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Hermitian formulation of the coupled-cluster approach

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Abstract. A Hermitian formulation of the coupled-cluster approach (CCA) is developed, based on the Jørgensen condition, $P\Omega^{\dagger}\Omega P = P$, Ω being the wave operator and P the projection operator for the model space. This leads to a formalism where the exact as well as the model functions are orthonormal, and the effective Hamiltonian has the manifestly Hermitian form $H_{\text{eff}} = P\Omega^{\dagger}H\Omega P$. It is shown that the Jørgensen condition is compatible with the connectivity criteria (connected cluster operator and effective Hamiltonian) for a general, incomplete model space. Even with an effective Hamiltonian of this form, however, non-Hermiticity may be introduced when the cluster expansion is truncated. This can be remedied by a reformulation of the coupled-cluster equations, where additional terms, which cancel in the complete expansion, preserve Hermiticity at each truncation. The new equations also lead to additional terms in the cluster operator itself, which make it possible, for instance, to include important effects in the pair approach that otherwise would require the evaluation of three- and four-body clusters.

1. Introduction

The many-body perturbation theory (MBPT) is often based on the so-called *intermediate normalization* (IN) (Brandow 1967, Lindgren 1974, Kvasnicka 1974, 1977), which implies that the zero-order wavefunction is the projection of the full wavefunction on a certain *model space*. This scheme has many advantages and leads to a simple form of the *effective Hamiltonian*, which yields the energies (energy splitting) of the system. On the other hand, the IN scheme also has certain disadvantages, such as a *non*-Hermitian effective Hamiltonian and non-orthogonal zero-order or model wavefunctions. Furthermore, as first pointed out by Mukherjee (1986a, b), in order to obtain connectivity in the coupled-cluster expansion for a general, incomplete model space, it is necessary to abandon the intermediate normalization.

The non-Hermiticity of the effective Hamiltonian in the IN scheme can be demonstrated in a simple way by means of the second-order diagrams (a) and (b) in figure 1. In this scheme the energy denominators are evaluated in the standard way 'from the bottom' (Lindgren and Morrison 1986), which leads to an asymmetry of the expressions. If the energies of the initial, final and intermediate states of diagram (a) are A, B and C, respectively, as indicated in the figure, then the denominator of that diagram becomes $(A-C)$, while for the 'Hermitian adjoint' diagram (b) the denominator is $(B-C)$. Hence, these diagrams are not exactly Hermitian adjoints in the case $A \neq B$, leading to non-Hermiticity of the effective Hamiltonian.

Several procedures have been proposed to 'Hermitize' the effective of the IN scheme by means of a non-unitary transformation, first discussed by des Cloizeaux (1960) and

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further developed particularly by the Toulouse group (see, for instance, Durand and Malrieu 1987). Another possibility is to impose a subsidiary condition, which forces the effective Hamiltonian to be Hermitian—a procedure first proposed by Jørgensen (1975). This procedure, which has previously been employed by Kvasnicka (1981, 1982) and by Haque and Mukherjee (1984, 1985), will be applied here. In the example mentioned above this procedure leads to an additional diagram (c), which compensates for the non-Hermiticity. An important advantage of the Hermitian formulation is that it is compatible with connectivity criteria also for an incomplete model space, as will be demonstrated below.

In IN non-Hermiticity can also be caused by the truncation, as illustrated in figure 2. If one- and two-body effects are considered, then the effective-operator diagram (a) will be generated in IN, while the corresponding Hermitian adjoint diagram (b) would in that scheme require that some three-body effects are included (namely single and double core excitations in combination with an unexcited valence electron). In the Hermitian formulation presented here, however, the latter diagram will be partly evaluated 'from the top', which requires only one- and two-body effects. The same kind of asymmetry appears in the wave operator. In IN the diagram (c) in figure 2 will be generated in the one- and two-body approximation, while the analogous diagram (d) would require that three-body effects were also considered. Again, in the Hermitian

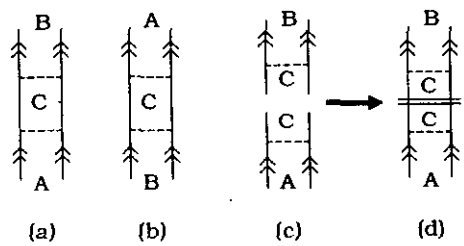

Figure 1. Illustration of the non-Hermiticity of the effective Hamiltonian in intermediate normalization. The broken lines represent the electron-electron interaction and the full lines the electron orbitals. Valence lines are marked with double arrows. The energy denominator of diagram (a) is $(A-C)$, while that of (b) is $(B-C)$. Hence the diagrams are not Hermitian adjoints when the initial and final energies are different, $A \neq B$. Diagram (c) is a correction to the effective Hamiltonian, which in the Hermitian formulation compensates for the non-Hermiticity (see equation (25)). The double line represents here the double energy denominator $(A-C)(B-C)$.

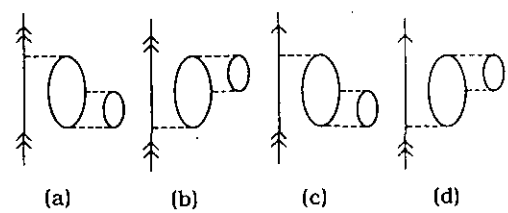

Figure 2. If single and double excitations are considered (without interaction with any passive valence orbital), then the effective-operator diagram (a) would be generated in intermediate normalization but not the corresponding Hermitian adjoint diagram (b). Similarly, the wave-operator diagram (c) would be included but not the analogous diagram (d), which involves a triple excitation, when viewed from the bottom. In the 'symmetrized' Hermitian formulation all these diagrams would be included in the approximation with singles and doubles.

formulation the latter can be evaluated from the top in the one- and two-body approximation.

In the Hermitian formulation presented here, it can be shown that the single-electron approximation leads to the full random-phase approximation (RPA), including the so-called 'ground-state correlations', while in IN the same approximation leads to the Tamm-Dankoff approximation (TDA) without these correlations. The situation is analogous in higher approximations, and the scheme yields a systematic way of generating approximations beyond RPA.

The present paper is organized as follows. First a review is given in section 2 of the general MBPT—with IN as well as with arbitrary normalization. In section 3 a Hermitian form of MBPT is presented, based on the condition of Jørgensen (1975). The equations for the wave operator and the effective Coulomb interaction are then expressed in a symmetric way in order to guarantee that the Hermiticity is preserved also for a truncated expansion. The effective operator corresponding to an *additional perturbation* is also discussed in this section. In section 4 the *coupled-cluster* formalism is presented, and the connectivity of the cluster operator is demonstrated for a general model space in the Hermitian formulation. In section 5 the one- and two-particle equations and their graphical representation are discussed.

The Jørgensen condition used here is a *sufficient but not necessary* condition for Hermiticity. A more complete analysis of the sufficient *and* the necessary conditions for Hermiticity and connectivity will be given in a forthcoming publication (Chowdhuri *et al* 1991).

2. General wave-operator equation

The *wave operator*, Ω, is defined by the relation

$$\Psi^{(a)} = \Omega \Psi_0^{(a)} \tag{1}$$

where $\Psi^{(a)}$ is a solution of the Schrödinger equation

$$H\Psi^{(a)} = E^{(a)}\Psi^{(a)} \tag{2}$$

and $\Psi_0^{(a)}$ is the corresponding *zero-order function*, confined to a subspace, called *model space*. We assume that the model space has the dimensionality d, and we consider d independent solutions ($a = 1, 2, \ldots, d$). We also assume that the zero-order functions are linearly independent, so that they span the entire model space.

The *effective Hamiltonian*, H_{eff}, is defined so that operating on the zero-order function it generates the corresponding *exact* energy,

$$H_{\text{eff}}\Psi_0^{(a)} = E^{(a)}\Psi_0^{(a)}. \tag{3}$$

Operating on this equation from the left with Ω, we get—using (1, 2)—

$$\Omega H_{\text{eff}}\Psi_0^{(a)} = E^{(a)}\Psi^{(a)} = H\Omega\Psi_0^{(a)}.$$

Since this relation holds for all $a = 1, 2, \ldots, d$, we can write it as an *operator relation*, often referred to as the (generalized) 'Bloch equation'

$$\Omega H_{\text{eff}} P = H\Omega P \tag{4}$$

where P is the *projection operator* for the model space. It follows directly from the definition (3) that the effective Hamiltonian cannot connect the model space with the

orthogonal space $(Q = 1 - P)$

$$QH_{\text{eff}}P = 0. \tag{5}$$

For the purpose of applying perturbation theory we *partition* the Hamiltonian, H, into a *zero-order Hamiltonian*, H_0, and a *perturbation*, V,

$$H = H_0 + V \tag{6}$$

and the effective Hamiltonian similarly into H_0 and an *effective* (*Coulomb*) *interaction*, V_{eff}

$$H_{\text{eff}}P = (H_0 + V_{\text{eff}})P. \tag{7}$$

It then follows that relation (4) can be written in the form of the commutator relation

$$[\Omega, H_0]P = (V\Omega - \Omega V_{\text{eff}})P. \tag{8}$$

By taking the projection onto the model space and the orthogonal space, respectively, we get

$$P[\Omega, H_0]P = P(V\Omega - \Omega V_{\text{eff}})P \tag{9a}$$

$$Q[\Omega, H_0]P = Q(V\Omega - \Omega V_{\text{eff}})P. \tag{9b}$$

The equations above hold in *any* scheme, regardless of the choice of the normalization. In *intermediate normalization* (IN), we have

$$\Psi_0^{(a)} = P\Psi^{(a)} \tag{10}$$

which together with (1) leads to

$$P\Omega P = P. \tag{11}$$

By projecting equation (4) to the left onto the model space, using (11), it follows that the effective Hamiltonian and the effective interaction are in the IN scheme

$$H_{\text{eff}}P = PH\Omega P \qquad V_{\text{eff}}P = PV\Omega P. \tag{12}$$

The relation (8) then becomes

$$[\Omega, H_0]P = (V\Omega - \Omega PV\Omega)P \tag{13}$$

which is a standard form of the wave-operator equation in intermediate normalization and the basis for several developments of MBPT using that scheme (Lindgren 1974, Kvasnicka 1974, 1977, Lindgren and Morrison 1986). Equation (8) is a generalization of this equation, valid in any scheme.

In the IN scheme the P projection (9a) of the commutator relation (8), (13) vanishes, and the wave operator can be generated by solving recursively the Q projection (9b) only. In the general case, on the other hand, the P projection is also non-vanishing, and both equations have to be treated simultaneously. Writing the wave operator in the form

$$\Omega = 1 + \chi \tag{14}$$

and using the relation (6), the projections (9) can be expressed

$$P[\Omega, H_0]P = P(V\Omega - V_{\text{eff}} - \chi V_{\text{eff}})P \tag{15a}$$

$$Q[\Omega, H_0]P = Q(V\Omega - \chi V_{\text{eff}})P. \tag{15b}$$

We have here used the fact that

$$QV_{\text{eff}}P = 0 \tag{16}$$

which follows directly from (5) and (7). In the recursive process the P projection (15a) is used to determine V_{eff}

$$V_{\text{eff}}P = P(V\Omega - \chi V_{\text{eff}} - [\Omega, H_0])P. \tag{17}$$

The P part (closed part) of the commutator appearing in this equation is determined by the choice of normalization and vanishes in IN. Note that it vanishes also for a degenerate model space, and that in the general case only elements of Ω between different zero-order energy appear in the effective interaction.

3. Hermitian form of the effective Hamiltonian

3.1. The Jørgensen condition

In order to find a formulation of MBPT with a Hermitian effective Hamiltonian, we start from the Schrödinger equation (2) in the form

$$H\Omega\Psi_0^{(a)} = E^{(a)}\Omega\Psi_0^{(a)} \tag{18}$$

and operate from the left with an operator X

$$XH\Omega\Psi_0^{(a)} = E^{(a)}X\Omega\Psi_0^{(a)}. \tag{19}$$

Then we see from definition (3) that the effective Hamiltonian is given by

$$H_{\text{eff}}P = XH\Omega P \tag{20}$$

provided

$$X\Omega P = P. \tag{21}$$

$X = P$ leads to the IN scheme (12) with $P\Omega P = P$. Another possible choice is $X = \Omega^{-1}$, which obviously satisfies (21) (Mukherjee 1989) and gives

$$H_{\text{eff}}P = \Omega^{-1}H\Omega P. \tag{22}$$

One way of making H_{eff} manifestly Hermitian is to set $X = P\Omega^{\dagger}$, which leads to

$$H_{\text{eff}}P = P\Omega^{\dagger}H\Omega P \tag{23}$$

and

$$P\Omega^{\dagger}\Omega P = P \qquad \text{or} \qquad P(\chi^{\dagger} + \chi + \chi^{\dagger}\chi)P = 0. \tag{24}$$

This is the 'isometry condition' of (Jørgensen (1975), which we shall use in the following. Since only the Hermitian part of $P\chi P$ is determined by this relation, there is some additional degree of freedom. The condition (24) has also been utilized in coupled-cluster developments by Kvasnicka (1981, 1982) and by Haque and Mukherjee (1985) (see also Mukherjee 1989).

The zero-order functions satisfy the eigenvalue equation (3), and it then follows that in the Hermitian scheme the *zero-order functions are orthogonal.*

In order to demonstrate explicitly that condition (24) actually leads to Hermiticity, we consider again the effective-operator diagrams (a) and (b) in figure 1. Diagrams of the same kind will appear in $P\chi^{\dagger}\chi P$, when two first-order wave-operator diagrams of $\chi^{\dagger}$ and χ are combined to form a closed diagram, as illustrated in figure 1(c). This diagram has a *double denominator*, $(A-C)(B-C)$, and inserted into the commutator in (18) this yields $(A-B)/(A-C)(B-C)$. This compensates exactly for the non-Hermiticity of the two effective-operator diagrams (a) and (b), regardless of the non-Hermitian part of χ.

3.2. The effect of truncation

We have shown above that the Jørgensen condition (24) leads to Hermitian effective operators when *all* effects are considered. It may still happen, however, that non-Hermiticity is introduced by truncation at a certain level. Using the partitioning (6) and the definition (7) of V_{eff}, we find from (23) and (24) that

$$\begin{aligned} H_{\text{eff}}P &= P\Omega^{\dagger}(H_0+V)\Omega P = P(\Omega^{\dagger}\Omega H_0+\Omega^{\dagger}[H_0,\Omega]+\Omega^{\dagger}V\Omega)P \\ V_{\text{eff}}P &= P(\Omega^{\dagger}V\Omega-\Omega^{\dagger}[\Omega,H_0])P. \end{aligned} \tag{25}$$

The last expression is identical to (17), when all effects are considered, but not necessarily so for a *truncated* expansion. Expression (25) is identical to (23) and therefore—in contrast to (17)—*Hermitian at each level of truncation.*

In order to demonstrate the relation between the two expressions (17) and (25) for V_{eff}, we operate on the wave-operator equation (8) from the left by $\Omega^{\dagger}$

$$\Omega^{\dagger}[\Omega,H_0]P = (\Omega^{\dagger}V\Omega-\Omega^{\dagger}\Omega V_{\text{eff}})P \tag{26a}$$

and move $\chi^{\dagger}[\Omega,H_0]P$ to the right-hand side

$$[\Omega,H_0]P = (\Omega^{\dagger}V\Omega-\Omega^{\dagger}\Omega V_{\text{eff}}-\chi^{\dagger}[\Omega,H_0])P. \tag{26b}$$

The Q projection of this equation yields

$$Q[\Omega,H_0]P = Q(\Omega^{\dagger}V\Omega-\Omega^{\dagger}\Omega V_{\text{eff}}-\chi^{\dagger}[\Omega,H_0])P \tag{26c}$$

while the P projection yields the expression (25).

In the equations (25) and (26) there are large cancellations between the different terms on the right-hand side, and therefore these equations are less convenient to use as they stand. For that reason we rewrite (26*b*) as an extension of (8)

$$[\Omega,H_0]P = (V\Omega-\Omega V_{\text{eff}}+\chi^{\dagger}(V\Omega-\Omega V_{\text{eff}}-[\Omega,H_0]))P. \tag{27}$$

Of course, due to relation (8), the 'extension term' here vanishes identically, if all contributions are considered. This is *not* the case for a *truncated* expansion, however, the reason being that *intermediate states* can reach beyond the approximation used. For instance, in the one- and two-body approximation considered above (figure 2), $V\Omega$ may contain triple excitations, which are reduced to double or single excitations by $\chi^{\dagger}$. Hence, the inner bracket in (27) will not cancel exactly at each level of approximation, and this introduces additional terms compared with the original equation (8). In this way diagrams like that in figure 2(*d*) will be produced and included in the wave operator in the approximation with singles and doubles.

In order to express the appearance of the additional terms more explicitly, we write the 'extended' equation (27) as

$$[\Omega,H_0]P = (V\Omega-\Omega V_{\text{eff}}+\chi^{\dagger}(V\Omega-\Omega V_{\text{eff}})_{+})P \tag{28}$$

where the subscript '+' is used to indicate effects *beyond the approximation used.* Obviously, the commutator $[\Omega,H_0]$ does not contain any such contributions. The Q and P projections of this equation lead to

$$Q[\Omega,H_0]P = Q(V\Omega-\chi V_{\text{eff}}+\chi^{\dagger}(V\Omega-\Omega V_{\text{eff}})_{+})P \tag{29a}$$

$$PV_{\text{eff}}P = P(V\Omega-\chi V_{\text{eff}}-[\Omega,H_0]+\chi^{\dagger}(V\Omega-\Omega V_{\text{eff}})_{+})P. \tag{29b}$$

The correction term represents the difference between the standard expressions (9) and (17) and the 'extended' ones (25) and (26). It vanishes when all effects are considered, but it has the important property of making *the effective interaction Hermitian at each level of truncation.*

3.3. Additional perturbation

The effect of an *additional perturbation*, h, on the effective Hamiltonian can be obtained by making the substitution

$$H \to H + h \tag{30}$$

and looking for the corresponding change of H_{eff}

$$H_{\text{eff}} \to H_{\text{eff}} + h_{\text{eff}}. \tag{31}$$

h_{eff} is the h-dependent part of the new effective Hamiltonian and is called the *effective operator*, corresponding to the perturbation h. Assuming that substitution (30) leads to the following change in the wave operator

$$\Omega \to \Omega + \Omega_h \tag{32}$$

we find that the form (23) of the effective Hamiltonian leads to

$$h_{\text{eff}} = P(\Omega_h^\dagger H\Omega + \Omega^\dagger H\Omega_h + \Omega^\dagger h\Omega)P \tag{33}$$

considering only terms *linear* in h. Using relation (4) and its Hermitian adjoint, this can be written

$$h_{\text{eff}} = P(\Omega_h^\dagger \Omega H_{\text{eff}} + H_{\text{eff}}\Omega^\dagger\Omega_h + \Omega^\dagger h\Omega)P. \tag{34}$$

The first two terms are here the Hermitian adjoints of each other, so the result can be expressed

$$h_{\text{eff}} = P(2\times\text{herm part}\,\{\Omega_h^\dagger \Omega H_{\text{eff}}\} + \Omega^\dagger h\Omega)P. \tag{35}$$

However, it follows from the Jørgensen condition (24) that

$$P(\Omega_h^\dagger\Omega + \Omega^\dagger\Omega_h)P = 0 \tag{36}$$

again considering only terms linear in h. Hence, the Hermitian part of $\Omega_h^\dagger\Omega$ vanishes, and we have in first order in h

$$h_{\text{eff}} = P\Omega^\dagger h\Omega P. \tag{37}$$

4. Coupled-cluster expansion. Proof of connectivity

4.1. General criteria for connectivity

The equations obtained above can be transformed into the coupled-cluster (CC) formalism following essentially the standard procedure. We start with the '*normal-ordered exponential ansatz*' (Lindgren 1978)

$$\Omega = \{\exp S\} = 1 + S + \tfrac{1}{2}\{S^2\} + \ldots \tag{38}$$

where the curly brackets are used to denote normal-ordering in the second-quantized (particle-hole) formalism (Lindgren and Morrison 1986). Equations for the cluster operator, S, corresponding to those of Ω given above, can then be derived, and, following the procedure of Mukherjee (1986a) and Lindgren and Mukherjee (1987), it will be shown below that the cluster operator can be *connected* for a general (incomplete) model space also in the Hermitian formulation.

We start by considering the basic equation (4) as a *Fock-space relation*

$$\Omega H_{\text{eff}} = H\Omega \tag{39}$$

implying that it holds for each *valence sector* (m) separately (*valence universality*)

$$(\Omega H_{\text{eff}})^{(m)} = (H\Omega)^{(m)}. \tag{40}$$

With a valence sector we understand all terms in the second-quantized formulation with a certain number of valence-electron absorption operators (or diagrams with a certain number of incoming valence lines). We consider only terms which give a non-zero result when operating to the right on P or on any of the 'subduced' model spaces, $P^{(m)}$ with $m < n$, obtained by removing one or several valence electrons from the original model space $P = P^{(n)}$ with n valence electrons. The m-valence sector can then be defined also as the collection of terms which give a non-zero result when operating to the right on $P^{(m)}$. (For simplicity we assume here that all valence electrons are of *particle* type. The formalism can easily be extended to the more general case with valence particles as well as *valence holes*, following the procedure of Lindgren and Mukherjee (1987).)

Relation (40) can be written in the form (see (A.1) in the appendix)

$$\{\overline{\Omega H_{\text{eff}}}\,\Omega\} = \{\overline{H\Omega}\,\Omega\} \tag{41}$$

where $\overline{H\Omega}$ ($\overline{\Omega H_{\text{eff}}}$) represents the part of $H\Omega(\Omega H_{\text{eff}})$ that is connected if S (and H_{eff}) are connected. (S or H_{eff} need not be connected at this stage.) Since this is a Fock-space relation, all terms are linearly independent. Therefore, the relation will hold for the connected parts separately,

$$\overline{\Omega H_{\text{eff}}} = \overline{H\Omega} \tag{42}$$

as before, considering only terms operating to the right on $P^{(m)}$ $(m \leqslant n)$. (The curly brackets are here deleted, since it is assumed that connected terms are always normal ordered.) With the partitioning (6) and (7) it then follows that

$$\overline{H_0\Omega} - \overline{\Omega H_0} = \overline{V\Omega} - \overline{\Omega V_{\text{eff}}}.$$

Assuming that H_0 is a one-body operator, it can connect only one S operator, giving

$$[S, H_0] = \overline{V\Omega} - \overline{\Omega V_{\text{eff}}}. \tag{43}$$

This is the cluster equation, corresponding to the wave-operator equation (8) above. (Note that the right-hand side is here connected in the sense that there are connections with all S operators in Ω, while the connectivity of S itself or of V_{eff} has not yet been shown.)

A *necessary* condition for connectivity for a general model space is that the effective Hamiltonian has no ('dummy') valence lines, not connected to the rest of the diagram (Lindgren and Mukherjee 1987). This has the consequence that relation (16) must hold for each valence sector separately,

$$QV_{\text{eff}}^{(m)}P = 0. \tag{44}$$

No part of V_{eff} is allowed to connect the P space with the orthogonal Q space, which with our definition implies that V_{eff} *must be closed.* We shall also follow the terminology of Mukhopadhyay and Mukherjee (1989) and refer to a term as '*quasi-open*', if it can excite from the model space into the *complementary model space*, $\bar{P}$, which together with P forms a complete model space. (We still use the definition $P + Q = 1$, so that $\bar{P}$ is a part of the Q space.) In defining $\bar{P}$ we disregard the exclusion principle. For instance, with a model space s^2d, an excitation $d \rightarrow s$ is defined as quasi-open, although it cannot operate by itself on the model space.

Sufficient conditions for connectivity can be derived from the P and Q projections of (43), considering one valence sector at a time (with $\Omega = 1 + \chi$),

$$Q[S, H_0]^{(m)}P = Q(\overline{V\Omega} - \overline{\chi V_{\text{eff}}})^{(m)}P \tag{45a}$$

$$PV_{\text{eff}}^{(m)}P = P(\overline{V\Omega} - \overline{\chi V_{\text{eff}}} - [S, H_0])^{(m)}P. \tag{45b}$$

The last equation refers to the *closed* components, while the first equation determines the *open* as well as *quasi-open* components, with the definitions given above. The relation between the closed parts of S and V_{eff} is not regulated here but is determined by the choice of normalization. It can now be shown by induction that S as well as V_{eff} is connected, *provided the closed part of S is connected* (Lindgren and Mukherjee 1987). We shall now show that this condition is compatible with the Hermiticity condition of Jørgensen (24).

4.2. Connectivity and Hermiticity

In our Fock-space treatment the various valence sectors are linearly independent, and the Jørgensen condition must then hold for each sector separately (Haque and Mukherjee 1985, Mukherjee 1989)

$$P(\Omega^\dagger\Omega)^{(m)}P = P. \tag{46}$$

In the appendix (section A.2) the following relation is shown

$$\Omega^\dagger\Omega = \{\exp W\} \qquad \text{with } W = S^\dagger + S + \overline{\chi^\dagger\chi} \tag{47}$$

where $\overline{\chi^\dagger\chi}$ represents the part of $\chi^\dagger\chi$ which is connected if S is connected. In our treatment this relation holds also for each valence sector separately. For a *complete model space* the closed part of $\{\exp W\}$ is given by the closed part of W, and hence a necessary and sufficient condition for the extended Jørgensen condition (46) in that special case is that the closed part of W vanishes, or

$$P(S^\dagger + S)^{(m)}P = -P(\overline{\chi^\dagger\chi})^{(m)}P. \tag{48}$$

Since $\overline{\chi^\dagger\chi}$ is rigorously connected, if S is connected, the conditions for connectivity given above can be satisfied with this subsidiary condition. Hence, *the conditions for connectivity and Hermiticity are compatible for a complete model space.*

The situation is somewhat more complicated for a general *incomplete model space*, since quasi-open terms may here form a closed combination *without* any contraction. Obviously, the Jørgensen condition (46) is satisfied, if all closed and quasi-open parts of W vanish. However, the non-diagonal, quasi-open part of S is given by (45*a*) and *cannot* be chosen freely. Below we shall show that the two conditions are in fact compatible also for a general model space.

From (44) it follows that $\bar{P}V_{\text{eff}}^{(m)}P = 0$, and Hermiticity requires that also

$$PV_{\text{eff}}^{(m)}\bar{P} = 0. \tag{49}$$

From equation (26*a*) and its Hermitian adjoint in the Fock-space formulation we get, assuming V_{eff} to be Hermitian

$$\Omega^\dagger[\Omega, H_0] = (\Omega^\dagger V\Omega - \Omega^\dagger\Omega V_{\text{eff}}) \tag{50a}$$

$$[H_0, \Omega^\dagger]\Omega = (\Omega^\dagger V\Omega - V_{\text{eff}}\Omega^\dagger\Omega). \tag{50b}$$

This leads to

$$[\Omega^\dagger\Omega, H_0] = [V_{\text{eff}}, \Omega^\dagger\Omega] \tag{51}$$

and, using relation (47), we have in analogy with (41)

$$[V_{\text{eff}}, \Omega^{\dagger}\Omega] = [V_{\text{eff}}, \{\exp W\}] = \{(\overline{V_{\text{eff}}\{\exp W\}} - \overline{\{\exp W\}V_{\text{eff}}}) \exp W\}. \tag{52a}$$

In the connected parts there are connections between V_{eff} and all W operators in $\{\exp W\}$ but no connection between the W operators in $\{\exp W\}$. Similarly, we get

$$[\Omega^{\dagger}\Omega, H_0] = [\{\exp W\}, H_0] = \{(\overline{\{\exp W\}H_0} - \overline{H_0\{\exp W\}}) \exp W\}$$
$$= \{(\overline{WH_0} - \overline{H_0 W}) \exp W\} \tag{52b}$$

since H_0 is assumed to be a one-body operator and can connect only one W operator. This leads with (51) to

$$\{(\overline{WH_0} - \overline{H_0 W}) \exp W\} = \{(\overline{V_{\text{eff}}\{\exp W\}} - \overline{\{\exp W\}V_{\text{eff}}}) \exp W\}$$

and since this is a Fock-space relation, we get in analogy with (42) and (43)

$$[W, H_0] = \overline{V_{\text{eff}}\{\exp W\}} - \overline{\{\exp W\}V_{\text{eff}}}. \tag{53}$$

We assume now that the closed, diagonal elements of $W^{(m)}$, i.e. elements between states of the same energy within the model space, vanish, and we shall show by induction that this leads with (53) to the vanishing of all closed and quasi-open elements of W.

In zero order $W = 1$, and the RHS of (53) vanishes in first order. Hence, also $[W, H_0]$ and the non-diagonal closed and quasi-open elements of W vanish in that order. Therefore, *all* closed and quasi-open elements of W *vanish in first order*. It then follows from (53) that the non-diagonal, closed and quasi-open elements of $[W, H_0]$ vanish in second order, and so on. Hence, the condition that the closed diagonal elements of W vanish has the consequence that *all closed and quasi-open diagrams of W vanish*, which implies that the Jørgensen condition (46) is satisfied. The closed diagonal elements of W can be made zero by choosing the closed part of S according to (48). Therefore, the conditions for Hermiticity and connectivity are compatible also for a general model space.

Assuming connectivity, we can now write the general cluster equation (43) as

$$[S, H_0] = (V\Omega - \Omega V_{\text{eff}})_{\text{c}} \tag{54}$$

where 'c' stands for *rigorously connected diagrams*, and the P and Q projections (45) as

$$Q[S, H_0]^{(m)}P = Q(V\Omega - \chi V_{\text{eff}})_{\text{c}}^{(m)}P \tag{55a}$$

$$V_{\text{eff}}^{(m)}P = P(V\Omega - \chi V_{\text{eff}} - [\Omega, H_0])_{\text{c}}^{(m)}P \tag{55b}$$

where the projections have the same meaning as in (45).

It is of interest to compare the condition of Jørgensen (24)

$$P\Omega^{\dagger}\Omega P = P\{\exp W\}P = P$$

with that of intermediate normalization (11)

$$P\Omega P = P\{\exp S\}P = P.$$

In order to see why the former is compatible with connectivity in the general case while the latter is not, we consider as an example an incomplete model space consisting of the electron configuration sd. The complementary model space, $\bar{P}$, consists here of the configurations $s^2 + d^2$. The excitations $s \rightarrow d$ and $d \rightarrow s$ are then quasi-open, since they lead from P to $\bar{P}$. The combination of the two excitations, on the other hand, is

closed, since it leads back to the model space. If we require S to be connected, we cannot at the same time require $P\chi P$ to vanish. Therefore connectivity is incompatible with intermediate normalization. The situation is different with the Jørgensen condition. It is easy to see that in the first-order W operator, $W^{(1)} = S^{(1)} + S^{(1)\dagger}$, the contributions from the excitations $s \to d$ and $d \to s$ cancel. In second order the corresponding contributions cancel between the terms in $W^{(2)} = S^{(2)} + S^{(2)\dagger} + \overline{S^{(1)\dagger} S^{(1)}}$ and so on. Therefore, there are no elements of W between the model space sd and the complementary model space $s^2 + d^2$, and no combination of disconnected (quasi-)open W operators can lead back to the model space. Hence, the condition $P\{\exp W\}P = P$ is not in conflict with connectivity.

4.3. The 'extended' coupled-cluster equations

We can now derive the coupled-cluster analogue of the 'extended' equations (27)–(29). We start from relation (26*a*) in the Fock-space formulation

$$\Omega^\dagger[\Omega, H_0] = (\Omega^\dagger V\Omega - \Omega^\dagger\Omega V_{\text{eff}}). \tag{56}$$

From relation (A.3) in the appendix we have

$$\Omega^\dagger[\Omega, H_0] = \{(\Omega^\dagger[\Omega, H_0])_c \exp W\} \tag{57a}$$

$$\Omega^\dagger V\Omega = \{(\Omega^\dagger V\Omega)_c \exp W\} \tag{57b}$$

$$\Omega^\dagger\Omega V_{\text{eff}} = \{(\Omega^\dagger\Omega V_{\text{eff}})_c \exp W\} \tag{57c}$$

since S is connected. We then get in analogy with (52)

$$(\Omega^\dagger[\Omega, H_0])_c = (\Omega^\dagger V\Omega - \Omega^\dagger\Omega V_{\text{eff}})_c \tag{58}$$

or

$$([\Omega, H_0])_c = [S, H_0] = (\Omega^\dagger V\Omega - \Omega^\dagger\Omega V_{\text{eff}} - \chi^\dagger[\Omega, H_0])_c. \tag{59}$$

The RHS is here the connected part of the corresponding equation for Ω (26), and in analogy with (28) we can then write this as

$$[S, H_0] = (V\Omega - \Omega V_{\text{eff}} + \chi^\dagger(V\Omega - \Omega V_{\text{eff}})_+)_c \tag{60}$$

where, as before, index '+' indicates terms beyond the approximation used. The projections then lead to the 'extended' coupled-cluster equations, which are the analogues of (29)

$$Q[S, H_0]^{(m)}P = Q(V\Omega - \chi V_{\text{eff}} + \chi^\dagger(V\Omega - \Omega V_{\text{eff}})_+)_c^{(m)}P \tag{61a}$$

$$V_{\text{eff}}^{(m)}P = P(V\Omega - \chi V_{\text{eff}} - [\Omega, H_0] + \chi^\dagger(V\Omega - \Omega V_{\text{eff}})_+)_c^{(m)}P. \tag{61b}$$

4.4. Normalization diagrams

In order to fulfil the extended Jørgensen condition (46), we include closed-cluster diagrams according to (48)

$$P(S^\dagger + S)^{(m)}P = -P(\overline{\chi^\dagger\chi})^{(m)}P. \tag{62}$$

Only the Hermitian part of *PSP* is determined by this relation, while the non-Hermitian part is optional. A few examples of such diagrams are illustrated in figure 3. It should be observed that in evaluating such diagrams there is a *double energy denominator* in

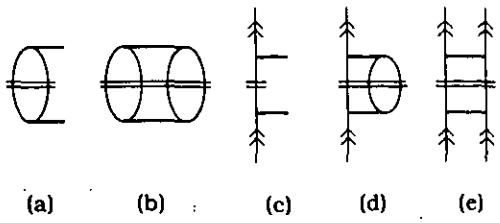

Figure 3. Graphical representation of some closed-cluster diagrams, which appear in order to satisfy the Hermiticity condition (24) and (48). The heavy lines represent the cluster operator S. Note that the diagrams without open valence lines (a) and (b) do not appear in the equations for S or V_{eff} (61). Note also that in the evaluation of these diagrams there is a double denominator in the intermediate state, denoted by the double bar.

the intermediate state, represented by the double bar. The closed S diagrams appear in the P as well as in the Q projections (61) above. The diagrams without any open valence line (a) and (b) do not appear in any equation, since they cannot form connected combinations.

The appearance of the closed S components has the consequence that the linked-diagram theorem has a different formulation in the Hermitian formulation presented here than in intermediate normalization. The wave operator may contain terms with disconnected closed parts. The cluster operator and the effective Hamiltonian, on the other hand, are rigorously connected, as demonstrated above†.

5. One- and two-particle equations

5.1. Single-particle approximation

Let us first consider the single-particle equation in the approximation

$$\Omega_{(1)} = 1 + S_1 + \tfrac{1}{2}\{S_1^2\}. \tag{63}$$

The equation for the single-particle cluster operator S_1 becomes in that approximation

$$[S_1, H_0] = (V + VS_1 + \tfrac{1}{2}VS_1^2 + S_1^\dagger V_2 + S_1^\dagger (VS_1)_2 - S_1 V_{\text{eff},1})_{1,c} \tag{64}$$

where subscript '2' represents two-body effects, which are beyond the approximation (63). This equation is illustrated in figure 4 for an excitation from the core. The single-particle cluster, S_1, can be regarded as an *orbital correction*, and consistent inclusion of that correction is equivalent to using *Brueckner orbitals* (Lindgren *et al* 1976, Ynnerman and Mårtensson-Pendrill 1990). It can be noted that when this formalism is applied to an open-shell system, there will be a symmetric correction to the incoming and outgoing valence lines due to the extension terms.

In figure 5 we have illustrated the single-particle equation for an excitation from the core with an interaction with an unexcited valence electron, leaving out the orbital corrections and the folded diagrams for simplicity. In this approximation, which we recognize as the 'random-phase approximation' (RPA), we observe that the extension

† The extended coupled cluster equations given here were first presented at the *Symp. on Many-Body Methods in Quantum Chemistry* (*Tel Aviv*) August 1988 (Lindgren 1989). Related equations were also discussed at the same symposium by Bartlett *et al* (1989) as a means of evaluating certain classes of diagrams (see also Noga *et al* 1989).

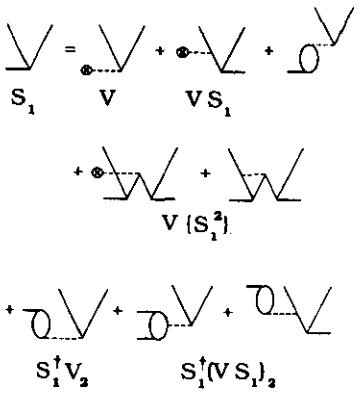

Figure 4. Graphical representation of the single-particle equation for excitation from the core, using the approximation (63). For simplicity the arrows are left out from the orbital lines. Only some representative diagrams are shown. The corresponding representation for excitation from a valence orbital is obtained by turning the incoming line down and adding a 'folded' diagram.

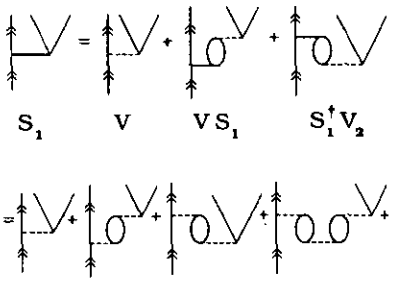

Figure 5. Graphical representation of the single-particle equation for excitation from the core with an interaction with an unexcited valence electron. The valence orbitals are marked with double arrows, while the general particle and hole lines are left unmarked, as before. Orbital corrections are left out as well as folded diagrams. These diagrams represent the random-phase approximation (RPA). Note that the $S_1^\dagger$ operator is needed to generate the 'backward' loops ('ground-state correlation').

term is vital in order to generate the 'backward' loops. Without that term only diagrams with 'forward' loops are generated, known as the Tamm–Dankoff approximation (TDA). The 'backward' loops appearing in RPA involve double excitations in the intermediate states, and the corresponding effect is often referred to as the 'ground-state correlation'. From a physical point of view, however, this is a single-particle effect, which is also manifested by the fact that it can be evaluated by means of a single-particle equation.

5.2. Pair approximation

Next we consider the pair approximation

$$\Omega_{(2)} = 1 + S_1 + S_2 + \tfrac{1}{2}\{S_1^2\} + \{S_1 S_2\} + \tfrac{1}{2}\{S_2^2\}. \tag{65}$$

The equation of S_1 then becomes

$$[S_1, H_0] = (V + VS_1 + VS_2 + \tfrac{1}{2}VS_1^2 + VS_1 S_2 + S_2^\dagger(VS_2)_3 + S_2^\dagger(VS_1^2)_3 + \ldots - S_1 V_{\mathrm{eff},1} - \ldots)_{1,c} \tag{66}$$

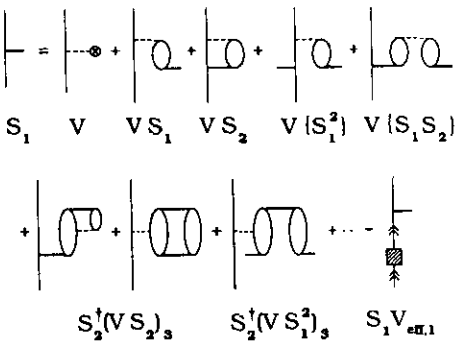

Figure 6. Graphical representation of the single-particle (66) in the approximation (65). The incoming line at the bottom can represent a valence or a core orbital. In the latter case there is no folded diagram.

which is illustrated in figure 6 for a general excitation. We observe here that the diagram in figure 2(d) is generated by the additional term, $S_2^\dagger(VS_2)_3$, while the analogous diagram in figure 2(c) is generated by VS_1. This illustrates the fact, mentioned previously, that the Hermitian procedure presented here yields a more symmetric and more complete expansion at each truncation than the standard procedure with intermediate normalization. In the pair approach, all 'physical' one- and two-body effects are included, represented by those Goldstone diagrams which after factorization can be expressed by means of one- and two-particle functions. In particular, this implies that *all third-order diagrams are included in such a pair approach.*

Similarly, the two-particle equation becomes

$$[S_2, H_0] = (V + VS_1 + VS_2 + \tfrac{1}{2}VS_1^2 + VS_1S_2 + \tfrac{1}{2}VS_2^2 + S_2^\dagger(VS_2^2)_4 + \ldots - S_2V_{\mathrm{eff},1} - S_1V_{\mathrm{eff},2} - S_2V_{\mathrm{eff},2} - \ldots)_{1,c}. \tag{67}$$

Here, the extension terms appear first in fourth order.

6. Summary and conclusions

In the treatment given here we have shown that it is possible to present the coupled-cluster theory in a form which is Hermitian at all truncations. This has the consequence that additional terms, not present in the conventional treatment, appear at each truncation, making these truncations less arbitrary and more 'physical'. It has also been shown that the formulation is compatible with the connectivity criteria for the cluster operator and the effective Hamiltonian for an arbitrary incomplete model space. Numerical tests are now under way of the significance of the new terms of the pair-correlation approach extended in this way, compared with genuine three-body effects left out in any pair approach.

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Appendix

A.1. Proof of the relation $V\Omega = \{\overline{V\Omega}\,\Omega\}$

(The proof here follows essentially that of Lindgren (1978) and Kvasnicka (1982))

Wick's theorem gives

$$V\Omega = \{V\Omega\} + \{\overbrace{V\chi}\}$$

where $\overbrace{V\chi}$ represents all terms with at least one connection between V and χ. With the definition (39) of Ω

$$\Omega = 1 + \chi = \{\exp S\} = \sum_{n=0}^{\infty} \frac{1}{n!}\{S^n\}$$

we get

$$\{\overbrace{V\chi}\} = \sum_{n=1}^{\infty} \frac{1}{n!}\overbrace{V\{S^n\}} = \sum_{n=1}^{\infty}\frac{1}{n!}\sum_{m=1}^{\infty}\binom{n}{m}\{\overline{V\{S^m\}}S^{n-m}\}$$

$$= \sum_{m,n=1}^{\infty}\frac{1}{m!(n-m)!}\{\overline{V\{S^m\}}S^{n-m}\}$$

$$= \left\{\sum_{m=1}^{\infty}\frac{1}{m!}\overline{V\{S^m\}}\sum_{r=0}^{\infty}\frac{1}{r!}\{S^r\}\right\} = \{\overline{V\chi}\Omega\}.$$

The bar represents a single cluster of operators with at least one connection between V and each of the S operators (but, of course, no connection between the latter). Thus

$$\overline{V\chi} = \overbrace{VS} + \frac{1}{2}\overbrace{VSS} + \frac{1}{3!}\overbrace{VSSS}\ldots$$

is the part of $V\chi$ that is connected if S is connected. With

$$V\Omega = V + V\chi$$

we get the final result

$$V\Omega = \{\overline{V\Omega}\,\Omega\}.$$

A.2. Proof of the relation $\Omega^\dagger\Omega = \{\exp W\}$ with $W = S^\dagger + S + \overline{\chi^\dagger\chi}$

Wick's theorem gives

$$\Omega^\dagger\Omega = \{\Omega^\dagger\Omega\} + \{\overbrace{\chi^\dagger\chi}\}$$

where $\{\overbrace{\chi^\dagger\chi}\}$ represents all possible contractions between $\chi^\dagger$ and χ,

$$\{\overbrace{\chi^\dagger\chi}\} = \sum_{m,n=1}^{\infty}\frac{1}{m!\,n!}\{\overbrace{S^{\dagger m}S^n}\}.$$

The contracted part can be separated into one, two, ... connected clusters, disconnected from each other. One such cluster corresponds to

$$\left\{\sum_{m,n=1}^{\infty}\frac{1}{m!\,n!}\sum_{r,s=1}^{\infty}\binom{m}{r}\binom{n}{s}\overline{\{S^{\dagger r}\}\{S^s\}}\{S^{\dagger m-r}\}\{S^{n-s}\}\right\}$$

$$= \left\{\sum_{r,s=1}^{\infty}\frac{1}{r!\,s!}\overline{\{S^{\dagger r}\}\{S^s\}}\sum_{m,n=1}^{\infty}\frac{1}{(m-r)!(n-s)!}\{S^{\dagger m-r}\}\{S^{n-s}\}\right\}$$

$$= \{\overline{\chi^\dagger\chi}\Omega^\dagger\Omega\}$$

where

$$\overbrace{\chi^\dagger\chi} = \overbrace{S^\dagger S} + \tfrac{1}{2}\overbrace{S^\dagger SS} + \tfrac{1}{2}\overbrace{S^\dagger S^\dagger S} + \tfrac{1}{2}\tfrac{1}{2}\overbrace{S^\dagger S^\dagger SS} + \ldots$$

represents the part of $\chi^\dagger\chi$ which is connected if S is connected.

Similarly, two clusters give rise to

$$\frac{1}{2}\left\{ \sum_{r,s=1}^{\infty} \frac{1}{r!\,s!} \overbrace{\{S^{\dagger r}\}\{S^s\}} \sum_{t,u=1}^{\infty} \frac{1}{t!\,u!} \overbrace{\{S^{\dagger t}\}\{S^u\}} \right.$$

$$\left. \times \sum_{m,n=1}^{\infty} \frac{1}{(m-r-t)!\,(n-s-u)!} \{S^{\dagger m-r-t}\}\{S^{n-s-u}\} \right\}$$

$$= \left\{ \tfrac{1}{2}(\overbrace{\chi^\dagger\chi})^2 \Omega^\dagger\Omega \right\}$$

etc. This gives

$$\{\overbrace{\chi^\dagger\chi}\} = \{(\overbrace{\chi^\dagger\chi} + \tfrac{1}{2}(\overbrace{\chi^\dagger\chi})^2 + \ldots)\Omega^\dagger\Omega\} = \{(\exp(\overbrace{\chi^\dagger\chi}) - 1)\exp(S^\dagger + S)\}$$

and the final result

$$\Omega^\dagger\Omega = \{\exp(S^\dagger + S + \overbrace{\chi^\dagger\chi})\}.$$

A.3. Proof of the relation $\Omega^\dagger V\Omega = \{\overbrace{\Omega^\dagger V\Omega}\ \exp W\}$

Wick's theorem gives

$$\Omega^\dagger V\Omega = \{\Omega^\dagger V\Omega\} + \{\overbrace{\chi^\dagger V\chi}\} + \{\Omega^\dagger \overbrace{V\chi}\} + \{\overbrace{\chi^\dagger V}\Omega\} + \{\overbrace{\chi^\dagger V\chi}\}$$

$$+ \{\overbrace{\chi^\dagger \overbrace{V\chi}}\} + \{\overbrace{\overbrace{\chi^\dagger V}\chi}\}$$

where the outer hook in the last two terms indicates that there are also connections between $\chi^\dagger$ and χ not involving V. In analogy with the previous case the following relations can be shown

$$\{\Omega^\dagger V\Omega\} + \{\overbrace{\chi^\dagger V\chi}\} = \{V(\Omega^\dagger\Omega + \overbrace{\chi^\dagger\chi})\} = \{V \exp W\}$$

$$\{\Omega^\dagger \overbrace{V\chi}\} + \{\overbrace{\chi^\dagger \overbrace{V\chi}}\} = \{\overbrace{V\chi}(\Omega^\dagger\Omega + \overbrace{\chi^\dagger\chi})\} = \{\overbrace{V\chi} \exp W\}$$

$$\{\overbrace{\chi^\dagger V}\Omega\} + \{\overbrace{\overbrace{\chi^\dagger V}\chi}\} = \{\overbrace{\chi^\dagger V}(\Omega^\dagger\Omega + \overbrace{\chi^\dagger\chi})\} = \{\overbrace{\chi^\dagger V} \exp W\}$$

$$\{\overbrace{\chi^\dagger \overbrace{V\chi}}\} = \{\overbrace{\chi^\dagger V\chi} \exp W\}$$

which lead to the final result

$$\Omega^\dagger V\Omega = \{\overbrace{\Omega^\dagger V\Omega} \exp W\}.$$

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