

Theory of Electronic Structures and Lattice Distortions in Polyacetylene and Itinerant Peierls Systems. II

— *Coulomb Interaction Dependences of
the HF Ground State, Lattice Dimerization and
 1B_u Excited State in Regular Trans-Polyacetylene* —

Hideo FUKUTOME and Masaki SASAI

Department of Physics, Kyoto University, Kyoto 606

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We study the Coulomb interaction dependences of the HF ground state, lattice dimerization and 1B_u excited state in regular trans-polyacetylene using the PPP hamiltonian model developed in a previous paper. The nature of the HF ground state is determined by the relative magnitudes of the on site and nearest neighbour parts and the screening of the longer range part of the effective Coulomb potential.

The Coulomb interaction with relatively large nearest neighbour part and not too strongly screened longer range part induces lattice dimerization. The driving force of the Coulomb induced dimerization is the nearest neighbour exchange interaction. The lattice dimerization in polyacetylene is due to the Coulomb mechanism.

The SSH model is implicitly taking into account the nearest neighbour exchange interaction.

The Franck-Condon band gap is mostly determined by the nearest neighbour exchange interaction. The 1B_u excited state is excitonic. The exciton binding energy is estimated for the effective Coulomb potential with the screened long range part. It is not large owing to very small effective mass of electron and hole. To explain the observed 1B_u excitation energy, the short range part of the effective Coulomb potential must be screened by about half compared to the one in small conjugate molecules. The condition for splitting of the exciton into a zwitterionic pair of charged solitons is discussed.

§ 1. Introduction

A major unsolved problem in polyacetylene is the role of the Coulomb interaction in it. The Su, Schrieffer and Heeger¹⁾ (SSH) model neglecting the Coulomb interaction was very successful. However, the success of the SSH model does not directly mean that the Coulomb interaction in polyacetylene is in fact weak. The SSH model utilizes the Hückel hamiltonian. It is well known that the Hückel theory is able to explain many properties of conjugate molecules in spite of the neglect of the Coulomb interaction. It, however, is eventually a crude approximation and the Coulomb interaction has important contributions in π electronic structures of small conjugate molecules. The success of the SSH model might be intuitive owing to implicit incorporation of some effects of the Coulomb interaction via empirical parametrization. There is also another possibility that the effective π electron Coulomb interaction might be suppressed

in polyacetylene by some mechanisms due to its unique structure and very long chain length.

In order to investigate the role of the Coulomb interaction in polyacetylene, it is necessary to start with a model with a sound quantum chemical background since polyacetylene is a typical conjugate molecule essentially of the same chemical character as small linear conjugate hydrocarbons, polyenes, except for its very long chain length. The Pariser-Parr-Pople (PPP) hamiltonian is best suited for this purpose because it is well established as a good semi-empirical effective hamiltonian for π electrons in small conjugate molecules.

We have developed in a previous paper²⁾ (hereafter referred to as I) a model of polyacetylene utilizing the PPP hamiltonian. To calculate π electronic structures and lattice distortions in polyacetylene we have developed the following method. i) We use for π electronic structures the temperature unrestricted Hartree-Fock (TUHF) approximation that incorporates an important part of electron correlation effects and is able to cover whole correlation regimes. ii) To solve the TUHF equation in an irregular lattice with solitons we use the transfer matrix technique that is able to get exact solutions in a one dimensional random system. We have shown in I that the transfer matrix technique can be adapted to the TUHF approximation with the long range Coulomb interaction. iii) To determine an irregular lattice structure with solitons we use the force equilibrium condition, i.e., the Hellmann-Feynman theorem. By combining ii) and iii) we can calculate the exact UHF solution and lattice geometry in a state with solitons. iv) To see whether the effective π electron Coulomb interaction in polyacetylene is similar to the one in small conjugate molecules or not, we first start with the parametrizations of the PPP hamiltonian and elastic potential well reproducing spectra and geometries of small conjugate molecules. We adopt ethane, ethylene and benzene as the reference molecules to determine the parameters. Thus determined parameter sets have been given in Table II of I. If the parameter sets are unable to explain experiments of polyacetylene, it is the case as we shall show in this and an accompanying papers, we next examine what modifications in the interaction parameters are necessary.

The purpose of this paper is to study how the nature of the HF ground state and physical properties of regular transpolyacetylene, especially the lattice dimerization, band gap and 1B_u absorption band, are dependent on the π electron Coulomb interaction. We shall study in an accompanying paper³⁾ (hereafter referred to as III) effects of the Coulomb interaction on solitons and search for the effective π electron Coulomb interaction that is consistent with experiments of polyacetylene. The results of this paper are useful as the basis to understand the mechanisms of the Coulomb interaction to affect properties of solitons.

The notations used in this paper are the same as those in I.

§ 2. Basic properties of the PPP hamiltonian model

We first consider some basic properties of the PPP hamiltonian model in the TUHF approximation that are important in considering how the Coulomb interaction affects π electronic structures of polyacetylene. The densities and bond orders of up and down spin π electrons can be represented in terms of the electron density (ED) q_n , the spin density (SD) s_n , the bond order (BO) p_n and the spin bond order (SBO) t_n as

$$q_n^\pm = q_n/2 \pm s_n, \quad p_n^\pm = p_n/2 \pm t_n. \quad (2.1)$$

The net charge density (CD) d_n is given by

$$q_n = 1 + d_n, \quad \sum_n d_n = \nu, \quad \nu = 0, \pm 1, \pm 2, \dots, \quad (2.2)$$

where ν is the total net charge of a chain. Our model has the four π electron order parameters d_n , s_n , p_n and t_n .

We assume as usually done that the effective Coulomb interactions γ_{mn} of π electrons, V_{mn} of σ cores and $-v_{mn}$ between π electrons and σ cores have the same shape

$$\gamma_{mn} = V_{mn} = v_{mn}. \quad (2.3)$$

Then the total energy $E^{\text{tot}} = E^\pi + E^\sigma$ (confer Eqs. (2.2) and (2.4) in I) and the force equilibrium condition (Eq. (2.29) in I) are given in terms of the order parameters as

$$E^{\text{tot}} = \frac{\gamma_0}{4}(N + 2\nu) + \sum_n \left\{ 2\beta_n p_n - 2\gamma_n \left(\frac{p_n^2}{4} + t_n^2 \right) + \gamma_0 \left(\frac{d_n^2}{4} - s_n^2 \right) + U(x_n) \right\} + \sum_{m,n}' \frac{1}{2} \gamma_{mn} d_m d_n, \quad (2.4)$$

$$-\frac{dU(x_n)}{dx_n} = 2 \frac{d\beta_n}{dx_n} p_n - \frac{1}{2} \frac{d\gamma_n}{dx_n} (p_n^2 + 4t_n^2) + \sum_{i,j}' \frac{1}{2} \frac{\partial \gamma_{ij}}{\partial x_n} d_i d_j, \quad (2.5)$$

where $\gamma_{nn} = \gamma_0$ and $\gamma_n = \gamma_{n+1}$. The TUHF equation (Eq. (2.6) in I) has the form

$$\left. \begin{aligned} B_n^\pm C_{n+1,a}^\pm + B_{n-1}^\pm C_{n-1,a}^\pm + A_n^\pm C_{n,a}^\pm &= \epsilon_a^\pm C_{n,a}^\pm, \\ A_n^\pm &= \gamma_0 q_n^\mp + \sum_n' \gamma_{mn} (q_m - 1) = \frac{\gamma_0}{2} - D_n \mp \Delta_n, \\ B_n^\pm &= \beta_n - \gamma_n p_n^\pm = B_n \mp b_n, \end{aligned} \right\} \quad (2.6)$$

where

$$\left. \begin{aligned} D_n &= -\frac{\gamma_0}{2}d_n - \sum'_m \gamma_{nm}d_m, & \Delta_n &= \gamma_0s_n, \\ B_n &= \beta_n - \frac{\gamma_n}{2}p_n, & b_n &= \gamma_n t_n, \end{aligned} \right\} \quad (2.7)$$

are the quantities having the significance of the gap parameters.

From Eqs. (2.4), (2.5) and (2.6), we have the following important properties of our model.

1°) Neutral UHF states with $d_n = 0$ depend only on the on site Coulomb force and the nearest neighbour exchange interaction but are independent of the different site Coulomb force.

2°) Anion-cation symmetry: If we have an anionic UHF solution with $q_n = 1 + d_n$, $d_n \neq 0$, then we have also a cationic solution with $q_n = 1 - d_n$ and the same equilibrium geometry. The energies of these solutions are related as

$$E^{\text{tot}}(\text{anion}) - E^{\text{tot}}(\text{cation}) = \nu\gamma_0. \quad (2.8)$$

The TUHF equation (2.6) and the force equilibrium condition (2.5) are invariant to the transformation

$$\left. \begin{aligned} \varepsilon_a^\pm - \gamma_0/2 &\rightarrow -(\varepsilon_a^\pm - \gamma_0/2), & \beta_n &\rightarrow -\beta_n, \\ d_n &\rightarrow -d_n, & p_n &\rightarrow -p_n, & s_n &\rightarrow -s_n, & t_n &\rightarrow -t_n. \end{aligned} \right\} \quad (2.9)$$

The total energy (2.4) is also invariant to (2.9) except for the change of the sign of ν . This shows that the orbital energy spectra of the anionic and cationic solutions are the mirror images to each other with respect to the origin $\varepsilon_a^\pm = \gamma_0/2$. This implies also that the orbital energy spectrum of a neutral UHF state is symmetric with respect to the origin.

3°) The TUHF equation (2.6) has the form of a Hückel equation with the effective transfer interaction B_n^\pm and the effective π electron- σ core interaction A_n^\pm . The nearest neighbour exchange interaction is renormalized into the effective transfer interaction B_n^\pm so that it has a larger value than the pure Hückel transfer interaction

$$|B_n^\pm| > |\beta_n|. \quad (2.10)$$

The on site and different site Coulomb forces between π electrons are renormalized into the effective π electron- σ core interaction A_n^\pm . The A_n^\pm depends on the CD d_n and is much affected by doping.

We note that the above properties are obtained on the assumption (2.3) and the neglect of the long range transfer and exchange interactions between sites farther than nearest neighbours. These approximations are reasonable and the error coming from them will not be so large to alter our conclusions.

§ 3. Coulomb interaction dependences of the UHF states in regular lattice

As we have shown in I, regular undoped trans-polyacetylene has five UHF states that may become the singlet HF ground state; BOW (bond order wave), SDW (spin density wave), CDW (charge density wave), SD-BOW (spin density-bond order wave) and CD-BOW (charge density-bond order wave). We show here that they have characteristic and different Coulomb interaction dependences. From this we can see how the nature of the HF ground state is determined by the Coulomb interaction.

The order parameters in the UHF states have alternating values

$$\left. \begin{aligned} d_n &= (-1)^{n-1} d, & s_n &= (-1)^{n-1} s, \\ p_n &= p + (-1)^{n-1} p', & t_n &= 0, \end{aligned} \right\} \quad (3.1)$$

where p is the average BO and d , s and p' are the amplitudes of the CD, SD and BO alternations, respectively. All the UHF states have no SBO. The UHF states are characterized by having one or two non-zero alternation amplitudes

$$\left. \begin{aligned} p'_0(\text{BOW}), & \quad s(\text{SDW}), & d(\text{CDW}), \\ s \text{ and } p'_0(\text{SD-BOW}), & & d \text{ and } p'_0(\text{CD-BOW}), \end{aligned} \right\} \quad (3.2)$$

where p'_0 is the value of p' in equidistant lattice. We note that lattice dimerization induces a BO alternation p'_D in all the UHF states and p' is the sum of the spontaneous and induced components, $p' = p'_0 + p'_D$. SDW and CDW have no spontaneous BO alternation, $p'_0 = 0$, whereas BOW, SD-BOW and CD-BOW have a spontaneous one, $p'_0 \neq 0$. The UHF states having no spontaneous SD(CD) alternation in equidistant lattice remain to have no SD(CD) alternation in dimerized lattice.

There is a restriction in the relative magnitudes of the alternation amplitudes. From the definitions of q_n^\pm and p_n^\pm (Eq. (2.3) in I) and the Schwartz inequality, we have

$$q_n^\pm q_{n+1}^\pm = q_n^\pm (1 - q_n^\pm) \geq |p_n^\pm|^2, \quad (3.3a)$$

that leads to

$$\left. \begin{aligned} 1 - 4s^2 &\geq (p \pm p')^2, \\ 1 - d^2 &\geq (p \pm p')^2, \end{aligned} \right\} \quad (3.3b)$$

showing that SD(CD) and BO alternations of large amplitudes are incompatible.

The gap parameters (2.7) in the UHF states are also alternating

$$\left. \begin{aligned} \Delta_n &= (-1)^{n-1} \Delta, & \Delta &= \gamma_0 s, \\ D_n &= (-1)^{n-1} D, & D &= \frac{\Gamma_0}{2} d, \\ B_{2m+1} &= B_1 = \beta_1 - \gamma_1 p_1 / 2, & B_{2m} &= B_2 = \beta_2 - \gamma_2 p_2 / 2, \\ p_1 &= p + p', & p_2 &= p - p', & b_n &= 0, \end{aligned} \right\} \quad (3.4)$$

where Γ_0 is a parameter to determine the stabilities of CDW and CD-BOW

$$\begin{aligned} \Gamma_0 &= -\gamma_0 + 2 \sum_m \gamma_{1,2m} - 2 \sum'_m \gamma_{1,2m+1} \\ &= 2(\gamma_{12} + \gamma_{14} + \dots + \gamma_{23} + \gamma_{25} + \dots) - \gamma_0 - 4(\gamma_{13} + \gamma_{15} + \dots). \end{aligned} \quad (3.5)$$

The total energy (2.4) per unit cell is given in terms of the alternation amplitudes as

$$\begin{aligned} E^{\text{tot}} &= \frac{\gamma_0}{2} + 2(\beta_1 + \beta_2)p - \frac{1}{2}(\gamma_1 + \gamma_2)(p^2 + p'^2) \\ &\quad + \{2(\beta_1 - \beta_2) - (\gamma_1 - \gamma_2)p\}p' - 2\gamma_0 s^2 - \frac{\Gamma_0}{2}d^2 + U(x_1) + U(x_2). \end{aligned} \quad (3.6)$$

We see from Eq. (3.6) what parts of the Coulomb interaction are responsible to produce the spontaneous alternations of the order parameters in the UHF states.

1°) The spontaneous BO alternation enhances the attractive nearest neighbour exchange interaction stabilizing the BOW class states.

2°) The spontaneous SD alternation suppresses the repulsive on site Coulomb force stabilizing the SDW class states.

3°) The net charges produced by the spontaneous CD alternation are of the same sign on even (on site, second, ...) neighbour sites but of the different signs on odd (nearest, third, ...) neighbour sites, so that the Coulomb potential due to the CD alternation is attractive between odd neighbour sites but repulsive between even neighbour sites. If the attractive contribution of odd neighbours exceeds the repulsive one of even neighbours, then the condition $\Gamma_0 > 0$ is satisfied and the different site Coulomb force stabilizes the CDW class states.

From 1°)~3°) and the list (3.2) of the spontaneously alternating order parameters in the UHF states, we obtain the Coulomb interaction dependences of the UHF states as summarized in Table I. We have some important remarks.

4°) BOW, SDW and SD-BOW are neutral states and independent of the different site Coulomb force. BOW is also independent of the on site Coulomb force because BOW has constant ED's, and consequently a constant contribution of the on site Coulomb force.

5°) Owing to the restriction (3.3b), the stabilizations by the Coulomb force and exchange interaction counteract. In SDW (CDW) without spontaneous BO

Table I. Coulomb interaction dependences of the UHF states.

	On site Coulomb	Nearest Neighbour		Long range Coulomb
		Coulomb	Exchange	
BOW (Dimerization, Gap)	×	×	⊙	×
SDW (Neutral solitons)	⊙	×	○	×
CDW (Charged solitons)	○	⊙	○	○
SD-BOW	⊙	×	⊙	×
CD-BOW	○	⊙	⊙	○

⊙ and ○ represent stabilizing and destabilizing contributions, respectively, and × independence of the heading part of the Coulomb interaction. The physical properties of trans-polyacetylene with the same Coulomb interaction dependence as the respective UHF state are also shown in parentheses. For solitons confer III.

alternation, development of the SD(CD) alternation produces not only a stabilization by the Coulomb force but also accompanies a destabilization by a suppression of the exchange interaction due to a decrease of BO's. In SD-BOW (CD-BOW) with both the BO and SD(CD) alternations, both the two interactions work stabilizingly but either one of them cannot become much superior to another. They must have moderate and balanced contributions.

6°) The stabilization of CDW and CD-BOW by the Coulomb force mainly comes from the nearest neighbour Coulomb attraction. The long range part of the Coulomb force farther than the nearest neighbour always contributes destabilizingly because the repulsive contribution of even neighbours is predominant in it. *If the effective Coulomb potential γ_{mn} has a relatively large nearest neighbour part and screened long range part, then the parameter Γ_0 has a large positive value leading to a large stabilization of CDW and CD-BOW.* We shall show in III that an enormous stabilization of charged solitons is brought about by screening of the long range part of the effective Coulomb potential due to this mechanism of the stabilization of CDW.

We have derived in I the conditions for the UHF states to become the HF ground state in equidistant lattice. We summarize here the conditions

$$\left. \begin{aligned}
 \text{BOW} & : K^{\text{BOW}} < 2/\gamma_0, \quad K^{\text{BOW}} < 2/\Gamma_0, \\
 \text{SDW} & : G^{\text{SDW}} < 1/\gamma, \quad \gamma_0 > \Gamma_0, \\
 \text{SD-BOW} & : K^{\text{BOW}} > 2/\gamma_0, \quad G^{\text{SDW}} > 1/\gamma, \quad \gamma_0 > \Gamma_0, \\
 \text{CDW} & : G^{\text{CDW}} < 1/\gamma, \quad \Gamma_0 > \gamma_0, \\
 \text{CD-BOW} & : K^{\text{BOW}} < 2/\Gamma_0, \quad G^{\text{CDW}} > 1/\gamma, \quad \Gamma_0 > \gamma_0,
 \end{aligned} \right\} \quad (3.7)$$

where $\gamma = \gamma_1 = \gamma_2$ and K and G are the quantities defined in Eq. (4.12) of I. As we have noted in I, there is a correspondence between the UHF states of the SDW class and those of the CDW class. The latter can be obtained from the former by replacing γ_0 by Γ_0 and Δ by D . The condition $\Gamma_0 > \gamma_0$ (Eq. (4.30) in I) for a CDW class state to become lower in energy than the corresponding SDW class state can be satisfied for the effective Coulomb potential with relatively large nearest neighbour part and screened long range part. The relative stability of the neutral states BOW, SDW and SD-BOW is determined by the relative strengths of the on site Coulomb and nearest neighbour exchange interactions, i.e., by the ratio γ/γ_0 . If γ/γ_0 is small, the stabilization by the on site Coulomb force is the larger and SDW becomes the HF ground state. If γ/γ_0 is near 1, the stabilization by the exchange interaction is the larger and BOW becomes the HF ground state. The SD-BOW ground state can be realized in a narrow range of γ/γ_0 where the two interactions can simultaneously produce moderate and balanced stabilizations whose sum exceeds the maximal stabilization by either one of them. This explains the structure of the phase map of the three states shown in Fig. 2 of I. The three states BOW, CDW and CD-BOW also have a phase map in the $\gamma/|\beta|$ vs $\Gamma_0/|\beta|$ plane with the same structure as Fig. 2 in I.

§ 4. Coulomb interaction dependence of the dimerization potential

We consider here how the Coulomb interaction affects the dimerization potential. As shown in I, the free energy of a UHF state with a spontaneous BO alternation changes linearly upon small dimerization of the lattice. This can clearly be seen in Eq. (3.6). For small dimerization, $x_1 = x + \delta x$ and $x_2 = x - \delta x$, the change of the total energy is

$$\delta E^{\text{tot}} = 4 \left\{ \frac{d\beta(x)}{dx} - \frac{1}{2} \frac{d\gamma(x)}{dx} p_0 \right\} p_0' \delta x, \quad (4.1)$$

where p_0 is the value of p in equidistant lattice. Equation (4.1) is a good approximation for the free energy change because the entropic term is negligibly small in regular lattice (in the order of 10^{-4} eV). The equilibrium geometries of BOW, SD-BOW and CD-BOW are therefore always dimerized. Equation (4.1) shows that the larger the spontaneous BO alternation p_0' , the larger the stabilization by lattice dimerization is. SDW and CDW have no p_0 , so that an equidistant lattice is their equilibrium geometry. It was shown that they cannot have a dimerized equilibrium geometry.⁴⁾

The correlation stabilizations of SDW and CDW at their equidistant equilibrium geometries are determined by γ_0 and Γ_0 , respectively, while the correlation and dimerization stabilization of BOW at its dimerized equilibrium geometry is determined by γ . To get larger stabilization of BOW than SDW and CDW, the

ratios γ/γ_0 and γ/Γ_0 must be larger than a critical value. Namely, to get a lattice dimerization, the effective Coulomb potential is necessary to have the nearest neighbour part exceeding a critical relative value to the on site part and Γ_0 . The values of γ/γ_0 for the Mataga-Nishimoto and Ohno potentials, that give equidistant and dimerized lattices, respectively, are 0.48 and 0.68 (at $r=1.412\text{\AA}$). The critical value of $\gamma/\gamma_0(\gamma/\Gamma_0)$ is therefore between these values. We note that the critical value is dependent on the transfer interaction and the elastic potential. We show in Fig. 1 how the barrier height of the dimerization potential of the HF ground state consisting of SDW and BOW changes upon the damping $c\gamma_n$, $0 \leq c \leq 1$, of the nearest neighbour part γ_n of the Ohno potential. We see that the barrier turns out negative and the lattice dimerization disappears if the damping factor c becomes smaller than a critical value.

Since equilibrium dimerized lattice is possible only in the BOW class states with a spontaneous BO alternation, the nearest neighbour exchange interaction to produce it is the driving force of the dimerization. The mechanism of the lattice dimerization by spontaneous BO alternation was first suggested by Čížek and Paldus.⁵⁾

Screening of the long range part of the effective Coulomb potential much affects the ratio γ/Γ_0 and consequently the dimerization. CDW and CD-BOW are very much stabilized by the screening and can become lower in energy than SDW and SD-BOW. We show in Fig. 2 how the exponential screening

$$\gamma_{mn} \exp(-r_{mn}/\alpha\bar{r}), \quad |m-n| > 1, \quad (4.2)$$

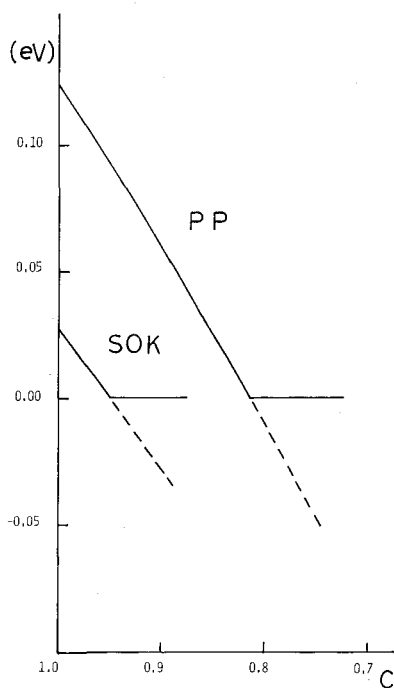


Fig. 1. Dependence of the dimerization potential barrier on the damping $c\gamma_n$, $0 \leq c \leq 1$, of the nearest neighbour part γ_n of the Ohno potential. The dimerization potential barrier of the HF ground state consisting of SDW and BOW, e.g., the difference of the energies of SDW and BOW at their equidistant and dimerized equilibrium geometries, is plotted against the damping factor c . The barrier is calculated for the SOK and PP parametrizations. In the dashed line region, the equidistant equilibrium geometry of SDW becomes lower in energy than the dimerized one of BOW.

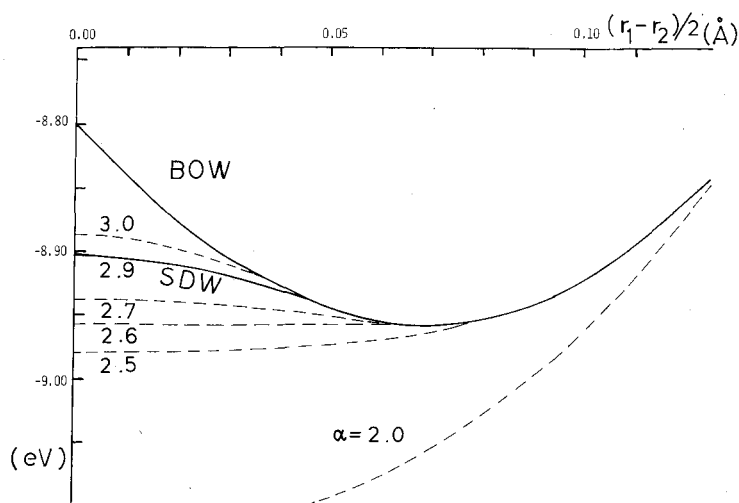


Fig. 2. Dependence of the dimerization potential of CDW on the exponential screening of the long range part of the Ohno potential. How the dimerization potential of CDW (-----) is affected by the exponential screening (4.2) of the Ohno potential is illustrated for various values of the screening parameter α . The parametrization is SOK and the average bond length $r = (r_1 + r_2)/2$ is fixed to the equilibrium value 1.412\AA . The dimerization potentials of SDW and BOW (—) are also shown.

of the long range part farther than the nearest neighbour of the Ohno potential affects the dimerization potential of CDW where $\bar{r} = 1.412\text{\AA}$ is the average bond length $(\bar{r}_1 + \bar{r}_2)/2$ of the dimerized equilibrium geometry. Note that the dimerization potential consisting of SDW and BOW is not affected by the screening since they depend only on the on site and nearest neighbour parts of the effective Coulomb potential. For α smaller than 2.9, the condition $\Gamma_0 > \gamma_0$ is satisfied and CDW becomes lower than SDW. Thus, *the screening of the long range part of the Coulomb potential can lead to a drastic change in the nature of the HF ground state, from neutral SDW with an antiferromagnetic SD alternation to ionic CDW with alternating CD's.* At this stage of the screening, however, the stable equilibrium geometry is still in the region of the BOW ground state and dimerized. Upon further decrease of α , the barrier of the dimerization potential becomes lower. For α smaller than 2.6, CDW at equidistant lattice turns out to have energy lower than the minimal energy of BOW and the barrier of the dimerization potential disappears. Therefore, *a sudden change of the equilibrium geometry from dimerized to equidistant takes place at this stage of the screening.*

We have shown in I that the SD-BOW ground state can be realized in a Peierls system consisting of an array of stacked organic ion radicals with a suitable effective Coulomb potential. An example of the parametrization for such a Peierls system has been given in Table II of I. Screening of the long range

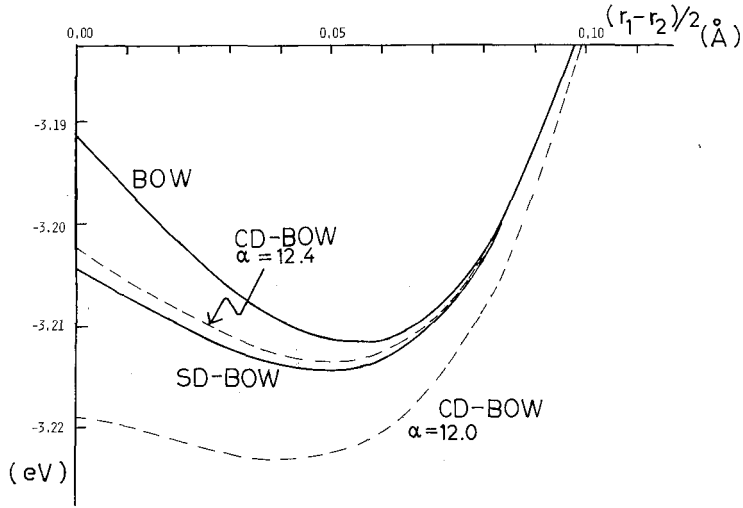


Fig. 3. Dependence of the dimerization potential of CD-BOW on the exponential screening of the long range part of the Ohno potential. How the dimerization potential of CD-BOW(-----) in the Peierls system whose parameters have been given in Table II of I is affected by the exponential screening (4·2) of the Ohno potential is illustrated for various values of α . The average bond length \bar{r} is fixed to the equilibrium value 3.4 Å. The dimerization potentials of SD-BOW and BOW(—) are also shown.

part of the effective Coulomb potential can change the nature of the HF ground state from SD-BOW to CD-BOW. We show in Fig. 3 how CD-BOW is stabilized by the screening (4·2). We see that a mild screening makes CD-BOW the HF ground state. Such a Peierls system is likely to have a rather strong screening of the long range part of the Coulomb potential. Then, much stabilized CDW becomes the HF ground state and lattice dimerization disappears.

The dimerization stabilization energy and the magnitude of the bond length alternation $\bar{r}' = (\bar{r}_1 - \bar{r}_2)/2$ is affected by the strength of the effective Coulomb potential. We show in Fig. 4 how the dimerization potential of BOW at $T = 300^\circ\text{K}$ is affected by the constant screening $(1/\epsilon)\gamma_{mn}$ of the Ohno potential. We show in Fig. 5(a) and (b) the $1/\epsilon$ dependences of \bar{r}' and the dimerization stabilization energy of BOW. In the limit $1/\epsilon \rightarrow 0$ of the complete constant screening, our model reduces to the SSH model and BOW becomes always the ground state of the system. In the lattice without the Coulomb interaction dimerization is caused by the transfer interaction. The extent of the lattice dimerization produced by the transfer interaction, however, is very much dependent on the gradient of the transfer integral $\beta(x)$.⁶⁾ The PP parametrization for $\beta(x)$ with a steep gradient yields a lattice dimerization at $T = 300\text{ K}$, though it is small, in the limit $1/\epsilon = 0$, but the SOK parametrization with a gentle gradient gives a very

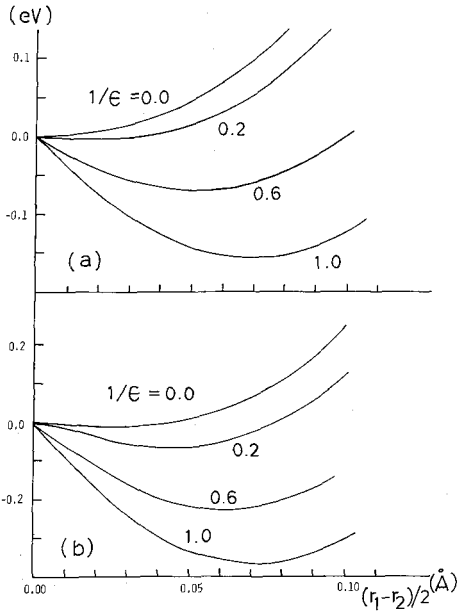


Fig. 4. Dependence of the dimerization potential of BOW on the constant screening $(1/\epsilon)\gamma_{mn}$ of the Ohno potential. How the dimerization potential of BOW is affected by the constant screening of the Ohno potential is illustrated for various values of $1/\epsilon$ in the SOK (a) and PP (b) parametrizations. The average bond length \bar{r} is fixed to the equilibrium value 1.412\AA (SOK) or 1.413\AA (PP).

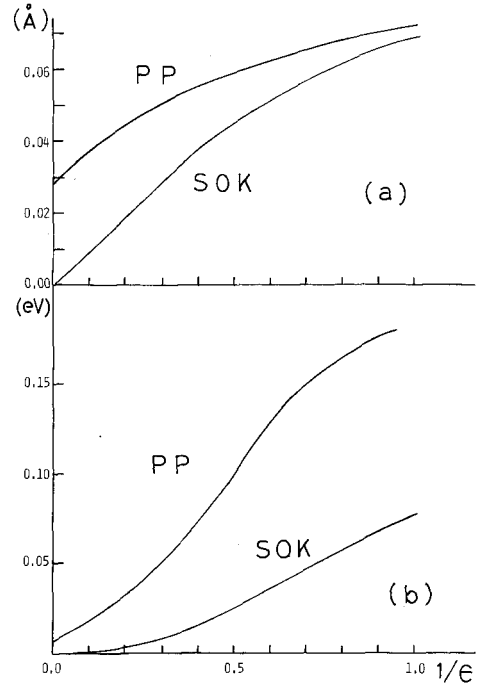


Fig. 5. Dependences of the bond length alternation (a) and the dimerization stabilization energy (b) of BOW on the constant screening $(1/\epsilon)\gamma_{mn}$ of the Ohno potential. The equilibrium bond length alternation $\bar{r}' = (\bar{r}_1 - \bar{r}_2)/2$ and the dimerization stabilization energy of BOW, e.g., the difference of the energies of BOW at the equidistant lattice with $r = \bar{r}$ and the dimerized equilibrium lattice, are plotted against $1/\epsilon$ for both the SOK and PP parametrizations.

small dimerization at $T=0\text{ K}$ (only in the order of 10^{-3}\AA) and it disappears at $T=300\text{ K}$. In the SOK case, therefore, the lattice dimerization is solely due to the Coulomb mechanism. In the PP case, the transfer interaction mechanism has a substantial contribution in the weak Coulomb regime. However, the Coulomb mechanism very effectively enhances the dimerization even in the weak Coulomb regime as seen in Fig. 5. If we try to explain the observed dimerization solely by the transfer interaction mechanism, as done in the SSH model, we need $\beta(x)$ with much steeper gradient than the PP case. Such a very steep $\beta(x)$ is difficult to justify quantum chemically. In both the parametrizations of $\beta(x)$, the average bond length \bar{r} ($=1.412\text{\AA}$ for the SOK case or $=1.413\text{\AA}$ for the PP case) is little affected but the magnitude of the bond length alternation \bar{r}' is much reduced

upon constant screening of the effective Coulomb potential. Fincher et al.⁷⁾ showed by X ray scattering that undoped trans-polyacetylene has a lattice dimerization with $\bar{r}=1.42\text{\AA}$ and $\bar{r}'=0.07\pm 0.02\text{\AA}$. Our result in Fig. 5(a) shows that to be consistent with the X ray scattering data the effective Coulomb potential in trans-polyacetylene cannot be very weak as long as the transfer interaction and elastic potential in it are similar to those in short polyenes. In the SOK and PP cases, the weakest plausible effective Coulomb potential are about 40~50% and 60~70% screened Ohno potentials, respectively. It is very unlikely possibility that not only the effective Coulomb potential but also the transfer interaction and the elastic potential are modified in polyacetylene from small conjugate molecules. As we shall show in III, the PP parametrization leads to an unreasonably narrow neutral soliton spreading and can be eliminated, while the SOK one gives results consistent with experiments. Therefore, the present result suggests that the effective Coulomb potential in trans-polyacetylene is not weaker than half of the one in small conjugate molecules.

§ 5. Equivalence of the SSH model to a BOW state

We show here that the SSH model is equivalent to a BOW state in our model under a reasonable approximation.⁴⁾ The energies of the SSH model and a BOW state in our model are

$$E^{\text{SSH}} = \sum_n (2\beta_n p_n + U(x_n)), \quad (5.1)$$

$$E^{\text{BOW}} = \sum_n (2\beta_n p_n - \gamma_n p_n^2 / 2 + U(x_n)). \quad (5.2)$$

We make the following approximations for the lattice distortion dependences of β_n , $U(x_n)$ and γ_n

$$\beta_n = \beta - \rho x_n, \quad U(x_n) = \frac{\kappa}{2} x_n^2, \quad \gamma_n = \gamma = \text{const}. \quad (5.3)$$

The neglect of the distortion dependence of the nearest neighbour Coulomb potential γ_n is reasonable since it is much weaker than that of β_n . With the approximation (5.3), the force equilibrium condition becomes

$$x_n = \frac{2\rho}{\kappa} p_n. \quad (5.4)$$

Using Eq. (5.4) we can eliminate the lattice distortion variables x_n from the energies (5.1) and (5.2)

$$E^{\text{SSH}} = \sum_n \left(2\beta p_n - \frac{2\rho^2}{\kappa} p_n^2 \right), \quad (5.5)$$

$$E^{\text{BOW}} = \sum_n \left\{ 2\beta p_n - \left(\frac{\gamma}{2} + \frac{2\rho^2}{\alpha} \right) p_n^2 \right\}. \quad (5.6)$$

Equations (5.5) and (5.6) show that the SSH model is equivalent to a BOW state in our model as long as an equilibrium lattice geometry concerns. This equivalence indicates that *the SSH model implicitly incorporates effects of the nearest neighbour exchange interaction that is the most important part of the Coulomb interaction for lattice distortions.* From Eqs. (5.5) and (5.6), the electron-lattice coupling parameter (the gradient of $\beta(x)$) in the SSH model can be related to the parameters in our model as

$$\rho^{\text{SSH}} = \sqrt{\rho^2 + \gamma\alpha/4}. \quad (5.7)$$

As we shall show in III, the SOK parametrization for $\beta(x)$ and the Ohno potential with 50~40% constant screening and an exponential screening of the long range part give soliton properties in agreement with experiments. The reasonable values of the parameters are therefore $\rho \approx 3 \text{ eV/\AA}$, $\gamma = 3.8 \sim 4.5 \text{ eV}$ (the values at $\bar{r} = 1.412 \text{ \AA}$) and $\alpha = 27.8 \text{ eV/\AA}^2$. Then Eq. (5.7) gives $\rho^{\text{SSH}} = 6.0 \sim 6.4 \text{ eV/\AA}$. This value is near the values $\rho^{\text{SSH}} = 8 \text{ eV/\AA}$ and $7.2 \pm 2.4 \text{ eV/\AA}$ proposed by Melé and Rice⁸⁾ and by Fincher et al.⁷⁾

§ 6. Coulomb interaction dependence of the band gap, a possible mechanism of splitting of exciton and evaluation of the exciton binding energy

As shown in § 4, the nearest neighbour Coulomb interaction of appreciable strength must be present in polyacetylene. It inevitably makes the optically allowed 1B_u absorption band excitonic. Here, we consider first the Coulomb interaction dependence of the band gap and next the condition to make splitting of the exciton into a zwitterionic pair of charged solitons possible. We lastly evaluate the exciton binding energy.

As shown in I, the energy bands in regular undoped trans-polyacetylene are given by

$$\varepsilon_{\pm}(\theta) = \frac{\gamma_0}{2} \pm [X^2 + B_1^2 + B_2^2 + 2B_1B_2 \cos \theta]^{1/2}, \quad (6.1)$$

where the plus and minus give the conduction and valence bands, respectively, and $X=0$ (BOW), Δ (SDW and SD-BOW) or D (CDW and CD-BOW). From Eq. (6.1), the band gap is given by

$$\left. \begin{aligned} \text{Gap} &= 2[X^2 + (B_1 - B_2)^2]^{1/2}, \\ B_1 - B_2 &= \beta_1 - \beta_2 - \frac{1}{2}(\gamma_1 - \gamma_2)p - \frac{1}{2}(\gamma_1 + \gamma_2)p'. \end{aligned} \right\} \quad (6.2)$$

Equation (6.2) shows that the band gap consists of the Hückel gap $2|\beta_1 - \beta_2|$, the

exchange correlation gap $|(\gamma_1 - \gamma_2)p + (\gamma_1 + \gamma_2)p'|$ and the Coulomb correlation gap $2X$. The exchange and Coulomb correlations make the gap always larger than the Hückel one. In a dimerized lattice, the HF ground state at the equilibrium geometry must be either BOW, SD-BOW or CD-BOW. In the dimerized lattice with the BOW ground state only the nearest neighbour exchange interaction contributes to the Franck-Condon band gap, while in the one with the SD-BOW (CD-BOW) ground state the on site part (all parts) of the Coulomb force also contributes to it via the Coulomb correlation gap. All the BOW class states have an appreciable exchange correlation gap because they have a spontaneous BO alternation p_0' that effectively contributes to it. The Franck-Condon band gap of the dimerized lattice with the effective Coulomb potential similar to the one in small conjugate molecules is quite large owing to a large exchange correlation gap. It is about 8 eV in the PP-Ohno parametrization and about 6 eV in the SOK-Ohno case as shown in Fig. 6.

The Franck-Condon band gap, however, is very sensitively decreased by reduction of the strength of the effective Coulomb potential. We show in Fig. 6 how the Franck-Condon band gap at $T=300$ K is affected by the constant screening $(1/\epsilon)\gamma_{mn}$ of the Ohno potential. The band gap in the SOK case reduces to zero in the limit $1/\epsilon \rightarrow 0$ because no lattice dimerization is present, while the one in the PP case remains to have a small finite value owing to the persistence of a dimerization. Figure 6 shows that the Franck-Condon band gap in trans-polyacetylene mostly arises from the exchange correlation.

Lauchlan et al.⁹⁾ showed that trans-polyacetylene has a photoconductivity starting from a threshold at about 1.0~1.3 eV that is well below the 1B_u absorption peak energy 1.9 eV. The threshold was interpreted as the energy necessary to make a zwitterionic pair of charged solitons. To be consistent with the photoconductivity data, the 1B_u exciton must be able to split into a zwitterionic pair of charged solitons. The splitting of the exciton is in principle possible. The exciton is a bound zwitterion as illustrated in Fig. 7(a) in the representation to use the localized Wannier functions. The lattice around the zwitterion of the Franck-Condon exciton makes a distortion to relax the lattice dimerization since the polarization of π electrons induced by the zwitterion makes nearby double bonds weaker. Then the zwitterion after the lattice relaxation is just equivalent to a colliding pair of charged solitons in close encounter (Fig. 7(b)). This lattice relaxation is always possible since it stabilizes the bound zwitterion. The last stage of the splitting of the exciton is separation of the colliding charged solitons (Fig. 7(c)). This process accompanies loss of the binding energy U_{bind} of the zwitterion. The key to make the process possible is in the fact that the separated charges induce much stronger polarization of π electrons around them than the polarization induced by the bound zwitterion since the charges in the bound zwitterion are compensated out and do not give strong long range influence to

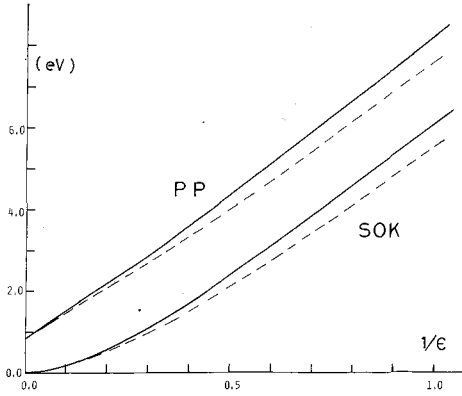


Fig. 6. Dependences of the Franck-Condon band gap (—) and 1B_u excitation energy (---) on the constant screening $(1/\epsilon)\gamma_{mn}$ of the Ohno potential. The Franck-Condon band gap and 1B_u excitation energy calculated by Eqs. (6.2) and (6.5) are plotted against $1/\epsilon$ for both the SOK and PP parametrizations.

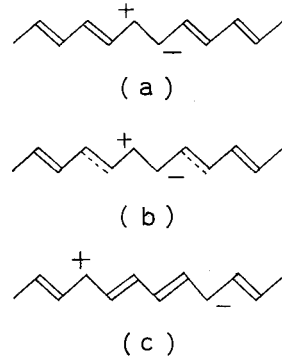


Fig. 7. Schematic illustration for the process of splitting of the 1B_u exciton. The Franck-Condon exciton (a) first relaxes to a colliding zwitterionic pair of charged solitons (b) and next separates into a plus and a minus charged solitons (c).

outside. If the correlation stabilization energy U_{pol} due to the polarization cloud around the separated charges is larger than the binding energy of the exciton, $U_{pol} > U_{bind}$, then the splitting of the exciton becomes possible. As we shall show in III, this condition is satisfied by the Ohno potential with a constant screening and an exponential screening of the long range part.

The effective Coulomb potential satisfying the above condition allows us to make approximate evaluation of the exciton binding energy. Since its long range part is screened, it can be approximated by a square well potential with the depth γ/ϵ and the range \bar{r} . The reduced mass m of the electron-hole pair is $m = m^*/2$ where m^* is the effective mass of an electron and a hole. The bound state energy U_{bind} of the square well potential is given by¹⁰⁾

$$\xi \tan \xi = \eta, \quad \xi^2 + \eta^2 = \frac{m^* \bar{r}^2 \gamma}{\hbar^2 \epsilon},$$

$$U_{bind} = \frac{\hbar^2}{m^* \bar{r}^2} \eta^2. \quad (6.3)$$

The effective mass m^* is obtained from Eq. (6.1) as

$$m^* = \hbar^2(B_1 - B_2)/a^2 B_1 B_2, \quad (6.4)$$

where $a \approx \sqrt{3} \bar{r}$ is the lattice constant of the dimerized regular lattice. We show in Fig. 8 the $1/\epsilon$ dependence of the effective mass. As seen in Fig. 8, m^* is very

small, in the order of one-tenth of the electron mass in the SOK case. From Eq. (6.4), we see that $m^* \bar{r}^2 \gamma / \hbar^2 \epsilon < 1$ and we can make the approximation $\tan \xi \approx \xi$. Therefore, we have

$$U_{\text{bind}} = \frac{4(B_1 - B_2)\gamma^2}{3B_1 B_2 \epsilon^2} \left(1 + \sqrt{1 + \frac{4(B_1 - B_2)\gamma^2}{3B_1 B_2 \epsilon^2}} \right). \quad (6.5)$$

We show in Fig. 6 the 1B_u excitation energy calculated by Eq. (6.5). The exciton binding energy is not large even for large γ/ϵ . This is due to the small effective mass of electron and hole. We see from Fig. 6 that *the effective Coulomb potential must have a constant screening about $1/\epsilon \sim 0.5$ in the SOK case together with an exponential screening of the long range part in order to get the 1B_u excitation energy in agreement with the observed energy 1.9 eV.* We shall show in III that this effective Coulomb potential also gives the formation energy of a zwitterionic pair of charged solitons in agreement with the observed photoconductivity threshold. Therefore, we can conclude that the 1B_u absorption band in trans-polyacetylene is excitonic but the exciton is able to split into a zwitterionic pair of charged solitons if the effective Coulomb potential in trans-polyacetylene is suitably screened compared to the one in small conjugate molecules.

§ 7. Conclusions

Summarizing the above results we can conclude

- 1°) The UHF states BOW, SDW, SD-BOW, CDW and CD-BOW have characteristic and different Coulomb interaction dependences. The factors in the effective Coulomb interaction to determine the nature of the HF ground state are the ratio γ/γ_0 of the nearest neighbour to on site parts and the screening of the longer range part.
- 2°) Lattice dimerization is possible only in the BOW class states with a sponta-

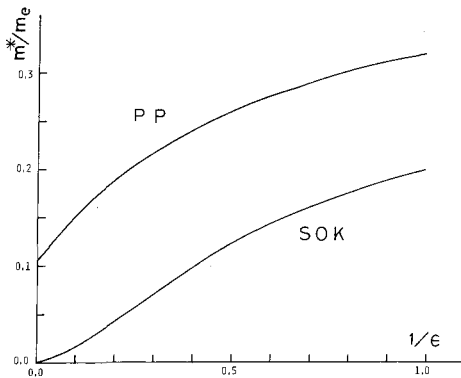


Fig. 8. Dependence of the ratio of the effective mass m^* of electron and hole to the electron mass m_e on the constant screening $(1/\epsilon)\gamma_{mn}$ of the Ohno potential. The m^*/m_e given by Eq. (6.4) is plotted against $1/\epsilon$ for both the SOK and PP parametrizations.

neous BO alternation. The effective Coulomb potential with relatively large nearest neighbour part and not too strongly screened longer range part induces lattice dimerization. As long as polyacetylene has the transfer interaction and the elastic potential similar to the ones in small conjugate molecules, the effective Coulomb interaction in it cannot be very weak to get a lattice dimerization consistent with the X ray scattering data.

3°) The SSH model is implicitly taking into account effects of the nearest neighbour exchange interaction that is the driving force of lattice distortions by the Coulomb interaction.

4°) The Franck-Condon band gap in a dimerized lattice is mainly determined by the nearest neighbour exchange interaction. The 1B_u excited state in the lattice with a Coulomb induced dimerization is excitonic. The binding energy of the exciton for the effective Coulomb interaction with screening of the long range part is not so large owing to the small effective mass of electron and hole. To get the 1B_u excitation energy consistent with the observed absorption spectrum of trans-polyacetylene, the short range part of the effective Coulomb interaction must be screened by about 50% compared to the one in small conjugate molecule. Splitting of the exciton to a zwitterionic pair of charged solitons is in principle possible. We shall study in III what effective Coulomb potential makes the splitting of the exciton possible.

The above conclusions have been obtained in the TUHF approximation. Since $0.8 \lesssim (\gamma_0 - \gamma_1) / \epsilon \beta \lesssim 1.5$ for the Ohno potential with the screening factor $0.5 \lesssim 1/\epsilon < 1$, the Coulomb interaction in polyacetylene belongs to an intermediate correlation regime. Therefore, correlation effects beyond TUHF might have an important contribution to lattice distortions in polyacetylene. Consideration of such higher order effects, however, is a difficult task. We add finally a comment about this. Cross and Fisher¹¹⁾ showed that the RPA correction has a substantial contribution to spin Peierls distortion. However, application of RPA to polyacetylene is inappropriate. As seen in Fig. 2, the HF ground state in the regular lattice with a dimerization consists of SDW and BOW or CDW and BOW. SDW and CDW bifurcate from BOW at points very close to the dimerized equilibrium geometry. Because of the equivalence of the HF and RPA instabilities,¹²⁾ RPA becomes unstable at the bifurcation points. Therefore, RPA is a bad approximation in polyacetylene. We confront the so-called mode-mode coupling problem if we want to proceed to a better approximation than TUHF.

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References

- 1) W. P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. Letters* **42** (1979), 1998; *Phys. Rev.* **B22** (1980), 2099.
M. J. Rice, *Phys. Letters* **71A** (1979), 152.
- 2) H. Fukutome and M. Sasai, *Prog. Theor. Phys.* **67** (1982), 41.
- 3) H. Fukutome and M. Sasai, *Prog. Theor. Phys.* **69**, (1982), No. 2 to appear.
- 4) H. Fukutome, *Prog. Theor. Phys.* **67** (1982), 977.
- 5) J. Čížek and J. Paldus, *J. Chem. Phys.* **47** (1967), 3976.
- 6) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **A251** (1959), 172.
- 7) C. R. Fincher, Jr., C. E. Chen, A. J. Heeger, A. G. MacDiarmid and J. B. Hastings, *Phys. Rev. Letters* **48** (1982), 100.
- 8) E. J. Melé and M. J. Rice, *Phys. Rev. Letters* **45** (1980), 926.
- 9) L. Lauchlan, S. Etemad, T. C. Chung, A. J. Heeger and A. G. MacDiarmid, *Phys. Rev.* **B24** (1981), 3701.
- 10) L. I. Schiff, "Quantum Mechanics" (McGraw-Hill, New York, 1955).
- 11) M. C. Cross and D. S. Fisher, *Phys. Rev.* **B19** (1979), 402.
- 12) D. J. Thouless, *Nucl. Phys.* **22** (1961), 78.