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Colour and Polarizability of Conjugated Chain-Molecule

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Electronic excitation of long conjugated chain-molecule is studied by Tomonaga's method of collective motion. One of the most elementary modes of collective motion is the dipole oscillation. Assuming the occurrence of this oscillation for pi-electrons in the conjugated chain, it is found that, for cyanine dyes which contain C-C bonds of equal length, we have the wavelength of absorption which increases nearly in proportion to their chain length, while for carotenoids which contain alternating bond lengths, we have the wavelength of absorption which approaches a finite value with increasing chain lengths of carotenoids. When the classical polarizability is introduced, we have the lower energies of excitation by a little amount. It is found that the introduction of the classical polarizability or the effect of depolarization corresponds to the mixing of configurations.

§ 1. Introduction

Colour of dye-molecules has been investigated by many authors since 1937 when Sklar succeeded in accounting for the spectrum of benzene. Simple molecules or highly symmetric molecules can be handled in a comparatively straightforward way. But as for large molecules, such as organic dyes, we must use drastic approximations owing to their complexity. Specifically, when we deal with the colour of organic dyes which contain the chain of conjugated double bonds, we usually assume that, in the lower electronic excitation of the molecule, the excitation occurs only for pi-electrons in the chain and remaining sigma-electrons play no role in the excitation. Such a pi-electron approximation is fully recognized and we will not discuss it further in the present paper.

In addition to pi-electron approximation, usually we use the method of one-electron approximation in dealing with such large molecules and we assume that the Coulomb energy or the correlation energy between electrons is small compared with the orbital energy of each electron. For comparatively simple molecules, several theories including Coulomb interaction have appeared recently and presented good results. Using the method of configurational mixing, one may find in principle a solution of the problem of correlation. But in order to investigate the electronic states of a large molecule, we must take into account so many configurations that it is hardly possible to carry out the practical computations.

Experimental studies for the spectra of chain molecules have been perform-
ed by Brooker and his coworkers\textsuperscript{39} and Karrer.\textsuperscript{40} Platt\textsuperscript{51} summarized their results and reached the following conclusions:

(a) The first absorption wavelength of long symmetrical odd-atom dye increases by 1000 ± 50 Å for every additional vinyl group in the chain, successive increases being "nonconvergent".

(b) In the first approximation, the wavelength of absorption of an unsymmetrical dye or chain molecule is given by the arithmetic mean of the wavelengths of its symmetrical parent dyes.

(c) This absorption is shifted to shorter wavelength by a small amount which is referred to as the Brooker deviation.

(d) In the case of polyenes, the spectra of vinylogous series lie at much shorter wavelengths than the cyanines and "converge" with increasing chain length, probably to a finite limiting wavelength of absorption.

We find numerous empirical and theoretical formulae which have been proposed to describe these phenomena in Platt's paper.\textsuperscript{51} Among them, we notice a theory proposed by Lewis and Calvin.\textsuperscript{6} They have described the chain molecule as an oscillator and have explained conclusion (a) but have failed to account for conclusion (d).

In the present paper, we shall reexamine the theory given by Lewis and Calvin and develop a collective description of the excitation of pi-electrons in the conjugated chain. We consider that the chain molecule corresponds to a long spheroid in which pi-electrons are contained and we assume that these pi-electrons form an electron gas in one-dimensional box and, when the molecule is excited, the center of mass of pi-electrons oscillates along the long axis of the spheroid, hence a dipole oscillation will be generated. Thus the method of collective motion proposed by Tomonaga\textsuperscript{7} will be applied to our problem of pi-electrons. We shall then show that our method corresponds to the method of configurational mixing and the question about what sort of configurations is included will be discussed in § 9.

§ 2. Theory of dipole oscillation

In the present section, we wish to study the one-dimensional oscillation of pi-electrons along the chain in the molecule. We begin with giving an outline of Tomonaga's method. The Hamiltonian for our system is written as

\[ H = \sum_{i=1}^{n} \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} - eV^p(x_i) \right) + \frac{e^2}{2} \sum_{i,j} G(x_i, x_j), \]  

where \( m \) represents the mass of the electron, \( V^p(x_i) \) the potential energy of the \( i \)-th electron and \( G(x_i, x_j) \) the Coulomb energy between the \( i \)-th and the \( j \)-th electron. We then define the collective coordinate \( \xi \) and the collective momentum \( \pi \) by means of...
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\[
\begin{align*}
\xi &= (1/N) \sum_i x_i , \\
\pi &= -i \hbar \sum_i \left( \partial / \partial x_i \right).
\end{align*}
\]  

(2.2)

Then the coordinate \( \xi \) satisfies the canonical commutation relation with the momentum \( \pi \),

\[
[\pi, \xi] = -i \hbar .
\]  

(2.3)

First we separate the kinetic energy into two parts,

\[
T = \sum_i -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} = T_{\text{coll}} + T_{\text{in}} ,
\]  

(2.4)

with

\[
T_{\text{coll}} = -\frac{1}{2I} \pi^2 ,
\]

\[
T_{\text{in}} = \sum_i -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} - \frac{1}{2I} \left( -i \hbar \sum_i \partial / \partial x_i \right)^2 ,
\]

where \( T_{\text{coll}} \) corresponds to the kinetic energy of the collective motion and \( T_{\text{in}} \) to the kinetic energy of the internal motion. The constant \( I \) is determined by the requirement that \( T_{\text{in}} \) should not contain \( \pi \). This requires that

\[
[\pi, \xi] = 0 .
\]  

(2.5)

This requirement determines \( I \) such that

\[
I = mN .
\]  

(2.6)

Then

\[
H_{\text{in}} = H - (1/2I) \pi^2
\]  

(2.7)

doest not contain \( \pi \), but it still contains the collective coordinate \( \xi \). In order to find the potential energy for the collective motion, we calculate the mean value of \( H_{\text{in}} \), using the Schrödinger function \( \Psi_{\text{in}} \) for the internal motion and expand the mean value in power series of \( \xi \). Then we shall have

\[
\langle \Psi_{\text{in}} | H_{\text{in}} | \Psi_{\text{in}} \rangle = V_0 + V_1 \xi + (1/2) V_2 \xi^2 + \ldots .
\]  

(2.8)

From this expansion, we obtain the potential energy for the collective motion \( V_1 \xi + (1/2) V_2 \xi^2 \). In our case \( V_1 \) vanishes as we shall show in Appendix I, hence the Schrödinger equation for our collective motion becomes

\[
\left( \frac{1}{2I} \pi^2 + \frac{1}{2} V_2 \xi^2 - E_{\text{coll}} \right) u(\xi) = 0 .
\]  

(2.9)

The equation for the internal motion will be introduced in Appendix I. Let the energy of the internal motion be denoted by \( E_{\text{in}} \), the total energy \( E \) of our system is then given by
The meaning of $E_{in}$ will be made clear in this Appendix.

So far we have given an outline of Tomonaga's method, but in this procedure the coefficient $V_2$ is defined by Eq. (2·8). Hence, in order to determine the magnitude of $V_2$, we must first determine the wave function $\psi_{in}$ for the internal motion. But this requires a very complicated calculation so that, in the present paper, we shall proceed in a different way and show that we can obtain $V_2$ by means of the following method without using $\psi_{in}$.

We introduce the system into an electric field of strength $F$. The Hamiltonian for our system then becomes

$$H' = H - eNF\xi.$$

As we shall show in Appendix I, the internal motion or $\psi_{in}$ will not be affected by the electric field, hence $V_2$ in Eq. (2·9) will be independent of the field $F$ and accordingly the variation due to $F$ will occur only in the collective part of the Hamiltonian. The Schrödinger equation for the collective motion in the presence of $F$ is then given by

$$\left(\frac{1}{2I} + \frac{1}{2} V_2 \xi^2 - eNF\xi - E_{coll}'\right)u'(\xi) = 0.$$

From Eq. (2·12), we have

$$u'(\xi) = u\left(\xi - \frac{eN}{V_2} F\right).$$

$$E_{coll}' = E_{coll} - \frac{1}{2} \frac{e^2N^2}{V_2} F^2.$$

The total energy then becomes

$$E' = E_{in} + E_{coll} - \frac{1}{2} \frac{e^2N^2}{V_2} F^2$$

$$= E - \frac{1}{2} \frac{e^2N^2}{V_2} F^2.$$

Thus it is found that, when we introduce the system into the electric field $F$, the center of mass $\xi$ is displaced by the amount

$$\Delta \xi = \frac{eN}{V_2} F$$

in the direction of $F$ and the energy is increased by the amount

$$\Delta E = -\frac{1}{2} \frac{e^2N^2}{V_2} F^2.$$

Owing to the displacement of $\xi$, the dipole moment $\mu$, i.e.
will be induced in the system. From the formula (2·18), it is found that the polarizability \( \alpha \) of the system is given by

\[
\alpha = \frac{e^2 N^2}{V_3}.
\]  

Using Eqs. (2·17), (2·18) and (2·19), we find

\[
\mu = \alpha F, \\
\Delta E = - \frac{1}{2} \alpha F^2,
\]

with

\[
V_3 = \frac{e^2 N^2}{\alpha}.
\]

Now it is found that, in order to obtain the potential energy for the collective motion, it is sufficient simply to calculate the polarizability \( \alpha \) in place of the direct calculation of \( V_3 \) by Eq. (2·8). The polarizability is obtained from \( \mu \) or \( \Delta E \). The merit of this method is that, in calculating \( \Delta E \) or \( \mu \), it is not necessary to separate the collective part from the internal part in the Hamiltonian. One has just to calculate the change of energy or the displacement of center of mass caused by the perturbation energy \( -eF \sum x_i \) added to the Hamiltonian (2·1). We can then obtain the polarizability and we can determine \( V_3 \) from it by Eq. (2·21). Then for the frequency of the collective motion we obtain

\[
\omega = \left( \frac{N e^2}{m \alpha} \right)^{1/3},
\]

from Eqs. (2·6), (2·9) and (2·21).

\section*{§ 3. Calculation of polarizability in the independent-particle approximation}

In order to calculate the polarizability, it is now necessary to determine the induced dipole moment or the variation of energy due to the external field \( F \); and this can be done by carrying out the perturbation calculation for the perturbed Hamiltonian \( H - eF \sum x_i \). But the unperturbed system itself is already a very complicated one which requires to solve a many-particle problem. Accordingly, we must begin with a very rough approximation, namely the independent-particle approximation. The meaning of this approximation and its bearing on a more improved approximation will be made clear in the course of calculation.
We have for our Hamiltonian

\[ H = \sum_{i} H_{i}^{2} + \frac{e^{2}}{2m} \sum_{i,j} G(x_{i}, x_{j}), \]  

(3.1)

where

\[ H_{i}^{2} = -\frac{\hbar^{2}}{2m} \frac{\partial^{2}}{\partial x_{i}^{2}} - eV_{p}(x_{i}), \]

and \( V_{p} \) represents the potential field due to the positive ions and \( G(x_{i}, x_{j}) \) the Coulomb energy between the \( i \)-th and the \( j \)-th electron. The problem we have to solve is

\[ (H-E)\Psi = 0. \]

(3.2)

In obtaining the solutions of Eq. (3.2), we use the independent-particle approximation. That is, in place of the exact Hamiltonian (3.1), we use the approximate Hamiltonian, in which we replace the potential for each electron by the mean value of the potential due to all electrons except for the electron itself. This means to use the approximate Hamiltonian

\[ \bar{H} = \sum_{i} \left(-\frac{\hbar^{2}}{2m} \frac{\partial^{2}}{\partial x_{i}^{2}} - eV_{p}(x_{i}) + e\bar{V}_{i}(x_{i}) \right) = \sum \bar{H}_{i}, \]

(3.3)

with

\[ \bar{V}_{i}(x) = e \sum_{j \neq i} G(x, x') \rho_{j}(x') dx', \]

(3.4)

where \( \rho_{j}(x) \) represents the density of the \( j \)-th electron. This approximation is very similar to the Hartree approximation but we shall distinguish between the independent-particle approximation and the Hartree approximation. The distinction will become clear in § 7.

Now we must solve

\[ (\sum_{i} \bar{H}_{i} - E)\Phi = 0. \]

(3.5)

Solving the equations

\[ (\bar{H}_{i} - E_{i}) \phi_{i}(x_{i}) = 0, \]

(3.6)

we find the eigenvalues \( E_{i} \) and the eigenfunctions \( \phi_{i}(x) \). We then obtain the solutions of Eq. (3.5), i.e.

\[ \begin{cases} E = \sum_{i} E_{i}, \\ \Phi = \prod_{i} \phi_{i}(x_{i}), \end{cases} \]

(3.7)

where the suffix \( i \) attached to \( E \) or \( \phi \) is used not only to specify electrons but also to specify the quantum state for the electron. More specifically, \( i, i', i'', \ldots, \)
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represent the various quantum states of the \(i\)-th electron.

Now we introduce the system into the electric field \(F\). Then we have the Hamiltonian for the perturbed system

\[
H' = \sum_i H_i - eF \sum_i x_i. \tag{3.8}
\]

According to the perturbation theory, \(\phi_i(x)\) and \(E_i\) in Eq. (3.7) will become \(\phi'_{i'}(x)\) and \(E'_{i'}\) respectively:

\[
\begin{align*}
\phi_{i'}(x_i) &= \phi_i(x_i) + eF \sum_{i'} \frac{\langle \phi_{i'}(x_i) | x_i | \phi_i(x_i) \rangle}{E_{i'} - E_i} \phi_{i'}(x_i) + \cdots \\
&= \phi_i(x_i) + \phi^0_i(x_i) + \cdots, \tag{3.9}
\end{align*}
\]

\[
\Delta E_{i'} = -e^2F^2 \sum_{i'} \frac{\langle \phi_{i'}(x_i) | x_i | \phi_{i'}(x_i) \rangle \langle \phi_{i'}(x_i) | x_i | \phi_{i'}(x_i) \rangle}{E_{i'} - E_i},
\]

where

\[
\Delta E_{i'} = E_{i'} - E_i.
\]

The perturbed eigenfunction \(\phi'_{i'}\) given by (3.9) enables us to calculate the mean displacement of the \(i\)-th electron, which is given by

\[
\langle \phi'_{i'}(x_i) | x_i | \phi_{i'}(x_i) \rangle = \langle \phi_i(x_i) | x_i | \phi^0_i(x_i) \rangle + \langle \phi^0_i(x_i) | x_i | \phi_i(x_i) \rangle = 2eF \sum_{i'} \frac{\langle \phi_{i'}(x_i) | x_i | \phi_{i'}(x_i) \rangle \langle \phi_{i'}(x_i) | x_i | \phi_{i'}(x_i) \rangle}{E_{i'} - E_i}.
\]

Summing the displacements over all electrons and multiplying the sum by the electronic charge \(e\), we obtain the induced dipole moment:

\[
\mu = 2e^2F \sum_i \frac{\sum_{i'} \langle \phi_{i'} | x_i | \phi_{i'} \rangle \langle \phi_{i'} | x_i | \phi_{i'} \rangle}{E_{i'} - E_i}. \tag{3.10}
\]

Summing \(\Delta E_{i'}\) given by (3.9) over all electrons, we obtain the variation of the total energy:

\[
\Delta E = -e^2F^2 \sum_i \frac{\sum_{i'} \langle \phi_{i'} | x_i | \phi_{i'} \rangle \langle \phi_{i'} | x_i | \phi_{i'} \rangle}{E_{i'} - E_i}. \tag{3.11}
\]

We then get for the polarizability

\[
\alpha = 2e^2 \sum_i \sum_{i'} \frac{\langle \phi_{i'} | x_i | \phi_{i'} \rangle \langle \phi_{i'} | x_i | \phi_{i'} \rangle}{E_{i'} - E_i}. \tag{3.12}
\]

From Eqs. (3.10), (3.11) and (3.12), it is found that the relations

\[
\begin{align*}
\mu &= \alpha F, \\
\Delta E &= -(1/2) \alpha F^2, \tag{3.13}
\end{align*}
\]
actually holds.

§ 4. Polarizability of free electrons in one-dimensional box

In the present section, we calculate the polarizability of pi-electrons by applying the general formula (3·12). First of all, we simplify our system, that is, we substitute a square-well potential for the potential \(-V_{\text{p}}+\bar{V}_{\text{e}}\) in Eq. (3·3) and we regard our system as a one-dimensional one. We may assume that this simple system corresponds well to the system of pi-electrons in the chain of conjugated linear molecule.

In this case, the solutions of Eq. (3·6) are given by

\[ \phi_j(x) = (2/L)^{1/2} \sin(j\pi x/L), \]
\[ E_j = \left( \frac{\hbar^2}{2m} \right) \left( \frac{\pi}{L} \right)^2 j^2, \quad j = 1, 2, \ldots \]

(4·1)

where \( L \) represents the length of the one-dimensional well.

Using (4·1), we can calculate the matrix elements of the coordinate \( x \):

\[ \langle \phi_{\nu'}|x_i|\phi_{\nu} \rangle = x_i \left\{ -\frac{2L}{\pi^2} \left[ \frac{1}{\nu^2} - \frac{1}{(2\nu' + \nu)^2} \right] \right\} ; \nu = 1, 3, 5, \ldots \]
\[ = 0 \quad ; \nu = 2, 4, 6, \ldots \]

(4·2)

In the ground state, we assume that all the levels from the bottom to the Fermi maximum are occupied by two electrons. From the formula (4·2), it is found that \( x_1 \) decreases very rapidly with increasing \( \nu \). Furthermore, transitions to the occupied levels are prohibited. Therefore, it will be a good approximation to take into account only the two electrons in level \( n(=N/2) \) and neglect all \( \langle \phi_{\nu'}|x_i|\phi_{\nu} \rangle \) except \( \langle \phi_n|x_i|\phi_{n+1} \rangle \). As we assume \( n \gg 1 \), the matrix element \( x_1 \) given by Eq. (4·2) is reduced to

\[ x_1 = -\left( \frac{2L}{\pi^2} \right). \]

(4·3)

Using Eq. (4·1), we find

\[ E_{n+1} - E_n = (2A/n), \]

(4·4)

with

\[ A = \left( \frac{\hbar^2}{2m} \right) \left( \frac{\pi}{L} \right)^2 n^2. \]

(4·5)

The length \( L \) of the chain increases proportionally to \( N(=2n) \), \( N \) being the number of pi-electrons. Hence \( A \) is a constant independent of the molecular length.

By the use of Eqs. (3·12), (4·3) and (4·4), we obtain the polarizability of free electrons in the independent-particle model. Denoting the polarizability in this case by \( a_{\text{ind}}^0 \), we obtain

\[ a_{\text{ind}}^0 = \left( \frac{8}{\pi^3} \right) \left( \frac{\epsilon^2 L^2 n}{A} \right) \]
\[ = \left( \frac{256}{\pi^6} \right) d^4 n^3 a_0^3, \]

(4·6)
where $a_0$ represents the Bohr radius ($\hbar^2/me^2 = 0.52917 \cdot 10^{-8} \text{ cm}$) and $d (= L/Na_0)$ the mean C-C distance in the conjugated chain in atomic units.

For $d \approx 2.63$ a.u., which corresponds to $1.39 \text{ Å}$ and is the empirical length of C-C bond of comparatively short conjugated molecules, the polarizability (4·6) becomes

$$\alpha_{\text{ind}}^2 = 18.8 \cdot n^3 \cdot 10^{-26} \text{ cm}^2. \quad (4·7)$$

In Appendix II, we shall give a more precise calculation of $\alpha_{\text{ind}}^2$ by the use of Eq. (3·12) and will get

$$\alpha_{\text{ind}}^2 = (8/3\pi^2) d^4 n^3 a_0^8, \quad (4·6)'$$

which yields almost the same numerical results as those calculated by using Eq. (4·6).

In 1952 Davies calculated the polarizabilities of long chain molecules using the method of molecular orbitals and derived a formula for the pi-electron polarizabilities and showed that the polarizabilities for long chain molecules increase proportionally to the cube of the molecular length. Our formulae (4·6) or (4·6)' also show the same dependence on the molecular length. Numerical results based on Eq. (4·7) and the polarizabilities calculated by Davies will be given in Table II.

§ 5. Bond alternation and Brillouin gap

As for long polyenes, many theories have been proposed to discuss whether or not the configuration with alternating longer and shorter C-C bonds is stable. If the configuration with alternating bonds is more stable than the configuration with equal bonds, the results in the preceding section are not valid because the alternation generates a potential with a period of two bond lengths, which perturbs the free electron orbitals and introduces a Brillouin gap between the highest occupied level and the lowest unoccupied level.

In dealing with this phenomenon, we have to consider the local variations of electron density. First, we assume that $N$ unit positive charges are embedded in the pi-electron clouds in an equal spacing. These positive point charges represent the carbon cores in the conjugated chain. Local variations of electron density, if they exist, should generate a field which displaces these positive charges.

The potential energy of the unit positive charge is given by

$$U(a) = \int \rho(x) G(|x-a|) \, dx, \quad (5·1)$$
where \( a \) denotes the coordinate of the positive charge and \( \rho(x) \) represents the density of electrons and \( G(|x-a|) \) the potential function between positive and negative charges. We assume that \( G(u) \) becomes a constant \( G(0) \) in the region \( u<\delta \). Then \( U(a) \) becomes

\[
U(a) = U_1(a) - U_2(a) \\
= \int_{a-\delta}^{a+\delta} G(0) \rho(x) \, dx - \int_{|x-a|>\delta} G(|x-a|) \rho(x) \, dx \\
= 2\delta G(0) \rho(a) - U_2(a). \tag{5.2}
\]

The first term, \( U_1(a) \), represents a potential which depends on the local variations of density of \( \pi \)-electrons. The second term, \( U_2(a) \), represents a potential which depends on the mean density of \( \pi \)-electrons and is independent of the local variations of the density. Because \( G(0) \) is a negative quantity, \( U_1(a) \) is in inverse phase with the variation of density of \( \pi \)-electrons.

Let \( N(=2n) \) electrons be in a one-dimensional box of length \( L \). In the ground state, the density of electrons is given by

\[
\rho(x) = \sum_{j=1}^{2n} |\phi_j(x)|^2 \\
= \frac{2n}{L} \left( \frac{\sin((2n+1)\pi x/L)}{(\pi x/L)} - 1 \right). \tag{5.3}
\]

In the neighbourhood of the middle of the box, the local variations of density are approximately given by

\[
\rho(x) \approx -(1/L) \cos(n\pi x/L). \tag{5.4}
\]

The coordinates of positive charges are given by

\[
a = d(m-1/2), \text{ with } m=1, 2, \ldots N. \tag{5.5}
\]

Then maxima and minima of the electron density, as shown in Figure 1, are situated alternatively nearly in the middle points between neighbouring positive charges. According to the potential \( U_1 \), the positive charges are displaced and distances between neighbouring positive charges, which correspond to C-C bond lengths, increase or decrease alternatively. Namely, the bond alternation is generated.

Once the bond alternation is generated in the conjugated chain, however small it may be, it gives rise to a potential given by

\[
V(x) = V_0 \cos(2n\pi x/L). \tag{5.6}
\]

This potential is referred to as Kuhn's potential.\textsuperscript{10} Kuhn's potential perturbs the wave functions of \( \pi \)-electrons and the density of \( \pi \)-electrons varies. Using the free electron orbitals (4.1) as the zeroth approximation, we obtain the following matrix elements of Kuhn's potential:
\[ \int \phi_i(x) V(x) \phi_j(x) \, dx = \begin{cases} -(1/2) V_0, & \text{if } i + j = 2n, \\ + (1/2) V_0, & \text{if } |i - j| = 2n, \\ 0, & \text{otherwise}. \end{cases} \] (5.7)

Here we neglect the matrix elements which correspond to \( |i - j| = 2n \), because each of these matrix elements combines the two states separated far apart energetically. Then we get the perturbed orbitals \( \varphi_j \) and the perturbed orbital energies \( E_j' \) for \( j \neq n \) by solving

\[ \begin{vmatrix} E_{n-\nu} - E' & -V_0/2 \\ -V_0/2 & E_{n+\nu} - E' \end{vmatrix} = 0, \] (5.8)

with

\[ E_j = \langle \hbar^2/2m \rangle (\pi/L)^2 j^2 = A(j/n)^2, \]

where \( \nu \) denotes a positive integer and \( 1 \leq \nu \leq n - 1 \). The perturbed orbital energy \( E_j' \) is given by, for \( \nu \neq 0 \),

\[ E_{n}^{'} = \frac{1}{2} \left( E_{n+\nu} + E_{n-\nu} \right) + \left\{ \left( \frac{E_{n+\nu} - E_{n-\nu}}{2} \right)^2 + \left( \frac{V_0}{2} \right)^2 \right\}^{1/2}, \]

and for \( \nu = 0 \), we have

\[ E_{n}^{'} = E_n - (1/2) V_0 = A - (1/2) V_0. \] (5.10)

Now it is found that the Brillouin gap \( V_0 (\sim E_{n+1} - E_n) \) is yielded for large \( n \). Due to the Brillouin gap, \( \varphi_j \) becomes \( \varphi_j' \) which is given by, for \( \nu \neq 0 \),

\[ \varphi_{n-\nu}(x) = (1 + c_{\nu}^2)^{-1/2} \{ \phi_{n-\nu}(x) + c_{\nu} \phi_{n+\nu}(x) \}, \] (5.11)

\[ \varphi_{n+\nu}(x) = (1 + c_{\nu}^2)^{-1/2} \{ \phi_{n+\nu}(x) - c_{\nu} \phi_{n-\nu}(x) \}, \] (5.12)

respectively and, for \( \nu = 0 \),

\[ \varphi_n(x) = \phi_n(x), \] (5.13)

with

\[ c_{\nu} = \sqrt{1 + \beta_{\nu}^2 - \beta_{\nu}}, \] (5.14)

\[ \beta_{\nu} = \frac{E_{n+\nu} - E_{n-\nu}}{V_0} = \left( \frac{4A}{V_0} \right) \left( \frac{\nu}{n} \right). \] (5.15)

In the ground state, \( \varphi_n \) and \( \varphi_{n-\nu} \) represent the occupied orbitals and \( \varphi_{n+\nu} \) represent the vacant orbitals.

From Eqs. (5.11) and (5.12), we can estimate the variations of the free electron orbitals \( \phi_j \) due to Kuhn's potential. At the positions, which corres-
pond to the middle points of C-C bonds in the conjugated chain whose coordinates are

\[ x = md, \] with \( d = L/N \) and \( m = 1, 2, \cdots (2n-1), \)

the eigenfunction \( \varphi_{n \pm \nu} \) is given by

\[ \varphi_{n \pm \nu}(md) = \varphi_{n \nu}(md) \{1 \pm (-1)^m c_n\} (1 + c_n^2)^{-1/2}. \] (5·16)

From Eq. (5·16), it is found that the amplitude of every occupied orbital increases for even \( m \) and decreases for odd \( m \) by the presence of Kuhn’s potential. Hence the local variations of electron density increase with the amplitude of Kuhn’s potential.

On the other hand, sum of the orbital energies of occupied levels decreases by the amount

\[ \sum_{\nu=0}^{n-1} (E_{n-\nu} - E_{n-\nu}) = \frac{1}{2} \sum_{\nu=0}^{n-1} \left(4A \frac{\nu}{n}\right)^2 + V_0^2 \left(\frac{2A}{n}\right) \sum_{\nu=0}^{n-1} \nu. \] (5·17)

If \( n \) is large, we may approximate the summation in Eq. (5·17) by integration. Then Eq. (5·17) becomes

\[ nA \left(\sqrt{1 + \gamma^3} - 1 + \gamma \log \frac{1 + \sqrt{1 + \gamma^3}}{\gamma}\right), \] (5·18)

with

\[ \gamma = V_0/4A. \]

If \( V_0 \) is small, (5·18) is proportional to \( V_0^2 (-\log \gamma) \).

Now it is found that the bond alternation will be generated in the following fashion: First we assume that there is a small bond alternation in the conjugated chain due to the local variations of electron density. This small bond alternation generates a small Kuhn’s potential. This Kuhn’s potential diminishes the sum of orbital energies of electrons and at the same time increases the local variations of electron density. This increased local variations of electron density generate the larger bond alternation. This feed-back mechanism makes the bond alternation larger and larger until the energy gain will be balanced by the energy loss of sigma-bonds which connect the neighbouring carbon cores quasi-elastically. Both the energy gain and the energy loss increase proportionally to the number of C-C bonds. Hence the magnitude of the bond alternation for long chain molecules will approach a definite value independent of the chain length.

If there are odd carbon atoms in the chain, the situation is completely different. In this case, carbon cores are situated on the positions corresponding to the maxima or the minima of the electron density. From Eq. (5·2), it is found that carbon cores do not receive any forces due to the local variations of electron density. Hence the feed-back mechanism does not appear and the bond alter-
Now it is found that the bond alternation occurs for the chain molecules with even carbon atoms, which correspond to polyenes or carotenoids, and the alternation does not occur for the molecules with odd carbon atoms, which correspond to cyanines or polymethine dyes. Then as for polyenes, we should take into account the Brillouin gap.

§ 6. Polarizability with Brillouin gap

In this section, we shall investigate the polarizability in the presence of Brillouin gap. In this case, we must calculate the polarizability using the perturbed orbitals \( \varphi_j \) given by Eqs. (5·11) and (5·12) in place of the free electron orbitals \( \phi_j \). Then we have

\[
\langle \varphi_n | x | \varphi_{n+1} \rangle^2 = \left( 1 - \frac{1}{\sqrt{1 + \beta_1^2}} \right) x_1^2, \tag{6·1}
\]

\[
\langle \varphi_{n+(\pm 1)} | x | \varphi_{n-\mu} \rangle^2 = \frac{1}{1 + c_\mu^2} \cdot \frac{1}{1 + c_{\mu \pm 1}^2} \cdot (c_\mu - c_{\mu \pm 1})^2 \cdot x_1^2, \tag{6·2}
\]

where \( x_1 \) represents the matrix element given by (4·3), and \( c_\mu \) and \( \beta_1 \) are given by Eqs. (5·14) and (5·15) respectively and \( \mu \) represents a positive integer. Because the matrix elements (6·2) do not vanish in our approximation, we cannot neglect the excitations of electrons lying in the lower levels.

Using the approximate relation

\[
c_{\mu \pm 1} - c_\mu \sim \pm \frac{d c_\mu}{d \mu} = \mp c_\mu \sqrt{1 + \mu^2 \beta^2}, \tag{6·3}
\]

matrix element (6·2) is reduced to

\[
\langle \varphi_{n+(\pm 1)} | x | \varphi_{n-\mu} \rangle^2 = \frac{c_\mu}{1 + c_\mu^2} \cdot \frac{c_{\mu \pm 1}}{1 + c_{\mu \pm 1}^2} \cdot \frac{\beta^2}{1 + \mu^2 \beta^2} \cdot x_1^2
\]

\[
= \frac{1}{4} \frac{\beta^2}{(1 + \mu^2 \beta^2)^2} x_1^2. \tag{6·4}
\]

We neglect \( x_1 \) given by Eq. (4·2) except for \( x_1 \) and we assume that every \( (E_{n+r} - E_n) \) is approximately equal to \( (E_{n+1} - E_n) \). From Eqs. (3·12), (6·1) and (6·4), we then obtain for the polarizability with Brillouin gap in the independent-particle approximation:

\[\text{...}\]

\(^{*)\text{It has been pointed out by Ooshika}^{211}\text{and others}^{12},^{19},^{22}\text{that in the infinitely long chain molecule the configuration in which the C-C bonds are alternatively long and short is the stable one even in the case of the chain molecule including odd carbon atoms. But for the dye molecules being of the finite length that are dealt with in the present paper, the discussions mentioned in this section are fruitful.}\]
\[ \alpha_{\text{ind}} = \frac{2e^2 x_1^2}{E_{n+1} - E_n} \left( 1 - \frac{1}{\sqrt{1 + \beta^2}} + \frac{1}{2} \sum_{r=1}^{n-1} \frac{1}{r(1 + r^2 \beta^2)} \right) \] (6.5)

with

\[ E_{n+1} - E_n = \frac{A}{n^2} + \frac{1}{2} \left[ V_0 + \left( \frac{4A}{n} \right)^2 \right]^{1/n} \]
\[ = \frac{V_0}{2} \left( \frac{\beta}{2n} + 1 + \sqrt{1 + \beta^2} \right). \] (6.6)

In place of the finite summation in Eq. (6.5), we may use the following infinite series without causing a serious error:

\[ \frac{1}{(1 + \beta^2)^2} + \frac{1}{(1 + 2\beta^2)^2} + \frac{1}{(1 + 3\beta^2)^2} + \cdots \]
\[ = \frac{\pi}{2\beta} \left( \frac{1}{2} \coth \left( \frac{\pi}{\beta} \right) + \left( \frac{\pi}{\beta} \right) \frac{1}{\cosh (2\pi/\beta) - 1} - \frac{\beta}{\pi} \right). \] (6.7)

On the other hand, \( (E'_{n+1} - E'_n) \) is given by Eq. (6.6) and \( (E_{n+1} - E_n) \) is by

\[ E_{n+1} - E_n = \left( \frac{A}{n^2} - \frac{2A}{n} \right) \]
\[ = \left( \frac{V_0}{2} \right) \left( \frac{\beta}{2n} + \beta \right), \]

hence we get

\[ \frac{E'_{n+1} - E'_n}{E_{n+1} - E_n} \sim \frac{1}{\beta} \left( 1 + \sqrt{1 + \beta^2} \right). \] (6.8)

Then the polarizability (6.5) is reduced to

\[ \alpha_{\text{ind}} = \alpha'_{\text{ind}} \frac{\beta}{1 + \sqrt{1 + \beta^2}} F(\beta), \] (6.9)

where \( \alpha'_{\text{ind}} \) represents the polarizability without Brillouin gap which is given by Eq. (4.6), while the function \( F(\beta) \) is defined by

\[ F(\beta) = 1 - \frac{1}{\sqrt{1 + \beta^2}} + \frac{\pi \beta}{4} \left[ \frac{1}{2} \coth \left( \frac{\pi}{\beta} \right) + \frac{(\pi/\beta)}{\cosh (2\pi/\beta) - 1} - \frac{\beta}{\pi} \right]. \] (6.10)

Numerical values of \( F(\beta) \) are given in Table I.

If \( \beta \) approaches zero, that is, the length of the chain is sufficiently long, the infinite series (6.7) approaches \( (\pi/4\beta) \). In this case, the polarizability (6.9) becomes

\[ \alpha_{\text{ind}} = \alpha'_{\text{ind}} (\pi/16) \beta^2 = (4\hbar e^2 / m n V_0^2) \cdot n. \] (6.11)

From Eq. (6.11), it is found that the polarizability increases proportionally to the length of the chain. In this case, we can consider that our system corresponds to a dielectric. On the contrary, when there is no Brillouin gap, the
Table I. Table of $F(\beta)$ given by Eq. (6.10).

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$F(\beta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0417</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0880</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1886</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2881</td>
</tr>
<tr>
<td>0.8</td>
<td>0.3754</td>
</tr>
<tr>
<td>1.0</td>
<td>0.4463</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6421</td>
</tr>
<tr>
<td>4.0</td>
<td>0.7877</td>
</tr>
<tr>
<td>6.0</td>
<td>0.8497</td>
</tr>
<tr>
<td>8.0</td>
<td>0.8847</td>
</tr>
<tr>
<td>10.0</td>
<td>0.9060</td>
</tr>
</tbody>
</table>

Polarizability increases proportionally to the cube of the chain length as shown in § 4, hence we cannot consider the system to be a dielectric.

If $\beta$ is large, that is, $V_0$ is small and the length of chain is not so long, the infinite series (6.7) approaches $(1/90) (\pi/\beta)^4$, hence we can neglect it. Then we obtain the polarizability

$$\alpha_{\text{ind}} = \alpha_{\text{ind}}^0 \left(1 - \frac{1}{\beta} \right)^2.$$  (6.12)

Polarizabilities calculated by Eq. (6.9) are given in Table II. Our formula (6.9) is not exact for short molecules, hence our result for short molecules, in Table II merely gives a rough estimate.

Table II. Polarizabilities based on the method of the independent-particle approximation in units of $10^{-26}$ cm$^3$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>n</th>
<th>$\alpha_{\text{ind}}^0 (V_0=0)$</th>
<th>$\alpha_{\text{ind}} (V_0=1.8\text{eV})$</th>
<th>Davies' results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>1</td>
<td>19</td>
<td>16</td>
<td>35</td>
</tr>
<tr>
<td>Butadiene</td>
<td>2</td>
<td>150</td>
<td>115</td>
<td>205</td>
</tr>
<tr>
<td>Hexatriene</td>
<td>3</td>
<td>507</td>
<td>296</td>
<td>600</td>
</tr>
<tr>
<td>Decapentaene</td>
<td>5</td>
<td>2350</td>
<td>990</td>
<td>2420</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>18800</td>
<td>3860</td>
<td>17200</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>63400</td>
<td>6970</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>150000</td>
<td>9900</td>
<td></td>
</tr>
</tbody>
</table>

§ 7. Classical polarizability of the spheroid and its quantum theoretical interpretation

So far we have calculated the polarizability by means of the independent-particle approximation. As was mentioned before, this approximation is too rough because the correlation of electrons is totally neglected. We shall now proceed to another approximation in which the correlation is, at least partly, taken into account. This is the classical treatment of the problem. In this section, we shall also discuss the relation between this method and the quantum theoretical equivalent. The fact that this approximation includes the correlation will be made clear in § 9.

The classical polarizability of dielectric spheroid is well known in electromagnetism. Let the longer semiprincipal axis of the spheroid and the shorter one be denoted by $a$ and $b$, respectively. Then the long axis component of polarizability of dielectric spheroid of permittivity $\varepsilon_1$, which is embedded in homogeneous dielectrics of permittivity $\varepsilon_2$, is given by
\[ \alpha_e = \frac{(ab^3/3) (\varepsilon_1 - 1)}{1 + (\mathcal{L}/4\pi) (\varepsilon_1 - 1)} , \]  

(7.1)

where \( \mathcal{L} \) represents the depolarizing factor and is given by

\[ \mathcal{L} = 4\pi \frac{1}{\varepsilon_2} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 - 1} A(x) , \]  

(7.2)

with \( x = (a/b) \). The function \( A(x) \) is given by

\[ A(x) = \frac{1}{x^3 - 1} \left( \frac{1}{2} \frac{x}{\sqrt{x^2 - 1}} \log \left( \frac{x + \sqrt{x^2 - 1}}{x - \sqrt{x^2 - 1}} \right) - 1 \right) . \]  

(7.3)

If \( x = 1, A(1) = 1/3, \) and if \( x \gg 1 \)

\[ A(x) \sim \log x - 0.30685 \frac{\log x}{x^3 - 1} . \]  

(7.4)

Numerical table of \( A(x) \) is given in Table III. If the spheroid is a conductor, we get the polarizability by regarding \( \varepsilon_1 \) in Eq. (7.1) as infinite. In this case, the polarizability (7.1) is reduced to

\[ \alpha_e = V / \mathcal{L} = V\varepsilon_2 / 4\pi A(x) , \]  

(7.5)

where \( V \) represents the volume of the spheroid \((4\pi/3)ab^3\).

If \( x \gg 1, \) or the axis \( a \) is sufficiently larger than the axis \( b, \) the polarizability (7.5) becomes

\[ \alpha_e = \varepsilon_2 \frac{a^3}{3 \log a} . \]  

(7.5')

From Eq. (7.1), it is found that, if we neglect the depolarizing factor \( \mathcal{L}, \) \( \alpha_e \) is represented by \( (ab^3/3) (\varepsilon_1 - 1) \). We now assume that, in case we neglect \( \mathcal{L}, \) the polarizability will be represented by \( \alpha_{\text{ind}} \) given by Eq. (6.9). That is, we assume

\[ (ab^3/3) (\varepsilon_1 - 1) = \alpha_{\text{ind}} , \]  

(7.6)

and rewrite Eq. (7.1) as

\[ \alpha_e = \frac{\alpha_{\text{ind}}}{1 + (\mathcal{L}/V) \alpha_{\text{ind}}} . \]  

(7.7)

The true meaning and the justification of this procedure will be given in the last part of this section; here we only point out the fact that so far as free electrons are concerned our assumption is quite conceivable, because in this case \( \alpha_{\text{ind}} \) becomes \( \alpha_{\text{ind}}^0 \) given by Eq. (4.6) and the latter increases proportionally to \( a^3 \). Inserting \( \alpha_{\text{ind}} \) into Eq. (7.7), we get Eq. (7.5') for large \( a. \)

If \( a \) approaches infinity, \( \alpha_{\text{ind}} \) will be represented by Eq. (6.11). Using the
relation \( (7 \cdot 6) \), we get the following relation between the permittivity and the Brillouin gap \( V_0 \):

\[
\varepsilon_1 - 1 = \frac{(12h^2e^2/m\pi V_0^2d)^2}{(12h^2e^2/m\pi V_0^2d^2)^2}.
\]

(7.6)

In obtaining this formula, we have assumed that \( L = 2a = 2nd \), where \( d \) represents the mean C-C distance. For example, in case \( d = 1.39 \text{ Å}, V_0 = 1 \text{ eV} \) and \( d = b \), \( \varepsilon_1 \) becomes 157. Polarizabilities given by Eq. \( (7 \cdot 7) \) are given in Table IV and Figure 2.

Table IV. Classical polarizabilities \( (7, 7) \) in units of \( 10^{-25} \text{ cm}^3 \). (Depolarizing factor is calculated by assuming \( b = 2d \).)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( V/L ) *</th>
<th>( \sigma_0(V_0=0) )</th>
<th>( \sigma_0(V_0=1.8 \text{ eV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>403</td>
<td>109</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>864</td>
<td>320</td>
<td>220</td>
</tr>
<tr>
<td>5</td>
<td>2520</td>
<td>1220</td>
<td>710</td>
</tr>
<tr>
<td>10</td>
<td>10000</td>
<td>7340</td>
<td>2920</td>
</tr>
<tr>
<td>15</td>
<td>32200</td>
<td>21400</td>
<td>5730</td>
</tr>
<tr>
<td>20</td>
<td>66200</td>
<td>46000</td>
<td>8610</td>
</tr>
</tbody>
</table>

* Values in this column correspond to the classical polarizabilities for conductive spheroid with \( a = nd \) and \( b = 2d \). See Eq. \( (7.5) \).

The meaning of Eq. \( (7 \cdot 7) \) is as follows: When a dielectric spheroid polarizes, the depolarizing field \( -LP \) will appear in the spheroid. \( L \) represents the depolarizing factor and \( P \) represents the polarization of unit volume of the spheroid. In the case of spheroid, the polarization is homogeneous, hence we have

\[
P = \frac{\mu}{V} = \frac{1}{V} eN\xi,
\]

(7.8)

where \( \mu \) represents the dipole moment induced by the external field and \( \xi \) represents the collective coordinate defined by Eq. \( (2 \cdot 2) \). Then we get for the energy due to the depolarization

\[
\frac{1}{2} \mu \cdot LP = \frac{1}{2} e^2N^2 \left( \frac{L}{V} \right) \xi^2.
\]

(7.9)

The potential energy for our collective motion in Eq. \( (2 \cdot 9) \) which has been given by Eq. \( (2 \cdot 21) \), i.e.
must be corrected for depolarization. That is, we have
\[ \frac{1}{2} \frac{e^2 N^2}{\alpha_{\text{ind}}} \]

where \( \alpha_e \) represents the corrected polarizability or the classical polarizability. From this formula, we find
\[ \frac{1}{\alpha_e} = \frac{1}{\alpha_{\text{ind}}} + \frac{F}{V}. \]

From Eq. (7.11), we obtain the formula (7.7).

We now proceed to the justification of our procedure quantum theoretically. To this end we recall that in § 3 we have drawn a distinction between the independent-particle approximation and the Hartree approximation. The distinctions are as follows: (a) In the independent-particle approximation we have considered \(-V^p + V^c\) to be the given external field and the sum of orbital energies of electrons, i.e.
\[ E = \sum_i E_{\nu} \]
gives the total energy. But according to the Hartree approximation, the true energy \( W \) is not given by \( E \) but is given by
\[ W = \sum_i E_{\nu} - \frac{e}{2} \sum_i \langle \phi_{\nu} (x_i) | \vec{V}_i^\prime (x_i) | \phi_{\nu} (x_i) \rangle. \]

(b) The external field \( F \) displaces the electron. Accordingly, \( V^p \) will be affected by \( F \) in the proper Hartree approximation.

We begin with the considerations of (b). In case of zero electric field, the Hamiltonian in the Hartree approximation is as well given by
\[ \vec{H} = \sum_i \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} - eV^p (x_i) + e\vec{V}_i^\prime (x_i) \right\} = \sum_i \vec{H}_i. \]

But in case we introduce the system into an external field \( F \), we have to use
\[ \vec{H}' = \sum_i \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} - eV^p (x_i) + e\vec{V}_i'' (x_i) - eFx_i \right\} = \sum_i \vec{H}_i', \]
with
\[ \vec{V}_i^\prime (x) = e \sum_{j \neq i} \int G(x, x') \rho_j (x') \, dx', \]
\[ \vec{V}_i'' (x) = e \sum_{j \neq i} \int G(x, x') \rho_j' (x') \, dx', \]
where \( \rho_j' \) represents the density of electrons which has been displaced by \( F \).
Then \( \overline{H}_i' \) in Eq. (7.14) is reduced to

\[
\overline{H}_i' = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} - eV^p(x_i) + e\overline{V}_i^e(x_i) - e\{ \overline{V}_i^e(x_i) - \overline{V}_i''(x_i) \} - eFx_i.
\]

(7.17)

From Eqs. (7.15) and (7.16), we find

\[
\overline{V}_i^e(x) - \overline{V}_i''(x) = \int G(x, x') \{ \sum_{j \neq i} \rho_j(x') + \sum_j \rho_j'(x') \} dx'.
\]

(7.18)

The difference between \( \rho_j \) and \( \rho_j' \) has the order of magnitude of the external field \( F \). Hence the difference of the fields given by Eq. (7.18) is also of the order of magnitude of \( F \) and we cannot neglect the difference. Accordingly, the treatment without the considerations of the field (7.18) is not correct. Now \( \sum \rho_j \) represents the density in the case of zero field and almost cancels the positive charges. But \( \sum \rho_j' \) represents the displaced density and cannot cancel the positive charges any longer. Then positive and negative charges will appear at the both ends of the molecule and Eq. (7.18) represents the field due to these charges. If we assume that the molecule has a spheroidal form, this field is just the depolarizing field which has been mentioned already. The depolarizing field for homogeneous polarization is given by

\[
-\mathcal{L}P = -\mathcal{L}(\mu/V),
\]

(7.19)

where \( \mathcal{L} \) represents the depolarizing factor for the system and \( \mu \) represents the dipole moment induced by the external field \( F \). Since it is anticipated that the induced moment is proportional to \( F \), we put

\[
\mu = \alpha_e F,
\]

(7.20)

with the yet unknown polarizability \( \alpha_e \).

The unknown \( \alpha_e \) is determined in the following manner: From Eqs. (7.19) and (7.20), the depolarizing potential is written as

\[
-\left( \frac{\mathcal{L}}{V} \right) \alpha_e F \sum_i x_i.
\]

(7.21)

Then we can use the potential (7.21) for the right-hand side of Eq. (7.18), that is, we can put

\[
\sum_i \{ \overline{V}_i^e(x_i) - \overline{V}_i''(x_i) \} = -\left( \frac{\mathcal{L}}{V} \right) \alpha_e F \sum_i x_i.
\]

(7.22)

Then \( \overline{H}_i' \) in the Hamiltonian (7.17) becomes

\[
\overline{H}_i' = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} - eV^p(x_i) + e\overline{V}_i^e(x_i) - e\left( 1 - \frac{\mathcal{L}}{V} \right) \alpha_e Fx_i.
\]

(7.23)

Comparing this Hamiltonian with the Hamiltonian (3.8), we see that the per-
turbing term $-eF \xi_t$ in the Hamiltonian (3.8) has been replaced by $-e \{1 - (L/V) \alpha_e \} F \xi_t$. Accordingly the polarization in our case is given by

$$\mu = \alpha_{\text{ind}} \left( 1 - \frac{L}{V} \alpha_e \right) F,$$

(7.24)

and

$$\Delta E = - \frac{1}{2} \alpha_{\text{ind}} \left( 1 - \frac{L}{V} \alpha_e \right)^2 F,$$

(7.24)'

by simply replacing $F$ in Eq. (3.13) by $\{1 - (L/V) \alpha_e \} F$. In Eqs. (7.24) and (7.24) ', we have used $\alpha_{\text{ind}}$ in place of $\alpha$, because $\alpha$ in Eq. (3.13) represents the polarizability which is calculated by the method of independent-particle approximation. Now, combining the formula (7.24) and the relation (7.20), we can determine $\alpha_e$ by

$$\alpha_e = \alpha_{\text{ind}} \left( 1 - \frac{L}{V} \alpha_e \right).$$

(7.25)

From Eq. (7.25), we obtain the formula (7.7). Thus the quantum theoretical justification of our procedure has been established.

Using Eq. (7.25), we find

$$\mu = \alpha_e F,$$

(7.26)

$$\Delta E = - \frac{1}{2} \alpha_e \left( 1 - \frac{L}{V} \alpha_e \right) F^2.$$

(7.26)'

From Eq. (7.26)', it is found that $\Delta E$ is not equal to $-(1/2) \alpha_e F^2$. This discrepancy is due to the situation mentioned in (a): that the energy $E$ calculated by Eq. (3.7) does not correspond to the true energy $W$. Now we must calculate the true energy $W$ by applying Eq. (7.12):

When we introduce the system into the electric field $F$, the true energy $W$ (7.12) becomes $W'$ given by

$$W' = E' - \frac{e}{2} \sum_i \langle \phi_{\nu} \psi_\xi (x_i) | \bar{\psi}_{\nu} \psi_\xi (x_i) | \phi_{\nu} \psi_\xi (x_i) \rangle,$$

(7.27)

with

$$E' = E + \Delta E,$$

(7.28)

where $\Delta E$, $\phi_{\nu} (x_i)$ and $\bar{\psi}_{\nu} (x_i)$ are given by Eqs. (7.26), (3.9) and (7.16) respectively. The second term in Eq. (7.27) is rewritten as

$$\langle \phi_{\nu} \psi_\xi (x_i) | \bar{\psi}_{\nu} \psi_\xi (x_i) | \phi_{\nu} \psi_\xi (x_i) \rangle$$

$$= \langle \phi_{\nu} | \bar{\psi}_{\nu} \psi_\xi | \phi_{\nu} \rangle$$

$$+ \langle \phi_{\nu} | - \bar{\psi}_{\nu} \psi_\xi | \phi_{\nu} \rangle + \langle \phi_{\nu} | \bar{\psi}_{\nu} - \phi_{\nu} | \bar{\psi}_{\nu} | \phi_{\nu} \rangle + \langle \phi_{\nu} | \bar{\psi}_{\nu} | \phi_{\nu} \rangle$$
where the first term represents the correction term in the case of zero field and the terms in the second and the fourth lines vanish because they are products of even and odd functions. Terms that we must calculate are the two terms in the third line. Using the wave functions (3.9), in which $F$ is replaced by $\{1-(L/V)\alpha_x\}F$, we find

$\phi_u' - \phi_u = e\left(1 - \frac{L}{V} \alpha_x\right) F \sum_{\nu} \frac{\langle \phi_{\nu u}(x_i) | x_i | \phi_u(x_i) \rangle}{E_{\nu u} - E_u} \phi_{\nu u}(x_i)$.

Using Eq. (7.22), we get

$\overline{V}_t - \overline{V}_t'' = - \frac{L}{V} \alpha_x F x_i$.

Then Eq. (7.29) is reduced to

$\langle \phi_u' | \overline{V}_t | \phi_u \rangle - \langle \phi_u | \overline{V}_t'' | \phi_u \rangle = - \langle \phi_u | \overline{V}_t - \overline{V}_t'' | \phi_u \rangle - \langle \phi_u' - \phi_u | \overline{V}_t - \overline{V}_t'' | \phi_u \rangle$

$= 2e\left(1 - \frac{L}{V} \alpha_x\right) \frac{L}{V} \alpha_x F \sum_{\nu} \frac{\langle \phi_{\nu u}(x_i) | x_i | \phi_u(x_i) \rangle \langle \phi_{\nu u}(x_i) | \phi_u \rangle}{E_{\nu u} - E_u} \frac{\alpha_{\text{ind}}}{2e^2}$

$= \frac{1}{e} \frac{L}{V} \alpha_x^2 F^2$.

In obtaining the above results, we have used Eq. (7.25). The true energy $W'$, (7.27), then becomes

$W' = E - \frac{1}{2} \alpha_x \left(1 - \frac{L}{V} \alpha_x\right) F^2 - \frac{e}{2} \langle \phi_u | \overline{V}_t | \phi_u \rangle - \frac{1}{2} \frac{L}{V} \alpha_x^2 F^2$

$= W - \frac{1}{2} \alpha_x F^2$.

Thus we obtain the correct result:

$$\begin{cases} 
\mu = \alpha_x F, \\
\Delta W = W' - W = - (1/2) \alpha_x F^2.
\end{cases} \quad (7.30)$$

In both of the classical and the Hartree approximations, the correlation of electrons are, at least partly, taken into account through the depolarizing field.
because the displacement of electrons at one place is affected by the displacement of other places through this field. In § 9, we shall make this point more clear by showing that our method just corresponds to the method of configurational mixing.

§ 8. Application to absorption wavelengths of conjugated chain molecules

Applying the formula (2·22) and the polarizabilities given in the preceding sections, we can obtain the frequency of our collective oscillation. We consider that the absorption of light of conjugated chain molecule corresponds to the excitation of the fundamental oscillation of our collective motion. We then get for the absorption wavelength

\[ \lambda = \frac{2\pi c}{\omega} = \frac{2\pi a_0}{s} \left( \frac{\alpha/a_0^3}{2n} \right)^{1/2} \]

\[ = 455.6 \left( \frac{\alpha/a_0^3}{2n} \right)^{1/2} \text{ Ångstrom}, \tag{8·1} \]

where \( a_0 \) is the Bohr radius and \( s \) the fine structure constant (\( = e^2/\hbar c \)) and \( \alpha \) the polarizability of the molecule.

First of all, we shall examine the frequency of the collective oscillation using the polarizabilities based on the method of the independent-particle approximation. Using \( \alpha_{\text{ind}}^2 \) given by Eq. (4·6), we get the frequency of oscillation for free electrons:

\[ \omega_{\text{ind}} = \left( \frac{N \pi^2}{m a_0^3} \right)^{1/2} = \left( \frac{N \cdot \pi^4}{8} \cdot \frac{A}{nL^3} \right)^{1/2}. \tag{8·2} \]

The excitation energy then becomes

\[ \hbar \omega_{\text{ind}} = \left( \frac{\hbar^2}{2m} \cdot \frac{\pi^2}{L^2} \cdot \frac{2n}{8} \right)^{1/2} \]

\[ = (E_{n+1} - E_n) (\pi^2/8)^{1/2} \simeq E_{n+1} - E_n, \tag{8·3} \]

where \( (E_{n+1} - E_n) \) is given by Eq. (4·4).

In the case where the Brillouin gap is present, we must substitute \( \alpha_{\text{ind}} \) given by Eq. (6·9) for \( \alpha_{\text{ind}}^2 \) in Eq. (8·2). When \( \beta \) is large or the Brillouin gap \( V_0 \) is small, we use the polarizability (6·12) and we find

\[ \hbar \omega_{\text{ind}} = \hbar \left( \frac{N e^3}{m a_{\text{ind}}^3} \right)^{1/2} \simeq E'_{n+1} - E'_n, \tag{8·4} \]

where \( (E'_{n+1} - E'_n) \) is given by Eq. (6·6). When \( \beta \) in (6·3) is small or the length of the chain is large, we use the polarizability (6·11) and we find

\[ \hbar \omega_{\text{ind}} = (\pi/2)^{1/2} V_0 \simeq V_0. \tag{8·5} \]
Here we notice that, according to the method of simple one-electron approximation in which we neglect the Coulomb interactions between electrons, the difference in energy between the lowest unoccupied \((n+1)\)-th level and the highest occupied \(n\)-th level corresponds to the excitation energy of the system. Namely, from Eqs. (8·3), (8·4) and (8·5), it is found that the excitation energy for our collective motion based on the method of the independent-particle approximation is equal to the excitation energy calculated by the method of simple one-electron approximation.

In order to obtain a closer approximation, we must use the classical polarizability \(a_c\) given by Eq. (7·7). In the case of free electrons, using Eqs. (4·6), (7·7) and (8·1), we obtain the absorption wavelength:

\[
\lambda = 166 \, d^2 \left[ 1 + \frac{3}{\varepsilon_\delta} \left( \frac{256}{\pi^2} \frac{n^2}{\delta^2} \cdot A \left( \frac{n}{\delta} \right) \right) \right]^{-1/2} \text{Å}, \tag{8·6}
\]

where \(\delta = (b/d)\). If the C-C distance \(d\) is 1.39Å, Eq. (8·6) becomes

\[
\lambda = 1147 \, n \left[ 1 + \frac{2.1}{\varepsilon_\delta} \frac{n^2}{\delta^2} \cdot A \left( \frac{n}{\delta} \right) \right]^{-1/2} \text{Å}. \tag{8·7}
\]

When the length of the chain becomes very large, that is, \(n \gg 1\), we have

\[
\lambda = \delta \sqrt{\varepsilon_\delta} \frac{792}{\sqrt{\log \left( n/\delta \right)}} \text{Å}. \tag{8·8}
\]

We consider that \(\sqrt{\varepsilon_\delta}\) represents the refractive index of the solvent, hence the magnitude of \(\sqrt{\varepsilon_\delta}\) will be about 1.4. Consequently, it is found from Eqs. (8·7) and (8·8) that, if \(\delta \sim 2\), the wavelength \(\lambda\) will increase about 1000Å for every additional \(n\). As shown in §5, the bond alternation does not occur for cyanines or polymethine dyes which contain the odd number of carbon atoms in the chain. Accordingly, we can use formulae (8·7) and (8·8) as the wavelength-formula of absorption for cyanines or polymethine dyes. We have thus obtained the conclusion (a) given by Platt.

As for long chain molecules, Mizuno and Izuyama\(^9\) have calculated the absorption wavelength according to the method of Tomonaga's sound waves\(^20\) and have shown that the absorption wavelength increases proportionally to \(L/\sqrt{\log L}\), where \(L\) represents the length of the conjugated chain. Their method is different from ours but the result is similar to ours.\(^1\)

\(^1\) In our previous paper on the carotenoids,\(^4\) we have expanded the Coulomb potential in one-dimensional space and obtained

\[
\left( e^2 \right)_{|x_i-x_j|} = \frac{L e^2}{\pi \delta} \sum_{\nu} \frac{1}{\nu} \exp \left[ i(2\pi/L)\nu|x_i-x_j| \right],
\]

where \(L\) represents the length of the space and \(\bar{A}\) represents a quantity which is referred to as the sectional area. According to the calculation in the present paper, \(\bar{A}\) is a function of \(L\) and \(R\) and is given by (continued on next page)
In the case of actually existing cyanines or polymethine dyes, various organic nuclei are combined with both ends of the conjugated chain. Conclusions (b) and (c) in § 1 are concerned with the dependence of the absorption wavelength upon the end nuclei. In order to explain conclusions (b) and (c), we must add some assumptions to our theory.

Because the energy necessary to displace the electrons is inversely proportional to the polarizability, we assume that the polarizability of an unsymmetrical dye with end nuclei $A$ and $B$, which is denoted by $\alpha(A, B)$, is given by

$$\frac{1}{\alpha(A, B)} = \frac{1}{2} \left( \frac{1}{\alpha(A)} + \frac{1}{\alpha(B)} \right), \quad (8.9)$$

where $\alpha(A)$ or $\alpha(B)$ represents the polarizability for the symmetric parent dye with the same end nuclei $A$ or $B$ respectively. We then get for the absorption wavelength

$$\frac{1}{\lambda(A, B)^2} = \frac{1}{2} \left( \frac{1}{\lambda(A)^2} + \frac{1}{\lambda(B)^2} \right).$$

If the difference in wavelength between $\lambda(A)$, $\lambda(B)$ and $\lambda(A, B)$ are small, we obtain

$$\lambda(A, B) = \frac{1}{2} \left( \lambda(A) + \lambda(B) \right) - \frac{3}{4} \left( \frac{\lambda(A) - \lambda(B)}{\lambda(A) + \lambda(B)} \right)^{\frac{3}{2}}. \quad (8.10)$$

The first term in Eq. (8.10) represents the conclusion (b) in § 1 and the second term, which corresponds to the Brooker deviation, represents the conclusion (c). Experimental results on the Brooker deviation cannot be described in detail by such a simple formula but the deviation given by Eq. (8.10) agrees qualitatively with the empirical results.

$$A = \frac{\pi R^2}{1 - 2I_1(kR) K_1(kR)},$$

where $k = 2\pi/L$ and other quantities are the same as used in Eq. (9.28). In the previous paper we have assumed that $A$ is a constant. This assumption implies that the radius $R$ is a function of $k$. If $Rk \ll 1$ or the length of our system becomes large, we have

$$1 - 2I_1(kR) K_1(kR) \approx Rk^2 \left\{ \frac{1}{8} - \frac{1}{2} (\tau + \log \frac{Rk}{2}) \right\}$$

$$\approx -\frac{1}{2} Rk^2 \log \frac{Rk}{2},$$

where $\tau$ represents the Euler's constant ($=0.57721\ldots$). If $R$ is given by

$$R = \frac{2}{k} \exp\{-(2\pi/A_0) (1/k^2)\},$$

the effective area $A$ becomes a constant $A_0$ for small $k$. If $R$ is a constant, we have the same result as the one given by Mizuno and Izuyama.9
As for polyenes, such as carotenoids, which contain even carbon atoms in the conjugated chain, we must take into account the Brillouin gap as mentioned in §5. Hence we must use the polarizability $a_{\text{ind}}$ given by Eq. (6.9). Usually we have $\varepsilon_1 \gg \varepsilon_2$. Then the depolarizing factor is given by

$$L = \frac{1}{\varepsilon_2} \frac{4\pi A(x)}{V}, \text{ with } x = a/b,$$

(8.11)

where $\varepsilon_2$ represents the permittivity of solvent and $A(x)$ represents the function given by Eq. (7.3). Using Eq. (7.11), we obtain

$$\frac{1}{\alpha_c} = \frac{1}{\alpha_{\text{ind}}} + \frac{4\pi}{V} \frac{A(x)}{\varepsilon_2},$$

$$= \frac{1}{\alpha_{\text{ind}}} + \frac{3}{ab^2} \frac{A(x)}{\varepsilon_2}.$$  

(8.12)

Using Eq. (8.1) and the polarizability $\alpha_c$ given by Eq. (8.12), we obtain for the absorption wavelength

$$\lambda = \frac{2\pi a_0}{s} \left[ \frac{1}{2n} \frac{a_{\text{ind}}/a_0^3}{1 + (3/ab^2)(A(a/b)/\varepsilon_2) \alpha_{\text{ind}}^2} \right]^{1/2},$$

(8.13)

Fig. 3. Wavelength of absorption of carotenoids.
where $a_0$ represents the Bohr radius and $s$ the hyperfine structure constant and $\varepsilon_s$ the permittivity or the square of the refractive index of the solvent. Using Eq. (8·13) with

$$a = nd, \quad b = 2d, \quad d = 2.63\text{ a.u.,} \quad V_0 = 1.83\text{ ev},$$

$$\varepsilon_s = \bar{n}^2 \quad (\bar{n} \text{ represents the refractive index of methyl alcohol and is shown in Fig. 4}),$$

we get the absorption wavelength which agrees satisfactorily with the absorption wavelength of carotenoids,10 as shown in Fig. 3.

![Fig. 4. Refractive index of methyl-alcohol.](https://academic.oup.com/ptp/article-abstract/27/5/899/1914425)

When the length of the chain approaches infinity, the second term in Eq. (8·12) vanishes and $a_{\text{ind}}$ approaches the magnitude given by Eq. (6·11). From Eq. (8·5), we see that the absorption wavelength converges to $2\pi hc/V_0$. Thus we get the conclusion (d) mentioned in §1.

Using Eq. (8·13), we can obtain a formula which describes the solvent effect for the absorption wavelength. The shift of the frequency of absorption is given by

$$\Delta \nu = \nu_0 - \nu = C \left(1 - \frac{1}{\varepsilon_s}\right), \quad (8·14)$$

with

$$C = \left(\frac{\nu_0}{2}\right) \left(\frac{k}{k + 1}\right), \quad k = \left(\frac{4\pi}{V}\right) A(a/b) \alpha_{\text{ind}},$$

where $\nu$ represents the frequency of absorption in the solvent of permittivity $\varepsilon_s$ and $\nu_0$ represents that of unit permittivity. Eq. (8·14), in which the permittivity of the solvent, $\varepsilon_s$, is replaced by the square of the refractive index, represents the Kundt's rule which holds good for nonpolar solvents.

We lastly investigate the oscillator strength of absorption. The oscillator strength $f$ is defined by

$$f = \frac{2}{3} \frac{m}{\hbar^2 \varepsilon_0} (\hbar \omega) \langle \Psi_0 | e^x | \Psi_1 \rangle, \quad (8·15)$$

where $\Psi_0$ represents the wave function for the ground state of the system and $\Psi_1$ represents the wave function for the excited state. According to our method of collective motion, the excitation occurs only in the part of collective motion.
Hence the oscillator strength is given by that of a harmonic oscillator, that is, we have

\[ f = N/3. \] \hspace{1cm} (8·16)

On the other hand, when we consider that the excitation corresponds to the transition of an electron from the highest occupied level to the lowest unoccupied level, we get the following results: When electrons can move freely, using the matrix elements (4·3), we find

\[ f = (2n/3)(8/\pi^2) \simeq (N/3). \] \hspace{1cm} (8·17)

In the presence of Brillouin gap, we find, using the matrix element (6·1),

\[ f = (N/3)(\beta/\sqrt{1+\beta^2}) , \] \hspace{1cm} (8·18)

with \( \beta = (4A/V_0n) \).

As an example, we shall compute the oscillator strength for lycopene which contains 22 pi-electrons in its conjugated chain. Empirical \( f \)-value for lycopene is 2.1. When C-C distance is 1.39 Å and the Brillouin gap \( V_0 \) is 1.8 eV, the constant \( \beta \) becomes about unity. For the oscillator strength, we have 7.3, using Eq. (8·16) or Eq. (8·17), and 5.2, using Eq. (8·18).

As for the comparison of empirical \( f \)-value with the theoretical one, Mulliken has shown that the calculation of \( f \)-value by means of Eq. (8·15) always leads to the results whose values are too high. Therefore, Mulliken used the correction factor in the range from 0.25 to 0.4. When Moffitt studied the intensities of the spectra of catacondensed hydrocarbons, he multiplied his theoretical results by 0.3. Following Moffitt, we multiply our calculated results by 0.3. Then, according to our collective model, the corrected \( f \)-value becomes 2.2 and agrees with the empirical \( f \)-value. By means of Eq. (8·18), the corrected \( f \)-value becomes 1.6, which is fairly smaller than the empirical one. In Table V, the corrected \( f \)-values calculated by means of Eq. (8·16) for lycopene-like molecules are shown and they agree excellently with the empirical results.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>( n )</th>
<th>( f_{\text{obs.}}^{10} )</th>
<th>( f_{\text{calc.}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoene</td>
<td>3</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Phytofluene</td>
<td>5</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>( \zeta )-carotene</td>
<td>7</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Neurosporene</td>
<td>9</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>( \delta )-carotene</td>
<td>10</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Lycopene</td>
<td>11</td>
<td>2.1</td>
<td>2.2</td>
</tr>
</tbody>
</table>

As for cyanines or polymethine dyes which contain nitrogen atoms in the conjugated chains, there is an ambiguity in counting the number of pi-electrons. For example, empirical \( f \)-value for dye
§ 9. Relation to the method of configurational mixing

In this last section, we shall investigate the relation between the method of our collective motion and the method of configurational mixing and we shall show that our collective treatment corresponds to a correct configurational mixing, at least qualitatively.

According to the method of the independent-particle approximation, the equation of our collective motion is given by Eq. (2·10):

$$\left( \frac{1}{2I} \pi^2 + \frac{1}{2} V_2 \xi^2 - E_{\text{col}} \right) u(\xi) = 0,$$

(9·1)

where $V_2$ is defined by Eq. (2·19) and is given by

$$V_2 = N^2 \varepsilon / \alpha_{\text{ind}},$$

(9·2)

where $\alpha_{\text{ind}}$ represents the polarizability of the system calculated according to the method of the independent-particle approximation and it is given by Eq. (4·6) or Eq. (6·9).

By means of the method of the Hartree approximation, the equation of motion is given by

$$\left( \frac{1}{2I} \pi^2 + \frac{1}{2} V_2' \xi^2 - E_{\text{col}} \right) u'(\xi) = 0,$$

(9·3)

where $V_2'$ is given by

$$V_2' = N^2 \varepsilon / \alpha_e,$$

(9·4)

where $\alpha_e$ is the polarizability given by Eq. (7·7), that is,

$$\alpha_e = \frac{\alpha_{\text{ind}}}{1 + (\mathcal{L}/V) \alpha_{\text{ind}}},$$

(9·5)

Since the potential energy in Eq. (9·3) differs from that in Eq. (9·1) only by the numerical factor, Eq. (9·3) can be derived from Eq. (9·1) by the simple canonical transformation

$$\xi \rightarrow \left( \frac{V_2'}{V_2} \right)^{1/4} \xi,$$

$$\pi \rightarrow \left( \frac{V_2}{V_2'} \right)^{1/4} \pi.$$

(9·6)
As a matter of fact, from the eigenvalue and the eigenfunction of Eq. (9·1):

\[ E_{\text{scit}} = \frac{\hbar}{2} \sqrt{V_s/I}, \tag{9·7} \]
\[ u(\xi) = \exp \left\{ -\frac{1}{2\hbar} \sqrt{IV_s} \xi \right\}, \tag{9·8} \]

we obtain by this transformation those of Eq. (9·3):

\[ E'_{\text{scit}} = \frac{\hbar}{2} \sqrt{V'_s/I}, \tag{9·9} \]
\[ u'(\xi) = \exp \left\{ -(1/2\hbar) \sqrt{IV'_s} \xi \right\}. \tag{9·10} \]

In general we have \( \alpha_s < \alpha_{\text{ind}} \). Hence \( u(\xi) \) and \( u'(\xi) \) are represented schematically by Fig. 5.

Now it can be immediately shown that the canonical transformation (9·6) is generated by the unitary transformation

\[ \xi \rightarrow U \xi \ U^{-1} \]
\[ \pi \rightarrow U \pi \ U^{-1} \]

with the unitary operator

\[ U = e^{(i/\hbar) \log(V'_s/V_s)(\pi \xi + \xi \pi)} \], \tag{9·11} \]

so that

\[ u'(\xi) = \exp \left\{ \left( \frac{i}{8\hbar} \right) \log \left( \frac{V'_s}{V_s} \right) \cdot (\pi \xi + \xi \pi) \right\} \cdot u(\xi). \tag{9·12} \]

Transformation of the wave function of the total system is then represented by

\[ \varphi_e = \exp \left\{ \left( \frac{i}{8\hbar N} \right) \log \left( 1 + \frac{\alpha_{\text{ind}}}{V} \sum_{i,j} (p_i x_j + x_i p_j) \right) \right\} \cdot \varphi_0. \tag{9·13} \]

In obtaining the relation (9·13), we have used Eqs. (9·2), (9·4), (9·5) and (2·2). \( \varphi_0 \) in Eq. (9·13) represents the single Slater determinantal wave function based on the method of the independent-particle approximation and is composed of the orbitals given by Eq. (4·1) or Eqs. (5·11) and (5·13). If we assume that \((\mathcal{L}/V)\alpha_{\text{ind}}\) is a small quantity, the transformation (9·11) becomes

\[ U = 1 + \left( \frac{i}{8\hbar N} \right) \left( \frac{\alpha_{\text{ind}}}{V} \right) \sum_{i,j} (p_i x_j + x_i p_j) + \cdots. \tag{9·14} \]

Now the operator

\( (p_i x_j + x_j p_i) \) or \( (p_i x_j + x_i p_j) \)

brings two electrons from the levels \( i \) and \( j \) to the levels \( i' \) and \( j' \), hence \( (p_i x_j + x_i p_j) \varphi_0 \) describes an excited configuration. Accordingly, \( \varphi_e \) represents a wave function which includes the mixing of configurations.
T. Murai

In order to determine the coefficient of the mixing, we must calculate

\[ \langle i' | p_i | i \rangle \langle j' | x_j | j \rangle + \langle i' | x_i | i \rangle \langle j' | p_j | j \rangle. \] (9·15)

For the sake of simplicity, we consider only the matrix elements with

\[ i = j = n = N/2, \]
\[ i' = i + 1, \quad j' = j + 1. \] (9·16)

In the case of free electrons, we find, using the orbitals (4·1),

\[ \langle i' | x_i | i \rangle = \langle j' | x_j | j \rangle = - (2L/\pi^2), \] (9·17)
\[ \langle i' | p_i | i \rangle = \langle j' | p_j | j \rangle = -i\hbar(2n/L). \] (9·18)

The quantity, (9·15), then becomes

\[ \langle i + 1 | p_i | x_j + 1 | j \rangle + \langle i + 1 | x_i | j + 1 | p_j | j \rangle = i\hbar(8n/\pi^2). \] (9·19)

The coefficient of mixing of the configuration is then given by

\[ - (1/\pi^2) (\mathcal{L}/V) \alpha_{\text{ind}}, \] (9·20)

where \( \mathcal{L} \) and \( \alpha_{\text{ind}} \) are given by Eqs. (7·4) and (4·6) respectively. For short molecules, \( \mathcal{L} \) approaches \((4\pi/3)\). Using \( \alpha_{\text{ind}} \) given by Eq. (4·6)', we find that the coefficient (9·20) becomes

\[ - (1/3\pi^2) (me^2/\hbar^2) (L^3/b^2n). \] (9·21)

Using Eq. (7·4), we obtain the coefficient of mixing for sufficiently long molecule

\[ - (8/\pi^4) (me^2/\hbar^2) (L/2n) (\log L - \log 2b). \] (9·22)

Notice that Eq. (9·13) clearly shows the origin of the configurational mixing in our procedure: It is the occurrence of \( \mathcal{L}/V \) in Eq. (9·13) and this fact corresponds to what was mentioned at the end of § 7.

Now, on the other hand, according to the usual orthodox method of configurational mixing, the coefficient of mixing is calculated by the perturbation theory and we find for the wave function

\[ \Psi'_e = \Psi_0 + \sum_v c_v \Psi_v, \] (9·23)

with the coefficient of mixing

\[ c_v = (\Psi_v, \sum_{i<j} G(x_i, x_j) \Psi_0) / (E_0 - E_v), \] (9·24)

where \( \Psi_0 \) represents the single Slater determinantal wave function for the ground state, the same wave function occurring in Eq. (9·13), and \( \Psi_v \) represents the single determinantal wave function of the excited configuration. \( E_0 \) represents the energy of the ground state and \( E_v \) represents the energy of the excited state.
$G(x_i, x_j)$ denotes the Coulomb potential between the $i$-th and the $j$-th electron.

The three-dimensional form of $G(x_i, x_j)$ is the usual Coulomb potential which can be represented by

$$\frac{e^2}{r_{ij}} = \frac{e^2}{2\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{1}{k^2} e^{ik(x_i - x_j)} dk_x dk_y dk_z. \quad (9.25)$$

Carrying out the integrations with respect to $k_x$ and $k_z$, we have

$$\frac{e^2}{r_{ij}} = \frac{e^2}{\pi} \int_{-\infty}^{+\infty} e^{ik_0(z_i - z_j)} K_0(r_0|k_z|) dk_z, \quad (9.26)$$

where

$$r_0 = \sqrt{(y_i - y_j)^2 - (z_i - z_j)^2},$$

with

$$y_i = r_i \cos \phi_i, \quad y_j = r_j \cos \phi_j,$$

$$z_i = r_i \sin \phi_i, \quad z_j = r_j \sin \phi_j,$$

and $K_0$ represents the Bessel function of the purely imaginary argument of the zero-th order. We expand $K_0(r_0|k_z|)$ into the following infinite series:

$$K_0(r_0|k_z|) = 1 + a > K_0 C r_0 \delta \right) = \sum_{m=-\infty}^{+\infty} K_m \left( |k_z| r_0 \right) \times I_m \left( |k_z| r_0 \right) \cos \left( \phi_i - \phi_j \right), \quad (9.27)$$

where $K_m$ and $I_m$ represent the Bessel functions of purely imaginary arguments of the $m$-th order and $r_0$ denotes the larger one among $r_i$ and $r_j$ and $r_0$ denotes the smaller one. Using the expansion (9.27), we average $K_0(r_0|k_z|)$ over the area of a circle with radius $R$ and we have

$$\overline{K_0(r_0|k_z|)} = \frac{1}{(\pi R^2)} \int \int K_0(r_0|k_z|) r_i dr_i r_j dr_j d\phi_i d\phi_j$$

$$= \left( \frac{2}{R^2 k_z^2} \right) \left\{ 1 - 2 I_1 (|k_z| R) \cdot K_1 (|k_z| R) \right\}. \quad (9.28)$$

If $|k_z|R \gg 1$, the average (9.28) becomes

$$\overline{K_0(r_0|k_z|)} = \left( \frac{2}{R^2 k_z^2} \right). \quad (9.29)$$

If $|k_z|R \ll 1$, we have

$$\overline{K_0(r_0|k_z|)} = \log \left( \frac{2}{|k_z| R} \right). \quad (9.30)$$

Accordingly, we use the following expression:

$$\overline{G}(x_i, x_j) = \frac{e^2}{\pi} \int_{-\infty}^{+\infty} e^{ik_0(z_i - z_j)} \overline{K_0(r_0|k_z|)} dk_z, \quad (9.31)$$

Fig. 6. Coordinate system used in the expansion (9.27).
for the one-dimensional Coulomb potential.

We consider only the configuration which has been considered in calculating the coefficients (9·21) and (9·22). In order to obtain the coefficient of mixing defined by Eq. (9·24), we first calculate the integral:

\[ \left( \frac{2}{L} \right)^2 \int_{0}^{L} \int_{0}^{L} G(x_i, x_j) \cdot \sin \frac{\pi}{L} i x_i \cdot \sin \frac{\pi}{L} (i+1) x_i \times \sin \frac{\pi}{L} j x_j \cdot \sin \frac{\pi}{L} (j+1) x_j \, dx_i \, dx_j. \tag{9·32} \]

This integral is reduced to

\[ \frac{e^2}{\pi} \int_{0}^{\infty} K_{0}(r_0/k_x) \left( \frac{1}{k_x L + \pi} + \frac{1}{k_x L - \pi} \right)^2 (1 + \cos k_x L) \, dk_x. \tag{9·33} \]

In obtaining (9·33), we have neglected the terms which include \( \cos \left[ \frac{(\pi x_i}{L} \times (2i + 1) \right] \) or \( \cos \left[ \frac{(\pi x_j}{L} \times (2j + 1) \right] \), because these terms oscillate violently. The term

\[ \left( \frac{1}{k_x L + \pi} + \frac{1}{k_x L - \pi} \right)^2 (1 + \cos k_x L) \]

has sharp maximums for \( k_x = \pm (\pi/L) \), hence the integral (9·33) is reduced to

\[ \frac{e^2}{L \pi} K_{0}(r_0/\pi L) \int_{0}^{\infty} \left( \frac{1}{k_x L + \pi} - \frac{1}{k_x L - \pi} \right)^2 (1 + \cos k_x L) \, dk_x \]

\[ = \frac{e^2}{L \pi} K_{0}(r_0/\pi L) \int_{-\infty}^{\infty} \frac{\sin^2 z}{z^2} \, dz, \quad \text{where} \quad z = \frac{1}{2} (k_x L - \pi), \tag{9·34} \]

Using formulae (9·29), (9·30) and (9·34) we have

\[ (\Psi_n, \sum_{i<j} G(x_i, x_j) \Psi_0) \]

\[ = (2e^2/L) (L^2/\pi^2 R^2), \quad \text{for} \quad (\pi R/L) \gg 1, \tag{9·35} \]

\[ = (e^2/L) \log (2L/\pi R), \quad \text{for} \quad (\pi R/L) \ll 1. \tag{9·36} \]

Putting (9·35) or (9·36) and

\[ E_n - E_0 = 2(\hbar^2/2m) (\pi/L)^2 n \tag{9·37} \]

into (9·24), we find that the coefficient of mixing \( c_1 \) is given by

\[ - (1/\pi^4) (me^2/\hbar^2) (L^8/R^8 n), \quad \text{for small} \ L, \tag{9·38} \]

\[ - (1/\pi^2) (me^2/\hbar^2) (L/2n) (\log L - \log (\pi R/2)), \quad \text{for large} \ L. \tag{9·39} \]
For long chain molecules, it is found that the coefficient of mixing (9·22) for the wave function of collective motion agrees well with the coefficient (9·39) which is obtained by the method of perturbation. For small $L$, the coefficients, (9·21) and (9·38), depend on $b$ and $R$ respectively. But such a short molecule is physically not realistic, hence nothing further will be discussed. We have thus justified that our transformed wave function $\Psi$, (9·14), describes the mixing of configurations correctly.

Thus the relation between our method and the method of configurational mixing has been made clear. At first sight, it may seem strange that our method based on the Hartree approximation leads to the configurational mixing. However, it was the finding of Tomonaga\(^2\) that configurational mixing can be properly described in terms of the zero-point amplitude of the collective sound oscillation. In our treatment the assumed collective motion is a dipole oscillation but not the sound wave, the difference being that we have assumed a uniform polarization while the sound wave corresponds to the polarization of the form of $\cos(2\pi x/L)$. But as far as the oscillation in the lowest mode in a long molecule is concerned, the fact that we are dealing with a long range interaction like Coulombian makes this difference insignificant. This is the reason why we obtained good agreement between (9·22) and (9·36). If we dealt with sound oscillation rather than dipole one, we could expect a closer agreement.

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Appendix I

In this appendix, we shall study the problems which have been left undiscussed in §2. That is, we must find the equation for the internal motion and we must justify that the term $(V_1\xi + 1/2 \cdot V_1\xi')$ represents the potential part of the collective motion and $V_1$ always vanishes and that the internal motion is independent of the external field $F$.

First we assume that the system is capable of performing the collective motion, that is, we assume that we can separate the motion of the whole system into the collective motion and the internal motion. Mathematically, this implies that we can represent the Schrödinger function for the system by

$$\Phi(x_1, x_2, \ldots x_N) = \Psi_{ta}(\zeta_1, \zeta_2, \ldots \zeta_{N-1}; \xi) u(\xi),$$  \hspace{1cm} (AI·1)

and we assume that the Schrödinger function for the internal motion, which is given by $\Psi_{tn}$, depends on $\xi$ only slightly, hence we can neglect its $\xi$-dependence.
\( \zeta_1, \zeta_2, \cdots \zeta_{N-1} \) represent the coordinates which describe the internal motion.

In order to obtain the Schrödinger equation for \( \Psi_{\text{in}} \) and \( u(\xi) \), we use the variational equation given by

\[
\delta \langle \Phi | H - eNF\xi - E | \Phi \rangle = 0. \tag{AI·2}
\]

Using Eqs. (2·7) and (AI·1), we have

\[
\langle \Phi | H - eNF\xi - E | \Phi \rangle = \int \int (\Psi_{\text{in}}^* H_{\text{in}} \Psi_{\text{in}}) (u^* u) d\zeta d\xi - eNF \int \int (\Psi_{\text{in}}^* \Psi_{\text{in}}) (u^* \xi u) d\zeta d\xi \\
+ \frac{1}{2i} \int \int (\Psi_{\text{in}}^* \Psi_{\text{in}}) (u^* \xi u) d\zeta d\xi - E \int \int (\Psi_{\text{in}}^* \Psi_{\text{in}}) (u^* u) d\zeta d\xi. \tag{AI·3}
\]

In obtaining (AI·3), we have neglected terms such as

\[
\frac{1}{2i} \int \int (\Psi_{\text{in}}^* \xi^2 \Psi_{\text{in}}) (u^* u) d\zeta d\xi,
\]

\[
\frac{1}{i} \int \int (\Psi_{\text{in}}^* \xi \Psi_{\text{in}}) (u^* u) d\zeta d\xi,
\]

because \( \Psi_{\text{in}} \) depends on \( \xi \) only slightly. By the variation of Eq. (AI·3) with respect to \( \Psi_{\text{in}}^* \), we obtain

\[
H_{\text{in}} \Psi_{\text{in}}(\zeta; \xi) - eNF\xi \Psi_{\text{in}}(\zeta; \xi) \\
+ \frac{1}{2i} \frac{u^*(\xi) \xi u(\xi)}{u^*(\xi) u(\xi)} \Psi_{\text{in}}(\zeta; \xi) - EF_{\text{in}}(\zeta; \xi) = 0. \tag{AI·4}
\]

By the variation of the same equation with respect to \( u^* \), we get

\[
\left( \frac{1}{2i} \xi^2 + \langle \Psi_{\text{in}} | H_{\text{in}} | \Psi_{\text{in}} \rangle - eNF\xi - E \right) u(\xi) = 0, \tag{AI·5}
\]

where \( \langle \Psi_{\text{in}} | H_{\text{in}} | \Psi_{\text{in}} \rangle \) is a function of \( \xi \) given by Eq. (2·8). This \( \langle \Psi_{\text{in}} | H_{\text{in}} | \Psi_{\text{in}} \rangle \) should be an even function of \( \xi \) when \( F \) is zero, because our system is symmetric, hence \( V_1 \) vanishes. But in our case, where \( F \) is present, we cannot decide whether \( V_1 \) should vanish or not. So we proceed with our investigation leaving \( V_1 \) as it is. Equation (AI·5) then becomes

\[
\left( \frac{1}{2i} \xi^2 + V_1\xi + \frac{1}{2} V_2\xi^2 - eNF\xi - E_{\text{coll}} \right) u(\xi) = 0, \tag{AI·6}
\]

where

\[
E_{\text{coll}} = E - V_0. \tag{AI·7}
\]

Equation (AI·6) represents the equation for the collective motion. Using Eq. (AI·6), we obtain

\[
\frac{1}{2i} \frac{u^*(\xi) \xi u(\xi)}{u^*(\xi) u(\xi)} = - (V_1\xi + \frac{1}{2} V_2\xi^2 - eNF\xi) + E_{\text{coll}}.
\]
Inserting this relation in Eq. (AI·4), we find
\[ \left\{ H_{tn} - \left( V_0 + V_1 \xi + \frac{1}{2} V_2 \xi^2 \right) \right\} \Psi_{tn} = 0, \]  
(AI·8)
and this equation represents the equation for the internal motion. In this equation, it is proper that the term \( (V_0 + V_1 \xi - 1/2 \cdot V_2 \xi^2) \) appears in place of the eigenvalue, because of the relation
\[ \left( V_0 + V_1 \xi + \frac{1}{2} V_2 \xi^2 \right) = \langle \Psi_{tn} | H_{tn} | \Psi_{tn} \rangle. \]
Comparing Eq. (AI·7) with Eq. (2·10), we find that
\[ E_{tn} = V_0. \]  
(AI·9)
The meaning of \( E_{tn} \) is thus made clear.

Equation (AI·8) does not contain the term \( (eNF\xi) \) any longer, hence the internal motion is entirely independent of \( F \). Accordingly, if \( V_1 \) vanishes in the absence of \( F \), \( V_1 \) should vanish even when \( F \) is present.

### Appendix II

In 1954, J. H. Gibbs\(^{10}\) calculated the polarizability of a charged particle in square-well potential by the use of the orbitals (4·1). Following Gibbs, we can obtain the polarizability for our system.

Using Eq. (3·12), we have for our polarizability
\[ \alpha = \sum_i \alpha_i, \]  
(AII·1)
where \( \alpha_i \) represents the polarizability of an electron in the \( i \)-th level, which is given by
\[ \alpha_i = 2\epsilon \sum_f \frac{\langle \phi_i | x | \phi_j \rangle \langle \phi_j | x | \phi_i \rangle}{E_j - E_i}. \]  
(AII·2)
Using
\[ \langle \phi_i (x) | x | \phi_j (x) \rangle = \begin{cases} -\frac{2L}{\pi^3} \left\{ \frac{1}{(i-j)^3} - \frac{1}{(i+j)^3} \right\} & ; \ i - j : \text{odd} \\
0 & ; \ i - j : \text{even}. \end{cases} \]  
(AII·3)
\[ E_j - E_i = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 (j^2 - i^2), \]  
(AII·4)
we find
\[ \alpha_i = \frac{512 m e^3 L^4}{\pi^3 \hbar^3} \cdot \Sigma_{i:j \text{ odd}}^{+\infty} \frac{j^2}{(j^2 - i^2)^{\delta}}. \]  
(AII·5)
Gibbs calculated the infinite series in (AII·5) by the following procedure:

\[
\frac{i^2 j^2}{(j^2-i^2)^5} = -\frac{5}{256} \frac{1}{i^8} \left( \frac{1}{j-i} - \frac{1}{j+i} \right)
+ \frac{5}{256} \frac{1}{i^4} \left( \frac{1}{(j-i)^3} + \frac{1}{(j+i)^3} \right)
- \frac{1}{128} \frac{1}{i^8} \left( \frac{1}{(j-i)^6} - \frac{1}{(j+i)^6} \right)
- \frac{1}{64} \frac{1}{i^4} \left( \frac{1}{(j-i)^4} + \frac{1}{(j+i)^4} \right)
+ \frac{1}{32} \frac{1}{i} \left( \frac{1}{(j-i)^5} - \frac{1}{(j+i)^5} \right).
\]

When we sum up these terms with respect to \( j \) from \( -\infty \) to \( +\infty \), the terms in the first, third and fifth lines vanish. Then, using

\[
\frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \ldots = \frac{\pi^2}{8},
\frac{1}{1^4} + \frac{1}{3^4} + \frac{1}{5^4} + \ldots = \frac{\pi^4}{96},
\]

we get

\[
\sum_{j=-\infty}^{\infty} \sum_{i: j \neq i} \left( \frac{1}{j-i} - \frac{1}{j+i} \right) = \frac{\pi^2}{1536} \left( \frac{15\pi^2}{i^2} \right).
\]

Gibbs thus obtained the polarizability of an electron in the \( i \)-th level:

\[
\alpha_i = \frac{m e^2 L^4}{3\pi^2 h^2} \left( \frac{15}{i^2} - \frac{\pi^2}{i^4} \right). \tag{AII·6}
\]

In order to obtain the total polarizability for our system, we must sum up \( \alpha_i \) given by Gibbs over all electrons and we get

\[
\alpha = 2 \sum_{i=1}^{n} \alpha_i = \frac{2 m e^2 L^4}{3\pi^2 h^2} \left( 15 \sum_{i=1}^{n} \frac{1}{i^2} - \pi^2 \sum_{i=1}^{n} \frac{1}{i^4} \right). \tag{AII·7}
\]

Here we use the infinite series which are given by

\[
\frac{1}{1^2} + \frac{1}{2^2} + \frac{1}{3^2} + \ldots = \frac{\pi^2}{6},
\frac{1}{1^4} + \frac{1}{2^4} + \frac{1}{3^4} + \ldots = \frac{\pi^4}{90}.
\]

The latter series with inverse fourth-power converges rapidly. Accordingly, if \( n \) is a large number, we can replace \( \sum_{i=1}^{n} (1/i^4) \) by \( \sum_{i=1}^{\infty} (1/i^4) \). Then we have
In general, we have

$$\frac{1}{n+1} \leq \sum_{i=n+1}^{\infty} \frac{1}{i^2} \leq \frac{1}{n}.$$ 

Hence, if $n$ is a large integer, we have

$$\sum_{i=n+1}^{\infty} \frac{1}{i^2} \approx \frac{1}{n}.$$ 

Consequently, $\alpha$ becomes

$$\alpha = \frac{2me^2L^4}{3\hbar^2n}$$

$$= \frac{8}{3\pi^2} d_n^a \alpha_0^a$$

$$= \alpha_{\text{ind}}^a (\pi^4/96) = \alpha_{\text{ind}}^a \times 1.01 \ldots,$$

(AII·8)

where $\alpha_{\text{ind}}^a$ represents the polarizability given by Eq. (4·6). It is thus found that we obtain almost the same result as the one obtained by our simplified calculations in § 4.

References

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