

## Intensities in Molecular Spectra.

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*Introduction.* Mulliken in his most interesting papers (1) made a serious attempt to interpret the intensities in molecular spectra on the quantum mechanical basis. His calculations were made in most cases with aid of the molecular orbital (MO) method.

The aim of this and subsequent papers is to treat the same problem by means of other quantum mechanical approximations. We shall compare the calculated values with the empirical ones and the accordance or deviation will serve as indicator for the degree of approximation by the method employed.

*The Oscillator Strength.* We shall use the method described by Mulliken (1) comparing the calculated and the observed oscillator strength.

In order to obtain the calculated oscillator strength,  $f_{\text{calc}}$  we compute the dipole strength  $D = Q^2$  (cf. II. 1) by means of the quantum mechanical  $\Psi$  functions describing the molecular states and from this

$$f_{\text{calc}} = 1.096 \cdot 10^{11} \cdot Q^2 \cdot \nu \quad (1)$$

where  $\nu$  is the place of the absorption maximum in  $\text{cm}^{-1}$ .

On the other hand we get the observed oscillator strength  $f_{\text{obs}}$  from the empirical absorption curve by means of the relation

$$f_{\text{obs}} = 4.32 \cdot 10^{-9} \cdot \int \epsilon_{\nu} d\nu \approx 4.32 \cdot 10^{-9} \cdot \epsilon^{\text{max}} \cdot \Delta\nu \quad (2)$$

in which  $\Delta\nu$  is the half width of the band,  $\epsilon$  the molar absorption coefficient.

The theoretically computed  $f_{\text{calc}}$  value refers to the gaseous state. In the case of solution we must make a correction due to the Lorenz-Lorentz forces. However some investigations (2) have shown that the agreement is better, when this correction is omitted.

Since the individual approximate methods treat the problem from different point of view and from the comparisons we will draw conclusions with respect to the method itself, we must make known by each the starting-point, the assumption and the simplifications used by the method.

In this paper we shall investigate the intensities in molecular spectra with aid of the Slater-Pauling method.

## I. The Outline of the Slater-Pauling Method.

1. *Starting point, assumptions (Heitler-London).* We shall investigate in the following only organic compounds in which the number of  $\pi$  electrons is equal to the number of C atoms forming the skeleton of the molecule. The electron cloud of each  $\pi$  electron forms a dumb bell the axis of which being perpendicular to the plane of the molecule, therefore it does not appreciably overlap with the  $\sigma$  electrons, the electron cloud of the latter being rotation-symmetrical around the joining line of two adjacent atoms.

The  $\pi$  electrons are less firmly bound than the  $\sigma$  electrons. They are responsible for many physical properties of the molecule among them for the visible and ultraviolet spectra. Investigating the intensity problem of the spectrum, we must only deal with the  $\pi$  electrons.

In the case of  $n$  C atoms and  $n$   $\pi$  electrons, we have an  $n$  electron problem what cannot be solved rigorously quantum mechanically. We must make some simplifications to get a first order approximation.

The idea of this simplification is due to Heitler and London and is the same as in the case of the hydrogen molecule. We think the atoms very far from each other, *one  $\pi$  electron being by each atom* (that is we exclude the ionic, polar cases in which two electrons are by one atom). We suppose that in this approximation only this atom acts upon the electron, in other words we take as perturbation the action of the other atoms and electrons.

In this approximation Schrödinger's equation is separable in  $n$  one-electron-problems and the solution is the product of  $n$  one-electron-functions:  $\psi = a(1) \cdot b(2) \cdot c(3) \dots$  (1, 2, ... denote the coordinatetriple of the first, second, ... electron,  $a, b, \dots$  mean the solution of the one-electron-problem by the first, second, ... atom.)

However the problem is a degenerate one because all the functions, which differ from the above mentioned only in the arbitrary permutation of the electrons among the atoms (e. g.  $\psi = a(2) \cdot b(1) \cdot c(3) \dots$ ) belong to the same energy. We have  $n!$  such functions.

When we treat the problem with aid of the perturbation theory introducing the interaction of the electrons as perturbation, we take these  $n!$  functions as of zero order approximation and we look for such linear combinations of them which approximate better the real states of the molecule.

The determination of these coefficients, which are necessary to the linear combination, requires the solution of a linear system of equations set up in taking account of the perturbation. This is possible only in the case when the determinant of the system vanishes. The roots of this so called *secular determinant* give the possible energy values of the perturbed system.

In this case the equation system consists of  $n!$  equations, the secular determinant has  $n!$  rows, the degree of the secular equation is  $n!$ . This is a very great number (e. g. in the case of benzene  $n = 6, n! = 720$ ) to deal with it.

2. *The Slater Method.* Slater achieved a very great simplifica-

tion of the problem introducing the spin variable and taking account of Pauli's exclusion principle. (3)

Neglecting the magnetic interactions we can write the one-electron-function as a product:  $\Psi(x, y, z, m_s) = u(x, y, z) \cdot \sigma(m_s)$  of two functions where  $u$  depends only upon the three space coordinates and  $\sigma$  only upon the spin coordinate ( $m$ ) The latter is the  $z$  component of the spin of the electron and can assume only two values:  $m = +1/2, m = -1/2$  (measured in  $\hbar/2\pi$  units).

The  $u$  function measures the probability to find the electron in the  $x, y, z$  place, the  $\sigma$  function measures the probability to find the  $z$  component of the spin of the electron ( $m$ ) with the values  $+1/2$  and  $-1/2$ , respectively.

When the electron spin has the value  $+1/2$ , then the values of the  $\sigma$  function are:

$$\alpha \left\{ \begin{array}{l} \text{for } m_s = +1/2 \quad \sigma(m_s) = 1 \quad (\text{certainty}) \\ \text{for } m_s = -1/2 \quad \sigma(m_s) = 0 \end{array} \right.$$

When the electron spin has the value  $-1/2$ , then the values of the  $\sigma$  function are:

$$\beta \left\{ \begin{array}{l} \text{for } m_s = +1/2 \quad \sigma(m_s) = 0 \\ \text{for } m_s = -1/2 \quad \sigma(m_s) = 1 \quad (\text{certainty}) \end{array} \right.$$

We call these functions  $\alpha$  and  $\beta$ , respectively. It follows from their definition that  $\alpha$  and  $\beta$  are mutually orthogonal:

$$\alpha(+1/2) \cdot \beta(+1/2) + \alpha(-1/2) \cdot \beta(-1/2) = 0 \quad (3)$$

and they are normalized

$$\alpha^2(+1/2) + \alpha^2(-1/2) = 1 \quad (4)$$

This is a very important fact by the calculation of the dipole strength integral.

Slater takes into account Pauli's exclusion principle using only wave functions antisymmetrized in the electrons. These functions must be written in determinant form or in the equivalent sum of permutations taking with  $+$  or  $-$  sign according to even or odd permutation. We denote these Slater functions by the following equivalent formulae:

#### *Slater function*

(e. g. in the case of four electrons one Slater function)

$$\varphi = \frac{1}{\sqrt{4!}} \begin{vmatrix} a(1) a(1) & a(2) a(2) & a(3) a(3) & a(4) a(4) \\ b(1) a(1) & b(2) a(2) & b(3) a(3) & b(4) a(4) \\ c(1) \beta(1) & c(2) \beta(2) & c(3) \beta(3) & c(4) \beta(4) \\ d(1) a(1) & d(2) a(2) & d(3) a(3) & d(4) a(4) \end{vmatrix} \quad (5a)$$

$$\varphi = \frac{1}{\sqrt{4!}} \sum_P (-1)^P P a(1) a(1) \cdot b(2) a(2) \cdot c(3) \beta(3) \cdot d(4) a(4) \quad (5b)$$

$$\varphi = \frac{1}{\sqrt{4!}} \begin{pmatrix} a & b & c & d \\ \alpha & \alpha & \beta & \alpha \end{pmatrix} \quad (5c)$$

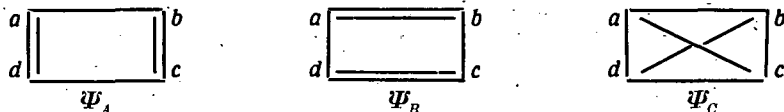
( $P$  means the permutation of the electrons (1, 2, ...) among the atoms. This function corresponds to the spin state, when the electrons by the first, second, third and fourth atom, respectively have the spin values  $+1/2, +1/2, -1/2$ , and  $+1/2$ , respectively.)

We can form  $2^n$  such functions because by each atom the spin can assume two values. That means that the degree of the secular equation is reduced from  $n!$  to  $2^n$ . (e. g. by benzene from 720 to 64).

Slater obtained a further simplification proving that by the linear combination we must use only functions by which the resultant spin has the same component on the  $z$  axis, or in other words which have the same number  $\alpha$  and  $\beta$ . The secular equation is dissolved in equations of minor degree. (e. g. in the case of benzene in equations of 1, 6, 15, 20, 15, 6, 1 degree, corresponding to the cases that the resultant spin has the following components: 3, 2, 1, 0, -1, -2, -3.) This is the method used by Hückel treating the benzene problem in his first paper (4).

3. *The vector-bond method (Eyring, Pauling)*. In the next step it was demonstrated (5) that in the linear combination one must use only functions by which the resultant spin has the same value (*not only his  $z$  component*) In classifying the states corresponding to these functions, we get singlet (resultant spin = 0), triplet (resultant spin = 1) and so on, states. The functions can be obtained from the Slater functions by means of the vector-bond diagrams.

Let us consider for example the singlet states. The resultant spin is 0. Connecting with bonds the atoms by which the spin is compensated ( $-1/2$  —  $+1/2$ ) we obtain many figures which are called vector-bond diagrams. (E. g. in the case of four atoms we can obtain the following three diagrams):



Each diagram is to be obtained from Slater functions (spin states) which are consistent with the figure. When we draw an arrow from the atom by which the electron spin is  $-1/2$ , to atom by which it is  $+1/2$ , we obtain, e. g. the first diagram as a sum of four Slater functions (spin states):

$$\Psi_A = \begin{array}{c} a \\ \downarrow \\ \square \\ \uparrow \\ c \end{array} \begin{array}{c} b \\ \downarrow \\ \square \\ \uparrow \\ d \end{array} = + \begin{array}{c} a \\ \uparrow \\ \square \\ \uparrow \\ c \end{array} \begin{array}{c} b \\ \uparrow \\ \square \\ \uparrow \\ d \end{array} - \begin{array}{c} a \\ \downarrow \\ \square \\ \uparrow \\ c \end{array} \begin{array}{c} b \\ \uparrow \\ \square \\ \uparrow \\ d \end{array} + \begin{array}{c} a \\ \downarrow \\ \square \\ \downarrow \\ c \end{array} \begin{array}{c} b \\ \downarrow \\ \square \\ \downarrow \\ d \end{array} - \begin{array}{c} a \\ \uparrow \\ \square \\ \downarrow \\ c \end{array} \begin{array}{c} b \\ \downarrow \\ \square \\ \downarrow \\ d \end{array}$$

$$\Psi_A = \frac{1}{\sqrt{4!}} \left\{ \begin{array}{ccc} a & b & c & d \\ \alpha & \alpha & \beta & \beta \end{array} \right\} - \begin{array}{ccc} a & b & c & d \\ \beta & \alpha & \beta & \alpha \end{array} \left\{ \begin{array}{ccc} a & b & c & d \\ \beta & \beta & \alpha & \alpha \end{array} \right\} - \begin{array}{ccc} a & b & c & d \\ \alpha & \beta & \alpha & \beta \end{array} \right\}$$

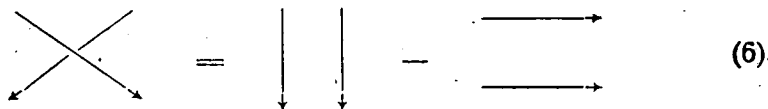
$$\Psi_A = \quad + \varphi_I \quad - \varphi_{II} \quad + \varphi_{III} \quad - \varphi_{IV}$$

(taking with + or - sign according to even or odd reverse of the arrows with respect to the first Slater function  $\varphi_I$ )

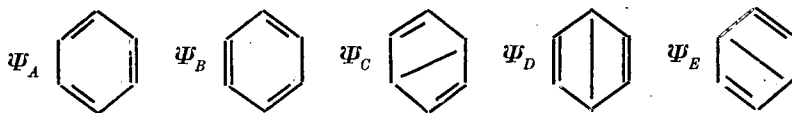
Rumer pointed out (6) that the functions corresponding to the vector-bond diagrams are not all linearly independent. According to his considerations we obtain the independent ones, writing the atoms on the circumference of a circle and forming all the possible vector-bond diagrams by which no two bond intersect each other. These are called *canonical structures* by Pauling (7)

(e. g. by the example mentioned above, only two are canonical, i. e. independent:  $\Psi_A$  and  $\Psi_B$ )

The other vector-bond diagrams can be resolved in the uncrossed ones by the repeated use of the following rule:



By the determination of the coefficients we must use only the independent set i. e. the canonical structures. This means that the secular determinant is further reduced. (e. g. by the benzene there are five linearly independent, canonical structures for the singlet state and we must solve an equation of the 5. degree



The real states of the molecule can be approximated by the linear composition of these five structures. The lowest state has less energy than any of the five structures according to the quantum mechanical perturbation computations.

After Pauling's comment this is due to the „resonance“ among the five structures. (7)

4. *Vector-bond method and mesomerism.* It is a close connection between these vector-bond (VB) functions derived on the basis of the quantum mechanics and the mesomeric structures introduced by the theoretical chemistry.

The two methods give the same conclusion referring to the stabilization of the molecule because of the resonance among the mesomeric (canonical) structures.

The difference between them is, that the mesomerism theory gives only qualitative conclusions, but the Slater-Pauling treatment makes possible the evaluation of many physical and chemical properties of the molecule. — In the following treatment we shall use for the evaluation of intensity of spectrum.

## II. Intensity calculations according to S—P method.

### 1. The dipole strength.

$$Q^2 = Q_x^2 + Q_y^2 + Q_z^2$$

In order to get the  $x$  component of the dipole strength  $Q_x$ , from a molecular state characterized by the function  $\Psi_i$  to other molecular states characterized by the functions  $\Psi_I, \Psi_{II}, \dots, \Psi_k$  ( $Q_x$  is proportional to the *probability of transition* from the state  $\Psi_i$  to states  $\Psi_I, \Psi_{II}, \dots$ , under the emission or absorption of light quanta polarized along the  $x$  axis), we must form the following product:  $X\Psi_i$  ( $X = \sum_{\nu} x_{\nu}$ )  $x_{\nu}$  means the  $x$  coordinate of the  $\nu$ -th electron) and expand in terms of the functions,  $\Psi_I, \Psi_{II}, \dots$  as follows:

$$X\Psi_i = c_{i1} \Psi_I + c_{i2} \Psi_{II} + c_{i3} \Psi_{III} + \dots \quad (7)$$



Taking into account the orthogonality and normalization of the spin variable

$$(\alpha_{(i)} \beta_{(i)}) = 0 \quad (\alpha_{(i)} \alpha_{(i)}) = 1 \quad (\beta_{(i)} \beta_{(i)}) = 1$$

we get the following rules for the integrals:

(We restrict ourselves to the transpositions. The essential is always the order of the spins by  $\varphi_i$  and  $\varphi_k$ )

a.) If there are more than one transpositions between the order of spins by  $\varphi_i$  and  $\varphi_k$  the integral vanishes.

b.) If one transposition is necessary to obtain the same order of spins by  $\varphi_i$  as  $\varphi_k$ , then we get one member from the sum, by which  $P$  is just the transposition which reestablishes the same order of spins.  $\int a(1) b(2) \dots X a(2) b(1) \dots d\tau = (ab)$ . We call this term, *exchange integral*.

c.) If  $\varphi_i = \varphi_k$ , we obtain one term of the following type:  $\int a(1) b(2) \dots X a(1) b(2) \dots d\tau$  *principal integral* ( $abc\dots$ ) and so many exchange integrals as many possibilities we have to permute the electrons having parallel spins.

(E. g. in the case of six electrons:

$$\int a(1) b(2) \dots X a(2) b(1) \dots d\tau = (ab)$$

$$\int a(1) b(2) \dots X a(1) b(2) \dots d\tau = (abcdef)$$

$$\varphi_I = \begin{pmatrix} a & b & c & d & e & f \\ \alpha & \alpha & \alpha & \beta & \beta & \beta \end{pmatrix} \quad \varphi_{II} = \begin{pmatrix} a & b & c & d & e & f \\ \alpha & \alpha & \beta & \alpha & \beta & \beta \end{pmatrix} \quad \varphi_{III} = \begin{pmatrix} a & b & c & d & e & f \\ \beta & \beta & \alpha & \beta & \alpha & \alpha \end{pmatrix} \quad \varphi_{IV} \dots$$

$$a) (\varphi_I \varphi_{III}) = 0 \quad b) (\varphi_I \varphi_{II}) = -(cd)$$

$$c) (\varphi_I \varphi_I) = (abcdef) - (ab) - (ac) - (bc) - (ed) - (df) - (ef)$$

$$(\varphi_{II} \varphi_{II}) = (abcdef) - (ab) - (ad) - (bd) - (ec) - (cf) - (ef)$$

3. *The principal integral.* We take for example the benzene. The molecule should be in the  $xy$  plane, the  $z$  axis being perpendicular to the plane of the molecule. The Slater-type form of a  $\pi$  electron function by the  $a$ -th C atom is then: (9)

$$a(1) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} z_a e^{-\alpha r_a} = k z_a e^{-\alpha r_a} = k r_a \cos \vartheta_a e^{-\alpha r_a}$$

where  $\vartheta_a, r_a$  means the spherical coordinates of the electron with respect to the  $a$ -th atom.

We take the origin of the coordinate system in the symmetry centre of the benzene molecule. The coordinates of the  $a$ -th atom then are:  $a_x$  and  $a_y$ . The coordinates of the electrons are:

$x, y$  with respect to the origin

$x_a, y_a$  with respect to the  $a$ -th atom

$$\left. \begin{aligned} x &= a_x + x_a \\ y &= a_y + y_a \end{aligned} \right\} (11) \quad \left. \begin{aligned} x_a &= r_a \sin \vartheta_a \cos \varphi_a \\ y_a &= r_a \sin \vartheta_a \sin \varphi_a \end{aligned} \right\} \quad z_a = r_a \cos \vartheta_a \quad (12)$$

a.) *The  $x$  principal integral.*

$$\int a(1) b(2) \dots f(6) [x_1 + x_2 + \dots + x_6] a(1) b(2) \dots d\tau_1 d\tau_2 \dots d\tau_6 = \\ = \int a(1) x_1 a(1) d\tau_1 \cdot \underbrace{\int b(2) b(2) d\tau_2}_{1} \cdot \underbrace{\int \dots \int f(6) f(6) d\tau_6}_{1} +$$

$$+ \int b(2)x_2 b(2)d\tau_2 + \int c(3)x_3 c(3)d\tau_3 + \dots + \int f(6)x_6 f(6)d\tau_6 \\ = J_1 + J_2 + \dots + J_6$$

$$J_1 = \int a(1)x_1 a(1)d\tau_1 = \int a(1)a(1)[a_x + x_a(1)]d\tau_1 = a_x \int \underbrace{a(1)a(1)d\tau_1}_1 +$$

$$+ \int a(1)a(1)x_a(1)d\tau_1 = a_x + \int \underbrace{k^2 z_a^2 e^{-2\alpha r_a}}_{a(1)a(1)} \cdot \underbrace{r_a \sin \vartheta_a \cos \varphi_a}_{x_a} \cdot \underbrace{r_a^2 \sin \vartheta_a dr_a d\vartheta_a d\varphi_a}_{d\tau(1)} =$$

$$= a_x + k^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} r^5 e^{-2\alpha r} \cdot \cos^2 \vartheta \sin^2 \vartheta \cdot \cos \varphi \cdot dr \cdot d\vartheta \cdot d\varphi =$$

$$= a_x + k^2 \int_0^\infty \int_0^\pi (r^5 e^{-2\alpha r} \cos^2 \vartheta \sin^2 \vartheta dr d\vartheta) \underbrace{\int_0^{2\pi} \cos \varphi d\varphi}_0 = a_x$$

Likewise  $J_2 = b_x \dots J_6 = f_x$   $J_1 + \dots + J_6 = a_x + b_x + c_x + d_x + e_x + f_x$  (12a)

b.) *The y principal integral.* We get in analogous manner

$$\int a(1)b(2)\dots[y_1 + y_2 + \dots + y_6] a(1)b(2)\dots d\tau = \\ = \underbrace{a_y + b_y + c_y + d_y + e_y + f_y}_{(12b)}$$

c.) *The z principal integral.* In the case of plane molecule  $z_a = z_1$ , and therefore

$$\int a(1)b(2)[z_1 + z_2 + \dots + z_6] a(1)b(2)\dots d\tau = \\ = \int a(1)z_1 a(1)d\tau_1 + \dots + \int f(6)z_6 f(6)d\tau_6 = J_1 + \dots + J_6$$

$$J_1 = \int a(1)a(1)z_a d\tau_1 = \int k^2 z_a^3 e^{-2\alpha r_a} d\tau = \\ = \int_0^\infty \int_0^\pi \int_0^{2\pi} \underbrace{k^2 r^3 \cos^3 \vartheta}_{z^3} \cdot e^{-2\alpha r} \cdot \underbrace{r^2 \sin \vartheta dr d\vartheta d\varphi}_{d\tau} = \\ = \int_0^\infty \int_0^\pi k^2 r^5 e^{-2\alpha r} \cdot dr d\vartheta \cdot \underbrace{\int_0^{2\pi} \cos^3 \vartheta \sin \vartheta d\vartheta}_0 = 0$$

Likewise  $J_2 = \dots = J_6 = 0$ . (12c)

Summarizing the results, we have obtained the following formulas in the case of plane molecule for the principal integral:

$$(abcdef)_x = a_x + b_x + c_x + d_x + e_x + f_x; \\ (abcdef)_y = a_y + b_y + c_y + d_y + e_y + f_y \quad (abcdef)_z = 0.$$

4. *The exchange integral.* Let us consider for example the following exchange integral:

$$(ab)_x = \int a(1)b(2)c(3)\dots[x_1 + x_2 + \dots + x_6] a(2)b(1)c(3)\dots d\tau$$



$$\begin{aligned}
 (ab)_x &= \underbrace{\int a(1)x_1 b(1) d\tau_1}_{J_1} \cdot \underbrace{\int a(2)b(2) d\tau_2}_{J_0} \cdot \underbrace{\int c(3)c(3) d\tau_3}_{1} \dots \underbrace{\int f(6)f(6) d\tau_6}_{1} + \\
 &+ \underbrace{\int a(1) b(1) d\tau_1}_{J_0} \cdot \underbrace{\int a(2) x_2 b(2) d\tau_2}_{J_1} \cdot \underbrace{\int c(3) c(3) d\tau_3}_{1} \dots \underbrace{\int f(6) f(6) d\tau_6}_{1} + \\
 &+ \underbrace{\int a(1) b(1) d\tau_1}_{J_0} \cdot \underbrace{\int a(2) b(2) d\tau_2}_{J_0} \cdot \underbrace{\int c(3) x_3 c(3) d\tau_3}_{c_x} \dots \underbrace{\int f(6) f(6) d\tau_6}_{1} + \dots + \\
 &+ \underbrace{\int a(1) b(1) d\tau_1}_{J_0} \cdot \underbrace{\int a(2) b(2) d\tau_2}_{J_0} \cdot \underbrace{\int c(3) c(3) d\tau_3}_{1} \dots \underbrace{\int f(6) x_6 f(6) d\tau_6}_{f_x} = \\
 &= 2J_0 J_1 + J_0^2 (c_x + d_x + e_x + f_x)
 \end{aligned}$$

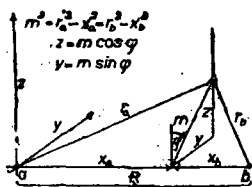
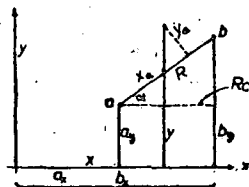
$$J_0 = \int a(1) b(1) d\tau_1 = \int a(2) b(2) d\tau_2 = \int k z_a e^{-\alpha r_a} \cdot k z_b e^{-\alpha r_b} d\tau = \int k^2 z^2 e^{-\alpha(r_a+r_b)} d\tau$$

$$J_1 = \int a(1) x_1 b(1) d\tau_1 = \int a(2) x_2 b(2) d\tau_2 = \int k^2 z^2 e^{-\alpha(r_a+r_b)} \cdot x \cdot d\tau$$

$$x = x_a + x_b \cos \alpha - y_b \sin \alpha \quad (13)$$

In order to evaluate  $J_0$  and  $J_1$  we use the transformation formula 13 and on the other hand we introduce elliptical coordinates

$\frac{r_a+r_b}{R} = \mu$   $\frac{r_a-r_b}{R} = \nu$  by means of which the integrals transform as follows:



$$x_a = \frac{R}{2}(1+\mu\nu) \quad x_b = \frac{R}{2}(1-\mu\nu) \quad z_a = z_b = z = \frac{R}{2}\sqrt{(\mu^2-1)(1-\nu^2)} \cos \varphi$$

$$y_a = y_b = y = \frac{R}{2}\sqrt{(\mu^2-1)(1-\nu^2)} \sin \varphi; \quad \iiint F d\tau = \frac{R^3}{8} \int_1^\infty d\mu \int_{-1}^1 d\nu \int_0^{2\pi} d\varphi (\mu^2 - \nu^2) F$$

$$\begin{aligned}
 J_0 &= \int_1^\infty \int_{-1}^1 \int_0^{2\pi} \frac{R^3}{8} (\mu^2 - \nu^2) k^2 \frac{R^2}{4} \underbrace{(\mu^2 - 1)(1 - \nu^2)}_{z^2} \cos^2 \varphi e^{-\alpha R \mu} d\mu d\nu d\varphi = \\
 &= \frac{e^{-\beta}}{5} \left( \frac{\beta^3}{3} + 2\beta^2 + 5\beta + 5 \right) \quad \beta = \alpha R.
 \end{aligned}$$

The value of  $R$  in aromatic molecules is 1.04 Å, the value of  $\alpha$  in the case of C atom is: 3.25. Substituting these values we get the following value for  $J_0$  (in atomic units)  $J_0 = 0.25995$  (10)  $J_0^2 = 0.06757$  (square of atomic unit).

$$\begin{aligned}
 J_1 &= \int_1^\infty \int_{-1}^+ \int_0^{2\pi} \frac{R^3}{8} (\mu^2 - \nu^2) \cdot k^2 \underbrace{\frac{R^2}{4} (\mu^2 - 1) (1 - \nu^2)}_{z^2} \cdot \underbrace{\cos^2 \varphi [a_x + x_a \cos \alpha - y_b \sin \alpha]}_x \cdot e^{-\alpha R \mu} d\mu d\nu d\varphi = \\
 &= a_x J_0 + \cos \alpha \underbrace{\int_1^\infty \int_{-1}^+ \int_0^{2\pi} \frac{R^3}{8} (\mu^2 - \nu^2) \cdot k^2 \frac{R^2}{4} (\mu^2 - 1) (1 - \nu^2) \cos^2 \varphi \frac{R}{2} (1 + \mu\nu)}_{J_2} \cdot e^{-\alpha R \mu} d\mu d\nu d\varphi - \\
 &- \sin \alpha \underbrace{\int_1^\infty \int_{-1}^+ \int_0^{2\pi} \frac{R^3}{8} (\mu^2 - \nu^2) \cdot k^2 \frac{R^2}{4} (\mu^2 - 1) (1 - \nu^2) \cos^2 \varphi \frac{R}{2} \sqrt{(\mu^2 - 1)(1 - \nu^2)} \sin \varphi}_{J_3} \cdot e^{-\alpha R \mu} d\mu d\nu d\varphi \\
 J_2 &= \frac{R}{2} J_0 + \underbrace{\int_1^\infty \int_{-1}^+ \int_0^{2\pi} \frac{R^3}{8} (\mu^2 - \nu^2) \cdot k^2 \frac{R^2}{4} (\mu^2 - 1) (1 - \nu^2) \cos^2 \varphi \cdot \frac{R}{2} \mu\nu}_{=0} \cdot e^{-\alpha R \mu} d\mu d\nu d\varphi \\
 J_3 &= \int_1^\infty \int_{-1}^+ \frac{R^3}{8} (\mu^2 - \nu^2) \cdot k^2 \frac{R^2}{4} (\mu^2 - 1) (1 - \nu^2) \cdot \frac{R}{2} \sqrt{(\mu^2 - 1)(1 - \nu^2)} \cdot e^{-\alpha R \mu} d\mu d\nu \cdot \underbrace{\int_0^{2\pi} \cos^2 \varphi \sin \varphi d\varphi}_{=0} = 0
 \end{aligned}$$

$$J_1 = a_x J_0 + \cos \alpha \cdot \frac{R}{2} J_0 = J_0 \left( a_x + \frac{R \cos \alpha}{2} \right) = J_0 \left( a_x + \frac{b_x - a_x}{2} \right) = \frac{J_0}{2} (a_x + b_x).$$

$$\begin{aligned}
 (ab)_x &= 2J_0 J_1 + J_0^2 (c_x + d_x + e_x + f_x) = \\
 &= J_0^2 (a_x + b_x + c_x + d_x + e_x + f_x)
 \end{aligned} \tag{14a}$$

We get in analogous manner

$$(ab)_y = J_0^2 (a_y + b_y + c_y + d_y + e_y + f_y) \tag{14b}$$

It can be proved that all exchange integral between adjacent atoms are of this form.

$(ab)_z = 0$ , in the case of plane molecule, as in the case of principal integral. 14c

It is obvious that by benzene, anthracene, naphthalene, the above mentioned sums (12 a b c, 14 a b c) are equal to zero because of the symmetry of the molecule.

### III. Conclusions. The comparison with the experiment.

We have reduced the dipole strength integral to two ground integrals: the principal integral and the exchange integral. We have evaluated the latter with aid of Slater-type eigenfunctions.

Our formulae show that in the case of a plane symmetrical molecule these ground integrals are zero and therefore the dipole strength which itself is a linear combination of them, is also zero. That means that the transition is forbidden.

A closer inspection of the formulae shows that there is a possibility of the transition when the sum differs from zero due to the deformation vibrations.

In this step our result is in good agreement with the experimental data. The first band of the benzene is very weak and has a vibrational structure and it is proved (11) that this transition is a

forbidden one. This is shown by the very little oscillator strength value  $f = 0.0006$ .

Our result differs from the experiment concerning the second band of the benzene which has a great oscillator strength. The same is the case by the naphthalene and anthracene. The deviations (and great deviations from the theoretical 0 osc. strength) show the lack of the Slater-Pauling method.

All the molecular states with which this method calculates are purely homopolar states. The ionic, polar states by which two electrons can be by the same atom, are excluded from this treatment.

The result obtained shows that there is no possibility of transition to these homopolar states. We interpret therefore the observed intensity as a transition to a molecular state which is a combination of the homopolar and ionic states.

In this step our result agrees with that of Sklar (12) with the difference that his considerations were only on group theoretical base while we evaluated the integrals, the value of which was easily determined on ground of the molecular structure (the spatial arrangement of the atoms).

Our result agrees with that of Mulliken's who starting from a different point of view found that the transitions of great intensity are always transitions to partly ionic states.

In the next paper we shall use this method by some asymmetrical molecules.

#### *Summary.*

We have treated the computation of transition probability on the base of the Slater-Pauling method by some organic symmetrical molecules (benzene, and so on).

The evaluation was reduced to some ground integrals and from these it was to observe that there is no transition between the pure homopolar states with which this method only deals.

The comparison with the experiment shows that the observed transition must be to a partly ionic state in agreement with Mulliken's result.

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