Pramāṇa, Vol. 13, No. 5, November 1979, pp. 535–544, © printed in India.

Symmetry-adapted many-body perturbation theory: use of the wave operator matrix elements

DEBASHIS MUKHERJEE and DIPAN BHATTACHARYYA*
Theory Group, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032
*Nuclear Reactions Section, Tata Institute of Fundamental Research, Bombay 400 005

MS received 21 April 1979; revised 7 September 1979

Abstract. In this paper we develop a simple method for adapting the closed-shell many-body perturbation theory to an arbitrary point group symmetry taking account of various classes of diagrams exactly to all orders. The method consists in deriving a linear operator equation for the closed-shell wave-operator W which is then symmetry-adapted to the pertinent point group G. It is shown that the system of equations thus derived enables one to include orbital-diagonal h-h, p-p and h-p ladders to all orders in a perturbative framework. The way to generalise the method through inclusion of a larger classes of diagrams to all orders is also indicated. Finally, the connection of the present mode of development with the non-perturbative coupled-cluster formalisms is briefly indicated.

Keywords. Many-body perturbation theory: atoms; molecules; perturbation theory; linear operator equation; wave operator; matrix elements.

1. Introduction

Recently we developed a method of incorporating spin-adapted configuration in the framework of many-body perturbation theory (MBPT) for closed-shell systems (Mukherjee *et al* 1977a; hereafter called I). The present paper serves to introduce another method, which is more suitable for adapting MBPT to an arbitrary point group symmetry.

The key-steps involved in the spin-adapted MBPT [I] may be summarised as follows:

(i) The Hugenholtz matrix-elements were cast into 'spin-free' form through the use of Wigner-Eckart theorem;
(ii) the hole-hole (h-h) and particle-particle (p-p) orbital-diagonal ladder insertions are shown to form a geometric series;
(iii) a certain class of orbital-diagonal hole-particle (h-p) ladders were also shown to form a geometric series; and
(iv) the remaining (h-p) orbital-diagonal ladders were shown to be summable by setting up two geometric series with, respectively, second, fourth, sixth... order and third, fifth, seventh...order perturbation terms (see e.g. equations (40) and (42) of I).

It appears that a similar procedure would not work out so neatly if we want to adapt MBPT to a general point group symmetry. The reason for this difference lies in the structure of the spin-adapted MBPT: When we use the reduced Hugenholtz matrix-elements in the process of spin-adaptation, we couple the spins of the ingoing and outgoing pair of electrons, respectively, to a given resultant spin S — which can take on only two values 0 and 1. But in a general point group G, the orbitals would be labelled by indices γ whose total number would depend on the dimensionality of the particular irreducible representation (IR) of the point group — so that the index Γ, analogous to S, for the coupled ingoing and outgoing electron pair states would take on more than two values in general. Moreover, for a particular IR, Γ may appear more than once from the coupling scheme (say, for example, for the point group K; Griffith 1962). In that case, the step (iv), described above, leading to two geometric series, cannot be attempted, and there does not seem to be any straightforward procedure to sum all the (h-p) orbital-diagonal ladders to all orders. We would resolve this difficulty by replacing the MBPT series by an equivalent one — written in terms of the associated symmetry-adapted wave-operation W (Lowdin 1966), and providing equations which determine the reduced matrix-elements of W. § 2 discusses this aspect. The equations for W derived by us are closely related to the closed-shell coupled-cluster equation (Čížek 1966, 1969; Paldus, 1977; Paldus and Čížek 1975) and also the direct CI equations of the vector method (Roos and Siegbahn 1977) in the non-perturbative framework. Recently Kvasnicka and Laurinc (1977) and Bartlett and Silver (1976) have used restrictive perturbative arguments to derive approximate equations analogous to ours. We have, however, derived a completely general equation for W, from which Kvasnicka-Bartlett type of recursive equations would follow as a special case. Because of the generality of our approach, we have been able to explore the connection between the perturbative and the non-perturbative approaches to the closed-shell problem*. This has been discussed in § 3.

2. Equation for the direct determination of W

Using the Hartree-Fock (HF) determined as the vacuum we may write the Hamiltonian H in normal order as follows:

$$H = E_{HF} + \sum_{A} \epsilon_A N[a_A^+ a_A] + \frac{1}{2!^2} \sum_{\substack{A,B,\\C,D}} \langle AB | v | CD \rangle_a N[a_A^+ a_B^+ a_D a_C] \tag{1}$$

Let us now suppose that we have a point-group G, commuting with H. For the closed-shells, the HF operator itself would commute with G, and the orbitals A would transform as bases for the various IRs of G. A general spin-orbital can then be labelled as

$$A \equiv a_\gamma^\Gamma \sigma_a, \tag{2}$$

*This same approach has proved profitable for elucidating the connection between perturbative and non-perturbative many-body theories for open-shells also (Mukherjee 1979). As a matter of fact, our success in the open-shells prompted us to look into the corresponding aspects for the closed-shell.

where Γ and γ stand for the index of the IR and the particular component of the IR corresponding to the orbital a, and the function σ_a is the associated spin function. We also classify all the spin-orbitals into hole orbitals and particle orbitals in the usual manner, and label holes by α, β, etc and particles p, q, etc. Specifically, any hole spin-orbital, say, would have the form $a_\gamma^\Gamma \sigma_a$.

We now partition H into the unperturbed and perturbed components H_0 and V in the usual manner (Kelly 1968), with V defined by the two-particle part of H in (1), and define the wave-operator W through the relation

$$|\psi\rangle = W|0\rangle, \tag{3}$$

with $|\psi\rangle$ as the exact ground state wave-function, satisfying the Schrödinger equation

$$H|\psi\rangle = E|\psi\rangle. \tag{4}$$

Using the Gell Mann-Low-Goldstone theorem (Kelly 1968; Fetter and Walecka 1971), W can be factored out as

$$W|0\rangle = W_L|0\rangle\langle 0|W|0\rangle, \tag{5}$$

where W_L is a collection of all operators which induces all the h-p excitations with the restriction that there are no closed-diagrams (that is, no ' vacuum fluctuations'). W_L thus stands for all the linked diagrams in W. Let us emphasise that the linked diagrams of W are not all ' connected ', they are linked only in the sense of having no vacuum fluctuations. From (4), it follows that

$$E = \langle 0|HW_L|0\rangle. \tag{6}$$

W_L can be written as a formal power series in V (Kelly 1968):

$$W_L = \sum_{n=0}^{\infty} \{[QV/(E_0 - H_0)]^n\}_L, \tag{7}$$

where Q is the projector on to the virtual space and $\{[QV/(E_0 - H_0)]^n\}_L$ stands for the nth order term in the expansion of W_L.

Now we show that, by a simple manipulation of (7), we may arrive at a linear equation in W_L. The derivation is analogous to, but simpler than, the one we followed in the open-shell case (Mukherjee 1979), and we shall therefore describe the procedure rather briefly:

We break up (7) as

$$W_L = 1 + \sum_{n=1}^{\infty} \{[QV/(E_0 - H_0)]^n\}_L, \tag{8}$$

and dissect one $[QV/(E_0 - H_0)]$ from the series in (8), then (7) can be rewritten as

$$W_L = 1 + \{[QV/(E_0 - H_0)]\ W_L'\}_L. \tag{9}$$

W_L' stands for classes of all diagrams left after dissecting the $[QV/(E_0 - H_0)]$ term.

If we now note that (i) the class of diagrams obtained by dissecting one $[QV/(E_0 - H_0)]$ term are all linked (as we cannot introduce vacuum fluctuations by the dissection procedure) and (ii) the terms in the infinite series in W_L' contain the same diagrams as would be obtained from W_L (i.e. (8)), clearly then $W_L' = W_L$ and we have

$$W_L = 1 + [QV/(E_0 - H_0)\, W_L]_L. \tag{10}$$

Writing W_L as $W_L = 1 + \overline{W}_L$.
we have, from (10)

$$\overline{W}_L = [QV/(E_0 - H_0)] + \{[QV/(E_0 - H_0)]\, \overline{W}_L\}_L. \tag{11}$$

Equation (10) or, equivalently (11), gives us a linear operator equation determining the wave-operator matrix-elements. Because of the presence of the projector Q, $\overline{W}_L$ can have matrix-elements only between virtual space states $\langle \phi_i^* |$ and the unperturbed ground state $|0\rangle$. From (11), we may easily derive

$$\langle \phi_i^* | \overline{W}_L | 0 \rangle = \left\langle \phi_i^* \left| \frac{V}{E_0 - H_0} \right| 0 \right\rangle + \sum\nolimits_m \left[\left\langle \phi_i^* \left| \frac{V}{E_0 - H_0} \right| \phi_m^* \right\rangle \langle \phi_m^* | \overline{W}_L | 0 \rangle \right]_L, \tag{12}$$

where, again only those terms in the sum over states ϕ_m^* are to be retained which lead to diagrams with no vacuum fluctuations.

We shall briefly show in § 3 that the equation (10) generates the coupled-cluster equations for W in the non-perturbative framework (Čížek 1966, 1969). For the present let us only remark that if one wants to include very many classes of diagrams, then it is advantageous to go over to the non-linear representation of W_L as an exponential operator (Coester 1958; Coester and Kummel 1960; Čížek 1966, 1969). This is because we are lumping together in the p-body operator component $W_L^{(p)}$ of W_L all the diagrams with p incoming and outgoing lines and are not explicitly keeping track of whether they are all connected or not. As a result, in the joining of $QV/(E_0 - H_0)$ and W_L in (11), we would not be sure that we are not introducing vacuum fluctuations. This difficulty would have been obviated in a coupled cluster representation of W_L where the connected and disconnected components are clearly differentiated*. For our present purpose, however, where we would really confine our attention to only the two-body part of W_L and would keep only certain special class of diagrams in (12), the linear representation suffices. We now invoke to the

*For a more extensive discussion regarding the difficulty concerning the disconnected diagrams we refer to our recent work on the connection between perturbative and non-perturbative open-shell theory (Mukherjee 1979).

usual approximation regarding the dominance of pair-correlations, and retain only the two-body part of W_L. The functions ϕ_l^* that would enter the equation (12) would be of the form

$$\phi_l^* \equiv \phi_l^* \begin{bmatrix} p_{\gamma_3}^{\Gamma_3}\sigma_3 & q_{\gamma_4}^{\Gamma_4}\sigma_4 \\ \uparrow & \uparrow \\ \alpha_{\gamma_1}^{\Gamma_1}\sigma_1 & \beta_{\gamma_2}^{\Gamma_2}\sigma_2 \end{bmatrix}.$$

We want to approximate (12) still further. For a given set of IR, characterising the hole and particle orbitals

$$\left\{\alpha_{\gamma_1}^{\Gamma_1}\sigma_1,\ \beta_{\gamma_2}^{\Gamma_2}\sigma_2,\ p_{\gamma_3}^{\Gamma_3}\sigma_3,\ q_{\gamma_4}^{\Gamma_4}\sigma_4\right\},$$

we choose only those doubly excited states ϕ_m^* which are formed by lifting two electrons-one from each of the degenerate components

$$\left\{\alpha_{\gamma_i}^{\Gamma_1}\sigma_l\right\} \text{ and } \left\{\beta_{\gamma_j}^{\Gamma_2}\sigma_j\right\}$$

and putting them—one in each again—into the degenerate components

$$\left\{p_{\gamma_k}^{\Gamma_3}\sigma_k\right\} \text{ and } \left\{q_{\gamma_l}^{\Gamma_4}\sigma_l\right\}.$$

It just means that, if we expand $W_L^{(2)}$ in (12), using (7), we would get a perturbation series in which scattering takes place only between the states involving hole and particle levels labelled by the same set of IRs Γ_1, Γ_2, Γ_3 and Γ_4 respectively. Diagram-wise this implies that all the diagrams which are orbital-diagonal (*h-h*), (*p-p*) and (*h-p*) ladders in all orders are taken into account in the calculation of E. An orbital-diagonal (*h-p*) insertion would, for example, involve a matrix-element

$$\langle \alpha_{\gamma_i}^{\Gamma_1}\sigma_i\, p_{\gamma_k}^{\Gamma_3}\sigma_k \mid v \mid \alpha_{\gamma_j}^{\Gamma_1}\sigma_j\, p_{\gamma_l}^{\Gamma_3}\sigma_l\rangle_a$$

with the same labels Γ_1 and Γ_3 on α and p respectively; the component indices γ_i, γ_k, γ_j and γ_l and the spin-functions σ_i, etc would take on all possible values however.

Clearly the equation (12)—as approximated above—is equivalent to the perturbation series analogous to the spin-adapted MBPT for an arbitrary point group. It only now remains to adapt this series explicitly to the point-group symmetry by way of introducing reduced Hugenholtz matrix-elements-analogous to what was done in I. We have, corresponding to the spin-adapted matrix-elements [see e.g. equation (10) of I], the defining relation

$$\begin{aligned}\langle a_{\gamma_1}^{\Gamma_1}\sigma_1\, b_{\gamma_2}^{\Gamma_2}\sigma_2 \mid v \mid c_{\gamma_3}^{\Gamma_3}\sigma_3\, d_{\gamma_4}^{\Gamma_4}\sigma_4\rangle_a \\ = \sum_{\substack{\Gamma,\gamma,n \\ S,M_S}} \{ab \parallel v \parallel cd\}_S^{\Gamma,n} \left\langle \begin{matrix}\Gamma_1 & \Gamma_2 \\ \gamma_1 & \gamma_2\end{matrix}\middle|\begin{matrix}\Gamma, n \\ \gamma\end{matrix}\right\rangle \left\langle \begin{matrix}\Gamma, n \\ \gamma\end{matrix}\middle|\begin{matrix}\Gamma_3 & \Gamma_4 \\ \gamma_3 & \gamma_4\end{matrix}\right\rangle \\ \left\langle \begin{matrix}\frac{1}{2} & \frac{1}{2} \\ \sigma_1 & \sigma_2\end{matrix}\middle|\begin{matrix}S \\ M_S\end{matrix}\right\rangle \left\langle \begin{matrix}S \\ M_S\end{matrix}\middle|\begin{matrix}\frac{1}{2} & \frac{1}{2} \\ \sigma_3 & \sigma_4\end{matrix}\right\rangle. \end{aligned} \tag{13}$$

The supercript n appearing in (13) would take care of the fact that the direct produce $\Gamma_1 \otimes \Gamma_2$, etc. for a general point group may not be simply reducible (Koster 1958). A similar equation also holds good for the reduced matrix-element for $\overline{W}_L$. Using the phase-convention as in Griffith (1962), and using the reduction procedure as outlined in I, through the graphical methods of spin-algebra (EI Baz and Castel 1972; Briggs 1971), we end up with the following system of linear simultaneous equations:

$$\{pq \parallel \overline{W}_2 \parallel \alpha\beta\}^{\Gamma k, n}_{S_k} = \frac{\{pq \parallel v \parallel \alpha\beta\}^{\Gamma k, n}_{S_k}}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q}$$

$$+ \frac{[\Gamma_k]\,[S_k]\,\{pq \parallel \overline{W}_2 \parallel \alpha\beta\}^{\Gamma k, n}_{S_k}}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q} [\{pq \parallel v \parallel pq\}^{\Gamma_{k,n}}_{S_k} \times$$

$$(2 - \delta_{pq})/2 + \{\alpha\beta \parallel v \parallel \alpha\beta\}^{\Gamma_{k,n}}_{S_k}\ (2 - \delta_{\alpha\beta})/2]$$

$$+ \sum_{\substack{\Gamma_i, \Gamma_j \\ S_i; S_j \\ m_i, m_j}} \frac{[\Gamma_k]\,[\Gamma_i]\,[\Gamma_j]\,[S_k]\,[S_i]\,[S_j]}{\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q} \times$$

$$\Big[\{p\alpha \parallel v \parallel \alpha p\}^{\Gamma_i, m_i}_{S_i} F^{S_i S_j}_{kn}(\Gamma_\alpha, \Gamma_\beta, \Gamma_p, \Gamma_q, \Gamma_i, \Gamma_j, m_i, m_j)$$

$$+ \{p\beta \parallel v \parallel \beta p\}^{\Gamma_i, m_i}_{S_i} F^{S_i S_j}_{kn}(\Gamma_\beta, \Gamma_\alpha, \Gamma_p, \Gamma_q, \Gamma_i, \Gamma_j, m_i, m_j)$$

$$+ \{q\alpha \parallel v \parallel \alpha q\}^{\Gamma_i, m_i}_{S_i} F^{S_i S_j}_{kn}(\Gamma_\alpha, \Gamma_\beta, \Gamma_q, \Gamma_p, \Gamma_i, \Gamma_j, m_i, m_j)$$

$$+ \{q\beta \parallel v \parallel \beta q\}^{\Gamma_i, m_i}_{S_i} F^{S_i S_j}_{kn}(\Gamma_\beta, \Gamma_\alpha, \Gamma_q, \Gamma_p, \Gamma_i, \Gamma_j, m_i, m_j)\Big] \times$$

$$\{pq \parallel \overline{W}_2 \parallel \alpha\beta\}^{\Gamma_j, m_j}_{S_j} \tag{14}$$

for all choices of (p, q), (α, β), k, n, and S_k. The quantity (Γ_k), etc. are the dimensionality of the corresponding IR. The quantity $F^{S_1 S_2}_{kn}$ is defined as

$$F^{S_1 S_2}_{kn}(\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5, \Gamma_6, m_1, m_2)$$

$$= \begin{pmatrix} \Gamma_1 & \Gamma_3 & \Gamma_5, m_1 \\ \Gamma_{k,n} & \Gamma_4 & \Gamma_3 \\ \Gamma_2 & \Gamma_6, m_2 & \Gamma_1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S_i \\ S_k & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & S_j & \frac{1}{2} \end{pmatrix}, \tag{15}$$

where the entries on the right hand side of (15) containing Γs is a 9-J symbol appropriate to the point group (labelled by 'extra' indices m_1, m_2 and n). Solution of (14) would provide us with the matrix-elements of $\overline{W}_L^{(2)}$ including all the (*h-h*), (*p-p*) and (*h-p*) orbital diagonal ladders to all orders.

The expression for correlation energy would be given by

$$\triangle E = \tfrac{1}{4} \sum_{\substack{\alpha,\beta,\\ p,q\\ \Gamma_k, S_k, n}} \{\alpha\beta \,\|\, v \,\|\, pq\}_{S_k}^{\Gamma_k, n} \{pq \,\|\, \overline{W}_2 \,|\, \alpha\beta\}_{S_k}^{\Gamma_k, n} [\Gamma_k]\ [S_k]. \tag{16}$$

3. Connection with the coupled-cluster theory

Let us first note that, in (12), if we include in the summation over ϕ_m^* all the doubly excited states for each ϕ_l^*, then the system of equations thus generated would embody all the (*h-h*), (*h-p*) and (*p-p*) ladders (diagonal as well as off-diagonal) to all orders. This is an obvious and straightforward extension of the scheme outlined in § 2 and follows closely the spirit expressed in I. An analogous systems of non-perturbative equations were derived recently by Paldus (1977) who has also discussed the relation of his work with those of Roos and Siegbahn (1977).

We now briefly show the connection of equation (10) with the coupled-cluster theory of Čížek (1966, 1969). Rewriting (10) as

$$(E_0 - H_0)\ W_L = (E_0 - H_0) + Q\,(VML)_L, \tag{17}$$

and pre-multiplying (17) with Q, post-multiplying by P, and using the idempotency of Q, we have

$$Q\ [E_0 - H_0]\ W_L\, P = Q\,(VW_L)_L\, P. \tag{18}$$

Using the relation

$$E_0 = PH_0P = PH_0 = H_0P, \tag{19}$$

we easily obtain from (18)

$$Q\ [H_0, W_L]\ P + Q\,(VWL)_L\, P = 0. \tag{20}$$

Now we shall use the linked-cluster factorisation theorem in the spirit of Čížek's theory, but shall use the algebraically expressed factored-out version as developed recently by Mukherjee *et al* (1975a, b; to be henceforth called IIa, and IIb respectively) in the context of a general non-perturbative formalism. Using the Ursell-Mayer representation of W_L:

$$W_L = \exp\,(T), \tag{21}$$

we have $$VW_L = V \exp(T) = \exp(T)\, U, \tag{22}$$

with $$U = \sum_{n=0}^{\infty} \sum_{\substack{n_1, n_2 \\ n_1+n_2=n}} (-1)^{n_1} \frac{1}{n_1!} \frac{1}{n_2!} \{T^{n_1} V T^{n_2}\}_{\text{conn}} \tag{23}$$

(see, e.g. equation 25(b) of IIa)

The quantity $\{T^{n_1} VT^{n_2}\}_{\text{conn}}$ was denoted as $\{T^{n_1} VT^{n_2}\}_L$ in IIa, but we have changed this notation here to emphasise that they consist of connected diagrams only—*though they may be closed.* Further, for closed shell, T's cannot be contracted to H from left, hence $n_1 = 0$.

Now, using (22) with V replaced by H_0, we have

$$H_0 W_L = H_0 \exp(T) = \exp(T)\, U_0 = W_L\, U_0 \tag{24}$$

where U_0 would be of the form (23) with H_0 replacing V. Writing U_0 as

$$U_0 = H_0 + \sum_{n=1}^{\infty} \frac{1}{n!} \{H_0 T^n\}_{\text{conn}} = H_0 + \bar{U}_0, \tag{25}$$

we have, from (24),

$$Q\,[H_0, W_L]\, P = Q\,[W_L\, \bar{U}_0]_{\text{conn}}\, P. \tag{26}$$

$\bar{U}_0$ consists of all the connected diagrams obtained by joining H_0 with several Ts. Now the Ts always induce transition from the P space to the Q space, and the operator H_0, being diagonal, when acting after the Ts would keep the resultant function still in the Q space. Hence $\bar{U}_0$ acting on a P space lifts it onto the Q space. Hence $P\, \bar{U}_0\, P = 0$ and we have no vacuum fluctuations. Equation (26) may thus be written as

$$Q\,[H_0, W_L]\, P = Q\,(W_L\, Q\, \bar{U}_0)_L\, P = Q\, W_L\, Q\, \bar{U}_0\, P. \tag{27}$$

Let us note that W_L does not have any line joining $Q\, \bar{U}_0$.

Dissecting U into closed-diagrams U_c and the linked diagrams U_L, we have

$$(HW_L)_L = \exp(T)\, U_L = W_L\, U_L. \tag{28}$$

Hence, $$Q\,(VW_L)_L\, P = Q\, W_L\, U_L\, P. \tag{29}$$

As U_L consists only of open diagrams, $P\, U_L\, P = 0$, and $Q\, U_L\, P = U_L\, P$, hence

$$Q\,(VW_L)_L\, P = Q\,(W_L\, Q\, U_L)\, P. \tag{30}$$

Hence equation (20) reduces to

$$Q\,W_L\,Q\,U_0\,P + Q\,W_L\,Q\,U_L\,P = 0, \tag{31}$$

whence $$Q\,\bar{U}_0\,P + Q\,U_L\,P = 0. \tag{32}$$

Now, from (23) and (25), we have

$$\bar{U}_0 + U_L = V + \sum_{n=1}^{\infty} \frac{1}{n!}\{H\,T^n\}_L, \tag{33}$$

where in U_L only the linked part of (25) is retained. Calling $U_0 + \bar{U}_L$ as $\bar{H}$, we have

$$Q\,\bar{H}\,P = 0, \tag{34}$$

which is the non-perturbative coupled-cluster equation of Čížek in algebraic form.*

Recently Kvasnicka and Laurinc (1977) and Bartlett and Silver (1976) gave recursive formulae which, in spirit, are related to the system of equations (11) derived by us. It appears that their recursive relations emphasise the structure of (11) in a limited sense in that disconnected diagrams are not considered at all, so that the problem of avoiding vacuum fluctuations has not been discussed. Kvasnicka and Laurinc (1977) however, observed that in general their procedure may lead to a problem of overcounting. We have shown in the present section how the problem of disconnected diagrams can be handled through the exp (T) representation. Thus we are on safer grounds—we know where we have to be careful while generalising the present scheme beyond ladder insertion and how to do it.

Let us also mention that very recently Lindgren (1978a, b) has developed a coupled-cluster formalism for open-shells starting from the open-shell perturbative theory of Bloch (1958) and Brandow (1967) from which the corresponding closed-shell version may be derived as a special case. This also leads to (34). The connection of Lindgren's approach with the Goldstone-like expansion scheme—as used in the present paper—has been discussed in detail in a recent paper (Mukherjee 1979) for open-shells. For closed shell, we merely observe that Lindgren's starting equation reduces to

$$Q\,[W_L, H_0]\,P = Q\,VW_L\,P - Q\,W_L\,PVW_L\,P, \tag{35}$$

(see equation (33) of Lindgren's paper (1978b)).

Noting that $PVW_L\,P$ consists of all closed diagrams of V and W_L connected together, we may identify $PVW_L\,P$ with the closed part U_c of U in (23). Using (22), (23), (25) and (29), we have

$$QW_L\,\bar{U}_0\,P + QW_L\,U_L\,P + QW_L\,U_C\,P - QW_L\,U_C\,P = 0, \tag{36}$$

from which (34) follows after cancellation of QW_L from the left.

*For a more extensive discussion on this point, see e.g. IIa and IIb.

4. Concluding remarks

The development outlined in this paper may be generalised to incorporate many other classes of diagrams to all orders. Furthermore, in the whole development, nowhere it is necessary to use explicitly the actual point group involved in the process. Thus, formal degeneracies, which are consequence of the special artifacts used in the calculations, may also be treated in the present formalism with equal facility. For example, in a PPP model benzene ground state calculation using localised HF orbitals, one may formally ascribe the three-fold degeneracy in the localised HF orbital energy of the bond orbitals as due to an abstract internal ' bond-space group ', and treat them as belonging to a convenient T-type of IR of any point group homomorphic with this ' bond-space group '. We are currently utilising this interesting observation in reducing the dimension of the coupled-cluster equations for systems showing alternancy symmetry. Systems for which the present formalism may be immediately useful are atoms, homonuclear diatomics, linear polyatomics and molecules belonging to the highly symmetric point groups like Td, Oh, etc.

Acknowledgements

The authors are thankful to Professor I Lindgren and Dr B Brandow for sending preprints of their work.

References

Bartlett R and Silver D M 1976 in *Quantum science* eds J L Calais, O Goscinski, J Linderberg and Y Ohrn (New York: Plenum Press)
Bloch C 1958 *Nucl. Phys.* **6** 329
Brandow B 1967 *Rev. Mod. Phys.* **39** 771
Briggs J S 1971 *Rev. Mod. Phys.* **43** 189
Čížek J 1966 *J. Chem. Phys.* **45** 4256
Čížek J 1969 *Adv. Chem. Phys.* **14** 35
Coester F 1958 *Nucl. Phys.* **7** 421
Coester F and Kunmel H 1960 *Nucl. Phys.* **17** 477
El Baz E and Castel B 1972 *Graphical methods of spin-algebra in atomic, nuclear and particle physics* (New York: Marcel Dekker)
Fetter A L and Walecka J D 1971 *Quantum theory of many-particle systems* (New York: McGraw Hill)
Griffith J S 1962 *Irreducible tensor methods for molecular symmetry groups* (New Jersy: Prentice Hall)
Kelly H P 1968 in *Adv. Theor. Phys.* and references therein (p. 75)
Koster G F 1958 *Phys. Rev.* **109** 227
Kvasnicka V and Laurinc V 1977 *Theor. Chim. Acta (Berlin)* **45** 197
Lindgren I 1978a preprint
Lindgren I 1978b *Int. J. Quantum. Chem. Symp.* **12** 33
Lowdin P O 1966 in *Perturbation theory and its applications in quantum mechanics* ed C H Will Cox (New York: John Wiley) and many references therein
Mukherjee D, Moitra R K and Mukhopadhyay A 1975a *Pramana* **4** 247
Mukherjee D, Moitra R K and Mukhopadhyay A 1975b *Mol. Phys.* **30** 1861
Mukherjee D and Bhattacharya D 1977 *Mol. Phys.* **34** 773
Mukherjee D 1979 *Pramana* **12** 203
Paldus J and Čížek J 1975 *Adv. Quantum Chem.* **9** 106
Paldus J 1977 *J. Chem. Phys.* **67** 303
Roos B O and Siegbahn P E M 1977 in *Methods of electronic structure theory* ed H F Schaefer (New York: Plenum Press) and many references therein