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Calculation of the Brueckner Orbitals and Generalized Natural Orbitals

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The diagrammatic-perturbation approach for the construction of the one-particle Hermitian pseudoeigenvalue problem determining the Brueckner orbitals and/or generalized natural orbitals is elaborated.

Key words: Brueckner orbitals – Generalized natural orbitals – Diagrammatic perturbation theory

1. Introduction

The independent-particle model [1] of the N-electron systems can be well established by the Hartree-Fock theory, which is often used as its synonym. Of course, there are other possibilities how to choose the "best" independent-particle wave function (Slater determinant). The most important and useful alternative methods for the determination of an orthonormal set of one-particle functions (orbitals) from which the independent-particle wave function is built up are the following.

1.1. The Brueckner (or Maximum-overlap) Orbitals (BO)

This type of orbitals has been suggested by Brueckner [2] in an attempt to surmount the difficulties associated with hard-core internuclear potential. The BO's are defined in two different (but completely equivalent [8]) ways:

(1) Through the Brillouin-Brueckner condition [3–4], which states that the matrix elements of the reaction operator [5] T (defined for the non-degenerate ground state) between the unperturbed state vector (independent-particle wave function) $|\Phi_0\rangle$ and the mono-excited configurations $X_p^+ X_h|\Phi_0\rangle$ vanish,

$$\langle\Phi_0| T X_p^+ X_h|\Phi_0\rangle = 0\,. \tag{1.1}$$

Here X_p^+ and X_h are creation and annihilation operators, respectively, related to the orthonormal set of BO's.

(2) And the maximum-overlap criterion [6, 7], according to which an overlap between the exact ground-state vector $|\Psi_0\rangle$ and the unperturbed state vector $|\Phi_0\rangle$ is maximized,

$$\langle\Psi_0|\Phi_0\rangle = \max\,. \tag{1.2}$$

If the variation of (1.2) is performed [8], the result is

$$\langle \Psi_0 | X_p^+ X_h | \Phi_0 \rangle = 0 , \tag{1.3}$$

i.e. the mono-excited configurations do not contribute to $|\Psi_0\rangle$. In the recent paper of Paldus *et al.* [9], some interesting points related to stability conditions of (1.2) have been clarified. The same result (and essentialy the same derivation) was discovered independently by Vojtík [10].

1.2. The Natural Orbitals (NO)

These orbitals have been introduced into general theory of N-electron systems by Löwdin [11] for the acceleration of the convergence of the CI-like expansion of the wave function. The NO's are defined through the condition that the first-order density matrix $\gamma \equiv \{\gamma_{ij}\}$ should be diagonal in the space of NO's,

$$\gamma_{ij} = \langle \Psi_0 | X_i^+ X_j | \Psi_0 \rangle = n_i \delta_{ij} . \tag{1.4}$$

The occupation numbers n_i which occure in this equation satisfy the conditions

$$0 \leqq n_i \leqq 1 , \tag{1.5a}$$

$$\sum_i n_i = N . \tag{1.5b}$$

The criterion (1.4) has been modified by Kobe [12] requiring that the number of electrons above (in) the Fermi sea (FS) be minimized (maximized), i.e.

$$N_> = \sum_{p \notin \mathrm{FS}} \langle \Psi_0 | X_p^+ X_p | \Psi_0 \rangle = \min , \tag{1.6a}$$

$$N_< = \sum_{h \in \mathrm{FS}} \langle \Psi_0 | X_h^+ X_h | \Psi_0 \rangle = \max , \tag{1.6b}$$

the total number of electrons is $N = N_< + N_>$. As was pointed out by Schäfer and Weidenmüller [13], it follows from this principle that

$$\gamma_{ph} = \langle \Psi_0 | X_p^+ X_h | \Psi_0 \rangle = 0 , \tag{1.7}$$

together with the complex conjugate condition. Orbitals that satisfy this condition are called *generalized natural orbitlas* [13] (GNO). The NO's are the special case where γ_{ij} are completely diagonal, i.e. $\gamma_{ij} = n_i \delta_{ij}$.

Unfortunately, there are some formal difficulties with the calculation of the BO's or (G) NO's. These difficulties arise from the fact that in their definition the exact wave function (or the exact reaction operator) appears. Thus an exact solution of a given N-electron Schrödinger equation is required for their calculation. In order to avoid this difficulty, a wide variety of approximate methods for the calculation of the BO's [14–18] as well as NO's [19–24] was suggested and applied to small many-electron systems. Indeed, up to the presence, these orbitals are of more theoretical [1, 7, 8, 12] than of practical significance.

Let us now interrupt our introductory remarks and turn our attention to some very interesting conclusions from the recent attempts of the direct calculations

of the low-lying ionization potentials [25–30] as well as excitation energies [30–32] by the diagrammatic perturbation theory, based on the Hartree-Fock orbitals. For the good agreement of the calculated ionization potentials with experimental values, at least the third-order diagrammatic contributions should be taken into account. Moreover, in special cases [26, 27], the third-order diagrammatic contributions should be completed by infinite summations of some pertinent diagrams. A similar situation, and probably even worse, exists also for the excitation energies [31, 32]. Here, even the complete third-order diagrammatic contributions do not provide a satisfactory agreement of the calculated with the exact low-lying excitation energies. A usual way to remove this drawback of the Hartree-Fock orbitals is based on the concept of the "new" renormalized one- and/or two-particle interaction a well-known method in the modern microscopic theory of nuclei [33–38]. The above mentioned infinite summations of some pertinent diagrams may be taken as a rudimentary realization of this concept. Unfortunately, a correct theoretical treatment of the renormalized interactions for finite nonhomogeneous N-electron systems is quite complex problem and contains many unresolved theoretical as well as computational pitfalls. For example, the problem of overcounting of diagrams should be treated very carefully.

From these remarks it follows that the Hartree-Fock theory does not form the best frame for the direct diagrammatic-perturbation calculation of the ionization potentials and excitation energies. In this connection it seems promising to turn attention to another type of the one-particle functions, namely, to the BO's and (G) NO's. This possibility has been shown in the recent works concerning the microscopic theory of nuclei [33–38], to be very closely related to the technique of the renormalized interactions. For example, Brandow [35] and Kirson [39] extensively studied the problem of the acceleration of the convergence of diagrammatic-perturbation expansions. They have introduced a special sort of the one-particle functions, which lie intermediate between BO's and NO's, and ensure that a maximal number of diagrams of the prescribed type is cancelled.

An applicability and potentiality of BO's and/or (G) NO's in the diagrammatic perturbation theory needs, however, that these orbitals should be determined through a one-particle Hermitian eigenvalue problem. Thus, we have obtained a promising linkage between the problem of the direct calculation of the low-lying excitation energies and ionization potentials, and the problem of the construction of the one-particle eigenvalue problem determining the BO's or GNO's, which is the scope of the present communication.

2. Auxiliary Remarks

Let us consider an atomic or molecular N-electron system with fixed skelet on of nuclei. Neglecting relativistic and magnetic effects, and assuming that in the zero-order approximation the above system is described by unperturbed (independent-particle) state vector

$$|\Phi_0\rangle = \prod_{i \in \mathrm{FS}} X_i^+ |0\rangle \,, \tag{2.1}$$

the Hamiltonian H can be written in the form [40]

$$H = \langle \Phi_0 | H | \Phi_0 \rangle + H_0 + H_1 , \tag{2.2a}$$

$$H_0 = \sum_i \varepsilon_i N[X_i^+ X_i] , \tag{2.2b}$$

$$H_1 = \bar{H}_1 - \bar{U} , \tag{2.2c}$$

$$\bar{H}_1 = (1/4) \sum_{ijkl} \langle ij|kl\rangle_A \, N[X_i^+ X_j X_l X_k] , \tag{2.2d}$$

$$\bar{U} = \sum_{ij} \langle i|u|j\rangle \, N[X_i^+ X_j] , \tag{2.2e}$$

where $N[\cdots]$ is the normal product (defined with respect to $|\Phi_0\rangle$) of the creation (X_i^+) and annihilation (X_j) operators, and $\langle ij|kl\rangle_A$ are the antisymmetrized two-particle matrix elements of the Coulomb repulsion between electrons. The creation and annihilation operators are defined on the orthonormal set of orbitals

$$\{|i\rangle; i = 1, 2, \ldots\} , \tag{2.3}$$

which are the eigenfunctions of the one-particle Hermitian characteristic problem

$$f|i\rangle = \varepsilon_i |i\rangle, \langle i|f|j\rangle = \varepsilon_i \delta_{ij} , \tag{2.4}$$

$$\langle i|f|j\rangle = \langle i|f_0|j\rangle + \langle i|u|j\rangle . \tag{2.4b}$$

Here f_0 is the well-known Hartree-Fock operator defined with respect to $|\Phi_0\rangle$. The Hermitian one-particle matrix elements $\langle i|u|j\rangle = \langle j|u|i\rangle^*$ [cf. also Eqs. (2.2c) and (2.2e)] will be specified in the following Section, and will depend on whether we calculate BO's or GNO's.

The perturbed exact ground-state vector $|\Psi_0\rangle$ (normalized in the "intermediate" way, i.e. by the requirement $\langle \Phi_0 | \Psi_0 \rangle = 1$) is, in the framework of the diagrammatic perturbation theory, determined by [41, 42]

$$|\Psi_0\rangle = \exp\left(\sum_{n=1}^{\infty} R_n \right) |\Phi_0\rangle . \tag{2.5}$$

Here the operator R_n generates the n-fold excited unperturbed states (configurations)

$$R_n = (n!)^{-2} \sum_{\substack{h_1 h_2 \ldots h_n \in \mathrm{FS} \\ p_1 p_2 \ldots p_n \notin \mathrm{FS}}} A(p_1 p_2 \ldots p_n; h_1 h_2 \ldots h_n) \, X_{p_1}^+ \ldots X_{p_n}^+ X_{h_n} \ldots X_{h_1} . \tag{2.6}$$

The matrix elements $A(p_1 \ldots; \ldots h_n)$ are determined by the following diagrammatic-perturbation expansion formula [41, 42]

$$A(p_1 p_2 \ldots p_n; h_1 h_2 \ldots h_n) = \sum_{q=0}^{\infty} A^{(q)}(p_1 p_2 \ldots p_n; h_1 h_2 \ldots h_n) , \tag{2.7a}$$

$$\begin{aligned} A^{(q+1)}(p_1 p_2 \ldots p_n; h_1 h_2 \ldots h_n) &= (\varepsilon_{h_1} + \varepsilon_{h_2} + \cdots + \varepsilon_{h_n} - \varepsilon_{p_1} - \varepsilon_{p_2} - \cdots - \varepsilon_{p_n})^{-1} \\ &\cdot \langle \Phi_0 | X_{h_1}^+ X_{h_2}^+ \ldots X_{h_n}^+ X_{p_n} \ldots X_{p_2} X_{p_1} H_1 \left(\frac{1}{-H_0} H_1 \right)^q |\Phi_0\rangle_{LC} , \end{aligned} \tag{2.7b}$$

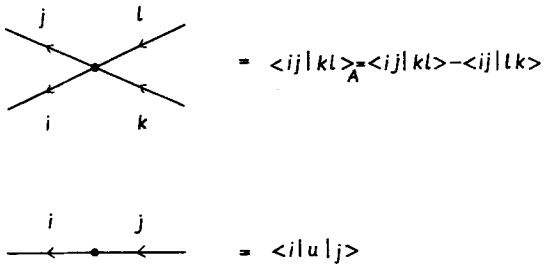

Fig. 1. The two- and one-particle vertices in the Hugenholtz graphology

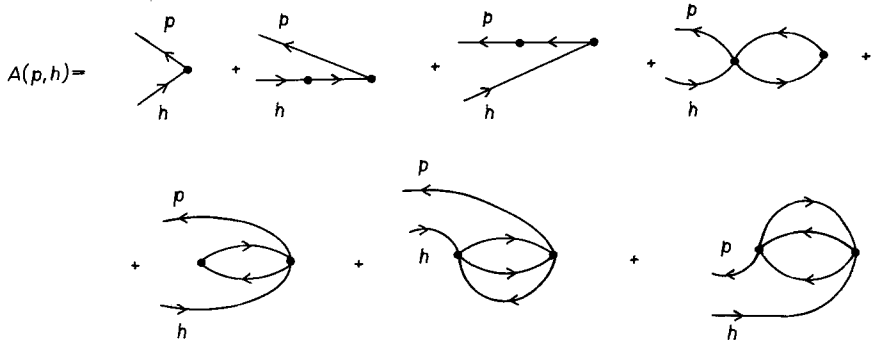

Fig. 2. Hugenholtz' diagrams contributing to the coefficient $A(p, h)$ up to the second order

where the subscript LC means that only linked-connected diagrams contribute (we use the Hugenholtz [41, 42] diagrammatic technique and his classification of diagrams, cf. also Fig. 1). For the 1 hole-1 particle case (when $n = 1$), this formula can be rewritten in the following form (cf. also Fig. 2)

$$A(p, h) = (\varepsilon_h - \varepsilon_p)^{-1} [- \langle p| u|h\rangle + \tilde{A}(p, h)], \tag{2.8a}$$

$$\tilde{A}(p, h) = \sum_{q=1}^{\infty} \langle \Phi_0| X_h^+ X_p H_1 \left(\frac{1}{-H_0} H_1\right)^q |\Phi_0\rangle_{LC}, \tag{2.8b}$$

where the matrix elements $\tilde{A}(p, h)$ express the higher-order contributions than first-order contributions to $(\varepsilon_h - \varepsilon_p) A(p, h)$.

Now, we turn our attention to the diagrammatic-perturbation calculation of the first-order reduced density matrix corresponding to the exact ground state. According to Thouless'linked-cluster theorem [43], the matrix elements γ_{ij} of the exact first-order reduced density matrix are equal to

$$\gamma_{ij} = \gamma_{ij}^{(0)} + \sum_{n=0}^{\infty} \langle \Phi_0| Y \left(\frac{1}{-H_0} Y\right)^n |\Phi_0\rangle_{C_{ij}}, \tag{2.9}$$

where $\gamma_{ij}^{(0)}$ is the zero-order (Hartree-Fock approximation) density matrix determined by

$$\gamma_{ij}^{(0)} = \begin{cases} \delta_{ij} & \text{for} \quad i, j \in \text{FS}, \\ 0 & \text{other cases}. \end{cases} \tag{2.10}$$

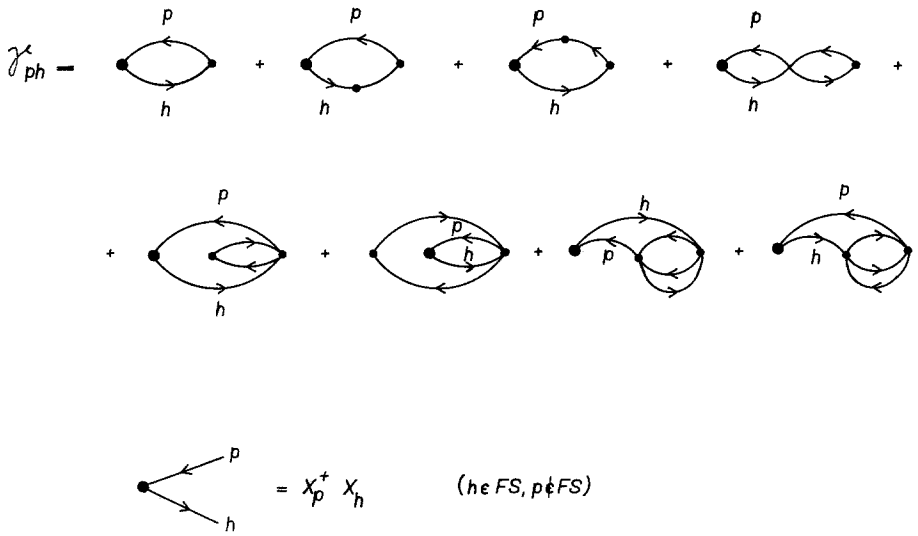

Fig. 3. The first and second order diagrammatic contributions to the element γ_{ph} of the first-order reduced density matrix. The heavy black dots correspond to the "virtual" one-particle vertex

The operator Y is equal either to $X_i^+ X_j$ or H_1 in such a way that the vertex corresponding to $X_i^+ X_j$ occurs only once in all succesive places. The subscript C_{ij} means that only those ground-state connected diagrams contribute in which summations corresponding to the hole and/or particle "external" lines where indices i and j are omitted. The Hugenholtz diagrams contributing to γ_{ph} ($h \in$ FS, $p \notin$ FS) up to the second order are illustrated in Fig. 3. Then, by using the rules of Hugenholtz' graphology [41, 42], we obtain from this diagrammatic expression

$$\gamma_{ph} = (\varepsilon_h - \varepsilon_p)^{-1} (-\langle p|\, u|h\rangle + \tilde{\gamma}_{ph}), \tag{2.11a}$$

$$\tilde{\gamma}_{ph} = (\varepsilon_h - \varepsilon_p) \sum_{n=1}^{\infty} \langle \Phi_0|\, Y \left(\frac{1}{-H_0} Y \right)^n |\Phi_0\rangle_{C_{ph}}. \tag{2.11b}$$

Here the matrix elements $\tilde{\gamma}_{ph}$ express the higher-order contributions than first-order contributions to $(\varepsilon_h - \varepsilon_p)\, \gamma_{ph}$.

3. Construction of the One Particle Pseudoeigenvalue Problem

As we have mentioned in Section 1, BO's can be determined by the Condition (1.3), which states that the exact ground-state vector does not contain the mono-excited configurations (1 particle- 1 hole unperturbed state vectors). Explicitly,

$$R_1 = 0, \tag{3.1}$$

where R_1 is the operator defined by (2.6) generating the mono-excited configurations in the linked-cluster expansion formula (2.5). According to (2.6) the necessary

and sufficient conditions for (3.1) are

$$A(p, h) = 0\,, \tag{3.2}$$

for all possible $p \notin \mathrm{FS}$ and $h \in \mathrm{FS}$. According to (2.8a) the above property is equivalent to

$$\langle p|\, u|h\rangle = \tilde{A}(p, h)\,, \tag{3.3}$$

where the quantities $\tilde{A}(p, h)$ are defined by (2.8b). The Condition (3.3) determines the matrix elements $\langle p|\, u|h\rangle$. Similarly, from the Hermitian conjugated form of (3.1), $R_1^+ = 0$, we obtain $\langle h|\, u|p\rangle = \tilde{A}(p, h)^*$, i.e.

$$\langle p|\, u|h\rangle = \langle h|\, u|p\rangle^*\,. \tag{3.4}$$

Accordingly, the "off-diagonal blocks" of the matrix elements $\{\langle p|\, u|h\rangle;\, p \notin \mathrm{FS},\, h \in \mathrm{FS}\}$ form a part of a Hermitian matrix. Thus, starting from the general Condition (3.1) determining the BO's we have determined the matrix elements $\langle p|\, u|h\rangle$ from the one-particle pseudoeigenvalue problem (2.4).

A similar approach may be used for the construction of the matrix elements $\langle p|\, u|h\rangle$ in the case of GNO's. Substitution of the Conditions (1.7) into (2.11a) gives

$$\langle p|\, u|h\rangle = \tilde{\gamma}_{ph}\,, \tag{3.5}$$

for all possible $p \notin \mathrm{FS}$ and $h \in \mathrm{FS}$. Here the Hermitian matrix elements $\tilde{\gamma}_{ph} = \tilde{\gamma}^*_{hp}$ are defined by (2.11b), i.e. the Condition (3.4) is automatically satisfied also for GNO's.

To summarize, starting from the Condition (1.3) or (1.7) we have obtained two alternative definitions of the matrix elements $\langle p|\, u|h\rangle$ from the one-particle psuedoeigenvalue problem (2.4) defining the orthonormal set either BO's or GNO's. For complete specification of the corresponding pseudoeigenvalue problem (2.4) we must know also "diagonal blocks" of the matrix elements $\{\langle p|\, u|p'\rangle;\, p, p' \notin \mathrm{FS}\}$ and $\{\langle h|\, u|h'\rangle;\, h, h' \in \mathrm{FS}\}$. Furthermore, as follows from the diagrammatic expressions for the matrix elements $\tilde{A}(p, h)$ and $\tilde{\gamma}_{ph}$ (cf. also Figs. 2 and 3), the matrix elements $\langle p|\, u|h\rangle$ are implicitly determined through the matrix elements $\langle h|\, u|h'\rangle$ and $\langle p|\, u|p'\rangle$. Unfortunately, these matrix elements are not determined directly by the Conditions (1.3) and (1.7). This paradoxical observation is in close relation to the fact that Conditions (1.3) and (1.7) describe merely a factorization of the space of orbitals into two orthogonal subspaces, namely, into the subspace of the occupied (within FS) and the subspace of the unoccupied (above FS) orbitals, respectively. Moreover, the Conditions (1.3) and (1.7) are invariant with respect to separate unitary transformations of the occupied and/or unoccupied orbitals. Physically relevant is only the above mentioned factorization uniquely determined by the matrix elements $\langle p|\, u|h\rangle$. The remaining matrix elements $\langle p|\, u|p'\rangle$ and $\langle h|\, u|h'\rangle$ where $h, h' \in \mathrm{FS}$ and $p, p' \notin \mathrm{FS}$ determine only an additional factorization within the subspaces of the occupied and unoccupied orbitals, respectively. A similar situation exists also in the Hartree-Fock theory based on the Brillouin theorem [44]. This theorem can be reduced to the form $\langle p|\, f_0|h\rangle = 0$, where f_0 is the Hartree-Fock operator defined with respect to $|\Phi_0\rangle$, and $h \in \mathrm{FS}$, $p \notin \mathrm{FS}$. Thus, the Brillouin theorem, similarly as the Condi-

tions (1.3) and (1.7), serves only as a factorization procedure of the orbitals into two orthogonal subspaces of the occupied and unoccupied orbitals. However, in the Hartree-Fock theory the situation is simpler than in the theory of the BO's or GNO's, since the explicit form of the Hartree-Fock operator f_0 is known. Postulating the "canonical" Hartree-Fock orbitals [44] (i.e. $\langle i|f_0|j\rangle = \varepsilon_i \delta_{ij}$), the Brillouin theorem is automatically satisfied. Unfortunately, in the theory of BO's as well as GNO's this approach cannot be used because the one-particle operator u is defined only through its matrix elements $\langle i|u|j\rangle$.

For an additional specification of the matrix elements $\langle h|u|h'\rangle$ and $\langle p|u|p'\rangle$ let us introduce an "ideal" requirement, that the one-particle energy ε_i be exactly equal to either minus ionization potential (for $i \in$ FS) or electron affinity (for $i \notin$ FS),

$$\varepsilon_h = -(IP)_h \quad (\text{for all } h \in \text{FS}), \tag{3.6a}$$

$$\varepsilon_p = (EA)_p \quad (\text{for all } p \notin \text{FS}). \tag{3.6b}$$

Here $(IP)_h = E_h(N-1) - E_0(N)$ is the "one-hole" ionization potential, $E_h(N-1)$ is the perturbed energy of $(N-1)$-electron system described in the zero-order approximation by $|\Phi_h\rangle = X_h|\Phi_0\rangle$, and $E_0(N)$ is the perturbed ground-state energy of original N-electron system.

Similarly, $(EA)_p = E_p(N+1) - E_0(N)$ is the "one-particle" electron affinity, $E_p(N+1)$ is the perturbed energy of $(N+1)$-electron system described in the zero-order approximation by $|\Phi_p\rangle = X_p^+|\Phi_0\rangle$. These both Conditions (3.6a) and (3.6b) are a generalization of the well-known Koopmans' theorem [45], which is valid in the Hartree-Fock theory only up to the first order.

For the construction of the matrix elements $\langle p|u|p'\rangle$ and $\langle h|u|h'\rangle$ satisfying Conditions (3.6a) and (3.6b), we now use the quasi-degenerate Rayleigh-Schrödinger perturbation theory [46]. Its main features have been published recently [29, 32], and therefore they will not be repeated here (cf. also Ref. [47]). Let us define two types of the model spaces, the "one-particle" model space

$$\Omega_0^{(+)} \equiv \{|\Phi_p\rangle = X_p^+|\Phi_0\rangle; \quad \text{for all} \quad p \notin \text{FS}\}, \tag{3.7a}$$

and the "one-hole" model space

$$\Omega_0^{(-)} \equiv \{|\Phi_h\rangle = X_h|\Phi_0\rangle; \quad \text{for all} \quad h \in \text{FS}\}. \tag{3.7b}$$

The projectors on these spaces are defined by

$$P_0^{(+)} = \sum_{p \notin \text{FS}} |\Phi_p\rangle\langle\Phi_p| = \sum_{p \notin \text{FS}} P_0(p), \tag{3.8a}$$

$$P_0^{(-)} = \sum_{h \in \text{FS}} |\Phi_h\rangle\langle\Phi_h| = \sum_{h \in \text{FS}} P_0(h). \tag{3.8b}$$

According to the above mentioned fact that the orbitals (BO's or GNO's) within the subspaces of the occupied and unoccupied one-particle states, respectively, are determined only up to an unitary transformation, the two model eigenvalue problems [29, 30, 46] defined in the model spaces $\Omega_0^{(+)}$ and $\Omega_0^{(-)}$ can be written in the form

$$(H_0 + G_{RS}^{(+)LC})|\Phi_p\rangle = \varepsilon_p|\Phi_p\rangle, \tag{3.9a}$$

$$(H_0 + G_{RS}^{(-)LC})|\Phi_h\rangle = -\varepsilon_h|\Phi_h\rangle, \tag{3.9b}$$

where the eigenvalues ε_p and $-\varepsilon_h$ satisfy the Conditions (3.6a) and (3.6b). The operators $G_{RS}^{(\pm)LC}$ are defined in the framework of the diagrammatic perturbation theory by

$$\langle \Phi_\alpha | G_{RS}^{(\pm)LC} | \Phi_\beta \rangle = \langle \Phi_\alpha | G_{RS}^{(\pm)} | \Phi_\beta \rangle_{LC}, \tag{3.10}$$

$|\Phi_{\alpha,\beta}\rangle \in \Omega_0^{(\pm)}$, the subscript LC means [cf. also Eq. (2.7b)] that only linked-connected diagrams contribute, and $G_{RS}^{(\pm)}$ are the Hermitian model interactions defined as follows [46]

$$G_{RS}^{(\pm)} = P_0^{(\pm)} H_1 P_0^{(\pm)} + \tilde{G}_{RS}^{(\pm)}, \tag{3.11a}$$

$$\tilde{G}_{RS}^{(+)} = \frac{1}{2} \sum_{p \notin \mathrm{FS}} \left\{ P_0^{(+)} H_1 \frac{1 - P_0^{(+)}}{\varepsilon_p - H_0} H_1 P_0(p) + h.c. \right\} + \cdots, \tag{3.11b}$$

$$\tilde{G}_{RS}^{(-)} = \frac{1}{2} \sum_{h \in \mathrm{FS}} \left\{ P_0^{(-)} H_1 \frac{1 - P_0^{(-)}}{-\varepsilon_h - H_0} H_1 P_0(h) + h.c. \right\} + \cdots. \tag{3.11c}$$

Multiplying (3.9a) from the left by $\langle \Phi_{p'}|$, and (3.9b) by $\langle \Phi_{h'}|$, and using the following identities: $\langle \Phi_{h'}| H_1 |\Phi_h\rangle_{LC} = \langle h| u |h'\rangle$, $\langle \Phi_p| H_1 |\Phi_{p'}\rangle_{LC} = -\langle p| u |p'\rangle$, $H_0|\Phi_h\rangle = -\varepsilon_h|\Phi_h\rangle$ and $H_0|\Phi_p\rangle = \varepsilon_p|\Phi_p\rangle$, we get the final expressions for the matrix elements

$$\langle p| u |p'\rangle = \langle \Phi_0| X_p \tilde{G}_{RS}^{(+)} X_{p'}^{+} |\Phi_0\rangle_{LC}, \tag{3.12a}$$

$$\langle h| u |h'\rangle = -\langle \Phi_0| X_{h'}^{+} \tilde{G}_{RS}^{(-)} X_h |\Phi_0\rangle_{LC}. \tag{3.12b}$$

To summarize, the matrix elements $\langle p| u |p'\rangle$ and $\langle h| u |h'\rangle$ are determined by (3.12a) and (3.12b) in such a way that the conditions (3.6a) and (3.6b) are satisfied. The diagrammatic interpretation of the individual contributions up to the second order is illustrated in Fig. 4. Then, using the standard rules of the Hugenholtz graphology [41, 42], the corresponding algebraic expressions to each diagram are obtained. In this connection we stress that the diagrammatic higher-order contributions to the matrix elements $\langle p| u |p'\rangle$ and $\langle h| u |h'\rangle$ are also properly interpreted by applying the Brandow [33] folded-diagram approach.

Several words about the mathematical structure of the model interactions $G_{RS}^{(\pm)}$ should be said. As follows from the formal quasi-degenerate Rayleigh-Schrödinger perturbation theory [46], the Hermitian model interaction can be expressed by a simple symmetrization of non-Hermitian model interaction. Unfortunately, in the quasi-degenerate perturbation theory, this is only true up to the third order. The problem when the many-body (i.e. with diagrammatic interpretation) model interaction is a Hermitian operator has been extensively studied by Brandow [35]. Similar conclusions are also given in our recent publication [47] concerning the diagrammatic quasi-degenerate Rayleigh-Schrödinger perturbation theory built up consequently on the theory of the resolvent operator. There exists one serious difficulty; namely, the mathematical structure of the higher-order contributions to the Hermitian model interaction is relatively complicated and without simple rules for their construction. Nevertheless, the diagrammatic Hermitian model interaction is a well established method in the many-body theory, and some additional difficulties of its construction are of more computational than of theoretical significance.

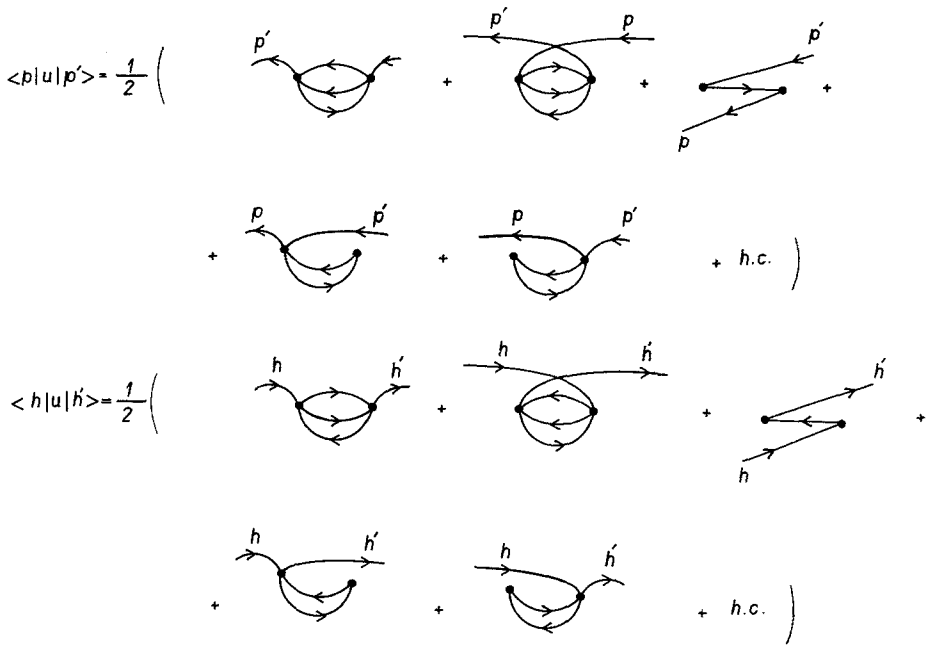

Fig. 4. The first and second order diagrammatic contributions to the matrix elements $\langle p|\, u|p'\rangle$ and $\langle h|\, u|h'\rangle$, where h.c. means a hermitian conjugated diagram

According to the dependence of the Hartree-Fock operator f_0 and the matrix elements $\langle i|\, u|j\rangle$ on the actual form of the one-particle eigensystem $\{|i\rangle, \varepsilon_i; i = 1,2,\ldots\}$, it is not possible to determine BO's or GNO's by a simple diagonalization of the one-particle eigenproblem (2.4). This means that (2.4) represents a nonlinear pseudo-eigenvalue problem which should be solved by an iterative procedure, for example, known from the Hartree-Fock theory [45]. We shall assume that the Hartree-Fock orbitals are a good starting approximation to BO's or GNO's, i.e. in the zeroth iterative step we solve the Hartree-Fock pseudo-eigenvalue problem $\langle i|\, f_0|j\rangle = \varepsilon_i \delta_{ij}$. In the next (first) step we shall use this Hartree-Fock eigensystem for the construction of the matrix elements $\langle i|\, f\,|j\rangle$ defined by (2.4b). For the calculation of these matrix elements, the matrix elements $\langle i|\, u|j\rangle$ will be approximated in such a way that only those terms are taken into account which contain merely two-particle antisymmetrized matrix elements $\langle ij|kl\rangle_A$. Then diagonalizing the Hermitian matrix eigenproblem, formed from the matrix elements $\langle i|\, f\,|j\rangle$, we obtain a new eigensystem $\{|i\rangle, \varepsilon_i; i = 1, 2,\ldots\}$. In the next iteration step we shall use this last eigensystem for the construction of the new version of the matrix elements $\langle i|\, f\,|j\rangle$, etc. until the self-consistency is obtained.

4. Discussion

Let us say a few words about the potentiality and applicability of the present approach to the theory of BO's and/or GNO's. First of all, the construction of the one-particle pseudo-eigenvalue problem, determining the BO's or GNO's, as a

straightforward generalization of the Hartree-Fock theory is, at least, a very interesting problem in the many-body theory of the finite-particle systems. In the course of the construction of the matrix elements $\langle i|\, u|j\rangle$ we have met with the fact that the basic Conditions (1.3) and (1.7) determine the matrix elements $\langle p|\, u|h\rangle$ only, where $h \in \mathrm{FS}$ and $p \notin \mathrm{FS}$. Therefore, for a complete specification of these matrix elements the additional conditions should be taken into consideration. In our case we have introduced an "ideal" assumption (3.6) in the framework of the independent-particle model, i.e. that the orbital energies are *exactly* equal to either minus ionization potential or electron affinity.

Secondly, as has been mentioned in the Introduction, the theory of the BO's or GNO's is very useful and fruitful method for the direct inclusion of some correlation effects on the independent-particle level. Or in other words, the infinite summations of the preselected diagrams are automatically implanted in the theory of BO's and GNO's. For example, in our recent communication [32] concerning the direct calculation of the low-lying excitation energies in the framework of the diagrammatic quasi-degenerate perturbation theory, we have shown that the model Hamiltonian can be exactly divided in the three terms, namely, 1 hole-1 hole, 1 particle-1 particle and 2 hole-2 particle terms. It is easy to see that if one uses the BO's or GNO's in this theory, the above mentioned 1 hole-1 hole and 1 particle-1 particle terms are automatically vanishing, i.e. the model Hamiltonian for the calculation of the low-lying excitation energies contains only one term describing the 2 hole-2 particle effective interactions. For better information in this very interesting field of the present many-body theory we recommend to read the papers of Brandow [34, 35] and Kirson [39] dealing with up to date "microscopic" theory of nuclei.

To close this Discussion we stress that this communication should be understood as a first attempt to solve the problem of the construction of a proper one-particle eigenproblem determining BO's or GNO's. While some theoretical as well as computational problems and questions still remain, we believe that the present communication might be of value as the first introductory step in this field.

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