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Hole-particle Formalism for the Electronic Spectra of Long Chain Polyenes

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From the hole-particle description of the many-Fermion system of long chain polyenes it has been shown that the convergence limit in the electronic spectra may be accounted for by the electron-hole pairing interaction.

It is well-known that the wavelength of the lowest N–V transition of polyenes does not grow proportionately with the number n of the conjugated double bonds as is true for symmetrical cyanines, but tends to a limit as n becomes large.1) Kuhn2) related this behavior to the unequal length of single and double bonds, which generates a perturbing potential with a period of the bond length and thus introduces a Brillouin gap between the highest occupied and the lowest unoccupied level. Dewar3) accounts for this phenomenon by assuming different exchange integrals for single and double bonds. On the other hand, simple free electron theory as well as molecular orbital theory predict a rapid equalization of bond lengths with increasing n and therefore invalidates the above reasoning. Further it has been found that mono- and dinegative ions of diphenyl polyenes show bond alternation,5) although dinegative ions show convergence and mono-negative ions do not. Unequal bonds do not appear to lead to convergence. Araki4) tried to correlate the convergence limit with the plasma oscillation in many-electron system, but it fails to explain different behavior of cyanines and polyenes.

In the usual treatment of many-Fermion problem each particle is supposed to move independently, the effect of the interaction between particles being simply replaced by an average field of force. This treatment does not take interparticle correlation into account. A step towards the improvement of the method so as to include correlation was taken by Euler,6) who calculated the effect of interparticle interaction, which causes the correlation, by perturbation theory assuming the interaction to be small. The calculation of such a type is carried out in the following manner. In the zeroth approximation each particle is in some one-particle quantum state, which we consider a "level". Let us consider the lowest state for the sake of definiteness. In this state all levels up to some highest, which we call the Fermi maximum (λ), are each filled by the particles. The perturbation energy due to the interparticle force, has non-vanishing matrix elements which cause virtual transitions to states in which particles are excited to levels higher than the Fermi maximum. The state which results from the interparticle force is thus a superposition of zero order state and various excited states. Such a mixture of excited states gives rise to correlation between particles.

Accepting the above model we may approach the problem of π-electronic spectra of long chain polyenes in a different way. In the single-particle level scheme of "electron in a box" the levels up to λ (Fermi level) are occupied and the levels above it are unoccupied. The state obtained by exciting a particle from an occupied level to an unoccupied level is called a state of one hole-one particle type, because in this process of excitation a vacancy (hole) is left in the occupied level and a "particle" is produced, instead, in one of the unoccupied level. If we use single-particle creation operator and destruction operator in the treatment of many-body-Hamiltonian, then we will be able to get the elementary excitation energy of a hole-particle pair or a quasiparticle.

The physics and mathematics of quasiparticles have been rigorously developed and applied with great success in nuclear physics8,8e) and in the theory of superconductivity.7) In what follows we use this formulation in a simplified and somewhat approximate form.

Quasiparticle Hamiltonian

The second quantized version of the many-body Hamiltonian is given as9)

$$H = \sum_{\alpha,\beta}\langle\alpha|T|\beta\rangle C_\alpha{}^+C_\beta + \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\langle\alpha\beta|v|\gamma\delta\rangle C_\alpha{}^+C_\beta{}^+C_\gamma C_\delta \cdots, \tag{1}$$

$$\left(v = \frac{1}{r_{ij}}\right)$$

where $C_\alpha{}^+$ is the creation operator for the state α and C_β, the destruction operator for the state β. The ground state $|\psi_0\rangle$ contains a set of occupied single particle states h, h^1, $\cdots$ and hence it is impossible to create another particle in an occupied state h. Therefore

$$C_h{}^+|\psi_0\rangle = 0$$

The state $|\psi_0\rangle$ does not contain any of the unoccupied single particle states p, p^1 $\cdots$ and hence it is impossible to destroy any such state in

$$C_p|\psi_0\rangle = 0$$

If we now define a new destruction operator for the single particle state by the following relation;

$$b_i = C_i{}^+ \text{ when } i = h,$$
$$= C_i \text{ when } i = p.$$

Then we have

$$b_i|\psi_0\rangle = 0 \text{ for all } i.$$

We interpret the state $|\psi_0\rangle$ as the vacuum state for the new object which we created by $b_i{}^+$, such that

$$b_i{}^+ = C_i \text{ where } i = h,$$
$$= C_i{}^+ \text{ where } i = p.$$

We call these new-objects quasiparticles and the $|\psi_0\rangle$ state plays the role of vacuum state for these objects.

We now replace the Hamiltonian (1) by its expectation value with respect to ground state $|\psi_0\rangle$ and get

$$\begin{aligned}\langle H\rangle &= \sum_{\alpha,\beta}\langle\alpha|T|\beta\rangle\langle C_\alpha{}^+C_\beta\rangle + \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\langle\alpha\beta|v|\gamma\delta\rangle \\ &\times\{\langle C_\alpha{}^+C_\beta{}^+\rangle\langle C_\gamma C_\delta\rangle + \langle C_\alpha{}^+C_\gamma\rangle\langle C_\beta{}^+C_\delta\rangle \\ &-\langle C_\alpha{}^+C_\delta\rangle\langle C_\beta{}^+C_\gamma\rangle\}\end{aligned} \tag{2}$$

where the exceptation values $\langle C_\alpha{}^+C_\beta\rangle$ *etc.* are pure numbers and is defined as density functions

$$\langle\beta|\rho|\alpha\rangle = \langle\psi_0|C_\alpha{}^+C_\beta|\psi_0\rangle \tag{3}$$

With this definition the last two terms combine to give us the self-consistent potential V, made up of both Coulomb and exchange terms. We then get

$$\begin{aligned}\langle H\rangle &= \sum_{\alpha,\beta}\langle\alpha|T+\frac{1}{2}V|\beta\rangle\langle\beta|\rho|\alpha\rangle \\ &+\frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\langle\alpha\beta|v|\gamma\delta\rangle\langle C_\alpha{}^+C_\beta{}^+\rangle\langle C_\gamma C_\delta\rangle\end{aligned} \tag{4}$$

We notice that the energy expression contains an extra-potential term than what is present in Hartree-Fock state, so these states are called Hartree-Fock-Bogolyubov (HFB) states.[8] Now following (3) we define $\langle C_\delta C_\gamma\rangle = K_{\delta\gamma}$ a density function and following anticommutation of destruction operators we have $\langle C_\gamma C_\delta\rangle = -K_{\delta\gamma}$. We therefore write the second term in (4) as

$$\frac{1}{4}\sum_{\alpha,\beta,\gamma,\delta}\langle\alpha\beta|v|\gamma\delta\rangle K^*_{\beta\alpha}(K_{\delta\gamma}-K_{\gamma\delta}) = \frac{1}{2}\sum_{\alpha,\beta}\Delta_{\alpha\beta}K^*_{\beta\alpha}, \tag{5}$$

where $\Delta_{\alpha\beta}$ may be defined as a pairing potential. So we get

$$\langle H\rangle = \sum_{\alpha,\beta}\{\langle\alpha|T+\frac{1}{2}V|\beta\rangle\langle\beta|\rho|\alpha\rangle + \frac{1}{2}\Delta_{\alpha\beta}K^*_{\beta\alpha}\} \tag{6}$$

Variation of Calculation of Quasiparticle Energy

We now try to determine the ground state energy by a variational calculation,[8] *i.e.*, we try to minimise $\langle\psi_0|H-\lambda N|\psi_0\rangle$ where λ is the Lagrangian multiplier and N is the operator for total number of particles

$$N = \sum_\alpha C_\alpha{}^+C_\alpha. \tag{7}$$

We now follow a two-step minimising procedure on $H(\lambda) = H-\lambda N$. We first omit the second term in (6) and define a single-particle state as

$$|i\rangle = \sum X_\alpha{}^i|\alpha\rangle \text{ and } H|i\rangle = \varepsilon_i|i\rangle$$

then the variation parameters X_{α^i} which makes $\langle H(\lambda)\rangle$ a minimum satisfy

$$\sum_\beta\langle\alpha|T-\lambda\mathbf{1}+\frac{1}{2}V|\beta\rangle X_\beta{}^i = (\varepsilon_i-\lambda)X_\alpha{}^i. \tag{8}$$

That is at this stage we now have single particles with energies $(\varepsilon_i-\lambda)$. In the next step we write $H(\lambda)$ using $|i\rangle$ as the basis

$$\langle H(\lambda)\rangle = \sum_{i,j}\langle i|T-\lambda\mathbf{1}+\frac{1}{2}V|j\rangle\langle j|\rho|i\rangle + \frac{1}{2}\sum_{ij}\Delta_{ij}K^*_{ij}, \tag{9}$$

Now we make a transformation[8]

$$b_i{}^+ = u_iC_i{}^+ + v_iC_{-i}, \tag{10}$$

where the coefficients u_i and v_i are the variation parameters. One can create a particle in a state if it is empty and destroy a particle if it is occupied. Therefore u_i^2 and v_i^2 are the probabilities of getting the state i empty and occupied respectively. We therefore have

$$u_i^2 + v_i^2 = 1,\ u_i = u_{-i},\ v_i = -v_{-i}. \tag{11}$$

Similarly we get

$$b_i = u_iC_i + v_iC_{-i}{}^+. \tag{12}$$

Inverting these relations we get

$$\begin{aligned}C_{-i}{}^+ &= u_ib_{-i}{}^+ + v_ib_i, \\ C_i &= u_ib_i - v_ib_{-i}{}^+.\end{aligned} \tag{13}$$

With this transformations we have

$$\begin{aligned}\langle j|\rho|i\rangle &= \langle C_i{}^+C_j\rangle \\ &= \langle\psi_0|(u_ib_i{}^+-v_ib_{-i})(u_jb_j-v_jb_{-j}{}^+)|\psi_0\rangle \\ &= \langle\psi_0|b_ib_j{}^+|\psi_0\rangle v_iv_j \\ &= v_i^2\delta_{ij},\end{aligned} \tag{14}$$

$$\begin{aligned}K_{ij} &= \langle\psi_0|(u_ib_i-v_ib_{-j}{}^+)(u_jb_j-v_jb_{-j}{}^+)|\psi_0\rangle \\ &= -\langle\psi_0|b_ib_j{}^+|\psi_0\rangle u_iv_j \\ &= u_iv_{-i}\delta_{i,-j}.\end{aligned} \tag{15}$$

Now b_i's in (10) and (12) are the creation and destruction operators for quasiparticles in the HFB[8] formulation and they differ from relations given for HF state because in HFB formulation the particle number is not conserved. In simplifying these relations we have used the Fermion anticommutation relations of quasiparticle operators

$$\{b_i, b_j\} = \{b_i{}^+, b_j{}^+\} = 0,$$

and $$\{b_i, b_j{}^+\} = \delta_{ij}.$$

With these transformation we get

$$\langle H(\lambda)\rangle = \sum_i\langle i|T-\lambda\mathbf{1}+\frac{1}{2}V|i\rangle v_i^2 + \frac{1}{2}\sum_i\Delta_{i,-i}u_iv_{-i}. \tag{16}$$

We now minimise (16) by requiring $\delta H(\lambda)/\delta v_i = 0$, using $u_i^2 = 1-v_i^2$, $v_{-i} = -v_i$ and we get

$$(\varepsilon_i-\lambda)2v_{-i}u_i + \frac{1}{2}\Delta_{i,-i}(u_i^2-v_i^2) = 0. \tag{17}$$

Putting $\cos\theta_i = u_i$ and $\sin\theta_i = v_{-i}$ we have

$$(\varepsilon_i-\lambda)\sin 2\theta_i = \Delta\cos 2\theta_i,\ \Delta = -\Delta_{i,-i}/2,$$

$$\text{or } \tan 2\theta_i = \frac{\Delta}{\varepsilon_i-\lambda},$$

$$2u_iv_{-i} = \sin 2\theta_i = \frac{\Delta}{\sqrt{(\varepsilon_i-\lambda)^2+\Delta^2}}, \tag{18}$$

$$u_i^2 - v_i^2 = \cos 2\theta_i = \frac{\Delta}{\sqrt{(\varepsilon_i-\lambda)^2+\Delta^2}}. \tag{19}$$

We set E_i equal to

$$E_i = \sqrt{(\varepsilon_i-\lambda)^2+\Delta^2}. \tag{20}$$

Significance of E_i

While simplifying the Eq. (1) we have used the product of the creation and destruction operator in the contracted form which gives us information about the ground state only. Terms containing the normal products of the operator will give us informations about the states in which there are one, two, three, four, *etc.* pairs of creation and destruction operators. If we pick up only terms in which there is only one pair of creation and destruction operator, then we have

$$H_1(\lambda) = \sum_j (\varepsilon_j - \lambda) C_j^+ C_j + \frac{1}{2} \sum_j \Delta_{j,-j} C_j^+ C_{-j}^+. \tag{21}$$

Expressing the creation operators in terms of quasiparticle operators and following the algebraic procedure outlined in the proceeding section we get

$$\begin{aligned} H_i(\lambda) &= \sum_j [(\varepsilon_j - \lambda)(u_j^2 - v_j^2) + \Delta_{j,-j} u_j v_{-j}] b_j^+ b_j \\ &= \sum_j [(\varepsilon_j - \lambda) \cos 2\theta_j + \Delta_{j,-j} \sin 2\theta_j] b_j^+ b_j \\ &= \sum_j E_j b_j^+ b_j. \end{aligned} \tag{22}$$

The new Hamiltonian is thus

$$H = \langle H_0(\lambda) \rangle + \sum_j E_j b_j^+ b_j. \tag{23}$$

Let us now consider a state i with one quasiparticle, *i.e.*, the state $b_i^+ |\psi_0>$. The energy of the state is given as

$$\begin{aligned} &\langle \psi_0 | b_i \{ \langle H_0(\lambda) \rangle + \sum_j E_j b_j^+ b_j \} b_i^+ | \psi_0 \rangle \\ &= \langle H_0(\lambda) \rangle \langle \psi_0 | b_i b_i^+ | \psi_0 \rangle + \sum_j E_j \langle \psi_0 | b_i b_j^+ b_j b_i^+ | \psi_0 \rangle \\ &= \langle H_0(\lambda) \rangle + E_i. \end{aligned} \tag{24}$$

The energy of the state ψ_0 is $<H_0(\lambda)>$ and the energy of the state with one quasiparticle is $<H_0(\lambda)>+E_i$. Hence we conclude that E_i is the energy carried by one hole-particle pair, *i.e.* a quasiparticle and it is given as

$$E_i = \sqrt{(\varepsilon_i - \lambda)^2 + \Delta^2}, \quad \Delta^2 = \left(\frac{\Delta_{i,-i}}{2} \right)^2. \tag{25}$$

Exactly same expression has been obtained by solving HFB equation by Green function technique.[11)] This partially justifies our assumption that Δ's are constant in variation calculation.

Significance of λ

From the relation

$$v_i^2 = \frac{1}{2} \left[1 - \frac{\varepsilon_i - \lambda}{E_i} \right] \tag{26}$$

it is evident that when ε_i is much greater than λ, $v_i^2 = 0$ while when it is much less than λ, $v_i^2 = 1$ assuming Δ to be small. In the usual description of π-electron system the levels upto Fermi-maximum are occupied while those above it are all empty. So the occupation probability above Fermi-maximum is zero and below it is one. This suggests that λ is to be associated with ε_F, the energy of the Fermi-maximum. Hence the quasiparticle energy is given.

$$E_i = \sqrt{(\varepsilon_i - \varepsilon_F)^2 + \Delta^2} \tag{27}$$

Convergence Limit and Δ

Equation (27) shows that when ε_i becomes equal to ε_F, the hole-particle energy is Δ and not zero and the minimum value of all quasiparticles is Δ. If the long-wavelength transition in linear polyene is associated with the electron jump from the top-most filled orbital to the first empty orbital, then in the quasiparticle scheme the energy should go over to Δ as the energy difference $\varepsilon_i - \varepsilon_F$ goes to zero, *i.e.*, as the length of the chain goes to infinity.

A Chemist's View of Δ

From the relation (18) we have

$$2u_i v_{-i} = \frac{\Delta}{\sqrt{(\varepsilon_i - \varepsilon_F)^2 + \Delta^2}}.$$

Now for HF state we have

$u_i = 1$ for a particle state
$= 0$ for a hole state,
$v_{-i} = 1$ for a hole state
$= 0$ for a particle state.

In HFB case u_i and v_i will deviate from these unique values and will be somewhere between zero and one. This means that even for HFB case should be positive. So Δ must be a positive quantity. Now Δ has been set equal to $-(\Delta_{i,-i})/2$, which means that $\Delta_{i,-i}$ must be negative. $\Delta_{i,-i}$ is related to pairing potential which in the present formulation must be Coulombic in origin as $v = 1/r_{ij}$. The Coulombic potential is negative if the interaction is between two particles of opposite charges. This suggests that we may associate this interaction with the attraction between a particle and a hole. This interaction is not taken into account at any stage in HF calculation.

If the Hamiltonian (1) is written out in full, then there will appear terms which can be correlated with interaction arising from hole-particle, particle-particle hole-hole, *etc.* These points have been thoroughly discussed in Random-Phase-Approximation Scheme.[10)] Instead of going into details of that calculation we only state that whenever we go over to calculate energy values for states other than ground state we must take into account interactions arising from hole-hole, hole-particle terms in the Hamiltonian (1).

With this formulation we now proceed to analyse the case of cyanine. In the π-electron calculation on cyanines, the systems are considered to be open-chain systems like polyenes, but carry a positive charge *i.e.* a hole in Fermi sea. The interaction of this charge with the π-electrons is taken into account in the usual HF calculation. In the expression for quasiparticle energy

$$E_i = \sqrt{(\varepsilon_i - \varepsilon_F)^2 + \Delta^2},$$

the Δ should be made up of two terms, the hole-particle attraction and the hole-hole repulsion, the terms which are not taken care of in HF calculation. It may not be too unfair to assume that these two terms will be nearly equal and cancel each other. The quasiparticle energy will then reduce to

$$E_i = (\varepsilon_i - \varepsilon_F),$$

and the system will not show any convergence limit as is actually the case.

While considering biphenyl-polyene dinegative and mononegative ions, we may consider the mononegative ion to be the same as dinegative ion with a formal hole in the Fermi sea. Consequently mononegative ion will show no convergence limit like cyanines, while dinegative ion will.

It appears that the hole-particle formulation with some chemical intuition can give a reasonable account for the convergence limit in π-electronic spectra of open-chain compounds.

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