

NOTE ON THE CORRELATION OF π -ELECTRONS IN ORGANIC DYES (III)

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§ I. Introduction

In order to take account the interaction between π -electrons in organic compounds, Kuhn¹⁾ has recently proposed to consider Coulombic potential between two electrons, which are considered as free electrons, running parallel each other. According to his model (if available), one of the two electrons, say electron 1, runs on the upper side of the molecular chain, being composed of atomic ions and σ -bonds. While, the other electron, say electron 2, runs on the under side of the molecular skeleton. The Coulombic interaction between the electrons is screened by positive atoms and σ -bonds, which result in the effective dielectric constant. One can calculate the wave-length of absorption band and that of phosphorescence or fluorescence band by perturbation or two-dimensional electronic digital computer,²⁾ taking into consideration the singlet and the triplet states.

In this paper, we shall consider another approach to solving the wave equations, and show that the wave function in the first approximation is expressed either by an elliptic function if one replaces Kuhn's interaction potential by δ -function, or by a Mathieu function if one takes successive approximation. In both cases, the results obtained agree quite well up to the terms of the first order of the correlation energy of the electrons.

§ II. Fundamental equations

We shall write the wave function for electron 1 of mass m as $\psi_1(x_1)$, where x_1 shows the coordinate measured along the orbit of electron 1, which is assumed to be subjected to a potential $V_1(x_1)$. The electron 1 is also suffered from the Coulombic repulsion of electron 2; then, the interaction potential shall be read

$$V_{\text{int}} = \frac{e^2}{D\sqrt{(x_1 - x_2)^2 + b^2}}, \quad (1)$$

with elementary charge e .

While, $\psi_2(x_2)$ means the wave function for electron 2, running on x_2 , which is measured along the other side of the molecular chain. The separation distance between x_1 and x_2 is equal to b , and D shows the effective dielectric constant of the medium, where the electrons 1 and 2 are inbeded (cf. Fig. 1).

Let us take the wave functions for the electrons in the Hartree approximation. The character of the electrons as fermions is taken into account, by putting two electrons which correspond to the parallel and the anti-parallel spin-states, into

the same orbit. Furthermore, if necessary, the singlet and the triplet states can be calculated by perturbation-method. Then, the wave equations for the electrons are written as

$$\frac{d^2}{dx_1^2} \phi_1(x_1) + \beta^2 \left\{ E^{(1)} - \left(V_1(x_1) + \int \phi_2^*(x_2) V_{\text{int}} \phi_2(x_2) dx_2 \right) \right\} \phi_1(x_1) = 0, \quad (3)$$

$$\frac{d^2}{dx_2^2} \phi_2(x_2) + \beta^2 \left\{ E^{(2)} - \left(V_2(x_2) + \int \phi_1^*(x_1) V_{\text{int}} \phi_1(x_1) dx_1 \right) \right\} \phi_2(x_2) = 0, \quad (4)$$

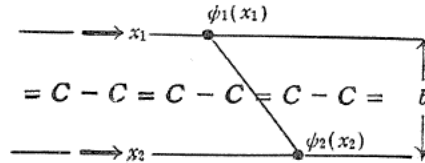


FIG. 1. Model of the system with two π -electrons.

with $\beta^2 = \frac{8\pi^2 m}{h^2}$, where the integration covers over the orbit parallel to the molecular chain. $E^{(1)}$ and $E^{(2)}$ represent the eigenvalues of energy for the electrons 1 and 2, respectively. From the nature of the problem about electrons in question, the functional form of the potentials V_1 and V_2 is to be chosen quite the same. We shall write it simply as $V(x)$. The precise form of the potential $V(x)$ shall be sinusoidal or complicated wavy form as shown by Kuhn.³⁾ For the simple calculation, however, it is already well known that one can take a potential box with infinitely high potential barrier at the both ends of the molecule, leading to a fairly good result for the problem of light-absorption of organic dyes. Accordingly, we shall take

$$\begin{aligned} V(x) &= 0 & \text{for } 0 < x < L \\ &= \infty & \text{for } x \leq 0, \text{ and } L \leq x, \end{aligned} \quad (5)$$

with the length of the molecular chain L , and x represents either x_1 or x_2 .

Let us consider the functional form of the interaction potential V_{int} . We can find at once that the function has a maximum at $x_1 = x_2$ and the value at the points, where x_1 is very different from x_2 , is quite small. Then, it may be possible to take the so-called "Sattelpunkt-Methode" to evaluate the Coulomb- or exchange-integral.

Here, however, the potential (1) is also seen quite resembled to δ -function, so we may perhaps put

$$V_{\text{int}} = \alpha \cdot \delta(x_1 - x_2), \quad (6)$$

where a constant α should be determined by the condition:

$$\frac{1}{D} \iint \frac{e^2 dx_1 dx_2}{\sqrt{(x_1 - x_2)^2 + b^2}} = \alpha \int \delta(x_1 - x_2) dx_1 dx_2, \quad (7)$$

or

$$\iint \phi_1^*(x_1) \phi_2^*(x_2) V_{\text{int}} \phi_1(x_1) \phi_2(x_2) dx_1 dx_2 =$$

$$= \alpha \iint \phi_1^*(x_1) \phi_2^*(x_2) \delta(x_1 - x_2) \phi_1(x_1) \phi_2(x_2) dx_1 dx_2. \quad (7')$$

One can also choose the value of α , so that the total interaction energy should be minimized. The assumption (6) may be applied the better, the shorter the length b becomes.

§ III. Solutions of wave equations

Under the assumptions (5) and (6), we shall be concerned with the solutions of (3) and (4).

Method I

If we are confined ourselves merely to the problem of light absorption of organic dyes, we could take the same functional form for the eigenfunctions ϕ_1 and ϕ_2 . This means that the electrons 1 and 2 interact each other at the same energy state and that the interaction among different states can be neglected.

Then, the equation (3) and (4) lead to the same form:

$$\frac{d^2}{dx_1^2} \phi_1(x_1) + \beta^2 (E^{(1)'} - \alpha \phi_1^*(x_1) \phi_1(x_1)) \phi_1(x_1) = 0, \quad (8)$$

$$\frac{d^2}{dx_2^2} \phi_2(x_2) + \beta^2 (E^{(2)'} - \alpha \phi_2^*(x_2) \phi_2(x_2)) \phi_2(x_2) = 0, \quad (9)$$

where $E^{(1)'} = E^{(2)'} = E - V$.

The expression (8) or (9) is just the fundamental equation⁴⁾ presented by the author in 1952.

For the real valued function, we obtain the exact solutions⁴⁾:

$$\phi_1(x_1) = \text{sn}(\beta \gamma x_1 + r', k), \quad (10)$$

$$\phi_2(x_2) = \text{sn}(\beta \gamma x_2 + r', k), \quad (11)$$

$$E^{(1)'} = E^{(2)'} = \gamma^2(1 + k^2), \quad (12)$$

$$k^2 = \frac{\alpha}{2\gamma^2}, \quad (13)$$

with integration constants γ and r' , $\text{Sn}(x, k)$ being an elliptic function.

Considering the condition at the both ends of the molecule

$$x_1 = 0; \phi_1 = 0 \quad \text{and} \quad x_1 = L; \phi_1 = 0, \quad (14)$$

we find

$$r' = 0, \quad (15)$$

$$\gamma = \frac{2}{\beta L} \{rK + isK'\}, \quad (16)$$

where r represents integers including zero, $i = \sqrt{-1}$ and $s = 0$ (ϕ is a real function), with

$$K = \int_0^{\pi/2} \frac{du}{\sqrt{1 - k^2 \sin^2 u}}, \quad (17)$$

$$K' = \int_0^{\pi/2} \frac{du}{\sqrt{1 - k'^2 \sin^2 u}}, \quad (18)$$

$$k' = \sqrt{1 - k^2}. \quad (19)$$

The eigenwert of energy is determined by

$$E' = r^2 + \frac{\alpha}{2}. \quad (20)$$

Method II

Other successive approximation can be carried out as follows. First, we neglect V_{int} in (3), and obtain the solution in the zero-th approximation under the assumption (6)

$$\psi_1(x_1) \propto \sin\left(\frac{r\pi}{L}x_1\right), \quad (21)$$

$$E^{(1)} = \frac{\hbar^2}{8m} \frac{r^2}{L^2}, \quad (22)$$

after considering the boundary condition (14), where r represents integers. Then we put (21) into (4) and obtain the equation in the first approximation:

$$\frac{d^2}{dx_2^2} \psi_2(x_2) + \beta^2 \left\{ E^{(2)} - V - \alpha \frac{1}{2} \left(1 - \cos \frac{2r\pi}{L} x_2 \right) \right\} \psi_2(x_2) = 0. \quad (23)$$

This equation with the boundary condition (14) gives

$$\psi_2(x_2) \propto Se_\nu(\mu x_2; H^2), \quad (24)$$

where Se_ν is a Mathieu function of order $\nu = \frac{n}{r}$ ($n = \text{integers}$),

$$\mu = \frac{r\pi}{L}, \quad (r = \text{integers}) \quad (25)$$

and

$$H^2 = -\frac{\alpha\beta^2}{4\mu^2}. \quad (26)$$

The normalization factor of the wave function ψ_2 should be determined in such a way that the electron finds itself in the π -orbital, *i.e.* in the whole (x_1, x_2) -space.

The eigenwert of energy for small H^2 is given by the following equation⁵⁾:

$$\cos \nu\pi = \cos \sqrt{A}\pi + H^4 \frac{\pi \sin \sqrt{A}\pi}{4\sqrt{A}(A-1)} + O(H^8), \quad (27)$$

where

$$A = \frac{\beta^2}{\mu^2} \left(E^{(2)} - V - \frac{\alpha}{2} \right). \quad (28)$$

For $H^2 \ll 1$, we find, up to the terms of $O(H^2)$, that the equation $\nu^2 \doteq A$ folds, *i.e.*

$$E' = E^{(2)} - V \doteq \frac{\nu^2 \mu^2}{\beta^2} + \frac{\alpha}{2} = \frac{\hbar^2 n^2}{8mL^2} + \frac{\alpha}{2}. \quad (n = \text{integers}) \quad (29)$$

It is interesting to mention that the expression (20) gives the eigenwert in the first approximation up to the terms of $O(\alpha)$

$$E' \doteq \frac{\hbar^2 s^2}{8mL^2} + \frac{\alpha}{2}, \quad (s = \text{integers}) \quad (20')$$

and the correction term $\alpha/2$ of the eigenwert of energy appears completely in the same form both in the expression (29) and in (20'). This term has a simple physical meaning. It shows that the first approximation of the eigenwert of the energy shifts towards the higher level from the energy level without interaction by a half of the interaction energy of the two electrons. The term $\alpha/2$ in (29) and (20') corresponds to the first order perturbation energy, when one considers the term $\frac{\alpha}{2} \left(1 - \cos \frac{2r\pi}{L} x_2\right)$ in (23) as a perturbed potential. Starting from an unperturbed eigenfunction

$$\phi_2^{(0)}(x_2) = \sin \frac{p\pi}{L} x_2$$

with eigenwert of energy $\frac{\hbar^2 p^2}{8mL^2}$ ($p = \text{integers}$), we can find at once that the first order perturbation energy is expressed by $\frac{\alpha}{2}$ if $p \neq r$, and $\frac{3}{4}\alpha$ if $p = r$.

By comparison with the experiment,^(6) 7) we can estimate the order of magnitude of α appeared in the present theory. The numerical value of α is seen to be about 0.12 eV for thiazolino-cyanine (1, 1'-dialkyl-2, 2'-trimethine-thiazolino-cyanine) with bond length of the chain elements 1.39 Å and bond number 1.5. The $C-C=C$ valency angle is $180^\circ - \varepsilon = 124^\circ$ and the number of electrons which contribute to the resonance structure is taken to be 8. For symmetrical 4, 4'-carbo-cyanine, we find $\alpha = 0.15$ eV for $j = 6$, where j means the number of double bonds counted in either of the resonance structure. In this case, the number of π -electrons contributing to the resonance is $2j + 2 = 14$. These figures for α are not physically very unreasonable, and it is seen that the expansion of eigenwert of energy in power series of α is quite reasonable in these examples.

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