RESEARCH REPORTS

ON THE SOLUTION OF SCHRÖDINGER EQUATION WITH PERIODIC POTENTIAL IN THE THREE DIMENSIONAL FINITE SPACE

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§ 0. Preliminaries

The solution of the one-dimensional Schrödinger equation with a potential composed of a number of square-well potentials of the same form, was presented by Oshida[1] in 1951. He has also given a brief comment about the generalization of his method to the case of one-dimensional potentials which are functions of coordinate.

The aim of this paper is to present a method to solve the three-dimensional Schrödinger equation with a potential composed of a finite number of potentials of the same form. The generalization to the n-dimensional case and to the case of differential equations of higher order, is also given. The application of this method to branched molecules is also briefly mentioned.

§ I. Matrix Representation of the Solution of the Schrödinger Equation

If the time-independent Schrödinger equation:

$$H\Psi = E\Psi, \tag{1}$$

with Hamiltonian operator H, is separable in the three-dimensional space, one can write in a suitable orthogonal coordinate-system (y_1, y_2, y_3),

$$\left.\begin{aligned} &H^{(p)}\Xi^{(p)}(y_p) = E^{(p)}\Xi(y_p), \qquad (p=1, 2, 3)\\ &\Psi(y_1, y_2, y_3) = \Xi^{(1)}(y_1)\,\Xi^{(2)}(y_2)\,\Xi^{(3)}(y_3), \end{aligned}\right\} \tag{2}$$

with constants $E^{(p)}$ and three differential operators $H^{(p)}$ of order 2. Further, let us consider a case where the differential equations (2) can be solved in each subspace. We shall now define

$$\xi^{(p)}(y_p) = \frac{d\Xi(y_p)}{dy_p}, \qquad (p=1, 2, 3) \tag{3}$$

and take a set of independent fundamental solutions which satisfy the following

conditions on the surfaces $y_p = y_p^\circ$, respectively.

Special solutions of type I: $\Xi_{\mathrm{I}}^{(p)}(y_p)$ satisfy

$$\left.\begin{aligned} &\Xi_{\mathrm{I}}^{(p)}(y_p^\circ) = 1 \quad \text{and} \quad \xi_{\mathrm{I}}^{(p)}(y_p^\circ) = 0, \qquad (p = 1, 2, 3) \\ &\text{Special solutions of type II: } \Xi_{\mathrm{II}}^{(p)}(y_p) \text{ satisfy} \\ &\Xi_{\mathrm{II}}^{(p)}(y_p^\circ) = 0 \quad \text{and} \quad \xi_{\mathrm{II}}^{(p)}(y_p^\circ) = 1. \qquad (p = 1, 2, 3) \end{aligned}\right\} \tag{4}$$

Then, the solutions which satisfy the conditions on the surfaces $y_p = y_p^\circ$:

$$\left.\begin{aligned} &\Xi^{(p)}(y_p^\circ) = \Xi_0^{(p)}, \\ &\xi^{(p)}(y_p^\circ) = \xi_0^{(p)}, \qquad (p = 1, 2, 3) \end{aligned}\right\} \tag{5}$$

are written as follows:

$$\Xi^{(p)}(y_p) = \Xi_0^{(p)} \cdot \Xi_{\mathrm{I}}^{(p)}(y_p) + \xi_0^{(p)} \cdot \Xi_{\mathrm{II}}^{(p)}(y_p). \qquad (p = 1, 2, 3) \tag{6}$$

Accordingly, we obtain

$$\xi^{(p)}(y_p) = \Xi_0^{(p)} \cdot \Xi_{\mathrm{I}}^{(p)\prime}(y_p) + \xi_0^{(p)} \cdot \Xi_{\mathrm{II}}^{(p)\prime}(y_p), \tag{7}$$

where the prime $'$ represents the differentiation with respect to the argument.

Let us take a column vector of six components:

$$\left.\begin{aligned} &\mathbf{X}(y_1, y_2, y_3) = \{\Xi^{(1)}(y_1), \xi^{(1)}(y_1), \Xi^{(2)}(y_2), \xi^{(2)}(y_2), \Xi^{(3)}(y_3), \xi^{(3)}(y_3)\}, \\ &\text{then the expressions (6) and (7) are written as} \\ &\mathbf{X}(y_1, y_2, y_3) = \mathbf{P}(y_1, y_2, y_3) \cdot \mathbf{X}(0, 0, 0), \\ &\text{with a column vector} \\ &\mathbf{X}(0, 0, 0) = \{\Xi_0^{(1)}, \xi_0^{(1)}, \Xi_0^{(2)}, \xi_0^{(2)}, \Xi_0^{(3)}, \xi_0^{(3)}\}, \end{aligned}\right\} \tag{8}$$

and a matrix $\mathbf{P}$ of order 6. This matrix is quasi-diagonal and is found to be

$$\mathbf{P} = \begin{Vmatrix} \mathbf{P}_1 & & 0 \\ & \mathbf{P}_2 & \\ 0 & & \mathbf{P}_3 \end{Vmatrix}, \tag{9}$$

with

$$\mathbf{P}_i = \begin{Vmatrix} \Xi_{\mathrm{I}}^{(i)}(y_i) & \Xi_{\mathrm{II}}^{(i)}(y_i) \\ \Xi_{\mathrm{I}}^{(i)\prime}(y_i) & \Xi_{\mathrm{II}}^{(i)\prime}(y_i) \end{Vmatrix}. \qquad (i = 1, 2, 3) \tag{10}$$

Thus we can find the value of a vector $\mathbf{X}(l_1, l_2, l_3)$ (*i.e.* the solution of the Schrödinger equation) on the surfaces $y_p = l_p$ $(p = 1, 2, 3)$ from a vector $\mathbf{X}(0, 0, 0)$ on the surfaces $y_p = y_p^\circ$ $(p = 1, 2, 3)$, by means of the transformation matrices $\mathbf{P}_i(y_1, y_2, y_3)$ whose determinants are Wronskian determinants of the differential equations (2).

When the potentials in the subspaces are composed of the same form appearing n times in each subspace, we have the transformation equations of the type:

$$\left.\begin{aligned} \mathbf{X}(L_1, L_2, L_3) &= \{\cdots \mathbf{RQP}\}^n \cdot \mathbf{X}(0, 0, 0), \\ L_p &= n \cdot l_p, \qquad (p=1, 2, 3) \end{aligned}\right\} \tag{11}$$

where $\mathbf{Q}$, $\mathbf{R}$ etc. represent the matrices similar to $\mathbf{P}$.

One can simplify the matrix $\{\cdots \mathbf{RQP}\}^n$ by means of Sylvester's theorem,[2] if one knows the eigen-values of the matrix $\{\cdots \mathbf{RQP}\}$. The theorem states: If λ_s $(s=1, 2, \ldots, q)$ are the different eigen-values (non-degenerate case) of the matrix $\mathbf{Z}$ of order q, then one has

$$\mathbf{Z}^n = \sum_{k=1}^{q} \frac{(\mathbf{Z}-\lambda_1\mathbf{I})\cdots(\mathbf{Z}-\lambda_{k-1}\mathbf{I})(\mathbf{Z}-\lambda_{k+1}\mathbf{I})\cdots(\mathbf{Z}-\lambda_q\mathbf{I})}{(\lambda_k-\lambda_1)\cdots(\lambda_k-\lambda_{k-1})(\lambda_k-\lambda_{k+1})\cdots(\lambda_k-\lambda_q)}\lambda_k^n. \tag{12}$$

In the degenerate case, however, one can have another expression for $\mathbf{Z}^n$ not very much different from (12).

It should be mentioned that the calculation of $\{\cdots \mathbf{RQP}\}^n$ is more simplified, if one takes into account that the matrices $\mathbf{P}$, $\mathbf{Q}$, $\mathbf{R}$ etc. are all quasi-diagonal. Then, we find

$$\{\cdots \mathbf{RQP}\}^n = \begin{Vmatrix} \{\cdots \mathbf{R}_1\mathbf{Q}_1\mathbf{P}_1\}^n & & 0 \\ & \{\cdots \mathbf{R}_2\mathbf{Q}_2\mathbf{P}_2\}^n & \\ 0 & & \{\cdots \mathbf{R}_3\mathbf{Q}_3\mathbf{P}_3\}^n \end{Vmatrix}. \tag{13}$$

Accordingly, it is quite sufficient to calculate each sub-matrix separately, without treating the original matrix (13) as a whole.

Moreover, it should be worth mentioning that the determinants of the transformation matrices (10) are not very complicated, because the matrices (10) correspond to the Wronskian determinants of (2).

By performing the calculation of the matrix (13), one can obtain the solution of equation (1) with a potential composed of a finite number of potentials of the same form connected in series in the three-dimensional configuration space.

The method presented here is very similar to the treatment in the circuit theory of four terminal networks.

§ II. Boundary Conditions

At the both ends of the potential, which appears in the Hamiltonian operator, we must take some boundary conditions for wave function. We shall consider two cases, as examples of the illustration of the boundary condition.

Case a. Infinitely high potential at the both ends.

Let us take a potential of the form:

$$W=\infty \quad \text{for} \quad y_p<0 \quad \text{and} \quad L_p<y_p, \tag{14}$$

then, we have

$$\Xi^{(p)}(y_p^0)=0 \quad \text{and} \quad \Xi^{(p)}(L_p)=0. \qquad (p=1, 2, 3) \tag{15}$$

These lead us to the conditions that the element in the first low and second

column of each matrix $\{\cdots \mathbf{R}_i\mathbf{Q}_i\mathbf{P}_i\}^n$ should vanish, whatever $\xi^{(p)}(y_p^\circ)$ and $\xi^{(p)}(L_p)$ they may be. Accordingly, the three equations

$$[\{\cdots \mathbf{R}_i\mathbf{Q}_i\mathbf{P}_i\}^n]_{12}=0, \qquad (i=1,\ 2,\ 3) \tag{16}$$

determine the eigen-values of the equations (2) under the conditions (14).

Case b. Potential of finite depth at the ends.
As for the potential

$$W=U_a<\infty \qquad \text{for} \quad y_p<0 \quad \text{and} \quad L_p<L_p, \tag{17}$$

we have somewhat complicated conditions, which involve the limiting operations $y_p\to\pm\infty$, and we can not practically evaluate the sub-matrices. On the other hand, we can sometimes determine equations which give eigen-values, starting from the values of the functions on the surfaces $y_p=y_p^\circ$, and demanding the conditions that $\Xi^{(p)}(y_p)$ and $\xi^{(p)}(y_p)$ should remain finite on the surfaces $y_p\to\pm\infty$. An example of such cases has been given by Oshida[1] for square-well potential.

§ III. Potential of Cylindrical or Spherical Symmetry

If any of the separated differential equations (2) has no singular point in the finite space, one can proceed by the method cited above. In some cases, however, such as the equations with a potential of cylindrical symmetry or spherical symmetry, we should avoid the singular point of the solutions, if necessary, by taking initial values of the wave functions not at the origin of the coordinates (in the case of the potential of spherical symmetry) or at the center-axis of the cylindrical coordinates (in the case of the potential of cylindrical symmetry), but at the point somewhat apart from the origin or on the surface somewhat apart from the center-axis.

§ IV. Potential in Power-Series and W.K.B.-Method

If the potential is expressed in power series or if the potential extends comparatively small length, one can obtain the approximate solution of wave equation in power series. For the potential of linear function of coordinates, the solution is expressed by Bessel function of order 1/3. The eigen-values of energy have been calculated by Sugiyama[3] after the method presented by Oshida. If the potential is of quadratic function of the coordinate, then one obtains, as is well known, Hermitian function, corresponding to the solution for the linear harmonic oscillator.

If the potential varies very slightly with regard to the coordinate, one can use W.B.K.-method in order to obtain the approximate solution for the wave functions.

§ V. Generalization to the n-Dimensional Case and Application to Differential Equations of Higher Order

The method presented in § I can be conveniently extended to the n-dimensional partial differential equations of second order, such as wave equation, diffusion equation etc. In these cases, one should take the $2n$-dimensional transformation

matrix as in the case of the circuit theory of $2n$ terminal networks. Naturally, the idea presented here is also applied to the differential equations of higher order. More generally, one can treat the solutions of linear functional equation, such as differential equations, integral equations, difference equations etc., in a manner similar to the method presented in § I. In these cases, however, the smooth continuation (or the linear boundary condition) for the individual solutions at the boundarys between the individual sub-potentials is demanded.

§ VI. Application to π-Electrons in Branched Organic Molecules

The matrix representation of the solution of Schrödinger equation presented in § I, can be conveniently applied to some branched molecules such as cata-condensed hydrocarbons, graphite etc.

In some molecules composed of four-valenced atoms, such as carbon, siliconium, germanium etc., their electronic state s^2p^2 is hybridized, the promoted electrons forming valence bond. For example, in a cata-condensed hydrocarbon, we take σ-electrons and π-electrons of carbon atoms into account, the latter being considered as free electrons running along the molecular skeleton. At the branching point, we have linear conditions[4] for the continuation of the wave functions lying on each line connecting the atoms. Accordingly, we can apply the idea presented in § I, to continuate the wave functions. In such a case, the transformation matrix similar to **P** is called a *branching matrix* (*Verzweigungsmatrix*), and a constant which represents the ratio of mixing of two wave functions (or more precisely, derivatives of two wave functions) in the branching matrix, is named a *mixing parameter* (*Mischungsparameter*).

In graphite, one treats the transformation matrix of higher order, and the column vector which includes wave functions and their derivatives is multi-dimensional. The calculation of the transformation matrix is very complicated, but the individual process of decomposing and finding the final form of the matrix is quite similar to the method presented in § I.

Literatures

1) I. Oshida: Busseiron-Kenkyû (Research in Chemical Physics) No. **37** (April 1951), 72.
2) For example,
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3) Y. Sugiyama: Memoirs of Faculty of Engineering, Nagoya Univ. **12** (1960), 64.
4) For example,
H. Kuhn: Zts. Elektrochem. **58** (1954), 219; J. Chem. Phys. **22** (1954), 2098; Zts. Naturforschung **9a** (1954), 989.