Theory of Molecular Deformation Due to the Vibronic Interaction between Two Closely-spaced Electronic Levels. I

Minoru Kimura,[†] Kiyoshi Nishikawa, and Shigeyuki Aono*
[†]*Department of Physics, Faculty of Science, Kanazawa University, Marunouchi, Kanazawa, 920*
Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi, Kanazawa, 920

(Received July 3, 1980)

An theoretical investigation was made of the vibronic interaction between two electronic levels which are degenerate or nearly degenerate. Within the mean field approximation we derive a simplified effective Hamiltonian to analyze the problem of bond distortion of a molecule; the effective Hamiltonian is diagonalized by a linear canonical transformation of electronic operators. Thermodynamic arguments predict a possibility for appearance of a distorted phase below a characteristic temperature. The distorted phase is realized under a sufficiently strong coupling condition in a non-degenerate case, but under an arbitrarily small coupling condition in a degenerate case. The shift of electronic spectrum, the stabilization energy of the distortion, and thermodynamic quantities are expressed in terms of the parameters associated with the Hamiltonian. Change in electromagnetic properties due to the distortion is discussed. Magnitudes of the bond distortion and energy stabilization in the ground state are numerically estimated for cyclobutadiene, with results in good agreement with literature values.

Let us consider an electronic system with two discrete levels which are degenerate or nearly degenerate and coupled with each other through a vibronic interaction. Such a system can be taken as a prototype model for the variety of molecular distortion phenomena such as the Jahn-Teller or the pseudo Jahn-Teller effect and the bond alternation in conjugated molecules so-called the Peierls transition.[1)]

One attractive point with the present model is that it gives us a simple physical picture for the mechanism of molecular distortion; one can derive analogues with other similar problems in physics, *e.g.*, lattice distortions caused by electron-phonon interactions. It should be noted that there is a marked difference between the two problems, the lattice distortion and the present distortion; the former treats macroscopically large systems whereas the latter considers a single molecule or, at least, an aggregate of independent molecules. In our problem, therefore, we cannot expect any clear-cut transition at a finite temperature but can only anticipate a possible tendency with a large fluctuation towards transition to a new distorted ground state as temperature is lowered. Our finite temperature treatment, presented below, shows that phenomena are characterized by a temperature T_c below which this distortive character is expected to become noticeable. Within our present approximation this characteristic temperature is given by the apparent non-analyticity in free energy and electronic spectrum.

If temperature is much lower than T_c the molecule exists at its ground state where the distorted phase is well defined and stable as compared with the normal undistorted phase, provided the vibronic interaction is sufficiently strong.

To orient ourselves we will recapitulate the theory of bond alternation presented by Longuet-Higgins and Salem[2)] for conjugated molecules of linear polyenes and also present the iterative procedure developed by Nakajima *et al.*[3)] As the first step we tentatively adopt a structure with equal bond lengths and use the Hükel theory. We can thus specify molecular orbitals and orbital energies. From the former we find a set of bond orders, P_{rs}, between the rth and sth atomic sites. Next, we assume the relation of bond order, bond length, R_{rs}, and of bond length, resonance integral, β_{rs}, as

$$R_{rs} = R^0_{rs} + aP_{rs}, \tag{1}$$

$$\beta_{rs} = \beta^0_{rs} \exp(-bR_{rs}), \tag{2}$$

where R^0_{rs} and β^0_{rs} refer to the standarad geometry. Constant a in Eq. 1 is related to the force constant of lattice vibration which is assumed to be harmonic.[2)] Applying the P_{rs} obtained in the first step to Eq. 1, we can get a new set of bond lengths which enables us to estimate new resonance integrals by Eq. 2. We can then proceed to the next step on the eigenvalue problem. Such iterative treatments are repeated until a stable structure has been found. In the present theory, however, we can estimate stabilization energy and stable bond lengths in a single step.

Hamiltonian

The system in question is assumed to be well described by the Hamiltonian in the second quantized representation:

$$H = \sum_i \varepsilon_i a_i{}^+ a_i + \sum_q \omega_q b_q{}^+ b_q + \sum_{ijq} g_{ij:q} \phi_q a_i{}^+ a_j, \tag{3}$$

where a_i^+ and a_i are the creation and annihilation operators for the electron at the ith level, ε_i its energy, ω_q the phonon energy for mode q, $g_{ij:g}$ vibronic interaction constant, and ϕ_q is the phonon operator defined by

$$\phi_q = b_q{}^+ + b_q. \tag{4}$$

Throughout this article, we will use the unit of $\hbar = k_B = 1$ (k_B is the Boltzmann constant).

As mentioned above, we are considering only two electronic levels and, in order to avoid unnecessary complexity, the relevant phonon mode is also assumed to be single. It is convenient to use the following notations:

$$\varepsilon_1 = -\varepsilon,\ \varepsilon_2 = \varepsilon(\varepsilon > 0), \tag{5}$$

$$C = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix},\ C^+ = (a_1{}^+, a_2{}^+), \tag{6}$$

$$\hat{g} = \begin{pmatrix} 0 & g \\ g & 0 \end{pmatrix} = g\sigma_1. \tag{7}$$

Vibronic interaction constant g can be taken as real and we arrive at the model Hamiltonian:

$$H = C^+(-\varepsilon\sigma_3 + q\sigma_1\phi)C + \omega b^+b, \tag{8}$$

where the Pauli matrices

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},\ \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix},\ \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{9}$$

are used.

We further introduce the effective Hamiltonian, a good approximation to that of Eq. 8:

$$H^{eff} = -\varepsilon C^+\sigma_3 C + g\langle\phi\rangle C^+\sigma_1 C + \omega|\langle b\rangle|^2. \tag{10}$$

This form is based on an expectation that the so-called coherent state impling $<\phi>\neq 0$ would be arranged by vibronic interaction.

Canonical Transformation

To diagonalize H^{eff} we will carry out a canonical transformation as follows:

$$\gamma = UC,\ \gamma^+ = C^+U^+, \tag{11}$$

where

$$U = \begin{pmatrix} u & -v \\ v & u \end{pmatrix},\ U^+ = \begin{pmatrix} u & v \\ -v & u \end{pmatrix}, \tag{12}$$

$$u^2 + v^2 = 1. \tag{13}$$

For these equations u and v are real and we have $u>0$. It is obvious that U is unitary ($U^+ = U^{-1}$), so we have

$$\begin{aligned} U &= u\sigma_0 - \mathrm{i}v\sigma_2, \\ U^+ &= u\sigma_0 + \mathrm{i}v\sigma_2. \end{aligned} \tag{14}$$

If we use the inverse transform of Eq. 11, Eq. 10 becomes

$$H^{eff} = \gamma^+(-\varepsilon U\sigma_3 U^+ + g\langle\phi\rangle U\sigma_1 U^+)\gamma + \omega|\langle b\rangle|^2. \tag{15}$$

Equation 14 readily gives

$$\begin{aligned} U\sigma_3 U^+ &= u^2\sigma_3 + 2uv\sigma_1 - v^2\sigma_3, \\ U\sigma_1 U^+ &= u^2\sigma_1 - 2uv\sigma_3 - v^2\sigma_1, \end{aligned} \tag{16}$$

so we have

$$H^{eff} = H^d + H^{od}, \tag{17}$$

where H^d and H^{od} are the diagonal and off-diagonal terms, respectively, as defined by

$$\begin{aligned} H^d &= -\gamma^+\{(u^2-v^2)\varepsilon + 2uvg\langle\phi\rangle\}\sigma_3\gamma + \omega|\langle b\rangle|^2, \\ H^{od} &= \gamma^+\{-2uv\varepsilon + (u^2-v^2)g\langle\phi\rangle\}\sigma_1\gamma. \end{aligned} \tag{18}$$

We determine u and v so as to make the off-diagonal term H^{od} vanish:

$$2uv\varepsilon = (u^2-v^2)g\langle\phi\rangle. \tag{19}$$

Combining this with Eq. 13, we get

$$\begin{aligned} u^2 &= \frac{1}{2}(1+\varepsilon/\sqrt{\varepsilon^2+\Delta^2}), \\ v^2 &= \frac{1}{2}(1-\varepsilon/\sqrt{\varepsilon^2+\Delta^2}), \end{aligned} \tag{20}$$

or alternatively,

$$\begin{aligned} u^2-v^2 &= \varepsilon/\sqrt{\varepsilon^2+\Delta^2}, \\ 2uv &= \Delta/\sqrt{\varepsilon^2+\Delta^2}, \end{aligned} \tag{21}$$

where

$$\Delta = g\langle\phi\rangle \quad (>0). \tag{22}$$

As will be explained in a later section, the molecular deformation arises from $<\phi>\neq 0$. The positive sign adopted in Eq. 22 corresponds to specifying that we set the coordinate direction so as to make the molecular deformation have positive sign.

Under the condition of Eq. 20 H^d becomes

$$H^d = -\gamma^+\tilde{\varepsilon}\sigma_3\gamma + \omega|\langle b\rangle|^2, \tag{23}$$

where

$$\begin{aligned} \tilde{\varepsilon} &= (u^2-v^2)\varepsilon + 2uvg\langle\phi\rangle \\ &= \sqrt{\varepsilon^2+\Delta^2}. \end{aligned} \tag{24}$$

At this stage, we will look for the solution for a static deformation of molecule which satisfies

$$\langle\dot{\phi}\rangle = 0. \tag{25}$$

To make this explicit, we examine the equation of motion for operators b and b^+. For b we have

$$\mathrm{i}\dot{b} = [b, H] = gC^+\sigma_1 C + \omega b. \tag{26}$$

The static condition of Eq. 25 leads to

$$\langle b\rangle = -\langle C^+\sigma_1 C\rangle\omega/g. \tag{27}$$

Since we can obtain entirely the same result for $<b^+>$, we conclude that $<b>$ and $<b^+>$ are real and given by

$$\langle b\rangle = \langle b^+\rangle = \frac{1}{2}\langle\phi\rangle. \tag{28}$$

Therefore, combining this with Eq. 23, we arrive at the result:

$$H^d = -\gamma^+\tilde{\varepsilon}\sigma_3\gamma + \frac{\omega}{4g^2}\Delta. \tag{29}$$

Parameter Δ should be determined self-consistently.

Thermodynamics

Let us study thermodynamic properties of an assembly of molecules on the basis of the approximate Hamiltonian of Eq. 29. The partition function (per molecule) defined by

$$Z \equiv \mathrm{Tr}\exp(-H^d/T) \tag{30}$$

is easily calculated by use of Eq. 29. Using the relation

$$\gamma^+\sigma_3\gamma = \gamma_1{}^+\gamma_1 - \gamma_2{}^+\gamma_2, \tag{31}$$

we obtain

$$\begin{aligned} Z &= \exp(-\omega\Delta^2/4g^2T)\mathrm{Tr}\exp(-\tilde{\varepsilon}\gamma_1{}^+\gamma_1/T) \\ &\quad \times \mathrm{Tr}\exp(\tilde{\varepsilon}\gamma_2{}^+\gamma_2/T) \\ &= \exp(-\omega\Delta^2/4g^2T)\{\exp(-\tilde{\varepsilon}/2T)+\exp(\tilde{\varepsilon}/2T)\}^2, \end{aligned} \tag{32}$$

for which we have used the fact that the eigenvalue of $\gamma_i^+\gamma_i$ is 0 or 1.

The free energy of this system is given by

$$\begin{aligned} F &\equiv -T\ln Z \\ &= \omega\Delta^2/4g^2 - 2T\ln\{2\cosh(\tilde{\varepsilon}/2T)\}. \end{aligned} \tag{33}$$

Now we minize the free energy with respect to Δ:

$$\frac{\partial F}{\partial\Delta} = \frac{\omega\Delta}{2g^2} - \tanh(\tilde{\varepsilon}/2T)\frac{\partial\tilde{\varepsilon}}{\partial\Delta} = 0. \tag{34}$$

On application of Eq. 24 we get

$$\Delta\left\{\frac{\omega}{2g^2} - \frac{1}{\tilde{\varepsilon}}\tanh(\tilde{\varepsilon}/2T)\right\} = 0. \tag{35}$$

The nontrivial solution for Δ is determined from the relation:

$$\omega\tilde{\varepsilon}/2g^2 = \tanh(\tilde{\varepsilon}/2T). \tag{36}$$

This is the gap equation for Δ and has a solution ($\Delta \neq 0$) if

$$\omega\tilde{\varepsilon}/2g^2 < 1. \tag{37}$$

This is an important relation among the parameters included in the original Hamiltonian. If the two levels are degenerate, the above condition is always satisfied. In the case of non-degenerate levels sufficiently strong vibronic interactions can satisfy Eq. 37.

Characteristic temperature T_c at which Δ vanishes is obtained from Eq. 36 as

$$\omega\varepsilon/2g^2 = \tanh(\varepsilon/2T_c). \tag{38}$$

Now, we will tentatively examine other thermodynamic quantities. The entropy S of this system is estimated as follows:

$$\begin{aligned} S \equiv -\frac{\partial F}{\partial T} &= -\left(\frac{\partial F}{\partial \Delta}\right)_T \frac{\partial \Delta}{\partial T} - \left(\frac{\partial F}{\partial T}\right)_\Delta \\ &= 2\ln\{2\cosh(\tilde{\varepsilon}/2T)\} - \frac{\tilde{\varepsilon}}{T}\tanh(\tilde{\varepsilon}/2T). \end{aligned} \tag{39}$$

In the above derivation, we have made use of Eq. 34. Using the gap equation (36), we get

$$S = 2\ln\{2\cosh(\tilde{\varepsilon}/2T)\} - \omega\tilde{\varepsilon}^2/2g^2T. \tag{40}$$

At the characteristic temperature,

$$S(T_c) = 2\ln\{2\cosh(\varepsilon/2T_c)\} - \frac{\varepsilon}{T_c}\tanh(\varepsilon/2T_c). \tag{41}$$

Since the entropy of the normal phase is given by

$$S_n(T) = 2\ln\{2\cosh(\varepsilon/2T)\} - \frac{\varepsilon}{T}\tanh(\varepsilon/2T), \tag{42}$$

the value of entropy changes continuously from the coherent phase ($\Delta \neq 0$) to the normal phase ($\Delta = 0$), *i.e.*,

$$S(T_c - 0) = S(T_c + 0). \tag{43}$$

On the other hand, heat capacity at constant volume

$$C \equiv T\frac{\partial S}{\partial T} \tag{44}$$

behaves in a different manner, as will be seen in what follows. From Eqs. 36 and 40 we get

$$\frac{\partial S}{\partial T} = -(\omega\tilde{\varepsilon}/2g^2T)\frac{\partial \tilde{\varepsilon}}{\partial T}. \tag{45}$$

We differenciate the gap equation (36) with respect to T and apply some algebraic treatments to have

$$\frac{\partial \tilde{\varepsilon}}{\partial T} = \tilde{\varepsilon}\{1 - (\omega\tilde{\varepsilon}/2g^2)^2\}/T\{(\omega T/g^2) + (\omega\tilde{\varepsilon}/2g^2)^2 - 1\}, \tag{46}$$

which, in conjunction with Eqs. 44 and 45, leads to the formulation of heat capacity:

$$\begin{aligned} C &= (\omega\tilde{\varepsilon}^2/2g^2T)\{1 - (\omega\tilde{\varepsilon}/2g^2)^2\}/\{(\omega T/g^2) + (\omega\tilde{\varepsilon}/2g^2)^2 - 1\} \\ &= \frac{\tilde{\varepsilon}}{T}\tanh(\tilde{\varepsilon}/2T)\,\mathrm{sech}^2(\tilde{\varepsilon}/2T)/\{(\omega T/g^2) - \mathrm{sech}^2(\tilde{\varepsilon}/2T)\}. \end{aligned} \tag{47}$$

The heat capacity of the normal phase is obtained from Eq. 42 as

$$C_n = (\varepsilon^2/2T^2)\,\mathrm{sech}^2(\varepsilon/2T). \tag{48}$$

At the characteristic temperature, the heat capacities of the coherent and normal phases are given by

$$\begin{aligned} C &= (\varepsilon^2/2T_c^2)\{1 - (\omega\varepsilon/2g^2)^2\}/\{1 + (g^2/\omega T_c)[(\omega\varepsilon/2g^2)^2 - 1]\} \\ C_n &= (\varepsilon^2/2T_c^2)\{1 - (\omega\varepsilon/2g^2)^2\}, \end{aligned} \tag{49}$$

hence

$$\frac{C}{C_n} = 1/\{1 + (g^2/\omega T_c)[(\omega\varepsilon/2g^2)^2 - 1]\} > 1. \tag{50}$$

We want to point out that, as T goes to 0, the heat capacities of these phases behave in accord with

$$\begin{aligned} C &= (\tilde{\varepsilon}^2/2T^2)\exp(-\tilde{\varepsilon}/T), \\ C_n &= (\varepsilon^2/2T^2)\exp(-\varepsilon/T). \end{aligned} \tag{51}$$

It is seen that the former decreases faster than the latter because $\tilde{\varepsilon} > \varepsilon$.

Ground State Properties

At the limit of $T=0$, the gap equation (36) becomes

$$\tilde{\varepsilon} = \sqrt{\varepsilon^2 + \Delta^2} = 2g^2/\omega, \tag{52}$$

which gives

$$\Delta^2 = (\varepsilon/s)^2(1 - s^2), \tag{53}$$

where s is a dimensionless quantity defined by

$$s = \omega\varepsilon/2g^2 \quad (<1). \tag{54}$$

The ground state energy of the coherent phase is given as a sum of electronic and lattice parts:

$$\begin{aligned} \tilde{E} &= -\tilde{\varepsilon} + \omega\Delta^2/4g^2 \\ &= -\varepsilon(1-s)^2/2s - \varepsilon. \end{aligned} \tag{55}$$

Since the energy of the normal phase is $E = -\varepsilon$, the stabilization energy is thus obtained as

$$\begin{aligned} \delta E \equiv E - \tilde{E} &= \varepsilon(1-s)^2/2s \\ &= 2g^2/\omega\{1 - (\omega\varepsilon/2g^2)\}^2. \end{aligned} \tag{56}$$

It is seen that, if the inequality (37) holds, we have an energy depression.

The deformation of lattice is expressed as

$$\delta R_\alpha = \sum_q \sqrt{\frac{\hbar}{2M\omega_q}} L_{\alpha q}\langle \phi_q \rangle, \tag{57}$$

where α refers to the site and coordinate indicies and $L_{\alpha q}$ is the transformation matrix from the normal mode q to the real displacement. $L_{\alpha q}$ is calculated by the standard method for actual systems. If we restrict ourselves to treatment of a single mode as we have done so far, we can simplify Eq. 57 to

$$\delta R_\alpha = \sqrt{\frac{\hbar}{2M\omega}} L_{\alpha q}(2g/\omega)\{1 - (\omega\varepsilon/2g^2)^2\}^{1/2}, \tag{58}$$

for which Eqs. 23 and 53 are used. The results obtained in this section will be applied to cyclobutadiene later.

Electromagnetic Properties

If the system has an induced dipole moment between levels 1 and 2, the interaction between the radiation field and the electron in our system is described as

$$\begin{aligned} H_{\mathrm{int}} &= -\mathbf{E}\cdot\mathbf{d}C^+\sigma_1 C \\ &= -\mathbf{E}\cdot\mathbf{d}\gamma^+ U\sigma_1 U^+\gamma, \end{aligned} \tag{59}$$

where $\mathbf{E}$ is the electric field associated with the applied radiation field and $\mathbf{d}$ is the induced dipole moment in the electronic system. Using Eq. 16, we can rewrite Eq. 59 as

$$H_{\rm int} = -\mathbf{E}\cdot\mathbf{d}\gamma^+\{(u^2-v^2)\sigma_1-2uv\sigma_3\}\gamma, \qquad (60)$$

hence we have for the radiative transition probability W_{21}

$$\begin{aligned} W_{21} &\propto (\mathbf{E}\cdot\mathbf{d})^2|\langle\tilde{2}|\gamma^+(u^2-v^2)\sigma_1\gamma|\tilde{1}\rangle|^2 \\ &= (\mathbf{E}\cdot\mathbf{d})^2(u^2-v^2)^2 \\ &= (\mathbf{E}\cdot\mathbf{d})^2\frac{\varepsilon^2}{\varepsilon^2+\Delta^2}. \end{aligned} \qquad (61)$$

We have an additional information that, even if there is no permanent dipole in the normal phase, there will appear a permanent dipole in the coherent phase, as embodied by

$$\begin{aligned} \mathbf{P} &= -2uv\mathbf{d}\langle\gamma^+\sigma_3\gamma\rangle \\ &= -\frac{\mathbf{d}\Delta}{\sqrt{\varepsilon^3+\Delta^2}}\{\exp(2\tilde{\varepsilon}/T)+1\}^{-1}. \end{aligned} \qquad (62)$$

It should be pointed out that increasing Δ causes the radiative transition probability to decrease but the permanent dipole to increase.

Illustrative Example. Cyclobutadiene

Cyclobutadiene is a fictious molecule, but has frequently been a subject for theoretical considerations. We will begin with an investigation on the assumption that cyclobutadiene is, in a crude approximation, a square molecule with bonds of equal length, 1.42 Å. This structure has two π electronic levels which are degenerate. The vibrational modes which connect these two levels have symmetries b_{1g} and b_{2g} as shown in Fig. 1. Those vibronic coupling constants referring to those modes are designated g_1 and g_2, respectively. These constants are evaluated by the method of Murrel and Pople[4] as

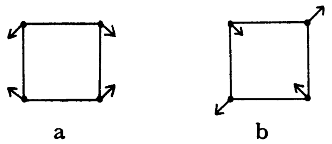

Fig. 1. Normal modes of molecular vibrations.
a: b_{1g} mode, b: b_{2g} mode.

$$\begin{aligned} g_1 &= 0.432/\sqrt{\nu_1}\ \text{eV}, \\ g_2 &= 0.112/\sqrt{\nu_2}\ \text{eV}, \end{aligned} \qquad (63)$$

where ν_i is the wave number of the vibration in question in units of 1000 cm^{-1}; we adopt $\nu_i=1.5$, as is usually the case with hydrocarbons having several carbon atoms.

Wave function for the degenerate π levels are written as

$$\begin{aligned} \phi_1 &= \frac{1}{2}(\chi_1+\chi_2-\chi_3-\chi_4), \\ \phi_2 &= \frac{1}{2}(\chi_1-\chi_2-\chi_3+\chi_4), \end{aligned} \qquad (64)$$

or alternatively,

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{2}}(\chi_1-\chi_3), \\ \phi_2 &= \frac{1}{\sqrt{2}}(\chi_2-\chi_4), \end{aligned} \qquad (65)$$

where χ_i is the 2pπ atomic orbital at site i. Equation 64 is suitable for considering the b_{1g} vibrational mode, whereas Eq. 65 is applicable to the b_{2g} mode, so that the coupling matrix $\hat{g}$ is written as Eq. 7.

We can calculate stabilization energies using Eq. 56 with $\varepsilon=0$ (degenerate case) as

$$\begin{aligned} \delta E(b_{1g}) &= 0.831\ \text{eV (rectangle)}, \\ \delta E(b_{2g}) &= 0.107\ \text{eV (diamond)}. \end{aligned} \qquad (66)$$

Apparently the former is much higher than the latter, in agreement with the most stable structure of this molecule being a rectangle. The stabilization energy, 0.831 eV, obtained here is very close to that obtained by Liehr, 0.907 eV.[5]

We turn to evaluation of δR_α ($\alpha=l,x$), with our interest restricted in the b_{1g} type distortion. Since $L_{\alpha q}$ has been estimated to be 0.0109 by the standard method,[6] we have from Eq. 58

$$\delta R_\alpha = 0.0325\ \text{Å}, \qquad (67)$$

hence the longer and shorter bond distances are evaluated as

$$D_l = 1.485\ \text{Å}, \quad D_s = 1.355\ \text{Å}. \qquad (68)$$

For reference, the following values have been obtained by Liehr[5] and by Salem:[7]

$$\begin{aligned} D_l &= 1.54\ \text{Å}, \quad D_s = 1.33\ \text{Å (Liehr)}, \\ D_l &= 1.463\ \text{Å}, \quad D_s = 1.388\ \text{Å (Salem)}. \end{aligned} \qquad (69)$$

Similar arguments may be applicable to conjugated chain molecules. In these case, the b_{1g} vibrational mode is expected also to contribute dominantly to the stabilization; however, ε is finite in these case, though we can expect the inequality (37), to be applicable; both the stabilization energy and bond distortion would be smaller than those in the degenerate case discussed in this paper.

Discussion

We have presented the mean field theory for such an electronic system as is composed of two closely-spaced levels and strongly coupled with a phonon mode. Even though we have adopted quite a simple Hamiltonian given by Eq. 8, we have successfully derived some physically interesting results; the appearance of coherent phase and the condition for this phase to be more stable than the normal phase. Expressions for the stabilization energy and associated bond distortion have been derived and their numerical values estimated for cyclobutadiene, with results in good agreement with those obtained by conventional methods.

It should be pointed out that, for usual finite molecules, the characteristic temperature at which the coherent phase appears is so high (over 10000 °C as estimated by Eq. 38) that common molecules should be in the well-established coherent phase with respect to the phonon modes even at room temperature.

As to long chain molecules, there is a leading opinion that the stabilization is caused mostly by electron correlation.[8] We agree to this but want to stress that the electron correlation term, if included in our Hamiltonian, would rise a new problem to us.

Finally, we shoud note that the appearance of non-analyticity of free energy at the finite temperature T_c is to be taken as a shortcoming of our simplest approximation. Nevertheless, we can regard it as an important step of theoretical development, though fluctuating, on the distortion. The thermodynamic properties derived above also must be considered as indicating characteristic features below T_c for the transition towards the distorted ground state. At any rate, a more satisfactory theory is expected which gose over the present framework of approximation.

The problem treated here can also be manipulated by means of Green's function, which will be discussed in the following paper.

References

1) R. E. Peierls, "Quantum Theory of Solids," Clarendon Press, Oxford (1955), p. 108.

2) H. L. Longuet-Higgins and L. Salem, *Proc. R. Soc. London, Ser. A*, **251**, 172 (1959).

3) H. Yamaguchi, T. Nakajima and, T. L. Kunii, *Theor, Chim. Acta*, **12**, 349 (1968).

4) J. N. Murrel and J. A. Pople, *Proc. R. Soc. London, Ser. A*, **69**, 245 (1956).

5) A. D. Liehr, *Z. Phys. Chem.*, **9**, 338 (1956).

6) G. Herzberg, "Molecular Spectra and Molecular Structure. II, IR and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York (1945), Chap. 2.

7) L. Salem, "Molecular Orbital Theory of Conjugated, System," W. A. Benjamin, Inc., New York (1966), Chap. 8.

8) A. A. Ovchinickov, I. I. Ukraiskii, and G. V. Kventsel, *Soviet Phys., Uspekhi*, **15**, 575 (1973). Other references are therein.