Progress of Theoretical Physics, Vol. 22, No. 5, November 1959

Electron Interaction in Very Long Linear Conjugated Molecules. II

——*Elementary Excitations in a System with Small Energy Gap*——

Takeo IZUYAMA

Research Institute for Fundamental Physics, Kyoto University, Kyoto

(Received June 8, 1959)

Lowlying excited states in a one-dimensional system which has a small energy gap (ϵ_g) in the spectra of H_0, the one-electron Hamiltonian, are investigated. Plasmons and excitons are our main interests. These states are investigated in the framework of the tight-binding approximation. In usual one-dimensional systems, such as very long linear conjugated molecules, the plasmon levels sink into the level continuum given by excitation energies of one-pair states. However, it is shown that the plasma oscillations are stable when their energies are sufficiently larger than the energy gap. On the other hand, the plasma oscillations with sufficiently small momentum whose energies in case of $\epsilon g=0$ were smaller than the present energy gap seem to be dissolved away into the level continuum.

A formulation to derive exciton solutions is given. The screening effect for the attractive force between the electron and the hole is investigated by means of the Gell-Mann and Brueckner technique and is found to grow larger as the energy gap becomes smaller. By this screening effect the possibility of getting the exciton-like bound state diminishes as $\epsilon g \to 0$. As a collorary we have found that the potential energy of two electric charges $z_1 e$ and $z_2 e$ separated by a distance r in a three dimensional system with small energy gap becomes $z_1 z_2 e^2 \exp(-\alpha r)/r$ if $r \ll |B/\Delta B|$, where $|B|$ is a measure of the Fermi energy and ΔB is a measure of the gap, while it becomes $z_1 z_2 e^2/\epsilon r$ if $r \gg |B/\Delta B|$, where $\epsilon \propto r_s^{-1}(|B|/(\Delta B)^2) \times (e^2/a_B)$.

§ 1. Introduction

In the previous paper[1] (hereafter referred to as I) low-energy electronic states with small wave numbers in the very long linear conjugated molecules with equal bond lengths and equal bond angles are investigated by means of Tomonaga's sound wave method[2] within the framework of Pariser-Parr's π electron approximation. The formulation employed may be regarded as the tight-binding approximation for plasma waves.

It has been an interesting problem to see whether very long linear conjugated molecules have alternating shorter and longer bonds even in their middle parts or they have equal bonds in the parts sufficiently far apart from the ends. Many physicists believe the existence of the alternation.[3] Accordingly, it will be interesting to investigate low energy electronic excitations in the molecule with alternating shorter and longer bonds. In order to simplify our problem, we here investigate the π electrons moving in an infinitely long molecular skelton with

fixed alternating bonds shown in Fig. 1. Then the one-electron energy of these π electrons has a Brillouin gap. In case of an infinitely long molecule the difference between the longer bond length and the shorter one will be very small. Then the gap should be very small. Thus our problem is similar to that of electronic excitations in graphites or intrinsic semiconductors. Qualitative aspects of our discussions seem to prevail in such three dimensional systems, though from quantitative point of view we should modify our treatment in each case. We will call the long linear molecules with equal bonds the N-molecules and those with alternating bonds the S-molecules.

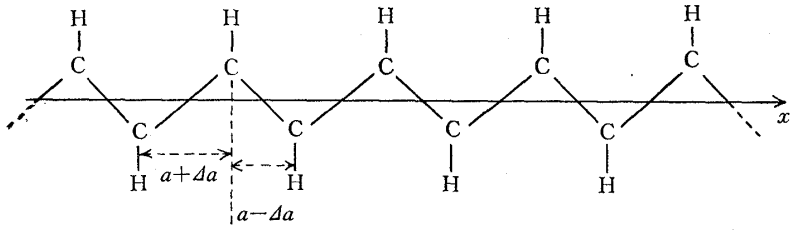


Fig. 1

§ 2 Review of the treatment for N-molecules

As shown in I, the Hamiltonian for the π electron system of an N-molecule is given by

$$\left.\begin{aligned} &H=H_0+H_I, \\ &H_0=\sum_k^{\sigma}\epsilon(k)N_{k\sigma}, \quad H_I=\tfrac{1}{2}\sum J_k\rho_k\rho_{-k}, \\ &N_{k\sigma}=a_{k\sigma}^{*}a_{k\sigma}, \quad \rho_k=\sum_l^{\sigma}a_{l+k\sigma}^{*}a_{l\sigma}, \end{aligned}\right\} \tag{2·1}$$

in the framework of Pariser-Parr's π electron approximation which has got a great success in the interpretation of optical spectra of organic molecules. In the above, a_k is the destruction operator for the Bloch orbital

$$\phi_k=\frac{1}{\sqrt{N}}\sum_{-N/2<R\leqq N/2}\exp(ikR)\varphi_R \tag{2·2}$$

where φ_R is the atomic orbital (or Wannier function) belonging to the R-th atom, k is given by

$$k=\frac{2\pi}{N}n \qquad (n=\text{integer}),$$

and σ denotes the spin function α or β.

(2·2) may be stated as follows,

$$a_{k\sigma}=N^{-1/2}\sum_{-N/2<R\leqq N/2}\exp(-ikR)b_{R\sigma}, \tag{2·3}$$

where b_R is the destruction operator for φ_R. Further, J_k, the Fourier component of the interaction, is given by

$$NJ_k=\frac{2e^2}{a}K_0(\gamma|k|)$$

in our one-dimensional system, K_0 being the modified Bessel function of the second kind, and γ being some dimensionless constant introduced in I. In Pariser-Parr's π electron approximation, the one-electron energy $\epsilon(k)$ is given by

$$\epsilon(k)=2B\cos k \tag{2·4}$$

where B is the resonance integral between two adjacent carbon atoms.

If the Tomonaga method of one-dimensional sound waves is applied to (2·1), lowlying excited states with small momenta are described by a Boson assembly which consists of two different groups of Bosons. One of the groups is composed of plasmons, each of which has the following energy quantum

$$W=|n|\sqrt{\epsilon'(n_F)[\epsilon'(n_F)+4J_n]} \tag{2·5}$$

where $k=(2\pi/N)n$ $(\ll\pi/2)$ is the wave vector of this Boson, n being an integer. Another group is described by Bosons corresponding to spin-density waves. The energy quantum of a Boson belonging to this group is given by

$$W=|n|\epsilon'(n_F). \tag{2·5′}$$

Same answer can be obtained by Sawada's useful method.[4] In this method only the interactions of the type shown in Fig. 2 are taken into account, the remaining interactions being neglected. Then the Coulomb interaction is replaced by

$$H_I\to H_C=\tfrac{1}{2}\sum J_n\zeta_n\zeta_{-n}$$

where

$$\zeta_n=\sum_{\substack{|n'|\leqq n_F\\ |n'+n|>n_F}}^{\sigma}(a^*_{n'+n\sigma}b^*_{n'\sigma}+b_{-n'\sigma}a_{-n'-n\sigma})$$

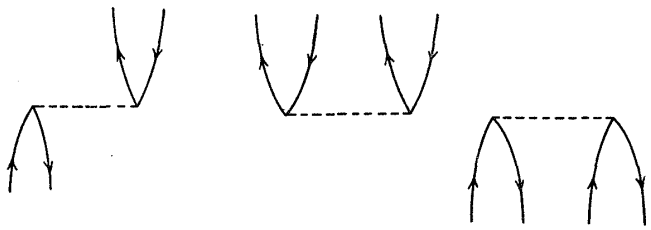


Fig. 2

in which $b^*_{n\sigma}=a_{n\sigma}$ $(n\leqq n_F)$. Further in the commutator

$$[H_C,\ a^*_{m\sigma}b^*_{n\sigma}]\quad\text{and}\quad[H_C,\ b_{n\sigma}a_{m\sigma}]$$

one may use the following commutation relation

$$[b_{n'\sigma'}a_{m'\sigma'},\ a^*_{m\sigma}b^*_{n\sigma}]=\delta_{\sigma\sigma'}\delta_{nn'}\delta_{mm'}$$

because the interaction diagrams are restricted as mentioned above. Then, one can find an excitation energy W given by

$$1=2J_n \sum_{\substack{n' \\ |n'|\leqq n_F \\ |n'+n|>n_F}} \left\{ \frac{1}{W-\epsilon(n'+n)+\epsilon(n')} - \frac{1}{W+\epsilon(n'+n)-\epsilon(n')} \right\}. \qquad (2\cdot6)$$

In the one-dimensional system, for sufficiently small n compared with n_F, we may use

$$\epsilon(n'+n)-\epsilon(n')=|n|\epsilon'(n_F) \qquad (2\cdot7)$$

in the denominator of the above eigenvalue equation. Then we get Eq. (2·5).

In Sawada's theory the plasma excitation connects with only the one pair excitation $\Psi_0 \to a^*_{n_F+n} b^*_{n_F} \Psi_0$ when the electron interaction is adiabatically switched off, where Ψ_0 represents the ground state when $e=0$ and n is here assumed to be positive. There are also " scattering solutions " whose excitation energies are almost equal to $\epsilon(n'+n)-\epsilon(n')$ and connect with those of one-pair excitations $\Psi_0 \to a^*_{n'+n} b^*_{n'} \Psi_0$ $(n'=n_F-n+1,\ n_F-n+2,\ \cdots,\ n_F-1)$ when the interaction is adiabatically switched off. According to Tomonaga's theory, on the other hand, the one-pair excitations which connect with the plasmon state are not limited to $\Psi_0 \to a^*_{n_F+n} b^*_{n_F} \Psi_0$ and are large in number. However, as mentioned in I, Tomonaga's proof to show the equivalence between the Boson Hamiltonian and the original Fermion Hamiltonian is not sufficient, though his theory as a whole is very ingenious and instructive. However, we must not jump to the conclusion that Tomonaga's result is incomplete, for there are no definite reason to show that the correspondence between one-pair states in the original Fermion system and the Boson states in Tomonaga's formulation is incomplete and, further, Sawada's method also contains a questionable point especially in one-dimensional systems. In our later discussions the difference between both theories is not important and we will not enter into this problem in more detail.

If the above scattering states could really exist, Araki's interpretation[5], according to which the excitation of a plasmon state with the lowest momentum is assigned to the first absorption band of a Carotenoid, would be very questionable. One might think at first that such scattering states could not absorb light quanta because of the conservation laws of energies and momenta. However, light waves can be absorbed by end effects, and dimensions of actual molecules are much smaller than the wave length of the light to be absorbed, that is, the conservation of momenta is out of question.

There are also low energy states of another type omitted in Tomonaga's theory, as mentioned by Nakajima[6]: Configurations each of which is given by $a^*_n b^*_m \overline{\Psi}_0$, n being slightly larger than n_F and m being slightly larger than $-n_F$, will not give plasmons and would give low-energy scattering states whose energies are nearly equal to $\epsilon(n)-\epsilon(m)$. These situations are illustrated in Fig. 3. These scattering states can absorb light quanta in actual molecules. Thus, a kind of energy-gap model in Kuhn's

sense[3] or so is required, in order to explain the convergency of the first absorption wave-length of the conjugated molecules.[1]

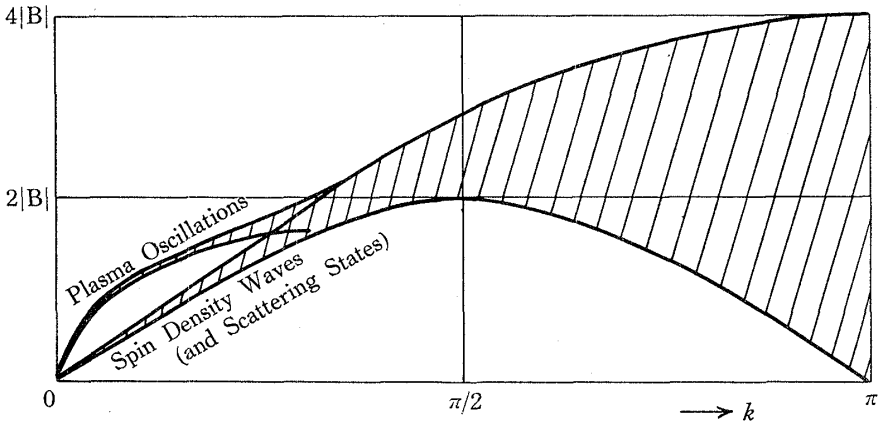


Fig. 3. Excitation energies of one-pair states in an N-molecule

§ 3. The Hamiltonian of the π electrons in a long molecule with alternating bonds

In our π electron Hamiltonian of an S-molecule the resonance integral defined in I is not merely B but $B+\Delta B$ or $B-\Delta B$, and further the Coulomb integral $J(R_1-R_2)$ defined in I depends not only on $R=|R_1-R_2|$ but on R_1 and R_2. Here we assume that these differences are not large. Adopting Pariser-Parr's π-electron approximation and neglecting the end effects as in I, we get the Hamiltonian $H=H_0+H_I$ given by

$$\begin{cases} H_0=H_0^0+\Delta H_0 \\ H_I=H_I^0+\Delta H_I, \end{cases}$$

where

$$\begin{aligned} H_0^0&=B\sum_{-N/2<R\leqq N/2}^{\sigma}(b_{R+1,\sigma}^* b_{R,\sigma}+b_{R-1,\sigma}^* b_{R,\sigma})=\sum_{-\pi<k\leqq\pi}^{\sigma}\epsilon(k)\,a_{k,\sigma}^* a_{k,\sigma}, \\ \Delta H_0&=\Delta B\sum_{-N/4<R\leqq N/4}^{\sigma}(b_{2R,\sigma}^* b_{2R+1,\sigma}+b_{2R+1,\sigma}^* b_{2R,\sigma}) \\ &\quad -\Delta B\sum_{-N/4\leqq R<N/4}^{\sigma}(b_{2R,\sigma}^* b_{2R-1,\sigma}+b_{2R-1,\sigma}^* b_{2R,\sigma}), \qquad (3\cdot1) \\ H_I^0&=\tfrac{1}{2}\sum_{-N/2<R_1,R_2\leqq N/2}\rho(R_1)\rho(R_2)J(R_1-R_2)=\tfrac{1}{2}\sum_k J_k\rho_k\rho_{-k}+\text{const}, \end{aligned}$$

and ΔH_I consists of the interaction between electric dipoles, each of which has dipole moment $(-1)^R e^2\cdot\Delta a\cdot\rho(R)$. Hence ΔH_I is a short-range interaction as well as weak one. Therefore, we neglect this.

We will express ΔH_0 in terms of a_k^* and a_k. Hereafter, we will omit the spin suffix σ in order to save notations, unless it is necessary. Using (2·3), we get

$$\sum_{-N/4<R\leqq N/4}(b_{2R}^{*}b_{2R-1}+b_{2R-1}^{*}b_{2R})$$
$$=\sum_{|k|\leqq\pi}(\cos k)a_k^{*}a_k+i\sum_{|k|,\,|k+\pi|\leqq\pi}(\sin k)a_{k+\pi}^{*}a_k+i\sum_{|k|,\,|k-\pi|\leqq\pi}(\sin k)a_{k-\pi}^{*}a_k,$$

and

$$\sum_{-N/4\leqq R<N/4}(b_{2R}^{*}b_{2R+1}+b_{2R+1}^{*}b_{2R})$$
$$=\sum_{|k|\leqq\pi}(\cos k)a_k^{*}a_k-i\sum_{|k|,\,|k+\pi|\leqq\pi}(\sin k)a_{k+\pi}^{*}a_k-i\sum_{|k|,\,|k-\pi|\leqq\pi}(\sin k)a_{k-\pi}^{*}a_k.$$

Substituting these into (3·1), we obtain

$$\Delta H_0=2i\Delta B\sum_{|k|,\,|k+\pi|\leqq\pi}(\sin k)a_{k+\pi}^{*}a_k+2i\Delta B\sum_{|k|,\,|k-\pi|\leqq\pi}(\sin k)a_{k-\pi}^{*}a_k.$$

Therefore

$$H_0=2B\sum_{-\pi<k\leqq\pi}(\cos k)a_k^{*}a_k$$
$$+2i\Delta B\sum_{|k|,\,|k+\pi|\leqq\pi}(\sin k)a_{k+\pi}^{*}a_k+2i\Delta B\sum_{|k|,\,|k-\pi|\leqq\pi}(\sin k)a_{k-\pi}^{*}a_k. \tag{3·2}$$

This is easily diagonalized by means of the following transformation

$$\left.\begin{aligned}a_{\pi/2-k}&=\left(\frac{1+\gamma_k}{2}\right)^{1/2}a_f(-k)-i\left(\frac{1-\gamma_k}{2}\right)^{1/2}a_c(-k)\\ a_{-\pi/2-k}&=-i\left(\frac{1-\gamma_k}{2}\right)^{1/2}a_f(-k)+\left(\frac{1+\gamma_k}{2}\right)^{1/2}a_c(-k)\end{aligned}\right\} \tag{3·3}$$

$$\left.\begin{aligned}a_{-\pi/2+k}&=-i\left(\frac{1+\gamma_k}{2}\right)^{1/2}a_f(k)+\left(\frac{1-\gamma_k}{2}\right)^{1/2}a_c(k)\\ a_{\pi/2+k}&=\left(\frac{1-\gamma_k}{2}\right)^{1/2}a_f(k)-i\left(\frac{1+\gamma_k}{2}\right)^{1/2}a_c(k)\end{aligned}\right\} \tag{3·3′}$$

where $\pi/2>k>0$ and

$$\gamma_k=\frac{|B\sin k|}{\sqrt{B^2\sin^2 k+(\Delta B)^2\cos^2 k}}. \tag{3·4}$$

Then (3·2) is written as

$$H_0=\sum_{-\pi/2<k\leqq\pi/2}E_c(k)a_c^{*}(k)a_c(k)+\sum_{-\pi/2<k\leqq\pi/2}E_f(k)a_f^{*}(k)a_f(k), \tag{3·5}$$

where

$$E_c(k)=-E_f(k)=2\sqrt{B^2\sin^2 k+(\Delta B)^2\cos^2 k}. \tag{3·6}$$

Thus we have a Brillouin gap $\epsilon_g=4\Delta B$, where we have chosen $\Delta B>0$. These spectra of H_0 are shown in Fig. 4.

Now we will express the Coulomb interaction

$$H_I=\sum_{\kappa>0}J_k\rho_k\rho_{-k}$$

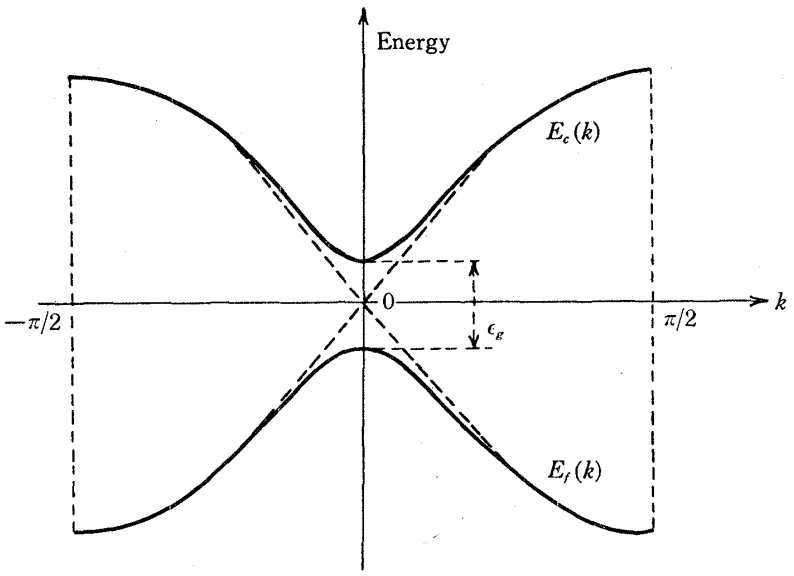


Fig. 4

in terms of $a_f(k)$ and $a_c(k)$. The result is as follows,

$$\begin{aligned}\rho_k=&\sum_{l>0}A_l^{l+k}\{a_f^*(l+k)a_f(l)+a_c^*(l+k)a_c(l)\\&\quad+a_f^*(-l)a_f(-l-k)+a_c^*(-l)a_c(-l-k)\}\\&+\sum_{k>l>0}B_l^{k-l}\{a_f^*(k-l)a_f(-l)+a_c^*(k-l)a_c(-l)\}\\&+\sum_{l>0}if_l^{l+k}\{a_c^*(l+k)a_f(l)+a_f^*(l+k)a_c(l)\\&\quad+a_f^*(-l)a_c(-l-k)+a_c^*(-l)a_f(-l-k)\}\\&+\sum_{k>l>0}ig_l^{k-l}\{a_f^*(k-l)a_c(-l)+a_c^*(k-l)a_f(-l)\},\end{aligned}\tag{3·7}$$

$$\rho_{-k}=\rho_k^*,$$

where

$$\left.\begin{aligned}A_l^{l+k}&\equiv\tfrac{1}{2}\{(1-\gamma_{l+k})^{1/2}(1-\gamma_l)^{1/2}+(1+\gamma_{l+k})^{1/2}(1+\gamma_l)^{1/2}\}\\B_l^{k-l}&\equiv\tfrac{1}{2}\{(1+\gamma_{k-l})^{1/2}(1-\gamma_l)^{1/2}+(1-\gamma_{k-l})^{1/2}(1+\gamma_l)^{1/2}\}\\f_l^{l+k}&\equiv\tfrac{1}{2}\{(1+\gamma_{l+k})^{1/2}(1-\gamma_l)^{1/2}-(1-\gamma_{l+k})^{1/2}(1+\gamma_l)^{1/2}\}\\g_l^{k-l}&\equiv\tfrac{1}{2}\{(1+\gamma_{k-l})^{1/2}(1+\gamma_l)^{1/2}-(1-\gamma_{k-l})^{1/2}(1-\gamma_l)^{1/2}\}\end{aligned}\right\}.\tag{3·8}$$

Here we adopt the following conventional notations,

$$a_c(k)\equiv a(k),$$

$$a_f(k)\equiv b^*(k),$$

$b^*(k)$ corresponding to the creation operator for a hole. Further, in order to simplify the notations in (3·7), we introduce the following quantities,

$$C_l^{l+k}\begin{cases}\equiv A_l^{l+k}(l>0), \\ \equiv B_{-l}^{k+l}(0>l>-k), \\ \equiv A_{-l-k}^{-l}(-k>l),\end{cases} \quad e_l^{l+k}\begin{cases}\equiv f_l^{l+k}(l>0), \\ \equiv g_{-l}^{k+l}(0>l>-k), \\ \equiv f_{-l-k}^{-l}(-k>l),\end{cases} \tag{3·9}$$

where $k>0$. Then we have

$$\rho_k=\sum_l C_l^{l+k}\{b(l+k)b^*(l)+a^*(l+k)a(l)\}-i\zeta_k \tag{3·10}$$

where

$$\zeta_k\equiv\sum_l e_l^{l+k}\{a^*(l+k)b^*(l)+b(l+k)a(l)\} \tag{3·11}$$

for $k>0$ and

$$\zeta_{-k}\equiv\zeta_k{}^*.$$

For our later discussions we give values of e_l^{l+k} in Table I.

Table I

k	$\ll \Delta B/\lvert B\rvert$		$\gg \Delta B/\lvert B\rvert$	
l	$\ll \Delta B/\lvert B\rvert$	$\gg \Delta B/\lvert B\rvert$	$\ll \Delta B/\lvert B\rvert$	$\gg \Delta B/\lvert B\rvert$
g_l^{k-l}	$\frac{k}{2}\Big/\frac{\Delta B}{\lvert B\rvert}$		$1/\sqrt{2}$	1
f_l^{l+k}	$\frac{k}{2}\Big/\frac{\Delta B}{\lvert B\rvert}$	$\frac{k}{2}\left(\frac{\Delta B}{\lvert B\rvert}\right)\mathrm{cosec}^2 l$	$1/\sqrt{2}$	$\frac{\Delta B}{2\lvert B\rvert}(\cot(l+k)-\cot l)$

§ 4. Plasma oscillations

Though our main purpose is to study the one-dimensional system, we will give some qualitative argument on the collective motions in a three-dimensional system. In general, if NJ_k is replaced by $4\pi e^2/ak^2$, our discussions on the one-dimensional model seem to be in essential points the ones on a three-dimensional system.

Excited states which may be interpreted as oscillating states of density waves might ordinarily be found even in insulators, if we seek such solutions among high energy states. However, many of them would be much different in character from the "usual" plasmon states in metals, and investigation of such high energy states is beyond our task. Our problem is to ascertain whether plasma oscillations similar to those in N-molecules ($\epsilon_g=0$) exist in S-molecules ($\epsilon_g>0$) or not.

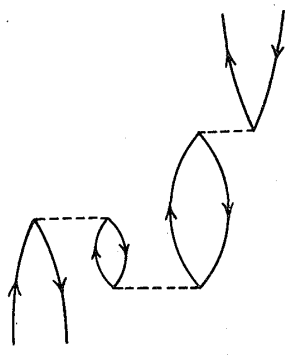


Fig. 5

Now the plasmon states in N-molecules are given by the diagrams of Gell-Mann and Brueckner's type[7] as shown in Fig. 5 which we call a plasmon diagram. Therefore, as in § 2, we seek for solutions within the framework of the plasmon diagrams and investigate the solutions to see

whether much difference can be found between these solutions and those of N-molecules. Then, according to Sawada,[4] we may replace the Coulomb interaction H_I by

$$H_I \to H_c = \sum_{k>0} J_k \zeta_k \zeta_{-k}$$

where ζ_k is given by (3·11) or

$$\zeta_k = \sum_l e_l^{l+k} \{\vartheta^*(l,\ l+k) + \vartheta(l+k,\ l)\}. \tag{4·1}$$

In the above

$$\vartheta(l,\ k) = b(l)a(k). \tag{4·2}$$

Then, in the framework of the plasmon diagrams, we get

$$[H_C,\ \vartheta^*(l,\ l+k)] = J_k \cdot e_l^{l+k} \cdot \zeta_k,$$
$$[H_C,\ \vartheta(l+k,\ l)] = -J_k \cdot e_l^{l+k} \cdot \zeta_k,$$
$$[H_0,\ \vartheta^*(l,\ l+k)] = E(l,\ l+k)\vartheta^*(l,\ l+k),$$
$$[H_0,\ \vartheta(l+k,\ l)] = -E(l,\ l+k)\vartheta(l+k,\ l),$$

where

$$E(l,\ k) \equiv E_c(k) - E_f(l). \tag{4·3}$$

From these, we get the following eigenvalue equation for excitation energy W:

$$1 = J_k \sum_l^{\sigma} |e_l^{l+k}|^2 \left\{ \frac{1}{W - E(l,\ l+k)} - \frac{1}{W + E(l,\ l+k)} \right\} \tag{4·4′}$$

or

$$1 = 4J_k \sum_l \frac{E(l,\ l+k)\,|e_l^{l+k}|^2}{W^2 - E^2(l,\ l+k)}. \tag{4·4}$$

We seek for solutions of (4·4) for some extreme values of k.

Case I. $|k| \ll \Delta B/|B|$

In this case (4·4) may be approximated as

$$1 = 8J_k \sum_{l>0} \frac{E(l,\ l+k)\,|f_l^{l+k}|^2}{W^2 - E^2(l,\ l+k)} = \frac{4}{\pi} N J_k \int_0^{\pi/2} \frac{E(l,\ l+k)\,|f_l^{l+k}|^2}{W^2 - E^2(l,\ l+k)}\, dl. \tag{4·5}$$

We calculate $E(l,\ l+k)\,|f_l^{l+k}|^2$ up to the lowest order term with respect to k. Then we get

$$E(l,\ l+k)\,|f_l^{l+k}|^2 = k^2 \frac{B^2 \Delta B^2}{(\Delta B^2 \cos^2 l + B^2 \sin^2 l)^{3/2}} + O(k^3). \tag{4·6}$$

(Case I·1) Three-dimensional system ($|k| \ll \Delta B/|B|$) ;

$$N \cdot J_k = \frac{4\pi e^2}{a} \frac{1}{k^2}.$$

At first we assume that the solution of (4·5) satisfies

$$W > \underset{l}{\mathrm{Max}}\{E(l,\ l+k)\}.$$

Now $NJ_k \cdot E(l,\ l+k)|f_l^{l+k}|^2$ in the numerator of (4·5) is extremely large only when $l \ll \Delta B/|B|$ and is practically zero when $l \gg \Delta B/|B|$, as is easily shown from (4·6). Further, for $l \ll \Delta B/|B|$,

$$W \gg E(l,\ l+k).$$

Then we get from (4·5)

$$W^2 = 8J_k \sum_{l>0} E(l,\ l+k)|f_l^{l+k}|^2.$$

Substituting (4·6) into the above and replacing the sum by the integral, we obtain

$$W^2 = \frac{16e^2}{a} B^2 \Delta B^2 \int_0^{\pi/2} \frac{dl}{(B^2 \sin^2 l + \Delta B^2 \cos^2 l)^{3/2}}$$

$$= \frac{16e^2}{a} |B| \left(\frac{\Delta B}{B}\right)^2 \int_0^{\pi/2} \frac{dl}{[1-\{1-(\Delta B/B)^2\}\cos^2 l]^{3/2}}.$$

In case $\Delta B \ll |B|$ we get, as shown in the Appendix,

$$\int_0^{\pi/2} \frac{dl}{[1-\{1-(\Delta B/B)^2\}\cos^2 l]^{3/2}} = \left(\frac{B}{\Delta B}\right)^2.$$

Therefore we obtain

$$W = 4\sqrt{\frac{e^2}{a} \cdot |B|} \equiv W_p.$$

This is nothing but the excitation energy of a plasmon given by substituting $NJ_k = (4\pi e^2/a) \cdot (1/k^2)$ into (2·5), i.e. the plasmon energy in the "normal state" ($\epsilon_g = 0$). For a very small k, the maximum value of $E(l,\ l+k)$ is almost equal to $4|B|$, as shown in Fig. 7. Therefore, $W_p > 4|B|$ has now been required. This means $e^2/a > |B|$. If this condition is satisfied, the plasmon level lies separately from the level continuum given by $E(l,\ l+k)$. On the other hand, if $e^2/a < |B|$, the plasmon level sinks into the level continuum. Even in this case, we cannot say that the plasma oscillation disappears when the gap appears. In this case the dispersion relation is written as[8]

$$1 = \frac{4}{\pi} NJ_k \cdot P\int \frac{E \cdot |e_l^{l+k}|^2}{W^2 - E^2} \Omega(E)\, dE \qquad (4\cdot7)$$

where P means the principal value,

$$E = E(l,\ l+k)$$

and

$$dl = \Omega(E)\, dE.$$

Then we get again the plasma frequency which is nearly equal to the one in the "normal state" ($\epsilon_g=0$). The electron excitations $(f, l)\to(c, l+k)$ in which $E(l, l+k)$'s are nearly equal to W should be treated separately. These excitations give the level width of our plasma oscillation. We estimate this width by means of the following formula,

$$\hbar\Gamma=\frac{1}{N}\frac{4\pi e^2}{ak^2}\sum_l E(l, l+k)\,|e_l^{l+k}|^2\,\delta(E(l, l+k)-W)$$

which has been derived by Kanazawa[9] in the framework of the time-dependent perturbation illustrated by Fig. 6. In order that

$$E(l, l+k)=W_p$$

is satisfied, $|l|$ should be very large compared with $\Delta B/|B|$. Then we get

$$E(l, l+k)\,|e_l^{l+k}|^2=k^2\cdot\Delta B/|B|\cdot\Delta B/\sin^3 l.$$

Therefore $\hbar\Gamma/B\propto(\Delta B/B)^2$. Consequently, if the gap is very small, the energy width of the plasmon level lying in the level continuum is very small.

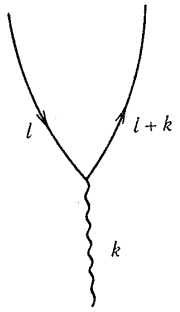


Fig. 6

(Case I·2) One-dimensional system ($|k|\ll\Delta B/|B|$)

In this case $NJ_k=(2e^2/a)K_0(\gamma|k|)$, then the dispersion relation (4·7) is written as

$$1=\frac{4e^2}{a}k^2K_0(\gamma|k|)\,P\int_{l=0}^{l=\pi/2}\frac{B^2\Delta B^2}{(B^2\sin^2 l+\Delta B^2\cos^2 l)^{3/2}}\frac{\Omega(E)\,dE}{W^2-E^2(l, l+k)}.$$

Now $\lim_{k\to0}k^2K_0(\gamma|k|)=0$. Therefore, W should be equal to $E(l, l+k)=E$, at which the above integrand rapidly changes. Then, it is very doubtful whether this solution does correspond to a real plasmon state. Indeed, one obtains the conclusion that there are no plasmons in the region of k satisfying $\Delta B/|B|\gg k$, if one is allowed to use the "existence criterion" of Bohm and Pines mentioned below. This criterion is stated as follows: For any k, the plasma oscillation exists if $I\equiv W_k/(\Phi|J_k\rho_k\rho_{-k}|\Phi)<1$, but it does not exist if $I>1$. In the above, Φ is a Slater determinant composed of a single particle state belonging to a degenerate Fermi sphere. In our case $W_k\cong\epsilon_g$. Further, noting that we are now considering the the case of $k\ll\Delta B/|B|$, we get

$$(\Phi|J_k\rho_k\rho_{-k}|\Phi)=J_k(\textstyle\sum_l^{\sigma}|e_l^{l+k}|^2)$$

$$\cong 2J_k\left(\frac{k}{2}\Big/\frac{\Delta B}{B}\right)^2\times\frac{N}{2\pi}\left(\frac{\Delta B}{|B|}\right)=\frac{1}{16}(W_k^{(0)})^2/\Delta B=\frac{1}{4}(W_k^{(0)})^2/\epsilon_g,$$

where $W_k^{(0)}=\sqrt{(4/\pi)k^2|B|NJ_k}$ is the energy of a plasmon in the case of $\epsilon_g=0$. Then we obtain

$$I \cong 4(\epsilon_g/W_k^{(0)})^2 \gg 1.$$

Thus, the plasmon levels which exist in N-molecules under the energy gap completely disappear in S-molecules and seem to be dissolved away into the level continuum above the gap.

Case II. $\pi/2 \gg k \gg \Delta B/|B|$

In the dispersion formula

$$1 = \frac{2NJ_k}{\pi} \cdot P \int_{l=-\pi/2}^{l=\pi/2} \frac{E(l,\ l+k)\,|e_l^{l+k}|^2}{W^2 - E^2(l,\ l+k)}\,\Omega(E)\,dE$$

we may use

$$e_l^{l+k} \begin{cases} = g_{-l}^{k+l}, & \text{if } -k < l < 0. \\ \cong 0, & \text{otherwise.} \end{cases}$$

Therfore, we get

$$1 = \frac{2NJ_k}{\pi} \int_{-k}^{0} \frac{E(l,\ l+k)}{W^2 - E^2(l,\ l+k)}\,dl.$$

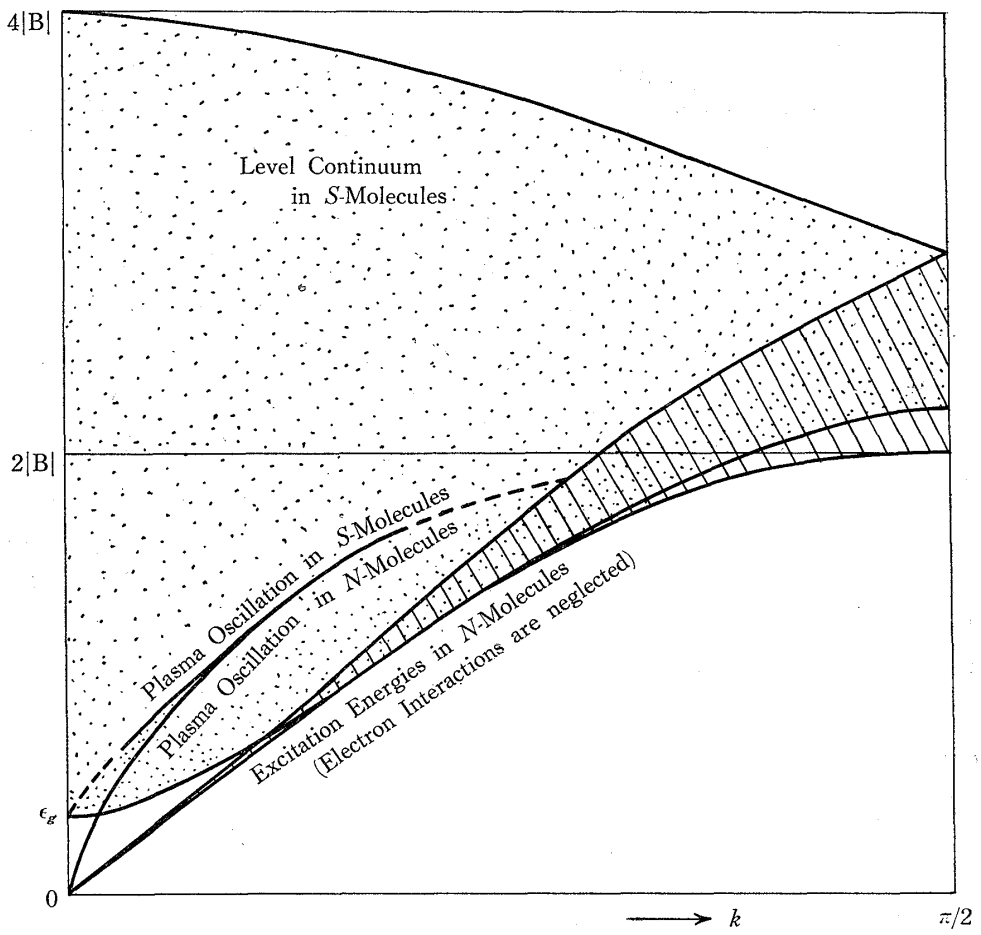


Fig. 7. Excitation energies of one-pair states

We can find a solution satisfying

$$W \gg E(l,\ l+k) \quad \text{for} \quad -k<l<0.$$

Further in the integrands, we may use

$$E(l,\ l+k)=2|B|k.$$

Then the above eigenvalue equation is nothing but the one in an N-molecule. This is true in the one-dimensional system as well as in the three-dimensional one. Especially, in the former the plasmon level always lies in the level continuum (unless $k^2NJ_k>4|B|$). The level width of this plasma oscillation is given by

$$\hbar\Gamma=J_k\sum_l E(l,\ l+k)\,|e_l^{l+k}|^2\,\delta(E(l,\ l+k)-W).$$

l should be very large compared with $\Delta B/|B|$ in order to satisfy $E(l,\ l+k)=W$. Then,

$$e_l^{l+k}\to f_l^{l+k}\propto\frac{\Delta B}{|B|}(\cot(l+k)-\cot l).$$

Thus, $\hbar\Gamma$ is sufficiently small and hence stable plasma oscillations may exist in S-molecules when $\Delta B\ll|B|$.

§ 5. Excitons

As is well known, the plasma oscillations come from the high mobility of electrons which leads to the screening of the Coulomb interaction between electrons. If the mobility were very large, the attractive force between an electron and a hole will also be screened and the possibility that the electron-hole pair has a bound state will be diminished. Thus excitons and plasmons are mutually exclusive. The exciton solution is given by the diagrams shown in Fig. 8. In the usual derivation[10),11),12)] of the equation describing the hydrogen-like internal motion of an exciton, one implicitly adopts only these diagrams and neglects all the other ones. Thus

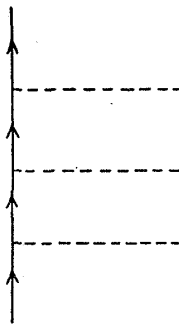


Fig. 8

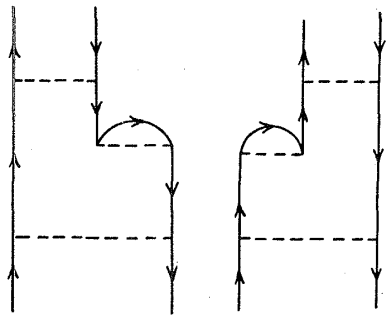


Fig. 9

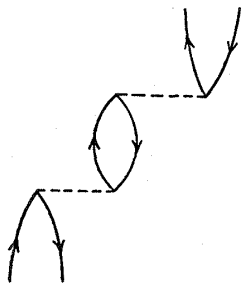
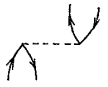


Fig. 10

we will call the diagrams shown in Fig. 8 the exciton diagrams. If the energy gap is very large as in case of insulators, the diagrams for an electron-hole pair which seem important at first sight are the exciton diagrams, exchange diagrams[13] (Fig. 9), and Macke's diagrams[14] (Fig. 10) (and of course, the ones given by mixing these diagrams). The remaining diagrams may be neglected, because they should be accompanied by "vacuum polarizations" which require a large energy in case of a large energy gap. The exchange diagrams will also play a minor role because they can be included in $E_c(k)$ or $E_f(k)$. One neglects Macke's diagrams, because in the off-diagonal element $(a^*(l'+k)b^*(l')\Psi_0|H_I|b(l)a(l+k)\Psi_0)$ the term  is generally small compared with  . However, the reason why other diagrams than exciton ones may be neglected in actual insulators would not be very clear. Indeed, the polarization waves in Mott-Pines' sense[15] which can never be given by exciton diagrams might exist in insulators.

At first we take only the exciton diagrams. Then

$$\rho_k \to \sum_l C_l^{l+k}\{b(l+k)b^*(l)+a^*(l+k)a(l)\}.$$

Further the Coulomb interaction

$$H_I=\sum_{\kappa>0} J_\kappa \rho_\kappa \rho_{-\kappa}$$

may be replaced by

$$H_I \to H_c=-\sum_{\kappa>0}\sum_{\lambda,\mu} J_\kappa \cdot C_\mu^{\mu+\kappa} C_\lambda^{\lambda+\kappa}\{a^*(\lambda)b^*(\mu)b(\mu+\kappa)a(\lambda+\kappa) + a^*(\lambda+\kappa)b^*(\mu+\kappa)b(\mu)a(\lambda)\}.$$

Introducing $\vartheta(\mu,\lambda)\equiv b(\mu)a(\lambda)$, we rewrite this as

$$H_C=-\sum_{\kappa\neq 0}\sum_{\lambda\mu} J_\kappa C_\mu^{\mu+\kappa} C_\lambda^{\lambda+\kappa}\vartheta^*(\mu,\lambda)\vartheta(\mu+\kappa,\lambda+\kappa).$$

As we limit ourselves in the exciton diagrams, we may use the commutation relation

$$[\vartheta(\lambda,\mu),\ \vartheta^*(\lambda',\mu')]=\delta_{\lambda\lambda'}\delta_{\mu\mu'}$$

in the evaluation of $[H_C, \vartheta^*(h-k,h)]$. Then we get

$$[H_C,\ \vartheta^*(h-k,h)]=-\sum_{\kappa\neq 0} J_\kappa C_{h-k-\kappa}^{h-k} C_{h-\kappa}^{h}\vartheta^*(h-k-\kappa,h-\kappa). \qquad (5\cdot 1)$$

Eq. (5·1) together with

$$[H_0,\ \vartheta^*(h-k,h)]=E(h-k,h)\vartheta^*(h-k,h)$$

determines the motion of our electron-hole pair.

Here we introduce the following quantity,

$$\mathcal{L}^*(k,R)=N^{-1/2}\sum_h \exp(ihR)\vartheta^*(h-k,h).$$

Then we have

$$[H_0,\ \mathfrak{L}^*(k,\ R)]=N^{-1/2}\sum_h \exp(ihR)\{E_C(h)-E_f(h-k)\}\vartheta^*(h-k,\ h)$$
$$=N^{-1}\sum_h\sum_{R'}\exp[ih(R-R')]\{E_C(h)-E_f(h-k)\}\mathfrak{L}^*(k,\ R')$$
$$=\sum_{R'}\{\mathcal{H}_C(R-R')-\exp[ik(R-R')]\mathcal{H}_f(R-R')\}\mathfrak{L}^*(k,\ R')$$

where

$$\mathcal{H}_C(R)=N^{-1}\sum_k \exp(ikR)E_C(k),\ \text{etc.} \tag{5·2}$$

Similarly we get

$$[H_C,\ \mathfrak{L}^*(k,\ R)]$$
$$=-N^{-1}\sum_{\varkappa\neq 0}\sum_h\sum_{R'}J_\varkappa\exp[ih(R-R')]\exp(i\varkappa R')C^{h-k}_{h-k-\varkappa}C^h_{h-\varkappa}\mathfrak{L}^*(k,\ R')$$
$$=-\sum_{\varkappa\neq 0}\sum_{R'}J_\varkappa\exp(i\varkappa R')C^k_\varkappa(R-R')\cdot\mathfrak{L}^*(k,\ R'),$$

where

$$N^{-1}\sum_h\exp(ihR)C^{h-k}_{h-k-\varkappa}C^h_{h-\varkappa}\equiv C^k_\varkappa(R). \tag{5·3}$$

Introducing

$$\sum_{\varkappa\neq 0}J_\varkappa\exp(i\varkappa R')C^k_\varkappa(R-R')=V_k(R',\ R), \tag{5·4}$$

which corresponds to a velocity dependent and non-local potential, we get

$$[H,\ \mathfrak{L}^*(k,\ R)]$$
$$=\sum_{R'}\{\mathcal{H}_C(R-R')-\exp[ik(R-R')]\mathcal{H}_f(R-R')-V_k(R',\ R)\}\mathfrak{L}^*(k,\ R'). \tag{5·5}$$

Now, the energy eigen-state of our electron-hole pair will, in general, be written as

$$\Psi(n,\ k)=\mathfrak{A}^*(n,\ k)\Psi_0,$$

where Ψ_0 is the vacuum state and

$$\mathfrak{A}^*(n,\ k)=\sum_R U_k(n,\ R)\cdot\mathfrak{L}^*(k,\ R). \tag{5·6}$$

In the above n is a quantum number describing the internal motion of our pair. As $H\Psi=0$, we get from $H\Psi(n,\ k)=W\Psi(n,\ k)$ the following equation,

$$[H,\ \mathfrak{A}^*(n,\ k)]\Psi_0=W\mathfrak{A}^*(n,\ k)\Psi_0.$$

Substituting (5·5) and (5·6) on the left side of the above equation, we get

$$\sum_{R'}\{\mathcal{H}_C(R'-R)-\exp[ik(R'-R)]\mathcal{H}_f(R'-R)-V_k(R,\ R')\}U_k(n,\ R')$$
$$=WU_k(n,\ R). \tag{5·7}$$

According to Wannier,[10] we sometimes regard the point function $U_k(n,\ R)$ defined at $R=0,\ \pm1,\ \cdots,\ \pm N/2$ as a continuous function of R in the range $(-N/2,\ N/2)$. Then, from (5·2) we obtain[10]

$$\sum_{R'} \mathcal{H}_c(R'-R)\cdot U_k(n,\ R') = E_c\left(\frac{1}{i}\frac{\partial}{\partial R}\right) U_k(n,\ R),$$

and

$$\sum_{R'} \exp[ik(R'-R)]\cdot \mathcal{H}_f(R'-R)\cdot U_k(n,\ R') = E_f\left(-k+\frac{1}{i}\frac{\partial}{\partial R}\right) U_k(n,\ R).$$

Therefore, Eq. (5·7) becomes

$$\left[E_c\left(\frac{1}{i}\frac{\partial}{\partial R}\right) - E_f\left(-k+\frac{1}{i}\frac{\partial}{\partial R}\right)\right] U_k(n,\ R)$$
$$-\int V_k(R,\ R')\, U_k(n,\ R')\, dR' = W U_k(n,\ R).$$

We here perform the following transformation,[10]

$$\exp\left(-\frac{i}{2}kR\right) U_k(n,\ R) = \Gamma_k(n,\ R).$$

Then, we get

$$\mathfrak{T}\cdot \Gamma_k(n,\ R) - \int V_k(R,\ R')\,\Gamma_k(n,\ R')\, dR' = W\cdot \Gamma_k(n,\ R), \tag{5·8}$$

where

$$\mathfrak{T} \equiv \exp\left(-\frac{i}{2}kR\right)\left[E_c\left(\frac{1}{i}\frac{\partial}{\partial R}\right) - E_f\left(-k+\frac{1}{i}\frac{\partial}{\partial R}\right)\right]\exp\left(\frac{i}{2}kR\right)$$
$$= E_c\left(\frac{k}{2}+\frac{1}{i}\frac{\partial}{\partial R}\right) - E_f\left(-\frac{k}{2}+\frac{1}{i}\frac{\partial}{\partial R}\right). \tag{5·9}$$

As we are now concerned with the very low energy states, we here consider the case $k\to 0$. Further, we replace $E_c(p)$ and $E_f(p)$ by

$$\left.\begin{aligned} E_c(p) \to \tilde{E}_c(p) &= 2\Delta B + \frac{\hbar^2}{2m^*}(p/a)^2 \\ -E_f(p) \to -\tilde{E}_f(p) &= 2\Delta B + \frac{\hbar^2}{2m^*}(p/a)^2 \end{aligned}\right\}, \tag{5·10}$$

where

$$\frac{\hbar^2}{m^* a^2} = \left[\frac{d^2}{dp^2}E_c(p)\right]_{p=0} = \left[\frac{d^2}{dp^2}E_f(p)\right]_{p=0} = 2\frac{B^2-\Delta B^2}{\Delta B}. \tag{5·11}$$

Then we obtain

$$\mathfrak{T} = 4\Delta B + \frac{\hbar^2 k^2}{2\cdot(2m^* a^2)} - \frac{\hbar^2}{m^* a^2}\frac{d^2}{dR^2}.$$

Omitting the kinetic energy due to the translational motion of the center of mass of the electron-hole pair, we get the following wave equation for the internal motion of our electron-hole pair,

$$-\frac{\hbar^2}{m^*a^2}\cdot\frac{d^2}{dR^2}\Gamma_k(n,\ R)-\int V_k(R,\ R')\Gamma_k(n,\ R')dR'=(W-\epsilon_g)\Gamma_k(n,\ R). \tag{5·12}$$

If $\Delta B\ll|B|$, (5·11) becomes

$$m^*=\frac{\Delta B\hbar^2}{2B^2a^2}=\frac{1}{2}\left(\frac{\Delta B}{|B|}\right)\cdot\frac{(e^2/a)}{|B|}\left(\frac{a_B}{a}\right)m, \tag{5·13}$$

where a_B is the Bohr radius and m denotes the usual electron mass. Therefore $\Delta B\ll|B|$ means $m^*\ll m$, for $a\sim a_B$ and $|B|\gtrsim(e^2/a)$. In this case, it is very difficult to localize the internal motion of our electron-hole pair, because of the uncertainty principle. Then, the bound state of this pair, if it could exist, should have a widely spreading orbital for the internal motion. Then, the long range part of the attracting force between the electron and the hole becomes important, while the short range part plays a less important role. Therefore, among the Fourier components of this potential, J_κ's with small κ play important roles.

One may think that such a widely spreading character of the internal motion is completely due to our "ad hoc" assumption (5·10). Indeed, $\tilde{E}(p)$ gives an unreasonably high energy for the pair configuration $\vartheta^*(p-k,\ p)$ when $|p|\gg\Delta B/|B|$ (cf. Fig. 11). Hence, the mixing of the configuration $\vartheta^*(p-k,\ p)\Psi_0$ (with $|p|\gg\Delta B/|B|$) might be undeservedly supressed. However, the mixing of such a configuration will actually be small, for J_κ(with $\pi/2\gg\kappa\gg\Delta B/|B|$) should be replaced by $\tilde{J}_\kappa(\ll J_\kappa)$, as shown in our later discussions, and then the matrix element between the above configuration and $\vartheta^*(p-k,\ p)\Psi_0$ (with $|p|\ll\Delta B/|B|$) will become very small. Now, we will examine the potential $V_k(R,\ R')$. When $k\to0$, we get

$$C_\kappa^k(R-R')=\frac{1}{N}\sum_h|C_{h-\kappa}^h|^2\exp[ih(R-R')].$$

For small κ, $C_{h-\kappa}^h=1$. Then we obtain

$$C_\kappa^\kappa(R-R')=\delta(R-R').$$

Therefore, for sufficiently large R, we get

$$V_k(R,\ R')=\sum_{\kappa\neq0}J_\kappa\cdot\exp(i\kappa R)\delta(R-R')$$

$$=\frac{e^2}{Ra}\cdot\delta(R-R').$$

This assures the existence of the bound state solution for Eq. (5·12). The dissociation energy of this bound state is roughly estimated as follows.

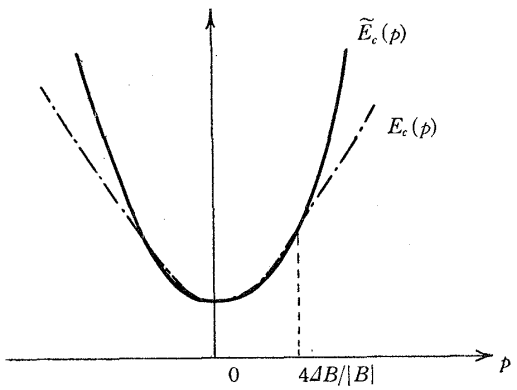


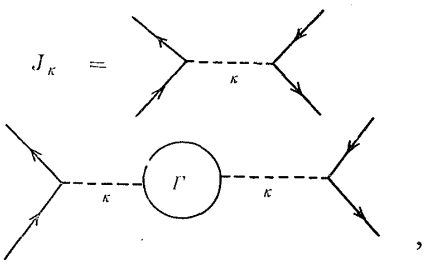
Fig. 11

$$W-\epsilon_g\cong-\frac{1}{4}\frac{e^2}{a_B}\frac{\Delta B\hbar^2}{B^2a^2}\frac{1}{m}=-\frac{1}{4}\Delta B\left(\frac{e^2}{a}\Big/|B|\right)^2=-\frac{1}{16}\epsilon_g\cdot\left(\frac{e^2}{a}\Big/|B|\right)^2 \tag{5·14}$$

It should be noted that $|B|$ is of the same order as that of e^2/a, though $|B|>e^2/a$. However, we must not jump to the conclusion that we can find an exciton level appreciably lower than the energy gap in an S-molecule.

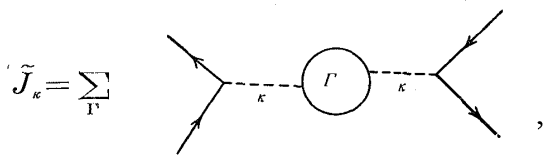
The reason why we have got such an exciton level is that we have taken into consideration only the exciton diagrams as shown in Fig. 8 or, in other words, we have completely neglected the screening effects for the long range Coulomb interaction between the electron and the hole. This interaction is not only

but also



,

where Γ is some polarization diagram.[16] Actually, for a scattering process with momentum transfer κ, the effective interaction should be given by



,

where the summation includes $\Gamma=0$. This $\tilde{J}_\kappa$ will be much smaller than J_κ.

Among various Γ's plasmon diagrams will be most important in case of a small gap. At first we consider the simplest case as shown in Fig. 12. The contribution from these diagrams is estimated as follows,

$$J^{(1)}(\kappa)\equiv -2J_\kappa^{\,2}\sum_\mu{}^{\sigma}\frac{|e_\mu^{\mu+\kappa}|^2}{E(\mu,\,\mu+\kappa)}=-\frac{2NJ_\kappa^{\,2}}{\pi}\int_{-\pi/2}^{\pi/2}\frac{|e_\mu^{\mu+\kappa}|^2\,d\mu}{E(\mu,\,\mu+\kappa)}. \qquad (5\cdot15)$$

This expression is not correct from the quantitative point of view, for in the energy denominator we have neglected the energy change induced by the intra-band transition of our electron-hole pair. For $\kappa\ll 4B/|B|$, however, (5·15) is a

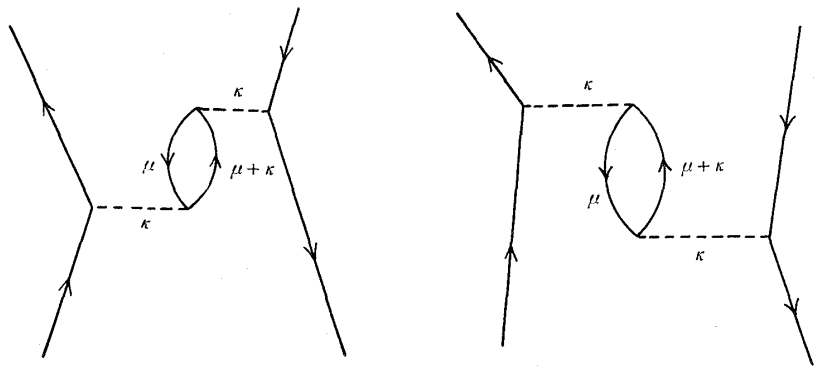


Fig. 12

sufficiently good approximation, for such an energy change is usually smaller than the polarization energy $E(\mu, \mu+\kappa)$. For $\pi/2 \gg \kappa \gg \Delta B/|B|$, on the other hand, the use of (5·15) can never be justified from the quantitative point of view. However, from the qualitative point of view, our result seems to remain unchanged, even if we take into account such an energy change. It should be noted that by using (5·15) we have replaced the screening for the interaction between the electron and the hole by the one for the interaction between two motionless charges placed in our many-electron system. In other words, we have neglected the retardation corresponding to the time spent by the interaction in polarizing the many-electron system. Though we can take this retardation into account by means of Hubbard's method[16] or else, we here neglect this, for the result including the retardation will complicate our later discussions. Here we adopt a similar technique to the one adopted by Gell-Mann and Brueckner[7], i.e. Feynman's path-integral method; we introduce the following function,

$$F_\kappa(t) \equiv \int_{-\pi/2}^{\pi/2} |e_\mu^{\mu+\kappa}|^2 \cdot \exp[-|t|E(\mu, \mu+\kappa)]\, d\mu.$$

Then (5·15) is written as

$$J^{(1)}(\kappa) = -\frac{NJ_\kappa^2}{\pi} \int_{-\infty}^{\infty} F_\kappa(t)\, dt.$$

This is further expressed as

$$J^{(1)}(\kappa) = -\frac{NJ_\kappa^2}{\pi} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt_1 \cdot F_\kappa(t_1)\, \delta(t_1 - t).$$

Next, we consider all plasmon diagrams shown in Fig. 13. Further, for our present qualitative arguments, we neglect all the other diagrams in the summation over Γ. Then we get

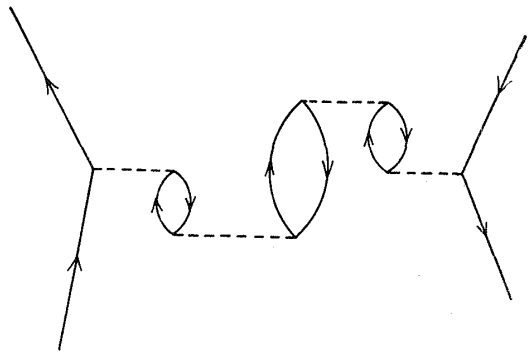


Fig. 13

$$\tilde{J}_\kappa = \sum_{n=0}^{\infty} J^{(n)}(\kappa),$$

$$J^{(n)}(\kappa) \equiv J_\kappa \cdot (-1)^n \left(\frac{NJ_\kappa}{\pi}\right)^n \cdot A_n(\kappa)$$

$$A_n(\kappa) \equiv \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n \cdot F_\kappa(t_1) \cdots F_\kappa(t_n) \cdot \delta(t_1 + \cdots + t_n - t).$$

Expanding the above δ-function into the Fourier series, we get

$$A_n(\kappa)=\frac{1}{2\pi}\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dt[Q_\kappa(u)]^n\exp(-iut)=[Q_\kappa(0)]^n,$$

where

$$Q_\kappa(u)\equiv\int_{-\infty}^{\infty}F_\kappa(t)\exp(itu)\,dt.$$

Therefore

$$\tilde{J}_\kappa=J_\kappa\sum_{n=0}^{\infty}(-1)^n\left(\frac{NJ_\kappa}{\pi}\right)^n[Q_\kappa(0)]^n=J_\kappa\frac{1}{1+(NJ_\kappa/\pi)Q_\kappa(0)},\qquad(5\cdot16)$$

where

$$Q_\kappa(0)=\int_{-\pi/2}^{\pi/2}d\mu\int_{-\infty}^{\infty}dt\cdot\exp[-|t|\cdot E(\mu,\mu+\kappa)]\cdot|e_\mu^{\mu+\kappa}|^2=2\int_{-\pi/2}^{\pi/2}d\mu\frac{|e_\mu^{\mu+\kappa}|^2}{E(\mu,\mu+\kappa)}.\qquad(5\cdot17)$$

(Case I) $\kappa\ll\Delta B/|B|$.

(5·17) may be safely replaced by

$$Q_\kappa(0)=4\int_0^{\pi/2}d\mu\frac{|f_\mu^{\mu+\kappa}|^2}{E(\mu,\mu+\kappa)}.$$

By means of (4·6) and (3·6), the above quantity is written as

$$Q_\kappa(0)=\kappa^2B^2(\Delta B)^2\int_0^{\pi/2}\frac{d\mu}{[(\Delta B)^2\cos^2\mu+B^2\sin^2\mu]^{5/2}}$$

$$=\frac{\kappa^2(\Delta B)^2}{|B|^3}\int_0^{\pi/2}\frac{d\mu}{[1-\{1-(\Delta B/B)^2\}\cos^2\mu]^{5/2}}.$$

This integral is evaluated in the Appendix, and is approximately equal to $\frac{2}{3}(B/\Delta B)^4$. Using this, we obtain

$$Q_\kappa(0)=\frac{2\kappa^2|B|}{3(\Delta B)^2}.$$

Then from (5·16) we obtain

$$\tilde{J}_\kappa=J_\kappa\cdot\frac{1}{1+2(NJ_\kappa)\cdot\kappa^2|B|/3\pi(\Delta B)^2}.\qquad(5\cdot18)$$

(Case II) $\pi/a\gg\kappa\gg\Delta B/|B|$.

(5·16) may be safely replaced by

$$Q_\kappa(0)=2\int_{-\infty}^{0}\frac{d\mu}{E(\mu,\,\mu+\kappa)}. \quad \text{(cf. Table I)}$$

Using $E(\mu,\,\mu+\kappa)=2|B|\kappa$, we get

$$Q_\kappa(0)=1/|B|.$$

Substituting the above into (5·16), we obtain

$$\tilde{J}_\kappa=J_\kappa\cdot\frac{1}{1+NJ_\kappa/\pi|B|}. \tag{5·19}$$

In Case II, the screened interaction in the S-molecule is equal to the one in the N-molecule. Note that $NJ_\kappa\gg|B|$, when $|\kappa|\ll\pi/2$. Especially, in three dimensional systems $(NJ_\kappa=(1/a)\cdot 4\pi e^2/\kappa^2)$, $\tilde{J}_\kappa$ is nothing but the Fourier coefficient of the potential $e^2\cdot\exp(-\alpha r)/r$. Then, the attractive potential between the electron and the hole separated by a distance r, $a|B|/\Delta B>r\gg a$, is not $-(e^2/r)$ but $-e^2\cdot\exp(-\alpha r)/r$. In Case I$(\kappa\ll\Delta B/|B|)$, the screening effect is weaker, though this effect grows stronger as $\Delta B\to 0$. Especially in three dimensional systems $\tilde{J}_\kappa=J_\kappa\cdot\dfrac{1}{1+(8/3)(e^2/a)|B|/\Delta B^2}$. Therefore, for $r\gg(|B|/\Delta B)\,a$, the interaction becomes $-e^2/\epsilon r$, where $\epsilon\cong 8/3\cdot e^2/a\cdot|B|/\Delta B^2$. Though this dielectric constant is extremely larger than unity, the interaction $-e^2/\epsilon r$ assures the existence of the excitons. Namely, the exciton solution is certainly obtained whenever the energy gap may arise and be compatible with the plasmon solution. However, the dissociation energy of the exciton in a three-dimensional system is extremely small compared with the gap, i.e., $(W-\epsilon_g/\epsilon_g)$ tends rapidly to zero in proportion to ϵ_g^2 as $\epsilon_g\to 0$, for the dielectric constant is inversely proportional to ϵ_g^2. Thus, the exciton cannot be observed if ϵ_g is sufficiently small, for the exciton level should have the energy width.[11]

In our one-dimensional system, however, $\tilde{J}_\kappa/J_\kappa$ for $\kappa\ll\Delta B/|B|$ is not so small as in the three-dimensional case. It should be noted that $\lim_{\kappa\to 0}\tilde{J}_\kappa=J_\kappa$. Namely, the interaction reduces to the completely unscreened form e^2/r, as $r\to\infty$. Accordingly, the possibility of observing the exciton in our one-dimensional system is much larger than that in the three-dimensional one. However, $(W-\epsilon_g/\epsilon_g)$ will tend to zero as $\epsilon_g\to 0$ even in this one-dimensional system because of the following reason. The classical distance of separation between the electron and the hole in their bound state whose dissociation energy is indicated by (5·14) is roughly equal to $(|B|/\Delta B)\,a_B$. Then $\tilde{J}_\kappa$'s with $\kappa\sim\Delta B/|B|$ should play important roles. The value of $\tilde{J}_\kappa/J_\kappa$ at $\kappa=\Delta B/|B|$ may be estimated by extrapolating the formula (5·17) or (5·18). Both formulae give about the same value for $\tilde{J}_\kappa/J_\kappa(\kappa=\Delta B/|B|)$, i.e. $\pi|B|/NJ_\kappa$. Note that $NJ_\kappa\gg|B|$. Hence $\tilde{J}_\kappa/J_\kappa\ll 1$ even for $\kappa\sim\Delta B/|B|$. Then the classical distance of separation should be much larger than $(|B|/\Delta B)\,a_B$, and so the dissociation energy $W-\epsilon_g$ of this exciton, if it could exist, would be much smaller than ϵ_g.

There are some possibilities of obtaining a large energy gap[3] in an S-molecule. Thus we could not reject the possibility that the lowest excited state corresponding to the first optical absorption would be the exciton state.

§ 6. Summary and discussions

One can never get the convergency, if one attributes its origin to the plasma oscillation of the one-dimensional electron gas in a long tube. Thus, a kind of energy-gap model in Kuhn's sense or the like is required, in order to explain the convergency.

When the energy-gap ϵ_g arises in the spectra of H_0, the plasma oscillations whose energy quanta $\hbar\omega$ are sufficiently large compared with ϵ_g remains stable even if their energies sink into the level-continuum of the pair excitation energies. On the other hand, the excited states which are represented in N-moleules by the plasmons with $\hbar\omega < \epsilon_g$ are much altered. The solution of Eq. (4·7) is always larger than ϵ_g, and in case $|k| \ll \Delta B/|B|$ it is almost equal to the gap. Moreover, it is very qeustionable to regard the solution as the one corresponding to a real plasma oscillation. Indeed, one obtains the conclusion that there are no plasmons in the region of k satisfying $|k| \ll \Delta B/|B|$, if one is allowed to use the " existence criterion " of Bohm and Pines. It should be noted that the above conclusions are limited to the one-dimensional system. Indeed, the plasma oscillations in the three-dimensional system remain unchanged when the small energy-gap arises.

Our discussions about the exciton are rather rough. Especially the use of (5·10) would be open to questions. However, we may reasonably conclude that the screening effect for the attractive force between the electron and the hole grows larger as the energy gap becomes smaller. By this screening effect the possibility of observing the exciton diminishes as ϵ_g becomes smaller. Further, our very rough arguments give the conclusion that the excitation energy of the lowest exciton-like bound state, if it could exist, would be nearly equal to the gap. Then, such a state would not be observed, for the exciton level should have energy width. Thus the lowest excitation energy of our many electron system with small energy gap in the spectra of H_0 seems to be practically equall to the gap.

§ 7. Acknowledgements

I would like to express my sincere thanks to Prof. M. Kotani and Dr. Y. Mizuno for their encouragements. I am very grateful to Prof. Y. Toyozawa for his valuable comments. It is also my pleasure to thank Prof. T. Muto for his kind comments on the manuscript.

Appendix

At first we calculate $\int_0^{\pi/2} \frac{d\mu}{[1-(1-k)\cos^2\mu]^{3/2}} \equiv I$ in case $k \ll 1$. The integrand

is overwhelmingly large only when $0 \lesssim \mu \ll 1$. Then we may use the following approximation,

$$I \simeqq \int_0^{\pi/2} \frac{\cos\mu\, d\mu}{[1-(1-k)\cos^2\mu]^{3/2}}$$
$$= \int_0^{\pi/2} \left[\cos\mu + \frac{3}{2}(1-k)\cos^3\mu + \frac{3\cdot 5}{2\cdot 4}(1-k)^2\cos^5\mu + \cdots\right] d\mu.$$

Using the well-known formula,

$$\int_0^{\pi/2} \cos^{2n+1}\mu\, d\mu = \frac{(2n)\cdot\cdots\cdot 4\cdot 2}{(2n+1)\cdot\cdots\cdot 5\cdot 3},$$

we get

$$I \simeqq 1+(1-k)+(1-k)^2+\cdots = \frac{1}{1-(1-k)} = \frac{1}{k}.$$

Next we calculate $\int_0^{\pi/2} \frac{d\mu}{[1-(1-k)\cos^2\mu]^{5/2}} \equiv\equiv I'$ in case $k \ll 1$. By the same reason as mentioned above the following technique may be used,

$$I' \simeqq \int_0^{\pi/2} \frac{\cos^3\mu\, d\mu}{[1-(1-k)\cos^2\mu]^{5/2}}$$
$$= \int_0^{\pi/2} \left[\cos^3\mu + \frac{5}{2}(1-k)\cos^5\mu + \frac{5\cdot 7}{2\cdot 4}(1-k)^2\cos^7\mu + \cdots\right] d\mu$$
$$= \frac{2}{3}[1+2(1-k)+3(1-k)^2+\cdots]$$
$$= \frac{2}{3}\frac{1}{[1-(1-k)]^2} = \frac{2}{3}k^{-2}.$$

References

1) Y. Mizuno and T. Izuyama, Prog. Theor. Phys. **21** (1959), 593.
2) S. Tomonaga, Prog. Theor. Phys. **5** (1950), 544.
3) H. Kuhn, J. Chem. Phys. **17** (1949), 1198.
   H. Lahbhart, J. Chem. Phys. **27** (1957), 957.
   Y. Ooshika, J. Phys. Soc. Japan **12** (1957), 1246.
   S. Huzinaga and T. Hasino, Prog. Theor. Phys. **18** (1957), 649.
4) K. Sawada, Phys. Rev. **106** (1957), 372.
   K. Sawada, K. A. Brueckner, N. Fukuda and F. Brout, Phys. Rev. **108** (1957), 1593.
   G. Wentzel, Phys. Rev. **108** (1957), 1593.
5) G. Araki and T. Murai, Prog. Theor. Phys. 8 (1952), 639.
6) S. Nakajima, Bussei Butsurigaku Kohza Vol. 8 (1958), 149 (Kyôritsu Shuppan, in Japanese).
7) M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106** (1957), 364.
8) P. Nozieres and D. Pines, Phys. Rev. **109** (1958), 741.
9) H. Kanazawa, Prog. Theor. Phys. **13** (1955), 227.
10) G. H. Wannier, Phys. Rev. **52** (1937), 191.
11) Y. Toyozawa, Prog. Theor. Phys. **20** (1958), 53.
12) C. Horie, Prog. Theor. Phys. **21** (1959), 113.
13) J. Goldstone, Proc. Roy. Soc. (London) **A239** (1957), 267.
14) W. Macke, Z. Naturforsch. **5a** (1950), 192.
15) D. Pines, Solid State Physics Vol. **1** (1955), 400.
16) J. Hubburd, Proc. Roy. Soc. (London) **A240** (1957), 539; **A243** (1957), 336.
    W. Kohn, Phys. Rev. **110** (1958), 857.