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A hermitian open-shell many-body perturbation theory for treating intruder states

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Abstract. In this paper we have formulated an open-shell many-body perturbation theory (MBPT) that applies to an incomplete model space. The effective Hamiltonian H^{eff} generated in our theory is hermitian. We follow the resolvent-operator based time-dependent formulation of MBPT of Banerjee *et al*, and show quite generally that, by classifying the various determinants spanning the Hilbert space as model valence space P, virtual valence space R and virtual space Q, a diagrammatic MBPT satisfying size consistency can be developed. The chief new features of the theory are (i) manifest hermiticity of H^{eff}; (ii) presence of disconnected diagrams no part of which is a legitimate diagram (irreducible disconnected diagrams); (iii) presence of folded diagrams with components that may be irreducible disconnected diagrams; (iv) a consistent treatment of the various n-valence sectors of the Hilbert space that may be interacting through H^{eff} if valence-holes are present—in particular a modified treatment of the core-valence separation. The generalisation afforded by the theory offers useful conceptual as well as computational advantages because the convergence difficulty encountered in a complete valence space formulation may be bypassed here by keeping the offending valence space determinants out of the model space. A brief critique of the development *vis-a-vis* the only other general model space development leading to a nonhermitian H^{eff} is also given.

Keywords. Many-body theory; open shell perturbation theory; intruder states.

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1. Introduction

Significant advances have been made over the last decade in the development of many-fermion correlation theories. Spurred by the earlier spectacular success of the Brueckner-Goldstone many-body perturbation theory (MBPT) for the closed-shells (Brueckner 1955; Goldstone 1957; Hugenholtz 1957) as applied to atomic and molecular correlation problems (Kelly 1964, 1969; Lee *et al* 1970; Kaldor 1973, 1975; Robb 1973; Bartlett and Silver 1975; Wilson and Silver 1977; Bartlett *et al* 1977; Wilson 1978; Bartlett 1981), attempts have been made to extend the formalism to encompass open-shell states as well. This requires a development of the open-shell analogue of the Brueckner-Goldstone expansion starting with a combination of the zeroth order determinants which are either degenerate or quasi-degenerate. Starting with the pioneering work of Brandow (1967, 1977), various alternative formalisms have been developed over the last decade (Oberlechner *et al* 1970; Kuo *et al* 1971; Lindgren 1974; Kvasnicka 1975; Banerjee *et al* 1982a, b) the interrelations between which are not very clear yet. The underlying basic idea of all these developments is the partitioning of the

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Hilbert space into a model space and a virtual space where the interaction between these two spaces is calculated perturbatively and the modified or "effective" Hamiltonian in the model space is diagonalised to generate the perturbed energies. All the formalisms pursue a diagrammatic approach, and choose an appropriate closed shell determinant as the physical vacuum. The zeroth order starting functions have additional valence occupancies (valence holes or valence particles) in addition to those present in the vacuum, but the valence occupancies are *partial* in the sense that out of M valence orbitals only a subset $N < M$ is filled in each determinant entering the zeroth order functions. Each theory then goes on to prove a linked-diagram theorem by assuming that the model space is *complete* with respect to valence orbitals in the sense that all the ${}^{M}C_{N}$ possible determinants corresponding to all possible valence occupancies have been included in the model space. While such an assumption lends an elegant property to these open shell MBPT's, *viz* the linked-diagram theorem, it has its operational difficulty as well. For valence orbitals which are not degenerate, this necessitates inclusion in the model space of determinants which lie considerably higher in energy compared to the lower lying states for describing even the low lying states. This not only implies handling a model space of large dimension, but also a potential convergence difficulty due to near degeneracy and consequently strong mixing of virtual space determinants with the higher lying model space determinants brought in solely for obtaining the linked-diagram expansion. Such offending virtual space determinants are called *intruder states* in the many-body literature (Schucan and Weidenmuller 1972, 1973). The appearance of intruder states is a perennial problem in any practical application of open-shell MBPT, and a proper handling of these states remains a major active area of the current day research. Although extrapolation techniques like Pade approximants (Wilson and Silver 1976) and related approaches have been extensively used (Hoffman *et al* 1973; Hoffman 1978; Hegarty and Robb 1979; Baker *et al* 1981; Shurpin *et al* 1977) to improve the convergence of the perturbation series that are beset with the appearance of divergent terms due to intruder state mixing, this improvement frequently occurs only if rather high order Pade or related approximants are calculated (Hoffman 1978). More significantly, the extrapolation techniques bypass the real physics of the situation: One should be able to formulate an open-shell MBPT in which the intruder states in principle should not occur at all.

Hose and Kaldor (1979, 1980, 1981, 1982) made significant advance in solving the intruder state problem by noting that if the model space determinants mixing strongly with the intruder states are kept outside the model space, the convergence of the perturbation series is dramatically improved. This of course implies that the model space is not complete with respect to the valence orbitals, which leads to the appearance of *disconnected diagrams* in the perturbation expansion of the effective Hamiltonian. Hose and Kaldor, however, made the important observation that although the effective Hamiltonian has disconnected diagrams, no disconnected components of these diagrams are legitimate diagrams as such of the effective Hamiltonian, so that appearance of disconnected diagrams do not spell a break down of the size-extensitivity or size consistency (Primas 1965; Pople *et al* 1976; Bartlett 1981) of the theory. In their formulation of the MBPT in the incomplete model space, Hose and Kaldor follow the time-independent approach of Brandow (1967) which is related to the works of Lindgren (1974) and Kvasnicka (1975) as also the time-dependent developments of Kuo *et al* (1971). All these formalisms lead to a *nonhermitian* effective Hamiltonian. The nonhermiticity essentially stems from the fact that in the calculation of the matrix-

elements $H_{ij}^{\text{eff}} = \langle \phi_i | H^{\text{eff}} | \phi_j \rangle$ of H^{eff} between model space determinants ϕ_i and ϕ_j, the energy denominators appearing in the perturbation expansion of H_{ij}^{eff} have as unperturbed energies only that of the *ket-function* ϕ_j and not of ϕ_i. Consequently, the matrix element H_{ij}^{eff} is *unsymmetric* with respect to the indices i and j and hence the nonhermiticity of H_{ij}^{eff}. Hose and Kaldor, however, exploits the nonhermiticity to its fullest advantage and chooses, in contrast to the works of Brandow (1967) and others, each ket ϕ_j as the vacuum to simplify the calculation of the matrix-elements H_{ij}^{eff} considerably. In so far as one likes to look upon the effective Hamiltonian as a bonafide Hamiltonian *per se*—sharing all the properties of a true Hamiltonian—the nonhermiticity of H^{eff} appears as aesthetically unpleasing. From a more pragmatic viewpoint, the nonhermiticity necessitates calculation of all the matrix elements of H^{eff} in the model space in contrast to only those in the upper triangle of a hermitian H^{eff}. The diagrammatics of Hose and Kaldor is moreover quite cumbersome making its application somewhat errorprone (Hose and Kaldor 1982).

There is thus clearly a need to develop a hermitian effective Hamiltonian of open-shell MBPT in an incomplete model space. This implies that we treat the ket and bra functions ϕ_j and ϕ_i in H_{ij}^{eff} on the same footing. In this paper we shall show it is possible to develop such a theory by generalising the hermitian formulation of MBPT in complete model space of Banerjee *et al* (1982a, b).

2. Theory

2.1 *Resolvent-based MBPT for complete valence space*

Here we give a brief resumé of our resolvent-based open-shell MBPT leading to a hermitian H^{eff} in a complete valence model space (Banerjee *et al* 1982a, b). This will fix the notations, introduce the basic formalism and also motivate the wanted generalisation to tackle the intruder states.

We partition the Hamiltonian H into an unperturbed part H_0 and a perturbation V:

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

where H_0 is a sum of one-body operators h_0. The orbitals entering the theory are taken as eigenstates of h_0, so that all the determinants built up from the orbital set are eigenstates of H_0. We choose as the vacuum for our problem a suitable closed-shell determinant ϕ which may have fewer, greater or equal number of particles than the set of unperturbed functions ψ_i^0 with unperturbed energies E_i^0 spanning the model space. The model space is taken to be *complete* with respect to the valence occupancies. The determinants ϕ_i comprising the unperturbed functions ψ_i^0 are obtained from ϕ through a set of valence creation operator products Ω_i^+(valence holes or valence particles):

$$\Omega_i^+ \phi = \phi_i. \tag{2}$$

We introduce Green function-like entities S_{ij} defined as

$$S_{ij}(t) = i \langle \phi_i | \exp [-i(H - E_c)t] | \psi_j \rangle / \langle \psi_j^0 | \psi_j \rangle, \tag{3}$$

where ψ_j is the exact eigenstate evolving from ψ_j^0, and E_c is the correlated energy of the vacuum ϕ. The one-sided Fourier transform of $S_{ij}(t)$ is given by

$$S_{ij}(\omega) = \int_{-\infty}^{0} \mathrm{d}t\, S_{ij}(t)\exp(i\omega t) = \langle \phi_i | (\omega + E_c - H)^{-1} | \psi_j \rangle / \langle \psi_j^0 | \psi_j \rangle \quad (4)$$

and has the structure of a matrix-element of a certain resolvent. The matrix $\mathbf{S}(\omega)$ has poles at $\omega = E_j - E_c$. Thus the energy differences between eigenstates ψ_j and the correlated vacuum may be found out from the poles of $\mathbf{S}(\omega)$. The resolvent-based open-shell MBPT seeks to derive a perturbation expansion for $\mathbf{S}(t)$ and to obtain a Dyson-like equation involving a self-energy matrix $\mathbf{\Sigma}(t)$. The Fourier transform of this equation then furnishes the equation for $\mathbf{S}(\omega)$ from which the desired poles are computed.

The key development of the formulation of Banerjee *et al* (1982a, b) is the observation that the series implied by the Dyson equation for $\mathbf{S}(t)$ ordinarily involves a time-delayed self-energy matrix $\mathbf{\Sigma}(t)$, and would thus produce an equation for $\mathbf{S}(\omega)$ involving an energy-dependent $\mathbf{\Sigma}(\omega)$. The resulting pole-search would then be analogous to the iterative solution strategy for an open-shell Brillouin-Wigner perturbation theory. In fact Banerjee *et al* demonstrate that the series involving $\mathbf{\Sigma}(\omega)$ is equivalent to the Bloch-Horowitz variant of the open-shell Brillouin-Wigner theory (Bloch and Horowitz 1958).

The Gellman-Low adiabatic theorem for open-shells can be expressed as

$$\frac{|\psi_j\rangle}{\langle \psi_j^0 | \psi_j \rangle} = \frac{U_I(0, -\infty)|\psi_j^0\rangle}{\langle \psi_j^0 | U_I(0, -\infty)|\psi_j^0\rangle}, \quad (5)$$

where U_I is the evolution operator in the interaction representation (Ratcliffe 1975). Using (5), $S_{ij}(t)$ can be expressed as

$$S_{ij}(t) = \frac{i\exp[i(E_c - E_i^0)t]\,\langle \phi_i | U_I(t, -\infty)|\psi_j^0\rangle}{\langle \psi_j^0 | U_I(0, -\infty)|\psi_j^0\rangle} = \frac{N_{ij}}{D_j}. \quad (6)$$

As D_j does not depend on t, it suffices to consider only the N_{ij}'s to study the pole structure of $\mathbf{S}(t)$. Using the perturbation expansion of $U_I(t, -\infty)$, N_{ij} may be written as

$$N_{ij} = i\exp[i(E_c - E_i^0)t] \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{t} \mathrm{d}t_1 \ldots \mathrm{d}t_n \times \langle \phi_i | T[V_I(t_1) \ldots V_I(t_n)] | \psi_j^0 \rangle. \quad (7)$$

Our motivation is to regroup the terms in the expansion of (7) to generate an implicit equation for $N_{ij}(t)$. Noting that each term in the expansion of (7) involves calculation of expectation values of the form $\langle \phi | \Omega_i T[\ ] \Omega_j^+ | \phi \rangle$ it easily follows from Wick's theorem that the only non vanishing terms of the normal product expansion of $T[\ ]$ will be those having valence to valence scatterings only, since only these will be capable of finally contracting with valence destruction/creation operators Ω_i/Ω_j^+. In diagrammatic language, the terms yielding non-zero contributions would correspond to a set of disjoint diagrammatic components having open lines (corresponding to uncontracted operators) labelled by valence lines only. We call such diagrams "valence G blocks". There may be valence G blocks having no open lines—they are thus closed blocks and are numbers. For a given ordering of the open blocks, if we now collect all possible time ordering of the closed blocks, then (7) can be factorised as

$$N_{ij}(t) = i \sum_{m=0}^{\infty} \frac{(-i)^m}{m!} \exp\left[i(E_c - E_i^0)t\right] \int_{-\infty}^{t} dt_1 \ldots dt_m \langle \phi_i | N[V_I(t_1) \ldots V_I(t_m)] | \psi_j^0 \rangle_{\text{open}} \times \left[\frac{1}{i} N^{\text{closed}}(t)\right], \tag{8}$$

where $N^{\text{closed}}(t)$ is given by

$$N^{\text{closed}}(t) = i \sum_{k=0}^{\infty} \frac{(-i)}{k!} \int_{-\infty}^{t} dt_1 \ldots dt_k \langle \phi | N[V_I(t_1) \ldots V_I(t_k)] | \phi \rangle = i \langle \phi | U_I(t, -\infty) | \phi \rangle. \tag{9}$$

Using Gellman-Low theorem for the closed shells, N^{closed} can be written as

$$N^{\text{closed}}(t) = i \exp\left[(E_0 - E_c)t\right] \langle \phi | \psi \rangle, \tag{10}$$

where ψ is the correlated vacuum state with exact energy E_c and E_0 is the unperturbed energy of the vacuum ϕ. Equation (10) allows us to eliminate the correlated vacuum energy E_c from (8) and obtain

$$N_{ij}(t) = i \sum_{m=0}^{\infty} \frac{(-i)^m}{m!} \exp\left[i(E_0 - E_i^0)t\right] \int_{-\infty}^{t} dt_1 \ldots dt_m \times \langle \phi_i | N[V_I(t_1) \ldots V_I(t_m)] | \psi_j^0 \rangle_{\text{open}} \langle \phi | \psi \rangle = N_{ij}^{\text{open}}(t) \langle \phi | \psi \rangle. \tag{11}$$

Again, as $\langle \phi | \psi \rangle$ does not contribute to the poles, it suffices to consider only $N_{ij}^{\text{open}}(t)$. Our next objective is to rewrite (11) in such a manner that the terms can be regrouped into a Dyson-like equation.

To facilitate further analysis, Banerjee *et al* (1982a, b) introduced the concept of a "box". A box is a part of the diagram which cannot be further subdivided into two sub boxes joined by *valence lines only*. Also, they introduced a "string" which is a connected set of boxes joined by valence lines only. The open G boxes of (11) will thus diagrammatically look like a set of disjoint strings having various numbers and types of boxes embedded in each string. A typical term of $N_{ij}^{\text{open}}(t)$ may be depicted as in figure 1. In each such term, there is a topmost time t_1 at which the interaction starts. If one scans the time arguments of the beginnings and endings of the boxes by going down the diagram for the term, one encounters an uppermost time level t_l lying below t_1 such that

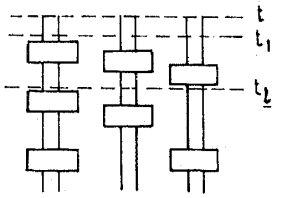

Figure 1. A typical term of $N^{\text{open}}(t)$ depicted in terms of boxes. The lines emanating from the boxes are all valence. The top-most possible time of the diagrams is t. The top-most time at which a box begins is t_1; t_1 is the top most time at which a horizontal line drawn across the vertical valence lines does not go through a box.

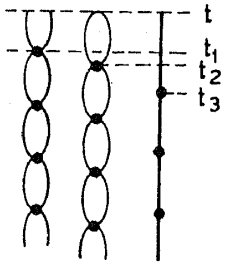

Figure 2. Conversion of string of boxes to a string of points. t is the top-most possible time of the diagram. t_1 is the time of the top-most point. We have also indicated a few time arguments of the succeeding points.

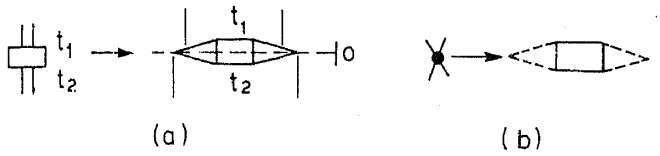

Figure 3. The procedure by which one converts a box showing a time-delayed interaction to a point. We choose the time-base t_0 midway between t_1 and t_2 and allow the valence lines to converge to t_0, **a.** shows how the effect of the extra propagators are annulled by folding back the "extra" propagators, **b.** depicts the internal disposition of the point.

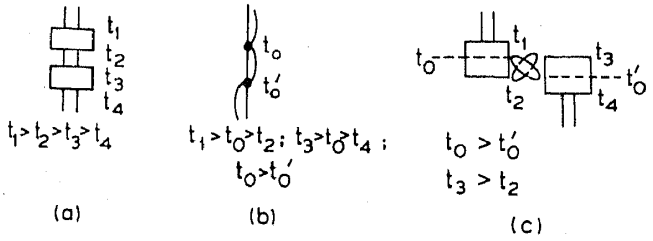

Figure 4. Emergence of folded diagrams as a result of iteration of a point, **a.** shows the time-arguments of the actual boxes joined in a string, **b.** shows the converted points joined in a string. The implied time-arguments are also displayed, **c.** shows the error incurred due to the implied time ordering of **b.** The time range which is wrongly included is shown in **c.** The diagram has a set of folded lines which are shown as encircled lines.

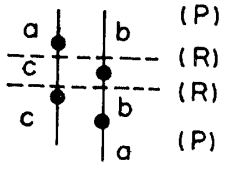

Figure 5. Set of points on two strings connecting determinants $|ab|$ and $|ac|$. These two determinants are in the set P. The dotted lines cutting the valence lines indicate the intermediate determinants. The figure displays that the intermediate determinants is $|bc|$ which is a virtual valence determinant in the set R. The whole diagram itself must be regarded as a part of Σ_{RS}.

a horizontal line drawn at t_l cuts *valence lines only* (*i.e.* cut at t_l does not go through a box). Calling the set of boxes above t_l as a "top" part of the diagram and the rest as the "bottom" part, it follows that the whole series for $N_{ij}^{\text{open}}(t)$ will involve a factorisation of terms involving all possible top parts and bottom parts, and as the latter has the highest time as t_l but has the same structure as $N_{ij}^{\text{open}}(t)$, it will have a form $N^{\text{open}}(t_l)$ with appropriate indices.

Introducing the resolution of identity in the model space as $\mathbf{1}_{\text{MP}} = \sum_k |\phi_k\rangle\langle\phi_k|$, we may show in a straightforward manner that

$$N_{ij}^{\text{open}}(t) = N_{0ij}^{\text{open}}(t) + \sum_k \int_{-\infty}^{t} \overline{N}_{0ii}^{\text{open}}(t) \sum_{ik}^{(t-t_l)} N_{kj}{}^{\text{open}}(t_l)\mathrm{d}t_l \tag{12}$$

where N_{0ij}^{open} and $\overline{N}_{0ij}^{\text{open}}$ are given by

$$N_{0ij}^{\text{open}}(t) = i\langle\phi_i|\exp\left[i(E_0 - E_i^0)t\right]|\psi_j^0\rangle, \tag{13a}$$

$$\overline{N}_{0ij}^{\text{open}}(t) = i\langle\phi_i|\exp\left(E_0 - E_i^0\right)t]|\phi_j\rangle\delta_{ij}. \tag{13b}$$

Equation (12) indicates clearly that a one-side Fourier transform on $N_{ij}^{\text{open}}(t)$ will yield an ω-dependent $\boldsymbol{\Sigma}(\omega)$ from $\boldsymbol{\Sigma}(t - t_l)$. Banerjee *et al* (1982a, b), however, further showed that by resorting to an alternative time-integration procedure it is possible to render $\boldsymbol{\Sigma}$ as instantaneous, so that the Fourier transform generates an ω-independent $\boldsymbol{\Sigma}$ and hence an open-shell MBPT of the Rayleigh-Schrödinger form.

If a box is replaced by an equivalent point-like or instantaneous vertex in which the valence lines enter and leave *at the same time*, then a string of boxes can be represented as a string of points. In such a situation, a typical term of $N_{ij}^{\text{open}}(t)$ will look like figure 2. If one now calls the part of the diagram having the topmost interaction t_l as the top part and the rest as bottom, then it follows that $N_{ij}^{\text{open}}(t)$ leads to a factorisation involving two parts: one containing collection of all the points of various internal structure, and the other containing just the collection of strings of points with highest time as t_1 yielding $N^{\text{opennn}}t_1$. $\boldsymbol{\Sigma}(t)$ in this case is then the collection of top parts and each term in $\boldsymbol{\Sigma}(t)$ is connected, and is time-instantaneous.

Johnson and Baranger (1971) gave a procedure by which it is possible to convert a time-delayed vertex into an instantaneous vertex. In this procedure, one chooses a convenient time base t_0, and propagators for the valence lines are allowed to converge on that time base. The point is then the part of the vertex containing corrections (*i.e.* additional propagators needed to bring the lines at t_0). Thus, for a box with time of entry and time of exit as t_2 and t_1 respectively, a point can be generated as shown in figure 3. The dotted lines in figure 3b indicate that the valence propagator lines have been "folded", and the genesis is depicted in figure 3a. A closer analysis reveals that the above procedure for replacing a box by an equivalent point does not simply convert a string of boxes to a string of points within the allowable time ranges unless correction terms are brought in. Johnson and Baranger (1971) as well as Benerjee *et al* (1982a, b), discussed at great length the various correction terms that one might have to invoke, and we refer to these works for these details. Here we simply demonstrate the emergence of one kind of correction terms by taking a concrete example. For a string of two boxes of the type shown in figure 3a, a simple replacement of the boxes by the points as in figure 3b would entail a time range absent in the original series. Terms having this time range are then *subtracted*. Figure 4a shows the string with two boxes and figure 4b the string with two points. In figures 4a and b the actual and implied time

restrictions are also shown. Figure 4c shows the term that is wrongly brought in. This is a situation in which the boxes overlap with $t_3 > t_2$ and the lines joining the two boxes "fold back". This term should therefore be subtracted. Finally, by choosing a time base for this correction term, this again may be made instantaneous. Again a correction term has to be invoked for this "correction" at a higher order. But the procedure is unique and can be carried through at each order systematically. Thus Banerjee *et al* finally obtain a $\Sigma(t)$ which is time-instantaneous so that the Fourier transform yields an ω-independent Σ. Following Johnson and Baranger (1971), they also demonstrate that if t_0 is chosen *midway* between the exit and entry points, then Σ can be made to be hermitian. With such a time base t_0, $N_{ij}^{\text{open}}(\omega)$ may be written as

$$N_{ij}^{\text{open}}(\omega) = N_{0ij}^{\text{open}}(\omega) + \sum_k \bar{N}_{0ii}^{\text{open}}(\omega) \Sigma_{ik}^{\text{RS}} N_{kj}^{\text{open}}(\omega), \tag{14a}$$

or, in matrix-notation

$$\mathbf{N}^{\text{open}}(\omega) = \mathbf{N}_0^{\text{open}}(\omega) + \bar{\mathbf{N}}_0^{\text{open}} \Sigma^{\text{RS}} \mathbf{N}^{\text{open}}(\omega), \tag{14b}$$

If we now expand the functions $|\psi_j^0\rangle$ in terms of the model space determinants $|\phi_k\rangle$ using

$$|\psi_j^0\rangle = \sum_k |\phi_k\rangle C_{kj}, \tag{15}$$

then it follows from the linear independence of the $|\psi_j^0\rangle$'s that

$$\bar{\mathbf{N}}^{\text{open}}(\omega) = \bar{\mathbf{N}}_0^{\text{open}}(\omega) + \bar{\mathbf{N}}_0^{\text{open}}(\omega) \Sigma^{\text{RS}} \bar{\mathbf{N}}^{\text{open}}(\omega), \tag{16}$$

where $$\mathbf{N}^{\text{open}} = \bar{\mathbf{N}}^{\text{open}} C. \tag{17}$$

The poles of $[N^{\text{open}}]^{-1}$ correspond to solutions of the following equation

$$[\bar{\mathbf{N}}_0^{\text{open}}(\omega)^{-1} - \Sigma^{\text{RS}}]\mathbf{A} = 0, \tag{18}$$

for nontrivial matrices A. Using the Fourier transform of (13b), we finally have the hermitian eigenvalue equation

$$[(E_j^0 - E_0)\mathbf{1} + \Sigma^{\text{RS}}]\mathbf{A}_j = \omega_j \mathbf{A}_j \tag{19}$$

furnishing the energies $\omega_j = (E_j - E_c)$.

2.2 *Resolvent-based open-shell MBPT for the incomplete valence space*

The above development clearly demonstrates that the key requirement in the factorisation leading to a product $\Sigma^{\text{RS}} N^{\text{open}}$ is that once the topmost point in a string is taken as the top part, the lines immediately under it joining with the bottom part must all be valence and any possible set of labelling these lines must define a model space-determinant for resolution of identity in the model space to hold good. The assumption of a complete valence model space was thus instrumental in the factorisation. In contrast, once we agree to deal with an incomplete model space, the valence lines immediately under the top part may not define a model space-determinant. In this case, we must always keep in mind the underlying determinantal states that characterise the labels on the bunch of valence lines joining the boxes. In a complete model space, any combination of the valence orbitals defines a model space determinant and any box is

automatically a legitimate diagram of Σ^{RS}. For an incomplete model space, this is not generally the case.

The crux of the problem is best illustrated by taking as a concrete example a two-valence problem with valence orbital labels a, b and c. The complete valence space consists of determinants $|ab|$, $|ac|$ and $|bc|$. Now let us suppose that we have an incomplete model space consisting of $|ab|$ and $|ac|$ and the determinant $|bc|$ is outside the model space. A typical term of $\mathbf{N}^{open}(t)$ consisting of two strings is shown in figure 5. If we identify the top point as the top part of the diagram, then it follows that, as labelled, the bunch of valence lines immediately under the point define the determinant $|bc|$ which is outside the model space. In this case the top part has to be taken as the part of the diagram under which there are only a bunch of valence lines labelled in such a way that they define model space-determinants. Clearly in figure 5 the whole diagram must be regarded as part of Σ^{RS}. This is disconnected. But a component of the diagram is then not a legitimate diagram, because it is impossible for any of the single strings to connect states $|ab|$ with $|ac|$ or $|ab|$. The appearance of disconnected diagrams thus does not indicate size-inconsistency of the theory. We call such disconnected diagrams as "irreducible disconnected diagrams".

The strategy that we advocate in this paper to generate H^{eff} can now be concretely stated. We start from the string of boxes. We next define three sets of determinants. The set of model space-determinants are called "model valence space" and is labelled as the set P. The set of valence determinants left out of the model space are called "virtual valence space" and is labelled as the set R. The set of virtual determinants are labelled as Q. We now label the lines joining the boxes in all possible manner. *Considering each box to be a point*, and scanning the diagram downwards we note whether the labels on the lines between the top-most point and the one under it characterise a term in P or in R. If the term is in P, the top vertex then is a legitimate top part. If the term is in R, we proceed downwards still further till we reach a stage where the nth point and $(n+1)$th point have for the first time a set of labels characterising a term in P. The points below this will form the bottom part, and the set of disconnected points on the top constitute a possible diagram in Σ^{RS}. For actual evaluation, we have to remember that the strings contain boxes and not points, and we have to convert them into points by folding the external lines onto a common time base t_0, following our earlier method (Banerjee *et al* 1982a, b) for complete valence space.

We have indicated in figure 5 the classification into P and R sets of a typical term for the incomplete model space with functions $|ab|$ and $|ac|$.

To illustrate the methodology still further we take a concrete example. Suppose we are interested to find out the low-lying states of He-like systems. The dominant configuration of the ground state is the determinant $|1S_\alpha 1S_\beta|$, and those for the excited singlet and triplet states are $|1S_\alpha 2S_\beta|$ and $|2S_\alpha 1S_\beta|$. For a complete model space, we should also include the function $|2S_\alpha 2S_\beta|$, which lies however far higher in energy (in the Auger continuum) and mixes strongly with virtual states like $|1S_\alpha 3S_\beta|$ etc., leading to an intruder state problem. Our strategy then would be to leave out the function $|2S_\alpha 2S_\beta|$ of the model space. The set of boxes labelled as in figure 6a are legitimate candidates for H^{eff}, as they connect the states $|1S_\alpha 1S_\beta|$, $|1S_\alpha 2S_\beta|$, $|2S_\alpha 1S_\beta|$ with $|1S_\alpha 1S_\beta|$, and indicate what kind of connected single boxes survive as bonafide terms. The set of diagrams shown in figure 6b are disconnected irreducible diagrams. The diagram on the left has a one-valence single box component with a passive valence line. This kind of diagram appears in a complete valence space calculation as well. However,

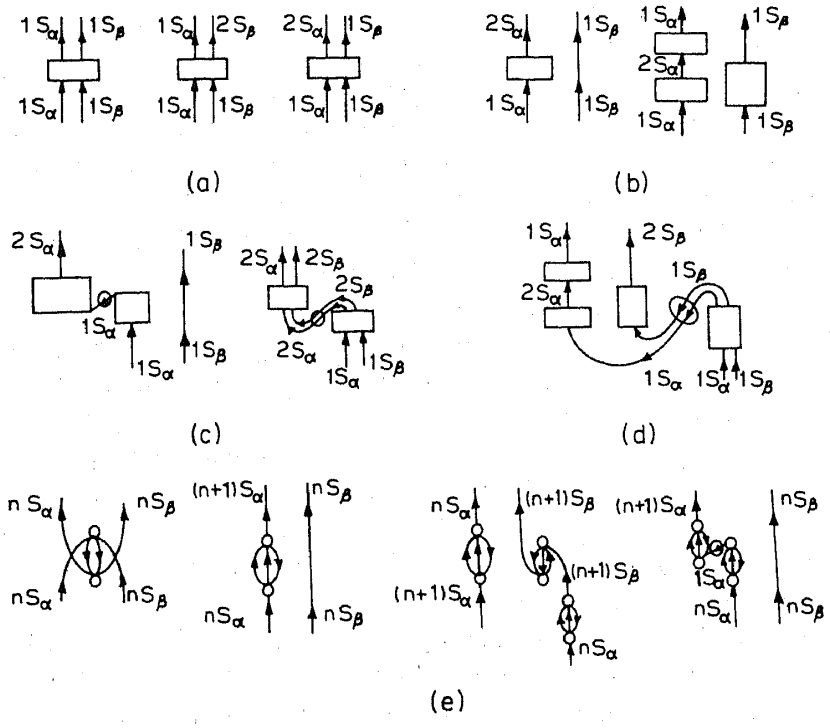

Figure 6. **a.** shows some typical single box diagrams for the two valence situations **b.** shows two diagrams. The one on the right is an irreducible disconnected diagram, **c.** is a set of folded diagrams brought in to correct the error during the conversion of boxes to points, **d.** is a folded diagram where an irreducible disconnected component is joined by folded lines to another single box, **e.** shows some typical diagrams for an incomplete model space calculation with function $|nS_\alpha nS_\beta|$, $|nS_\alpha(n+1)S_\beta|$ and $|(n+1)S_\alpha nS_\beta|$.

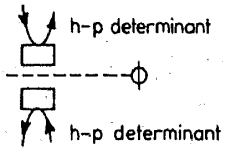

Figure 7. A typical disconnected diagram in which the intermediate determinant is the Hartree-Fock function ϕ. This diagram spells a breakdown of the core-valence situation.

the diagram appearing on the right of figure 6b is a true disconnected irreducible diagram which is characteristic of our present formulation. Let us note carefully, that a horizontal line passing just under the topmost box cuts a bunch of R valence lines, characterising the determinant $|2S_\alpha 2S_\beta|$, and thus the topmost box by itself cannot form a legitimate diagram of H^{eff}. The diagrams in figure 6c are the "correction terms" brought in during the replacement of string of boxes by an equivalent string of points, as discussed in §2.1. The lines that are folded are encircled to indicate that the associated propagators run "backwards". These folded diagrams are all connected because they stem from the conversion of connected boxes to points. In our formulation there are, however, disconnected irreducible boxes as well, as shown in figure 6b. Conversion of such boxes into a point by folding onto a common time base will entail again errors in diagrams containing two or more such points. The corresponding correction terms will then appear as disconnected diagrams having boxes joined by folded lines. In this

process of joining, a previously disconnected set of boxes might form a connected diagram. This is illustrated in figure 6d. The set of boxes on the top joined by folded lines are the irreducible disconnected diagrams of figure 6b. Upon joining by folded lines to the lower box, the composite diagram becomes connected. However it should be borne in mind that in general there will also be disconnected irreducible diagrams having folded lines joining the various components. We do not show such a term explicitly here because it will appear at a pretty high order of perturbation theory. For the formal point of view, however, their presence must be taken into account.

To illustrate concretely the internal structure of the boxes, we depict in figure 6e a few typical Hugenholtz diagrams for a model space consisting of nS^2 and $ns(n+1)S$ functions. The arrows on the internal lines indicate the associated hole or particle orbitals participating in the internal part of the boxes. Starting from the left, the first diagram of figure 6e is a legitimate connected single box diagram and is a correlation term. Its general shape is that of a diagram of figure 6a. The second one is a single box diagram with a spectator valence line. Its general structure is that of the left diagram of figure 6b. The third diagram is a disconnected irreducible diagram of the general structure of the right diagram of figure 6b. The last diagram of figure 6c is a folded diagram.

It should be clear from the foregoing discussions that, because of the underlying book-keeping procedure for the determinants of the P and R space, no general rule for drawing the diagrams can be given. However the general strategy is quite simple. The new set of terms that we encounter are the disconnected irreducible diagrams which have intermediate R space valence determinants and the folded diagrams in which one or more components of the boxes joined by folding can be disconnected irreducible boxes.

We have elaborated above on the formalism by taking as examples the cases where the valence lines are valence particles. In these cases the H^{eff} conserves the number of valence lines before and after the interaction. This leads to a number of simplifications. In particular, the various n-valence sectors of the Hilbert space become automatically noninteracting with one another due to the particle conservation superselection rule:

$$H^{\text{eff}} = \bigoplus_n H_n^{\text{eff}}, \tag{20}$$

where H_n^{eff} refers to the n-valence projection of H^{eff}. Clearly this spells an "aufbau" development of the H^{eff} starting from the $n = 0$ valence state (*i.e.* the vacuum). The very fact that each H_n^{eff} is noninteracting with respect to one another makes it possible to calculate the vacuum exact energy E_c first, the one valence energies by calculating H_1^{eff} next, and so on, so that the shift in energy upon addition of valence particles can be easily evaluated, if desired. This simplicity of structure is, however, somewhat modified if there are valence holes as well in the model space determinants. In that case the number of valence lines entering into and leaving from the bottom and the top respectively are not necessarily the same. As a result, various n-valence sectors of the Hilbert space are coupled together. In particular, the following couplings are generally present:

$$H_{\text{eff}} = \bigoplus_{n = \text{odd, even}} H_n^{\text{eff}}, \tag{21a}$$

or

$$\begin{aligned} &n = 1, 3, 5, \ldots, \text{for odd} \\ &n = 0, 2, 4, \ldots, \text{for even} \end{aligned} \tag{21b}$$

which follows from the fact that determinants which are related by various hole-particle excitations have the same number of electrons and thus can generally interact through H^{eff}. The most striking consequences of this observation is the breakdown of the so-called "core-valence" separation (Brandow 1967). Let us suppose that we are interested in finding out the low-lying excitation energies of a closed shell ground state. The natural choice for the model space functions are the hole particle excited determinants of the Hartree-Fock ground state ϕ. If the model space contains no other functions, ϕ itself becomes a part of the virtual space functions Q! One thus has an awkward situation where the vacuum itself interacts with the model space functions, and this leads to certain disconnected diagrams involving the hole-particle determinants and ϕ, as shown in figure 7. As a result the core-exact energy E_c cannot be calculated independently, and the core-valence separation breaks down. In a recent article, Brandow (1983) has pointed this out, which he regarded as a malady. In the light of our present development, this is no longer a major problem. For a general model space one can leave out or bring in any determinant that is deemed as instrumental in smoothing the convergence of the perturbation series. For determinants involving valence holes and even number of electrons, (21a) generally holds true. Once we decide as to which determinants are to be included in P, we add to P the determinant ϕ as well, corresponding to the $n = 0$ valence problem. The $n = 4, 6 \ldots\ldots$ virtual valence and other virtual space determinants then form the complementary spaces R and Q. If needed, one may leave out even some $n = 2$ hole-particle excited determinants out of P. Particularly, the more highly excited hole-particle determinants mix very strongly with 2 hole-2 particle excited determinants and may cause convergence problems if included in P. Once ϕ is included in the model space, the diagram of figure 7 cannot appear, for ϕ is a part of P now, and the final diagonalisation of H^{eff} would furnish us with both the excited state energies and the ground state correlation energy. The core-valence separation thus figures in this theory in a somewhat modified manner.

3. Concluding remarks

In this paper we have formulated an open-shell MBPT which is not restricted for its performance to complete valence model spaces. The effective Hamiltonian H^{eff} thus generated is hermitian which results in considerable computational simplification and offers stability to the calculated energies. The formalism relies on a resolvent operator approach to MBPT put forward recently by Banerjee *et al* (1982a, b) and it has been shown that by a simple modification of the concept of valence space a completely general formalism may be developed in a transparent manner.

A brief comparison with the only other MBPT involving the general model space may not be out of place here. The formalism of Hose and Kaldor (1979, 1980, 1981, 1982) relies on the nonhermitian formulation of Brandow (1967) for its development. Hose and Kaldor claim that, by choosing each ket ϕ_j as the vacuum for calculating $\langle\phi_i|H^{\text{eff}}|\phi_j\rangle$, they eliminate many diagrams which would otherwise cancel among each other. While this may have advantages in a nonhermitian formulation where there is a manifest asymmetry between ϕ_i and ϕ_j, it becomes difficult to extend this formalism to generate a hermitian H^{eff}. Operationally speaking, the choice of multiple vaccua for the calculation makes the general diagrammatic classification in Hose-Kaldor formalism quite cumbersome and generation of the diagrams error prone (Hose *et al* 1982). In

the present formulation, one simply needs to classify the diagrams into various boxes first and regroup them according to connected single boxes and disconnected irreducible boxes. In contrast, Hose and Kaldor classifies the diagrams as closed diagrams, cut-reducible diagrams and so on, whose manipulations can be quite complicated in practice. More significantly, Hose and Kaldor did not consider the interacting nature of the H^{eff} for hole-valence situations and did not discuss the breakdown of the core-valence separation as a consequence.

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