Partial Description of Quantum-Mechanical System

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(Received March 30, 1956)

A quantum-mechanical system is divided into several partial systems which are interacting each other. The general and practical methods of extracting one of the partial systems are discussed. If a one-dimensional partial system is extracted the two-particle interaction in the partial system is a long range part of the two-particle interaction in the original system and its short range part is absorbed in the average field due to the remaining part of the system. It is noted that the light absorption of long carotenoids is due to the plasma oscillation of \( \pi \) electrons caused by the long range part of the Coulomb interaction. The mechanism of screening the short range part is somewhat different from that of the three-dimensional case.

Introduction

As has been generally realized, it is hopelessly difficult to obtain the exact solution for most quantum-mechanical problems of real significance. Various ways for obtaining approximate solutions have been devised. Though they are only mathematical in some case, the device often introduces the method of physically important significance in which the approximation means a kind of the physical idealization. In such a case the physically significant conclusion can be drawn by the idealization and realization (the analysis and synthesis) which have been the general method in the science.

There are two ways for the idealization. The first is to introduce the physically ideal basic states. For example, one has often preferred the idea of configurations to the neat mathematical expression for studying nuclear, atomic and molecular states. The second is to divide a given quantum-mechanical system into several parts which are interacting each other, as is the case with molecules which have preferably been considered as consisting of atoms in order to fit the chemical idea of elements and compounds. The division can be done with respect to the coordinates as is the case with the use of relative and centre-of-mass coordinates in various problems.

In a certain case only one partial system is extracted and the state of the remaining parts is made asleep by an appropriate way. This may be called the method of the partial description. The sleeping partial system is often called a core or a skeleton. The energy levels of atoms are usually discussed by making the state of their nuclei sleep and the latter is ignored from the outset. This may be an extreme, trivial case, while the idea of valence electrons outside a closed atomic core may be a better example. The separation of the electronic and nuclear systems in molecular problems and extracting the \( \pi \)-
electron system from the large conjugated molecules are the same kind of examples. A special way of the partial description is to extract a system of partial coordinates from the partial or total system after the suitable coordinate transformation. The separation of vibrational and rotational coordinates of molecules and the free-electron model for the \(\pi\)-electron system belong to this category. The theory of collective motion is also of the same kind.

In what follows a general method to extract the partial system will first be discussed in order to see what is the kind of its approximation. The method itself will not be a new one but a generalization of those used in various cases. The practical method will be accounted for in the cases of helium and complex atoms. It will next be shown that the one-dimensional partial description results in dividing the two-particle interaction into the short and long range parts and adopting the latter as the two-particle interaction in the extracted partial system, the short range part being absorbed in the skeleton field. Though this will be shown for the Coulomb interaction in the present paper, the result can be generalized to the case of other types of interactions. The theory of carotenoids and polyacenes previously worked out by the author and his collaborator will be interpreted from this viewpoint. That this method is really useful will further be shown with actual examples in the separate papers in which we shall see that the result is in fairly good agreement with experiment in spite of the simpleness of the model and the calculation.

Finally it will be noted that the light absorption by long carotenoids is really caused by the plasma oscillation of \(\pi\) electrons contained in the conjugated chains. This plasma oscillation is excited by the long range part of the Coulomb interaction between \(\pi\)-electrons but the reason of screening is somewhat different from that of the three-dimensional case.

It is due to the excitation of only a one-dimensional motion and sleeping of the motion in the remaining two dimensions, while the three-dimensional plasma oscillation is caused by the charge screening which results in a cut-off of the high frequency Fourier components of the Coulomb interaction. However, the one-dimensional and three-dimensional cases may both be considered as belonging to the same kind of phenomena from the viewpoint of the partial description.

The present idea of the partial description by extracting the partial two-particle interaction could successfully be applied to various problems, for example, including nuclear problems as well as atomic and molecular ones, if the method of extracting the partial system and the partial two-particle interaction would ingeniously be devised.

\section{General method}

We consider a quantum-mechanical system of \(N\) coordinates. After an appropriate transformation of the coordinates we divide all coordinates into two sets: \((\xi_1, \xi_2, \xi_3, \ldots, \xi_n)\) and \((x_1, x_2, x_3, \ldots, x_{N-n})\). Their canonically conjugate momenta are denoted by \((\pi_1, \pi_2, \pi_3, \ldots, \pi_n)\) and \((p_1, p_2, p_3, \ldots, p_{N-n})\) respectively. For the sake of simplicity we shall denote these sets of coordinates and momenta by \(\xi, \pi, p\) respectively. The Hamiltonian of the total system consequently takes the following form:
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\[ H = T(\pi, \xi) + V(\xi) + H_0(p, x) + H_1(\pi, \xi; p, x). \]  (1.1)

The total system is thus divided into two partial systems which are represented by the Hamiltonians denoted by \( T(\pi, \xi) + V(\xi) \) and \( H_0(p, x) \). The interaction between these two systems is given by \( H_1(\pi, \xi; p, x) \).

In order to extract a partial system we have to make the other sleep. This process can be carried out in the following way. First we solve the eigenvalue problem:

\[ [H_0(p, x) + H_1(0, \xi; p, x)] \phi(\xi, x) = U(\xi) \phi(\xi, x) \]  (1.2)

where \( \xi \) is considered as the constant parameter, \( U(\xi) \) is the eigenvalue, and \( \phi \) is normalized for every value of \( \xi \). If a set of all \( \phi(\xi, x) \) as the functions of \( x \) is complete for every value of \( \xi \), any eigenfunction \( \Psi \) of the total Hamiltonian can be expanded in an infinite series of \( \phi(\xi, x) \) for every value of \( \xi \):

\[ \Psi(\xi, x) = \sum \phi(\xi) \phi(\xi, x). \]  (1.3a)

The coefficient \( \phi(\xi) \) of the expansion can be so determined that \((H-E)\Psi = 0\) is satisfied by the series. For the present purpose we should assume that the series consists of only a few terms. For the sake of simplicity we consider the simplest case in which the series consists of a single term:

\[ \Psi(\xi, x) = \phi(\xi) \phi(\xi, x). \]  (1.3b)

Of course this can not be an exact solution but an approximate one for the eigenvalue problem of the total Hamiltonian, except for the accidentally fortunate case.

The eigenvalue equation, \((H-E)\Psi = 0\), for the total system reduces to

\[ [T(\pi, \xi) + V(\xi) + U(\xi) + H_1(\pi, \xi; p, x) - H_1(0, \xi; p, x) - E] \psi(\xi, \phi(\xi, x)) = 0. \]  (1.4)

Further if we multiply this by \( \phi^* \) and integrate with respect to \( x \), we have the equation for \( \psi \) as follows:

\[ [T(\pi, \xi) + V(\xi) + U(\xi) + T_1(\pi, \xi) - E] \phi(\xi) = 0 \]  (1.5a)

where

\[ T_1(\pi, \xi) = \int \phi^*(\xi, x)[H_1(\pi, \xi; p, x) - H_1(0, \xi; p, x)] \phi(\xi, x) dx \]

\[ + \int \phi(\xi, x)[T(\pi, \xi) \phi(\xi, x) - \phi(\pi, \xi) T(\pi, \xi)] dx. \]  (1.5b)

Generally speaking, \( \phi(\xi) \) must contain \( x \) as a parameter in order to satisfy (1.4). This contradicts the starting assumption, (1.3b). Therefore the influence of \( T_1 \) on the eigenvalue problem should be very small in order that the assumption given by (1.3b) is nearly correct. If this requirement is satisfied, \( \phi(\xi) \) can be determined by solving the equation (1.5). When \( T_1 \) is ignored the approximate Hamiltonian of the extracted system is given by
where $T$ is the kinetic energy and $U$ is the potential of the average field due to the skeleton. In this case it may be natural to take into account the effect of $T_1$ as a perturbation. If the total system is an isolated system of particles and if the partial $\xi$-system contains a number of particles, $V(\xi)$ represents the interaction between particles in the extracted system. In such a case $V$ and $U$ are usually given in the form

$$V = \sum_j [\xi(j) - \xi(0)], \quad U = \sum_k G(\xi_k).$$

The present method can equally be applied to the nuclear, atomic and molecular systems.

A practical way of determining the potential $U(\xi)$ is to make use of the variational method in which the function $\phi(\xi, x)$ is determined so as to minimize the variation integral for every value of $f$:

$$U(\xi) = \int \phi^* \left( H_0(p, x) + H_1(0, \xi; p, x) \right) \phi(\xi, x) dx.$$  \hspace{1cm} (1.8)

The adiabatic potential between atoms is often calculated in this way. More simply we can calculate $U(\xi)$ by assuming a suitable function for $\phi(\xi, x)$ in this integral. For example, if the $\xi$-system consists of valence electrons of an atom we can replace the self-consistent function of the core for $\phi(\xi, x)$ which is then eventually independent of $\xi$. In the extreme case the $x$-system is frozen, namely the integral (1.8) is calculated by assuming that $p_1 = p_2 = p_3 = \cdots = p_{N-n} = 0$ and $\phi^* \phi = \delta(x_1 - a_1) \delta(x_2 - a_2) \cdots \delta(x_{N-n} - a_{N-n})$ where $a_1, a_2, \cdots a_{N-n}$ are constants. This is the case with the nucleus in the consideration of the electronic states of an atom. A short cut is to assume a suitable, functional form of $U(\xi)$ on a certain physical ground. The free-electron model for the $\pi$-electron system is its example.

How to separate the partial Hamiltonian is most important. This procedure is not unique. Whether the method succeeds or not is due mainly to the way of this separating procedure. An ingenious device of dividing the total Hamiltonian is often capable of absorbing the greater part of the effect of $V(\xi)$ into $U(\xi)$. For this reason the particle interaction is not necessarily the same as the one contained in the original Hamiltonian. The way of the division should be devised so as to make the succeeding calculation as easy as possible or to make the effect of $V$ as small as possible. In the most fortunate case we have an independent-particle model.

§ 2. Practical application

In this section the application of the general method mentioned in the preceding section to the practical problem will briefly be accounted for in order to obtain the better understanding of the actual meaning of the method. To begin with the simplest problem we first take up the electronic state of the helium atom in which the nucleus is frozen, and examine whether the requirement for the smallness of the effect of $T_1$ is satisfied.

The Hamiltonian of the helium-like atom is given by (in atomic units)

$$H = -(d_1 + d_2)/2 - Z/r_1 - Z/r_2 + 1/r_{12}. \hspace{1cm} (2.1)$$
In this case the Hamiltonians of partial systems are $-\frac{\hbar^2}{2} - Z/r_1$ and $-\frac{\hbar^2}{2} - Z/r_2$ respectively and the interaction between them is $1/r_{12}$ which contains no momentum. If $\Psi(x_1, x_2)$ is a solution of $(H-E)\Psi = 0$ any linear combination of $\Psi(x_1, x_2)$ and $\Psi(x_2, x_1)$ also satisfies the same equation. Since $\Psi(x_1, x_2) + \Psi(x_2, x_1)$ and $\Psi(x_1, x_2) - \Psi(x_2, x_1)$ are the orbital functions for the singlet and triplet states respectively we have only to seek $\Psi(x_1, x_2)$. According to the procedure (1·2) we first consider the following equation:

$$
(-\frac{\hbar^2}{2} - Z/r_1 + 1/r_{12})\phi(x_1, x_2) = U\phi(x_1, x_2)
$$

(2·2)

where $U$ is an eigenvalue depending on $x_a$.

We want to have $\Psi(x_1, x_2)$ corresponding to the 1s1l configuration and let $\phi(x_1, x_2)$ have the $s$ symmetry for the space rotation. For this purpose we expand the interaction and the wave function in the Legendre series as follows:

$$
\phi(x_1, x_2) = \sum_{k=0}^{\infty} u_k(r_1, r_2) P_k(\cos \theta_{12})
$$

$$
1/r_{12} = \sum_{k=0}^{\infty} a_k(r_1, r_2) P_k(\cos \theta_{12}),
$$

(2·3)

where $\theta_{12}$ is the angle between $x_1$ and $x_2$. If we substitute these series for $\phi$ and $1/r_{12}$ in (2·2) we have the following set of equations for $u_k(r_1, r_2)$'s on account of the linear independence of the Legendre polynomials:

$$
\left[ \frac{1}{2r_1} \frac{\partial^2}{\partial r_1^2} r_1 - k(k+1)/(2r_1^2) + Z/r_1 + U(r_2) \right] u_k(r_1, r_2)
$$

$$
= \sum_{s=0}^{\infty} W(k, s; r_1, r_2) u_s(r_1, r_2)
$$

(2·4)

for $k=0, 1, 2, \cdots$ where

$$
W(k, s; r_1, r_2) = (2k+1) \sum_{\alpha=0}^{s} b(k, s, \gamma+2\alpha) a_{\gamma+2\alpha}(r_1, r_2), \quad \gamma = |k-s|, \quad \gamma+2\beta=k+s
$$

(2·5)

$$
b(l, m, n) = (1/2) \int_{-1}^{1} P_l(x) P_m(x) P_n(x) dx
$$

which appear when we expand the product of $\phi$ and $1/r_{12}$ in the Legendre series. We see from (2·4) that the eigenvalue, $U$, depends only on $r_2$, so that we write explicitly $U(r_2)$ in (2·4). $W(k, s; r_1, r_2)$ may be interpreted as a kind of the coupling energy between $u_k P_k$ and $u_s P_s$ states.

As is well known the expansion coefficients in (2·3) and (2·5) are given by

$$
a_k(r_1, r_2) = r_1^{\lambda/2} r_2^{\lambda+1} \quad \text{for} \quad r_1 < r_2
$$

$$
= r_2^{\lambda/2} r_1^{\lambda+1} \quad \text{for} \quad r_1 > r_2
$$

$$
b(l, m, n) = \frac{1 \cdot 3 \cdot 5 \cdots (l+m-n-1) \cdot 1 \cdot 3 \cdot 5 \cdots (m+n-l-1)}{2 \cdot 4 \cdot 6 \cdots (l+m-n) \cdot 2 \cdot 4 \cdot 6 \cdots (m+n-l)}
$$
where \( b(l, m, n) = 0 \) otherwise.

For \( k=0 \) and \( k=1 \) the equation (2.4) reduces to

\[
\left[ \frac{1}{2r_1} \frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1} + Z/r_1 - a_0(r_1, r_2) + U(r_2) \right] u_0(r_1, r_2) = 0
\]

\[
\left[ \frac{1}{2r_1} \frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1} + Z/r_1 - a_0(r_1, r_2) - \frac{2}{5} a_0(r_1, r_2) + U(r_2) \right] u_1(r_1, r_2)
\]

\[
= a_1(r_1, r_2) u_0(r_1, r_2) + \sum_{s=0}^{m} \frac{3 u_s(r_1, r_2)}{2s+1} \left( \frac{s}{2s-1} a_{s-1}(r_1, r_2) + \left( \frac{s+1}{2s+3} \right) a_{s+1}(r_1, r_2) \right).
\]

In order to determine \( u_0 \) and \( u_1 \) in an approximate way we assume that the main part of \( u_0 \) is the \( s \) orbital of the lowest energy and \( u_1, u_2 \ldots \) are small corrections. Since these corrections arise from \( 1/r_1^2 \) in (2.2), the summands under the \( \sum \) signs in the r.h.s. of (2.7a) and (2.7b) are the correction terms of respective equations. In order to have the first approximation we omit these terms altogether. Then we have a homogeneous equation for \( u_0 \) and an inhomogeneous equation for \( u_1 \). These equations still contain the correction terms, namely \( a_0 \) and \( a_2 \) terms in the l.h.s., the former being more important. We replace the former by \( 1/r_2 \) and ignore \( a_0(r_1, r_2) - 1/r_2 \) and \( a_2(r_1, r_2) \). Since we are seeking \( \psi(x_1, x_2) \) corresponding to the \( 1s \) configuration the ignorance of \( a_0(r_1, r_2) - 1/r_2 \) is nearly correct as it vanishes for \( r_1 < r_2 \) where the wave function is large. In this approximation we readily have the solution of (2.7) as follows:

\[
U(r_2) = -Z/2 + 1/r_2, \quad u_0 = \sqrt{Z^2/\pi} N(r_2) e^{-Zr_2}.
\]

\[
u_1(r_1, r_2) = \sqrt{Z/(4\pi)} N(r_2) \left[ \frac{3}{2} \left( e^{\rho_1} - e^{-\rho_2} (1 + 2 \rho_1 + 2 \rho_2) \right) (1 + \rho_2 e^{-\rho_2}) \right.
\]

\[
\left. - (2 \rho_1 + \rho_2 e^{-\rho_2}) e^{-\rho_1} / \rho_2 \right],
\]

for \( \rho_1 < \rho_2 \)

\[
\left[ \rho_2^2 + (3/2) \left( 1 - \rho_2^2 - [1 + \rho_2 e^{-\rho_2}] \right) (1 + 2 \rho_1 + 2 \rho_2) \right] e^{-\rho_1}
\]

\[
/ (\rho_1 \rho_2) e^{\rho_1} - 2 \rho_2 e^{-\rho_1}, \quad \text{for} \ \rho_1 > \rho_2
\]

where \( N(r_2) \) is the normalization constant, \( \rho_1 = Zr_1 \), and \( \rho_2 = Zr_2 \). The function \( u_0 \) is the \( 1s \) orbital of the hydrogen-like atom with the nuclear charge \( Z \). The Hamiltonian of the second partial system defined by (1.6) is given by \( H_2 = -d_2/2 - Z/r_2 + U(r_2) = -d_2/2 - (Z-1)/r_2 - Z/2 \). Therefore its eigenfunction, \( \psi(x_2) \), is the \( n \) orbital of the
hydrogen-like atom with the nuclear charge $Z - 1$. The first approximation of the searched solution is given by

$$\Psi(x_1, x_2) = \phi(x_1, x_2) \psi(x_2) = \{u_0(r_1) + u_1(r_1, r_2) \cos \theta_{12}\} \psi(x_2).$$ \hspace{1cm} (2.9)

The more exact solution and eigenvalue-function, $U(r_2)$, can be obtained by reviving some of the neglected terms or by proceeding to the higher stages of the successive approximation. It is also possible to apply the variation method. The details of such calculations will later be reported elsewhere. The correction term including $\cos \theta_{12}$ in (2.9) means the angular deformation of the $1s$ orbital by the electrostatic influence of the $n\ell$ orbital. This can be interpreted as the influence of the $pd$ and other $sp$ configurations. The more exact solution includes the radial and angular deformations of higher order or the influence of higher configurations.

Now we shall examine whether the effect of $T_1(\pi, \xi)$, which appeared in (1.56), is small in the present case. We saw that if the contribution of $T_1(\pi, \xi)$ to the eigenvalue of the total Hamiltonian is small, the basic assumption, (1.33), is nearly correct. In the present case $T_1(\pi, \xi)$ is given by

$$T_1(p_\pi, x_2) \psi(x_2) = -2^{-1} \int \phi(x_1, x_2) [\Delta\phi(x_1, x_2) - \phi(x_1, x_2) \Delta\phi] d(x_1) \psi(x_2).$$ \hspace{1cm} (2.10a)

Since $\phi(\Delta\phi - \Delta\phi) \psi = \phi\Delta\phi + (p_\pi \phi) (\nabla \phi)$, and $\phi$ is real and normalized for every value of $x_2$ as the function of $x_1$ the integral is reduced to

$$T_1(p_\pi, x_2) \psi(x_2) = -2^{-1} \int \phi(x_1, x_2) \Delta\phi(x_1, x_2) d(x_1).$$ \hspace{1cm} (2.10b)

If we again make use of $\phi\Delta\phi = \Delta\phi^2/2 - (\nabla \phi)^2$ and the normalization property of $\phi(x_1, x_2)$ we have

$$T_1(p_\pi, x_2) = (1/2) \int [\nabla \phi(x_1, x_2)]^2 d(x_1).$$ \hspace{1cm} (2.11)

Therefore $T_1$ is the positive function of $x_2$ and independent of $p_\pi$.

The contribution of $T_1$ to the eigenvalue, $E_1$ of the total Hamiltonian is given by

$$E_1 = \int \phi^*(x_2) T_1 \psi(x_2) d(x_2)$$ \hspace{1cm} (2.12)

which has the anti-binding effect as $T_1$ is positive. If we make use of (1.56) we have

$$E_1 = E - \int \phi^*(x_2) [-\Delta\phi/2 - Z/r_2 + U(r_2)] \psi(x_2) d(x_2).$$ \hspace{1cm} (2.13)

The numerical values of the integral were computed by Bethe in an approximate way in which $U(r_2)$ was calculated more exactly than the one given by (2.8). We can estimate $E_1$ if we subtract his value from the observed $E$. The results are $|E_1/E| = 10^{-6}$ for He $3D$ and $|E_1/E| = 6 \times 10^{-7}$ for He $4D$.

Next we briefly consider the case of a complex atom. The method illustrated in
the case of helium can be generalized to this case. The total number of electrons is denoted by $N$. We ignore the state of the nucleus as before. The system of atomic electrons is divided into two partial systems which consist of $N_0$ and $N$ electrons respectively where $N_0 = 2, 4, 10, 12, 18, 28, \cdots = \Sigma 2(2l+1)$. According to the procedure (1·1), the total Hamiltonian is divided into three parts:

$$H = H_a + H_0 + H_1$$

$$H_a = -\sum_{k=1}^{N} (d_k/2 + Z/r_k) + \sum_{k=1}^{N} \sum_{j=k+1}^{N} 1/r_{kj}$$

$$H_0 = -\sum_{a=1}^{N_0} (d_a/2 + Z/r_a) + \sum_{a=N+1}^{N} \sum_{b=a+1}^{N} 1/r_{ab}.$$  

If $\Psi(x_1, x_2, \cdots, x_N)$ is an eigenfunction of $H$ belonging to the eigenvalue $E$, the function given by $\sum_F c_F P \Psi$ is also an eigenfunction of $H$ belonging to the same eigenvalue, where $P$ denotes the permutation of coordinates, $c_F$ is the arbitrary coefficient which may or may not depend on the electron spins, and the summation should be extended over all possible permutations. Therefore if $\phi$ is a solution of (1·2) including the spin functions of $N_0$ electrons we can write the eigenfunction of the total Hamiltonian in the form

$$\Psi = \sum_F c_F P \phi(\xi) \phi(\xi, x)$$  

where $\xi$ denotes $(x_1, x_2, \cdots, x_N)$, $\phi$ denotes $(x_{N+1}, x_{N+2}, \cdots, x_N)$, and the coefficient $c_F$ should contain the spin functions of $N$ electrons so as to satisfy the Pauli principle. The equation (1·2) may be solved in the way that the first approximation of $\phi(\xi, x)$ is the Hartree-Fock function corresponding to the solution of the equation, $H_0 \phi = U_0 \phi$. In this case the first approximation of $\phi(\xi, x)$ represents a closed shell structure. Therefore one may speak that the atom consists of $N$ valence electrons and a closed shell core of $N_0$ electrons, and $U(\xi)$ is the potential energy of valence electrons due to the atomic core. The deviation of exact $\phi(\xi, x)$ from the Hartree-Fock function represents the deformation of the core function due to the electrostatic influence of valence electrons or it can be interpreted as the configuration interactions. The $\pi$ electron system and the skeleton of a conjugated molecule can be considered quite in the same way.

§ 3. Linear model

In this section we consider the linear model. In order to make the discussion clear-cut we take up the $\pi$-electron system, although the consideration is equally applicable to other system. The partial system is separated in two steps. First the $\pi$-electron system is extracted from a conjugated molecule where $\xi$-coordinates correspond to the three-dimensional cartesian coordinates of $\pi$-electrons. We next divide the $\pi$-electron system into two parts, the $x$ and $\gamma x$ systems. Although the interaction between $\pi$-electrons is not necessarily Coulombian as was mentioned in the previous section, we derive the one-dimensional two-electron interaction in the extracted system by assuming the Coulomb interaction between
π-electrons in order to avoid the unnecessary confusion. If the Fourier coefficient of the
Coulomb potential is given by \( F(k_1, k_2, k_3) \), the interaction (measured in atomic units)
between electrons can be divided into three parts as follows:

\[
1/r_{ij} = J(x_i - x_j) + G(\rho_{ij}) + G_i(x_i - x_j),
\]

\[
\rho_{ij}^2 = (y_i - y_j)^2 + (z_i - z_j)^2,
\]

\[ x_i = (x_i, y_i, z_i), \quad i = 1, 2 \quad (3\cdot1) \]

where

\[
J(x) = \sum_{k} F(k, 0, 0) \exp \left( i k \cdot x \right)
\]

\[
G(\rho_{ij}) = \sum_{k, k_2} F(0, k_2, k_3) \exp \left[ i (k_2 (y_i - y_j) + k_3 (z_i - z_j)) \right], \quad k_2^2 + k_3^2 > 0
\]

\[
G_i(x) = \sum_{k} F(k, k_2, k_3) \exp \left( i k \cdot x \right) \quad |k_2| > 0, \quad k_2^2 + k_3^2 > 0 \quad (3\cdot2)
\]

\[ \mathbf{k} = (k_1, k_2, k_3), \quad j = 2\pi n_j/L_{y}, \quad n_j = 0, \pm 1, \pm 2, \ldots, \quad j = 1, 2, 3. \]

The Fourier series converges to the Coulomb potential in the domain given by
\( 2|x_i - x_j| < L_1, \quad 2|y_i - y_j| < L_2, \) and \( 2|z_i - z_j| < L_3. \) We consider
\( J(x_i - x_j) \) as the two-electron interaction in the partial \( x \)-system, \( G(\rho_{ij}) \) as that in the \( yz \)-system, and \( \sum_{i=1}^{n} \sum_{j=i+1}^{n} G_i(x_i - x_j) \) as the
interaction between these two systems where \( n \) is the number of π electrons.

In order to see how \( J(x) \) depends on \( x \), we have to evaluate the sum of the series.
This can easily be carried out because \( J(x) \) is the average of the Coulomb potential in the
\( yz \) domain. Therefore we have

\[
J(x) = (4ab)^{-1} \int_{b}^{a} dy \int_{-\pi}^{\pi} r^{-1} dz \quad (3\cdot3)
\]

where \( r = \sqrt{x^2 + y^2 + z^2}, \quad r \geq 0, \quad 2a = L_y, \) and \( 2b = L_y. \) This integral can be evaluated in an
elementary way. The result is given by

\[
J(x) = \frac{1}{2} \log \left( \frac{\sqrt{c^2 + x^2} + d}{\sqrt{c^2 + x^2} - d} \right)^{1/a} \left( \frac{\sqrt{c^2 + x^2} + b}{\sqrt{c^2 + x^2} - b} \right)^{1/b} - \frac{x}{ab} \tan^{-1} \left( \frac{ab}{x\sqrt{c^2 + x^2}} \right) \quad (3\cdot4)
\]

where \( c = a^2 + b^2. \) The asymptotic form of this function is \( 1/|x| \) as is expected. If we
denote the difference of \( 1/|x| \) and \( J(x) \) by \( J_0(x) \) we can divide the Coulomb potential
into the sum of these two functions:

\[
1/|x| = J_0(x) + J(x) \quad (3\cdot5)
\]

The value of \( J(x) \) at the origin is given by \( J(0) = [\log(3 + 2\sqrt{2})]/a = 1.76/a \) when \( a \)
and \( b \) are the same. Therefore the most part of the Coulomb potential is reserved in
\( J_0(x) \) near the origin and in \( J(x) \) at the distant point.

The function given by \( (3\cdot4) \) is too complicated to see the qualitative behaviour of
\( J(x). \) The behaviour can easily be seen if we evaluate the sum in an approximate way
by taking the average over the circular domain restricted by \( \gamma^2 + \zeta^2 \leq a^2, \) instead of the
Fig. 1.
- : \( J(x) \) given by (3.6)
- - - - - - - - - - : Coulomb potential

Fig. 2.
- : \( J(x) \) given by (3.7) \((a=1)\)

rectangular domain. We have then *

\[
J(x) = (2/\alpha^2)\left[ \sqrt{\alpha^2 + x^2} - |x| \right]. \tag{3.6}
\]

Its value at the origin is somewhat larger than the former case, namely \( J(0) = 2/\alpha \), because of the smaller area of the domain. It may be natural to refer \( J_0(x) \) and \( J(x) \) as the short range and long range parts of the Coulomb potential respectively. The division given by (3.5) depends on the value of \( \alpha \). Therefore \( \alpha \) is the division constant which discriminates two parts and its genetic history illustrated above has no significance so far as the exact functional form itself of \( J(x) \) at the short distance is unimportant for the final result. It is then only important that \( J(x) \) is the long range part of the Coulomb potential. Another functional form is equally possible in this case. For example, the following function has the same property:

\[
J(x) = \begin{cases} 
0 & \text{for } |x| < \alpha \\
1/|x| & \text{for } |x| \geq \alpha.
\end{cases} \tag{3.7}
\]

The functional form of \( J(x) \) given by (3.4) was applied to the one-dimensional free-electron model of carotenoids\(^1\) and cyanins\(^2\) and the very good agreement between theory and experiment was obtained. In the former case the value of the division constant \( \alpha \) was equal to 7.12\( \text{Å} \) \((a-b)\), and in the latter case it was equal to 16.7\( \text{Å} \). The greater value of the constant means that the effect of two-electron interaction is absorbed

---

* If the interaction is the Yukawa potential, \( e^{-kr}/r \), we have

\[
J(x) = \left\{ 2/(\alpha^2) \right\} \left[ \exp(-\kappa |x|) - \exp\left(-\kappa \sqrt{\alpha^2 + x^2}\right) \right].
\]
the more in the skeleton field. Nevertheless the latter value is still too large compared with the total length of the conjugated chain, while the former value is reasonable. Although, in the first paper, \( \sigma^2 \) was interpreted as the sectional area of the pipe in which \( \pi \) electrons are enclosed, the interpretation may not be adequate but the present idea be better. This will further be justified by the example in the next section. However, another interpretation is still possible\(^{(24)}\).

When we extract the two-dimensional partial system we can consider \( G(\rho_{12}) + F(0, 0, 0) \) as the two-electron interaction in the extracted system which is given by

\[
G(\rho) + F(0, 0, 0) = \frac{1}{2a} \int_{-a}^{a} r^{-1} dr = \frac{1}{2a} \log \frac{\sqrt{a^2 + \rho^2} + a}{\sqrt{a^2 + \rho^2} - a}, \quad \rho^2 = x^2 + y^2. \quad (3 \cdot 8)
\]

This function asymptotically behaves as \( 1/\rho \). Still it has a weaker logarithmic singularity at \( \rho = 0 \). This interaction was examined in the two-dimensional free-electron model of naphthalene by Huzinaga\(^9\).

§ 4. Ring model

We next consider the ring model in which electrons are confined to move freely in a ring by means of suitably assumed form of \( U(\xi) \). We want to derive a one-dimensional interaction in the similar way as the preceding case. Let the radius of the ring be \( R \). The one-dimensional coordinate of a point on the ring can be given by the arc length between the point and a definite point on the ring where the coordinate and the definite point are referred to as the ring coordinate and its origin respectively. We denote the ring coordinate by \( s \). Let the positions of two electrons be denoted by \( (\rho_1, \theta_1, z_1) \) and \( (\rho_2, \theta_2, z_2) \) in the cylindrical coordinates, where \( \rho^2 = x^2 + y^2 \) and \( \theta \) is the azimuthal angle. The distance, \( r_{12} \), between these electrons is given by

\[
r_{12}^2 = (\rho_1 - \rho_2)^2 + \rho_1 \rho_2 [2 \sin \{ ((\theta_1 - \theta_2)/2) \}]^2 + (z_1 - z_2)^2. \quad (4 \cdot 1)
\]

We define a function of \( \rho, \theta \) and \( z \) by

\[
W(\rho, \theta, z; R^2) = [\rho^2 + (2R \sin \theta/2)^2 + z^2]^{-1/2}. \quad (4 \cdot 2)
\]

If \( F(k_n, k_3; R^2) \) is the Fourier coefficient of this function we can separate its \( \theta \)-part as was done in the previous section. If we replace \( \theta \) by \( s/R \), the \( \theta \)-part of the function is given by

\[
f(s) = \sum_{n=0}^{m} F(0, n, 0; R^2) e^{i n s/R}. \quad (4 \cdot 3)
\]

By making use of the same Fourier coefficient we can expand the Coulomb interac-
tion between two electrons in the exponential series as follows:

\[
1/r_{12} = W(\rho_1 - \rho_2, \theta_1 - \theta_2, z_1 - z_2; \rho_1, \rho_2)
\]

\[
= \sum_{k_{nm}} F(k_1, n, k_2; \rho_1, \rho_2) \exp \left[ ik_1 (\rho_1 - \rho_2) + n(\theta_1 - \theta_2) + k_2 (z_1 - z_2) \right]
\]

\[
k_i = 2\pi n_i / L_i, \quad i = 1, 2; \quad n_1, n_2, n_0 = 0, \pm 1, \pm 2, \ldots\]

(4.4)

The function \( f(s_1 - s_2) \) can be obtained by replacing \( R^2 \) for \( \rho_1, \rho_2 \) and \( (s_1 - s_2) / R \) for \( \theta_1 - \theta_2 \) in the \( \theta \)-series part of this expansion. Therefore we can consider the two-electron function given by \( f(s_1 - s_2) \) as the \( s \)-part (on the ring) of the Coulomb interaction between two electrons. The sum of the Fourier series in the right-hand side of (4.3) can be evaluated by taking the average of \( W(\rho, \theta, z; R^2) \) with respect to \( \rho \) and \( z \) over the domain defined by \( 2|\rho| \leq L_\rho \) and \( 2|z| \leq L_z \). The result is given by the similar expression as (3.4). As was done in the previous section, if we approximately calculate the average over the circular domain restricted by \( \rho^2 + z^2 \leq d^2 \), we have

\[
f(s) = (2/\pi)^2 \left[ \sqrt{d^2 + 2R \sin \{s/(2R)\}} \right]^2 - 2R \sin \{s/(2R)\}.\]

(4.5)

Since the distance between two electrons on the ring is equal to \( 2R \sin (s_1 - s_2) / (2R) \) as is seen from the equation (4.1) by putting \( z_1 = z_2 \) and replacing \( R \) for \( \rho_1 \) and \( \rho_2 \), the above equation has the same meaning as (3.6). Therefore the function can be replaced by

\[
f(s) = 0 \quad \text{for} \quad s < s_0
\]

\[
= \left| 2R \sin \{s/(2R)\} \right|^{-1} \quad \text{for} \quad s \geq s_0.
\]

(4.6)

Making use of this form of the two-electron interaction the energy levels of \( \pi \)-electron systems were calculated by assuming a free-electron model for polyacenes, a preliminary account of which was already given\(^3\). The length of the division constant, \( s_0 \), was 0.68\( l \) where \( l = 1.4\AA \) is the bond length in benzene. We saw that the variation of the wave length of the absorption maxima with the number of benzene rings was reproduced fairly well. The detail of the calculation and the application of the same method to the energy levels of benzene by taking into account the configuration interaction will be reported in the separate papers. We shall see that the result is fairly good in spite of the simpleness of the model and the calculation.

§ 5. Plasma oscillation of \( \pi \) electrons in carotenoids

The excitation energy of the \( \pi \)-electron system of carotenoids was calculated by assuming the linear model in a previous paper\(^3\). The result is given by

\[
\Delta E = \sum_{\nu = -\infty}^{\infty} N_\nu \sqrt{T_\nu^2 + 2T_\nu U_\nu}
\]

(5.1)

where \( N_\nu \) is the number of sound Bosons whose energy is equal to \( \sqrt{T_\nu^2 + 2T_\nu U_\nu} \). \( T_\nu \) and \( U_\nu \) come from the kinetic energy and the interaction between \( \pi \) electrons respectively and they are given by
Partial Description of Quantum-Mechanical System

\[ T_v = \frac{(\hbar/L)^2 \cdot (n_0/m) |\psi|}{2}, \quad U_v = 2 |\psi| J_v \]

(5.2)

where \( L \) is the length of the conjugated chain, \( m \) is the electron mass, \( n_0 \) is the Fermi maximum, and \( J_v \) is the Fourier coefficient of the one-dimensional interaction between \( \pi \) electrons. If we assume that the interaction is given by \( J(x_1 - x_2) \) of (3.4) we have

\[ J_v = \left( \frac{\epsilon L}{\pi A} \right) \cdot \frac{1}{\nu^2} (\nu = \pm 1, \pm 2, \ldots) \]  

(5.3)

where \( L_1 \) is replaced by \( L \) and \( L_2 \) by \( A \). In this case the second term under the square root sign of (5.1) is independent of \( \nu^0 \).

If we denote the total number of \( \pi \) electrons by \( N \) we have \( N = 4n_0 + 2 \). When \( N \) is very large we can replace \( 4n_0 \) with \( N \) and we have approximately

\[ 2T_v U_v = (\hbar \omega)^2 \]  

(5.4)

where \( \omega \) is the so-called plasma frequency \( \omega^{(0)} \) :

\[ \omega = \sqrt{4\pi \epsilon^2 N/(mLA)} \]  

(5.5)

The linear density, \( N/L \), of \( \pi \) electrons is the same for all carotenoids. Therefore the plasma frequency is independent of the molecular length of carotenoids. Since \( T_v \) is inversely proportional to the molecular length the energy of sound Bosons approaches to the limit, \( \hbar \omega \), the energy of the plasma oscillation, when the molecule becomes longer and longer. The energy of low-energy (small-\( \nu \)) Bosons in long carotenoids is approximately equal to the limit. The limit of the excitation energy of carotenoids is equal to

\[ (\Delta E)_0 = N_\infty \hbar \omega \]  

(5.6)

where \( N_\infty \) is the total number of sound Bosons.

As is well known, the wave length of the absorption maxima of carotenoids becomes longer and longer with the molecular length but ultimately converges to a limit. The first excitation energy of carotenoid is given by (5.1) with \( N_\nu = 1 \) and \( N_\nu = 0 \) for \( \nu \neq 1 \). Therefore the convergence limit of the absorption energy is equal to the energy, \( \hbar \omega \), of the plasma oscillation. The corresponding wave length can be calculated by employing the parameter value previously determined \(^{1}\), namely \( A = 724 \cdot 3 \) atomic units. The linear density of \( \pi \) electrons is equal to \( N/L = 1/l \) where \( l \) is the mean bond length between carbons in the conjugated chain and is assumed to be the bond length in benzene \( (l = 1 \cdot 4A = 2 \cdot 646 \) atomic units). The calculated values of the wave length and the wave number of the plasma oscillation are equal to \( 563 \) m\( \mu \) and \( 1 \cdot 78 \times 10^4 \) cm\(^{-1} \) respectively. Whether the energy of the plasma oscillation is greater or less than the kinetic part of the absorption energy can be indicated by the ratio, \( \delta = 2U_\nu /T_\nu \) \( = (\hbar \omega /T_\nu)^2 \). In fact the values of this ratio are large compared with unity for long carotenoids as is seen from Table 1. Therefore we see that the light absorption of long carotenoids is due mainly to the plasma oscillation of \( \pi \)-electrons contained in their conjugated chains. We see, from the reasoning of the third and fifth sections, that the plasma oscillation is caused by the long range part of the Coulomb interaction between
\(\pi\)-electrons. The screening of the short range part arises from extracting the one-dimensional partial system and making sleep the motion of \(\pi\)-electrons in the remaining two dimensions, while this is the charge screening which results in a cut-off of the high frequency Fourier components of the Coulomb interaction by introducing the collective coordinates in the case of the three-dimensional plasma oscillation\(^{5,10}\). The effective electron density of plasma oscillation may be defined as \(N/(LA) = 1/(LA)\) though \(A\) does not mean the real sectional dimension of the electron vessel in the present case. The calculated value of the effective density for carotenoids is equal to \(3 \cdot 5 \times 10^{21} \text{cm}^{-3}\). The calculated and observed values of absorption maxima are also shown in Table 1.

Table 1. Absorption Maxima of Long Carotenoids

<table>
<thead>
<tr>
<th>(N)</th>
<th>(\delta)</th>
<th>(\lambda_{\text{calc}})</th>
<th>(\lambda_{\text{obs}})*</th>
<th>Carotenoids</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.47</td>
<td>457</td>
<td>450</td>
<td>Antheraxanthin</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>461</td>
<td>Rubixanthinmonoeoxyde</td>
</tr>
<tr>
<td>22</td>
<td>1.76</td>
<td>471</td>
<td>466</td>
<td>Astaxanthin</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>471</td>
<td>Rhodopin</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>472</td>
<td>Lycoxanthin</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>473</td>
<td>Lycopophyll</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>473</td>
<td>Lycopene</td>
</tr>
<tr>
<td>24</td>
<td>2.07</td>
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<td>478</td>
<td>Eschscholtzxanthin</td>
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<tr>
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<td>482</td>
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<td>2.42</td>
<td>493</td>
<td>493</td>
<td>Rhodoviolascin</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>495</td>
<td>Decapreno-(\delta)-carotene</td>
</tr>
<tr>
<td>28</td>
<td>2.79</td>
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<td>500</td>
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</tr>
<tr>
<td>30</td>
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<tr>
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<td></td>
<td></td>
<td>508</td>
<td>Decapreno-(\beta)-carotene</td>
</tr>
<tr>
<td>38</td>
<td>5.03</td>
<td>528</td>
<td>537</td>
<td>Dodecapreno-(\beta)-carotene</td>
</tr>
<tr>
<td>(\infty)</td>
<td>(\infty)</td>
<td>553</td>
<td></td>
<td>(plasma oscillation)</td>
</tr>
</tbody>
</table>

*Sources were given in reference (1).
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References

5) D. Bohm and D. Pines, Phys. Rev. 92(1953), 609.
9) H. Bethe, Geiger-Scheel's Handb. der Phys., 24/1 (1933), 339.

Note added in proof. Recently Ta-You-Wu and A. B. Bhatia [J. Chem. Phys., 24 (1956), 48, 444] calculated the operator $T_1$ in the case of ionic and neutral hydrogen molecules and two normal helium atoms which were divided into electronic and nuclear systems. They found that $T_1$ is of the same order of magnitude as the van der Waals interaction and that $T_1$ is represented by a repulsive potential. The latter result can be seen from (2.11) in the present paper.

The estimation of $|E_1/E|$ in the present paper may include a certain error because Bethe's calculation is not sufficiently accurate for the purpose of calculating $E_1$ according to Equation (2.13). It is better to calculate $E_1$ directly by making use of Equations (2.11) and (2.12). The eigenvalue of $-\Delta_2/2Z/r_2 + U(r_2)$ is lower than the eigenvalue of the Hamiltonian given by (2.1) because $T_1$ is repulsive as is seen from (2.11). If the former eigenvalue is calculated in an approximate way the difference of these eigenvalues is partly compensated by the error of the calculation. We consequently underestimate the value of $E_1$ if we make use of (2.13). Thus the estimated value of $|E_1/E|$ in the present paper may be too small. The result of direct calculation of $E_1$ will be reported elsewhere.