

Solution of Schrödinger Equation for a Periodic Lattice. II

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We extend to $\mathbf{k} \neq 0$ the work in a previous paper on the solution of the Schrödinger equation in a periodic potential. We begin with a perturbation method, and expand the wave function and energy in powers of k . The equations determining the wave function to any given order in k are then just inhomogeneous linear equations, which are practical to solve. We give formulas for evaluating the energy from these wave functions: For bands which are not degenerate at $\mathbf{k}=0$ these involve straightforward summations over the reciprocal lattice; for bands which are degenerate at $\mathbf{k}=0$, we show how to derive the secular determinant which gives the splitting of these bands. The elements of this determinant can also be calculated as sums, which are practical to evaluate, over the reciprocal lattice. We present a simple numerical example

to show how some of the above results work out in practice. Next, we discuss tight-binding formulas in the present formalism, and the practical problem of evaluating these formulas. We give simple expressions, involving the radial derivatives of the atomic momentum space wave functions, for evaluating the energy in powers of k ; these formulas do not make near-neighbor approximations. Then, for those cases for which neither the tight-binding approximation nor an expansion in powers of k is appropriate, we discuss the direct numerical solution of the equations and give a convenient partial wave expansion for this purpose. Finally, we briefly discuss the relation to each other of the various approximations presented in this paper.

I. INTRODUCTION

IN a previous paper by the same title¹ we have presented, mainly for $\mathbf{k}=0$, a new method for solving the Schrödinger equation for a periodic lattice. In this paper, we discuss the extension of the method to the case $\mathbf{k} \neq 0$.

For convenience, we reproduce here a few of the equations of I. The problem is defined by the crystal potential $V_c(\mathbf{r})$, the sum of the atomic potentials $V^a(\mathbf{r}_i)$. If we write the wave function in Bloch form, and expand the periodic part in Fourier series with coefficients $C(\mathbf{K}_j)$, we get an equation for the Fourier coefficients

$$[\beta - (\mathbf{K}_i + \mathbf{k})^2]C(\mathbf{K}_i) = \sum_j C(\mathbf{K}_j)w(\mathbf{K}_i - \mathbf{K}_j). \quad (1)$$

Here, $v_c = 2mV_c/\hbar^2$, $v^a = 2mV^a/\hbar^2$, $\beta = 2mE/\hbar^2$, and we have expanded v_c in Fourier series,

$$v_c(\mathbf{r}) = \sum_j w(\mathbf{K}_j)e^{i\mathbf{K}_j \cdot \mathbf{r}}.$$

In this paper we discuss three different methods for the solution of the basic Eq. (1). We briefly describe these methods here. First, assuming we have solved Eq. (1) for $\mathbf{k}=0$ by the method of I, or otherwise, we try to use these solutions to develop a perturbation series in powers of k . This is, of course, the same idea as that of the well-known " $\mathbf{k} \cdot \mathbf{p}$ perturbation method" for the Schrödinger equation in coordinate space, but the present perturbation formalism seems to have appreciable advantages over the ordinary one. We discuss both the case when the band is nondegenerate at $\mathbf{k}=0$, and when it is degenerate. This work is presented in Sec. II.

In Sec. III we extend the discussion of the tight-binding method, which we have already discussed in I for $\mathbf{k}=0$, to the case $\mathbf{k} \neq 0$. As in I we find that in the tight-binding limit one can get an expression for the energy which involves summations over the different

absolute magnitudes of the reciprocal lattice points and which does not involve near-neighbor approximations. In the particular case that one wants only an expansion of the tight-binding formulas in powers of k , the functions that one has to sum are simply the derivatives of the atomic radial momentum space wave function.

For those cases for which neither a perturbation series in k nor tight binding is appropriate, we discuss in the next section a method which is the analogue of that presented in I; namely, the direct solution of Eq. (1) as a homogeneous secular equation, after we have broken up the $C(\mathbf{K}_i)$ into radial and angular parts. The additional complicating factor in the present case is of course that the term $[\beta - (\mathbf{K}_i + \mathbf{k})^2]$ introduces an additional angular dependence in Ω_i , the solid angle corresponding to \mathbf{K}_i , and the question is how to introduce this in a way that makes for least additional difficulty. We give at least a partial answer to this question in Sec. IV.

Finally, in Sec. V we discuss the first two of the above approximation methods and show that they can be considered as special cases of a general perturbation theory in which we start from the free atom equations, and expand either in powers of k , or of d/a (where d is the "range" of the atomic potentials and a is the lattice spacing), or of both simultaneously.

II. EXPANSION IN POWERS OF k —THE EFFECTIVE MASS

A. General Discussion

We now discuss the perturbation solution of Eq. (1) for $\mathbf{k} \neq 0$, supposing that we know the solution for $\mathbf{k}=0$. We begin with unperturbed bands that are nondegenerate; later we discuss the degenerate case.

In Eq. (1) the term in k^2 can be incorporated with the β and makes for no problem; it is the term $\mathbf{K}_i \cdot \mathbf{k}$ that causes difficulty. Hence it is convenient to define

$$\beta' = \beta - k^2$$

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¹ L. Eyges, Phys. Rev. **123**, 1673 (1961). Hereafter we refer to this paper as I.

and rewrite Eq. (1) as

$$\sum_j C(\mathbf{K}_j)w(\mathbf{K}_i - \mathbf{K}_j) + K_i^2 C(\mathbf{K}_i) + 2\mathbf{k} \cdot \mathbf{K}_i = \beta' C(\mathbf{K}_i).$$

We can write this in the form convenient for our purposes:

$$(\hat{H}_0 + kH')C(\mathbf{K}_i) = \beta' C(\mathbf{K}_i), \quad (2)$$

where the operator \hat{H}_0 is defined by

$$\hat{H}_0 C(\mathbf{K}_i) = \sum_j C(\mathbf{K}_j)w(\mathbf{K}_i - \mathbf{K}_j) + K_i^2 C(\mathbf{K}_i), \quad (3)$$

and

$$H' = 2K_i \cos \gamma = 2(\mathbf{k} \cdot \mathbf{K}_i)/k, \quad (4)$$

with γ the angle between \mathbf{K}_i and \mathbf{k} .

Now we expand the eigenfunction and eigenvalue in (2) in powers² of k :

$$\beta' = \beta'^{(0)} + k\beta'^{(1)} + k^2\beta'^{(2)} + \dots, \quad (5)$$

$$C(\mathbf{K}_i) = C^{(0)}(\mathbf{K}_i) + kC^{(1)}(\mathbf{K}_i) + k^2C^{(2)}(\mathbf{K}_i) + \dots \quad (6)$$

Equating powers of k , we get a set of coupled equations for $C^{(0)}$, $C^{(1)}$...:

$$\hat{H}_0 C^{(0)} = \beta'^{(0)} C^{(0)}, \quad (7a)$$

$$\hat{H}_0 C^{(1)} + H' C^{(0)} = \beta'^{(0)} C^{(1)} + \beta'^{(1)} C^{(0)}, \quad (7b)$$

$$\hat{H}_0 C^{(2)} + H' C^{(1)} = \beta'^{(0)} C^{(2)} + \beta'^{(1)} C^{(1)} + \beta'^{(2)} C^{(0)}. \quad (7c)$$

From these, we can calculate the "energy" eigenvalues $\beta'^{(1)}$, $\beta'^{(2)}$... successively.³ For example, to calculate $\beta'^{(2)}$ multiply (7a) by $C^{(2)}$ and sum over \mathbf{K}_i ; multiply (7c) by $C^{(0)}$ and sum over \mathbf{K}_i ; then subtract the two resultant equations to give the expression⁴ (among others below) for $\beta'^{(2)}$,

$$\beta'^{(1)} = \sum H'(C^{(0)})^2 / \sum (C^{(0)})^2, \quad (8a)$$

$$\beta'^{(2)} = (\sum C^{(0)} H' C^{(1)} - \beta'^{(1)} \sum C^{(0)} C^{(1)}) / \sum (C^{(0)})^2, \quad (8b)$$

$$\beta'^{(3)} = [\sum H'(C^{(1)})^2 - \beta'^{(1)} \sum (C^{(1)})^2 - 2\beta'^{(2)} \sum C^{(1)} C^{(0)}] / \sum (C^{(0)})^2, \quad (8c)$$

$$\beta'^{(4)} = [\beta'^{(0)} \sum (C^{(2)})^2 - \beta'^{(1)} \sum C^{(1)} C^{(0)} - \beta'^{(2)} \sum (C^{(1)})^2 - \beta'^{(3)} \sum C^{(1)} C^{(0)} - \sum C^{(2)} H_0 C^{(2)}] / \sum (C^{(0)})^2. \quad (8d)$$

Equations (7a, b ...) are inhomogeneous linear equations in the successive amplitudes $C^{(1)}$, $C^{(2)}$, and

² The fact that we formally assume a solution in powers of the magnitude k does not of course preclude our getting an answer which depends on k_x , k_y , k_z , since these of course enter into the perturbation H' . What we are doing is simply using the scalar magnitude k as our expansion parameter. This point may be clearer if one imagines a parameter λ introduced into the perturbation and writes it as $\lambda 2\mathbf{K}_i \cdot \mathbf{k}$, then expands in powers of λ and finally sets $\lambda = 1$. This procedure is of course equivalent to the simpler one we adopt above. Alternatively we can, in $2(\mathbf{K}_i \cdot \mathbf{k})/k$, express (\mathbf{k}/k) in terms of angles in \mathbf{k} space, and the perturbation is then clearly of the form of k times a function of these angles.

³ The results that follow are a trivial adaptation of those in: H. A. Bethe and E. Salpeter, *Quantum Mechanics of the One- and Two-Electron Problem* (Academic Press Inc., New York, 1952), p. 122.

⁴ For neatness we have in these expressions suppressed the argument \mathbf{K}_i of the functions $C^{(0)}(\mathbf{K}_i)$ etc., and the summation index as well, but it is of course understood that, for example, $\sum H'(C^{(0)})^2$ means $\sum_i H'(\mathbf{K}_i)[C^{(0)}(\mathbf{K}_i)]^2$.

one can try to solve them directly as such. As has been pointed out many times, for each successive amplitude that we find, we calculate two additional terms (in powers of k) for the energy. That is, knowing $C^{(0)}$ we can calculate $\beta'^{(0)}$ and $\beta'^{(1)}$, knowing $C^{(1)}$ we can calculate $\beta'^{(2)}$ and $\beta'^{(3)}$ etc. We also note parenthetically that we can get the effective mass m^* from $\beta'^{(2)}$, and hence from $C^{(1)}$, from the formula

$$m^* = m / (1 + \beta'^{(2)}). \quad (9)$$

We would like to emphasize here that, formally, the calculation of $C^{(n)}$ is the same for all orders n , in the sense that it is calculated from

$$(\hat{H}_0 - \beta'^{(0)})C^{(n)} = (\text{inhomogeneous terms}),$$

where the (inhomogeneous terms) involve the $C^{(n-1)}$ and those of still lower order. Once one has a computer program which programs the left hand side of this equation, then it is simply a matter of successively feeding in different inhomogeneous terms on the right-hand side to get successive $C^{(n)}$. In practice then, and in contrast with ordinary perturbation theory, it would seem to be feasible to calculate perturbation theory to fairly high orders. It is true that the higher $C^{(n)}$ will be progressively more complicated in their angular dependence in \mathbf{K}_i space, but the order of magnitude of the problem of calculating $C^{(2)}$ say, is the same as that for $C^{(1)}$. And we shall show, for at least a few numerical examples, that the calculation of $C^{(1)}$ is, as calculations go in this field, quite simple.

Before presenting these numerical examples, we shall discuss the form that the perturbation theory takes for degenerate states. Now, a general discussion of this problem would be so cumbersome as to be unenlightening, so what we shall rather do, is to calculate the second order splitting in the p band of a cubic lattice. This is a problem general enough to serve as a model for other cases, and yet simple enough that it can be worked out in illuminating detail. Also, it is one for which we can compare our results with those of previous authors.⁵

For a cubic lattice there are three p states for $\mathbf{k} = 0$ that correspond to the same $\beta'^{(0)}$. We call the wave functions for these states $C_x^{(0)}(\mathbf{K}_i)$, $C_y^{(0)}(\mathbf{K}_i)$, $C_z^{(0)}(\mathbf{K}_i)$. They satisfy, for example

$$\hat{H}_0 C_x^{(0)}(\mathbf{K}_i) = \beta'^{(0)} C_x^{(0)}(\mathbf{K}_i). \quad (10)$$

For each of these states there is an expansion in Kubic harmonics of type δ . For example in the notation for Kubic harmonics introduced in I we have

$$C_z^{(0)}(\mathbf{K}_i) = \sum_{l=1,3,5,\dots} C_{zl}^{(0)}(K_i) H_{l3}^{(\delta)}(\Omega_i). \quad (11)$$

As always in degenerate perturbation theory, we want

⁵ W. Shockley, Phys. Rev. **78**, 173 (1950); R. J. Elliott, Phys. Rev. **96**, 266 (1954); F. Herman, thesis, Columbia University (unpublished); G. Dresselhaus, A. F. Kip and C. Kittel, Phys. Rev. **98**, 368 (1955).

to find the correct linear combination of $C_x^{(0)}$, $C_y^{(0)}$, $C_z^{(0)}$, i.e., that linear combination which is approached by the solution of the perturbed problem as the perturbation goes to zero. Hence we take for $C^{(0)}$

$$C^{(0)} = a_x C_x^{(0)} + a_y C_y^{(0)} + a_z C_z^{(0)}. \quad (12)$$

Now we want to calculate $\beta'^{(1)}$. Of course, we shall find that $\beta'^{(1)}$ vanishes identically for a cubic crystal but it will clarify matters to show this explicitly. We put Eq. (12) into Eq. (7b), multiply by $C_x^{(0)}$ and sum over the reciprocal lattice.⁶ Then we multiply (10) by $C^{(1)}$ and sum over the lattice. Subtracting the two resulting equations we get

$$a_x [M_{xx} - \beta'^{(1)}] + a_y M_{xy} + a_z M_{xz} = 0,$$

where, for example

$$M_{xx} = \sum C_x^{(0)} H' C_x^{(0)}.$$

If we do the same for $C_y^{(0)}$ and $C_z^{(0)}$ we get two other equations in a_x , a_y , a_z . Equating to zero the determinant of this set of three equations we get a secular determinant which would, *in general*, give three different values for $\beta'^{(1)}$ and for each of these values a set of coefficients a_x , a_y , a_z would be determined. With these coefficients we would have three different determinate expressions for $C^{(0)}$, and could then calculate unambiguously from Eq. (7b) three corresponding expressions for $C^{(1)}$.

Now, since all the matrix elements M_{xx} etc. vanish, this does not happen in the present case. Rather we get that $\beta'^{(1)} = 0$, and that a_x , a_y , a_z are not determined but are still arbitrary. This means that there is an arbitrariness in calculating $C^{(1)}$. To resolve this, consider the function $C_z^{(1)}$ which is generated from $C_z^{(0)}$ in the same way as [according to Eq. (7b)] $C^{(1)}$ is generated from $C^{(0)}$. That is, consider $C_z^{(1)}$ defined by⁷

$$(\hat{H}_0 - \beta'^{(0)}) C_z^{(1)} = -H' C_z^{(0)}. \quad (13)$$

With two other functions $C_x^{(1)}$ and $C_y^{(1)}$ defined similarly we take for $C^{(1)}$ the linear combination

$$C^{(1)} = a_x C_x^{(1)} + a_y C_y^{(1)} + a_z C_z^{(1)}. \quad (14)$$

Obviously the $C^{(0)}$ and $C^{(1)}$ defined by (12) and (14) satisfy Eqs. (7a) and (7b), so they represent a solution if a_x , a_y , a_z can be determined. To do this we put these expressions for $C^{(0)}$ and $C^{(1)}$ into (7c)

$$\begin{aligned} \hat{H}_0 C^{(2)} + H' (a_x C_x^{(1)} + a_y C_y^{(1)} + a_z C_z^{(1)}) \\ = \beta'^{(0)} C^{(2)} + \beta'^{(2)} (a_x C_x^{(0)} + a_y C_y^{(0)} + a_z C_z^{(0)}). \end{aligned}$$

We multiply this equation by $C_x^{(0)}$, and sum over the reciprocal lattice; we multiply Eq. (10) by $C^{(2)}$ and sum; we then subtract these two resulting equations to get⁶

$$\begin{aligned} a_x \sum C_x^{(0)} H' C_x^{(1)} + a_y \sum C_x^{(0)} H' C_y^{(1)} \\ + a_z \sum C_x^{(0)} H' C_z^{(1)} = a_x \beta'^{(2)}. \end{aligned}$$

⁶ We assume that $C_x^{(0)}$ is normalized such that

$$\sum_i [C_x^{(0)}(\mathbf{K}_i)]^2 = 1.$$

⁷ We recognize here that $\beta'^{(1)}$ is zero.

Working similarly with $C_y^{(0)}$ and $C_z^{(0)}$ we get two other linear equations in a_x , a_y , a_z ; equating their determinant to zero gives the familiar secular equation which determines $\beta'^{(2)}$, and hence the coefficients a_x , a_y , a_z .

$$\begin{vmatrix} \Gamma_{xx} - \beta'^{(2)} & \Gamma_{xy} & \Gamma_{xz} \\ \Gamma_{yx} & \Gamma_{yy} - \beta'^{(2)} & \Gamma_{yz} \\ \Gamma_{zx} & \Gamma_{zy} & \Gamma_{zz} - \beta'^{(2)} \end{vmatrix} = 0.$$

In this determinant the definition of Γ_{xy} , for example, is

$$\Gamma_{xy} = \sum_i C_x^{(0)}(\mathbf{K}_i) H' C_y^{(1)}(\mathbf{K}_i).$$

We now compute these Γ 's to bring out explicitly the dependence of the secular determinant on k_x , k_y , k_z . Consider for example Γ_{zz} which is just $\sum_i C_z^{(0)}(\mathbf{K}_i) H' C_z^{(1)}(\mathbf{K}_i)$. The basic problem in evaluating it is to calculate $C_z^{(1)}$ since H' is given and $C_z^{(0)}$ is assumed known. $C_z^{(1)}$ satisfies Eq. (13) which involves $C_z^{(0)}$ on the right-hand side. Now $C_z^{(0)}$ can be expanded in Kubic harmonics according to Eq. (11) and in principle, all l values must be considered in this series. But in practice, we expect that only a small number of these are important; otherwise in fact we could not have solved the zero-order problem. Now the analysis we are about to make, is essentially the same for each $C_z^{(0)}$ contained in $C_z^{(0)}$. Partly for simplicity of exposition then, and partly because in fact it will often be a good approximation, we shall assume that only the term $l=1$ is important in Eq. (11). Then we can write

$$C_z^{(0)}(\mathbf{K}_i) = C_{z1}^{(0)}(K_i) Y_{10}(\Omega_i). \quad (15)$$

To calculate $C_z^{(1)}(\mathbf{K}_i)$ we begin by expanding the right-hand side of Eq. (13). We have

$$\begin{aligned} H' C_z^{(0)}(K_i) &= (2\mathbf{K}_i \cdot \mathbf{k}/k) C_z^{(0)}(\mathbf{K}_i) \\ &= \frac{8\pi}{3} K_i \left[\sum_{m=-1}^1 Y_{1m}(\Omega_i) Y_{1m}^*(\Omega_k) \right] C_{z1}^{(0)}(K_i) Y_{10}(\Omega_i). \end{aligned}$$

We expand the products of spherical harmonics in this expression⁸ in terms of single spherical harmonics to get

$$\begin{aligned} H' C_z^{(0)}(\mathbf{K}_i) &= \frac{K_i C_{z1}^{(0)}(K_i)}{k\sqrt{3}} \left[2k_z Y_{00}(\Omega_i) + \frac{4k_z}{(5)^{\frac{1}{2}}} Y_{20}(\Omega_i) \right. \\ &\quad \left. - \frac{\sqrt{2}(k_x - ik_y)}{5} Y_{21}(\Omega_i) + \frac{\sqrt{2}(k_x + ik_y)}{5} Y_{2-1}(\Omega_i) \right]. \quad (16) \end{aligned}$$

We put this expression into Eq. (13), which we then multiply by Y_{00}^* , Y_{20}^* , Y_{21}^* , Y_{2-1}^* successively and, for reasons discussed in I, are permitted to *integrate*

⁸ It is more convenient to use spherical harmonics than Kubic harmonics from this point on.

over $d\Omega_i$. We get

$$\begin{aligned}
\int Y_{00}^*(\hat{H}_0 - \beta'^{(0)})C_z^{(1)}(\mathbf{K}_i)d\Omega_i &= -2k_z K_i C_{z1}^{(0)}(K_i)/\sqrt{3}k, \\
\int Y_{20}^*(\hat{H}_0 - \beta'^{(0)})C_z^{(1)}(\mathbf{K}_i)d\Omega_i &= -4k_z K_i C_{z1}^{(0)}(K_i)/(15)^{1/2}k, \\
\int Y_{21}^*(\hat{H}_0 - \beta'^{(0)})C_z^{(1)}(\mathbf{K}_i)d\Omega_i &= \sqrt{2}(k_x - ik_y)K_i C_{z1}^{(0)}(K_i)/5\sqrt{3}k, \\
\int Y_{2-1}^*(\hat{H}_0 - \beta'^{(0)})C_z^{(1)}(\mathbf{K}_i)d\Omega_i &= -\sqrt{2}(k_x + ik_y)K_i C_{z1}^{(0)}(K_i)/5\sqrt{3}k.
\end{aligned} \tag{17}$$

Now we expand $C_z^{(1)}(\mathbf{K}_i)$ in spherical harmonics:

$$C_z^{(1)}(\mathbf{K}_i) = \sum_{l,m} C_{z,lm}^{(1)}(K_i) Y_{lm}(\Omega_i).$$

We put this expansion into Eqs. (17) and do the angular integrations to get a set of four equations, a typical one of which we write out explicitly for the sake of clarity. For example, the equation involving Y_{21} is

$$\begin{aligned}
(K_i^2 - \beta'^{(0)})C_{z,21}^{(1)}(K_i) &+ 4\pi \sum_{l'm'} \sum_{K_j} C_{z,l'm'}^{(1)}(K_j) w_2(K_i, K_j) \\
&\sum_{\Omega_j} Y_{21}^*(\Omega_j) Y_{l'm'}(\Omega_j) \\
&= \sqrt{2}(k_x - ik_y)K_i C_{z1}^{(0)}(K_i)/5\sqrt{3}k. \tag{18}
\end{aligned}$$

It is easy to verify that we get a solution of Eq. (18) and its three counterparts by assuming that the only non-vanishing amplitudes are $C_{z,00}^{(1)}$, $C_{z,20}^{(0)}$, $C_{z,21}^{(1)}$, $C_{z,2-1}^{(1)}$. With this assumption we then have⁹

$$\begin{aligned}
(K_i^2 - \beta'^{(0)})C_{z,00}^{(1)}(K_i) &+ \sum_{K_j} C_{z,00}^{(1)}(K_j) w_0(K_i, K_j) n_i \\
&= -2k_z K_i C_{z1}^{(0)}(K_i)/\sqrt{3}k, \\
(K_i^2 - \beta'^{(0)})C_{z,20}^{(1)}(K_i) &+ 4\pi \sum_{K_j} C_{z,20}^{(1)}(K_j) w_2(K_i, K_j) \sum_{\Omega_j} |Y_{20}(\Omega_j)|^2 \\
&= -4k_z K_i C_{z1}^{(0)}(K_i)/(15)^{1/2}k, \\
(K_i^2 - \beta'^{(0)})C_{z,21}^{(1)}(K_i) &+ 4\pi \sum_{K_j} C_{z,21}^{(1)}(K_j) w_2(K_i, K_j) \sum_{\Omega_j} |Y_{21}(\Omega_j)|^2 \\
&= \sqrt{2}(k_x - ik_y)K_i C_{z1}^{(0)}(K_i)/5\sqrt{3}k, \\
(K_i^2 - \beta'^{(0)})C_{z,2-1}^{(1)}(K_i) &+ 4\pi \sum_{K_j} C_{z,2-1}^{(1)}(K_j) w_2(K_i, K_j) \sum_{\Omega_j} |Y_{2-1}(\Omega_j)|^2 \\
&= -\sqrt{2}(k_x + ik_y)K_i C_{z1}^{(0)}(K_i)/5\sqrt{3}k.
\end{aligned} \tag{19}$$

⁹ In the first equation, n_i represents (as it does in I) $4\pi \sum_{\Omega_j} |Y_{00}|^2$, and is just equal to the number of reciprocal lattice vectors of magnitude K_j .

Actually, the last two of the above equations are essentially identical, i.e., $C_{z,21}^{(0)}$ and $C_{z,2-1}^{(0)}$ are the same functions within a factor. We see this and at the same time bring out the dependence on k_x , k_y , k_z clearly by defining three new functions $A(K_i)$, $B(K_i)$, $D(K_i)$.

$$\begin{aligned}
C_{z,00}^{(1)}(K_i) &= -A(K_i)2k_z/\sqrt{3}k, \\
C_{z,20}^{(1)}(K_i) &= -B(K_i)4k_z/(15)^{1/2}k, \\
C_{z,21}^{(1)}(K_i) &= \sqrt{2}D(K_i)(k_x - ik_y)/5\sqrt{3}k, \\
C_{z,2-1}^{(1)}(K_i) &= -\sqrt{2}D(K_i)(k_x + ik_y)/5\sqrt{3}k.
\end{aligned}$$

Then A , B , and D satisfy the following equations

$$\begin{aligned}
(K_i^2 - \beta'^{(0)})A(K_i) &+ \sum_{K_j} A(K_j) w_0(K_i, K_j) n_j \\
&= K_i C_{z1}^{(0)}(K_i), \\
(K_i^2 - \beta'^{(0)})B(K_i) &+ 4\pi \sum_{K_j} B(K_j) w_2(K_i, K_j) \sum_{\Omega_j} |Y_{20}|^2 \\
&= K_i C_{z1}^{(0)}(K_i), \\
(K_i^2 - \beta'^{(0)})D(K_i) &+ 4\pi \sum_{K_j} C(K_j) w_2(K_i, K_j) \sum_{\Omega_j} |Y_{21}|^2 \\
&= K_i C_{z1}^{(0)}(K_i).
\end{aligned}$$

In terms of A , B , D then

$$\begin{aligned}
k\sqrt{3}C_z^{(1)}(K_i) &= [2k_z A(K_i)Y_{00} + 4k_z B(K_i)Y_{20}/(5)^{1/2} \\
&- \sqrt{2}(k_x - ik_y)D(K_i)Y_{21}/5 \\
&+ \sqrt{2}(k_x + ik_y)D(K_i)Y_{2-1}/5]. \tag{20}
\end{aligned}$$

If we now combine this with (16), we get for Γ_{zz} , noting that many of the spherical harmonics products that arise will vanish when summed over the reciprocal lattice,

$$\Gamma_{zz} = \mu(k_x^2 + k_y^2) + \eta k_z^2, \tag{21}$$

where

$$\begin{aligned}
\mu &= -\frac{4}{75k^2} \sum_{K_i} K_i D(K_i) C_{z1}^{(0)}(K_i) \sum_{\Omega_i} |Y_{21}|^2, \\
\eta &= \frac{1}{3\pi k^2} \sum_{K_i} K_i A(K_i) C_{z1}^{(0)}(K_i) n_i \\
&\quad + \frac{16}{15k^2} \sum_{K_i} K_i B(K_i) C_{z1}^{(0)}(K_i) \sum_{\Omega_i} |Y_{20}|^2.
\end{aligned}$$

Similarly we get for Γ_{xz}

$$\Gamma_{xz} = \rho k_x k_z, \tag{22}$$

where

$$\begin{aligned}
\rho &= \frac{2\sqrt{2}}{3k^2} \sum_{K_i} K_i C_{z1}^{(0)}(K_i) \left\{ \frac{A(K_i) n_i}{4\pi} - \frac{2B(K_i)}{5\sqrt{5}} \sum_{\Omega_i} Y_{20}^2 \right. \\
&\quad \left. - \frac{D(K_i)}{25} \sum_{\Omega_i} |Y_{21}|^2 \right\}.
\end{aligned}$$

With these results, our secular equation is then of a form which has been given before⁵:

$$\begin{vmatrix} \mu(k_y^2 + k_z^2) + \eta k_x^2 - \beta'^{(2)} & \rho k_x k_y & \rho k_x k_z \\ \rho k_y k_x & \mu(k_x^2 + k_z^2) + \eta k_y^2 - \beta'^{(2)} & \rho k_y k_z \\ \rho k_z k_x & \rho k_z k_y & \mu(k_x^2 + k_y^2) + \eta k_z^2 - \beta'^{(2)} \end{vmatrix} = 0.$$

B. Numerical Example

To illustrate the above results, we briefly present a numerical example based on them. We undertake the calculation of $C^{(1)}(\mathbf{K}_i)$ for the s -like states of the bcc lattice of exponential potentials that we have discussed in I. Knowing $C^{(1)}$, we can then calculate $\beta'^{(2)}$ from Eq. (8b) and hence the effective mass. This calculation is representative in the sense that the calculation of, say, the p -band splitting is essentially identical except that there we have not one but three functions $C_x^{(1)}$, $C_y^{(1)}$, $C_z^{(1)}$ to consider. However, each of these functions satisfies an equation similar to the one we are about to discuss.

In calculating $C^{(1)}$ we must use our previous results for $C^{(0)}$. Here we must make essentially the same remark that we did in calculating the p -state splitting in the last section. Namely, although in principle $C^{(0)}$ is expanded in an infinite series of Kubic harmonics, we found in I that the term $C_0^{(0)}$ corresponding to the Kubic harmonic with $l=0$ harmonic was important, and that the next highest amplitude, corresponding to $l=4$, was very small. We shall keep this approximation, i.e., we shall assume

$$C^{(0)}(\mathbf{K}_i) \rightarrow C_0^{(0)}(K_i). \quad (23)$$

Now if we suppose that $C^{(1)}(\mathbf{K}_i)$ is expanded in spherical harmonics, it is easy to see that we get a solution to (7b) by assuming that $C^{(1)}$ involves only spherical harmonics with $l=1$, and that in fact we can write

$$C^{(1)}(\mathbf{K}_i) = C_1^{(1)}(K_i) P_1(\cos \gamma), \quad (24)$$

where we assume that \mathbf{k} is along the z axis, and γ is the angle between \mathbf{k} and \mathbf{K}_i . If we put this and the expansion given in I for $w(\mathbf{K}_i - \mathbf{K}_j)$ into (7b) and integrate

over Ω_i we get in a familiar way

$$C_1^{(1)}(K_i) K_i^2 + 4\pi \sum_{K_j} C_1^{(1)}(K_j) w_1(K_i, K_j) \sum_{\Omega_j} Y_{10}^2(\Omega_j) + 2K_i C_0^{(0)}(K_i) = \beta'^{(0)} C_1^{(1)}(K_i). \quad (25)$$

This is the basic equation for the amplitude $C_1^{(1)}(K_i)$ evaluated at the absolute magnitudes of the different reciprocal lattice vectors. We now specialize it to the bcc lattice of exponential potentials considered in I. We introduce dimensionless variables

$$x_i = K_i d$$

and use the expression for $w_1(x_i, x_j)$ derived in I,

$$w_1(x_i, x_j) = \frac{\pi b^2 d^3 \Omega_b}{x_i^2 x_j^2} \left(\ln \frac{S+1}{S-1} - \frac{2S}{S^2-1} \right),$$

where

$$S(x_i, x_j) = \frac{1 + x_i^2 + x_j^2}{2x_i x_j}.$$

We get

$$C_1^{(1)}(x_i) (x_i^2 - \beta'^{(0)}) + \sum_{x_j} C_1^{(1)}(x_j) w_1(x_i, x_j) n_j = -2x_i C_0^{(0)}(x_i). \quad (26)$$

We have solved Eq. (26), which is really an infinite set of inhomogeneous equations for the $C_1^{(1)}(x_i)$, on the IBM 709.¹⁰ In so doing, we had of course to truncate the equations, i.e., to assume that $C_1^{(1)}(x_i)$ is zero for i greater than some N . We have tested this procedure by solving the same equation for different values of N . The values of N we used ranged from 8 to 18. The results for the wave functions are given in Table I, from which we see, *a posteriori*, that the $C_1^{(1)}(x_i)$ do drop to zero for large enough x_i . We also observe that $C_1^{(1)}(0)$ is always zero—this can be seen directly from Eq. (26). With the wave functions of Table I we have calculated

TABLE I. The functions $C_0^{(0)}(x_i)$ and $C_1^{(1)}(x_i)$ for "1S" and "2S" states of a bcc lattice at each lattice point of which there is an exponential potential $v^{(a)}(r) = -b^2 e^{-r/d}$. The lattice spacing a is given in terms of $\alpha = a/(\sqrt{2}\pi d)$, and $bd = 3.5001$.

i	x_i	$\alpha = 0.7500$				x_i	$\alpha = 1.000$				x_i	$\alpha = 1.5000$			
		1S	$C_1^{(1)}$	$C_0^{(0)}$	2S		1S	$C_1^{(1)}$	$C_0^{(0)}$	2S		1S	$C_1^{(1)}$	$C_0^{(0)}$	2S
1	0.0	99.85	0.0	-5.405	0.0	0.0	98.41	0.0	-17.74	0.0	0.0	63.92	0.0	-7.68	0.000
2	2.666	1.524	-0.4590	28.47	-122.3	2.000	4.903	-2.831	+27.33	-87.1	1.333	19.31	-21.3	1.54	-7.80
3	3.771	0.3764	-0.1115	5.323	-11.7	2.818	1.510	-0.7860	8.252	-14.9	1.885	9.323	-8.43	0.865	-2.24
4	4.619	0.1910	-0.0780	1.651	-10.7	3.464	0.6485	-0.6309	3.282	-16.4	2.309	5.147	-10.4	0.487	-3.59
5	5.333	0.0725	-0.0243	0.6699	-2.12	4.000	0.2480	-0.1827	1.556	-3.99	2.667	3.097	-3.90	0.291	-1.10
6	5.963	0.0401	-0.0153	0.3198	-1.54	4.472	0.1859	-0.1516	0.828	-3.02	2.981	1.973	-3.50	0.183	-1.00
7	6.532	0.0242	-0.0066	0.1737	-0.330	4.899	0.1138	-0.0556	0.474	-2.20	3.266	1.319	-1.25	0.121	-0.293
8	7.055			0.1042	-0.968	5.292			0.297	-0.772	3.528	0.9166	-2.99	0.083	-0.936
9						5.656			0.195	-0.229	3.771	0.6567	-2.508	0.058	-0.103
10						6.000			0.133	-0.676	4.000	0.4821	-1.17	0.042	-0.330
11						6.324			0.100	-0.313	4.216	0.3618	-0.617	0.031	-0.160

¹⁰ I am grateful to Mrs. Virginia Mason for programming and running these equations.

TABLE II. The effective mass ratio m^*/m as calculated from Eq. (9) and the wave functions given in Table I. The "energy" parameter λ is $\lambda = 2mEd^2/\hbar^2$.

α	1S		2S	
	m^*/m	λ	m^*/m	λ
0.2500			-0.00887	+43.006
0.500			-0.0531	+5.533
0.7500	1.000231	-16.693	-0.1501	+0.07219
1.000	1.0273	-7.2063	-0.3035	-1.3400
1.250	1.664	-4.1429	-0.5046	-1.5980
1.50	4.845	-3.063	-0.7695	-1.2479
∞	∞	-3.0625	$-\infty$	-0.2500

the corresponding effective masses. The results are given in Table II. We know from general principles that the effective mass should become infinite as the lattice spacing becomes infinite and we can see this trend from the numerical results, particularly for the 1S state.

III. TIGHT BINDING

In I, we wrote down a variational expression for the energy eigenvalue parameter β for $\mathbf{k}=0$ based on the fact that (for $\mathbf{k}=0$) the solution of Eq. (1) was, in the limit of large lattice spacing, just $C_a(\mathbf{K})$, an atomic momentum space wave function. We would now like to ask the same question when $\mathbf{k} \neq 0$; i.e., what is the solution of Eq. (1) for large lattice spacing? For knowing this, we can then, in the spirit of the tight-binding approximation, use it as a variational function. The answer is: When the lattice spacing becomes infinite, the solution $C(\mathbf{K}_i)$ of Eq. (1) is just the atomic momentum space wave function of argument $(\mathbf{K}+\mathbf{k})$.

$$C(\mathbf{K}_i) \rightarrow C_a(\mathbf{K}+\mathbf{k}), \quad \text{lattice spacing} \rightarrow \text{infinity}. \quad (27)$$

This result can be easily derived by writing the usual Bloch sum of atomic orbitals and making a Fourier transform, but it is instructive to derive it from the equations themselves. In the limit of large lattice spacing, Eq. (1) becomes

$$C(\mathbf{K})[\beta - (\mathbf{K}+\mathbf{k})^2] = \int w^a(\mathbf{K}-\mathbf{K}')C(\mathbf{K}')d\mathbf{K}', \quad (28)$$

and for $\mathbf{k}=0$, the solution of (28) is just an atomic orbital $C_a(\mathbf{K})$;

$$C_a(\mathbf{K})(\beta - K^2) = \int w^a(\mathbf{K}-\mathbf{K}')C_a(\mathbf{K}')d\mathbf{K}'. \quad (29)$$

By changing the argument in (28) we get

$$C(\mathbf{K}-\mathbf{k})(\beta - K^2) = \int w^a(\mathbf{K}-\mathbf{K}'-\mathbf{k})C(\mathbf{K}')d\mathbf{K}'.$$

With the change of integration variable $\mathbf{K}'+\mathbf{k}=\mathbf{K}'$ this last equation becomes

$$C(\mathbf{K}-\mathbf{k})(\beta - K^2) = \int w^a(\mathbf{K}-\mathbf{K}')C(\mathbf{K}'-\mathbf{k})d\mathbf{K}',$$

which is an equation of the same form as (29) and which therefore has as solution

$$C(\mathbf{K}-\mathbf{k}) = C_a(\mathbf{K}).$$

Equation (27) then follows.

In using this result for tight-binding calculations we must, as in I, proceed somewhat differently for states which are nondegenerate, and for those which are degenerate, at $\mathbf{k}=0$. We first consider the former. For this case we have the variational expression for the energy

$$\beta = [\sum_i C_a^2(\mathbf{K}_i+\mathbf{k})(\mathbf{K}_i+\mathbf{k})^2 + \sum_i \sum_j C_a(\mathbf{K}_i+\mathbf{k}) \times C_a(\mathbf{K}_j+\mathbf{k})w(\mathbf{K}_i-\mathbf{K}_j)] / [\sum_i C_a^2(\mathbf{K}_i+\mathbf{K})]. \quad (30)$$

We have discussed in I the evaluation of (30) for $\mathbf{k}=0$ when $C_a(\mathbf{K})$ is expanded in Kubic harmonics, and have given examples of the accuracy obtained from this formula. If the atomic wave functions are known analytically, one can in principle do the same thing here, for if we know the atomic wave function $\psi_a(\mathbf{r})$ of which $C_a(\mathbf{K})$ is the Fourier transform,

$$C_a(\mathbf{K}) = \int \psi_a(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r}$$

then

$$\begin{aligned} C_a(\mathbf{K}-\mathbf{k}) &= \int \psi_a(\mathbf{r}) \exp[i(\mathbf{K}-\mathbf{k}) \cdot \mathbf{r}] d\mathbf{r} \\ &= (4\pi)^2 \int \psi_a(\mathbf{r}) \left[\sum_{l,m} i^l j_l(Kr) Y_{lm}^*(\Omega_k) Y_{lm}(\Omega_r) \right] \\ &\quad \times \left[\sum_{l',m'} (-i)^{l'} j_{l'}(kr) Y_{l'm'}(\Omega_k) Y_{l'm}^*(\Omega_r) \right] d\mathbf{r}. \end{aligned} \quad (31)$$

If we can do the integrations over \mathbf{r} , we have $C_a(\mathbf{K}-\mathbf{k})$ in terms of spherical (or Kubic) harmonics of Ω_K . In (30) then we can sum over Ω_i using the theorem in I for this kind of sum, and so are left with a sum over the different absolute magnitudes K_i of the reciprocal lattice vectors.

If the atomic state that gives rise to the band is degenerate, we must, as in I, proceed somewhat differently. That is, we must look at the variational calculation in the light of perturbation theory, and consider it as the first-order perturbation calculation of the energy splitting due to the perturbation $\mathbf{H}_p - \mathbf{H}_a$. We then get a secular equation for the energy splitting which involves matrix elements of $\mathbf{H}_p - \mathbf{H}_a$ with respect to however many unperturbed degenerate wave functions $C_a(\mathbf{K})$ there are. But there is not much new in principle in this that is not discussed either above or in I, so we do not elaborate further.

If the integrals in Eq. (30) are too difficult, or if one is only interested in small k , one can get simpler integrals by expanding the $j_l(kr)$ in this equation in powers of k . However, if one is committed to expanding in powers of k , it is probably best not to go about it in

this way, but rather to use the formulae we have given in Sec. II for the energy in powers of k , in terms of the wave function in powers of k . The reason is that these formulas give the simplest possible results in the sense that they always give energy eigenvalues of any order in terms of wave functions of lower order. But if one does not take care, one can get results which are equally valid, but not so simple. For example, one can get $\beta'^{(2)}$ in terms of $C^{(2)}$ from Eq. (7c), but clearly this is not as useful as Eq. (8b), which gives $\beta'^{(2)}$ in terms of $C^{(1)}$. In short, in calculating energies in powers of k , it would seem to be almost always advantageous to start from the formulas in Eqs. (8a, b ...).

We can use these in the context of the tight-binding approximation by expanding the tight-binding formulas in powers of k . We have

$$C_a(\mathbf{K}+\mathbf{k}) = C_a(\mathbf{K}) + (\mathbf{k} \cdot \nabla) C_a(\mathbf{K}) + \frac{1}{2} (\mathbf{k} \cdot \nabla)^2 C_a(\mathbf{K}) + \dots, \quad (32)$$

where of course ∇ operates on \mathbf{K} . We have thus generated, in this approximation, the functions which we called $C^{(0)}(\mathbf{K})$, $C^{(1)}(\mathbf{K})$, ... in Sec. II. Thus

$$C^{(0)}(\mathbf{K}) = C_a(\mathbf{K}), \quad (32a)$$

$$kC^{(1)}(K) = (\mathbf{k} \cdot \nabla) C_a(\mathbf{K}), \quad (32b)$$

and so on, and with them one can immediately use the formulas of that section. Note that, since $C_a(\mathbf{K})$ is an atomic function of the form $\Phi(K)Y_{lm}(\Omega_K)$, it is easy to evaluate Eq. (32b) with the help of the gradient formula.¹¹ For example, for an S state, for which $C_a(\mathbf{K}+\mathbf{k})$ is a function only of $|\mathbf{K}+\mathbf{k}|$, we get either from the gradient formulas or directly,

$$C_a(\mathbf{K}+\mathbf{k}) = C_a(K) + \frac{(\mathbf{k} \cdot \mathbf{K})}{K} \frac{dC_a(K)}{dK} + \frac{(\mathbf{k} \cdot \mathbf{K})^2}{2K^2} \left(\frac{d^2 C_a(K)}{dK^2} - \frac{1}{K} \frac{dC_a(K)}{dK} \right) + \frac{k^2}{2K} \frac{dC_a(K)}{dK} + \dots$$

Thus

$$C^{(1)}(K) = [(\mathbf{k} \cdot \mathbf{K})/kK] [dC_a(K)/dK].$$

We can, incidentally, compare this with the function $C^{(1)}(\mathbf{K})$ given by Eq. (24) of Sec. II. If, as in that section, we take \mathbf{k} along the z axis we find, referring to Eq. (24), the tight-binding approximation for $C_1^{(1)}(K)$,

$$C_1^{(1)}(K) \approx dC_a(K)/dK.$$

Qualitatively we can see, with reference to I, where $C_a(K)$ is plotted for $1S$ and $2S$ states, that $dC_a(K)/dK$ does have the same behavior as the $C_1^{(1)}(K)$ tabulated in Table I; namely, it is zero at the origin, rises rapidly, and then drops to zero in about the same distance that $C_a(K)$ itself drops to zero.

Equations (32) can equally well be used for degener-

ate states, to calculate the splitting at $\mathbf{k}=0$ in the tight-binding approximation. Thus consider the p -band splitting we calculated previously. The crucial point there was to calculate the first-order wave functions $C_x^{(1)}$, $C_y^{(1)}$, $C_z^{(1)}$. Take for example $C_z^{(1)}$; now, since there are three degenerate atomic functions, which we can call $C_{a,x}(\mathbf{K}_i)$, $C_{a,y}(\mathbf{K}_i)$, $C_{a,z}(\mathbf{K}_i)$, there will be three variational functions $C_{a,x}(\mathbf{K}+\mathbf{k})$, etc. Just as in (32a) and (32b) then we have, for example,

$$C_z^{(0)}(\mathbf{K}) = C_{a,z}(\mathbf{K}), \\ C_z^{(1)}(\mathbf{K}) = (1/k)(\mathbf{k} \cdot \nabla) C_{a,z}(\mathbf{K}).$$

Working out this last expression we get with $C_{a,z}(\mathbf{K}) = \Phi(K)Y_{10}(\Omega_K)$

$$k\sqrt{3}C_z^{(1)}(K_i) = \left\{ 2k_z Y_{00}(\Omega_i) \left(\frac{1}{2} \frac{\partial}{\partial K} + \frac{1}{K} \right) \Phi(K) \right. \\ + \frac{2k_z}{(5)^{1/2}} Y_{20}(\Omega_i) \left(\frac{\partial}{\partial K} - \frac{1}{K} \right) \Phi(K) \\ - \frac{\sqrt{3}(k_x - ik_y)}{2(5)^{1/2}} Y_{21}(\Omega_i) \left(\frac{\partial}{\partial K} - \frac{1}{K} \right) \Phi(K) \\ \left. + \frac{\sqrt{3}(k_x + ik_y)}{2(5)^{1/2}} Y_{2-1}(\Omega_i) \left(\frac{\partial}{\partial K} - \frac{1}{K} \right) \Phi(K) \right\}.$$

This is to be compared with Eq. (20).

IV. DIRECT NUMERICAL SOLUTION; A CONVENIENT PARTIAL WAVE EXPANSION

Now we discuss the third possibility mentioned in the Introduction; namely, the direct numerical solution of Eq. (1), once we have separated $C(\mathbf{K}_i)$ into radial and spherical parts. The general idea is the same as in I. We expand the $C(\mathbf{K}_i)$ into appropriate (according to group theory) series of Kubic harmonics, with corresponding radial functions. Then, as before, we truncate the Kubic harmonic expansion, assume the $C(\mathbf{K}_i)$ are zero for K_i large enough and so get a finite set of homogeneous equations and a corresponding secular equation for the energy. The present problem is, of course, more difficult than that for $\mathbf{k}=0$; here one has to deal with the angle-dependent factor $\beta - (\mathbf{K}_i + \mathbf{k})^2$, which both complicates the equations and makes the group theory more difficult to apply.

This latter difficulty aside, there are two obvious ways of proceeding. The first is to take the angle-dependent factor as it stands in Eq. (1) and expand it,

$$\beta - (\mathbf{K}_i + \mathbf{k})^2 = \beta - K_i^2 - k^2 \\ - \frac{8\pi K_i k}{3} \sum_{m=-1}^1 Y_{1m}(\Omega_i) Y_{1m}^*(\Omega_k). \quad (33)$$

If we then expand the $C(\mathbf{K}_i)$ as we have done previously, we get an infinite set of coupled equations for the radial

¹¹ A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

parts of the $C(\mathbf{K}_i)$ and can proceed as before to solve them.

There is, however, another way of doing this which seems to have appreciable advantages, especially for β negative, which we now assume, and this is the main subject of this section. To introduce it, we rewrite Eq. (1) as

$$C(\mathbf{K}_i) = [\sum_j C(\mathbf{K}_j) w(\mathbf{K}_i - \mathbf{K}_j)] / [\beta - (\mathbf{K}_i + \mathbf{k})^2]. \quad (34)$$

Now we expand $1/[\beta - (\mathbf{K}_i + \mathbf{k})^2]$ in a series of Legendre polynomials. From the Appendix

$$\frac{1}{\beta - (\mathbf{K}_i + \mathbf{k})^2} = \sum_{l=0}^{\infty} (2l+1) f_l(k, K_i, \beta) P_l(\cos\theta). \quad (35)$$

We give explicit expressions for the f_l there, but what is important for our purposes is that the dependence of the f_l on k , K_i , β comes in essentially through a single parameter κ

$$\kappa = 2kK_i / (K_i^2 + k^2 - \beta).$$

We see this in the series expansion

$$f_l = \frac{\kappa^l l! (-)^{l+1}}{(K_i^2 + k^2 - \beta) 1 \cdot 3 \cdot 5 \cdots (2l+1)} \times \left[1 + \sum_{s=1}^{\infty} (-)^s \frac{\{1 \cdot 3 \cdot 5 \cdots (2l+1)\} (l+2s)}{1 \cdot 3 \cdot 5 \cdots (2l+2s+1)} (\kappa/2)^{2s} \right]. \quad (36)$$

Now our main point is this: We are committed by assumption to a numerical solution of Eq. (1). Taken as they stand, they are an infinite set of equations and hence are not practical for computation. Somehow they must be truncated, and reduced to a finite set of equations in a finite number of unknowns. Of course this can be done by trial and error, but it is obvious that anything one can do in advance to get an idea of how and where to truncate will be useful. The truncation of the $C(\mathbf{K}_i)$ is twofold: We expand them in a *finite* number of spherical harmonics and we limit the volume of \mathbf{K}_i space. Now it is clear that the more partial waves we must take in practice in the expansion (35), the more partial waves we must take in the expansion of $C(\mathbf{K}_i)$. Thus, if we can estimate in advance the number of f_l we must take in (35) we have significantly simplified the problem of truncating the partial wave expansion of the $C(\mathbf{K}_i)$.

But we can do just this. First, for small and moderate k we can, if we have even a rough idea of the value of β , which we usually do, estimate the values of κ (as a function of K_i) that are of interest and then use Eq. (36) to make an estimate of the ratios of successive f_l , and so to truncate this expansion. For k not small we can still get an upper limit on κ ; i.e., although k may be large, it is still restricted to the first Brillouin zone. Thus, the worst case for our purpose (largest κ) occurs

when \mathbf{k} terminates near the surface of this first zone. Let us consider κ as a function of \mathbf{K}_i for this case. For $\mathbf{K}_i = 0$ of course $\kappa = 0$. Now the first Brillouin zone is formed by drawing the shortest \mathbf{K}_i vectors and then bisecting them with planes. For these shortest (except for $\mathbf{K}_i = 0$) vectors then $k \approx K_i/2$ and

$$\kappa \approx \frac{K_i^2}{(5/4)K_i^2 - \beta}. \quad (37)$$

But even this can be small, depending on the value of β . For everything else fixed, i.e., lattice distance, shape of potential, etc., it is clear that as the potential strength is increased, the magnitude of β increases (i.e., it becomes more negative) and if it is large, κ will be small. For larger K_i than those that correspond to (37), κ is still smaller, approaching the limit $2k/K_i$ when K_i gets very large. It is clear then that there can be a considerable range of potential strengths which make κ small for all K_i .

There is one new problem that presents itself with a direct numerical solution using the expansion (35) and we discuss it briefly here. We are interested in finding the energy eigenvalue parameter β . Now, for the case $\mathbf{k} = 0$ [or using the expansion (33)], this parameter occurs in a convenient form, multiplying $C(\mathbf{K}_i)$, and this makes for a conventional linear eigenvalue problem. In the present case, the eigenvalue β is much more effectively hidden in the functions $f_l(k, K_i, \beta)$, and it is useful to adopt a somewhat different procedure, as follows. We note that $w(\mathbf{K}_i - \mathbf{K}_j)$ is proportional for a given potential *shape*, to the potential *strength* b^2 . Usually what we do is take k^2 and b^2 as given and then find β as a function of them. But in the present case, it is obviously easier to turn this around and assume β and k^2 are given and then find the value of b^2 that corresponds to these values. If we do this for several different values of b^2 , we can then by interpolation plot β versus k^2 for given value of b .

V. DISCUSSION

It is worth noting that, assuming the wave functions for the atom are known, one can think of the various approximations discussed in this paper in terms of two parameters of expansion. These are: the wave number k and the ratio d/a , where a is the lattice spacing and d is the "range" of one of the atomic potentials. Now unlike k , the ratio d/a never enters our equations explicitly as an expansion parameter, but it is clear that it is really such if as in I we write

$$\hat{H}_p = \hat{H}_a + (\hat{H}_p - \hat{H}_a),$$

where \hat{H}_p is the Hamiltonian for the periodic lattice, and \hat{H}_a that for the atom, and recognize that when d/a becomes very small the term $\hat{H}_p - \hat{H}_a$ can be considered a perturbation on \hat{H}_a . Effectively then we can think of \hat{H}_p as the sum of the atomic Hamiltonian plus a per-

turbation term for which the expansion parameter is d/a (or some power of d/a).

With this idea in mind, we can characterize the tight-binding and perturbation methods as follows. The tight-binding method gives results correct to all orders in k , but only to first order in d/a . The perturbation method gives results accurate to all orders in d/a but only to whatever order in k one calculates. There are of course additional intermediate possibilities. If we expand the tight-binding wave functions in powers of k we have results accurate to that power of k and to the first order in d/a .

The above remarks have to be supplemented for potentials like the Coulomb potential which do not have a range. For these, the effective range that one must consider is the distance over which the wave function is appreciable; for example, the Bohr radius for the case of a "hydrogen lattice."

It is worth noting that if the variational tight-binding calculation as done here is not quite accurate enough, it would seem to be promising to apply a variation-iteration technique¹² for improving the wave function, especially since we know that the variational atomic functions are good approximations to the correct functions for large values of K_i , and hence the iteration method need only correct them for small values.

Finally, we would like to add a word on the relation of the present method for solving the Schrödinger equation to other plane wave expansions,¹³ for example, the orthogonalized plane wave method. In both the latter method and the present one, we expand the wave function in plane waves with Fourier coefficients $C(\mathbf{K}_i)$ and in both cases we use group theory to limit the form of $C(\mathbf{K}_i)$. But beyond this there is still a choice to be made: we can elect to express \mathbf{K}_i either in rectangular coordinates or in spherical coordinates. Doing the former we are led to equations for functions of the *rectangular* components K_{ix}, K_{iy}, K_{iz} ; doing the latter we are led to the equations of this and the previous paper for the function $C_l(K_i)$, which depends on the absolute magnitude of \mathbf{K}_i . Now there is no reason to believe that one of these choices is not more advantageous than the other; and it is our contention that it is the latter that is preferable, at least for the kinds of lattice and potentials we have been considering. The basic reason is that with it the connection with the atomic case is immediate: in the limit of large lattice spacing the $C(\mathbf{K}_i)$ go over into atomic functions. This immediately gives us an insight that is lacking if we expand in rectangular coordinates. It gives us approximations for the tails of the wave functions, and enables us to reformulate the tight-binding approximation without using near neigh-

bor approximations. Moreover, the fact that it is essentially a partial wave expansion helps in the crucial question of truncating the infinite set of equations for the $C(\mathbf{K}_i)$, by limiting the number of l values that we need take, as well as by limiting the region of K_i space.

APPENDIX

We want to expand the function $1/[\beta - (\mathbf{K}_i + \mathbf{k})^2]$ in a series of Legendre polynomials of $\cos\theta$, where θ is the angle between \mathbf{k} and \mathbf{K}_i . To do this, we write the integral representation

$$\begin{aligned} \frac{1}{\beta - (\mathbf{K}_i + \mathbf{k})^2} &= - \int_0^\infty \exp\{-x[(\mathbf{K}_i + \mathbf{k})^2 - \beta]\} dx \\ &= - \int_0^\infty \exp[-x(K_i^2 + k^2 - \beta) - 2x\mathbf{K}_i \cdot \mathbf{k}] dx. \end{aligned}$$

We put into the last integral a slight variant of the well-known partial wave expansion of a plane wave,

$$\exp(-2x\mathbf{K}_i \cdot \mathbf{k}) = \sum_{l=0}^{\infty} i^l (2l+1) j_l(2iK_i kx) P_l(\cos\theta).$$

We then get

$$\frac{1}{\beta - (\mathbf{K}_i + \mathbf{k})^2} = \sum_{l=0}^{\infty} (2l+1) f_l(k, K_i, \beta) P_l(\cos\theta),$$

where

$$f_l(k, K_i, \beta) = \frac{i^l}{\beta - (K_i^2 + k^2)} \int_0^\infty e^{-y} j_l(iky) dy \quad (\text{A1})$$

and

$$\kappa = 2kK_i / (K_i^2 + k^2 - \beta).$$

The integral defining $f_l(k, K_i, \beta)$ is a standard one in terms of hypergeometric functions,¹⁴ or it can be done directly in terms of elementary functions by using in it an integral representation for $j_l(z)$

$$j_l(z) = \frac{1}{2i^l} \int_{-1}^1 e^{izy} P_l(y) dy.$$

The resultant double integration is simple and one gets, for example,

$$\begin{aligned} f_0 &= \frac{1}{4kK_i} \ln \frac{(K_i + k)^2 - \beta}{(K_i - k)^2 - \beta}, \\ f_1 &= \frac{1}{2kK_i} \left[1 - \frac{K_i^2 + k^2 - \beta}{4kK_i} \ln \frac{(K_i + k)^2 - \beta}{(K_i - k)^2 - \beta} \right]. \end{aligned}$$

For our purposes what is often more useful than these expressions is an explicit expansion of $f_l(k, K_i, \beta)$ in

¹² P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

¹³ For a summary and critical review of these methods see Frank Herman, *Revs. Modern Phys.* **30**, 103 (1958).

¹⁴ Reference 12, p. 1575.

powers of κ . To get this, we use the series expansion

$$i^l j_l(i\kappa y) = \frac{(\kappa y)^l}{1 \cdot 3 \cdot 5 \cdots (2l+1)} \\ \times \sum_{s=0}^{\infty} (-1)^{l+s} \frac{1 \cdot 3 \cdot 5 \cdots (2l+1)}{1 \cdot 3 \cdot 5 \cdots (2l+2s+1)} (\kappa y/2)^{2s}.$$

Putting this into the integral, (A1), we get the desired expression

$$f_l(k, K_i, \beta) = \frac{\kappa^l l! (-1)^{l+1}}{(K_i^2 + k^2 - \beta) 1 \cdot 3 \cdot 5 \cdots (2l+1)} \\ \times \left[1 + \sum_{s=1}^{\infty} (-1)^s \frac{\{1 \cdot 3 \cdot 5 \cdots (2l+1)\} (l+2s)}{1 \cdot 3 \cdot 5 \cdots (2l+2s+1)} (\kappa/2)^{2s} \right].$$

Ferrimagnetic Structure of a Magnetite Crystal as Revealed by Electron Diffraction

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The process of thermal perturbation in electron diffraction is used to find the direction of easy magnetization, $[111]$, of the lattice of magnetite. In the diffraction pattern of magnetite with incidence along the $[1\bar{1}0]$ direction, the thermomagnetic displacement of the diffraction spots takes place perpendicular to the $[111]$ axis. This fact leads to the direction of the magnetization according to the Lorentz force.

INTRODUCTION

THE lattice planes in a crystal of magnetite which are parallel to the electron spin planes oriented magnetically can be assigned by means of neutron diffraction.¹ In the present study it is demonstrated that a procedure of electron diffraction is able to detect these ferrimagnetic net planes.

EXPERIMENTAL

A thin and homogeneous magnetic field is established at the two sharp edges of magnetized razor blades

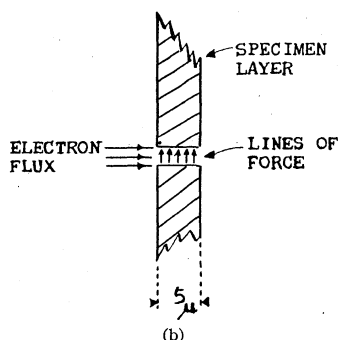
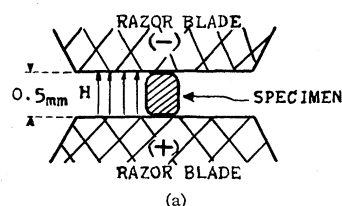


FIG. 1. Arrangement for the magnetization and for the diffraction experiment of the Fe_3O_4 layer. In (a) the electron beam runs perpendicular to the paper face; (b) shows the diffraction process through a pinhole of the magnetized Fe_3O_4 layer.

of hard steel (remanence: about 5000 gauss). Here these two sharp edges are situated in a narrow gap (0.5 mm), as shown in Fig. 1. The minimum thickness of the wedge-shaped truncated edge is about 0.5μ . A thin layer of magnetite crystal which was prepared by mechanical polishing was employed as a specimen for the experiment. The thickness and the area of this specimen were 5μ and $0.5 \times 0.5 \text{ mm}^2$, respectively, and it contained some pinholes (of about 1μ). The specimen was magnetized in the field (5000 oe) described above (see Fig. 1). An electron beam was passed in grazing incidence through one of the pinholes in the magnetized specimen in order to give rise to a diffraction pattern.

The Lorentz force of the specimen acting on the electrons was observed as a function of temperature. Here a procedure of double exposure was utilized to observe the thermally perturbed diffraction patterns. The diffraction pattern from the cold specimen (i.e., at 40°C) was first photographed, and then that of the hot specimen at 300°C was superimposed upon the former pattern. The position of the specimen and that of the photographic plate as well as the wavelength of the incident electron beam were all kept constant during this double exposure process. The double diagram obtained in this way is shown in Fig. 2, where the incident beam runs parallel to the $[1\bar{1}0]$ axis of the magnetite crystal.

The temperatures of the specimen, 40°C and 300°C , were controlled by the irradiation of the electron beam.² The conditions of this electronic bombardment are characterized as follows: The current of the beam was

¹ G. E. Bacon, *Neutron Diffraction* (Clarendon Press, Oxford, 1955), p. 241.

² S. Yamaguchi, *Z. angew. Phys.* **13**, 253 (1961).