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Intensity Calculation by Expansion of Scattering Matrix

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A new formulation of the intensity calculation of electron diffraction by scattering matrix which is applicable to thicker crystal is obtained with the use of the Feynman expansion. The results are compared with Bethe's 2nd approximation. It is shown that this method is practically useful so far as v_g/b_1^2 (v_g: Fourier potential, b_1: reciprocal lattice vector) is small.

The scattering matrix method in electron diffraction was developed by Sturkey[1], Niehrs[2] and the present author[3),5)]. More recently, the author extended this method and calculated the intensity of the reflected wave applying the Feynman expansion to the scattering matrix[4]. This expansion is, however, not suitable for the intensity calculation of reflected wave from a thick crystal, since each term of the expansion diverges at large thickness. The aim of the present paper is to deduce the formula which is applicable even to a thick crystal.

In the Laue-case of electron diffraction, the amplitude of the h-wave is given by the h,0-component of the following matrix,

$$\exp\left(i\frac{D}{2k}\mathrm{M}\right). \tag{1}$$

Here, D is the thickness of crystal, $k=2\pi/\lambda$, and M the matrix whose elements are $\mathrm{M}_{hg}=v_{h-g}(h\neq g)$ and $\mathrm{M}_{hh}=p_h=2k\rho_h$, where v is the Fourier potential multiplied by $8\pi^2m/h^2$, and ρ_h "Anregungsfehler". If the matrix M can be expressed in the form,

$$\mathrm{M}=\mathrm{M}_0+\varepsilon\mathrm{M}' \tag{2}$$

with M_0 having non-degenerate eigenvalue, the amplitude of the h-wave calculated from the Feynman expansion is

$$\begin{aligned}\Psi_h=\left[\exp\left(i\frac{D}{2k}\mathrm{M}\right)\right]_{h0}=&\sum_i \psi_h{}^i\psi_0{}^{i*}\exp\left(i\frac{D}{2k}x^i\right)+\varepsilon\sum_i\sum_{g,l}\left\{\sum_{j(\neq i)}(\psi_h{}^i\psi_g{}^{i*}\psi_l{}^j\psi_0{}^{j*}+\psi_h{}^j\psi_g{}^{j*}\psi_l{}^i\psi_0{}^{i*})\frac{1}{x^i-x^j}\right.\\
&\left.+i\frac{D}{2k}\psi_h{}^i\psi_g{}^{i*}\psi_l{}^i\psi_0{}^{i*}\right\}\mathrm{M}'_{gl}\exp\left(i\frac{D}{2k}x^i\right)+\varepsilon^2\sum_i\sum_{g,l,m,n}\left\{\sum_{j,k(\neq i)}(\psi_h{}^i\psi_g{}^{i*}\psi_l{}^j\psi_m{}^{j*}\psi_n{}^k\psi_0{}^{k*}\right.\\
&+\psi_h{}^j\psi_g{}^{j*}\psi_l{}^i\psi_m{}^{i*}\psi_n{}^k\psi_0{}^{k*}+\psi_h{}^j\psi_g{}^{j*}\psi_l{}^k\psi_m{}^{k*}\psi_n{}^i\psi_0{}^{i*})\frac{1}{(x^i-x^j)(x^i-x^k)}+\sum_{j(\neq i)}(\psi_h{}^i\psi_g{}^{i*}\psi_l{}^i\psi_m{}^{i*}\psi_n{}^j\psi_0{}^{j*}\\
&+\psi_h{}^i\psi_g{}^{i*}\psi_l{}^j\psi_m{}^{j*}\psi_n{}^i\psi_{0i}{}^*+\psi_h{}^j\psi_g{}^{j*}\psi_l{}^i\psi_m{}^{i*}\psi_n{}^i\psi_0{}^{i*})\left(i\frac{D}{2k}\frac{1}{(x^i-x^j)}-\frac{1}{(x^i-x^j)^2}\right)\\
&\left.-\frac{1}{2}\left(\frac{D}{2k}\right)^2\psi_h{}^i\psi_g{}^{i*}\psi_l{}^i\psi_m{}^{i*}\psi_n{}^i\psi_0{}^{i*}\right\}\mathrm{M}'_{gl}\mathrm{M}'_{mn}\exp\left(i\frac{D}{2k}x^i\right)+\cdots,\end{aligned} \tag{3}$$

where $\psi_h{}^i$ is the component of the eigenvector ψ^i of M_0, x^i the corresponding eigenvalue, and * indicates the conjugate complex.

On the other hand, the amplitude of the h-wave is given by

$$\Psi_h=\sum_i U_h{}^i\exp\left(i\frac{D}{2k}X^i\right), \tag{4}$$

where $U_h{}^i$ is the amplitude of the h-wave belonging to the i-th wave field, and $U_h{}^i$ and X^i may be written as

$$\begin{aligned}U_h{}^i&=u^i_{h(0)}+\varepsilon u^i_{h(1)}+\varepsilon^2u^i_{h(2)}+\cdots\\
X^i&=x^i_{(0)}+\varepsilon x^i_{(1)}+\varepsilon^2x^i_{(2)}+\cdots.\end{aligned} \tag{5}$$

Substitution from (5) to (4) leads to

$$\Psi_h=\sum_i\left[u^i_{h(0)}+\varepsilon\left(u^i_{h(1)}+i\frac{D}{2k}u^i_{h(0)}x^i_{(1)}\right)+\varepsilon^2\left\{u^i_{h(2)}+i\frac{D}{2k}(u^i_{h(1)}x^i_{(1)}+u^i_{h(0)}x^i_{(2)})\right.\right.$$
$$\left.\left.-\frac{1}{2}\left(\frac{D}{2k}\right)^2u^i_{h(0)}(x^i_{(1)})^2\right\}+\cdots\right]\exp\left(i\frac{D}{2k}x^i_{(0)}\right). \qquad (6)$$

Equating the coefficients of each power of ε in (3) and (6), we easily obtain

$$\begin{cases} u^i_{h(0)}=\psi_h{}^i\psi_0{}^{i*} \\ x^i_{(0)}=x^i \end{cases}$$

$$\begin{cases} u^i_{h(1)}=\sum_{g,l}\sum_{j(\neq i)}(\psi_h{}^i\psi_g{}^{i*}\psi_l{}^j\psi_0{}^{j*}+\psi_h{}^j\psi_g{}^{j*}\psi_l{}^i\psi_0{}^{i*})\dfrac{\mathrm{M}'_{gl}}{x^i-x^j} \\ x^i_{(1)}=\sum_{g,l}\psi_g{}^{i*}\psi_l{}^i\mathrm{M}'_{gl} \end{cases}$$

$$\begin{cases} u^i_{h(2)}=\sum_{g,l,m,n}\left\{\sum_{j,k(\neq i)}(\psi_h{}^i\psi_g{}^{i*}\psi_l{}^j\psi_m{}^{j*}\psi_n{}^k\psi_0\psi_0{}^{k*}+\psi_h{}^j\psi_g{}^{j*}\psi_l{}^i\psi_m{}^{i*}\psi_n{}^k\psi_0{}^{k*}\right. \\ \qquad +\psi_h{}^j\psi_g{}^{j*}\psi_l{}^k\psi_m{}^{k*}\psi_n{}^i\psi_0{}^{i*})\dfrac{1}{(x^i-x^j)(x^i-x^k)}-\sum_{j(\neq i)}(\psi_h{}^i\psi_g{}^{i*}\psi_l{}^i\psi_m{}^{i*}\psi_n{}^j\psi_0{}^{j*} \\ \qquad \left.+\psi_h{}^i\psi_g{}^{i*}\psi_l{}^j\psi_m{}^{j*}\psi_n{}^i\psi_0{}^{i*}+\psi_h{}^j\psi_g{}^{j*}\psi_l{}^i\psi_m{}^{i*}\psi_n{}^i\psi_0{}^{i*})\dfrac{1}{(x^i-x^j)^2}\right\}\mathrm{M}'_{gl}\mathrm{M}'_{mn} \\ x^i_{(2)}=\sum_{g,l,m,n}\sum_{j(\neq i)}\psi_g{}^{i*}\psi_l{}^j\psi_m{}^{j*}\psi_n{}^i\dfrac{1}{(x^i-x^j)}\mathrm{M}'_{gl}\mathrm{M}'_{mn} \end{cases}$$

etc.

Putting $\varepsilon=1$ in (5), we get the amplitudes belonging to each wave field and eigenvalue. The boundary conditions are satisfied for each order of perturbation, i.e. $\sum_i u^i_{h(n)}=0$ $(h, n\neq 0)$ and $\sum_i u^i_{0(0)}=1$.

In order to consider the physical meaning of each term of (5), we take M_0 as

$$\mathrm{M}_0=\begin{pmatrix} \ddots & & & & \ddots \\ & \ddots & & \iddots & \\ & & p_{h-g} \quad 0 \quad v_{h-2g} & & \\ & & \ddots \quad \ddots & & \\ & & p_0 \quad v_{-h} & & \\ 0 & & & & 0 \\ & & v_h \quad p_h & & \\ & & \ddots \quad \ddots & & \\ & \iddots & & \ddots & \\ v_{2g-h} & & 0 & & p_g \\ \ddots & & & & \ddots \\ & \ddots & & \iddots & \\ \ddots & & & & \ddots \end{pmatrix} \qquad (8)$$

in which $p_0=p_h$, $p_g=p_{h-g}$, $\cdots$, and v's are assumed to be real, for simplicity. Then, 0 and h-waves, $h-g$ and g-waves, $\cdots$ constitute the pairs of resonance states, respectively. The order of each term in the Feynman expansion (3) corresponds to how many times the interaction appears in it. Therefore, we see that the second order term in (5) approximately involves the multiple times of interaction among 0, h-group and other ones (the first order one vanishes in this case). The second order term of the eigenvalue

$$x^i_{(2)}=\sum_{g,l,m,n}\sum_{j(\neq i)}\psi_g{}^{i*}\psi_l{}^j\psi_m{}^{j*}\psi_n{}^i\frac{\mathrm{M}'_{gl}\mathrm{M}'_{mn}}{x^i-x^j}$$

is the same as that deduced from the Bethe's third order approximation, and $X^i=x^i_{(0)}+x^i_{(2)}$ represents the dynamic potential.

It is difficult to discuss the convergence of the series in (5). Therefore, the intensity for the following three cases where the effect of other reflection waves may be large were calculated. In Table, the numerical values are shown.

Table. Values of v_{hhh}/b^2_{111}.

	111	222	333	444	555
Ge	0.563	0	−0.184		
Al	0.214	0.073	0.036	0.018	0.009
Au	0.770	0.362	0.190	0.092	0.059

Case I. The forbidden 222-reflection from Ge at the Bragg position.

As the unperturbed crystal potential, we take the sinusoidal type as

$$M_0=\begin{pmatrix} \ddots & \ddots & & & & & \\ \ddots & \ddots & \ddots & & & & \\ & \ddots & p_{-2} & v_1 & & & \\ & & v_1 & p_{-1} & v_1 & & 0 \\ & & & v_1 & p_0 & v_1 & \\ & 0 & & & v_1 & p_1 & v_1 \\ & & & & & v_1 & p_2 \ddots \\ & & & & & & \ddots \ddots \end{pmatrix} \tag{9}$$

In this case, we can obtain the exact solution with use of the Mathieu function. In the perturbation matrix, we take only the 333-potential as given by

$$M'=\begin{pmatrix} \ddots & \ddots & \ddots & \ddots & & & & & \\ \ddots & \ddots & \ddots & \ddots & \ddots & & & & \\ \ddots & \ddots & 0 & 0 & 0 & v_3 & & 0 & \\ \ddots & \ddots & 0 & 0 & 0 & 0 & v_3 & & \\ & \ddots & 0 & 0 & 0 & 0 & 0 & v_3 & \\ & & v_3 & 0 & 0 & 0 & 0 & 0 & \ddots \\ & & & v_3 & 0 & 0 & 0 & 0 & \ddots \ddots \\ & & 0 & & v_3 & 0 & 0 & 0 & \ddots \ddots \\ & & & & & \ddots & \ddots & \ddots & \ddots \ddots \\ & & & & & & \ddots & \ddots & \ddots \ddots \end{pmatrix} \tag{10}$$

The results are shown in Fig. 1. In this case, the convergence is so rapid that the intensity curves calculated up to the 1st and 2nd orders almost agree, but they are fairly different from that of the 0th order.

Case II. The 333-reflection from Al at the Bragg position.

We take (8) as M_0, in which we consider

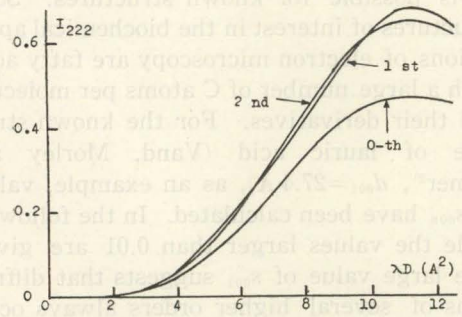

Fig. 1. The intensity curves of 222-reflection of Ge at the Bragg position which are calculated by taking account of the perturbation up to the 1st and 2nd orders.

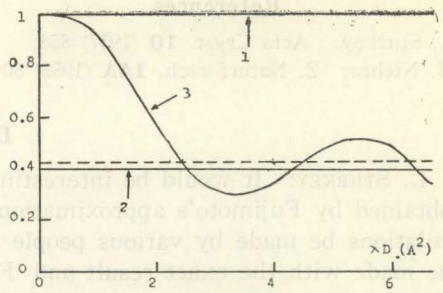

Fig. 2. The intensity ratios of 333-reflection from Al between each calculation and kinematical one. 1) Kinematical and 2-wave approximation, 2) Bethe's 2nd approximation, 3) Present method.

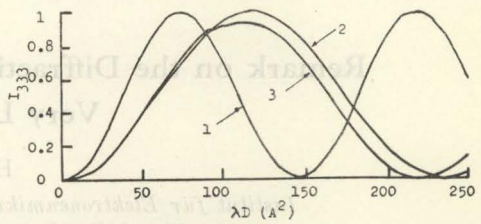

Fig. 3. The intensity curves of 333-reflection from Al calculated by 1) 2-wave approximation, 2) Bethe's 2nd approximation, 3) Present method

the waves from $\bar{1}\bar{1}\bar{1}$ to 444. The results are shown in Fig. 2 and 3. In this case, the convergence is very rapid, and, therefore, we calculate up to the 3rd order. In Fig. 2, the curves of intensity ratio to the kinematical value are shown at small range of λD. In Fig. 3 the intensity curves are shown up to the larger range. In these two figures, the results obtained from the 2-wave and Bethe's 2nd approximations are compared with our results. These figures show that Bethe's 2nd approximation is fairly good.

Case III. The 333-reflection from Au at the Bragg position.

The convergence of amplitude is rapid while the convergence of eigenvalue is not so rapid.

From the above results, this method is useful for the intensity calculation for thick crystals so far as v_g/b_1^2 are small, and we can say that Bethe's 2nd approximation is also effective in the same case. This formulation is, of course, useful in the case of the reflection which does not satisfy the Bragg condition and even in the presence of accidental interactions.

Details will be published in J. Phys. Soc. Japan.

References

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DISCUSSION

L. STURKEY: It would be interesting to compare exact calculations with the values obtained by Fujimoto's approximation process. Therefore, I suggest that several calculations be made by various people using their various systems and that comparisons be made with the exact result and Fujimoto's results. I will volunteer (if no one else does) to make the exact calculations be evaluating the complete scattering matrix.

Remark on the Diffracting Power of Net Planes with Very Large Spacing

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The approximative procedures in the theories of electron diffraction may generally be regarded as expansions with respect to reciprocal powers of the interaction constant $h^2/2m = 150\text{eV}\cdot\text{Å}^2$. Considerations of some problems of recent interest, indicate that the ratio $s_h = \Phi_h \cdot d_h^2/(150\text{V Å}^2)$ plays an important role in determining the type of diffraction pattern to be expected from a space lattice, and in deciding for a suitable method of treating a problem. In this quantity which might be called "diffraction power of lattice planes h," d_h is the plane spacing of order h, and Φ_h is the Fourier coefficient of inner potential related to that order. In unit cells containing only a few atoms, which are mostly studied by diffraction, the spacing d_h remains always smaller than a few angstroms, and s_h rarely approaches the value 1. However, in the large cells of the complicated lattices characteristic of many organic compounds and silicates, and in crystals with superlattice structures, the spacing d_h can be rather large. Although Φ_h is then known to be very small, it can seldom be calculated because only a few lattice structures with large cells have been thoroughly investigated. A table given by Ibers[2] provides scattering powers of atoms at very small values of $2\cdot\sin(\theta/2)/\lambda = 1/d_h$, and although tedious, the calculation of Φ_h is possible for known structures. Some structures of interest in the biochemical applications of electron microscopy are fatty acids with a large number of C atoms per molecule, and their derivatives. For the known structure of lauric acid (Vand, Morley and Lomer[2], $d_{001} = 27.4$ Å), as an example, values of s_{00n} have been calculated. In the following table the values larger than 0.01 are given. The large value of s_{001} suggests that diffractions of several higher orders always occur simultaneously with (001). They must contribute significantly to the diffraction pattern, as well as to the fringe contrast in an electron micrograph. The range of incident angle

Table

n	s_{00n}
1	3.60
2	0.22
3	0.44
4	−0.074
5	0.062
6	−0.014
.....	.....
10	−0.018
12	−0.021
14	0.020