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On a note concerning the linked-cluster factorisation in an open-shell theory

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In this note we present a few formulae related to the linked-cluster factorisation in a non-perturbatic approach to the calculation of Correlation energy of a degenerate or nearly degenerate system. A similar theory for the non-degenerate systems has earlier been given by Cizek (1966). With the starting wave-function ψ_0 to be a combination of components ϕ_i of the form

$$|\psi_0> = \sum_i a_i |\phi_i>, \qquad \ldots (1)$$

the *exact* wave-function $|\psi_{ex}>$ may always be generated by the action of an *excitation* operator e^S on ψ_0

$$|\psi_{ex}> = e^S |\psi_0>. \qquad \ldots (2)$$

We have found that the matrix-elements of the operators in S may be determined from the Schrödinger equation for $|\psi_{ex}>$ using various identities and operator equalities. In this connection, we have derived a theorem which is of central importance in providing the desirable property of a linked-cluster factorisation of the relevant equations. The theorem states that, if, for the choice of any of the components ϕ_i as the vacuum the contractions of the operators in $\hat{S}$ are zero, then the following relation holds good

$$He^{\hat{S}} |\phi_i> = e^{\hat{S}} u_i |\phi_i>, \qquad \ldots (3)$$

where H is the Hamiltonian, and u_i is a set of linked contracted operators. Writing $\hat{S}$ in the form

$$\hat{S} = \sum_{p=1}^{N} \hat{S}_p, \qquad \ldots (4)$$

where $\hat{S}_p$ is the p-particle *excitation* operator for an N-electron system, the operator u_i is given by

$$u_i = \sum_{k=0}^{\infty} \frac{1}{k} \sum_{\substack{R_1 = S_1,\, S_N \\ R_k = S_1,\, S_N}} \sum_{\substack{k_1,\, k_2 = 0,\, k \\ k_1 + k_2 = k}} (-1)^{k_1} \{R_1 \ldots Rk_1 (f+v)_i Rk_1+1 \ldots R_k\}_L + <\phi_i | H | \phi_i> \qquad (5)$$

where f and v are the one- and two-particle parts of the Hamiltonian put in *normal order* with respect to ϕ_i as the vacuum. The subscript 'i' on $(f+v)$ denotes that it is dependent on the choice of $|\phi_i>$ as the vacuum. The quantity $\{R_1 \ldots R_{k_1}(f+v)_i R_{k_1+1} \ldots R_k\}_L$ consists of a number of terms, all of which are linked in the sense that the associated product of operators do not factor out as mutually uncontracted subsets.

Using this theorem, the Schrodinger equation may be written in the form

$$He^{\hat{S}}|\psi_0> = e^{\hat{S}} \sum_i C_i u_i |\phi_i> = Ee^{\hat{S}} \sum_i C_i \phi_i, \qquad \ldots (6a)$$

and the exact energy E is given by

$$E = \sum_{i,j} C_i C_j <\phi_j|u_i|\phi_i \qquad \ldots (6b)$$

The equations determining the matrix-elements of $\hat{S}$ may be found out by projecting eq. (6a) onto the excited states $|\phi_m^*>$ orthogonal to all ϕ_i's, and are given by

$$<\phi_m^*|u_i|\phi_i> = 0, \qquad \text{for all } i \text{ and } m. \qquad \ldots (6c)$$

Defining an operator u by the relation

$$u|\phi_i> = u_i|\phi_i>, \qquad \ldots (7)$$

the eq. (6b) may be re-written as follows

$$E = \sum_i C_i C_j <\phi_j|u|\phi_i>. \qquad \ldots (8)$$

The operator u may thus be thought of as an *effective operator* which acting entirely within the space of the components ϕ_i generates the exact energy of the state $|\phi_{ex}>$. From the manner of construction of u_i's, it is clear that they are independent of the coefficients C_i so that for k components $|\phi_i>$, the exact energies E^k of the k states having starting wave-functions $\psi^k{}_0$ may be found out from the relation

$$E^k = \sum_{i,j} C_i{}^k C_j{}^k <\phi_j|u|\phi_i>. \qquad \ldots (9)$$

For states where the coefficients $C_i{}^k$ are determined purely by symmetry, the energies E^k are known whenever u_i's are known. However when $C_i{}^k$'s are not determined by symmetry alone, as is the case for near degenerate systems, they may be found out from the condition that the associated energies E^k are extremum. This leads to an eigen-value equation of the form

$$\sum_i <\phi_j|u|\phi_i> C_i{}^k = E^k C_j. \qquad (10)$$

By choosing the operators in $\hat{S}$ to be anti-hermitean, the effective operator u may always be chosen to be hermitean, so that solution of the eigen-value eq. (10) leads to real energies E and orthonormal wave-functions $\psi_{ex}{}^{k}$. Thus, the use of the theorem described in this note enables one to define an effective operator u, which may be made hermitean, such that it generates the exact energy eigen-values E^k of various states by acting entirely within the space spanned by the components ϕ_t. The restrictions imposed on $\hat{S}$ are fairly trivial, so that the theorem holds true under quite general conditions.

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On the choice of virtual orbitals in a many-body perturbation calculation of pair-correlation energies

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In a perturbation calculation of the Correlation energy, one usually starts with the Hartree-Fock (HF) function as the unperturbed wave-function, and improves on the associated energy by a perturbation expansion. The partition of the total electronic Hamiltonian H into an unperturbed part H_0 and a perturbation H_1 in a perturbation calculation may be achieved in many ways. However, only those partitionings are preferred which keep the perturbation as small as possible. The oldest partitioning is that of Moller and Plesset (MP), where H_0 is taken to be a sum of HF one-electron Hamiltonian. This partition introduces large diagonal matrix-elements of the perturbation in the associated perturbation series and thus suffers from a slow convergence. A vastly better partition is, however, that of Epstein and Nesbet (EN) where H_0 is so chosen that the above matrix-elements do not appear at all. In this partition, the diagonal