

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

— *UHF Transfer Matrix Method Adapted
to the Long Range Coulomb Interaction
and UHF States in Regular Bond Alternated Lattice* —

Hideo FUKUTOME and Masaki SASAI

Department of Physics, Kyoto University, Kyoto 606

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We develop in this series a theory of itinerant Peierls systems that mainly aims to study polyacetylene. In order to investigate roles of the long range Coulomb interaction in electronic structures and lattice distortions in a Peierls system, we develop a transfer matrix technique adapted to the unrestricted Hartree-Fock (UHF) approximation. The method makes it possible to calculate UHF states and equilibrium lattice geometries in a lattice with any aperiodic structure due to the presence of solitons.

Applying the method, we obtain the UHF states in the case of regular lattice that may become the HF ground state. There are at least eight such UHF states which are distinguished by the long range orders in the spin and charge densities and the bond orders. The nearest neighbour exchange interaction is responsible to produce such plentiful UHF states. We calculate the bond alternation potential and the band gap in trans polyacetylene using parametrizations of the Hamiltonian and the elastic potential that are able to well reproduce spectra and equilibrium geometries of small conjugated hydrocarbons. The bond alternation potential is very sensitive to the strength of the nearest neighbour Coulomb interaction. The Coulomb potential with fast damping prevents the bond alternation. The band gap is much larger than the energy 2 eV of the lowest absorption band as long as the Coulomb interaction in polyacetylene is similar to that in small conjugated hydrocarbons, suggesting the excitonic nature of the absorption band. We make also an illustrative calculation for an itinerant spin Peierls system with an antiferromagnetic spin order as well as a lattice dimerization.

§ 1. Introduction

The soliton (bond alternation domain wall) model of polyacetylene developed by Su, Schrieffer and Heeger¹⁾ (SSH) and by Rice²⁾ has achieved a great success. It is able to explain the conductivity,^{1),2)} optical properties,^{3),4)} magnetic resonances⁵⁾ and other properties of polyacetylene. It therefore seems to be a fundamentally correct model for polyacetylene. The model, however, utilizes the Hückel π electron Hamiltonian and no effect of the Coulomb interaction of π electrons is explicitly taken into consideration. It is well established that the Hückel Hamiltonian is a too crude approximation and explicit consideration of the electron Coulomb interaction is indispensable to obtain a good description of π electronic structures of conjugated molecules. In particular, the electron correlation in polyenes is by no means in a weak correlation regime. To explain

the existence of the lowest lying singlet A_g excited state in polyenes, it is necessary to take a lot of electron correlation effects into account.⁶⁾ Models of polyacetylene in the strong correlation regime were proposed by Kondo⁷⁾ and by Nakano and Fukuyama.⁸⁾ Their models start with the Heisenberg Hamiltonian for π electrons. However, the Coulomb interaction of π electrons in conjugated hydrocarbons is not so strong enough to yield the Heisenberg Hamiltonian as a good effective Hamiltonian. The ratio $(\gamma_0 - \gamma_1)/|\beta|$ is in order of 1~3 in the effective π electron Hamiltonian with reasonable parametrizations, where γ_0 and γ_1 are the one center and nearest neighbour two center Coulomb repulsion integrals and β is the nearest neighbour resonance integral. Therefore, the electron correlation in polyacetylene seems to be in an intermediate regime as long as the Coulomb interaction in it has the strength similar to the one in smaller conjugated molecules.

The long range Coulomb interaction may have important roles in polyacetylene. It may have serious effects on the energy and interaction of charged solitons. Magnetic susceptibility experiments⁹⁾ have shown that the Pauli susceptibility develops beyond a high doping concentration, indicating that highly doped polyacetylene becomes metallic. The continuum version of the SSH model proposed by Takayama, Lin-Liu and Maki¹⁰⁾ predicts the stability of high density soliton lattice¹¹⁾ in contradiction to the experiments. The possibility of a soliton-metal transition due to the Coulomb interaction was pointed out by Horovitz.¹²⁾

The purpose of this series is to develop a theory of polyacetylene that explicitly takes the long range Coulomb interaction of π electrons into account and connects the weak and strong correlation regimes. For this purpose, we use the unrestricted Hartree-Fock (UHF) approximation for the π electron Hamiltonian. The UHF approximation gives the exact ground state energy in both the weak and strong correlation limits and connects the two limits. A difficulty of polyacetylene problems lies in the fact that polyacetylene with solitons has in general an aperiodic structure. To overcome this difficulty, we develop a transfer matrix technique adapted to the UHF approximation. The transfer matrix technique¹³⁾ was very powerful to the studies of one dimensional random systems.¹⁴⁾ It was applied also to Hückel molecular orbital studies of conjugated chain polymers¹⁵⁾ and substituent effects on the bond alternation in polyacetylene.¹⁶⁾ By means of the UHF transfer matrix technique, it becomes possible to carry out computations for polyacetylene with arbitrary arrangements of solitons.

We give, in this paper, a general formulation of the UHF transfer matrix method adapted to the long range Coulomb interaction and obtain the UHF ground state in undoped trans polyacetylene with a regular bond alternated lattice. We discuss also itinerant spin Peierls systems that are realizable in one

dimensional crystals composed of stacked array of ion radicals of conjugated molecules. In succeeding papers, we shall apply the method to the problems of solitons, soliton-soliton interactions and the instability of high density solitons.

**§ 2. UHF-transfer matrix method for a polyacetylene chain
with the long range Coulomb interaction
and variable bond lengths**

We develop here a method of calculating π electronic structures and equilibrium geometries of a polyacetylene chain with the long range Coulomb interaction and variable C-C bond lengths. We use the geometrical parameter x_n that is the deviation of the bond length r_n between the n - and $n+1$ -th carbon atoms from the single bond length r_0 ; $x_n = r_0 - r_n$. We assume that all the C-C bond angles are fixed at 120° . Then, the geometries of the trans and cis isomers of a polyacetylene chain are specified by the x_n 's. We adopt, as the π electron Hamiltonian, the Pariser-Parr-Pople¹⁷⁾ (PPP) type one with the nearest neighbour transfer and exchange interactions and the long range Coulomb force.

The Coulomb integral α_n of the n -th π atomic orbital (AO), the resonance integral β_n between the n - and $n+1$ -th π AO's and the Coulomb repulsion integrals γ_{mn} between the m - and n -th π AO's are functions of x_n 's

$$\left. \begin{aligned} \alpha_n &= -\sum'_m v_{mn}, & v_{mn} &= v(r_{mn}), \\ \beta_n &= \beta(x_n), & \gamma_{mn} &= \gamma(r_{mn}), \end{aligned} \right\} \quad (2.1)$$

where $-v_{mn}$ is the Coulomb potential between the n -th π AO and the m -th σ core, r_{mn} is the distance between the m - and n -th π centers that is a function of x_n, \dots, x_{m-1} , $m > n$, and the primed sum denotes the summation over $m \neq n$.

We solve the Schrödinger equation of π electrons in the temperature UHF approximation. We consider a UHF state with the DODS (different orbitals for different spins) molecular orbital (MO) coefficients $C_{n,a}^\pm$, where \pm denote the up and down spins and the index a specifies an MO. We impose a restriction for the UHF state that for an MO a with complex MO coefficients $C_{n,a}^\pm$ there is always another MO $-a$ with the complex conjugate MO coefficients $C_{n,-a}^\pm = C_{n,a}^{\pm*}$. This restriction means that all the elements of the HF density matrix including the bond orders are real.

The π energy in the temperature UHF approximation is given by

$$\begin{aligned} E^\pi &= \sum_n \{ \alpha_n q_n + 2\beta_n p_n + \gamma_0 q_n^+ q_n^- - \gamma_n ((p_n^+)^2 + (p_n^-)^2) \} \\ &+ \frac{1}{2} \sum'_{m,n} \gamma_{mn} q_m q_n. \end{aligned} \quad (2.2)$$

Here, q_n^\pm are the densities of up and down spin π electrons on the n -th π AO and p_n^\pm are the bond orders between the n - and $n+1$ -th π AO's

$$\left. \begin{aligned} q_n^\pm &= \sum_a |C_{\bar{n},a}^\pm|^2 f_a^\pm, & q_n &= q_n^+ + q_n^-, \\ p_n^\pm &= \sum_a C_{\bar{n}+1,a}^\pm C_{\bar{n},a}^{\pm*} f_a^\pm, & p_n &= p_n^+ + p_n^-, \end{aligned} \right\} \quad (2.3)$$

where f_a^\pm are the statistical weights of the a -th up and down spin MO's. The γ_0 and $\gamma_n = \gamma_{n+1n}$ are the Coulomb repulsion integrals on the same π center and between nearest neighbour π centers, respectively.

The energy of the σ skelton is the sum of the elastic energy and the Coulomb potential between σ cores

$$\left. \begin{aligned} E^\sigma &= \sum_n U(x_n) + V, \\ V &= \frac{1}{2} \sum'_{m,n} V_{m,n}, & V_{m,n} &= V(r_{mn}), \end{aligned} \right\} \quad (2.4)$$

where $V_{m,n}$ is the Coulomb potential between the m - and n -th σ cores and U is the elastic potential of the C-C single bond whose explicit form will be given later.

The free energy of the system with the x_n 's as the adiabatic parameters is

$$\left. \begin{aligned} F &= E^{\text{tot}} - TS, & E^{\text{tot}} &= E^\pi + E^\sigma, \\ -TS &= kT \sum_a \sum_s \{ f_a^s \ln f_a^s + (1 - f_a^s) \ln(1 - f_a^s) \}, \end{aligned} \right\} \quad (2.5)$$

where k is the Boltzman constant and $s = \pm$ represents spin.

From the variation of the free energy with respect to $C_{\bar{n},a}^{\pm*}$ and f_a^\pm we obtain the UHF equation and the Fermi weights

$$\begin{aligned} &(\beta_n - \gamma_n p_n^\pm) C_{\bar{n}+1,a}^\pm + (\beta_{n-1} - \gamma_{n-1} p_{\bar{n}-1}^\pm) C_{\bar{n}-1,a}^\pm \\ &+ (\alpha_n + \gamma_0 q_n^\pm + \sum'_m \gamma_{nm} q_m) C_{\bar{n},a}^\pm = \varepsilon_a^\pm C_{\bar{n},a}^\pm, \end{aligned} \quad (2.6)$$

$$f_a^\pm = [\exp\{(\varepsilon_a^\pm - \varepsilon_F)/kT\} + 1]^{-1} = f(\varepsilon_a^\pm - \varepsilon_F), \quad (2.7)$$

where ε_a^\pm 's are the orbital energies and ε_F is the Fermi energy. Using Eq. (2.6), we obtain another expression of E^π

$$\begin{aligned} E^\pi &= \sum_a (\varepsilon_a^+ f_a^+ + \varepsilon_a^- f_a^-) \\ &- \sum'_n \{ \gamma_0 q_n^+ q_n^- - \gamma_n ((p_n^+)^2 + (p_n^-)^2) \} - \frac{1}{2} \sum'_{m,n} \gamma_{mn} q_m q_n. \end{aligned} \quad (2.8)$$

To solve Eq. (2.6), we use the transfer matrix technique. We define the transfer matrix T_n^\pm by

$$T_n^\pm(\varepsilon) = \begin{bmatrix} (\varepsilon - A_n^\pm)/B_n^\pm, & -B_{\bar{n}-1}^\pm/B_n^\pm \\ 1, & 0 \end{bmatrix}, \quad (2.9)$$

where

$$\left. \begin{aligned} A_n^\pm &= \alpha_n + \gamma_0 q_n^\pm + \sum'_m \gamma_{nm} q_m = A_n \mp \Delta_n, \\ A_n &= \alpha_n + \frac{\gamma_0}{2} q_n + \sum'_m \gamma_{nm} q_m, \quad \Delta_n = \gamma_0 (q_n^+ - q_n^-)/2, \\ B_n^\pm &= \beta_n - \gamma_n p_n^\pm. \end{aligned} \right\} \quad (2.10)$$

In the following, we consider a polyacetylene chain with N (an even number) carbon atoms and solve Eq. (2.6) with the periodic boundary condition $C_{\bar{n}+N,a}^\pm = C_{\bar{n},a}^\pm$ to avoid the complexity due to the end effect. Then, according to Ref. 15), Eq. (2.6) can be written

$$C_{\bar{n}+1}^\pm = T_n^\pm C_n^\pm = T_n^\pm \cdots T_1^\pm C_1^\pm, \quad C_n^\pm = \begin{bmatrix} C_n^\pm \\ C_{\bar{n}-1}^\pm \end{bmatrix}. \quad (2.11)$$

From Eq. (2.11) and the periodic boundary condition, we obtain

$$C_{\bar{N}+1}^\pm = C_1^\pm = T_N^\pm \cdots T_1^\pm C_1, \quad (2.12)$$

so that the secular equation to determine the orbital energies is given by

$$\left. \begin{aligned} \det[X^\pm(\varepsilon) - 1] &= 2 - \text{Tr}[X^\pm(\varepsilon)] = 0, \\ X^\pm &= T_N^\pm \cdots T_1^\pm, \quad \varepsilon = \varepsilon_a^\pm, \end{aligned} \right\} \quad (2.13)$$

where \det and Tr mean determinant and trace, respectively, and we have used the relation $\det(A - 1) = 1 + \det(A) - \text{Tr}(A)$ that holds for a two dimensional matrix A and the unimodularity of X^\pm ; $\det(X^\pm) = 1$.

To calculate the electron densities and bond orders, we introduce the Green functions

$$G_{\bar{n}m}^\pm(\varepsilon) = \sum_a C_{\bar{n},a}^\pm C_{m,a}^{*\pm} / (\varepsilon_a^\pm - \varepsilon). \quad (2.14)$$

They satisfy

$$\begin{aligned} \mathbf{G}_{\bar{n}+1m}^\pm &= T_n^\pm \mathbf{G}_{\bar{n}m}^\pm + \boldsymbol{\rho}_n^\pm \delta_{nm}, \quad \mathbf{G}_{\bar{n}m}^\pm = \begin{bmatrix} G_{\bar{n}m}^\pm \\ G_{\bar{n}-1m}^\pm \end{bmatrix}, \quad \boldsymbol{\rho}_n^\pm = \begin{bmatrix} 1/B_n^\pm \\ 0 \end{bmatrix}, \\ &= T_n^\pm \cdots T_m^\pm \mathbf{G}_{\bar{m}n}^\pm + T_n^\pm \cdots T_{m+1}^\pm \boldsymbol{\rho}_m^\pm, \quad n > m. \end{aligned} \quad (2.15)$$

From Eq. (2.15) and the periodic boundary condition, we obtain

$$\left. \begin{aligned} \mathbf{G}_{\bar{n}n}^\pm &= \mathbf{G}_{\bar{n}+Nn}^\pm = J_n^\pm T_n^\pm \mathbf{G}_{\bar{n}n}^\pm + J_n^\pm \boldsymbol{\rho}_n^\pm, \\ J_n^\pm &= T_{\bar{n}-1}^\pm \cdots T_1^\pm T_N^\pm \cdots T_{n+1}^\pm, \end{aligned} \right\} \quad (2.16)$$

that leads to

$$G_{\bar{n}n}^\pm = [(1 - J_n^\pm T_n^\pm)^{-1} J_n^\pm]_{11} / B_n^\pm. \quad (2.17)$$

From Eqs. (2.15) and (2.17), we obtain also

$$G_{\bar{n}+1n}^{\pm} = [(1 - T_n^{\pm} J_n^{\pm})^{-1}]_{11} / B_n^{\pm}. \quad (2\cdot18)$$

By using the relation

$$A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \quad A^{-1} = \begin{bmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{bmatrix} / \det(A), \quad (2\cdot19)$$

Eqs. (2\cdot17) and (2\cdot18) become

$$\left. \begin{aligned} G_{\bar{n}n}^{\pm} &= (J_n^{\pm})_{11} / B_n^{\pm} \{2 - \text{Tr}(X^{\pm})\}, \\ G_{\bar{n}+1n}^{\pm} &= \{1 - (J_n^{\pm})_{12}\} / B_n^{\pm} \{2 - \text{Tr}(X^{\pm})\}, \end{aligned} \right\} \quad (2\cdot20)$$

where we have used $\text{Tr}(J_n^{\pm} T_n^{\pm}) = \text{Tr}(X^{\pm})$ and $(T_n^{\pm} J_n^{\pm})_{22} = (J_n^{\pm})_{12}$.

Calculating from Eq. (2\cdot20) the residues of $G_{\bar{n}n}^{\pm}$ and $G_{\bar{n}+1n}^{\pm}$ at $\varepsilon = \varepsilon_a^{\pm}$, we obtain the following expressions for the electron densities and bond orders:

$$\left. \begin{aligned} q_n^{\pm} &= \sum_a Q_n^{\pm}(\varepsilon_a^{\pm}) f_a^{\pm}, & p_n^{\pm} &= \sum_a P_n^{\pm}(\varepsilon_a^{\pm}) f_a^{\pm}, \\ |C_{\bar{n},a}^{\pm}|^2 &= Q_n^{\pm}(\varepsilon_a^{\pm}), & \text{Re}[C_{\bar{n}+1,a}^{\pm} C_{\bar{n},a}^{\pm*}] &= P_n^{\pm}(\varepsilon_a^{\pm}), \\ Q_n^{\pm}(\varepsilon) &= \{J_n^{\pm}(\varepsilon)\}_{11} / B_n^{\pm} \sum_{m=1}^N \{J_m^{\pm}(\varepsilon)\}_{11} / B_m^{\pm}, \\ P_n^{\pm}(\varepsilon) &= (1 - \{J_n^{\pm}(\varepsilon)\}_{12}) / B_n^{\pm} \sum_{m=1}^N \{J_m^{\pm}(\varepsilon)\}_{11} / B_m^{\pm}. \end{aligned} \right\} \quad (2\cdot21)$$

The q_n^{\pm} and p_n^{\pm} of Eq. (2\cdot21) satisfy the stationary conditions

$$\partial F / \partial q_n^{\pm} = 0, \quad \partial F / \partial p_n^{\pm} = 0, \quad (2\cdot22)$$

as we shall prove in the Appendix.

Equations (2\cdot13) and (2\cdot21) are the SCF equations to determine ε_a^{\pm} , q_n^{\pm} and p_n^{\pm} and make it in principle possible to calculate them for a chain with any structure. However, $\text{Tr}(X^{\pm})$ is a function of ε very rapidly oscillating for large N and it is practically difficult to compute ε_a^{\pm} from it except for the case of periodic structures. To overcome this difficulty, we utilize the following technique. The Green functions (2\cdot14) have poles at $\varepsilon = \varepsilon_a^{\pm}$. The Fermi weight $f(z)$ also has poles at $z = \pm kT\pi(2l-1)i$, $l=1, 2, \dots$. It can be expanded as

$$f(z) = \frac{1}{2} - \sum_{l=1}^{\infty} kT \left\{ \frac{1}{z - kT\pi(2l-1)i} + \frac{1}{z + kT\pi(2l-1)i} \right\}. \quad (2\cdot23)$$

We make the path integration of the functions $G_{\bar{m}n}^{\pm}(z)f(z-\varepsilon)$ on the rectangular contour shown in Fig. 1. The parameters E and Γ of the contour are chosen in such a way that

$$E \gg 2 \max|\beta_n|, \quad \Gamma = 2\pi kT\nu \gg 4 \max|\beta_n|/N, \quad (2\cdot24)$$

where ν is an integer. The condition (2\cdot24) ensures that the contour contains all the poles of $G_{\bar{m}n}^{\pm}$ and Γ is larger than the average level spacing of the orbital

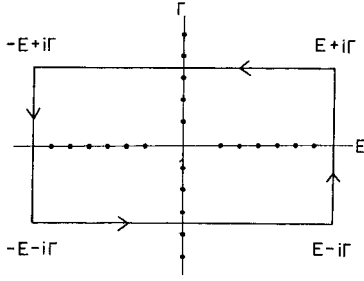


Fig. 1. The contour for the path integration of Eq. (2·25). The poles of the Green functions G_{mn}^{\pm} are on the real axis and those of the Fermi distribution function on the imaginary axis.

energies. The latter condition makes $G_{mn}^{\pm}(E+i\Gamma)$ smooth functions of E . From the Cauchy theorem, we obtain

$$\begin{aligned}
 q_{mn}^{\pm}(\varepsilon) &= \sum_a C_{m,a}^{\pm} C_{n,a}^{\pm*} f(\varepsilon_a^{\pm} - \varepsilon) \\
 &= \frac{1}{\pi i} \int_{-E}^E \text{Im}\{G_{mn}^{\pm}(E+i\Gamma)\} f(E-\varepsilon) dE \\
 &\quad + \frac{1}{\pi} \int_0^{\Gamma} \text{Re}\{G_{mn}^{\pm}(-E+i\Gamma)\} f(-E-\varepsilon+i\Gamma) \\
 &\quad - G_{mn}^{\pm}(E+i\Gamma) f(E-\varepsilon+i\Gamma) d\Gamma \\
 &\quad - \sum_{l=1}^{\nu} 2kT \text{Re}\{G_{mn}^{\pm}(\varepsilon+kT\pi(2l-1)i)\}, \quad \Gamma=2\pi kT\nu. \quad (2\cdot25)
 \end{aligned}$$

The electron densities and the bond orders are given by

$$q_n^{\pm} = q_{nn}^{\pm}(\varepsilon_F), \quad p_n^{\pm} = q_{n+1n}^{\pm}(\varepsilon_F). \quad (2\cdot26)$$

Equation (2·25) gives also the integrated level density weighted by the Fermi distribution function

$$\rho^{\pm}(\varepsilon) = \int_{-\infty}^{\infty} \nu^{\pm}(E) f(E-\varepsilon) dE = \sum_n q_{nn}^{\pm}(\varepsilon), \quad (2\cdot27)$$

where $\nu^{\pm}(E)$ are the level densities of up and down spin π electrons. Numerical integration of Eq. (2·25) is feasible owing to the smoothness of $G_{mn}^{\pm}(E+i\Gamma)$.

By virtue of the Hellman-Feymann theorem for the temperature UHF approximation, we have the condition for the equilibrium geometry as

$$\frac{\partial F}{\partial x_n} = \frac{\partial E^{\sigma}}{\partial x_n} + \frac{\partial E^{\pi}}{\partial x_n} = 0, \quad (2\cdot28)$$

where $\delta/\delta x_n$ is the differentiation operating only on the parameters in E^{π} but not on q_n^{\pm} and p_n^{\pm} . From Eqs. (2·28), (2·2) and (2·4), we obtain the equations to determine the equilibrium x_n 's

$$\begin{aligned}
-\frac{dU(x_n)}{dx_n} &= 2\frac{d\beta_n}{dx_n}p_n - \frac{d\gamma_n}{dx_n}((p_n^+)^2 + (p_n^-)^2) \\
&+ \sum_i \frac{\partial\alpha_i}{\partial x_n}q_i + \frac{1}{2}\sum'_{ij} \left(\frac{\partial\gamma_{ij}}{\partial x_n}q_iq_j + \frac{\partial V_{ij}}{\partial x_n} \right). \quad (2\cdot29)
\end{aligned}$$

By means of the above formalism, we can calculate iteratively the physical quantities and the equilibrium geometry in any possible lattice structure of polyacetylene. We note that this formalism can be applied with slight modifications to any one dimensional system composed of segments each of which has only one electron orbital that predominantly contributes to the electronic structure governing lattice distortions of the system.

§ 3. Case of periodic lattices

When the lattice has a periodic structure, the formulas derived in § 2 can be brought into the forms explicitly taking the periodic structure into account. Let the MO coefficients and the transfer matrices satisfy the periodic condition

$$\left. \begin{aligned} C_{\bar{n}+M,\lambda\theta}^\pm &= e^{i\theta} C_{\bar{n},\lambda\theta}^\pm, \quad T_{\bar{n}+M}^\pm = T_{\bar{n}}^\pm, \\ N &= LM, \quad \theta = 2\pi l/L, \quad l=0, 1, \dots, L-1, \quad \lambda=1, \dots, M, \end{aligned} \right\} \quad (3\cdot1)$$

where we specify the MO's by the pseudo-momentum θ and the band index λ . Note that the unit cell length M of the UHF MO's and transfer matrices may be twice the lattice period when an odd number of electrons is contained in a lattice unit cell. Owing to the periodic condition (3·1), we obtain

$$C_{\bar{M}+1}^\pm = e^{i\theta} C_1^\pm = T_M^\pm \dots T_1^\pm C_1^\pm, \quad (3\cdot2)$$

that leads to the secular equation

$$\left. \begin{aligned} \det[Y^\pm(\varepsilon) - e^{i\theta}] &= e^{i\theta}(2 \cos \theta - \text{Tr}[Y^\pm(\varepsilon)]) = 0, \\ Y^\pm &= T_M^\pm \dots T_1^\pm, \quad \varepsilon = \varepsilon_\lambda^\pm(\theta). \end{aligned} \right\} \quad (3\cdot3)$$

The Green functions (2·14) now become

$$G_{\bar{n}m}^\pm = \sum_\theta G_{\bar{n}m}^\pm(\theta) = \sum_\theta \sum_\lambda \frac{C_{\bar{n},\lambda\theta}^\pm C_{m,\lambda\theta}^{\pm*}}{\varepsilon_\lambda^\pm(\theta) - \varepsilon}. \quad (3\cdot4)$$

Equations (2·15) and (3·1) give

$$\left. \begin{aligned} \sum_\theta e^{i\theta} \mathbf{G}_{\bar{m}m}^\pm(\theta) &= (Y_m^\pm)^l \mathbf{G}_{\bar{m}m}^\pm + (Y_m^\pm)^{l-1} K_m^\pm \boldsymbol{\rho}_m^\pm, \quad L-1 \geq l \geq 1, \\ \mathbf{G}_{\bar{m}m}^\pm &= (Y_m^\pm)^L \mathbf{G}_{\bar{m}m}^\pm + (Y_m^\pm)^{L-1} K_m^\pm \boldsymbol{\rho}_m^\pm, \\ K_m^\pm &= T_{\bar{m}-1}^\pm \dots T_1^\pm T_M^\pm \dots T_{\bar{m}+1}^\pm, \quad Y_m^\pm = K_m^\pm T_m^\pm, \quad M > m > 1. \end{aligned} \right\} \quad (3\cdot5)$$

Using the relation $\sum_{l=0}^{L-1} e^{il(\theta-\theta')} = L\delta_{\theta,\theta'}$, we have from Eq. (3·5)

$$\begin{aligned} G_{mm}^{\pm}(\theta) &= \frac{1}{L} \sum_{l=1}^{L-1} e^{-i(l+1)\theta} (Y_m^{\pm})^l (1 - (Y_m^{\pm})^L)^{-1} K_m^{\pm} \rho_m^{\pm} \\ &= \frac{1}{L} (e^{i\theta} - Y_m^{\pm})^{-1} K_m^{\pm} \rho_m^{\pm}. \end{aligned} \quad (3.6)$$

We obtain from Eqs. (2.15) and (3.6)

$$G_{m+1,m}^{\pm}(\theta) = \frac{1}{L} (e^{i\theta} - T_m^{\pm} J_m^{\pm})^{-1} \rho_m^{\pm}. \quad (3.7)$$

Equations (3.6), (3.7) and (3.4) lead to

$$\left. \begin{aligned} G_{mm}^{\pm} &= \frac{1}{L} \sum_{\theta} (K_m^{\pm})_{11} / B_m^{\pm} \{2 \cos \theta - \text{Tr}(Y^{\pm})\}, \\ G_{m+1,m}^{\pm} &= \frac{1}{L} \sum_{\theta} \{e^{i\theta} - (K_m^{\pm})_{12}\} / B_m^{\pm} \{2 \cos \theta - \text{Tr}(Y^{\pm})\}. \end{aligned} \right\} \quad (3.8)$$

Calculating the residues of Eq. (3.8) and replacing the summation over θ by the integration, we get

$$\left. \begin{aligned} q_m^{\pm} &= \sum_{\lambda=1}^M \frac{1}{\pi} \int_0^{\pi} \bar{Q}_m^{\pm}(\varepsilon_{\lambda}^{\pm}(\theta)) f(\varepsilon_{\lambda}^{\pm}(\theta) - \varepsilon_F) d\theta, \\ p_m^{\pm} &= \sum_{\lambda=1}^M \frac{1}{\pi} \int_0^{\pi} \bar{P}_m^{\pm}(\theta, \varepsilon_{\lambda}^{\pm}(\theta)) f(\varepsilon_{\lambda}^{\pm}(\theta) - \varepsilon_F) d\theta, \\ \bar{Q}_m^{\pm}(\varepsilon) &= [K_m^{\pm}(\varepsilon)]_{11} / \{B_m^{\pm} \sum_{i=1}^M [K_i^{\pm}(\varepsilon)]_{11} / B_i^{\pm}\}, \\ \bar{P}_m^{\pm}(\theta, \varepsilon) &= \{\cos \theta - [K_m^{\pm}(\varepsilon)]_{12}\} / \{B_m^{\pm} \sum_{i=1}^M [K_i^{\pm}(\varepsilon)]_{11} / B_i^{\pm}\}. \end{aligned} \right\} \quad (3.9)$$

The level density in the periodic lattice is given by

$$\nu^{\pm}(\varepsilon) = 1 / (\pi d\varepsilon^{\pm} / d\theta). \quad (3.10)$$

From Eq. (3.3), we have

$$\frac{d}{d\theta} \text{Tr}(Y^{\pm}) = \frac{d\varepsilon^{\pm}}{d\theta} \frac{\partial}{\partial \varepsilon} \text{Tr}(Y^{\pm}) = \frac{d\varepsilon^{\pm}}{d\theta} \sum_{m=1}^M (K_m^{\pm})_{11} / B_m^{\pm} = -2 \sin \theta, \quad (3.11)$$

so that we get

$$\begin{aligned} \nu^{\pm}(\varepsilon) &= -\frac{1}{2\pi} \sum_m (K_m^{\pm})_{11} / B_m^{\pm} \sin \theta \\ &= -\frac{1}{\pi} \sum_m (K_m^{\pm})_{11} / B_m^{\pm} [4 - \{\text{Tr}(Y^{\pm})\}^2]^{1/2}. \end{aligned} \quad (3.12)$$

$\nu^{\pm}(\varepsilon)$ is zero for the ε 's such that $|\text{Tr}(Y^{\pm})| > 2$. By using Eq. (3.12), Eq. (3.9) can be rewritten

$$\left. \begin{aligned} q_m^\pm &= -\frac{1}{\pi B_m^\pm} \int [K_m^\pm(\varepsilon)]_{11} [4 - \{\text{Tr}(Y^\pm(\varepsilon))\}^2]^{-1/2} f(\varepsilon - \varepsilon_F) d\varepsilon, \\ p_m^\pm &= -\frac{1}{\pi B_m^\pm} \int \left\{ \frac{1}{2} \text{Tr}(Y^\pm) - (K_m^\pm)_{12} \right\} \\ &\quad \times [4 - \{\text{Tr}(Y^\pm)\}^2]^{-1/2} f(\varepsilon - \varepsilon_F) d\varepsilon, \end{aligned} \right\} \quad (3.13)$$

where the integration is made in the range $|\text{Tr}(Y^\pm(\varepsilon))| \leq 2$. The total energy per unit cell is obtained from Eqs. (2.8) and (2.4) as

$$\begin{aligned} E^{\text{tot}} &= \sum_\lambda \frac{1}{\pi} \int_0^\pi \sum_s \varepsilon_\lambda^s(\theta) f(\varepsilon_\lambda^s(\theta) - \varepsilon_F) d\theta \\ &\quad + \sum_{m=1}^M \left\{ \frac{1}{\gamma_0} \Delta_m^2 - \frac{\gamma_0}{4} q_m^2 + \gamma_m ((p_m^+)^2 + (p_m^-)^2) \right\} \\ &\quad + \frac{1}{2} \sum_{m=1}^M \sum_n' (V_{mn} - \gamma_{mn} q_m q_n) + \sum_{m=1}^M U(x_m). \end{aligned} \quad (3.14)$$

§ 4. UHF states in regular trans polyacetylene

We consider here undoped trans polyacetylene with a regular bond alternated lattice. Applying the formalism given in § 3, we derive the UHF SCF equations and obtain the UHF states that may become the HF ground state of the system. The results of this paragraph can be applied also to other regular one dimensional systems. The parameters of a unit cell have the properties

$$\left. \begin{aligned} \alpha_1 &= \alpha_2 = \alpha, & \beta_1 &\neq \beta_2, \\ \gamma_{12m-1} &= \gamma_{22m}, & \gamma_{12m} &= \gamma_{22m+1}, & \sum_n' \gamma_{1n} &= \sum_n' \gamma_{2n}. \end{aligned} \right\} \quad (4.1)$$

Two electrons are present in a unit cell and the electron densities in it satisfy $q_1^+ + q_2^+ = q_1^- + q_2^- = 1$. Hence, we can put

$$\Delta_1 = -\Delta_2 = \Delta, \quad q_1 = 1 + d, \quad q_2 = 1 - d. \quad (4.2)$$

Then, the parameters A_n^\pm of Eq. (2.10) in a unit cell can be expressed as

$$\left. \begin{aligned} A_1^\pm &= A - D^\pm, & A_2^\pm &= A + D^\pm, & D^\pm &= D \pm \Delta, \\ A &= \alpha + \frac{\gamma_0}{2} + \sum_n' \gamma_{1n}, & D &= \frac{\Gamma_0}{2} d, \\ -\Gamma_0 &= \gamma_0 + 2 \sum_m' \gamma_{12m+1} - 2 \sum_m' \gamma_{12m}. \end{aligned} \right\} \quad (4.3)$$

The transfer matrices and the matrices K_m^\pm are given by

$$\left. \begin{aligned} T_1^\pm &= \begin{bmatrix} (\varepsilon - A + D^\pm)/B_1^\pm, & -B_2^\pm/B_1^\pm \\ 1, & 0 \end{bmatrix}, & T_2^\pm &= \begin{bmatrix} (\varepsilon - A - D^\pm)/B_2^\pm, & -B_1^\pm/B_2^\pm \\ 1, & 0 \end{bmatrix}, \\ K_1^\pm &= T_2^\pm, & K_2^\pm &= T_1^\pm. \end{aligned} \right\} \quad (4.4)$$

The secular equation (3.3) becomes

$$\text{Tr}(T_2^\pm T_1^\pm) = \{(\varepsilon - A)^2 - (D^\pm)^2 - (B_1^\pm)^2 - (B_2^\pm)^2\} / B_1^\pm B_2^\pm = 2 \cos \theta, \quad (4.5)$$

so that the orbital energies are obtained as

$$\varepsilon_\pm^s(\theta) = A \pm \varepsilon_\theta^s, \quad \varepsilon_\theta^s = [(D^s)^2 + (B_1^s)^2 + (B_2^s)^2 + 2B_1^s B_2^s \cos \theta]^{1/2}. \quad (4.6)$$

The subscripts + and - denote the conduction and valence bands of π electrons, respectively. Equation (4.6) shows that a UHF state has the band gaps $2[(D^\pm)^2 + (B_1^\pm - B_2^\pm)^2]^{1/2}$. By substituting Eqs. (4.2) and (4.6) into Eq. (3.14) and putting $\varepsilon_F = A$, the total energy per unit cell is obtained as

$$\begin{aligned} E^{\text{tot}} = & 2\alpha + \frac{\gamma_0}{2} + \sum_n' \gamma_{1n} + \frac{2}{\gamma_0} \Delta^2 + \frac{2}{\Gamma_0} D^2 + \gamma_1 \sum_s (p_1^s)^2 + \gamma_2 \sum_s (p_2^s)^2 \\ & - \sum_s \frac{1}{\pi} \int_0^\pi \varepsilon_\theta^s \text{th}(\varepsilon_\theta^s / 2kT) d\theta + \sum_n' V_{1n} + U(x_1) + U(x_2). \end{aligned} \quad (4.7)$$

From Eqs. (3.9), (4.4) and (4.6), we have the SCF equations to determine Δ , D , p_1^\pm and p_2^\pm

$$\left. \begin{aligned} \Delta &= \frac{\gamma_0}{4\pi} \sum_s \int_0^\pi (\Delta - sD) \text{th}(\varepsilon_\theta^s / 2kT) / \varepsilon_\theta^s d\theta, \\ D &= \frac{\Gamma_0}{4\pi} \sum_s \int_0^\pi (D - s\Delta) \text{th}(\varepsilon_\theta^s / 2kT) / \varepsilon_\theta^s d\theta, \end{aligned} \right\} \quad (4.8)$$

$$\left. \begin{aligned} p_1^s &= -\frac{1}{2\pi} \int_0^\pi (B_1^s + B_2^s \cos \theta) \text{th}(\varepsilon_\theta^s / 2kT) / \varepsilon_\theta^s d\theta, \\ p_2^s &= -\frac{1}{2\pi} \int_0^\pi (B_2^s + B_1^s \cos \theta) \text{th}(\varepsilon_\theta^s / 2kT) / \varepsilon_\theta^s d\theta. \end{aligned} \right\} \quad (4.9)$$

These equations can be rewritten as

$$\left. \begin{aligned} \Delta &= \frac{\gamma_0}{4} \{ \Delta(K^+ + K^-) - D(K^+ - K^-) \}, \\ D &= \frac{\Gamma_0}{4} \{ D(K^+ + K^-) - \Delta(K^+ - K^-) \}, \end{aligned} \right\} \quad (4.10)$$

$$\left. \begin{aligned} p_1^\pm + p_2^\pm &= -(B_1^\pm + B_2^\pm)(K^\pm - G^\pm), \\ p_1^\pm - p_2^\pm &= -(B_1^\pm - B_2^\pm)G^\pm, \end{aligned} \right\} \quad (4.11)$$

where

$$\left. \begin{aligned} K^\pm &= \frac{1}{\pi} \int_0^\pi \text{th}(\varepsilon_\theta^\pm / 2kT) / \varepsilon_\theta^\pm d\theta, \\ G^\pm &= \frac{1}{\pi} \int_0^\pi \sin^2 \frac{\theta}{2} \text{th}(\varepsilon_\theta^\pm / 2kT) / \varepsilon_\theta^\pm d\theta. \end{aligned} \right\} \quad (4.12)$$

Equations (4.10) and (4.11) yield solutions of the following types:

$$\left. \begin{array}{l} \text{A) } \Delta \neq 0, \quad D=0, \quad p_1^\pm = p_1/2, \quad p_2^\pm = p_2/2, \\ \text{B) } D \neq 0, \quad \Delta=0, \quad p_1^\pm = p_1/2, \quad p_2^\pm = p_2/2, \\ \text{C) } \Delta=0, \quad D=0, \quad \left\{ \begin{array}{l} (1) \quad p_1^\pm = p_1/2, \quad p_2^\pm = p_2/2, \\ (2) \quad p_1^+ \neq p_1^-, \quad p_2^+ \neq p_2^-, \end{array} \right. \\ \text{D) } \Delta \neq 0 \quad \text{and/or} \quad D \neq 0, \quad p_1^+ \neq p_1^-, \quad p_2^+ \neq p_2^-. \end{array} \right\} \quad (4.13)$$

Solutions of the type A have an alternating modulation of the spin densities and those of the type B one of the charge densities. Solutions of the type C have neither modulation of the spin nor charge density. Equation (4.11) in this case is decoupled for the up and down spin bond orders. Its each spin component has the same form as the SCF equation of the spinless Fermion system obtained by Kondo.⁷⁾ Consequently, any combination of up and down spin solutions is allowed as an SCF solution. We subdivide this class into the solutions with the same up and down spin bond orders, C1 type solutions, and those with different up and down spin ones, C2 type solutions. Solutions of the type D have modulations in both or either one of the spin and/or charge densities and different up and down spin bond orders. The up and down spin energy bands in solutions of the types A, B and C1 are identical:

$$\left. \begin{array}{l} \varepsilon_\theta^\pm = \varepsilon_\theta = [Z^2 + B_1^2 + B_2^2 + 2B_1B_2 \cos \theta]^{1/2}, \\ B_1 = \beta_1 - \gamma_1 p_1/2, \quad B_2 = \beta_2 - \gamma_2 p_2/2, \end{array} \right\} \quad (4.14)$$

where $Z = \Delta$, D and 0 for the cases A, B and C1, respectively. Consequently, Eq. (4.10) for the cases A and B reduces to

$$\left. \begin{array}{l} \text{A) } \quad K^\pm = K = 2/\gamma_0, \\ \text{B) } \quad K^\pm = K = 2/\Gamma_0. \end{array} \right\} \quad (4.15)$$

The up and down spin energy bands in solutions of the other types are different except for equi-spaced lattices where the stronger symmetry of the lattice may make the bands identical.

In order to get more concrete information about possible solutions, we consider an equi-spaced lattice. Then, $\beta_1 = \beta_2 = \beta$, $\gamma_1 = \gamma_2 = \gamma$ and Eq. (4.11) becomes

$$p_1^\pm + p_2^\pm = -\{2\beta - \gamma(p_1^\pm + p_2^\pm)\}(K^\pm - G^\pm), \quad (4.16a)$$

$$p_1^\pm - p_2^\pm = \gamma(p_1^\pm - p_2^\pm)G^\pm. \quad (4.16b)$$

Equation (4.16b) yields solutions of the two types:

$$\left. \begin{array}{l} \text{a) } \quad p_1^\pm = p_2^\pm = p^\pm, \\ \text{b) } \quad p_1^\pm \neq p_2^\pm, \quad G^\pm = 1/\gamma. \end{array} \right\} \quad (4.17)$$

Solutions of the type a have uniform bond orders, whereas those of the type b have a spontaneous alternation of the bond orders even in the equi-spaced lattice. Combining Eqs. (4·13) and (4·17), we get a catalogue of possible UHF solutions of different types. We list up here the solutions with the identical up and down spin energy bands:

$$\left. \begin{array}{lll} \text{A-a,} & \text{B-a,} & \text{C1-a: } p_1^\pm = p_2^\pm = p/2, \\ \text{A-b,} & \text{B-b,} & \text{C1-b: } p_1^\pm = p_1/2, \quad p_2^\pm = p_2/2, \quad p_1 \neq p_2, \\ \text{DA-b,} & \text{DB-b,} & \text{C2-b: } p_1^\pm = p_2^\mp, \quad p_1^\pm \neq p_2^\pm, \\ & & p_1^+ + p_1^- = p_2^+ + p_2^- = p. \end{array} \right\} \quad (4\cdot18)$$

In Eq. (4·18), we subdivide the D-b combination into the subcases DA-b with $\Delta \neq 0$, $D=0$ and DB-b with $D \neq 0$, $\Delta=0$. Solutions of the types A-b, B-b and C1-b have an alternating modulation of the bond orders with the same phase for the up and down spin components. They are called bond order wave (BOW) type. Solutions of the types DA-b, DB-b and C2-b also have alternating modulations of the bond orders but the modulations of the up and down spin components are in the opposite phases so that they have uniform total bond orders. They are called spin bond order wave (SBOW) type. Thus, these nine solutions are distinguished by the different modes in the modulations of the spin densities (SD), charge densities (CD) and bond orders (BO). We therefore give these solutions the names shown in Table I.

The ϵ_θ of the energy bands in these nine kinds of UHF solutions is

$$\epsilon_\theta = [Z^2 + 4B^2 - (4B^2 - \gamma^2 p'^2) \sin^2 \frac{\theta}{2}]^{1/2},$$

$$B = \beta - \gamma p/2, \quad (4\cdot19)$$

where $p = (p_1 + p_2)/2$, p' is 0 (no BOW class), $(p_1 - p_2)/2$ (BOW class) or $p_1^+ - p_2^+ = -(p_1^- - p_2^-)$ (SBOW class) and Z is Δ (SDW class), D (CDW class) or 0 (no SD-CDW class). Equation (4·16a) has the common form

Table I. Possible UHF solutions at equi-spaced lattice.

	No BOW class	BOW class	SBOW class
SDW class	A-a	A-b	DA-b
	SDW	SD-BOW	SD-SBOW
CDW class	B-a	B-b	DB-b
	CDW	CD-BOW	CD-SBOW
No SD-CDW class	C1-a	C1-b	C2-b
	RHF	BOW	SBOW

$$p = -(2\beta - \gamma p)(K - G), \quad (4\cdot20)$$

for all the UHF solutions and determines the average bond order p . The spontaneous bond order fluctuation p' and the correlation gap parameter Δ or D are determined by the following combinations of Eqs. (4\cdot16b) and (4\cdot15):

$$\left. \begin{array}{ll} \text{BOW, SBOW} & : G = 1/\gamma, \\ \text{SDW} & : K = 2/\gamma_0, \\ \text{SD-BOW, SD-SBOW} & : K = 2/\gamma_0, \quad G = 1/\gamma, \\ \text{CDW} & : K = 2/\Gamma_0, \\ \text{CD-BOW, CD-SBOW} & : K = 2/\Gamma_0, \quad G = 1/\gamma. \end{array} \right\} \quad (4\cdot21)$$

We see from Eqs. (4\cdot19)~(4\cdot21) that if a solution of a BOW type exists, then there is always a solution of the corresponding SBOW type that is degenerate in energy. We note also that solutions of BOW types exist always in pair since the exchange of p_1 and p_2 of a solution gives another solution that has an inequivalent bond order alternation but is degenerate in energy. We discriminate the two degenerate BOW type solutions by the subscripts 1 and 2.

In the following, we shall discuss each UHF solution. RHF: Substituting (4\cdot19) with $Z=0$ and $p'=0$ into Eq. (4\cdot20), we obtain

$$p = \frac{1}{\pi} \int_0^\pi \cos^2 \frac{\theta}{2} \text{th} \left(|B| \cos \frac{\theta}{2} / kT \right) d\theta. \quad (4\cdot22)$$

At $T=0$, Eq. (4\cdot22) gives $p=2/\pi$ that is just the bond order of the conventional RHF solution.

BOW and SBOW: These solutions in polyenes were obtained by Čížek and Paldus.¹⁸⁾ Kondo's solution⁷⁾ for the spinless Fermion system is just formally identical with each spin component of BOW and SBOW. They exist always below RHF as proved by the instability of RHF.^{7),18)} The nearest neighbour exchange interaction is essential in producing these solutions. The Hubbard Hamiltonian cannot have them. Their stability or instability for spin density fluctuation can be seen as follows. Using Eqs. (4\cdot7) and (A\cdot2) of the Appendix, we obtain the second order variation of the free energy with respect to Δ as

$$\begin{aligned} \left. \frac{\partial F}{\partial \Delta^2} \right|_{\Delta=0} &= \frac{2}{\gamma_0} - \frac{2}{\pi} \int_0^\pi \frac{\partial \varepsilon_\theta}{\partial \Delta^2} \text{th}(\varepsilon_\theta / 2kT) \Big|_{\Delta=0} d\theta \\ &= \frac{2}{\gamma_0} - K^{\text{BOW}}. \end{aligned} \quad (4\cdot23)$$

Equation (4\cdot23) shows that if

$$K^{\text{BOW}} > 2/\gamma_0, \quad (4\cdot24a)$$

then BOW (and SBOW) is unstable for spontaneous alternation of the spin

densities. By using Eqs. (4·20) and (4·21), the condition (4·24a) can be transformed to the following condition for the average bond order of BOW:

$$p^{\text{BOW}} = -2\beta(K - G)^{\text{BOW}} / \{1 - \gamma(K - G)^{\text{BOW}}\} > -\beta(2\gamma - \gamma_0) / \gamma(\gamma_0 - \gamma). \quad (4\cdot24b)$$

SDW: The SDW solution in polyenes and polyacetylene was obtained by Misurkin and Ovchinnikov¹⁹⁾ for the Hubbard Hamiltonian and by the author²⁰⁾ for the PPP Hamiltonian. Its extension to the bond alternated lattice was calculated by Tric.²¹⁾ It exists always below RHF as proved by the instability of RHF.²⁰⁾ It is the HF ground state of the Hubbard Hamiltonian in equi-spaced lattices. In the PPP Hamiltonian, however, it may become unstable for spontaneous alternation of the bond orders. The condition for the instability of SDW can be obtained by the same manner as the derivations of Eqs. (4·24a) and (4·24b) as

$$\left. \begin{aligned} \frac{\partial F}{\partial p'^2} \Big|_{p'=0} &= \gamma - \gamma^2 G^{\text{SDW}} < 0, \\ p^{\text{SDW}} &< -\beta(2\gamma - \gamma_0) / \gamma(\gamma_0 - \gamma). \end{aligned} \right\} \quad (4\cdot25)$$

SD-BOW and SD-SBOW: They are UHF solutions of hitherto unknown types. From Eqs. (4·20) and (4·21), the average bond order in them is given by

$$p^{\text{SD-BOW}} = -\beta(2\gamma - \gamma_0) / \gamma(\gamma_0 - \gamma). \quad (4\cdot26)$$

Since $\beta < 0$, $\gamma_0 > \gamma$ and $0 \leq p \leq 1$, we obtain from Eq. (4·26) the condition for the existence of SD-BOW and SD-SBOW as

$$\frac{1}{2}(2\beta + \gamma_0 + \sqrt{4\beta^2 + \gamma_0^2}) \geq \gamma \geq \gamma_0/2. \quad (4\cdot27)$$

They are not solutions bifurcating from the instability of SDW. They may exist above SDW even if SDW is stable, but become lower in energy than SDW when SDW becomes unstable.

CDW, CD-BOW and CD-SBOW: The SCF equations for the CDW class have the same forms as those of the SDW class except for the replacements of γ_0 by Γ_0 and \mathcal{A} by D . In order for solutions of the CDW class to exist, Γ_0 must be positive, e.g. the inequality

$$\Gamma_0 = 4 \sum_{m \geq 1} (\gamma_{12m} - \gamma_{12m+1}) - \gamma_0 > 0, \quad (4\cdot28)$$

must be satisfied. Of course, no solution of the CDW class exists in the Hubbard Hamiltonian. The CDW solution in the PPP Hamiltonian was obtained by the author²⁰⁾ and Paldus and Čížek.¹⁸⁾ CD-BOW and CD-SBOW are solutions of hitherto unknown types. By the same way as the derivation of Eq. (4·27), we obtain the condition for their existence as

$$2\gamma \geq \Gamma_0 \geq \gamma \left(1 - \frac{\beta}{\gamma - \beta}\right). \quad (4.29)$$

A CDW type solution may become lower in energy than the corresponding SDW type solution if the condition

$$\Gamma_0 > \gamma_0, \quad (4.30)$$

is satisfied. The condition (4.28) is satisfied for the effective Coulomb interaction unscreened at long distances. The conditions (4.29) and (4.30), on the other hand, impose rather severe restrictions on the distance dependence of the effective Coulomb interaction though there may be the possibility of realizing them under special circumstances.

The above results indicate that each of the solutions, BOW (SBOW), SDW, SD-BOW (SD-SBOW), CDW and CD-BOW (CD-SBOW) has the possibility of becoming the HF ground state in a uniform one dimensional system. The nature of the HF ground state may change according to the distance dependence of the effective electron Coulomb interaction. We show in Fig. 2 the domains of the BOW, SDW and SD-BOW ground states in the parameter space of $\gamma_0/|\beta|$ and $\gamma/|\beta|$ calculated by the instability conditions (4.24) and (4.25). We show also the existence domain (4.27) of SD-BOW. The region of the SD-BOW ground state is a very narrow zone between the domains of the BOW and SDW ground states.

All the BOW type solutions are linearly unstable for a small alternating distortion $x_1 = x + u$ and $x_2 = x - u$ of the lattice. The β_m 's and γ_m 's with the distortion are $\beta_1 = \beta + \beta' u$, $\beta_2 = \beta - \beta' u$, $\gamma_1 = \gamma + \gamma' u$ and $\gamma_2 = \gamma - \gamma' u$. Then by using Eq. (A.2) of the Appendix, the variation of the free energy for the lattice distortion is obtained from Eq. (4.7) as

$$\frac{\partial F}{\partial u} \Big|_{u=0} = \gamma' (p_1^2 - p_2^2) / 2 - \frac{2}{\pi} \int_0^\pi \left[\left(\frac{\partial B_1}{\partial u} \frac{\partial \varepsilon_\theta}{\partial B_1} + \frac{\partial B_2}{\partial u} \frac{\partial \varepsilon_\theta}{\partial B_2} \right) \text{th}(\varepsilon_\theta / 2kT) \right]_{u=0} d\theta$$

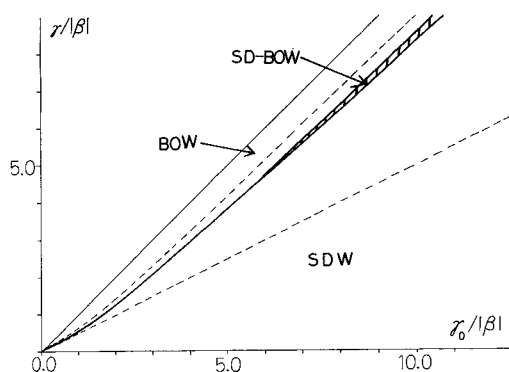


Fig. 2. The domains of the SDW, SD-BOW and BOW ground states of a one dimensional equi-spaced lattice system in the parameter space of $\gamma_0/|\beta|$ and $\gamma/|\beta|$. The domain of the SD-BOW ground state is the narrow zone with hatching. The existence domain of SD-BOW is the region bounded by the dashed lines. The region with $\gamma/|\beta| > \gamma_0/|\beta|$ is not realizable for the Coulomb interaction.

$$\begin{aligned}
&= \gamma'(p_1^2 - p_2^2)/2 - (2\beta' - \gamma' p_1)\{(B_1 + B_2)K - 2B_2 G\} \\
&\quad + (2\beta' - \gamma' p_2)\{(B_1 + B_2)K - 2B_1 G\} \\
&= \gamma G(p_1 - p_2)\{2\beta' - \gamma'(p_1 - p_2)/2\}, \tag{4.31}
\end{aligned}$$

where we have used Eq. (4.11). Equation (4.31) shows that the free energy linearly decreases for the small lattice distortion to shorten the bond 1 and to lengthen the bond 2 for the BOW₁ type solution with $p_1 > p_2$ but it linearly increases for the BOW₂ type solution with p_1 and p_2 exchanged. The first order variations of the up and down spin components of the free energy of an SBOW class solution have non-zero values with the same magnitude but of the opposite signs, so that the total first order variation vanishes. Therefore, the degeneracy of the BOW₁, BOW₂ and SBOW type solutions is lifted in bond alternated lattices and the BOW₁ type solution comes to have the lowest energy. The free energies of the RHF, SDW and CDW solutions without spontaneous alternation of the bond orders have no linear term in u . The above result indicates that an equilibrium geometry of a BOW class solution is always bond alternated. If a system has the BOW ground state at the bond alternated equilibrium geometry, the system is non-magnetic. A system with the SD-BOW ground state has an antiferromagnetic spin order as well as a lattice dimerization.

§ 5. The bond alternation potential and the band gap in trans polyacetylene

According to the theory developed in § 4, we calculate here the UHF states, their potentials and band gaps in regular trans polyacetylene. We make also an illustrative calculation for an itinerant spin Peierls system.

The parametrization of the PPP Hamiltonian and the elastic potential in polyacetylene is made as follows. The resonance integral is put in the exponential form

$$\beta(x) = \beta_0 e^{\delta x}. \tag{5.1}$$

We assume that the effective Coulomb potentials of π electrons and σ cores are the same

$$\gamma_{mn} = v_{mn} = V_{mn}. \tag{5.2}$$

We use for the Coulomb repulsion integrals $\gamma_{mn} = \gamma(r_{mn})$ the Ohno or Mataga-Nishimoto (MN) formula²²⁾

$$\left. \begin{aligned}
\text{Ohno: } & \gamma(r) = \gamma_0/[1 + (r/a_0)^2]^{1/2}, \\
\text{MN: } & \gamma(r) = \gamma_0/[1 + r/a_0].
\end{aligned} \right\} \tag{5.3}$$

We use the elastic potential $U(x)$ of the single bond with the anharmonic terms

since C-C bonds in polyacetylene much deviate from the single bond length:

$$U(x) = \frac{\kappa}{2} x^2 \left(1 + \frac{2}{3} ax + \frac{1}{2} bx^2 \right). \quad (5.4)$$

The parameters in Eqs. (5.1)~(5.4) are determined using ethane, ethylene and benzene with the C-C bond lengths 1.536, 1.337 and 1.397 Å, respectively, as the reference molecules. We use as the single bond length r_0 the C-C bond length of ethane. The parameters β_0 and δ are determined so as to give the values of $\beta(x)$ for ethylene and benzene proposed by Pariser and Parr¹⁷⁾ (PP) or by Schulten, Ohmine and Karplus⁶⁾ (SOK), namely, β (ethylene) = -2.92 eV, β (benzene) = -2.39 eV (PP) or β (ethylene) = -2.62 eV, β (benzene) = -2.43 eV (SOK). The SOK parametrization gives much slower distance dependence of $\beta(x)$ than the PP parametrization. Since the distance dependence of $\beta(x)$ directly affects the bond alternation potential, we examine both the parametrizations. For the one center Coulomb repulsion integral γ_0 , the standard semi-empirical value $I-A$ is used where I is the valence state ionization potential and A is the electron affinity. The parameter a_0 is assumed to satisfy the constraint $\gamma_0 a_0 = e^2$, where e is the electron charge, that gives the unscreened Coulomb potential at long distances. The Ohno formula gives much larger nearest neighbour Coulomb interaction than the MN one. Since the nearest neighbour Coulomb interaction is of crucial importance, we examine both the formulas. We use for the force constant κ of the C-C single bond the value of n -alkanes determined by Shimanouchi.²³⁾ The parameters a and b of the anharmonic terms are determined so as to give the equilibrium geometries of ethylene and benzene. For the RHF ground state in equi-spaced lattices, Eq. (2.29) to determine the equilibrium geometry becomes

$$\frac{dU(x)}{dx} = 2 \frac{d\beta(x)}{dx} p - \frac{1}{2} \frac{d\gamma(x)}{dx} p^2. \quad (5.5)$$

The values of a and b are determined to satisfy Eq. (5.5) for $x=0.199$ Å, $p=1$ (ethylene) and $x=0.139$ Å, $p=2/3$ (benzene). In the determination of a and b , the Ohno formula for $\gamma(x)$ is used. In the following calculations using the MN formula, no readjustment of a and b is made to make possible direct comparison of the π electronic energy with the one in the Ohno formula case. The parameters thus determined are shown in Table II. Both the parameter sets given in

Table II. Parametrizations of the Hamiltonian and elastic potential.

	β_0 (eV)	δ (Å ⁻¹)	γ_0 (eV)	a_0 (Å)	κ (eV/Å ²)	a (Å ⁻¹)	b (Å ⁻²)
PP ^{a)}	-1.5027	3.3382	11.13	1.2935	27.8	12.95	3.738
SOK ^{a)}	-2.0419	1.2518	11.13	1.2935	27.8	-0.46	12.11
Spin-Peierls	-0.2	1.2518	6.0	8.35	2.70	35.7	357.2

a) For trans polyacetylene.

Table II are able to well reproduce spectra and equilibrium geometries of small conjugated hydrocarbons with the RHF ground state.

Calculations of the UHF states are made by solving iteratively Eqs. (4·10) and (4·11) under the constraints A, B and C1 of Eq. (4·13). Namely, the right-hand sides of Eqs. (4·10) and (4·11) are calculated by feeding trial values of Δ (or D), p_1 and p_2 . Then, their next iteration values are obtained from the left-hand sides of Eq. (4·10) and (4·11). The iteration is stopped when the differences of q_m^\pm and p_m between consecutive iterations become smaller than 10^{-6} .

In the PP-Ohno and SOK-Ohno parametrizations, the condition (4·27) for the existence of SD-BOW is satisfied, but the condition (4·25) for the instability of SDW is not. Hence, SD-BOW is higher in energy than SDW. In the PP-MN and SOK-MN parametrizations, both the conditions are not satisfied because of the faster damping of the MN Coulomb potential than the Ohno one. The condition (4·28) for the existence of CDW is satisfied for both the Ohno and MN formulas. The value of Γ_0 in the equi-spaced lattice with $r=1.41 \text{ \AA}$ is 6.2492 eV (Ohno) and 1.0149 eV (MN). The conditions (4·29) for the existence of CD-BOW and (4·30) for the CDW type ground state are not satisfied in all the parametrizations. Therefore, the HF ground state in regular trans polyacetylene is either SDW or BOW.

We show in Fig. 3 the free energy potentials at 300°K of SDW and BOW plotted against the distortion $(r_1 - r_2)/2$ of the two bonds at an average bond length $(r_1 + r_2)/2 = 1.41 \text{ \AA}$ that is close to the equilibrium average bond length. Because of the large band gap as shown later, the entropic term and the temperature dependence of the free energy are negligibly small at temperatures below 300°K. Figures 3(a) and (b) show that the Ohno formula gives the HF ground state consisting of SDW and BOW and a bond alternated equilibrium lattice geometry in the region of the BOW ground state. Figure 3(a) shows the linear distortion dependence of the BOW potential near the equi-spaced lattice and the splitting of BOW_1 and BOW_2 upon lattice distortion. On the other hand, Figs. 3(c) and (d) show that the HF ground state in the case of the MN formula is SDW in all (SOK case) or almost all (PP case) lattice distortions. The equilibrium geometry of the HF ground state is equi-spaced and no bond alternation occurs. This large contrast of the Ohno and MN cases indicates that the bond alternation potential is very sensitive to the strength of the nearest neighbour Coulomb interaction. The value of $(\gamma_0 - \gamma)/|\beta|$, that determines the extent of electron correlation, is about 1 for the Ohno case but about 3 for the MN case. The electron correlation in the MN case is stronger than the Ohno case bringing about a large stabilization of SDW. The MN parametrization was shown to make even the HF ground states of short polyenes to be SDW.⁶⁾ This and no occurrence of the bond alternation definitely indicate the inappropriateness of the MN parametrization in polyenes and polyacetylene. We do not know how the non-

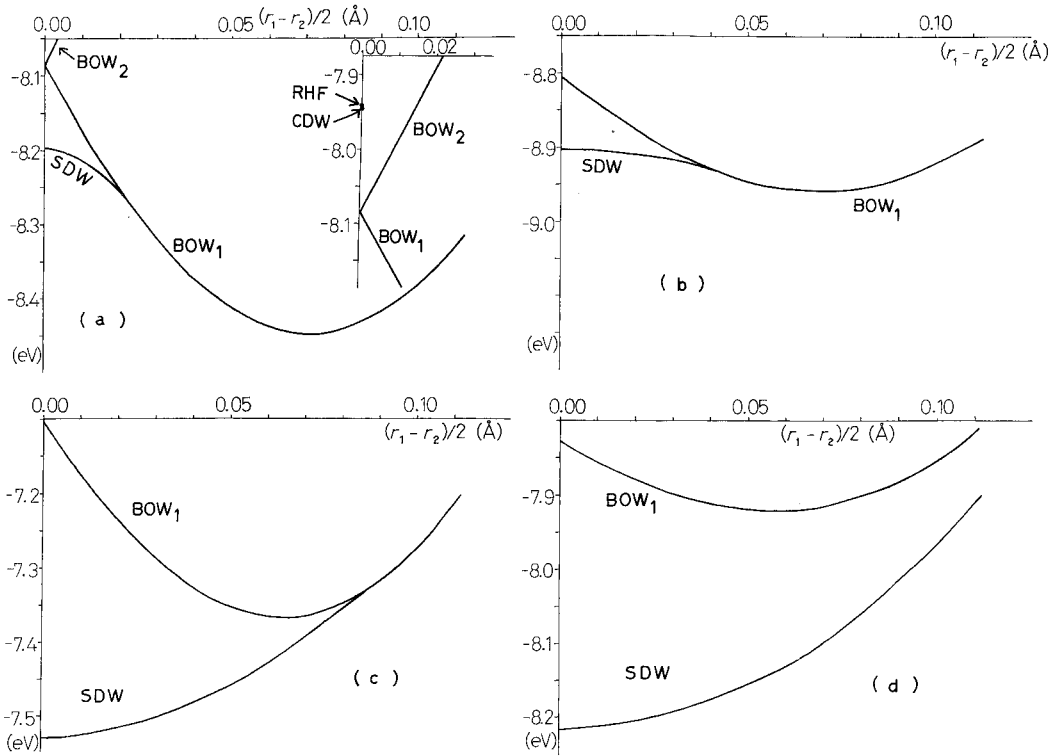


Fig. 3. The bond alternation potentials of the BOW and SDW states in regular trans polyacetylene with the average bond length 1.41 Å. (a) for the PP-Ohno, (b) for the SOK-Ohno, (c) for the PP-MN and (d) for the SOK-MN parametrizations. The inset of (a) shows in an enlarged scale the BOW₁ and BOW₂ potentials near the equi-spaced lattice and the energies of RHF and CDW at the equi-spaced lattice.

empirical effective π electron Coulomb interaction derived from the all valence electron Hamiltonian looks like in polyacetylene. However, a calculation of the effective π electron Hamiltonian of ethylene by Iwata and Freed²⁴⁾ showed that the suppression of the effective Coulomb repulsion integrals is larger in the one center part than the two center one, suggesting that the distance dependence of the Ohno formula, which gives the nearest neighbour Coulomb repulsion not so much different from the non-empirical value, may be a good approximation at least in a short distance. The longer range part of the effective Coulomb interaction may suffer a large suppression due to the dielectric screening by σ electrons. However, the screening of the long range part does not affect SDW and BOW though it affects CDW.

The bond alternation potential in the case of the Ohno formula is much shallower in the SOK parametrization with the $\beta(x)$ of slower distance depen-

dence than the PP parametrization with the steeper $\beta(x)$. Electron correlation also has an important effect for the bond alternation potential. The correlation stabilization of SDW makes the barrier of the bond alternation potential at the equi-spaced lattice lower. The occurrence of the SDW ground state near equi-spaced lattices indicates that the state of π electrons around a neutral soliton is SDW like since the lattice dimerizations in the vicinity of a soliton are small. The presence of an unpaired electron in a neutral soliton is nicely described by the SDW like electronic structure near the soliton as schematically illustrated in Fig. 4(a). The correlation stabilization of the SDW like electronic structure brings about a lowering of the formation energy of a neutral soliton. The barrier height of the bond alternation potential gives an approximate estimation of the soliton formation energy. The barrier height is about 0.25 and 0.05 eV for the PP and SOK parametrizations, respectively. The observed density of neutral solitons in undoped trans polyacetylene is about 850 ppm.⁹⁾ The density of thermally formed solitons is below this observed figure for the value 0.25 eV of the soliton formation energy but the value 0.05 eV is too small and yields a much larger population of thermally formed solitons. Thus, the PP-Ohno parametrization is consistent with the observed neutral soliton density but the SOK-Ohno one is not.

We show in Fig. 5 the contour map of the bond alternation potential in the PP-Ohno parametrization that is plotted against $(r_1 - r_2)/2$ and $(r_1 + r_2)/2$. The equilibrium geometry has the bond distortion $(r_1 - r_2)/2 = 0.073 \text{ \AA}$ and the average bond length $(r_1 + r_2)/2 = 1.413 \text{ \AA}$ that are in good agreement with the values $0.07 \pm 0.02 \text{ \AA}$ and 1.42 \AA , respectively (assuming 120° bond angles) observed by X ray scattering.²⁵⁾ The bond orders of the BOW ground state at the equilibrium geometry are shown in Table III. They show that the bond dimerization in the equilibrium BOW state is nearly complete.

In order to see the energetic relations of the UHF states, we show in Fig. 6 the potentials of RHF, CDW, BOW and SDW in the equi-spaced lattice plotted against the bond length r in the case of the PP-Ohno parametrization. In the parametrization, SD-BOW exists above SDW. However, we failed to calculate it because the iteration procedure starting with all trial values tested converged

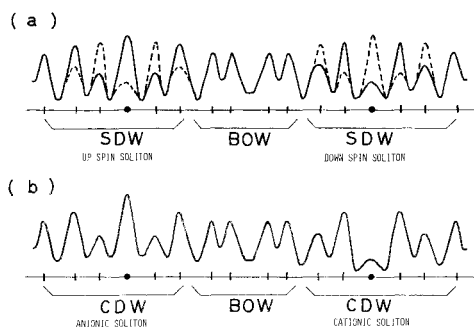


Fig. 4. Schematic illustrations of the SDW like π electronic structure around a neutral soliton (a) and the CDW like π electronic structure around a charged soliton (b) in trans polyacetylene. The real and dashed lines in (a) represent the densities of up and down spin π electrons, respectively. The π electronic structure at the lattice in between two solitons is BOW like. The centers of solitons are marked by black dots. These electronic structures are suggested ones.

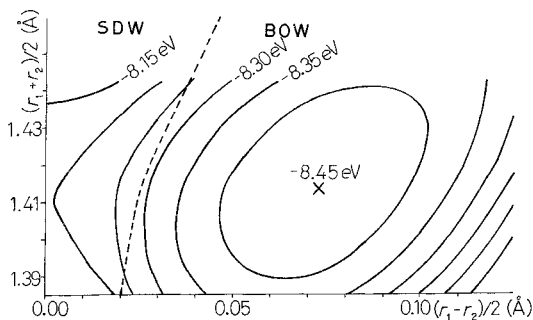


Fig. 5. The contour map of the bond alternation potential of the HF ground state in regular trans polyacetylene. The parametrization is the PP-Ohno. The boundary between the BOW and SDW ground states is indicated by a dashed line. The equilibrium geometry is indicated by a cross.

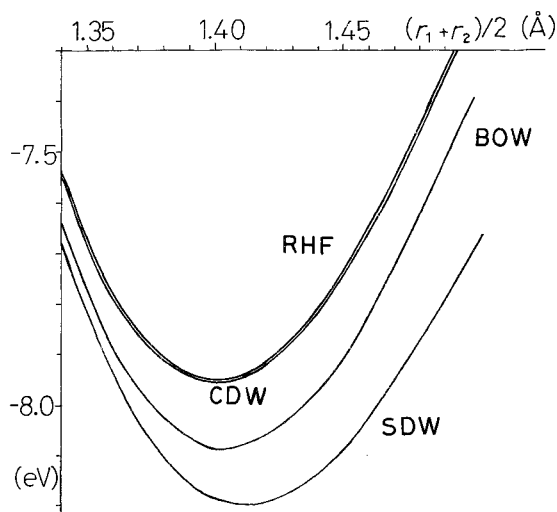


Fig. 6. The potentials of the RHF, CDW, BOW and SDW states in equi-spaced trans polyacetylene. The parametrization is the PP-Ohno.

Table III. Physical quantities of UHF states in trans polyacetylene.

		E total (eV)	Band gap (eV)	p_1	p_2	Δ or D (eV)	$q_+ - q_-$	$q_+ - q_-$
Equi-Spaced ($r=1.41 \text{ \AA}$)	RHF	-7.9424	0	0.63662(2/ π)		0	0	0
	CDW	-7.9462	0.6780	0.63486		0.3390	0.1085	0
	BOW	-8.0847	4.2348	0.33075	0.89360	0	0	0
	SDW	-8.1988	5.5706	0.57434		2.7853	0	0.5005
Bond-Alternated ^{a)}	BOW	-8.4491	8.2474	0.19132	0.96373	0	0	0

a) At the equilibrium geometry with $(r_1 + r_2)/2 = 1.413 \text{ \AA}$ and $(r_1 - r_2)/2 = 0.073 \text{ \AA}$.

to SDW. This is considered to be due to that the condition $p_1 \neq p_2$ for SD-BOW does not definitely eliminate the case $p_1 = p_2$ of SDW in the numerical calculation procedure and the iteration slips down to SDW when SD-BOW is higher in energy than SDW. We show in Table III the extent of the charge or spin density alternation, the bond orders and other physical quantities of the UHF states at $r = 1.41 \text{ \AA}$. The charge alternation in CDW is so small that its correlation stabilization relative to RHF is small. BOW has a large spontaneous bond order alternation that leads to a large stabilization due to the exchange interaction. SDW has a large spin density alternation that gives the largest correlation stabilization of SDW.

We show in Fig. 7 the band gaps of BOW and SDW and the correlation gap parameter Δ of SDW plotted against $(r_1 - r_2)/2$ at $(r_1 + r_2)/2 = 1.41 \text{ \AA}$. The band

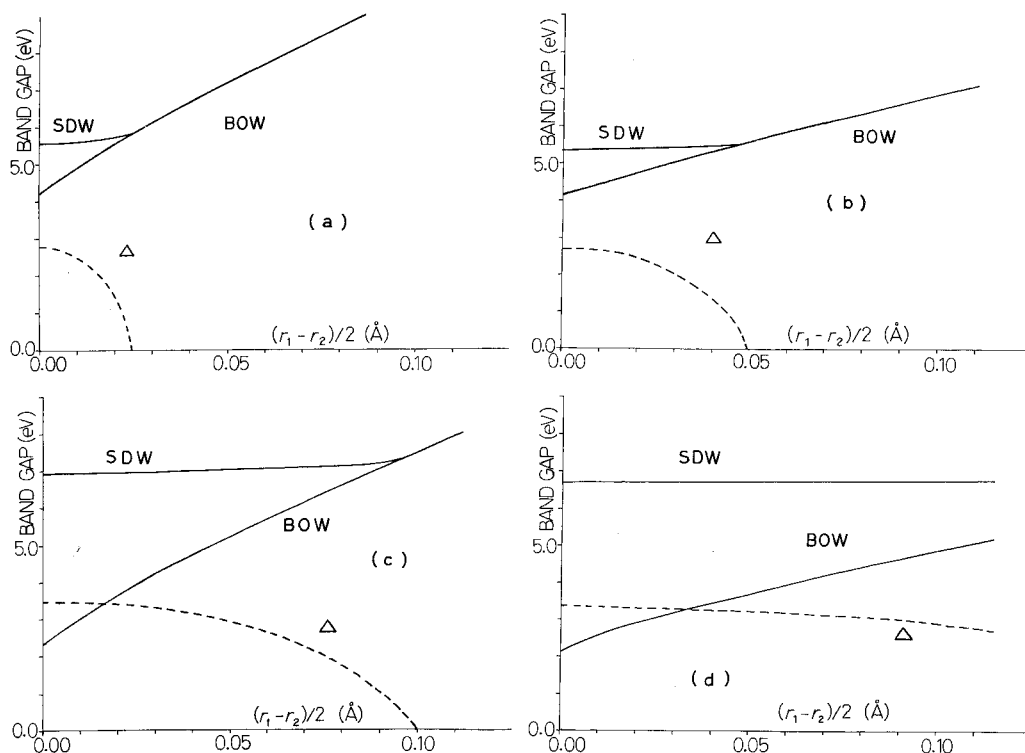


Fig. 7. The lattice distortion dependences of the band gaps of the BOW and SDW states in regular trans polyacetylene with the average bond length 1.41 \AA . The correlation gap parameter Δ of SDW is also shown by dashed line. (a) for the PP-Ohno, (b) for the SOK-Ohno, (c) for the PP-MN and (d) for the SOK-MN parametrizations.

gap of BOW increases roughly linearly with $(r_1 - r_2)/2$, while that of SDW is nearly constant. The band gaps in all the parametrizations are much larger than the energy 2 eV of the lowest strong absorption band in undoped trans polyacetylene. Suzuki et al.³⁾ assigned the 2 eV band as due to the interband transition based on the SSH model. The SSH model is consistent with the behaviour of the band for doping and photo-conductivity experiments²⁶⁾ as they showed. However, our result shows that the band should be excitonic as long as the one center and nearest neighbour Coulomb repulsion integrals in polyacetylene have values similar to those in small conjugated hydrocarbons. The nearest neighbour exchange interaction is the cause to produce the large band gap. All the non-empirical and semi-empirical band calculations for polyacetylene made so far gave values of the band gap much larger than 2 eV ²⁷⁾ in agreement with our result.

The Franck-Condon band gap at the equilibrium geometry of the PP-Ohno case (Fig. 7(a)), that gives the most reasonable bond alternation potential, is

about 8 eV. This band gap is just at the position of the edge of the absorption band in the vacuum ultraviolet region observed by an SOR experiment.²⁸⁾ The band, of course, should contain $\sigma-\sigma^*$ transitions since its edge position is the same as the absorptions of polyethylene and long chain *n*-alkanes. Our result shows a possibility that it contains also the interband $\pi-\pi^*$ transition.

If the 2 eV band is excitonic as suggested by our and other calculations, we have to explain how the photoconductivity can emerge from the excitation to the band. A possible mechanism is suggested by the distortion dependence of the band gap. As seen in Fig. 7(a), the band gap decreases toward the equi-spaced lattice. The gap of the exciton band is considered to have a similar lattice distortion dependence. The lattice around the bound electron-hole pair is expected to make a distortion toward equi-spacing. The lattice distortion might finally lead to splitting of an exciton into a zwitter ionic pair of charged solitons. We note that the state of π electrons around a charged soliton may be CDW like as schematically illustrated in Fig. 4(b). Though the correlation stabilization of the neutral CDW is small, the CDW like electronic structure around a charged soliton may have a large charge density alternation, that brings about a large correlation stabilization, owing to the absence or excess of an electron. If this picture of charged solitons is correct, the Coulomb interaction between charged solitons may be strongly screened by the CDW like polarization of π electrons around them and the zwitter ionic pair of charged solitons might relatively easily split into free solitons. We shall examine this idea in a succeeding paper of this series.

We finally show an example of itinerant spin Peierls system to have the SD-BOW ground state. We make a parametrization of the Hamiltonian and the elastic potential that mimics an array of ion radicals of conjugated molecule like TTF or TCNQ which forms a van der Waals stacked column. A possible parametrization is given in Table II. The parameters of the elastic potential are obtained by expanding the van der Waals potential $A/r^{12} - B/r^6$ with the binding energy 0.433 eV and the equilibrium van der Waals distance $r_0 = 3.4 \text{ \AA}$. The value of β_0 is estimated from the overlap of π lobes at $r_0 = 3.4 \text{ \AA}$. The values of $\gamma_0 = I - A$ for ion radicals of conjugated molecules are unknown but values in the order of $7 \sim 4 \text{ eV}$ are considered to be reasonable. To obtain the SD-BOW ground state, it is necessary to make the nearest neighbour Coulomb interaction γ be in a narrow range near 90% of γ_0 . A large value of a_0 is chosen to make γ be in the range. The bond alternation potentials of SD-BOW and BOW in the system are shown in Fig. 8. The SD-BOW potential has a linear distortion dependence in the vicinity of the equi-spaced lattice and the splitting of SD-BOW₁ and SD-BOW₂ is seen as expected. We show in Table IV the physical quantities of the SD-BOW, SDW and BOW states in the system. The spontaneous bond order alternation of SD-BOW at the equi-spaced lattice is smaller than that of

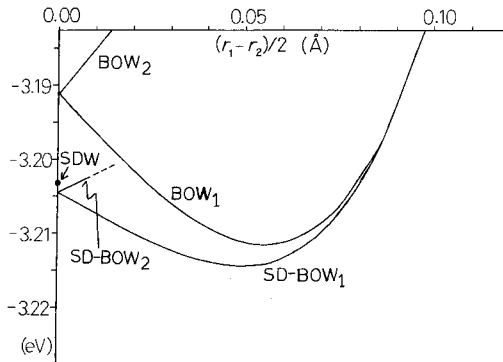


Fig. 8. The bond alternation potentials of the SD-BOW and BOW states in an itinerant spin Peierls system. Both the potentials of SD-BOW₁ and SD-BOW₂ and those of BOW₁ and BOW₂ are shown near the equi-spaced lattice. The energy of SDW is also indicated at the equi-spaced lattice. The parametrization of the system is given in Table II.

Table IV. Physical quantities of UHF states in an itinerant spin Peierls system.

		E total (eV)	Band gap (eV)	p_1	p_2	Δ (eV)	$q_+ - q_-$
Equi-Spaced ($r = 3.4 \text{ \AA}$)	BOW	-3.1910	5.0808	0.06362	0.99596	0	0
	SDW	-3.2032	4.9710	0.38742		2.4855	0.8285
	SD-BOW	-3.2044	5.0780	0.19279	0.63747	2.2182	0.7394
Bond-Alternated ^{a)}	BOW	-3.2115	5.2818	0.05840	0.99659	0	0
	SD-BOW	-3.2144	5.2340	0.09382	0.85494	1.5154	0.5051

a) At the equilibrium geometries with $(r_1 + r_2)/2 = 3.4 \text{ \AA}$ and $(r_1 - r_2)/2 = 0.055 \text{ \AA}$ (BOW) or $= 0.050 \text{ \AA}$ (SD-BOW).

BOW. Its spin density alternation also is smaller than that of SDW. This is due to the coexistence of the two kinds of long range orders in SD-BOW. The narrowness of the domain of the SD-BOW ground state is due to the exclusive nature of the two long range orders.

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Appendix

We prove here that the q_n^{\pm} 's and p_n^{\pm} 's given by Eq. (2·21) satisfy the stationary condition (2·22). To do this, we calculate the derivative of the free energy by an arbitrary quantity R . From Eqs. (2·5) and (2·7), we have

$$\frac{\partial}{\partial R} [\sum_a \sum_s (\varepsilon_a^s - \varepsilon_f) f_a^s - TS] = \sum_a \sum_s \frac{\partial \varepsilon_a^s}{\partial R} f_a^s. \quad (\text{A} \cdot 1)$$

We obtain from Eqs. (A·1) and (2·8)

$$\begin{aligned} \frac{\partial F}{\partial R} &= \frac{\partial}{\partial R} \{ F - \varepsilon_F (\sum_a \sum_s f_a^s - N) \} \\ &= \sum_a \sum_s \frac{\partial \varepsilon_a^s}{\partial R} f_a^s + \frac{\partial}{\partial R} \left[- \sum_n \{ \gamma_0 q_n^+ q_n^- - \gamma_n ((p_n^+)^2 + (p_n^-)^2) \} \right. \\ &\quad \left. - \frac{1}{2} \sum'_{m,n} \gamma_{mn} q_m q_n + E^\sigma \right]. \end{aligned} \quad (\text{A} \cdot 2)$$

Taking the derivative of the secular equation (2·13), we have

$$\begin{aligned} \frac{\partial}{\partial R} \text{Tr}[X^\pm(\varepsilon_a^\pm)] &= \sum_n \left\{ \frac{\partial}{\partial R} (T_n^\pm)_{11} \cdot (J_n^\pm)_{11} + \frac{\partial}{\partial R} (T_n^\pm)_{12} \cdot (J_n^\pm)_{21} \right\} \\ &= \sum_n \left[\frac{\partial}{\partial R} (\varepsilon_a^\pm - A_n^\pm) \frac{(J_n^\pm)_{11}}{B_n^\pm} - \frac{\partial B_n}{\partial R} \left\{ \frac{\varepsilon_a^\pm - A_n^\pm}{(B_n^\pm)^2} (J_n^\pm)_{11} \right. \right. \\ &\quad \left. \left. - \frac{B_{n-1}^\pm}{(B_n^\pm)^2} (J_n^\pm)_{21} + \frac{1}{B_{n+1}^\pm} (J_{n+1}^\pm)_{21} \right\} \right]. \end{aligned} \quad (\text{A} \cdot 3)$$

We have also the relation

$$\begin{aligned} \text{Tr}(X^\pm) &= \text{Tr}(J_n^\pm T_n^\pm) \\ &= \frac{\varepsilon_a^\pm - A_n^\pm}{B_n^\pm} (J_n^\pm)_{11} - \frac{B_{n-1}^\pm}{B_n^\pm} (J_n^\pm)_{21} + (J_n^\pm)_{12} = 2. \end{aligned} \quad (\text{A} \cdot 4)$$

From Eqs. (A·3) and (A·4), we get

$$\sum_n \left\{ \frac{\partial}{\partial R} (\varepsilon_a^\pm - A_n^\pm) (J_n^\pm)_{11} - \frac{\partial B_n^\pm}{\partial R} (1 - (J_n^\pm)_{12}) \right\} / B_n^\pm = 0, \quad (\text{A} \cdot 5)$$

where we have used

$$\left. \begin{aligned} (J_n^\pm)_{12} &= - \frac{B_n^\pm}{B_{n+1}^\pm} (Z_n^\pm)_{11}, \quad (J_{n+1}^\pm)_{21} = (Z_n^\pm)_{11}, \\ J_n^\pm &= Z_n^\pm T_{n+1}^\pm, \quad J_{n+1}^\pm = T_n^\pm Z_n^\pm, \\ Z_n^\pm &= T_{n-1}^\pm \cdots T_1^\pm T_n^\pm \cdots T_{n+2}^\pm. \end{aligned} \right\} \quad (\text{A} \cdot 6)$$

When q_n^\pm 's and p_n^\pm 's satisfy Eq. (2·21), Eq. (A·5) gives the relation

$$\sum_a \frac{\partial \varepsilon_a^\pm}{\partial R} f_a^\pm = \sum_n \left(\frac{\partial A_n^\pm}{\partial R} q_n^\pm + \frac{\partial B_n^\pm}{\partial R} p_n^\pm \right). \quad (\text{A} \cdot 7)$$

For $R = q_n^\pm$ and p_n^\pm , Eqs. (A·2) and (A·7) lead to Eq. (2·22). We note also that Eq. (2·29) can be obtained from Eqs. (A·2) and (A·7) for $R = x_n$.

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