Theoret. chim. Acta (Berl.) 8, 367—375 (1967)

A Semiempirical Method for Treating Unsaturated Molecules in Terms of Electron Pair Functions

GY. BÜTI

Research Group for Theoretical Physics of the Hungarian Academy of Sciences, Budapest

Received May 19, 1967

It is proposed to use the treatment of GIRARDEAU for the calculation of energies of unsaturated molecular systems. This involves a second quantized formalism with electron pair basis functions. No strong orthogonality is assumed, instead a subsidiary condition is imposed on the state vectors. However this does not involve any approximation. Information regarding the ground and excited states can be obtained from various propagators. In order to determine these propagators the Green function method of the many body problem can be used.

Es wird vorgeschlagen, Moleküle mit konjugierten Systemen nach einem Verfahren von GIRARDEAU zu behandeln, das mit Geminalen ohne starke Orthogonalität arbeitet. Man kann dabei die Greensche Funktion in der üblichen Weise benützen.

Une théorie du type N-corps est formulée pour l'étude des molécules non-saturées avec les effects de corrélation en utilisant un formalisme de GIRARDEAU avec une base de fonctions de paires électroniques, ou on ne suppose pas l'orthogonalité forte, mais impose à la place une condition sur les vecteurs d'état. Cependant ceci ne comporte aucune approximation. L'information relative à l'état fondamental et aux états excités peut être obtenue à partir des différents propagateurs. Ces propagateurs peuvent être déterminés à l'aide de la méthode de la fonction de Green du problème à N corps.

1. Introduction

It is believed that an adequate way of treating two electron correlations could give the bulk of correlation effects in atoms and molecules [15]. Besides Sinanoğlu's many electron theory [17] the separated electron pair approach [12] yields a very promising way to this problem. However this method in the present form suffers from some defects:

a) the strong orthogonality condition (SOC) may limit the applicability of the method; (see however [13], and the recent numerical check [6]);

b) even under the SOC the actual calculations are very troublesome, hence this method was applied only for very simple systems.

Present computing facilities do not allow even full Hartree-Fock calculations for larger unsaturated molecules, hence an adequate treatment of the correlation problem seems improbable here with these methods. However for these molecules some semi-empirical methods (Hückel, Pariser-Parr-Pople) became very useful. It is a common feature of these methods that they are rather "many body methods", i.e. instead of detailed "orbital calculations" characteristic of the atomic Hartree-Fock method they concentrate on the "combinatorial" aspects of the problem and the few parameters that should be obtained in principle from "orbital calculations" are fitted in a semiempirical way. This is justified by the natural separability of the molecular problem, i.e. electronic repulsion and overlap integrals of atomic orbitals sitting on nuclei far from each other are really small, etc. This paper is an attempt to construct such a "many body theory" for conjugated molecules in terms of not strong orthogonal electron-pair basis functions. The introduction of such basis functions makes the problem rather involved as regards permutation antisymmetry of the wave function. This was treated by GIRARDEAU [9], and the second section of this paper is devoted to the summary of his results. In Sec. 3 a Green's function formalism is introduced similar to that of LINDERBERG and ÖHRN [14]. Various approximations are treated in sections 3 and 4 for various propagators and it is shown how to extract information from their analytic structure. The self-consistency consitions are discussed in Sec. 5. The last section is devoted to a discussion of applications, etc.

2. Second Quantized Formalism for Electron Pair Funtions

This section is devoted to a brief summary of Girardeau's treatment of the many body problem [9]. We shall restrict ourselves to the special case of expanding the wave function in terms of electron pair functions. The Schrödinger equation of the molecular system can be written within the framework of the Born-Oppenheimer approximation as ($\hbar = m_e = e = 1$)

$$H\,\Phi(\xi) = \left[\sum_{i=1}^{2n} - \tfrac{1}{2}\Delta_i + U(r_i) + \sum_{i<j} \frac{1}{r_{ij}}\right]\Phi\,(\xi) = E\,\Phi\,(\xi)\,, \qquad (1)$$

where $\xi = \{x_1, x_2, \ldots, x_{2n}\}$, $x_i = \{\boldsymbol{r}_i, \sigma_i\}$, $r_{ij} = |\,\boldsymbol{r}_i - \boldsymbol{r}_j\,|$. Now we shall introduce a complete set of two electron functions $\{\varphi_\alpha(x_1, x_2)\}$, where α denotes the whole system of quantum numbers characterizing the two electron function. These functions have the properties

$$\begin{aligned} &\varphi_\alpha(x_j, x_{j+1}) = - \varphi_\alpha(x_{j+1}, x_j)\,, \\ &\int \varphi_\alpha^*(x_1, x_2)\, \varphi_\beta(x_1, x_2)\, dx_1\, dx_2 = \delta_{\alpha\beta}\,, \\ &\sum_\alpha \varphi_\alpha(x_1, x_2)\, \varphi_\alpha^*(x_1', x_2') = \tfrac{1}{2}\,[\delta(x_1 - x_1')\,\delta(x_2 - x_2') - \delta(x_1 - x_2')\,\delta(x_2 - x_1')]\,, \end{aligned} \qquad (2)$$

and the suitable asymptotic behaviour.

Integration includes a summation over the spin indices, e.g. $\delta(x_1 - x_1') = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_1')\,\delta_{\sigma_1\sigma_2}$. Using these completness and symmetry relations any wave function can be expanded as

$$\Phi\,(\xi) = \sum_{\{\alpha_1 \ldots \alpha_n\}} c(\alpha_1, \alpha_2, \ldots, \alpha_n)\, \varphi_{\alpha_1}^{(1)}\,(x_1, x_2)\, \varphi_{\alpha_2}^{(2)}\,(x_3, x_4) \ldots \varphi_{\alpha_n}^{(n)}\,(x_{2n-1}, x_{2n})\,. \qquad (3)$$

However the converse is not true, i.e. it is not true, that any expansion of the form (3) represents a physical wave function. In order to satisfy the usual antisymmetry condition of $\Phi\,(\xi)$, the following restriction should be imposed on the coefficients $c(\alpha_1, \alpha_2, \ldots, \alpha_n)$:

$$\begin{aligned} \sum_{i\leq j} \sum_{\beta\gamma} \langle \alpha_i\, \alpha_j \,|\, I \,|\, \beta\gamma \rangle\, c(\alpha_1, \alpha_2, \ldots \alpha_{i-1}, \beta, \alpha_{i+1}, \ldots, \alpha_{j-1}, \gamma, \alpha_{j+1}, \ldots \alpha_n) = \\ = - \tfrac{1}{2}\, n(n-1)\, c(\alpha_1, \alpha_2, \ldots, \alpha_n)\,, \end{aligned} \qquad (4)$$

where the matrix element is defined as:

$$\langle \alpha_i \, \alpha_j \mid I \mid \beta\gamma \rangle = \int \varphi^*_{\alpha_i}(x_1, x_2) \, \varphi^*_{\alpha_j}(x_3, x_4) \, \varphi_\beta(x_3, x_2) \, \varphi_\gamma(x_1, x_4) \, dx_1 \, dx_2 \, dx_3 \, dx_4 \tag{5}$$

and

$$c(\alpha_1, \ldots, \beta, \ldots, \gamma, \ldots, \alpha_n) = + \, c(\alpha_1, \ldots, \gamma, \ldots, \beta, \ldots, \alpha_n). \tag{6}$$

These coefficients can be regarded as a Fock space representation of the wave function (see e.g. [10]). The Schrödinger equation can be transformed to this representation in the usual way. Introducing creation and destruction operators with boson commutation rules [cf. (6)]

$$\begin{gathered} [a_\alpha, a_\beta] = [a^\dagger_\alpha, a^\dagger_\beta] = 0 \\ [a_\alpha, a^\dagger_\beta] = \delta_{\alpha\beta} \, , \end{gathered} \tag{7}$$

we have the expression for the Hamiltonian

$$H = H_0 + V \, , \tag{8}$$

where

$$\begin{gathered} H_0 = \sum_{\alpha\beta} a^\dagger_\alpha \langle \alpha \mid H_0 \mid \beta \rangle \, a_\beta \\ V = \tfrac{1}{2} \sum_{\alpha\beta\gamma\delta} a^\dagger_\alpha \, a^\dagger_\beta \, \langle \alpha\beta \mid V \mid \gamma\delta \rangle \, a_\gamma \, a_\delta \, . \end{gathered} \tag{9}$$

The matrix elements are defined as

$$\langle \alpha \mid H_0 \mid \beta \rangle = \int \varphi^\dagger_\alpha(x_1, x_2) \left[- \Delta_1 + 2U(\boldsymbol{r}_1) + \frac{1}{r_{12}} \right] \varphi_\beta(x_1, x_2) \, dx_1 \, dx_2$$

$$\langle \alpha\beta \mid V \mid \gamma\delta \rangle = \int \varphi^\dagger_\alpha(x_1, x_2) \, \varphi^\dagger_\beta(x_3, x_4) \, \frac{4}{r_{13}} \, \varphi_\alpha(x_1, x_2) \, \varphi_\sigma(x_3, x_4) \, dx_1 \, dx_2 \, dx_3 \, dx_4 \, .$$

Sometimes $U(\boldsymbol{r})$ means an effective core potential instead of the potential of the nuclei. Thus we can treat the π-electron system separately. Otherwise we can treat σ-π interactions, bound-π interactions, etc.

Condition (4) can be written as

$$I \mid \Phi \rangle = - \tfrac{1}{2} \, n(n-1) \mid \Phi \rangle \, ,$$

where

$$I = \tfrac{1}{2} \sum_{\alpha\beta\gamma\delta} a^\dagger_\alpha \, a^\dagger_\beta \, \langle \alpha\beta \mid I \mid \gamma\delta \rangle \, a_\gamma \, a_\delta \, .$$

A generalized Hamiltonian will be defined as

$$\mathscr{H} = H - \mu N + \lambda I \, ,$$

where

$$N = \sum_\alpha a^\dagger_\alpha \, a_\alpha$$

is the total number of electron pairs and μ and λ are Lagrange multipliers associated with the conditions that any physical state must satisfy the equations

$$\begin{gathered} N \mid \Phi \rangle = n \mid \Phi \rangle \\ I \mid \Phi \rangle = - \tfrac{1}{2} \, n(n-1) \mid \Phi \rangle \, . \end{gathered}$$

We should diagonalize H in the Hilbert space of states with these conditions. A generalized grand canonical ensemble will be introduced with the density operator and grand partition function [$\beta = (kT)^{-1}$, k = Boltzmann's constant]

$$\varrho = \mathcal{Z}_g^{-1} e^{-\beta \mathscr{H}}$$
$$\mathcal{Z}_g = tr\, e^{-\beta \mathscr{H}} \, .$$

The thermodynamic potential is defined [1] as

$$W = -\frac{1}{\beta} \ln \mathcal{Z}_g \, .$$

Using this definition of W and the relation

$$\langle O \rangle = tr\, \varrho\, O \, ,$$

we have

$$\frac{\partial}{\partial \mu} W = - n$$
$$\frac{\partial}{\partial \lambda} W = - \tfrac{1}{2} n(n-1) \, . \tag{10}$$

According to these conditions the thermodynamic potential should be calculated using the undetermined constants μ and λ, and at the end of the calculation they should be fixed from (10). Generally the limit $\beta \to \infty$ will be performed. It can be shown [16] that in this limit the average is over the state with the lowest energy, hence "fluctuations" in the generalized grand canonical ensemble are negligible. Thus in this limit we have the average over the *true* ground state when (10) holds.

Up to this point we have treated the problem in Schrödinger picture, e.g. the coefficients in (3) were functions of the time variable. We can go to Dirac or Heisenberg picture in the usual way, e.g. in the latter case

$$i \frac{\partial}{\partial t} O = [O, \mathscr{H}]$$
$$O(t) = e^{i \mathscr{H} t}\, O(t=0)\, e^{i \mathscr{H} t} \, , \tag{11}$$

etc.

3. Green's Functions. The "Hartree-Fock" Approximation

Green's functions are defined as averages of chronological products of operators. The simplest one is

$$G(\alpha, \alpha'; t) = - i \, \langle T a_\alpha(t_\alpha)\, a_{\alpha'}^\dagger(t_{\alpha'}) \rangle \, , \tag{12}$$

where $t = t_\alpha - t_{\alpha'}$ (translation invariance in time is supposed). The Fourier transform with respect to the time variable is

$$G(\alpha, \alpha'; \omega) = \int_{-\infty}^{\infty} G(\alpha, \alpha'; t)\, e^{i\omega t}\, dt \, . \tag{13}$$

Proceeding in the usual way [19] the equation for the Green's function is

$$\begin{aligned}(\omega - \varepsilon_\alpha)\, G(\alpha, \alpha'; \omega) = \delta_{\alpha\alpha'} + \sum_{\beta \neq \alpha} \langle \alpha \mid H_0 \mid \beta \rangle\, G(\beta, \alpha'; \omega) + \\ + \sum_{\beta\gamma\delta} \langle \alpha\beta \mid \mathscr{V} \mid \gamma\delta \rangle\, \Gamma(\beta\gamma\delta, \alpha'; \omega) \, ,\end{aligned} \tag{14}$$

where

$$\langle \alpha\beta \mid \mathscr{V} \mid \gamma\delta \rangle = \langle \alpha\beta \mid V \mid \gamma\delta \rangle + \lambda \, \langle \alpha\beta \mid I \mid \gamma\delta \rangle$$
$$\varepsilon_\alpha = \langle \alpha \mid H_0 \mid \alpha \rangle - \mu \tag{15}$$
$$\Gamma(\beta\gamma\delta, \alpha'; \omega) = - i \int_{-\infty}^{\infty} \langle T a_\beta^\dagger(t+0)\, a_\gamma(t)\, a_\delta(t)\, a_{\alpha'}^\dagger\, (0) \rangle\, e^{i\omega t}\, dt \, .$$

$\Gamma(\beta\gamma\delta, \alpha'; \omega)$ can be determined from the two-particle Green's function, the two-particle Green's function is connected with the three-particle Green's function, etc. This sequence of equations should be terminated by an appropriate decomposition of higher Green's functions into lower ones. The simplest decomposition is a "Hartree-Fock" approximation [16]

$$\Gamma(\beta\gamma\delta, \alpha'; \omega) \cong n(\beta\gamma)\, G(\delta, \alpha'; \omega) + n(\beta\delta)\, G(\gamma\, \alpha'; \omega)\,, \tag{16}$$

where

$$n(\beta\gamma) = \langle a_\beta^\dagger(t)\, a_\gamma(t)\rangle = iG(\gamma, \beta;\, -0) \tag{17}$$

is independent of time.

Thus for the Green's function we have the following inhomogeneous equation:

$$\begin{aligned}(\omega - \varepsilon_\alpha)\, G_{\mathrm{HF}}\,(\alpha,\alpha'; \omega) - \sum_{\beta \neq \alpha} \langle \alpha \mid H_0 \mid \beta\rangle\, G(\beta, \alpha'; \omega) - \sum_{\beta\gamma\delta} \langle \alpha\beta \mid \mathscr{V} \mid \gamma\delta\rangle\, n(\beta\gamma) \times \\ \times\, G_{\mathrm{HF}}(\delta, \alpha'; \omega) - \sum_{\beta\gamma\delta} \langle \alpha\beta \mid \mathscr{V} \mid \gamma\delta\rangle\, n(\beta\delta)\, G_{\mathrm{HF}}(\gamma, \alpha'; \omega) = \delta_{\alpha\alpha'}\,.\end{aligned} \tag{18}$$

Eq. (18) can be written as

$$(\omega - \varepsilon_\alpha)\, G_{\mathrm{HF}}(\alpha, \alpha'; \omega) - \sum_\delta M_{\mathrm{HF}}(\alpha, \delta)\, G_{\mathrm{HF}}(\delta, \alpha'; \omega) = \delta_{\alpha\alpha'}\,, \tag{19}$$

and $M_{\mathrm{HF}}(\alpha, \delta)$ is the mass operator [1] in the Hartree-Fock approximation. This equation should be solved self-consistently together with conditions (10).

Using the Källen-Lehman spectral representation [7]

$$\begin{aligned}G(\alpha, \alpha'; \omega) = -\, \mathscr{L}_g^{-1} \sum_{ij} e^{-\beta E_i} \Bigg[\langle \Phi_i \mid a_{\alpha'}^\dagger \mid \Phi_j^+\rangle \langle \Phi_j^+ \mid a_\alpha \mid \Phi_i\rangle \frac{1}{\omega + E_j^+ - E - i\varepsilon} - \\ - \langle \Phi_i \mid a \mid \Phi_j^-\rangle \langle \Phi_j^- \mid a_{\alpha'}^\dagger \mid \Phi_i\rangle \frac{1}{\omega + E_i - E_j^- + i\varepsilon} \Bigg]\,,\end{aligned} \tag{20}$$

where $\mathscr{H} \mid \Phi_i^\pm\rangle = E_i^\pm \mid \Phi_i^\pm\rangle$, and $\mid \Phi_i\rangle$ or $\mid \Phi_j^\pm\rangle$ is a complete set of states of the neutral molecule and the twice ionized states. The operators should be taken at time $t = 0$. Suppose that the ground state of the molecular system [i.e. the state with the lowest (free) energy and compatible with conditions (10)] is $\mid \Phi_0\rangle$, then in the limit $\beta \to \infty$ we have

$$\begin{aligned}G(\alpha, \alpha'; \omega) = \sum_j \Bigg[\langle \Phi_0 \mid a_{\alpha'}^\dagger \mid \Phi_j^+\rangle \langle \Phi_j^+ \mid a_\alpha \mid \Phi_0\rangle \frac{1}{E_0 - E_j^+ - \omega + i\varepsilon} - \\ - \langle \Phi_0 \mid a_\alpha \mid \Phi_j^-\rangle \langle \Phi_j^- \mid a_{\alpha'}^\dagger \mid \Phi_0\rangle \frac{1}{E_j^- - E_0 - \omega - i\varepsilon} \Bigg]\,.\end{aligned} \tag{21}$$

Thus "quasi-boson" electron pair energies are determined by the singularities of $G(\alpha, \alpha'; \omega)$. These quasibosons are just the "independent" modes of electron pair states. Of course in a real system these modes are interacting, i.e. there is a finite imaginary part of the poles of the Green's function [7], however experience suggests that this picture does give a rather faithful description of physical systems. Using the notations $\langle \Phi_0 \mid a_\alpha^\dagger \mid \Phi_i^+\rangle = c_\alpha^i$, $\langle \Phi_0 \mid a_\alpha \mid \Phi_i^-\rangle = \mathrm{d}_\alpha^i$, the energies of quasi-bosons can be determined from the homogeneous equations [8, 14]

$$(\omega - \varepsilon_\alpha)\, c_\alpha^{i*} - \sum_\delta M_{\mathrm{HF}}(\alpha, \delta)\, c_\alpha^{i*} = 0 \tag{22}$$

and

$$(\omega - \varepsilon_\alpha)\, d_\alpha^i - \sum_\delta M_{\mathrm{HF}}(\alpha, \delta)\, d_\delta^i = 0\,, \tag{23}$$

i.e. from the condition

$$\left| (\omega - \varepsilon_\alpha)\, \delta_{\alpha\beta} - M_{\mathrm{HF}}(\alpha, \beta) \right| = 0 \,. \tag{24}$$

In order to determine $M_{\mathrm{HF}}(\alpha, \beta)$, $n(\alpha\beta)$ should be known. Using (17) and (21)

$$n(\alpha\beta) = \lim_{\varepsilon \to +0} i \int_{-\infty}^{\infty} G(\beta, \alpha; \omega)\, e^{+i\omega\varepsilon} \frac{d\omega}{2\pi} = \sum_j c^j_\alpha c^{j*}_\beta \,. \tag{25}$$

After having determined $\omega = E_0 - E_i^+$ or $\omega = E_i^- - E_0$ from (24), the coefficients can be found from (22) and (23). In order to determine the complete solution of (19) we should also determine the inhomogeneous solution. This is the condition fixing the normalization of the solutions of (22) and (23). The following relation can be valuable in this affair

$$\sum_j d^j_\alpha d^{j*}_{\alpha'} - \sum_j c^{j*}_{\alpha'} c^j_\alpha = \delta_{\alpha\alpha'}, \tag{26}$$

which can be proved from the equal time commutator. Eqs. (22) – (26) together with the prescription for $M_{\mathrm{HF}}(\alpha, \beta)$ [c.f. (18) and (19)] constitute the basis for a complete SCF calculation. Unfortunately this work can be very tedious, since a great many off-diagonal elements of the Green's function are needed. Of course in an actual calculation we use only a restricted set of two electron basis functions. This makes our mathematical scheme a finite dimensional one. The complexity of the calculational work can be further reduced if the mass operator is approximated by

$$M(\alpha, \beta) \cong M_{\mathrm{model}}\, (\alpha, \beta) + M'(\alpha, \beta)\,, \tag{27}$$

where $M_{\mathrm{model}}\, (\alpha, \beta)$ is fixed, and we make a SCF calculation in terms of a reduced set of basis functions. This leads to various forms of π approximations. Note that there might be a possibility to incorporate into $M_{\mathrm{model}}\, (\alpha, \beta)$ the "exchange interaction" as well as a certain amount of correlation effects. Under favourable conditions this $M_{\mathrm{model}}\, (\alpha, \beta)$ should be transferable (within certain types of molecules).

4. Other Approximations. Excitation Spectrum

This section is devoted to the study of higher approximations to Eq. [14]. Although we feel, that within the framework of the "Hartree-Fock" approximation described in the preceding section it is possible to take into account the bulk of correlation, it is interesting to speculate about the possibility of including intergeminal correlations into our scheme. The Hamiltonian can be written as

$$\mathscr{H} = H_0 - \mu N + \mathscr{V} = (H_0 - \mu N + \mathscr{V}_{\mathrm{HF}}) + (\mathscr{V} - \mathscr{V}_{\mathrm{HF}})\,, \tag{28}$$

where

$$\mathscr{V}_{\mathrm{HF}} = \sum_{\alpha\beta} a^\dagger_\alpha \langle \alpha \mid \mathscr{V}_{\mathrm{HF}} \mid \beta \rangle\, a_\beta\,, \tag{29}$$

is the "Hartree-Fock" potential. The matrix element is defined as

$$\langle \alpha \mid \mathscr{V}_{\mathrm{HF}} \mid \beta \rangle = \sum_{\gamma\delta} [\langle \alpha\gamma \mid \mathscr{V} \mid \beta\delta \rangle + \langle \alpha\gamma \mid \mathscr{V} \mid \delta\beta \rangle]\, n(\gamma\delta)\,.$$

The SCF procedure described in the preceding section diagonalizes the operator $(H_0 - \mu N + \mathscr{V}_{\mathrm{HF}})$, i.e. we have the equation

$$G(\alpha, \alpha'; \omega) = G_{\mathrm{HF}}(\alpha, \alpha'; \omega) + \sum_{\beta\gamma\delta\varepsilon} G_{\mathrm{HF}}(\alpha, \beta; \omega) \langle \beta\gamma \mid \mathscr{V} \mid \delta\varepsilon \rangle\, \Gamma(\gamma\delta\varepsilon, \alpha'; \omega) -$$

$$- \sum_{\beta\gamma} G_{\mathrm{HF}}(\alpha, \beta; \omega) \langle \beta \mid \mathscr{V}_{\mathrm{HF}} \mid \gamma \rangle\, G(\gamma, \alpha'; \omega)\,,$$

where $G_{\mathrm{HF}}(\alpha, \alpha'; \omega)$ is the "unperturbed" Hartree-Fock propagator determined in the previous section. The "fluctuation interaction" [17] as introduced above can be treated e.g. in a perturbational way. The details of such a procedure will be described elsewhere [5].

The next task is to describe excitation spectra. In the case of an unsaturated molecule it is difficult to see excited states as composed of a ground state wave function in which one spin-orbital is substituted by an excited one. Instead, the system should be regarded, as a whole i.e. excitation spectrum should be the outcome of "collective" phenomena. Therefore we feel, that the energy differences of the "Hartree-Fock" geminals which can be determined from the solutions of (24) cannot give a really satisfactory answer. In unsaturated systems the situation is somewhat similar to that in nuclei (for a discussion of the situation in nuclei see [18]).

Information about these "collective" phenomena can be extracted from the two-particle Green's function. In principle two-particle Green's functions can be determined from a Bethe-Salpeter equation [7], which can be derived in the usual way also in the case of a molecular system. However a perturbational approach (Random Phase Approximation) will be used here. This method was used [4] for the treatment of plasmons in homogeneous electron gas, but the usefullness for finite systems was pointed out too. [18, 2, 14, 3, 11] Within the RPA the unperturbated particle-hole propagator is

$$Q^0_{\mathrm{RPA}}(\alpha, \alpha'; \omega) = \int_{-\infty}^{\infty} G(\alpha, \alpha'; \omega')\, G(\alpha, \alpha'; \omega + \omega') \frac{d\omega'}{2\pi}, \tag{30}$$

where $G(\alpha, \alpha'; \omega)$ should be inserted within an available approximation. The full particle-hole propagator can be obtained within the RPA as

$$Q_{\mathrm{RPA}}(\alpha, \alpha'; \omega) = Q^0_{\mathrm{RPA}}(\alpha, \alpha'; \omega) + \sum_{\beta\gamma} Q^0_{\mathrm{RPA}}(\alpha, \beta; \omega) \langle \beta\gamma \mid \mathscr{V} \mid \beta\gamma \rangle\, Q_{\mathrm{RPA}}(\gamma, \alpha'; \omega)\,. \tag{31}$$

Excitation spectra can be obtained from the poles of $Q(\alpha, \alpha'; \omega)$. In the homogeneous electron gas it is possible to determine the analytic structure explicitely [4]. In a molecular system we must evaluate (30) and then determine the poles of $Q(\alpha, \alpha'; \omega)$ from (31). This can be made by a similar procedure which was described in the previous section, i.e. truncating (31) to a homogeneous equation and seeking the conditions of nontrivial solutions. However we do not go into detail here in this point.

5. Termodynamic Potential

After having discussed the calculation and information content of various Green's functions we go back to the problem of Lagrange multipliers. The values of μ and λ should be determined from (10), therefore the construction of W is needed. In the actual calculations we have concentrated on the limit $\beta \to \infty$. It can be proved [1, 16], that in this limit $W = \mathscr{E}$, where

$$\mathscr{E} = \langle \Phi_0 \mid \mathscr{H} \mid \Phi_0 \rangle\,,$$

i.e. $\mathscr{E}$ is the generalized free energy. This can be determined from the one-particle Green's function in the following way [7]. The average of that part of $\mathscr{H}$ which is bilinear in particle operators is

$$\begin{aligned}\langle\Phi_0 \mid H - \mu N \mid \Phi_0\rangle &= i \sum_{\alpha\beta} (\langle\alpha \mid H \mid \beta\rangle - \mu\delta_{\alpha\beta})\, G(\beta, \alpha; t = -0) = \\ &= \frac{i}{2\pi} \sum_{\alpha\beta} \int_{-\infty}^{\infty} (\langle\alpha \mid H_0 \mid \beta\rangle - \mu\delta_{\alpha\beta})\, G(\beta, \alpha; \omega)\, d\omega = \\ &= \sum_j \sum_{\alpha\beta} (\langle\alpha \mid H_0 \mid \beta\rangle - \mu\delta_{\alpha\beta})\, c^j_\alpha c^{j*}_\beta\,, \end{aligned} \tag{32}$$

since the integration path can be closed with a semicircle on the upper half of the ω plane. Now using (12), (11) and the relations

$$\sum_\alpha a^\dagger_\alpha [H_0 - \mu N, a_\alpha] = -(H_0 - \mu N)$$

$$\sum_\alpha a^\dagger_\alpha [\mathscr{V}, a_\alpha] = -2\,\mathscr{V}\,,$$

we have

$$\langle\Phi_0 \mid \sum_\alpha a^\dagger_\alpha\, [\mathscr{H}, a_\alpha] \mid \Phi_0\rangle = -\langle\Phi_0 \mid H - \mu N + 2\mathscr{V} \mid \Phi_0\rangle = -i \sum_\alpha \frac{d}{dt} G(\alpha, \alpha; t)\, \Big|_{t=-0}\,,$$

i.e.

$$-\langle\Phi_0 \mid H_0 - \mu N + 2\mathscr{V} \mid \Phi_0\rangle = \sum_\alpha \int_{-\infty}^{\infty} G(\alpha, \alpha; \omega)\, \omega\, \frac{d\omega}{2\pi i} = \sum_\alpha \sum_i |\, c^i_\alpha\,|^2\, \Delta E_j\,. \tag{33}$$

Here $\Delta E_j = E^+_j - E_0$ are the energies of the quasi-bosons as can be obtained from the poles of the Green's function [cf. (21)]. $E_0 = \mathscr{E}$, however, only the energy differences enter. This is the main advantage of Green's function technique, which makes the interpretation, incorporation of empirical data, etc. very easy.

From (32) and (33)

$$\begin{aligned} W = \mathscr{E} &= \tfrac{1}{2}\, [\langle\Phi_0 \mid H_0 - \mu N \mid \Phi_0\rangle + \langle\Phi_0 \mid H_0 - \mu N + 2\mathscr{V} \mid \Phi_0\rangle] = \\ &= \tfrac{1}{2} \sum_j \sum_{\alpha\beta} c^j_\alpha\, c^{j*}_\beta\, [\langle\alpha \mid H_0 \mid \beta\rangle - \delta_{\alpha\beta}(\mu - \Delta E_j)]\,. \end{aligned} \tag{34}$$

This should be inserted into (10). Note, that c^j_α and ΔE_j are functions of μ, therefore

$$\frac{\partial W}{\partial\mu} \neq -\tfrac{1}{2} \sum_j \sum_\alpha |\, c^j_\alpha\,|^2\,.$$

Of course on physical grounds

$$\frac{\partial W}{\partial\mu} = -n = -\sum_j \sum_\alpha |\, c^j_\alpha\,|^2\,.$$

6. Discussion

In this paper a Green's function technique using non strong orthogonal electron pair basis functions was studied for molecular systems. Like in every molecular theory, where we have no explicitely diagonalized unperturbated Green's function with a complete basis system, we should perform the calculations with a finite set of geminals made from atomic or Löwdin orbitals. This requires the diagonalization of finite matrices. With the appropriate choice of basis functions we can treat "vertical" correlation, etc. We have not worried up to now about the various interaction and exchange operator matrix elements given explicitely in the second section. Since this techniques works with observable quantities it can be possible to incorporate spectroscopical data in a similar way as described in [14], using the concept of "molecules in molecules". However, since the interpretation of spectra is not clear, it can be more advantageous to make ab initio calculations on smaller molecules or on model systems and then to incorporate the results of these calculations. It can be imagined that after sufficient experience has been accumulated about the best values of various matrix elements, Lagrange multipliers, etc., a reasonable amount of work could be enough to treat correlations even in larger molecules.

Acknowledgements. The author is grateful to Prof. P. GOMBÁS for his kind interest in this work. Thanks are also due to Dr. E. KAPUY for reading the manuscript.

References

1. BONCH-BRUEVICH, V. L., and S. V. TYABLIKOV: The Green's function method in statistical mechanics. Amsterdam: North-Holland 1962.
2. BRANDT, W., and S. LUNDQUIST: Physic. Rev. **132**, 2135 (1963).
3. BROWN, G. E.: Lectures on many-body problems. Copenhagen: Nordita 1961.
4. DU BOIS, D. V.: Ann. Phys. **7**, 174; **8**, 24 (1959).
5. BÜTI, GY.: To be published.
6. EBBING, D. D., and L. E. POPLAWSKI: J. chem. Physics **45**, 2657 (1966).
7. GALITSKII, V., and A. MIGDAL: Soviet Physics JETP **7**, 96 (1958).
8. GELL-MANN, M., and F. LOW: Physic. Rev. **84**, 350 (1951).
9. GIRARDEAU, M.: J. math. Physics **4**, 1096 (1963).
10. GOMBAS, P.: Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik. Basel: Birkhäuser, 1950.
11. HERZENBERG, A., D. SHERRINGTON, and M. SÜVEGES: Proc. physic. Soc. (London) **84**, 465 (1964).
12. HURLEY, A. C., J. E. LENNARD-JONES, and J. A. POPLE: Proc. Roy. Soc. (London) **A220**, 446 (1953).
13. KAPUY, E.: Theoret. chim. Acta **6**, 281 (1966).
14. LINDERBERG, J., and Y. ÖHRN: Proc. Roy. Soc. (London) **A285**, 445 (1965).
15. LÖWDIN, P. O.: Advan. chem. Physics **2**, 207 (1959).
16. MARTIN, P. C., and J. SCHWINGER: Physic. Rev. **115**, 1342 (1959).
17. SINANOĞLU, O.: Proc. Natl. Acad. Sci. U.S. **47**, 1217 (1961).
18. THOULESS, D. J.: Nucl. Physics **22**, 78 (1961).
19. ZUBAREV, D. N.: Soviet Physics, USP **3**, 320 (1960).

Dr. GY. BÜTI
Research Group for Theoretical Physics
The Hungarian Academy of Sciences
XI. Budafoki ut 8
Budapest, Hungary