

## Spin Density Wave and Charge Transfer Wave in Long Conjugated Molecules<sup>\*)</sup>

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### § 6. Instability of the conventional diamagnetic ground state of long polyenes

In this section, we examine the stability of the conventional diamagnetic ground state of long even numbered polyenes by applying the criteria derived in § 4.

The polyenes considered here are those without bond alternation. The polyenes are employed as the simplest example of long conjugated molecules. The essence of the following discussions holds also for any one-dimensionally long conjugated molecules with metallic level distribution, that is, the energy gap between the highest occupied and lowest unoccupied orbitals tending to zero when the length of the molecule tends infinite.

In order to avoid unnecessary complication, we consider the  $4\nu + 2$  numbered ring polyenes.

The conventional LCAO MO DMO solution of ring polyene with  $2N = (4\nu + 2)$  electrons are given by

$$\phi_k^0(x) = \frac{1}{\sqrt{2N}} \sum_{n=0}^{2N-1} e^{ink} \theta_n(x), \quad (6.1)$$

where  $\theta_n(x)$  is the Löwdin atomic orbital of the  $\pi$ -electron of  $n$ -th carbon and the pseudomomentum  $k$  takes the values

$$k = \frac{n\pi}{N}, \quad n = N, N-1, \dots, (N-1). \quad (6.2)$$

The orbitals with the momentum  $k$ ,  $|k| < \pi/2$ , are occupied and those with  $k$ ,  $|k| > \pi/2$ , are unoccupied.

The orbital energy  $W_k^0$  is given by

$$W_k^0 = C - \frac{W}{2} \cos k + \sum_{|l| < \pi/2} \{2\langle k, k|l, l \rangle^0 - \langle k, l|l, k \rangle^0\}, \quad (6.3)$$

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where  $C$  is the core Coulomb integral and  $-W/4$  is the core resonance integral.

By using the conservation law for the pseudomomentum, the instability conditions (4.12) and (4.13) for ring polyene become

$$\sum'_{k,l} f_{K+k,k}^* \{ (W_{K+k}^0 - W_k^0) \delta_{kl} + 4 \langle K+k, k | l, K+l \rangle^0 - \langle K+k, K+l | l, k \rangle^0 - \langle K+k, -l | -k, K+l \rangle^0 \} f_{K+l,l} < 0, \quad (6.4)$$

$$\sum'_{k,l} f_{K+k,k}^* \{ (W_{K+k}^0 - W_k^0) \delta_{kl} - \langle K+k, K+l | l, k \rangle^0 - \langle K+k, -l | -k, K+l \rangle^0 \} f_{K+l,l} < 0, \quad (6.5)$$

where we have denoted the momentum of the unoccupied orbital forming a pair with the occupied orbital with momentum  $k$  by  $K+k$ , that is,  $K$  is the total momentum of the electron-hole pair, and the summation for  $k$  and  $l$  in (6.4) and (6.5) must be carried out in the range such that

$$\left. \begin{aligned} |K+k| > \pi/2, & \quad |k| < \pi/2, \\ |K+l| > \pi/2, & \quad |l| < \pi/2. \end{aligned} \right\} \quad (6.6)$$

By neglecting the differential overlap between the atomic orbitals, the instability conditions (6.4) and (6.5) become

$$\sum'_{k,l} f_{K+k,k}^* \left\{ (W_{K+k}^0 - W_k^0) \delta_{kl} + \frac{1}{N} (4G(K) - G(k-l) - G(K+k+l)) \right\} f_{K+l,l} < 0, \quad (6.7)$$

$$\sum'_{k,l} f_{K+k,k}^* \left\{ (W_{K+k}^0 - W_k^0) \delta_{kl} - \frac{1}{N} (G(k-l) + G(K+k+l)) \right\} f_{K+l,l} < 0, \quad (6.8)$$

where

$$G(K) = \frac{1}{2} (00|00) + \sum_{n=1}^{N-1} \cos(nK) (nn|00) + \frac{1}{2} e^{iNK} (NN|00), \quad (6.9)$$

and  $(nn|00)$  is the two-center Coulomb repulsion integral between the atomic orbitals of  $n$ -th and 0-th carbon atoms.

We have similarly

$$W_{K+k}^0 - W_k^0 = \frac{W}{2} (\cos k - \cos(K+k)) + \frac{1}{N} \sum_{|l| < \pi/2} (G(k-l) - G(K+k-l)). \quad (6.10)$$

Now, let us consider the case in which the deformation parameters  $f_{K+k,k}$  and  $f_{K+l,l}$  have non-vanishing values only at a fixed value of  $k$ . Then the instability conditions (6.7) and (6.8) become

$$W_{K+k}^0 - W_k^0 + \frac{1}{N}(4G(K) - G(0) - G(K+2k)) < 0, \quad (6.11)$$

$$W_{K+k}^0 - W_k^0 - \frac{1}{N}(G(0) + G(K+2k)) < 0. \quad (6.12)$$

Let the momentum  $k$  be close to either of the Fermi momenta  $\pm\pi/2$  and the total momentum  $K$  of the electron-hole pair be close to the momenta  $\mp\pi$ :

$$\left. \begin{aligned} k &= \pm \frac{(\nu-n)\pi}{2\nu+1}, & 0 \leq n \ll \nu, \\ K &= \mp \left( \pi - \frac{m\pi}{2\nu+1} \right), & 0 \leq m \leq n. \end{aligned} \right\} \quad (6.13)$$

where the restrictions on  $n$  and  $m$  in (6.13) are imposed to satisfy the condition (6.6) and the double sign must be taken in the same order. When the length  $2N$  of the polyene is large, the conditions (6.11) and (6.12), with the momenta  $k$  and  $K$  given by (6.13), become

$$\frac{\pi W}{2N}(1+2n-m) + \frac{1}{N}(4G(\pi) - 2G(0)) < 0, \quad (6.14)$$

$$\frac{\pi W}{2N}(1+2n-m) - \frac{2}{N}G(0) < 0, \quad (6.15)$$

where we have neglected the terms of the order of  $N^{-2}$ .

On the other hand, we see from (6.9) that, when  $N$  becomes large,  $G(0)$  tends to have the value of the order of  $\log N$  since the two center Coulomb integral  $(nn|00)$  turns out to have the value  $e^2/na$  for large  $n$ , where  $a$  is the distance for C-C bond.

$$\begin{aligned} G(0) &= \frac{1}{2}(00|00) + \sum_{n=1}^{N-1} (nn|00) + \frac{1}{2}(NN|00) \\ &\sim \frac{1}{2}(00|00) + \sum_{n=1}^N \frac{e^2}{na} \sim \frac{e^2}{a} \log N, \end{aligned} \quad (6.16)$$

while,  $G(\pi)$  converges to a finite value.

$$\begin{aligned} G(\pi) &= \frac{1}{2}(00|00) + \sum_{n=1}^{N-1} (-1)^n (nn|00) + \frac{(-1)^N}{2}(NN|00) \\ &\sim \frac{1}{2}(00|00) + \sum_{n=1}^N (-1)^n \frac{e^2}{na} \sim \frac{1}{2}(00|00) - \frac{e^2}{a} \log 2. \end{aligned} \quad (6.17)$$

Therefore, the second terms in (6.14) and (6.15) come to have negative values exceeding the positive first term when  $N$  becomes large. Thus, the conventional diamagnetic ground state of long ring polyene is unstable to both of number density and spin density fluctuations.

The above proof of instability indicates that the essential reason of the instability is that the Coulomb attraction and exchange energies between the electron and hole closely lying to the Fermi surface are of the order of  $\log N/N$  due to long range nature of Coulomb interaction, while the energy gaps between these levels are of the order of  $1/N$ , so that the gain of the interaction energy between the electron and hole exceeds the loss of the orbital energy by the excitation of the pair. This situation is common for all one-dimensionally long conjugated molecules with metallic level distribution.

It is interesting to estimate the minimal length of polyene at which the instability arises. The instability conditions (6.11) and (6.12) come to be satisfied for smallest  $N$  when the momenta  $k$  and  $K$  of the transition causing the instability are

$$\left. \begin{aligned} k &= \pm \frac{\nu\pi}{2\nu+1}, \\ K &= \pi. \end{aligned} \right\} \quad (6.18)$$

( $-\pi$  is equivalent to  $\pi$ )

The instability to spin density fluctuation arises at smaller  $N$  than that to number density fluctuation.

The values of (6.11) and (6.12) were evaluated by using the semi-empirical method of Pariser and Parr.<sup>11)</sup> The result is shown in Table I. From Table I,

Table I.

Length	6	10	14	18	22	26
$C_T^{\omega}$	3.183	1.324	0.565	0.193	-0.012	-0.133
$C_S^{\omega}$	4.193	1.874	0.948	0.487	0.227	0.068

  

Length	30	34	38	42	46
$C_T^{\omega}$	-0.209	-0.257	-0.288	-0.309	-0.322
$C_S^{\omega}$	-0.035	-0.104	-0.151	-0.185	-0.209

<sup>ω)</sup>  $C_T$  and  $C_S$  are respectively the values of (6.12) and (6.11) in eV. The distance of C-C bond is assumed to be 1.39 Å.

we see that, in the case of ring polyenes, the minimal lengths to give rise to the instabilities to spin density and number density fluctuations are 22 and 30 respectively. Similar calculation was performed also for linear polyenes with all trans-configuration. The result is shown in Table II. In the case of linear polyenes the instability to spin density fluctuation arises at the length 10 which is shorter than that of the ring polyenes, while the instability to number density fluctuation was found not to arise below the length 100, on account of slow decrease of the energy transfer type interaction  $\langle ma|am \rangle$  for increasing length.

Table. II.

Length	2	4	6	8	10	12
$C_T^{(a)}$	1.63	0.834	0.369	0.115	-0.033	-0.125
$C_S^{(a)}$	7.93	6.72	5.80	5.15	4.65	4.25

  

Length	14	16	18	20	30	60	100
$C_T^{(a)}$	-0.183	-0.222	-0.248	-0.266	-0.293	-0.255	-0.204
$C_S^{(a)}$	3.93	3.66	3.43	3.24	2.54	1.62	1.13

<sup>a)</sup> The orbitals in the form of  $\phi_l^0(x) = (1/\sqrt{2N}) \sum_{n=1}^{2N} \sin(nl\pi/(2N+1)) \theta_n(x)$ ,  $l=1 \dots 2N$ , were used.  $C_T$  and  $C_S$  are respectively (4.13) and (4.12) with  $f_{ma}$  and  $f_{ma}$  having the non-vanishing value 1 only for the transition between the highest occupied and lowest unoccupied levels.

Thus, we arrive at an important conclusion that the instability, at least to spin density fluctuation, may arise in the length realized by the polyenes now available.

When the length of the polyene becomes more and more longer exceeding the critical lengths, more transitions with the momenta in the form of (6.13) come to contribute to the instability. However, since the total momentum  $K$  of the electron-hole pair is a good quantum number in the ring polyenes, the instabilities due to transitions with different values of  $K$  will not mutually interfere. Therefore, in the case of ring polyenes, the instability may be classified according to the value of the total momentum  $K$  of the electron-hole pair causing the instability.

Finally, we note that the transitions with the momenta in the form

$$\left. \begin{aligned} k &= \pm \frac{\nu - n}{2\nu + 1} \pi, \\ K &= \pm \frac{m}{2\nu + 1} \pi, \quad 0 \leq n < m \ll \nu \end{aligned} \right\} \quad (6.19)$$

may also cause the instability to spin density fluctuation, but transitions of this type do not cause the instability to number density fluctuation.

### § 7. The spin density wave and charge transfer wave solutions of the Hartree-Fock equation of long ring polyenes

Since the conventional diamagnetic ground state of long polyene is unstable, as shown in the preceding section, it is expected that the Hartree-Fock equation has another solution with lower ground state energy than it. We consider here the solutions which appear accompanying the instability caused by the electron-hole pair with the total momentum  $\pi$ . Such solutions are expected to appear as soon as the length of polyene exceeds the critical lengths described in the

preceding section.

Such new solutions will be constructed by mixing the conventional DMO's with momenta  $k$  and  $k+\pi$ . We put the new solution in the following form:

$$\begin{aligned} \varphi_{rk}(s, x) = & \eta_r(s) \cos \omega_k (\cos \theta_k \phi_k^0(x) + \sin \theta_k \phi_{k+\pi}^0(x)) \\ & + (\eta(s) \mathbf{e} \cdot \boldsymbol{\sigma})_r \sin \omega_k (\cos \theta_k \phi_{k+\pi}^0(x) - \sin \theta_k \phi_k^0(x)). \end{aligned} \quad (7.1)$$

The orbital (7.1) is an ASWO, and may be rewritten in the form of (3.19):

$$\varphi_{rk}(s, x) = \frac{1}{2} \{ \eta(s) (1 + \mathbf{e} \cdot \boldsymbol{\sigma}) \}_r \phi_k^+(x) + \frac{1}{2} \{ \eta(s) (1 - \mathbf{e} \cdot \boldsymbol{\sigma}) \}_r \phi_k^-(x), \quad (7.2)$$

where

$$\left. \begin{aligned} \phi_k^\pm(x) &= \cos \lambda_k^\pm \phi_k^0(x) + \sin \lambda_k^\pm \phi_{k+\pi}^0(x), \\ \lambda_k^\pm &= \omega_k \pm \theta_k. \end{aligned} \right\} \quad (7.3)$$

The Dirac density matrix of the solution (7.1) is given by

$$Q(rx, sy) = \frac{1}{2} (1 + \mathbf{e} \cdot \boldsymbol{\sigma})_{rs} Q^+(x, y) + \frac{1}{2} (1 - \mathbf{e} \cdot \boldsymbol{\sigma})_{rs} Q^-(x, y), \quad (7.4)$$

where

$$\begin{aligned} Q^\pm(x, y) = & \sum_{|k| < \pi/2} \{ \cos^2 \lambda_k^\pm \phi_k^0(x) \phi_k^{0*}(y) + \sin^2 \lambda_k^\pm \phi_{k+\pi}^0(x) \phi_{k+\pi}^{0*}(y) \\ & + \cos \lambda_k^\pm \sin \lambda_k^\pm (\phi_k^0(x) \phi_{k+\pi}^{0*}(y) + \phi_{k+\pi}^0(x) \phi_k^{0*}(y)) \}. \end{aligned} \quad (7.5)$$

From (7.4) and (7.5), the deformation matrix  $G$  has non-vanishing matrix elements only between the states with momenta  $k+\pi$  and  $k$ .

$$\left. \begin{aligned} G_{r, k+\pi, sk} &= \frac{1}{2} (1 + \mathbf{e} \cdot \boldsymbol{\sigma})_{rs} G_{k+\pi, k}^+ + \frac{1}{2} (1 - \mathbf{e} \cdot \boldsymbol{\sigma})_{rs} G_{k+\pi, k}^-, \\ G_{k+\pi, k}^\pm &= \tan \lambda_k^\pm. \end{aligned} \right\} \quad (7.6)$$

The spin dependence of the Hartree-Fock operator is given similarly by

$$H(rx, sy) = \frac{1}{2} (1 + \mathbf{e} \cdot \boldsymbol{\sigma})_{rs} H^+(x, y) + \frac{1}{2} (1 - \mathbf{e} \cdot \boldsymbol{\sigma})_{rs} H^-(x, y), \quad (7.7)$$

and from (5.9) the matrix elements of the operators  $H^\pm$  are given by

$$\left. \begin{aligned} H_{k+\pi, k}^\pm &= \frac{1}{2} \sum_{|l| < \pi/2} \{ (\langle k+\pi, k|l, l+\pi\rangle^0 + \langle k+\pi, k|l+\pi, l\rangle^0) \\ & \quad \times (\sin 2\lambda_l^+ + \sin 2\lambda_l^-) - (\langle k+\pi, l+\pi|l, k\rangle^0 + \langle k+\pi, l|l+\pi, k\rangle^0) \sin 2\lambda_l^\pm \}, \\ H_{k, k}^\pm &= W_k^0 + \sum_{|l| < \pi/2} \{ (\langle k, k|l+\pi, l+\pi\rangle^0 - \langle k, k|l, l\rangle^0) \\ & \quad \times (\sin^2 \lambda_l^+ + \sin^2 \lambda_l^-) - (\langle k, l+\pi|l+\pi, k\rangle^0 - \langle k, l|l, k\rangle^0) \sin^2 \lambda_l^\pm \}, \\ H_{k+\pi, k+\pi}^\pm &= W_{k+\pi}^0 + \sum_{|l| < \pi/2} \{ (\langle k+\pi, k+\pi|l+\pi, l+\pi\rangle^0 - \langle k+\pi, k+\pi|l, l\rangle^0) \\ & \quad \times (\sin^2 \lambda_l^+ + \sin^2 \lambda_l^-) \\ & \quad - (\langle k+\pi, l+\pi|l+\pi, k+\pi\rangle^0 - \langle k+\pi, l|l, k+\pi\rangle^0) \sin^2 \lambda_l^\pm \}. \end{aligned} \right\} \quad (7.8)$$

All other matrix elements of  $H^\pm$  are zero. By neglecting the differential overlap between the atomic orbitals, (7.8) are simplified as

$$\left. \begin{aligned} H_{k+\pi, k}^\pm &= \frac{1}{N} \sum_{|l| < \pi/2} \{G(\pi) (\sin 2\lambda_l^+ + \sin 2\lambda_l^-) - G(k-l) \sin 2\lambda_l^\pm\}, \\ H_{k, k}^\pm &= W_k^0 + \frac{1}{N} \sum_{|l| < \pi/2} (G(k-l) - G(\pi+k-l)) \sin^2 \lambda_l^\pm, \\ H_{k+\pi, k+\pi}^\pm &= W_{k+\pi}^0 - \frac{1}{N} \sum_{|l| < \pi/2} (G(k-l) - G(\pi+k-l)) \sin^2 \lambda_l^\pm. \end{aligned} \right\} \quad (7.9)$$

Substituting (7.6), (7.7) and (7.8) into (5.18), we have the equation to determine  $\lambda_k^\pm$ :

$$\alpha_k^\pm \sin 2\lambda_k^\pm = \beta_k^\pm \cos 2\lambda_k^\pm, \quad (7.10)$$

where

$$\left. \begin{aligned} \alpha_k^\pm &= H_{k+\pi, k+\pi}^\pm - H_{k, k}^\pm, \\ \beta_k^\pm &= -2H_{k+\pi, k}^\pm. \end{aligned} \right\} \quad (7.11)$$

From (7.10), we have

$$\left. \begin{aligned} \cos 2\lambda_k^\pm &= \alpha_k^\pm (A_k^\pm)^{-1}, \\ \sin 2\lambda_k^\pm &= \beta_k^\pm (A_k^\pm)^{-1}, \\ A_k^\pm &= \{(\alpha_k^\pm)^2 + (\beta_k^\pm)^2\}^{1/2}. \end{aligned} \right\} \quad (7.12)$$

By substituting (7.12) into (7.9), the equations in (7.11) become

$$\left. \begin{aligned} \alpha_k^\pm &= W_{k+\pi}^0 - W_k^0 + \frac{1}{N} \sum_{|l| < \pi/2} (G(\pi+k-l) - G(k-l)) (1 - \alpha_l^\pm (A_l^\pm)^{-1}), \\ \beta_k^\pm &= \frac{1}{N} \sum_{|l| < \pi/2} (G(\pi+k-l) + G(k-l)) \beta_l^\pm (A_l^\pm)^{-1} \\ &\quad - \frac{2}{N} G(\pi) \sum_{|l| < \pi/2} (\beta_l^+ (A_l^+)^{-1} + \beta_l^- (A_l^-)^{-1}). \end{aligned} \right\} \quad (7.13)$$

Equations (7.13) are the equations to determine  $\alpha_k^\pm$  and  $\beta_k^\pm$ . Note the close resemblance of the equations in (7.13) to Bogoliubov's equation of superconductivity.<sup>12)</sup> Equations (7.13) may be written in terms of  $\lambda_k^\pm$  as

$$\left. \begin{aligned} A_k^\pm \cos 2\lambda_k^\pm &= W_{k+\pi}^0 - W_k^0 \\ &\quad + \frac{1}{N} \sum_{|l| < \pi/2} (G(\pi+k-l) - G(k-l)) (1 - \cos 2\lambda_l^\pm), \\ A_k^\pm \sin 2\lambda_k^\pm &= \frac{1}{N} \sum_{|l| < \pi/2} \{ (G(\pi+k-l) + G(k-l)) \sin 2\lambda_l^\pm \\ &\quad - 2G(\pi) (\sin 2\lambda_l^+ + \sin 2\lambda_l^-) \}. \end{aligned} \right\} \quad (7.14)$$

It is extremely difficult to get a strict solution of the equations in (7.13) or (7.14). However, in the case of two-electron system, that is, the case  $N=1$  corresponding to ethylene or hydrogen molecule, we may get a strict solution.

In the case of two-electron system, Eq. (7.14) becomes

$$\left. \begin{aligned} A^\pm \cos 2\lambda^\pm &= W_\pi^0 - W_0^0 + (G(\pi) - G(0)) (1 - \cos 2\lambda^\pm), \\ A^\pm \sin 2\lambda^\pm &= (G(\pi) + G(0)) \sin 2\lambda^\pm - 2G(\pi) (\sin 2\lambda^+ + \sin 2\lambda^-), \end{aligned} \right\} \quad (7.15)$$

where  $W_\pi^0$  and  $W_0^0$  are the orbital energies of the antibonding and bonding orbitals of the standard solution and

$$\left. \begin{aligned} G(\pi) &= \frac{1}{2} \{ (00|00) - (11|00) \}, \\ G(0) &= \frac{1}{2} \{ (00|00) + (11|00) \}. \end{aligned} \right\} \quad (7.16)$$

Eliminating  $A^\pm$  from the equations in (7.15) and rearranging the resultant equation, we have

$$(W_\pi^0 - W_0^0 + G(\pi) - G(0)) \sin 2\lambda^\pm = -2G(\pi) \sin 2\lambda^\pm \cos 2\lambda^\pm. \quad (7.17)$$

Equation (7.17) has two non-trivial solutions (it has also the trivial solution  $\sin 2\lambda^\pm = 0$ ),

$$\cos 2\lambda^+ = \cos 2\lambda^- = (W_\pi^0 - W_0^0 + G(\pi) - G(0)) / 2G(\pi), \quad \sin 2\lambda^- = -\sin 2\lambda^+, \quad (7.18)$$

$$\cos 2\lambda^+ = \cos 2\lambda^- = -(W_\pi^0 - W_0^0 + G(\pi) - G(0)) / 2G(\pi), \quad \sin 2\lambda^- = \sin 2\lambda^+. \quad (7.19)$$

In order for the solutions (7.18) and (7.19) to give real values for  $\lambda^\pm$ , the following inequalities must respectively be satisfied.

$$W_\pi^0 - W_0^0 - G(\pi) - G(0) < 0, \quad W_\pi^0 - W_0^0 + 3G(\pi) - G(0) > 0, \quad G(\pi) > 0, \quad (7.20)$$

$$W_\pi^0 - W_0^0 + 3G(\pi) - G(0) < 0, \quad W_\pi^0 - W_0^0 - G(\pi) - G(0) > 0, \quad G(\pi) < 0. \quad (7.21)$$

The first inequalities in (7.20) and (7.21) are respectively nothing but the instability conditions (6.12) and (6.11) for the two-electron system. Therefore, the solution (7.18) is the solution which appears when the conventional solution becomes unstable to spin density fluctuation. As easily be seen from (7.16) the inequalities (7.20) come to be satisfied when the interatomic distance of the two atoms tends to be large. It is well known that the conventional Hartree-Fock ground state of the two-electron system tends to wrong limit when the interatomic distance tends to infinity. This classic discrepancy is a manifestation of the instability of the conventional diamagnetic ground state at large interatomic distance. The new solution (7.18) gives the bonding orbital in the following form;



$$\begin{aligned} \varphi_r(s, x) = & \frac{1}{2} \{ \eta(s) (1 + \mathbf{e} \cdot \boldsymbol{\sigma}) \}_r (\cos \lambda \phi_0^0(x) + \sin \lambda \phi_\pi^0(x)) \\ & + \frac{1}{2} \{ \eta(s) (1 - \mathbf{e} \cdot \boldsymbol{\sigma}) \}_r (\cos \lambda \phi_0^0(x) - \sin \lambda \phi_\pi^0(x)), \end{aligned} \quad (7.22)$$

where  $\cos \lambda = \cos \lambda^+ = \cos \lambda^-$  and  $\phi_0^0$  and  $\phi_\pi^0$  are respectively the conventional bonding and antibonding orbitals. From (7.18), we see that  $\lambda$  tends to  $\pi/4$  when the interatomic distance tends to infinity. Therefore, the orbital (7.22) converges correctly to the atomic orbitals of the two atoms when the distance between the two atoms tends to infinity.

On the other hand, (7.19) is the solution which appears accompanying the instability of the conventional solution to number density fluctuation. However, on the contrary to (7.20), the inequalities (7.21) are never satisfied for the two-electron system with repulsive Coulomb interaction. They may come to be satisfied for the fictitious two-electron system with attractive interaction. The important point, however, is the fact that Eq. (7.15) may have two distinct solutions corresponding to the two kinds of the instability. The solution (7.19) leads to the orbital in the following form:

$$\varphi_r(s, x) = \eta_r(s) (\cos \lambda \phi_0^0(x) + \sin \lambda \phi_\pi^0(x)). \quad (7.23)$$

The orbital (7.23) is diamagnetic.

The above analysis on the solutions of Eq. (7.15) for the two-electron system suggests that Eq. (7.13) may have two types of solutions which are characterized respectively by the relations

$$\left. \begin{aligned} \sin 2\lambda_k^+ &= -\sin 2\lambda_k^-, & \cos 2\lambda_k^+ &= \cos 2\lambda_k^-, \\ \beta_k^+ &= -\beta_k^-, & \alpha_k^+ &= \alpha_k^-, \end{aligned} \right\} \quad (7.24)$$

$$\left. \begin{aligned} \sin 2\lambda_k^+ &= \sin 2\lambda_k^-, & \cos 2\lambda_k^+ &= \cos 2\lambda_k^-, \\ \beta_k^+ &= \beta_k^-, & \alpha_k^+ &= \alpha_k^-. \end{aligned} \right\} \quad (7.25)$$

The solution of the former type is expected to appear when the conventional diamagnetic solution becomes unstable to spin density fluctuation and the solution of the latter type accompanying the instability to number density fluctuation.

With the postulate (7.24), Eq. (7.13) becomes

$$\left. \begin{aligned} \alpha_k &= W_{k+\pi}^0 - W_k^0 + \frac{1}{N} \sum_{|l| < \pi/2} (G(\pi + k - l) - G(k - l)) \left( 1 - \frac{\alpha_l}{\sqrt{\alpha_l^2 + \beta_l^2}} \right), \\ \beta_k &= \frac{1}{N} \sum_{|l| < \pi/2} (G(\pi + k - l) + G(k - l)) \frac{\beta_l}{\sqrt{\alpha_l^2 + \beta_l^2}}, \end{aligned} \right\} \quad (7.26)$$

where  $\alpha_k = \alpha_k^+ = \alpha_k^-$  and  $\beta_k = \beta_k^+ = -\beta_k^-$ . The solution of this type leads to the orbitals of ASWO type.

$$\begin{aligned} \varphi_{rk}(s, x) = & \frac{1}{2} \{ \eta(s) (1 + \mathbf{e} \cdot \boldsymbol{\sigma}) \}_r (\cos \lambda_k \phi_k^0(x) + \sin \lambda_k \phi_{k+\pi}^0(x)) \\ & + \frac{1}{2} \{ \eta(s) (1 - \mathbf{e} \cdot \boldsymbol{\sigma}) \}_r (\cos \lambda_k \phi_k^0(x) - \sin \lambda_k \phi_{k+\pi}^0(x)). \end{aligned} \quad (7.27)$$

The same kind of solution of the Hartree-Fock equation was discussed by Matsubara and Yokota<sup>13)</sup> in their split band model of antiferromagnet.

With the postulate (7.25), Eq. (7.13) becomes

$$\left. \begin{aligned} \alpha_k &= W_{k+\pi}^0 - W_k^0 + \frac{1}{N} \sum_{|l| < \pi/2} (G(\pi+k-l) - G(k-l)) \left(1 - \frac{\alpha_l}{\sqrt{\alpha_l^2 + \beta_l^2}}\right), \\ \beta_k &= \frac{1}{N} \sum_{|l| < \pi/2} (G(\pi+k-l) + G(k-l) - 4G(\pi)) \frac{\beta_l}{\sqrt{\alpha_l^2 + \beta_l^2}}, \end{aligned} \right\} \quad (7.28)$$

where  $\beta_k = \beta_k^+ = \beta_k^-$ . The solution of this type leads to the DMO type orbitals.

$$\varphi_{rk}(s, x) = \eta_r(s) (\cos \lambda_k \phi_k^0(x) + \sin \lambda_k \phi_{k+\pi}^0(x)). \quad (7.29)$$

We call the orbital in the form of (7.29) the charge transfer wave orbital (CTWO). Meaning of this name will be discussed in the next section. The same kind of solution as (7.29) for low density electron gas has recently been discussed by Kohn<sup>5)</sup> and he call it the excitonic phase which we do not think a good naming.

When the length of the polyene is large, the summation in (7.26) and (7.28) may be replaced by the integration, and they become

$$\left. \begin{aligned} \alpha_k &= W_{k+\pi}^0 - W_k^0 + \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} \bar{\mathcal{G}}(k, l) \left(1 - \frac{\alpha_l}{\sqrt{\alpha_l^2 + \beta_l^2}}\right) dl, \\ \beta_k &= \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} \underline{\mathcal{G}}(k, l) \frac{\beta_l}{\sqrt{\alpha_l^2 + \beta_l^2}} dl, \end{aligned} \right\} \quad (7.30)$$

where

$$\bar{\mathcal{G}}(k, l) = G(\pi+k-l) - G(k-l) \quad (7.31)$$

and

$$\underline{\mathcal{G}}(k, l) = G(\pi+k-l) + G(k-l) \quad (7.32)$$

for the ASWO type solution, and

$$\underline{\mathcal{G}}(k, l) = G(\pi+k-l) + G(k-l) - 4G(\pi) \quad (7.33)$$

for the CTWO type solution.

Equation (7.30) is quite the same form as the Bogoliubov equation of superconductivity, and an approximate solution may be obtained in the same way as employed in it.<sup>12)</sup> Assuming that  $\beta_k$  is exponentially small quantity decreasing rapidly to zero except the neighbourhoods of the Fermi momenta  $k_F = \pm \pi/2$ , we have the solution near the Fermi momenta:

$$\left. \begin{aligned} \alpha_k &\simeq W(k - k_F), \\ \beta_k &\simeq \pi W \frac{\underline{\mathcal{G}}(k, k_F)}{\underline{\mathcal{G}}(k_F, k_F)} \exp(-\pi W / 2 \underline{\mathcal{G}}(k_F, k_F)). \end{aligned} \right\} \quad (7.34)$$

However, in the present case, the solution (7.34) contradicts the assumption from which it is derived. Since

$$\mathcal{G}(k_F, k_F) = G(0) + G(\pi) \quad \text{or} \quad G(0) - 3G(\pi), \quad (7.35)$$

and  $G(0)$  is the quantity with the value of the order of  $\log N$ ,  $\mathcal{G}^{-1}(k_F, k_F)$  tends to zero when  $N$  tends to infinity. Therefore, in the limit of infinite  $N$ , we have

$$\lim_{N \rightarrow \infty} \beta_{k_F} = \pi W. \quad (7.36)$$

Thus,  $\beta_k$  given by (7.34) takes a value of the order of 30 eV at the Fermi momenta, which contradicts the assumption for  $\beta_k$  to be a small quantity. Therefore, the validity of the approximate solution (7.34) is dubious, but it suggests that  $\beta_k$  satisfying (7.30) is a quantity which might take a value of several eV at the Fermi momenta.

### § 8. Properties of the spin density wave and the charge transfer wave solutions

Solving the eigenvalue equation (5.25) and using (7.11), we have the orbital energies of the ASWO and the CTWO solutions as

$$\left. \begin{aligned} W_k &= \frac{1}{2} (W_{k+\pi}^0 + W_k^0 - \sqrt{\alpha_k^2 + \beta_k^2}), \\ W_{k+\pi} &= \frac{1}{2} (W_{k+\pi}^0 + W_k^0 + \sqrt{\alpha_k^2 + \beta_k^2}). \end{aligned} \right\} |k| < \pi/2 \quad (8.1)$$

Since  $\beta_k$  has a finite value at the Fermi momenta  $\pm\pi/2$ , the formula (8.1) means that the occupied and unoccupied orbitals in the ASWO and CTWO solutions are separated by a finite energy gap. The energy gap persists even in the polyene with infinite length and, as discussed in the previous section, it might have the value of the order of several eV.

Substituting (7.6), (7.11) and (7.12) into (5.23), we have the ground state energy of the ASWO and the CTWO solutions as

$$E_0 = E_0^0 + \frac{1}{2} \sum_{|k| < \pi/2} (W_{k+\pi}^0 - W_k^0 - \sqrt{\alpha_k^2 + \beta_k^2}) \left( 1 - \frac{\alpha_k}{\sqrt{\alpha_k^2 + \beta_k^2}} \right). \quad (8.2)$$

Since  $\beta_k$  is considered to have a finite value near the Fermi momenta and decrease rapidly when the momentum  $k$  departs from them, the summands of (8.2) with the momentum  $k$  near the Fermi momenta will mainly contribute to (8.2), leading to a lower ground state energy than  $E_0^0$ . Lowering of the ground state energy than  $E_0^0$  is strictly demonstrated for the two-electron system. From (7.15), (7.18) and (7.19), the ground state energy (8.2) for the two-electron system becomes for the ASWO solution

$$E_0 = E_0^0 - \frac{1}{4G(\pi)} (W_\pi^0 - W_0^0 - G(\pi) - G(0))^2 \quad (8.3)$$

and for the CTWO solution

$$E_0 = E_0^0 + \frac{1}{4G(\pi)} (W_\pi^0 - W_0^0 + 3G(\pi) - G(0))^2. \quad (8.4)$$

From (7.20) and (7.21), the second terms in (8.3) and (8.4) are negative.

From (3.21), (3.6) and (7.27), the number density distribution in the ASWO ground state is given by

$$\langle n(x) \rangle = 2 \sum_{|k| < \pi/2} \{ \cos^2 \lambda_k |\phi_k^0(x)|^2 + \sin^2 \lambda_k |\phi_{k+\pi}^0(x)|^2 \}. \quad (8.5)$$

By neglecting the differential overlap between the atomic orbitals, (8.5) becomes

$$\langle n(x) \rangle = \sum_{n=1}^{2N-1} |\theta_n(x)|^2. \quad (8.6)$$

Thus, the electrons in the ASWO ground state are uniformly distributed at every carbon atoms as in the case of the conventional DMO ground state.

From (3.21), (3.7) and (7.27), the spin density distribution in the ASWO ground state is given by

$$\langle \mathbf{S}(x) \rangle = \frac{e}{2} \sum_{|k| < \pi/2} \sin 2\lambda_k \operatorname{Re} (\phi_k^0(x) \phi_{k+\pi}^0(x)), \quad (8.7)$$

where  $\operatorname{Re} X$  denotes the real part of  $X$ . By neglecting the differential overlap between the atomic orbitals, (8.7) becomes

$$\langle \mathbf{S}(x) \rangle = \frac{e}{4N} \sum_{|k| < \pi/2} \sin 2\lambda_k \sum_{n=0}^{2N-1} (-1)^n |\theta_n(x)|^2. \quad (8.8)$$

Thus, in the ASWO ground state, spin is distributed to the carbon atoms with equal weight but with alternately reversing direction.

The number density distribution in the CTWO ground state is given by

$$\langle n(x) \rangle = 2 \sum_{|k| < \pi/2} |\cos \lambda_k \phi_k^0(x) + \sin \lambda_k \phi_{k+\pi}^0(x)|^2. \quad (8.9)$$

By neglecting the differential overlap between the atomic orbitals, (8.9) becomes

$$\left. \begin{aligned} \langle n(x) \rangle &= \sum_{n=0}^{2N-1} (1 + (-1)^n c) |\theta_n(x)|^2, \\ c &= \frac{1}{N} \sum_{|k| < \pi/2} \sin 2\lambda_k. \end{aligned} \right\} \quad (8.10)$$

Thus, in the CTWO ground state, electrons are distributed to the carbon atoms with non-uniform and alternately modulated weights, that is, the effective number of the electrons around the carbon atoms takes two values  $1 \pm c$  alternately from atom to atom. Therefore, the CTWO ground state may be regarded as a state of corrective charge transfer complex, the electron donating and accepting carbons being arranged alternately.

In the case of even numbered linear polyene, the CTWO ground state is a

state with spontaneous polarization, since the effective charge of the carbon atoms is reversed alternately, so that the carbon atoms at the two terminals have effective charges with opposite signs.

Both of the ASWO and CTWO ground states are degenerated.

In the case of the ASWO solution, the direction  $\mathbf{e}$  of spin is quite arbitrary and the ground states  $\Psi_0^{\mathbf{e}}$  with different  $\mathbf{e}$  are different states and degenerated, as discussed before. The inner product between two ASWO ground states is given, from (2.21) and (7.27), as

$$\langle \Psi_0^{\mathbf{e}} | \Psi_0^{\mathbf{e}'} \rangle = \prod_{|k| < \pi/2} \{1 - \frac{1}{2}(1 - \mathbf{e} \cdot \mathbf{e}') \sin^2 2\lambda_k\}. \quad (8.11)$$

We have, on the other hand, from (3.22) and (7.27) the expectation value of the square of the total spin by the ASWO ground state:

$$\langle \mathbf{S}^2 \rangle = N - \sum_{|k| < \pi/2} \cos^2 2\lambda_k = \sum_{|k| < \pi/2} \sin^2 2\lambda_k. \quad (8.12)$$

The square of the total spin (8.12) is presumed to be large for very long polyenes, and the inner product (8.11) to be very small. If (8.12) is divergent for infinite  $N$ , then the inner product (8.11) tends to zero, that is, the degenerated ASWO ground states become orthogonal for infinite polyene.

From the degenerated ASWO ground states, we may construct the ground states as (3.35) which are eigenstates of total spin. The degeneracy of the ASWO ground states is split off in the ground states (3.35) and the magnitude of the energy splitting is of the order of the inner product (8.11). Therefore, we get a series of closely lying states with different total spin for long polyenes. In the limit of infinite polyene, the energy splitting tends to zero, and the ground states (3.35) again become degenerated.

In the case of the CTWO solution, the ground state is degenerated two-fold. As seen from (7.28), if  $\beta_k$  is a solution of (7.28) then  $-\beta_k$  too is. The solution  $-\beta_k$  corresponds to the orbital

$$\varphi'_{rk}(s, x) = \eta_r(s) (\cos \lambda_k \phi_k^0(x) - \sin \lambda_k \phi_{k+\pi}^0(x)). \quad (8.13)$$

The solution (8.13) leads to the number density distribution as

$$\langle n(x) \rangle' = \sum_{n=0}^{2N-1} (1 - (-1)^n c) |\theta_n(x)|^2. \quad (8.14)$$

Therefore, the CTWO ground state  $\Psi_0'$  constructed from the CTWO (8.13) has an effective charge distribution with sign reversed to that of the ground state  $\Psi_0$  constructed from (7.29), that is, the electron excess and electron deficient carbons in the state  $\Psi_0$  become electron deficient and electron excess respectively in the state  $\Psi_0'$ . Both of the CTWO ground states  $\Psi_0$  and  $\Psi_0'$  violate the space inversion symmetry of molecule. However, we may construct the ground states satisfying the symmetry requirement:

$$\Phi_0^{\pm} = (\Psi_0 \pm \Psi_0') \{2(1 \pm \langle \Psi_0 | \Psi_0' \rangle)\}^{-1/2}. \quad (8.15)$$

where the inner product between two CTWO ground states is given by

$$(\Psi_0|\Psi_0') = \prod_{|k| < \pi/2} \cos^2 2\lambda_k \quad (8.16)$$

and the  $\pm$  sign in (8.15) represents the parity for space inversion.

In the new CTWO ground states (8.15), the degeneracy in the states  $\Psi_0$  and  $\Psi_0'$  is split off and the uneven charge distributions in them are also eliminated.

### § 9. Other possible solutions of the Hartree-Fock equation in long polyenes

The solutions discussed above are those which appear accompanying the instabilities caused by the electron-hole pair with total momentum  $\pi$ . When the length of polyene is sufficiently long, the instabilities caused by the transitions of the types (6.13) and (6.19) may arise. Accompanying the instabilities caused by the electron-hole pair with total momentum not equal to  $\pi$ , other types of the solutions appear. We describe briefly these solutions which are expected to appear in very long polyenes.

#### i) SWO solution with spiral spin arrangement

Accompanying the instability to spin density fluctuation caused by the triplet electron-hole pair with total momentum  $K$  in the form of (6.13) and (6.19), the SWO type solution in the following form appears:

$$\begin{aligned} \varphi_{rk}(s, x) = \sum_u \eta_u(s) \{ \cos \lambda_k \phi_k^0(x) + \frac{1}{2} \boldsymbol{\sigma} \cdot (\mathbf{e}_1 + i\mathbf{e}_2) \sin \lambda_k \phi_{k+K}^0(x) \\ + \frac{1}{2} \boldsymbol{\sigma} \cdot (\mathbf{e}_1 - i\mathbf{e}_2) \sin \lambda_k \phi_{k-K}^0(x) \}_{ur}, \end{aligned} \quad (9.1)$$

where  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are unit vectors mutually orthogonal and, in order for the orbitals (9.1) to be orthonormal, the parameter  $\lambda_k$  must satisfy the relation

$$\sin(\lambda_{k+K} + \lambda_k) = 0. \quad (9.2)$$

The solution in the form of (9.1) is the analogue of Overhauser's spiral spin density wave<sup>4)</sup> in polyene. The parameter  $\lambda_k$  is determined from the following equations.

$$\left. \begin{aligned} \alpha_k &= W_{k\pm K}^0 - W_k^0 + \frac{1}{2N} \left( \sum_l^{(+)} + \sum_l^{(-)} \right) (G(\pm K + k - l) - G(k - l)) \\ &\quad \times \left( 1 - \frac{\alpha_l}{\sqrt{\alpha_l^2 + \beta_l^2}} \right), \\ \beta_k &= \frac{1}{N} \left\{ \sum_l^{(\pm)} G(k - l) + \sum_l^{(\mp)} G(\pm K + k - l) \right\} \frac{\beta_l}{\sqrt{\alpha_l^2 + \beta_l^2}}, \end{aligned} \right\} \quad (9.3)$$

where the upper or the lower of the double signs in (9.3) must be taken according to whether  $k$  is in either of the ranges

$$|k+K| > \pi/2, \quad |k| < \pi/2 \quad (9.4)$$

or

$$|k-K| > \pi/2, \quad |k| < \pi/2. \quad (9.5)$$

The summation  $\sum^{(+)}$  and  $\sum^{(-)}$  are carried out respectively in the ranges (9.4) and (9.5).  $\alpha_k$ ,  $\beta_k$  and  $\lambda_k$  are related in the same way as (7.12). In the SWO ground state constructed from the solution (9.1), the direction of spin at the position of carbon atom is rotated by the angle  $K$  around the axis  $\mathbf{e}_1 \times \mathbf{e}_2$  relative to the spin direction at the nearest neighbouring carbon.

ii) *CTWO solution with beated number density wave*

Accompanying the instability to number density fluctuation caused by the singlet electron-hole pair with total momentum  $K$  in the form of (6.13), the CTWO solution in the following form appears:

$$\varphi_{rk}(s, x) = \eta_r(s) (\cos \lambda_k \phi_k^0(x) + \sin \lambda_k \phi_{k+K}^0(x)). \quad (9.6)$$

The parameter  $\lambda_k$  must satisfy (9.2) and

$$\sin \lambda_k = 0 \quad (9.7)$$

for  $k$  in the range

$$|k+K| < \pi/2, \quad |k| < \pi/2. \quad (9.8)$$

$\lambda_k$  is determined from the equations

$$\left. \begin{aligned} \alpha_k &= W_{k+K}^0 - W_k^0 + \frac{1}{2N} (\sum_l^{(+)} + \sum_l^{(-)}) (G(K+k-l) - G(k-l)) \\ &\quad \times \left( 1 - \frac{\alpha_l}{\sqrt{\alpha_l^2 + \beta_l^2}} \right), \\ \beta_k &= \frac{1}{N} \{ \sum_l^{(+)} (G(k-l) - 2G(K)) + \sum_l^{(-)} (G(K+k-l) - 2G(K)) \} \\ &\quad \times \frac{\beta_l}{\sqrt{\alpha_l^2 + \beta_l^2}}, \end{aligned} \right\} \quad (9.9)$$

where  $\alpha_k$ ,  $\beta_k$  and  $\lambda_k$  are related by the same way as (7.12) and  $k$  is in the range (9.4).

The solution (9.6) leads to the ground state number density distribution in the following form:

$$\left. \begin{aligned} \langle n(x) \rangle &= \sum_{n=0}^{2N-1} (1 + c \cos(nK)) |0_n(x)|^2, \\ c &= \frac{1}{N} \sum_l^{(+)} \sin 2\lambda_k. \end{aligned} \right\} \quad (9.10)$$

Since the total momentum  $K$  is close to  $\pm\pi$ , the number density distribution

(9.10) gives a beated wave.

iii) *CTWO solution with non-vanishing ground state current*

Accompanying each CTWO solution (7.29) or (9.6), there are CTWO solutions in the following form:

$$\varphi_{rk}(s, x) = \eta_r(s) (\cos \lambda_k \varphi_{k+p}^0(x) + \sin \lambda_k \varphi_{k+p+K}^0(x)). \quad (9.11)$$

The parameter  $\lambda_k$  is determined from the equations

$$\left. \begin{aligned} \alpha_k &= W_{k+p+K}^0 - W_{k+p}^0 + \frac{1}{2N} (\sum_l^{(+)} + \sum_l^{(-)}) (G(K+k-l) - G(k-l)) \\ &\quad \times \left(1 - \frac{\alpha_l}{\sqrt{\alpha_l^2 + \beta_l^2}}\right), \\ \beta_k &= \frac{1}{N} \{ \sum_l^{(+)} (G(k-l) - 2G(K)) + \sum_l^{(-)} (G(K+k-l) - 2G(K)) \} \\ &\quad \times \frac{\beta_l}{\sqrt{\alpha_l^2 + \beta_l^2}}. \end{aligned} \right\} \quad (9.12)$$

When the momentum  $p$  is sufficiently small, then Eq. (9.12) has solution if Eq. (9.9) has solution.

The orbitals (9.11) represent the state in which all electrons in the orbitals (9.6) move with momentum  $p$  relative to the nuclei. Therefore, the ground state obtained from the orbitals (9.11) has non-vanishing electric current. The solution of this type is possible only for ring molecules or infinite linear molecules without terminals.

These solutions discussed above appear when the length of polyene becomes much longer than the critical lengths, and seem to give higher ground state energies than those of the solutions discussed in § 7 and § 8. Since the ASWO type solution appears at shortest length, they are presumed to be the solution that give the lowest ground state energy.

## § 10. Discussion

### i) *Experimental implications*

Existence of the converging limit of the maximum absorption wave-lengths in series of polyenes with increasing lengths,<sup>14)</sup> has been a subject of wide discussion and controversy. The explanation of the phenomenon based upon bond alternation<sup>15)</sup> has been considered to be the most satisfactory one. However, firm experimental verification of bond alternation has been lacking and the present theory offers an entirely new explanation of the phenomenon based upon the instability of the conventional ground state of polyene *without bond alternation*. The conventional ground state of polyene without bond alternation becomes unstable to spin density fluctuation when the length of polyene exceeds a critical



length, which is estimated to be about 10 for the linear polyene, and new kind of ground state having spin density wave appears. The new ground state is separated by a finite energy gap from the excited state even in the limit of infinite polyene. Reliable numerical estimation of the energy gap is extremely difficult but is presumed to be of the order of several eV. If this suggested figure is correct, the energy gap may explain the convergence of the maximum absorption wavelength.

Another important consequence of the present theory is concerned with the magnetic property of long conjugated molecules. As discussed in § 8, the ground state of long conjugated molecule is approximated by the wave function (3.35) constructed by superposition of the degenerated ASWO ground states, and there appears a series of the ground states with different values of total spin. When the length of the molecule is very long, the spacing between these states is presumed to be small. Among these states, the state with total spin zero is presumably the state with lowest energy, but in long molecule the states with non-zero spin may come to mix thermally with it, and the molecule becomes paramagnetic. In the limit of infinitely long molecule, they become again degenerated and the ASWO ground state itself becomes a good approximation to the true ground state. Therefore, the infinitely long conjugated molecule is expected to behave as an antiferromagnet. In the case of very long but finite molecule, many states with non-zero total spin may become thermally accessible, and complicated magnetic behavior is expected. It will be interesting to examine magnetic property of long conjugated molecule in both of experimental and theoretical points of view.

ii) *Instability in two-dimensionally large molecules*

In the case of one-dimensionally long conjugated molecules, the instability is considered to be a universal situation, but, in the case of two-dimensionally large conjugated molecules, the situation is different and we may show that in some cases no instability arises. As discussed in § 4, the instability arises when the sum of the Coulomb attraction energy between electron and hole and the exchange energy between the pairs exceeds the energy gap between the highest occupied and the lowest empty orbitals. The magnitudes of the Coulomb attraction energy and the exchange energy in two-dimensional molecules are of the order of  $1/\sqrt{N}$ , where  $N$  is the total number of  $\pi$ -electrons. In the case of the polyacene having the same symmetry as graphite,<sup>16)</sup> the energy gap is also of the order of  $1/\sqrt{N}$ , and no instability by the size effect arises. Diamagnetism of infinite polyacene graphite is consistent with this conclusion.

iii) *Electron correlation in large conjugated molecules*

This work was motivated from the finding that the calculation of configuration interaction of long polyene in the Sawada approximation<sup>17),18)</sup> or equivalently

by the time dependent Hartree-Fock approximation<sup>19)</sup> leads to imaginary excitation energy. Appearance of imaginary excitation energy in the Sawada approximation is equivalent to the instability of the Hartree-Fock ground state. The coincidence of the stability conditions for the Hartree-Fock approximation and the Sawada approximation was first noted by Sawada and Fukuda.<sup>1)</sup> As discussed in § 6, the instability of the conventional Hartree-Fock ground state is a universal situation in long conjugated molecules, and equivalently the conventional Sawada approximation fails to be applicable to them. Even for moderately long conjugated molecules or two-dimensionally large molecules in which no instability arises, the Sawada approximation cannot be considered to be a good approximation. The Sawada approximation is a good approximation in weakly excited system, that is, when the electron density of the system is high or the excited state of the system is separated by a large energy gap from the ground state. Large conjugated molecules are, however, not weakly excited system, both of the electron density and the energy gap being small. Therefore, approximation method beyond the Sawada approximation is needed. It is a very difficult task to get such an approximation. When the instability arises, the new solutions of the Hartree-Fock equation may be used as an initial approximation. However, as shown in this paper, the new solutions always lead to degenerated ground states, and direct use of them as the approximation for the true ground state is inappropriate. But, the superposition of these degenerated ground state in the form of (3·34), (3·35) or (8·15) might be a good approximation for the true ground state. Further study of this type of approximation is needed. For instance, treatment of excited state in this approximation remains to be uninvestigated problem.

In the case of large molecules without instability, use of the new solution of the Hartree-Fock equation is impossible, and other method must be developed. The variation procedure to the wave function in the form of (3·34) or (3·35) might be a promising approach.

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