP})^{(p)}\Big]P$$

$$+\,QN\Big[\sum_{k,l=1}^{\infty}\frac{(-1)^l}{l!}\,\frac{1}{k!}\sum_{n=0}^{\infty}\frac{1}{n!}(\{T_V{}^l\,\{T_V{}^k\,\{H_C\,T_V{}^n\}_C^{PP}\}_C^{QP}\}_C^{QP})^{(p)}\Big]P \tag{50}$$

In (50), we have separated the $l=0$ term from the first term of r.h.s. of (49), and made use of the fact that $l=0$ form is by definition zero for the second term of the r.h.s. of (49). We now collect together all the terms having identical powers of T_V that appear on the left of H_C for the last two terms of (50). For such total power $M\geqslant 2$, we can rewrite these two terms as

$$QN\Big[\sum_{M=2}^{\infty}\sum_{t=1}^{M}\sum_{n=0}^{\infty}\frac{(-1)^r}{(M-r)!}\,\frac{1}{r!}\,\frac{1}{n!}\,(\{T_V{}^r\,\{T_V{}^{M-r}\,\{H_C\,T_V{}^n\}_C^{PP}\}_C^{QP}\}_C^{QP})^{(p)}\Big]P$$

$$= -\,QN\Big[\sum_{M=2}^{\infty}\sum_{n=0}^{\infty}\frac{1}{M!}\,\frac{1}{n!}\,(\{T_V{}^M\,\{H_C\,T_V{}^n\}_C^{PP}\}_C^{QP})^{(p)}\Big]P. \tag{51}$$

The $M=1$ term is left out, and simply read as

$$-\frac{1}{n!}\,(\{T_V\,\{H_C\,T_V{}^n\}_C^{PP}\}_C^{QP})^{(p)}.$$

So, finally, (49) yields, through (50) and (51)

$$0 = QN\left[\sum_{n=0}^{\infty}\frac{1}{n!}\left(\{H_c\, T_v^n\}_c^{QP}\right)^{(p)}\right]P$$

$$-QN\left[\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{m=1}^{\infty}\frac{1}{m!}\left(\{T_v^m\,\{H_c\, T_v^n\}_c^{PP}\}_c^{QP}\right)^{(p)}\right]P. \tag{52}$$

Substitution of H_c from (27) completes the equivalence of (52) with (25), and it thus follows that the perturbative and the non-perturbative approaches are structurally equivalent. The derivation, moreover, brings out the lineage of the non-perturbative theory in an explicit manner. The above equivalence essentially carries through with very little modification where valence-orbitals contain ' active hole levels ' as well. We consider this explicitly elsewhere.

The representation (14) for W_{FL} is an ansatz, however, and is by no means the only representation possible. In the following we consider several alternative forms, all of which might not lead equally easily to the equivalence of the perturbative and non-perturbative approaches.

4. Alternative expansions for W_{FL}

Brandow (1975) and Kuo *et al* (1971) have discussed how W_{FL} can be factored into a pure core-excitation component and one containing core-valence interaction component. Instead of the explicitly factored out representation for W_{FL}, we might use the historically oldest representation (Coester and Kummel 1958; Cizek 1966):

$$W_{FL} = \exp\,(T_c + \bar{T}_v). \tag{53}$$

Using the Baker-Hausdorff expansion, we can rewrite this as (For more rigorous forms, see, e.g. Buzano 1978)

$$W_{FL} = \exp\,(T_c + \bar{T}_v) \sim \exp\,(T_c)\,\exp\,(\bar{T}_v)\,\exp\,[-\tfrac{1}{2}\,(T_c, \bar{T}_v)]. \tag{54}$$

Let us note that the presence of the commutator $[T_c, \bar{T}_v]$ ensures that $\exp\,[-\frac{1}{2}(T_c, \bar{T}_v)]$ is also linked. The alternative ansatz is equally capable of exciting ψ_i^0's to various excited determinants, but is less compact. The ansatz (14) is such that the combined effect of $\exp\,(\bar{T}_v)$ and $\exp\,[-\frac{1}{2}(T_c, \bar{T}_v)$ are all lumped together to give a compact representation $\exp\,(T_v)$. Each T_v thus contains many contracted components of T_c and $\bar{T}_v$ coming through the commutator $(T_c, \bar{T}_v)$. One wonders whether it might be more economical to have a representation of W_{FL} which avoids explicit appearance of commutators between the various components of T_c and T_v. In the ansatze (14) or (53) these commutators invariably appear through contractions of the type

$$\overbrace{T_v^{(p)}\, T_c^{(p)}} \quad \text{or} \quad \overbrace{T_v^{(p)}\, T_v^{(p)}}$$

etc. and makes the expression of H_{eff} rather complex at higher orders. We may easily verify that a representation of W_{FL} as W_{FL} = normal ordered part of

$$\left[1+T+\frac{T^2}{2!}+\frac{T^3}{3!}+\cdots\right], \tag{55}$$

with $T=T_{\text{c}}+T_{\text{v}}$, is also perfectly general, but being in normal order, avoids contractions between various components of T. We may compactly write

$$W_{\text{FL}} = M\,[\exp\,(T_{\text{c}}+T_{\text{v}})] \tag{56}$$

where M may be called a 'block normal ordering operator', which keeps normally ordered part of a given operator-algebraic expression:

$$M\,[\exp\,(T_{\text{c}}+T_{\text{v}})] = \sum_{n=0}^{\infty}\frac{1}{n!}\,N\,[T^n]. \tag{57a}$$

The operator M is frequently used in the operator solutions appearing in Quantum Field Theory (*see*, e.g., Coleman *et al* 1975; Coleman 1975), and is also called 'Mandelstam ordering' (Mandelstam 1975). For (57), we have

$$\begin{aligned} M\,[\exp\,(T_{\text{c}}+T_{\text{v}})] &= M\,[\exp\,(T_{\text{c}})\exp\,(T_{\text{v}})] \\ &= \exp\,(T_{\text{c}})\;M\,[\exp\,(T_{\text{v}})] \end{aligned} \tag{57b}$$

and the complexity of the Baker-Hausdorff expansion is bypassed. Very recently, Ey (1978) has used this form of W_{FL} to generate non-perturbative equations for open-shell systems. This is a generalisation of an earlier work (Offermann *et al* 1976). After the submission of the first draft of this paper, we have come to know that Lindgren also has used the same representation to derive a set of non-perturbative equations similar to those derived by Ey (Lindgren 1978). Before discussing their equations, let us first indicate how the earlier developed non-perturbative theory gets modified in this new representation of W_{FL}.

As we have proved in the appendix, the linked cluster theorem gets modified as follows

$$H\,M\,[\exp\,(T)] = M\,[\exp\,(T)]\;H_{\text{c-v}} \tag{58a}$$

with
$$H_{\text{c-v}} = \sum_{n=0}^{\infty}\sum_{\substack{n_1,\,n_2\\ n_1+n_2=n}}(-1)^{n_1}\frac{1}{n_1!}\frac{1}{n_2!}\,\overbrace{\{T_{\text{v}}^{n_1}\{\overbrace{H_{\text{c}}\,T_{\text{v}}^{n_2}}\}_{\text{c}}\}_{\text{c}}}, \tag{58b}$$

with
$$\text{H}_{\text{c}} = \sum_{m=0}^{\infty}\frac{1}{m!}\,\{\overbrace{H\,T_{\text{c}}^{m}}\}_{\text{c}} \tag{58c}$$

where *all* the operators on the left and right of $\{\ \}_c$ are contracted with H and there is no contraction between the various T's on the same side of H. We may remark here that, due to the presence of at most two-body terms in H, the series in (58a) terminates after the fourth power. This parallels the situation in closed-shells. In contrast, the expression (30) for H_{C-V} remains essentially infinite, as there may be terms with arbitrary power of T having contractions connecting the various T's. By virtue of (58a), the equivalence of the perturbative and non-perturbative equations derived above remain virtually the same, with the only difference that quantities $\{\ \}_c$ have to be interpreted as ones containing contractions with H only. Thus, the block introduced in figure 3a and 3c contain contractions of T's with H and not in a string like $\overbrace{T_c}\,\overbrace{T_c}\,T_v$, etc. The cluster shown in figure 3b similarly contains disconnected T's and no contracted components.

Ey (1978) has used the representation (56) and showed that a relation like (25) may be derived from an equation analogous to (38) through a rather laborious Wick algebra. He did not make use of the simplification afforded by connected components and diagrams and kept the use of bi-orthogonal completeness relation implicit. The relation with the perturbative approach was not explicitly demonstrated, though an order by order expansion analysis was indicated showing the emergence of folded-diagrams from their equations. This is very similar to a method used earlier by us to indicate that certain folded diagrams also emerge from our non-perturbative equations (Mukherjee *et al* 1975b). After the submission of the first draft of the paper for publication, we came to know about the very recent work of Lindgren (1978) and Brandow (1978) where he has explicitly derived (25) from the many-body open-shell perturbative theory put forward earlier (Lindgren 1974). Lindgren also used the representation (56) for W_{FL} but did not demonstrate how the seemingly quite different expression (34) obtained by a straightforward use of the linked cluster theorem (Mukherjee *et al* 1975a, b) is related to (25). The present work uses Brandow representation of W_{FL} in the perturbative context and uses a different route to arrive at (25) first and then shows how the expression (34) from the non-perturbative theory is related to (25). This probably thus conflates both sides of the problem. Let us note that equivalence of our work with that of Ey and Lindgren (i.e. equivalence of (34) and (25)) is valid only at infinite order of expansion; their structures are inequivalent for truncated expressions.

5. Calculation of difference energies in the Mandelstam-ordered representation of W_{FL}

In this section we shall indicate how the use of the representation (56) leads to a rather compact expression of H_{C-V} leading to a very convenient theory for the direct calculation of difference energies in a non-perturbative manner. This is a generalisation of the work done recently by us (Mukhopadhyay *et al* 1978).

Let us assume that we have a HF representation ψ_{H-F} as the first approximation of a closed-shell ground state, and we have a similar set of approximations ψ_K for either an excited or an ionised state. We would like to find the differences in the exact energies for the corresponding exact states.

In this formulation, *we define the HF state itself as the vacuum*, and thus

redefine our hole orbitals accordingly. We first solve for the ground state problem by defining the exact ground state function ψ_{gr} as

$$\psi_{gr} = \exp(T_c)\,\psi_{HF}. \tag{59}$$

Starting with the ground state Schrödinger equation and using the relation (57b), we have, using the linked cluster theorem proved in the appendix, the relation:

$$H_c\,\psi_{HF} = E_{gr}\,\psi_{HF}, \tag{60}$$

where
$$H_c = \sum_{n=0}^{\infty} \frac{1}{n!}\,\{\overbrace{HT_c n}\}_c. \tag{61}$$

H_c is really the expression derived by Čižek in the development of the corresponding closed-shell non-perturbative theory (Čižek 1966). We now separate the completely closed component $\overline{H}_c$ from H_c, and write it as

$$H_c = \overline{H}_c + H_c^{op}, \tag{62a}$$

so that
$$\overline{H}_c = E_{gr}. \tag{62b}$$

Projecting (60) on to appropriate excited states we have

$$\langle \psi_l^* \mid H_c^{op} \mid \psi_{HF} \rangle = 0, \tag{63}$$

as the defining equation for T_c. Let us now use the following ansatz for the states ψ_k^0

$$H \exp(T_c)\,M\ [\exp(T_v)]\,\psi_k^0 = E^k \exp(T_c)\,M\,[\exp(T_v)]\,\psi_k^0. \tag{64}$$

Using (61) and (62b), we have

$$H_c^{op} M\,[\exp(T_v)]\,\psi_k^0 = \triangle E^k\,M\,[\exp(T_v)]\,\psi_k^0, \tag{65}$$

where $\triangle E^k$'s are the difference energies of interest H_c may be interpreted as the 'dressed' hamiltonian for the system (Mukherjee *et al* 1977a). Using the linked-cluster theorem (58) once again, we have

$$\overline{H}_{c-v}\,\psi_k^0 = \triangle E^k\,\psi_k^0 \tag{66}$$

with
$$\overline{H}_{c-v} = \sum_{n=0}^{\infty} \sum_{\substack{n_1,n_2 \\ n_1+n_2=n}} (-1)^{n_1} \frac{1}{n_1!}\frac{1}{n_2!} \left\{ \overbrace{T_v^{n_1}\{\overbrace{H_c^{op} T_v^{n_2}}\}_c} \right\}_c \tag{67}$$

The series terminates after $n = 4$. Writing ψ_k^0 in terms of model space functions, we have

$$\sum_j \langle \psi_i^o \mid \overline{H}_{c-v} \mid \psi_j^o \rangle C_{jk} = \triangle E^k\,C_{ik}. \tag{68}$$

The equations determining T_V are given by

$$\langle \psi_e^* \mid H_{C-V} \mid \psi_i^c \rangle = 0 \tag{69}$$

In (69) N- or $(N-1)$-electron excited states have to be considered depending on whether we are calculating transition energy or ionisation potential. It is clear that just as in the closed-shell case there would be only a few diagrams contributing to the matrix-elements (69) because of the rather compact nature of (67), and this has come about due to the Mandelstam-ordered product representation of W_{FL}.

6. Summary of the main results

In this paper the following things are shown.

(a) Using the Gell Mann-Low analogue of the linked part of the W_{FL} open-shell wave operator, a non-perturbative linear operator equation in W_{FL} may be derived.

(b) For a consistent treatment of the above equation, one must keep track of the connected and disconnected components of W_{FL}, and this is achieved if one uses a coupled cluster ansatz for W_{FL}.

(c) Using a factorisation theorem, which we call the linked cluster theorem, it is possible to convert the equation in W_{FL} to a set of coupled equations which contain only connected components if one uses the ansatz $W_{FL} = \exp(T_V) \exp(T_C)$ and the 'corevalence separation' and the more general 'subsystem embedding' condition. This set may be further shown to be equivalent to the equations previously derived by us during the development of a purely non-perturbative many body theory. Thus a connection is established between the non-perturbative and perturbative approaches to the open-shell problem.

(d) By an analysis of the terms contained in the perturbative expression for W_{FL}, it is shown that several alternative exponential representation of W_{FL} is possible and they correspond to different ways of writing the corevalence interaction terms of W_{FL}. Using the concept of Mandelstam or block-normal ordering, it is shown that a rather compact form for W_{FL} may be found. The equations derived for the $\exp(T_C) \exp(T_V)$ are converted to the appropriate forms for the Mandelstam-ordered representation, and the relation of these equations with the recent non-perturbative equations of Ey (1978) and Lindgren (1978) is indicated. It is shown that the present work conflates these two approaches.

(e) The Mandelstam ordering is exploited to develop a purely non-perturbative theory for difference energy—which parallels closely the non-perturbative theory for open-shells.

Appendix

We shall show here that, for the representation $W_{FL} = M[\exp(T)]$, we have

$$HM[\exp(T)] = M[\exp(T)]\,\bar{H}, \tag{A1}$$

with

$$\bar{H} = \sum_n \sum_{n_1, n_2 = n} (-1)^{n_1} \frac{1}{n_1!} \cdot \frac{1}{n_2!} \{T^{n_1} \{\overbrace{H T^{n_2}}\}_C\}_C. \tag{A2}$$

Expanding M [exp (T)], we have

$$HM\ [\exp\ (T)] = \sum_{n=0}^{\infty} \frac{1}{n!} HM\ [(T^n)], \tag{A3}$$

where $M\ [(T^n)]$ is the normally ordered part of T^n. Using Generalised Wick Theorem (GWT), we have

$$\sum_{n=0}^{\infty} \frac{1}{n!} HM\ [T^n] = \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{n_2=0}^{n} M\ [\overbrace{H\ T^{n_2}}\ T^{n-n_2}]\ {}^{n}C_{n_2}, \tag{A4}$$

where all the T's in $M\ [\overbrace{H\ T^{n_2}}\ T^{n-n_2}]$ shown under contraction are joined exclusively to H, and never among themselves. As all the T operators contain *even* number of creation/destruction operators, we have

$$M\ [\overbrace{H\ T^{n_2}}\ T^{n-n_2}] = M\ [T^{n-n_2}\ \overbrace{H\ T^{n_2}}]. \tag{A5}$$

Let us write the operator $\overbrace{HT^{n_2}}$ as B, and try to use GWT backwards to write $M\ [T^{n-n_2}\ B]$ in (A5) as a product of two disjoint terms:

$$M\ [T^{n-n_2}\ B] = M\ [T^{n-n_2}]\ M\ [B]$$

$$- \sum_{k=1}^{n-n_2} {}^{n-n_2}C_k\ M\ [T^{n-n_2-k}\ \overbrace{T^k\ B}]. \tag{A6}$$

Continuing the operation of splitting up terms of the type $M(T^r B)$ into two parts we finally have

$$M\ (T^{n-n_2}\ B) = \sum_{n_1=0}^{n-n_2} \frac{(n-n_2)!}{(n-n_2-n_1)!}\ T^{n-n_2-n_1} \sum_{\substack{q=1 \\ (\sum k_i = n_1) \\ i=1,\ p}}^{n_1} (-1)^p\ M\ [\overbrace{T^{n_1}\ B}]\ \frac{1}{\prod\limits_{i=1,\ p} k_i!}. \tag{A7}$$

Now, the sum

$$\sum_{p=1}^{n_1} (-1)^p \frac{1}{\prod\limits_i k_i\ !}$$

is the coefficient of the term x^{n_1} in the expansion of $[1 - x - x^2 - \ldots]^{n_1}$ and may be shown to be just $(-1)^{n_1}$. We thus have

$$M\ [T^{n-n_2}\ B] = \sum_{n_1=0}^{n-n_2} \frac{(n-n_2)!}{(n-n_2-n_1)!}\ (-1)^{n_1}\ M\ [\overbrace{T^{n_1}\ B}]. \tag{A8}$$

Thus, (A4) becomes

$$\sum_{n=0}^{\infty}\frac{1}{n!}HM\ [T^n] = \sum_{n=0}^{\infty}\ \frac{1}{n!}\sum_{n_2=0}^{n}\ \frac{n!}{(n-n_2)!\,n_2!}\sum_{n_1=0}^{n-n_2}\frac{(n-n_2)!}{(n-n_2-n_1)!}$$

$$\times(-1)^{n_1}\,M\ [\overbrace{T^{n_1}\,(\overbrace{HT^{n_2}})}]$$

$$=\sum_{n=0}^{\infty}\ \sum_{n_2=0}^{n}\ \sum_{n_1=0}^{n-n_2}\ \frac{(T^{n-n_1-n_2})}{(n-n_2-n_1)!}\ \frac{1}{n_1!}\frac{1}{n_2!}(-1)^{n}_{1}\,M\ [\overbrace{T^{n}_{1}\,[\overbrace{H\,T^{n_2}}]}] \tag{A9}$$

Changing variables in the sum, and using the fact that $1/(n-n_1-n_2)!$ is zero for $n < n_1+n_2$, we have

$$\sum_{n=0}^{\infty}\ \frac{1}{n!}\ HM\ [T^n] = \sum_{k=0}^{\infty}\ \frac{T^k}{k!}\sum_{n_1=0}^{\infty}\ \sum_{n_2=0}^{\infty}\ \frac{1}{n_1!}\frac{1}{n_2!}(-1)^{n_1}\,M\ (\overbrace{T^{n_1}\,[\overbrace{H\,T^{n_2}}]}] \tag{A10}$$

In order to emphasise that all the terms of the form

$$M\ [\overbrace{T^{n_1}\,[\overbrace{H\,T^{n_2}}]}]$$

for a fixed (n_1+n_2) should be lumped together, we formally keep a sum over n. Thus

$$HM\ [\exp\,(T)] = M\ [\exp\,(T)]\,\overline{H} \tag{A11}$$

$$\text{where}\quad \overline{H} = \sum_{n=0}^{\infty}\ \sum_{\substack{n_1,\,n_2\\ n_1+n_2=n}}(-1)^{n_1}\frac{1}{n_1!}\frac{1}{n_2!}M\ \overbrace{[T^{n_1}\,[\overbrace{H\,T^{n_2}}]}] \tag{A12}$$

Clearly, the quantities $M[\overbrace{T^{n_1}\,[\overbrace{H\,T^{n}_{2}}]}]$ are all connected and linked, and we call them as connected terms $\left\{\overbrace{T^{n_1}\left\{\overbrace{HT^{n_1}}\right\}_{c}}\right\}_{c}$.

Thus,

$$\overline{H} = \sum_{n=0}^{\infty}\ \sum_{n_1+n_2=1}^{\infty}(-1)^{n_1}\frac{1}{n_1!}\frac{1}{n_2!}\left\{\overbrace{T^{n_1}\left\{\overbrace{H\,T^{n_2}}\right\}_{c}}\right\}_{c} \tag{A13}$$

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