

Simplified Impurity Calculation*

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(Received August 30, 1954)

The methods of previous papers by the authors are applied to a simplified impurity calculation. This is the case of a localized perturbation in a simple cubic lattice. We consider the effect of the perturbation on a single band which is describable in terms of a Wannier function which only has nearest neighbor interactions. The results of this calculation are compared with some approximate treatments of impurity calculations.

I. INTRODUCTION

IN two previous papers,^{1,2} the authors have proposed a treatment of the impurity problem in solids. This method consisted of expanding the perturbed wave function in terms of a linear combination of the Wannier functions of the unperturbed crystal. The coefficients in this linear expansion were shown to satisfy a set of simultaneous linear equations which had the form of difference equations. The method used to solve these equations was a Green's function method for the difference equations. The procedure was applied to simple cases drawn almost exclusively from one-dimensional crystals. These are quite unrealistic and it is desirable to work through, by this method, a three-dimensional impurity problem.

Fortunately, there exists a three-dimensional impurity problem which can be carried through analytically in some detail. This does not correspond to any crystal found in nature but it will have features in common with more realistic computations. The problem concerns itself with the effect of an impurity on the wave functions of a single band in a simple cubic lattice. This band is assumed to be cosine-like in the x , y , and z directions of reciprocal space. This is to say that the dependence of energy on the propagation vector is a sum of cosines of k_x , k_y , and k_z . If this is the case, the evaluation of the Green's function for the difference equations can be carried out analytically and the solutions can be studied in detail.

We are able to study the manner in which the bound state appears below the band as we vary the perturbative potential. The wave function of the bound state can be found numerically. This enables us to compare the wave function found in this precise manner with the wave functions found by approximate procedures. In particular, we can compare it with the wave function that appears from replacing the exact difference equations by approximate differential equations. Another

approximation can be studied. This approximation consists of cutting the crystal off after a finite number of lattice spacings. We shall be able to see how valid it is to replace the infinite crystal by a small finite crystal. In addition to the bound states, the scattering problem in this lattice can be carried through. It is hoped that this simple example will illustrate the use of the method of treating the impurity problem proposed in the previous papers and will also indicate features which we might expect to find in more precise impurity problems.

II. STATEMENT AND DIRECT SOLUTION OF THE PROBLEM

We shall assume that we have a simple cubic lattice whose primitive translations are given by

$$\mathbf{R}_{pqr} = p\mathbf{R}_i + q\mathbf{R}_j + r\mathbf{R}_k. \quad (1)$$

Here R is the lattice spacing and \mathbf{i} , \mathbf{j} , and \mathbf{k} are unit vectors in the x , y , and z directions respectively. Each lattice site will be further assumed to have full cubic symmetry. Let us imagine that associated with this solid there is a band of energies which has associated with it Wannier functions³ which have full cubic symmetry with respect to the lattice site about which they are defined. These energies are the eigenstates of some one-electron Hamiltonian. We assume in addition that the Wannier functions only have interactions between each other when they are nearest neighbor or closer. If we denote the Wannier function associated with the lattice site \mathbf{R}_{pqr} by $a(\mathbf{r} - \mathbf{R}_{pqr})$ and the one-electron Hamiltonian by H , this means that the only nonvanishing matrix elements of the Hamiltonian are given by

$$\begin{aligned} \mathcal{E}(0) &= \int a(\mathbf{r} - \mathbf{R}_{pqr}) H a(\mathbf{r} - \mathbf{R}_{pqr}) dv, \\ \mathcal{E}(1) &= \int a(\mathbf{r} - \mathbf{R}_{pqr}) H a(\mathbf{r} - \mathbf{R}_{p+1, q, r}) dv \\ &= \int a(\mathbf{r} - \mathbf{R}_{pqr}) H a(\mathbf{r} - \mathbf{R}_{p, q+1, r}) dv, \text{ etc.} \end{aligned} \quad (2)$$

We wish to study the effects of a perturbation on this perfect periodic lattice. We restrict ourselves in this

³ G. H. Wannier, Phys. Rev. **52**, 191 (1937).

* The research in this document was supported jointly by the U. S. Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

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¹ G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954). This paper will be referred to as (I).

² G. F. Koster, Phys. Rev. **95**, 1436 (1954). This paper will be referred to as (II).

section to a perturbative potential which extends over only one lattice site. If we call the perturbative potential $V(\mathbf{r})$, this means that the only nonvanishing matrix component of the perturbative potential is

$$V(0) = \int a(\mathbf{r}-0)V(\mathbf{r})a(\mathbf{r}-0)d\mathbf{r}. \quad (3)$$

The perturbative potential has, for convenience, been assumed to be centered at the central lattice site.

Following the procedure outlined in an earlier paper¹ by the authors, we expand our perturbed wave function in terms of the Wannier functions of the band which we have described:

$$\psi(\mathbf{r}) = \sum (p, q, r) U_{p, q, r} a(\mathbf{r} - \mathbf{R}_{p, q, r}). \quad (4)$$

ψ is the perturbed wave function and the U 's are unknown coefficients which are to be determined by minimizing the expectation value of the perturbed Hamiltonian. This minimization gives rise to a set of difference equations for the U 's [Eqs. (8) of (I)] which in this case reduce to

$$[\mathcal{E}(0) - E]U_{p, q, r} + \mathcal{E}(1)[U_{p+1, q, r} + U_{p-1, q, r} + U_{p, q+1, r} + U_{p, q-1, r} + U_{p, q, r+1} + U_{p, q, r-1}] = 0, \quad (5)$$

unless $p = q = r = 0$,

$$[\mathcal{E}(0) + V(0) - E]U_{0, 0, 0} + \mathcal{E}(1)[U_{1, 0, 0} + U_{-1, 0, 0} + U_{0, 1, 0} + U_{0, -1, 0} + U_{0, 0, 1} + U_{0, 0, -1}] = 0.$$

E is the energy of the perturbed state. If the perturbative term were set equal to zero, the solutions to this difference equation would just give rise to the Bloch solutions to the unperturbed lattice and the energies would be just the energies in the energy band which would be given by

$$E = \mathcal{E}(0) + 2\mathcal{E}(1)[\cos k_1 R + \cos k_2 R + \cos k_3 R]. \quad (6)$$

Here k_1, k_2, k_3 can take on arbitrary values. We must now look for the solutions to the difference equations for the states when the perturbation does not vanish. Instead of solving the problem of the perturbed lattice by the method proposed in (I), we solve it in this section by direct solution of the difference equations. We do this since we shall treat in a later section the case of the finite lattice and this method of solution easily gives us the proper results for this case. In a later section, we shall solve the same problem by the method proposed in (I) which will be much simpler for the case of an infinite lattice.

Our problem has the symmetry properties of the cube, and our solution to the problem must form a basis function for one of the irreducible representations of the cubic group. We know that we are looking for a function which forms a basis for the identity representation of the cubic group. We know this because any other representation of the cubic group would have a

vanishing contribution from the Wannier function at the origin and hence would not be perturbed by our localized potential. We therefore know that we are looking for a function which is an even function of p , of q , and of r . This is the same type of symmetry shown by the s function; only here since we do not have spherical symmetry, we must not expect that the function $U_{p, q, r}$ will show spherical symmetry.

The difference equations (5) fortunately can be solved, though the solution does not appear in the literature. The writers are indebted to Dr. H. C. Schweinler for pointing out that an analogous problem has been solved by McCrae and Whipple.⁴ The same method of solution can be applied to the present problem. What we shall do is find solutions of the difference equations with the energy E for those equations not involving the perturbation and then form a linear combination of them to satisfy the special equation which involves the perturbation $V(0)$. For boundary conditions, we shall assume that $U_{p, q, r}$ vanishes on the faces of a cube which extends N atoms in the plus x direction and in the minus x direction and the same distances in the plus and minus y and z directions.

The method of solution introduces an apparent lack of symmetry between the three directions in space: one axis, which we shall take to be the r axis, must be treated differently from the others. Though the solution appears unsymmetrical, this is only in the way of writing it, not in the solution itself. Let us take a function

$$U_{p, q, r} = \cos \left[\frac{(2m+1)\pi}{2N} p \right] \cos \left[\frac{(2n+1)\pi}{2N} q \right] \times \sinh[(r-N)\beta], \quad r \geq 0. \quad (7)$$

Here m and n are integers which take values up to $N-1$. This function satisfies the boundary conditions in the x and y directions and also in the positive z direction. If we substitute this into the first of Eqs. (5), we find that we have a solution provided

$$E = \mathcal{E}(0) + 2\mathcal{E}(1) \left\{ \cos \left[\frac{(2m+1)\pi}{2N} \right] + \cos \left[\frac{(2n+1)\pi}{2N} \right] + \cosh \beta \right\}. \quad (8)$$

For a given energy value, the quantity β is determined from Eq. (8) in terms of m, n , and E . Now let us make up a solution as a sum of $(N-1)^2$ such terms, all corresponding to the same E ; it will clearly be a solution of the first of Eqs. (5), and we have merely to satisfy the second. However, before we go on we must look at the symmetry properties of the solution.

The solutions in Eq. (7) have even symmetry with respect to the p and q axes. In order to give the solution

⁴ W. H. McCrae and F. J. W. Whipple, Proc. Roy. Soc. Edinburgh, **60**, 281 (1940).

the proper symmetry with respect to the r axis, we must for negative values of r replace $\sinh(r-N)\beta$ by $\sinh(-r-N)\beta$. We shall then have a condition of joining these two solutions along the plane $r=0$, as well as the condition which we must satisfy at $p=q=r=0$. We can now write our solution in the form

$$U_{p,q,r} = \sum (m,n) c(m,n) \cos \left[\frac{(2m+1)\pi}{2N} p \right] \times \cos \left[\frac{(2n+1)\pi}{2N} q \right] \sinh[(r-N)\beta], \quad r \geq 0. \quad (9)$$

In the summation, m and n are to run up to the values $N-1$, and the c 's are coefficients to be determined. The solution above applies only when $r \geq 0$; for negative r we use $\sinh[(-r-N)\beta]$. The quantity β is to be determined in terms of m and n by the use of Eq. (8). We shall now apply the condition of continuity over the plane $r=0$, but for the case where p and q are not both equal to zero.

To do this we substitute Eq. (9) into the first equation of (5), for the special case where $r=0$, remembering the situation for negative r 's. We find at once that the result, when we make use of Eq. (7), reduces to the statement that the expression in Eq. (9), computed for $r=-1$, must equal the same expression computed for $r=1$. In other words, though the expansion in Eq. (9) is correct only for positive r 's, this shows that it must still converge for $r=-1$ (so long as we do not have $p=q=0$), and must give the correct value at such a point. We can then write this condition in the form

$$\sum (m,n) c(m,n) \cos \left[\frac{(2m+1)\pi}{2N} p \right] \cos \left[\frac{(2n+1)\pi}{2N} q \right] \times \cosh N\beta \sinh \beta = 0. \quad (10)$$

We shall now show that all such equations, provided p and q are not both zero, can be satisfied by the assumption,

$$c(m,n) = 1/(\cosh N\beta \sinh \beta), \quad (11)$$

where β is defined in terms of m and n by Eq. (8).

To do this we note that in case Eq. (11) holds the summation in Eq. (10) becomes $\sum (m,n) \cos[(2m+1)\pi/2N] \cos[(2n+1)\pi/2N]$. Such a sum is immediately shown to be zero on account of the familiar theorems on the orthogonality of the cosine functions. We thus see that our expression (9), in which the c 's are given by Eq. (11), forms an exact solution to our difference equations (5) everywhere, except that we have not yet considered the point $p=q=r=0$.

If we substitute our solution in the second of Eqs. (5) and make use of (8) we find that we must have

$$V(0) \sum (m,n) [\sinh N\beta] / [\cosh N\beta \sinh \beta] = 2N^2 \mathcal{E}(1). \quad (12)$$

The quantity being summed depends on m and n through the relation in Eq. (8). This is the eigenvalue condition which determines the energy as a function of the perturbative potential $V(0)$. We shall now go on and let our lattice become infinite to see how this modifies our expressions.

If we allow N to become infinite, Eq. (12) reduces to

$$V(0) \sum (m,n) 1/\sinh \beta = 2N^2 \mathcal{E}(1). \quad (13)$$

We can now replace the summations over m and n by integrations over continuous variables α_1 and α_2 . If we do this, and also express the \sinh in (13) in terms of the cosh, and the cosh in terms of $\alpha_1 = (2m+1)\pi/2N$ and $\alpha_2 = (2n+1)\pi/2N$ through the use of (8), we obtain for the eigenvalue condition (13) the result that

$$\frac{V}{\pi^2} \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \left[\left(\frac{E - \mathcal{E}(0)}{2\mathcal{E}(1)} - \cos \alpha_1 - \cos \alpha_2 \right)^2 - 1 \right]^{-\frac{1}{2}} = 2\mathcal{E}(1). \quad (14)$$

The wave function can also be expressed in terms of an integral by substituting (11) into (9) and passing to the limit as N becomes infinite. In this case the wave function $U_{p,q,r}$ would be proportional to

$$\int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \frac{\cos \alpha_1 p \cos \alpha_2 q e^{-r\beta}}{\sinh \beta}, \quad (15)$$

where once again β must be expressed in terms of α_1 and α_2 through the energy expression. We shall defer the study of the wave function and the energy until the next section where we shall formulate the same problem in terms of the method of solution proposed in (I).

III. SOLUTION OF THE PROBLEM BY MEANS OF THE GREEN'S FUNCTION FOR DIFFERENCE EQUATIONS

In this section, we shall solve the difference equations for the infinite perturbed lattice by means of the method proposed in (I). In that paper, we have discussed just the case of a perturbation localized on one lattice site. If we apply the results for the wave function summed up in Eq. (42) of (I) and for the eigenvalue condition summed up in Eq. (43) of (I), we get in our case for the wave function,

$$U_{p,q,r} = (1/N) V(0) \sum (\mathbf{k}) [\exp(i\mathbf{k} \cdot \mathbf{R}_{p,q,r})] / [E - E(\mathbf{k})] U(0), \quad (16)$$

and for the condition determining the energy,

$$(V(0)/N) \sum (\mathbf{k}) [E - E(\mathbf{k})]^{-1} = 1. \quad (17)$$

In these expressions, the energies $E(\mathbf{k})$ are given by Eq. (6) of this paper. If we replace $k_1 R$, $k_2 R$ and $k_3 R$ by α_1 , α_2 , and α_3 , respectively, we can convert these

summations to integrations over the α 's. If this is done, the solutions to the difference equations are given by

$$U_{p,q,r} = \frac{V(0)}{\pi^3} \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\alpha_3 \times \frac{\cos p\alpha_1 \cos q\alpha_2 \cos r\alpha_3}{E - \mathcal{E}(0) - 2\mathcal{E}(1)[\cos\alpha_1 + \cos\alpha_2 + \cos\alpha_3]} U(0), \quad (18)$$

and the eigenvalue conditions become

$$\frac{V(0)}{\pi^3} \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\alpha_3 \{E - \mathcal{E}(0) - 2\mathcal{E}(1)[\cos\alpha_1 + \cos\alpha_2 + \cos\alpha_3]\}^{-1} = 1. \quad (19)$$

The eigenvalue condition when written in this form looks different from the eigenvalue condition expressed in Eq. (14). It is easy to show, however, that by integration over α_3 , Eq. (14) may be obtained from Eq. (18). The integration over α_3 is a simple integral.

The wave function and eigenvalue condition could be evaluated by numerical integration in the form indicated. This however is not a convenient form in which to do the integrals. In the Appendix, we show a method by which these conditions can be rewritten which will reduce both of these integrals to single integrals. Taking the results from the Appendix we find that the solution to the difference equations is given by

$$U_{p,q,r} = V'(0)U(0) \int_0^\infty e^{-E't} I_p(t) I_q(t) I_r(t) dt, \quad (20)$$

and the eigenvalue condition by

$$V'(0) \int_0^\infty e^{-E't} [I_0(t)]^3 dt = 1. \quad (21)$$

The I 's are the Bessel functions of imaginary argument and we have let

$$V'(0) = V(0)/2\mathcal{E}(1) \quad \text{and} \quad E' = [E - \mathcal{E}(0)]/2\mathcal{E}(1).$$

This is a more convenient form in which to do the integrals and they can easily be done numerically.

We are now in a position to study the dependence of the energy E' on the perturbative potential $V'(0)$. We first notice that if the energy E' is greater than 3, the integral (21) diverges. This can most easily be seen by considering the asymptotic form of the function $I_0(t)$. For large values of t , the asymptotic form of $I_0(t)$ contains a factor e^t . This means that the integrand in (21) will go as $\exp[(3-E')t]$. Thus for $E' < 3$ the integrand will become infinite as we approach the upper limit and the integral will diverge. This result can also be seen by consideration of the integral in the form (14). In this case for $E' < 3$ the integrand will develop a singularity which makes the integral infinite.

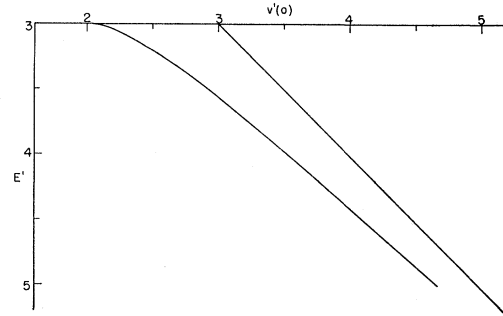


FIG. 1. Energy of bound state as a function of perturbative potential.

Thus for this case there is no solution to our problem. The case where $E' = 3$ is easy to interpret. This corresponds to the case $E = \mathcal{E}(0) + 6\mathcal{E}(1)$, which is the value of the energy at the center of the Brillouin zone, from (6). If $\mathcal{E}(1)$ is positive, this is the top of the energy band, and in this case we find a discrete state only when E is above the top of the band; when $\mathcal{E}(1)$ is negative, it is the bottom of the band, and we have a discrete state only below the bottom of the band. This of course is as it should be. Since the integral in Eq. (21) is positive by its definition, this means that from Eq. (21) we have a solution when $V(0)$ has the same sign as $\mathcal{E}(1)$ [$V'(0)$ positive]. We shall not take up the opposite case, where the discrete level appears at the value of energy corresponding to the corner of the Brillouin zone rather than the center, but it can easily be handled by putting in a change in the sign of the U 's associated with adjacent lattice points.

The value of the integral in Eq. (21), when carried out numerically for the case $E' = 3$, turns out to be 0.4990. As the value of E' increases above three the value of the integral decreases. Thus in order to satisfy Eq. (21) the perturbative potential $V'(0)$ must increase. In other words, in order to have a discrete state, $V(0)$ must be at least equal to $2\mathcal{E}(1)/0.4990$, which is approximately $4\mathcal{E}(1)$. That is, from the difference equations we have shown that there is no discrete state unless the perturbative potential is greater than a critical value. Furthermore, we have been able to evaluate this critical value, for the simple cubic lattice with nearest neighbor interaction. The total width of the band in this case is $12\mathcal{E}(1)$ [since each of the cosines in the energy expression (6) can go through the values from -1 to 1]. In other words, the quantity $V(0)$ must be equal to at least a third of the width of the band, in order that there be a discrete state.

In addition to the value $E' = 3$, the integral in Eq. (21) has been carried out for a number of other values of E' greater than three in order to study the dependence of energy of the bound state on the perturbative potential. In Fig. 1 we plot the energy of the bound state E' in terms of the perturbative potential $V'(0)$. We notice that in the graph the bound state appears to leave the graph quadratically with the perturbation. We also

notice that as we increase the perturbation the energy of the bound state becomes linear with the perturbation $V'(0)$. Both of these facts can be checked by consideration of the expressions which determine the energy in terms of $V'(0)$.

The most convenient expression from which to study the dependence of the energy on perturbation near the point where the bound state first leaves the band is Eq. (19). Let us define the integral which multiplies $V'(0)/\pi^3$ as $I(E')$. What we must first do is to find the difference between $I(E')$ and $I(3)$. $I(3)$ is, of course, the value of the integral which determines the value of the perturbation which first gives rise to a bound state. By comparison with Eq. (21), we see that $I(3) = \pi^3(0.4990)$. From Eq. (19) we see that the aforementioned difference is given by

$$I(E') - I(3) = \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\alpha_3 \times \{ [E' - \cos\alpha_1 - \cos\alpha_2 - \cos\alpha_3]^{-1} - [3 - \cos\alpha_1 - \cos\alpha_2 - \cos\alpha_3]^{-1} \}. \quad (22)$$

We are to study this difference for values of E' very close to 3. Because of this the principal contribution to this difference will come from values of α_1 , α_2 , and α_3 very close to zero. We shall expand the cosines in terms of the first two terms of their power series and introduce polar coordinates in the space of α_1 , α_2 , and α_3 , defining $r^2 = \alpha_1^2 + \alpha_2^2 + \alpha_3^2$. If this is done, Eq. (22) can be rewritten as

$$I(E') - I(3) = (4\pi/8) \int_0^\infty \{ [E' - 3 + r^2/2]^{-1} - (\frac{1}{2}r^2)^{-1} \} r^2 dr. \quad (23)$$

We have extended the upper limit to infinity since we know that the principal contribution to this integral comes from small values of the argument on account of the small size of $E' - 3$. In Eq. (23), the fractions can be given a common denominator. When this is done, the integral reduces to an elementary integral which gives the result:

$$I'(E) - I(3) = (-\pi^2/\sqrt{2})(E' - 3)^{1/2}. \quad (24)$$

Let us now substitute this result into the eigenvalue condition (19):

$$[V'(0)/\pi^3][-(\pi^2/\sqrt{2})(E' - 3)^{1/2} + I(3)] = 1. \quad (25)$$

We can now solve this relation for $E' - 3$ in order to obtain the result:

$$E' - 3 = 2\pi^2 \{ 1/V'(0) - I(3)/\pi^3 \}^2. \quad (26)$$

The second term in the curly brackets we recognize as the value $V'(0)$ of the perturbation potential which first produces a bound state. Since the value of $V'(0)$ for a value of energy near 3 will differ from this by a small quantity this expression can be rewritten (correct

to terms of the second order)

$$E' - 3 = 2\pi^2 (I(3)/\pi^3)^4 \{ V'(0) - \pi^3/I(3) \}^2. \quad (27)$$

We have thus demonstrated our contention that the energy of the bound state behaves quadratically with the perturbative potential as the bound state leaves the bottom of the band. Of course, this quadratic dependence is with the difference between the potential and the value of the potential that first produces a bound state.

We are also interested in the dependence of the energy on perturbation for large values of E' . Returning to Eq. (19) the integrand is seen to become essentially independent of the α 's for large values of E' . Thus, in this case, Eq. (19) reduces to

$$[V'(0)/\pi^3][\pi^3/E'] = 1, \quad V'(0) = E'. \quad (28)$$

We have plotted the straight line defined by Eq. (28) in Fig. 1 and it can be seen that the curve of energy *versus* perturbation approaches this straight line asymptotically for large values of $V'(0)$.

We have now completed the discussion of the dependence of the energy on the perturbing potential. In the next section, we shall study the dependence of the wave function on the perturbative potential and compare these results with those of the differential equation approach to the impurity problem.

IV. THE WAVE FUNCTION FOR THE IMPURITY LEVEL

In this section, we shall study the wave function of the bound state as expressed in terms of the coefficients of the Wannier functions. These coefficients are given by either Eq. (15), (18), or (20). Before we give the results of these computations it is instructive to do the problem by the differential equation approach in order to have an approximate solution with which we can compare our exact solution. This differential equation approach was briefly described in (I) and we shall make use of the equations as written there.

The coefficients of the Wannier functions $U_{p,q,r}$ when expressed as a function of the continuous variables p , q , and r can be shown to satisfy approximately the differential equation,

$$-\frac{\hbar^2}{8\pi^2 m} \nabla^2 U + [E_0 + V(r)]U = EU \quad (29)$$

This is essentially Eq. (12) of (I). We have specialized that equation to the case at hand. For our case, near $\mathbf{k} = 0$ there is only one effective mass since for small values of \mathbf{k} the band is spherically symmetric. E_0 is the value of the energy at the bottom of the band and $V(\mathbf{r})$ is the perturbing potential. In the problem as solved by the difference equations, the only property of this potential that we have used is the fact that it only has matrix elements between two Wannier functions

located at the central lattice site. In order to carry out this differential equation approach, we must specify this potential in more detail. We shall assume that it is a three-dimensional square well.

If we look for a solution of Eq. (29) which is independent of angle, the radial Schrödinger function will satisfy the equation,

$$\frac{-\hbar^2}{8\pi^2m} \frac{d^2}{dr^2}(rU) + VrU = ErU. \quad (30)$$

We have adjusted our zero of energy to lie at the bottom of the band. Now if V is zero, as we have outside our potential well, the quantity rU satisfies the differential equation for a free particle, so that it can be written in the form $\exp(ikr)$, where $k = (2\pi/\hbar)(2mE)^{1/2}$. Inside the potential well, in a similar way, where we shall assume the potential energy to be $-V_0$, we have a solution of the form $\exp(ik_0r)$, where $k_0 = (2/\hbar)(2m(E+V_0))^{1/2}$. For a bound state, we must assume that $E+V_0$ is positive, but that E , the kinetic energy outside the potential well, is negative. Inside, then, we must use the solution $rU = \sin k_0r$; for only by using such a solution will the actual wave function U be finite at the origin. We must use outside a solution $\exp(-\gamma r)$, where $\gamma = (2\pi/\hbar) \times (-2mE)^{1/2}$, the energy being negative. These two functions must join smoothly at the boundary of the well. Now the exponential must be sloping down at the boundary of the well, or in the limit where γ is very small it will have a horizontal tangent. Thus we cannot join the functions smoothly unless the sine function has gone through at least a quarter wavelength within the well, so as to rise to its first maximum at the boundary of the well. In this limit, then, where E is zero, and the wavelength within the well is $\hbar(2mV_0)^{-1/2}$, the condition for the existence of a bound state is that $4R_0$ should be at least a wavelength, or that V_0 must be at least $\hbar^2/(32mR_0^2)$. (R_0 is the radius of the square well.) The fact that the differential equation approach gives a finite value of the perturbation necessary for the appearance of a bound state agrees with the result of the last section. Actually, closer examination of this approach would even show that for small increases of V_0 over the critical value, the energy will be proportional to $(V_0 - V_{crit})^2$, but at sufficiently great V_0 , the energy will be proportional to V_0 . The wave function will become more and more concentrated in the potential well as V_0 increases, falling off more and more rapidly in the exponential region outside the well, where it has the form $\exp(-\gamma r)/r$. Finally, for an extremely deep well, the wave function will be negligible outside the well, and will become identical with that of a particle in a well with infinitely high barriers at the boundary.

Before going on to a detailed discussion of the wave function, it is interesting, though probably not very significant, to compare the condition for the critical value of $V(0)$ which we find from the difference equation

approach with the corresponding value for the square potential well and Schrödinger's equation. We have seen that in that case we have a discrete state provided V_0 , the depth of the potential well, is greater than $\hbar^2/(32mR_0^2)$, where R_0 is the radius of the well. To compare these, we must first substitute for the effective mass: if the energy as a function of \mathbf{k} is given by Eq. (6) then the effective mass is $-\hbar^2/2\mathcal{E}(1)R^2$ (the negative sign because it is positive at the bottom of a band, which comes at $k=0$ is $\mathcal{E}(1)$ is negative). If we had a Schrödinger equation with this effective mass, then, we find that the critical value of V_0 is $(\pi^2/4)(R^2/R_0^2)\mathcal{E}(1)$. We may ask what value R_0 , the radius of the square well, must be, in order that this critical value of V_0 should agree with $4\mathcal{E}(1)$, the approximate critical value of $V(0)$. Clearly $R_0 = (\pi/4)R$, so that R_0 is of atomic dimensions, R being the interatomic distance in the simple cubic lattice. The volume of the sphere within which the potential is V_0 is $(4\pi/3)R_0^3$, which equals $(\pi^4/48)R^3$, or roughly $2R^3$, or twice the volume per atom in the simple cubic lattice. It seems likely, therefore, that the solution of Schrödinger's equation for such a potential well might give a fair approximation to the solution of the difference equations.

In order to calculate the coefficients of the Wannier functions ($U_{p,q,r}$), we shall use the form in Eq. (20). We shall not present here the normalized values of the coefficients $U_{p,q,r}$ but instead the values of the integral in Eq. (20), namely

$$\int_0^\infty e^{-E't} I_p(t) I_q(t) I_r(t) dt. \quad (31)$$

For any given value of E' this gives the proper dependence of the coefficients of the distance from the origin. It does not however (since the wave function is not normalized) give the proper dependence of a given coefficient on the energy. In Table I we give the results of the calculation of the quantity in Eq. (31) carried out numerically using Simpson's rule. The table gives the values of the quantity in Eq. (31) for points along the x direction where y and z are equal to zero, for a number of values of the energy. From Fig. 1 we can of course get the corresponding value of the perturbing potential. In Fig. 2, we plot the quantity $pU_{p,0,0}/U_{1,0,0}$ as a function of p for various values of E' on semilog paper. With this type of plot we can compare the results of our rigorous solution of the difference equations with the results of the differential equation approach.

TABLE I. $\int_0^\infty dt e^{-E't} [I_0(t)]^2 I_p(t)$ as a function of E' and p .

$\begin{smallmatrix} E' \\ p \end{smallmatrix}$	3.0	3.1	3.2	3.5	4.2	5.0
0	0.4990	0.4311	0.4001	0.3410	0.2646	0.2137
1	0.1658	0.1123	0.0935	0.0645	0.0371	0.0238
2	0.0778	0.0376	0.0270	0.0141	0.00564	0.00278
3	0.0501	0.0154	0.00929	0.00350	0.000924	0.000343
4	0.0411	0.00717	0.00365	0.000964	0.000162	0.0000439

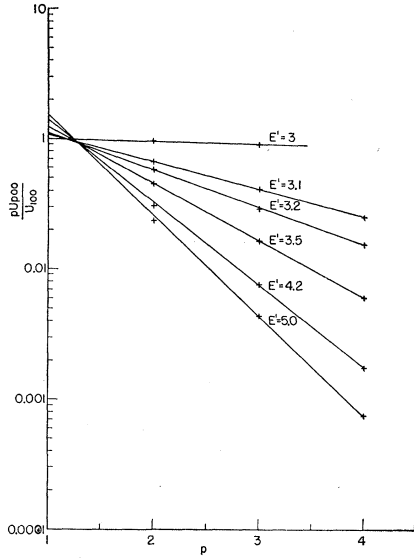


FIG. 2. Coefficients of the Wannier function in the (100) direction ($p(U_{p,0,0}/U_{1,0,0})$) as a function of p for various values of E' .

We have seen above that the differential equation approach would give as the wave function $\exp(-\gamma r)/r$. This would mean that if the exact solutions of the difference equations were well approximated by the solution of the differential equation when these results were plotted semilogarithmically, as they are in Fig. 2, the result would be a straight line. We have not plotted the points $U_{0,0,0}$ since the differential equation solution which falls off exponentially does not apply at this point. We notice that for $E'=3$ the graph is very nearly linear and horizontal. This is what would be predicted by the differential equation approach ($\gamma=0$). For $E'>3$ the linearity becomes quite good for points removed from the impurity atom (i.e., $p=2, 3, 4$ lie nearly on a straight line). We can actually compare these results with another approximation which we mentioned in (I).

In (I) we expanded the denominator in the expression for the Green's function in a power series in \mathbf{k} . This type of expansion would give an approximation to the solution of the difference equations for the values of the energy close to the point where the bound state appears beneath the band. This resulting approximate form of the Green's function is Eq. (46) of (I). If we specialize this expression to the case we consider in this paper, we get the result that

$$U_{p,q,r} \approx (p^2 + q^2 + r^2)^{-\frac{1}{2}} \times \exp\{-[2(E'-3)]^{\frac{1}{2}}[p^2 + q^2 + r^2]^{\frac{1}{2}}\}. \quad (32)$$

We notice that this result agrees in form with the result of the differential equation approach. It is based however on the difference equation approach since it involves an approximation to the Green's function. Furthermore, in order to derive this expression no

assumption had to be made about the form of the potential besides those made in the original difference equations. This expression also gives the dependence of the falloff of the wave function with distance on the energy. We can actually compare the slopes on the semilog plot with those approximated by the expression (32). Equation (32) predicts a slope,

$$(\log_{10} e)/[2(E'-3)]^{\frac{1}{2}}. \quad (33)$$

For $E'=3.1$ this gives a value 0.193; for $E'=3.2$ the value is 0.275. The corresponding slopes calculated from the actual values of $U_{p,0,0}$ are 0.209 for $E'=3.1$ and 0.285 for $E'=3.2$. We can see therefore that the approximation to the slope gives a value to within 5 percent of the true value.

We also notice that both Eq. (32) and the differential equation approach make an additional prediction about the wave function. These expressions predict that the solutions of the difference equations should be spherically symmetric. In order to check this dependence on angle, for $E'=3.5$ we have computed the values of (31) for other directions than the 100 direction. The results are given in Table II. We have plotted in Fig. 3

$$(p^2 + q^2 + r^2)^{\frac{1}{2}} \int_0^\infty e^{-E't} I_p(t) I_q(t) I_r(t) dt,$$

which is proportional to the distance from the origin multiplied by $U_{p,q,r}$, versus the distance from the origin $[(p^2 + q^2 + r^2)^{\frac{1}{2}}]$. The plot is again on semilog paper. The straight line in the plot connects the points in the 100 direction. If the approximate expressions were valid and the coefficients of the Wannier function did display spherical symmetry, then all the points in the graph would be on a single straight line. It is clear from the graph that this is not the case. The approximate expression seems to give the proper dependence on

TABLE II. $I_{p,q,r} = \int_0^\infty dt e^{-E't} I_p(t) I_q(t) I_r(t)$ for $E'=3.5$ as a function of p, q , and r .

p	q	r	$I_{p,q,r}$
0	0	0	0.3410
0	0	1	0.0645
0	0	2	0.0141
0	0	3	0.00350
0	0	4	0.000964
0	1	1	0.0242
0	1	2	0.00765
0	1	3	0.00236
0	2	2	0.00318
0	2	3	0.00120
0	3	3	0.000527
1	1	1	0.0125
1	1	2	0.00486
1	1	3	0.00172
1	2	2	0.00228
1	2	3	0.000935
1	3	3	0.000435
2	2	2	0.00122
2	2	3	0.000553
2	3	3	0.000277
3	3	3	0.000150

distance in a given direction but fails to give the proper dependence on direction. We can, therefore, see from this simple example that the differential equation approach gives results that are qualitatively correct but faulty in some of the aspects of the wave function.

In all of the preceding we have assumed that the perturbative potential extends over only one lattice site. This is, of course, a rather unrealistic assumption. It has, in addition, the bad feature that the only bound state is a state which is completely symmetric under the operations of the point group. In order to have bound states with higher types of symmetry, we must have our perturbative potential extend over more lattice sites. In the next section we shall carry out the impurity problem for a more extended perturbation. We shall let it extend over the nearest neighbors of the central lattice site. Unfortunately, we shall have to assume a shape for the potential. This we shall do in a completely arbitrary manner, the object being to illustrate the use of the general procedure for solving for states of higher types of symmetry rather than to have a model which has any exact physical counterpart.

V. A MORE EXTENDED PERTURBATION

If our perturbative potential $V(\mathbf{r})$ extends over more than one lattice site, we must solve the general difference equations which are Eqs. (8) of (I). In (I) we showed that we could solve these equations in the form of Eq. (38) of that same paper. For the special case under consideration in this paper, these equations reduce to

$$U_{p,q,r} + \frac{1}{\pi^3} \sum (p',q',r'; p'',q'',r'') \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\alpha_3 \times \frac{\exp i[(p-p')\alpha_1 + (q-q')\alpha_2 + (r-r')\alpha_3]}{E' - \cos\alpha_1 - \cos\alpha_2 - \cos\alpha_3} \times V'(p',q',r'; p'',q'',r'') U_{p'',q'',r''} = 0. \quad (34)$$

In this equation,

$$V(p',q',r'; p'',q'',r'') = \frac{1}{2\mathcal{E}(1)} \int a(\mathbf{r} - \mathbf{R}_{p',q',r'}) V(\mathbf{r}) a(\mathbf{r} - \mathbf{R}_{p'',q'',r''}) dv \quad (35)$$

We shall now specialize this relation by assuming that the only nonvanishing matrix elements of the perturbation are

$$\begin{aligned} V'(0) &= \frac{1}{2\mathcal{E}(1)} \int a(\mathbf{r} - \mathbf{0}) V(\mathbf{r}) a(\mathbf{r} - \mathbf{0}) dv, \\ V'(1) &= \frac{1}{2\mathcal{E}(1)} \int a(\mathbf{r} - \mathbf{R}_{1,0,0}) V(\mathbf{r}) a(\mathbf{r} - \mathbf{R}_{1,0,0}) dv \quad (36) \\ &= \frac{1}{2\mathcal{E}(1)} \int a(\mathbf{r} - \mathbf{R}_{0,1,0}) V(\mathbf{r}) a(\mathbf{r} - \mathbf{R}_{0,1,0}) dv \\ &= \text{etc.} \end{aligned}$$

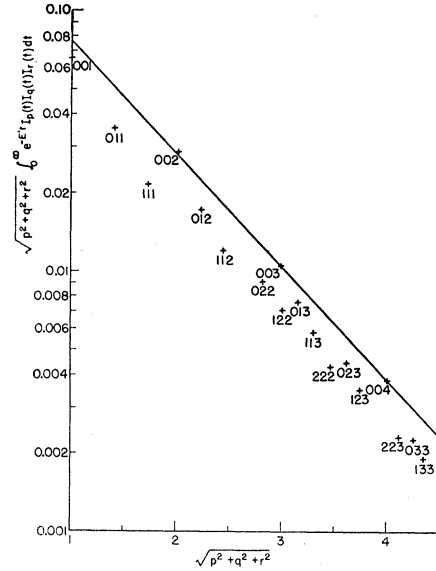


FIG. 3. The coefficients of the Wannier function times the distance from the origin as a function of the distance from the origin.

The "etc." in the last equation means that there are further nonvanishing matrix elements where both Wannier functions are located at the six nearest neighbors of the central atom and that the values of these matrix elements are the same as those which are indicated. We have assumed that our potential has full cubic symmetry and that there are only two distinct nonvanishing matrix elements of our perturbation; $V'(0)$ and $V'(1)$. From this we can conclude that the solutions of this perturbed periodic potential problem must form bases for the irreducible representations of the full cubic group.

In (I), we saw that the method of solving the set of simultaneous equations embodied in Eq. (34) of this paper was to cause the determinant of the coefficients of the U 's to vanish for those U 's which were associated with the lattice sites over which the perturbation extends. In the case of the perturbative potential of limited range which we set up in the last paragraph, this would mean that we would have to solve a set of simultaneous linear homogeneous equations of the seventh order. This is because $V(r)$ only has matrix elements for Wannier functions on the central lattice site and the six nearest neighbors. Symmetry further reduces the order of this set of equations since we know that the wave functions must form bases for irreducible representations of the full cubic group.

Let us first look for those solutions which have the symmetry of the p states with respect to the cubic group. This implies a certain relation between the U 's. Let us set up the state which has the symmetry of the z -like p state. (The p states are of course triply degenerate, the y -like and the z -like being degenerate with the x -like.) The relations that this implies between our

U 's are

$$\begin{aligned} U_{0,0,1} &= -U_{0,0,-1}, \\ U_{1,0,0} &= U_{-1,0,0} = U_{0,1,0} = U_{0,-1,0} = 0, \\ U_{0,0,0} &= 0. \end{aligned} \quad (37)$$

We can now insert these restrictions into Eq. (34). Since there is now only one independent coefficient, the Eqs. (34) reduce to one equation.

$$U_{0,0,1} - \left\{ \frac{V'(1)}{\pi^3} \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\alpha_3 \right. \\ \left. \times \frac{1 - \cos 2\alpha_3}{E' - \cos \alpha_1 - \cos \alpha_2 - \cos \alpha_3} \right\} U_{0,0,1} = 0. \quad (38)$$

This gives at once for the eigenvalue condition for the triply degenerate p states that

$$1 = \frac{V'(1)}{\pi^3} \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\alpha_3 \\ \times \frac{1 - \cos 2\alpha_3}{E' - \cos \alpha_1 - \cos \alpha_2 - \cos \alpha_3}. \quad (39)$$

We can of course carry out the same process which brought us from Eq. (18) to Eq. (20) and finally express the eigenvalue condition in the form,

$$V'(1) \int_0^\infty e^{-E't} \{ [I_0(t)]^3 - [I_0(t)]^2 I_2(t) \} dt = 1. \quad (40)$$

In (I) we also showed that the wave function for regions beyond the extent of the perturbation was expressible in terms of the coefficients of the Wannier functions within the region of the perturbation. In the case at hand, for the p states, this would mean that

$$U_{p,q,r} = V'(1) U_{0,0,1} \int_0^\infty e^{-E't} \{ I_{r-1}(t) - I_{r+1}(t) \} \\ \times I_q(t) I_p(t) dt. \quad (41)$$

Using the fact that $I_n(t) = I_{-n}(t)$, we can easily show that the solution to the difference equations (41) shows the symmetry of a p state with z -like symmetry. The states degenerate with this state can be obtained by permuting the indices p , q , and r .

We know that there are two d -like irreducible representations to the cubic group. We can look for bound states of these symmetries. The first are the d functions with symmetry properties like xy , xz , and yz . If we determine the relations between values of the coefficients of the Wannier functions for the seven lattice sites over which the perturbation extends for this type of symmetry, we find that all seven coefficients vanish. This means that there is no triply degenerate d -like bound state.

The other representation of the cubic group with d -like symmetry is doubly degenerate and has basis functions which transform as $x^2 - y^2$ and $3z^2 - r^2$. Let us consider the partner in this irreducible representation which has $x^2 - y^2$ -like symmetry. The relations between the seven coefficients of the Wannier functions which this symmetry induces are

$$\begin{aligned} U_{0,0,1} &= U_{0,0,-1} = U_{0,0,0} = 0, \\ U_{1,0,0} &= U_{-1,0,0} = U_{0,1,0} = -U_{0,-1,0}. \end{aligned} \quad (42)$$

If we use these relations in Eq. (34), we notice that we only have one independent coefficient of the seven under consideration. We can proceed as we did for the p -like states and obtain for the eigenvalue condition,

$$V'(1) \int_0^\infty e^{-E't} I_0(t) \{ [I_0(t)]^2 + I_2(t) I_0(t) \\ - 2[I_1(t)]^2 \} dt = 1. \quad (43)$$

We can also, once again, write the solutions of the difference equations in terms of the coefficients of the Wannier functions for those lattice sites over which the impurity extends. For the $x^2 - y^2$ states this gives us

$$\begin{aligned} U_{p,q,r} &= V'(1) U_{1,0,0} \int_0^\infty e^{-E't} \{ I_{p-1}(t) I_q(t) I_r(t) \\ &\quad + I_{p+1}(t) I_q(t) I_r(t) - I_p(t) I_{q+1}(t) I_r(t) \\ &\quad - I_p(t) I_{q-1}(t) I_r(t) \} dt. \end{aligned} \quad (44)$$

The other partner in this irreducible representation would of course have the same eigenvalue condition, but the solutions to the difference equations would be given by

$$\begin{aligned} U_{p,q,r} &= V'(1) U_{1,0,0} \int_0^\infty e^{-E't} \{ I_p(t) I_q(t) I_{r+1}(t) \\ &\quad + I_p(t) I_q(t) I_{r-1}(t) - \frac{1}{2} I_{p+1}(t) I_q(t) I_r(t) \\ &\quad - \frac{1}{2} I_{p-1}(t) I_q(t) I_r(t) - \frac{1}{2} I_p(t) I_{q+1}(t) I_r(t) \\ &\quad - \frac{1}{2} I_p(t) I_{q-1}(t) I_r(t) \} dt. \end{aligned} \quad (45)$$

This is the state with $3z^2 - r^2$ symmetry.

We have now found the eigenvalue conditions for five bound states: three p -like states and two d -like states. We might expect that the solution of our simultaneous linear equations for the seven lattice sites over which the impurity extends would give rise to a total of seven states. This is indeed the case. The two solutions which we are lacking have s -like symmetry. For these solutions we can again find the relations that symmetry introduces between the coefficients of the Wannier functions. In this case they are as follows:

$$U_{1,0,0} = U_{-1,0,0} = U_{0,1,0} = U_{0,-1,0} = U_{0,0,1} = U_{0,0,-1}. \quad (46)$$

The remaining coefficient $U_{0,0,0}$ need not vanish because of symmetry. We see that for the case of s -like symmetry we have two independent coefficients instead of only one as we had for the p - and d -like states. If we now put these relations in Eq. (34), we obtain a pair of simultaneous linear equations for the two independent U 's.

$$\begin{aligned} & \left\{ 1 - V'(0) \int_0^\infty e^{-E't} [I_0(t)]^2 dt \right\} U_{0,0,0} \\ & - \left\{ (\sqrt{6}) V'(1) \int_0^\infty e^{-E't} [I_0(t)]^2 I_1(t) dt \right\} U_{1,0,0} = 0, \\ & - \left\{ (\sqrt{6}) V'(0) \int_0^\infty e^{-E't} [I_0(t)]^2 I_1(t) dt \right\} U_{0,0,0} \\ & + \left\{ 1 - V'(1) \left[\int_0^\infty e^{-E't} I_0(t) [I_0(t) I_0(t) \right. \right. \right. \\ & \quad \left. \left. + I_2(t) I_0(t) + 4 I_1(t) I_1(t) \right] dt \right\} U_{1,0,0} = 0. \end{aligned} \quad (47)$$

In order to find the energies of the bound s -like states, we must make the determinant of the coefficients vanish. This would be done by the variation of E' giving rise to two s -like states of different energies. The solution of the difference equations for regions outside of the perturbation would take the form, in this case,

$$\begin{aligned} U_{p,q,r} = & V'(0) U_{0,0,0} \int_0^\infty e^{-E't} I_p(t) I_q(t) I_r(t) dt \\ & + 6 V'(1) U_{1,0,0} \int_0^\infty e^{-E't} \{ I_{p+1,q,r} \\ & + I_{p-1,q,r} + \text{Per.} \} dt. \end{aligned} \quad (48)$$

In Eq. (48) the symbol “+Per.” means that one is to add the terms with p, q , and r cyclically permuted. We can see from Eqs. (47) and (48) that if we let the perturbation extend over only one lattice site, as we did in the earlier section, we should obtain Eq. (20) for the solution of the difference equations and Eq. (21) for the eigenvalue condition. This means, of course, that we set $V'(1)$ equal to zero.

This is about as far as we can carry the discussion of the states arising from this perturbation without some further assumption. The additional assumption that we make is that there is a known ratio between $V'(0)$ and $V'(1)$. In order to calculate the energy levels of the bound states numerically, we assume that

$$V'(0) = 2V'(1). \quad (49)$$

This is, of course, completely arbitrary but it will enable us to study the energies of the bound states as a function of $V'(0)$.

Using the expressions in Eqs. (40), (43), and (47) for the eigenvalue conditions we have calculated the energies of the bound states as a function of $V'(0)$. The re-

sults are shown graphically in Fig. 4. In this figure, we plot the energies of the bound states *versus* the matrix element of perturbation on the central atom [$V'(0)$]. The straight lines on the graph are the asymptotes of the energies of the bound states. The lowest s -like state becomes asymptotic to the line $E' = V'(0)$ while the energies of the higher s - and the p - and d -like states become asymptotic to the line $E' = V'(1) = \frac{1}{2} V'(0)$. We can see at once from the graph that for small values of the perturbation there will be no bound state. For a certain critical value of the perturbation a bound, s -like state will appear. For some higher value of the perturbation a second s -like state will appear as a bound state. Increasing the perturbation finally causes the appearance of bound p - and d -like states. The order in which these higher states become bound is probably a function of the shape of potential we have assumed, and is not general. Even in the model we have assumed we notice that, whereas the higher s state comes out of the band before the p -like state for higher values of the perturbative potential, it crosses over the p -like state and finally lies above this p state in energy. It always remains, however, below the d -like state.

The fact that an s state is the first one to become bound upon increasing the perturbation is not surprising, since this is the only type of symmetry which allows us to have a nonvanishing coefficient of the Wannier function at the central atom. It is this central atom which has the largest perturbation associated with it and consequently it is very favorable energetically to have the wave function with a nonvanishing value at the central lattice site. Changing the ratio of $V'(0)$ and $V'(1)$ would not have any effect on the qualitative appearance of this graph. Since the eigenvalue conditions for the bound p - and d -like states depends only on the value of $V'(1)$ increasing $V'(0)/V'(1)$ would have the effect of requiring a larger value of $V'(0)$ to cause the appearance of bound states of these symmetries. This means that the three high states s' , p , and d would be shifted to the right on the graph if we increased the ratio in Eq. (49).

This completes the discussion of the bound states which appear under the assumption that our wave

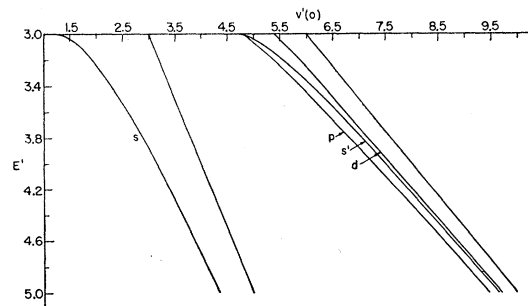


FIG. 4. Energy of the bound states of s , p , and d -like symmetry as a function of the perturbative potential.

function vanishes at infinity. In the next section, we discuss the case where we assume somewhat different boundary conditions. We shall assume that our wave function vanishes on the surface of a cube of finite size which surrounds the impurity.

VI. BOUNDARY CONDITIONS ON A FINITE CUBE

In the previous sections, we demanded that the solution for the bound state of our perturbed problem vanish at infinity. We might well ask how quickly the energies of the bound states would converge to the energy of the bound state of the infinite crystal, if we demand that our wave function vanish at the surface of a cube and then let the cube increase in size. In order to do this, we return to Eq. (5). These are the difference equations which are to be satisfied subject to the boundary condition that $U_{p,q,r}$ vanish when either p , q , or r are $\pm N$. This means we are solving the problem of an impurity which extends over only one lattice site within a box of dimensions $2N \times 2N \times 2N$. If we look back at Sec. II, we find that we have already accomplished this before we let our boundary conditions go to infinity. The eigenvalue condition for this case was given in Eq. (12). This equation can be rewritten in the form

$$V'(0) \sum_0^{N-1} (n) \sum_0^{N-1} (m) \frac{\tanh N\beta_{mn}}{\sinh \beta_{mn}} = N^2, \quad (50)$$

where the dependence of β_{mn} on its indices is given by Eq. (8); that is,

$$\cosh \beta_{mn} = E' - \cos \frac{(2m+1)\pi}{2N} - \cos \frac{(2n+1)\pi}{2N}. \quad (51)$$

In order to calculate the dependence of the energy on the perturbation for various values of N , all we need do is solve Eq. (51) for the various values of $\cosh \beta_{mn}$ corresponding to a given value of E' and then carry out the summation in Eq. (50) to find the value of the perturbation corresponding to this value of E' . This has been done for a number of values of N . In particular, the values of N used were 3, 6, and 10. The results are plotted in Fig. 5 where we have plotted the energy of

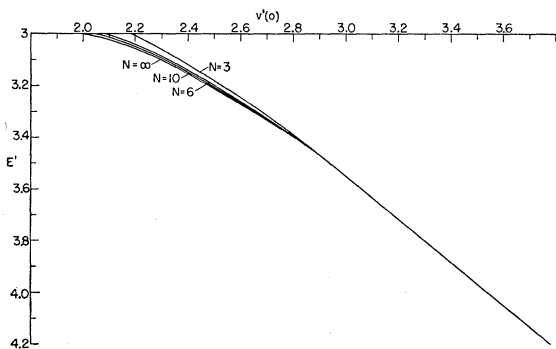


FIG. 5. Energy of the bound state as a function of perturbation for boundary conditions on a cube of half width N .

the lowest state (bound state) as a function of the perturbative potential as well as a function of N for the values indicated. This diagram is, of course, completely analogous to Fig. 1 and we have included on this graph the case of $N = \infty$. We notice that as we increase the size of the crystal the curves approach the curve for $N = \infty$ very rapidly. The curve for $N = 10$ is indistinguishable from the case of the infinite boundary conditions. We can also notice from these graphs that for larger values of the perturbation the difference between the curves for the various values of N becomes smaller and smaller.

These results are not difficult to interpret. We are dealing with a bound state. This means that the wave function falls off as a function of the distance from the origin. Thus, in the case of the infinite crystal, by the time the distance from the origin is about ten lattice sites, the coefficients of the Wannier function have fallen off to essentially zero. Taking as our boundary conditions the vanishing of the wave function at any point beyond this should give the same results as the infinite case, since the wave function is essentially zero anyway. We also know that, as we increase the value of the perturbative potential, the coefficients fall off more and more rapidly as a function of distance. For the case of an infinite perturbation, the wave function of the bound state would be completely localized at the central lattice site, regardless of the size of the cube which we used for the boundary conditions. This means that, as we increase the size of the perturbation, we should expect that the value of N would make less and less difference in determining the energy of the lowest state.

These results are actually of some interest since they illustrate the validity of an approximation method. The energies which we obtained from Eq. (50) are, of course, the same as we should have obtained by solving the secular equation in Eq. (5) where we cut off the secular equation after some finite size. In this case, we let the size be $(N-2)^3$. (Symmetry would reduce this order considerably.) This is, of course, quite different from solving the determinant of the Green's function method, since this is equivalent to solving the secular equation like Eq. (5) only of infinite size. This finite secular equation forms the basis of an approximation, therefore, and we can see that this approximation will be quite good, provided the coefficients of the Wannier functions for the atoms most distant from the perturbation have dropped off to a very small value. This method of approximation is used quite often in the discussion of F -centers in alkali halides. In particular, Inui and Uemura⁵ have calculated the energy levels of F -centers using just the approximation which we mentioned. They calculated these energy levels by solving the secular equation, cutting it off after some finite number of neighbors. In the case mentioned, they cut the secular equation off in one case after nearest neighbors and in

⁵ T. Inui and Y. Uemura, Progr. Theoret. Phys. (Japan) **5**, 252 (1950).

another case after second nearest neighbors. From their results it appears that they are getting reasonably good results by cutting off the wave function after second nearest neighbors judging by the improvement of the second nearest neighbor results over the nearest neighbor results. This would lead one to suspect that the effect of the perturbation is sufficiently strong to make the approximation they have used quite valid.

VII. EFFECT OF THE PERTURBATION OF THE WAVE FUNCTIONS IN THE BAND

In this section, we shall discuss the case where the energy of the perturbed state lies in the allowed band of energies. This is the case where $-3 \leq E' \leq 3$. In order to do this, we shall apply the method developed in (II). If we follow the method of that paper, we assume that our solution to the difference equations consists of two parts. The first is the incident Bloch wave and the second is the wave scattered by the impurity. For the problem at hand the solution of the difference equations is given by

$$U_{p,q,r} = \exp(i\mathbf{k} \cdot \mathbf{R}_{p,q,r}) + \sum (\phi', q', r') c_{p',q',r'} \times K_{E'}(\mathbf{R}_{p,q,r} - \mathbf{R}_{p',q',r'}). \quad (52)$$

This is Eq. (25) of (II). The c 's are unknown coefficients to be determined and represent the strength of the scattered wave. The quantity $K_{E'}(\mathbf{R}_{p,q,r} - \mathbf{R}_{p',q',r'})$ is the Green's function which is useful for the case of energies lying in the band. For our simplified impurity calculation, we can see from the Appendix and (II) that this Green's function will be given by

$$K_{E'}(\mathbf{R}_{p,q,r}) = (1/i) \sum (\mathbf{k}) \int_0^\infty \{ \exp[iEt - iE(\mathbf{k})t] \} \times \{ \exp(i\mathbf{k} \cdot \mathbf{R}_{p,q,r}) \} dt \quad (53)$$

$$= (N/i) \int_0^\infty dt J_p(t) J_q(t) J_r(t) \exp[iE't].$$

In deriving this form of the Green's function we have converted the summation over \mathbf{k} to an integration and have then made use of the explicit form of $E(\mathbf{k})$ given by Eq. (6) to carry out this integration in order to arrive at the Bessel functions in the right-hand side of (53).

In order to solve the scattering problem, we must find the c 's. In (II) they were shown to satisfy a set of simultaneous linear inhomogeneous equations [Eq. (19) of (II)]. In this section, we shall specialize to the case of the impurity extending over only one lattice site. If this is done, the only quantity which appears of all the c 's is $c_{0,0,0} = c(0)$ and this is given by the condition,

$$\left\{ -N + V'(0)(N/i) \int_0^\infty dt [J_0(t)]^3 \exp(iE't) \right\} c(0) = -V'(0). \quad (54)$$

TABLE III. $I_c = \int_0^\infty dt [J_0(t)]^3 \cos E't$; $I_s = \int_0^\infty dt [J_0(t)]^3 \sin E't$ as a function of E' .

E'	I_c	I_s
0.0	0.8963	0.0000
0.2	0.8970	0.0740
0.4	0.8967	0.1530
0.6	0.8999	0.2416
0.8	0.9071	0.3557
1.0	0.8691	0.6027
1.2	0.6171	0.6268
1.4	0.5063	0.6057
1.5	0.4631	0.5988
1.6	0.4259	0.5909
1.8	0.3602	0.5762
2.0	0.3038	0.5621
2.2	0.2537	0.5496
2.4	0.2055	0.5378
2.5	0.1826	0.5321
2.6	0.1585	0.5260
2.8	0.1062	0.5167
3.0	0.0134	0.4926

In terms of $c(0)$, the solution to the difference equations is given by

$$U_{p,q,r} = \exp(i\mathbf{k} \cdot \mathbf{R}_{p,q,r}) + c(0)(N/i) \int_0^\infty dt J_p(t) J_q(t) J_r(t) \exp[iE't]. \quad (55)$$

We can see from this that the quantity $c(0)$ is the amplitude of the scattered wave. The square of its absolute value, which is the intensity of the scattered wave, is then given by

$$|c(0)|^2 = \{ [1/V'(0) - I_s]^2 + I_c^2 \}^{-1}. \quad (56)$$

Equation (56) was obtained from Eq. (55) and I_c and I_s are given by

$$\frac{i}{N} K_{E'}(0) = \int_0^\infty dt [J_0(t)]^3 \exp(iE't)$$

$$= \int_0^\infty dt [J_0(t)]^3 [\cos E't + i \sin E't] = I_c + i I_s. \quad (57)$$

The quantities I_c and I_s were approximately evaluated by the Whirlwind computer at M.I.T.⁶ Simpson's rule and an interval of 0.2 in t was used. The integral was carried out to $t=48$ at which point the convergence was fairly good. The results are given in Table III. From the table, we can see at once that there is some error in the calculation of these integrals as a function of E' . In (II) we showed that for energies outside the band the imaginary part of the Green's function must vanish. This means that for $E'=3$, I_c should be zero instead of 0.013. In addition in the Appendix we have shown

⁶ Availability of Digital Computer Laboratory time for this problem was made possible by the U. S. Office of Naval Research.

that for $E' \geq 3$ we should have the equality

$$\int_0^\infty dt e^{-E't} [I_0(t)]^3 = \frac{1}{i} \int_0^\infty dt e^{iE't} [J_0(t)]^3 = \int_0^\infty dt [J_0(t)]^3 \sin Et. \quad (58)$$

Comparison of Tables II and III shows that for $E'=3$ the integral involving the Bessel function of imaginary argument gives the value 0.4990 whereas the integral involving the Bessel function of real argument gives the value 0.4926. We see therefore that the numerical evaluation of the integrals in this section is probably accurate to within about 2 percent, but this is sufficient for our purposes. In Fig. 6 we have plotted the values of $|c(0)|^2$ as a function of the perturbative potential for a number of values of the energy using Eq. (56).

Let us see what we can learn about the nature of scattering in a solid from this simple example. We notice that the intensity of the scattered wave is independent of the \mathbf{k} vector of the incident wave. The scattered intensity depends only on the energy of the incident wave. This result arises from the fact that our impurity extends over only one lattice site and is not peculiar to the particular form of the energy band which we have assumed in this paper. In any problem of scattering in a solid in which the impurity is localized to one lattice site, the scattered intensity will be independent of the \mathbf{k} vector of the incident wave. Another feature of the intensity of the scattered wave can be seen from Fig. 6. We notice that for $E'=3$ (when the energy is at the top or bottom of the band) there is a singularity of the scattered intensity for a certain value of the perturbative potential. For $E'=3$ we notice that this singularity arises when $I_s = 1/V'(0)$. This however is nothing more than the condition that a bound state appear. Thus we see that for that strength of perturbation for which a bound state can first appear at the bottom of the band the scattered intensity for energies at the bottom of the band becomes infinite.

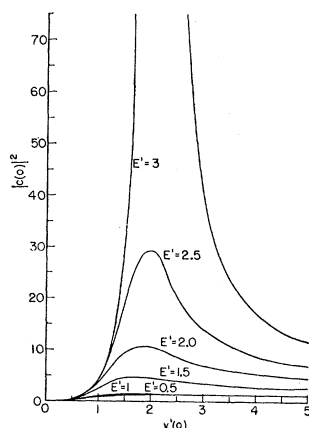


FIG. 6. Intensity of the scattered waves as a function of the perturbative potential for various values of the energy of the incident wave.

This same effect is familiar in scattering in free space. If we scatter a plane wave from a square well potential in three dimensions a similar thing happens. The scattering cross section for zero energy becomes infinite for that value of the well depth for which a bound state is first allowed.⁷ We can see how this will arise even for the general case of scattering in solids.

In (II), we saw that the c 's were given by the solution of the set of simultaneous equations [Eq. (19) of that paper]. The condition for the solution of this set of simultaneous inhomogeneous equations is that the determinant of the coefficients of the c 's must not vanish. It has already been pointed out in that paper that for energies lying outside the bands the vanishing of this determinant is just the eigenvalue condition for the appearance of bound states. If we choose an energy at the bottom or top of a band and then vary the perturbative potential, there will be a value of this potential for which the bound state can first appear, and this value of the perturbative potential will cause the determinant of the coefficients of the c 's to vanish. This will mean that the c 's will become infinite as the perturbative potential approaches this value. This can most easily be seen from the well known method of expressing the solution of a set of simultaneous linear inhomogeneous equations as the ratio of two determinants. The denominator is the determinant of the coefficients of the unknowns, and the numerator is the determinant of the coefficients of the unknowns where one column has been replaced by the inhomogeneous terms. As the coefficients of the unknowns approach values which make their determinant vanish, in general the unknowns will develop singularities.

We have seen in this section that the method of treating scattering in a solid can be applied to the simplified impurity calculation presented in this paper. This example shows us that the scattering is strongest for those energies in the band which lie near the energies of the bound states which appear as a result of the perturbation. There appears to be reason to believe that this result can be generalized to more realistic impurity calculations.

VIII. DISCUSSION

From the preceding discussion, we get a fairly complete understanding of the problem of a single perturbing atom in a simple cubic lattice, and a general idea of the effect of a perturbation extending over a number of lattice sites. The results of the single perturbed atom when compared with the differential equation approach turned out to be at least qualitatively close to this approximate approach. We may assume that the same thing will hold without qualitative change in other types of lattices. We may expect, therefore, that if a perturbation extends over a number of lattice sites for

⁷ N. F. Mott and H. S. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), pp. 28-38.

sufficiently large perturbations, a number of bound states will appear. As a general rule, the discussion which we have given makes it fairly plain that as the perturbative potential increases, these discrete levels may split off from the continuum successively, rather than all at once. The various wave functions will have different types of symmetry. These functions must belong to the various irreducible representations of the point symmetry group of the crystal with respect to the center of perturbation, provided the perturbation also has the symmetry of the point group of the crystal. Thus, as we have seen, if the perturbative potential and the crystal both have cubic symmetry, we shall have the various possible symmetry types of the cubic group, one being *s*-like, a threefold degenerate *p*-like type and so on. We might try to apply what we learned in our simple case to give a qualitative discussion of more physical cases. In doing so we shall repeat many things already known and discussed by other authors, but it may be useful to review their discussions in the light of what we have learned about difference equations.

The particularly interesting problem in three dimensions is the Coulomb potential. The reason for this comes from its occurrence in semiconductors. We are not going to examine the nature of the perturbing field to be expected in the various types of problems; this is a problem in self-consistent fields, rather than of solving the periodic potential problem, and we wish to separate these two parts of the question, first understanding the nature of the solutions of the one-electron Schrödinger equation before we build up determinantal many-electron wave functions and apply a condition of self-consistency. However, we may anticipate enough to state the general situation encountered when an impurity atom is introduced substitutionally into a crystal. The result is quite different, depending on whether we are dealing with a good conductor like a metal, or a poor conductor like a semiconductor. Let us assume that the impurity atom has a nuclear charge greater or less than that of the crystal by a few units. If there were no shielding, this would introduce a perturbation of the Coulomb type, which outside the impurity atom itself would be proportional to the difference between the nuclear charges of the impurity atom and the atoms of the crystal. In an actual case, most of this field will be shielded by a rearrangement of the electronic charge. There will usually be enough discrete levels with wave functions concentrated close to the impurity atom so that these levels can be occupied by electrons, or emptied, as the case may be, to make the impurity atom approximately uncharged. In a good conductor, the conduction electrons will rearrange their charge distributions so as to shield this Coulomb potential almost completely, just as any electric field in a metal is almost completely neutralized by the conduction electrons. Ordinarily in a metal, then, the perturbative potential arising from the self-consistent problem is confined almost entirely to the perturbing

atom. In other words, we have almost precisely the case which we have been taking up in this paper, leading to discrete levels if the perturbative term $V(0)$ is great enough, but to no new energy levels if it is below a critical value.

An impurity atom in a metal, as we have just stated, has its field almost completely neutralized even at the position of its nearest neighbors by the conductivity, just as we should conclude from looking at the electrical properties of a metal from the macroscopic point of view. In a semiconductor, on the contrary, the conductivity is not great enough for this to happen, and the problem is much more like the electrostatic one of a charge in a dielectric. The dielectric constants of some of the important semiconductors are very high, that of germanium being of the order of magnitude of 16. The electric field of a point charge in such a dielectric will be less than in empty space, being inversely proportional to the dielectric constant. This dielectric constant is itself a manifestation of the self-consistent field. If we look at it microscopically, we see that the charge polarizes all the surrounding atoms, displacing their electrons with respect to their nuclei so as to produce dipoles on them; and it is well known that it is the superposition of the fields of these dipoles which cancels most of the field of the polarizing charge. We should get at this effect, in a completely logical treatment of our problem, by solving for the wave functions of the polarized atoms in the external polarizing field, which would be part of the self-consistent field, and by making the problem self-consistent, which would imply that each atom had just such a dipole moment that the sums of these dipole fields produce the dielectric effect by simple electrostatics. Ordinarily, however, we are willing not to look into the problem in such a fundamental way, but to accept the value of the macroscopic dielectric constant as being given, and to assume that it correctly describes the self-consistent effect of the polarizing charge in the dielectric.

We conclude, then, that if a dielectric contains an impurity atom which normally has an excess or deficiency of charge, the potential produced by this atom at a distance will be that produced by its net charge, computed for the actual dielectric constant. That is, we shall have a Coulomb potential, but one ordinarily a good deal less in magnitude than in free space, on account of the large dielectric constant. We might thus assume that it is a fairly good approximation to replace our difference equations by the approximate differential equation. We shall then have Schrödinger's equation for a hydrogen-like problem, but with a potential decreased in proportion to the dielectric constant, and an effective mass instead of the real mass. The solutions will then be the ordinary hydrogenic solutions, but the wave functions will be much more spread out, and the energies will be less. In this case we have an infinite number of stationary states, instead of a finite number as with the perturbation located only on a finite number of lattice

sites. Furthermore, we do not have any critical lower limit for the magnitude of the perturbation potential, below which we do not find discrete states; that is a characteristic of the problem where the perturbations are confined to a finite number of atoms.

We also find something in the Coulomb case which we do not in the case of a single perturbing atom: The differential equation forms a good approximation to the solution of the difference equations. The reason is that in this case the solution really varies slowly from atom to atom, and we have seen in (I) that this is the condition for the applicability of the differential equation method. Thus, for the ground state of hydrogen, the wave function is $\exp(-\gamma r)$, which remains finite at $r=0$, and varies slowly from atom to atom, if γR is small compared to unity, where R is the interatomic distance. We have this situation in the cases we are interested in. This is in striking contrast to the case of a single perturbing atom, where we have seen that the wave function is of the form $[\exp(-\gamma r)]/r$. We can thus feel that the conventional derivation of the impurity levels in a semiconductor, on the basis of the hydrogenic wave function, is generally legitimate.

There is, however, a feature of the situation which has generally been overlooked, and which can be very important. The dielectric effect shields the field of the perturbing atom at the positions of all of the neighbors, but does not affect the perturbative potential on the perturbing atom itself. In other words, the perturbation $V(0)$, the average of the perturbative potential over the Wannier function located on the impurity atom, can be just as great in a semiconductor as in a metal. This is larger than the value which would be consistent with the hydrogenic problem, roughly in the ratio of the dielectric constant. In other words, the Schrödinger problem which is really appropriate in this case is one with a Coulomb potential at all neighboring atoms, with a dielectric term to make it small, but in addition a potential well at the central atom. We may now legitimately combine the types of arguments which we have used in discussing the potential well problem, and the Coulomb problem. We may assume that unless the potential well becomes too deep, exceeding a critical value, the wave function and energy level will not be appreciably affected by it. In other words, it is likely that the hydrogenic wave function and energy level corresponding to the Coulomb potential can, so to speak, resist the effect of a perturbation on the central atom, provided this perturbation is not too large. The wave function will be modified in the immediate neighborhood of the central atom, but it extends over so many atoms that this modification is not very important, and will not change the energy very much. If the perturbation of the central atom becomes too great, however, the problem will change completely. The energy level will fall far below the hydrogenic value (we are assuming that the perturbing potential is negative, as it would be if the perturbing ion were posi-

tively charged, or as in the case of a donor atom below the bottom of the conduction band). At the same time, the wave function will become much more concentrated around the perturbing atom, as in the discrete level, in the problem of the single perturbing atom.

This situation can very likely occur in practice. We understand, in the first place, on the basis of this argument, why in so many cases we seem to get good agreement, quantitative as well as qualitative, between the simple hydrogenic theory and the observed impurity levels in semiconductors. These are the cases in which the perturbative energy on the perturbing atom is less than the critical value. Different perturbative atoms, under these circumstances, would have almost, though not quite, the same wave function and energy levels, the discrepancies coming only in the immediate neighborhood of the perturbing atom. On the other hand, we should also expect cases of greater perturbations, in which the whole character of the wave functions and energy level changes, and the energy level is much further below the conduction bands (or much further above the valence bands, if we are dealing with acceptor impurities). This may well be the explanation of the deep traps, which seem to occur particularly in silicon. Such trapping levels seem to explain the long time constants observed in some experiments with silicon,⁸ and similar levels have been postulated in silicon after neutron bombardment;⁹ these, of course, may well come from interstitial rather than substitutional impurity atoms, and this is a problem slightly different from those we have discussed, but the principle is not different.

Finally, we should mention that if the dielectric constant of a semiconductor is not very great, the Coulomb type of problem will lead to a wave function which is no longer extended over many atoms, but is more concentrated. In such a case it will no longer be justified to replace the difference equations by the differential equation, and we must anticipate quantitative errors in the use of the hydrogenic solution. We hardly expect, however, any very striking qualitative change in the situation.

The authors wish to express their gratitude to the Project Lincoln and the Research Laboratory of Electronics computing groups for their help with the numerical calculations involved in this paper.

APPENDIX

We recall that in (I) the quantity which formed the Green's function for the difference equations and played a central role in the solution of the perturbed periodic lattice was the quantity,

$$\int (d\mathbf{k}) \frac{e^{i\mathbf{k} \cdot \mathbf{R}_p}}{E - E(\mathbf{k})}. \quad (\text{A1})$$

⁸ J. R. Haynes and J. A. Hornbeck, *Phys. Rev.* **90**, 152 (1953).

⁹ W. E. Johnson and K. Lark-Horovitz, *Phys. Rev.* **76**, 442 (1949).

\mathbf{R}_p was a lattice vector of the crystal and $E(\mathbf{k})$ was the energy in one of the energy bands as a function of position in reciprocal space. The integration was to be carried out over the first Brillouin zone. (The crystal is assumed to be infinite.) Let us consider the case where the energy E , the energy of the state we are considering, does not lie in the band. We shall assume that it lies above the band. (The case where it lies below the band can easily be worked out by similar methods.) In this case $E > E(\mathbf{k})$, for all values of \mathbf{k} . Since this is the case we can replace Eq. (A1) by

$$\int_0^\infty dt \int (d\mathbf{k}) e^{-[E-E(\mathbf{k})]t} e^{i\mathbf{k} \cdot \mathbf{R}_p}. \quad (\text{A2})$$

The integration over t can be carried out at once to give the previous form of the Green's function.

We notice, at once, that this expression in Eq. (A2) has a striking resemblance to the Green's function which we proposed in (II) for the solution of the perturbed periodic potential problem,

$$\frac{1}{i} \int_0^\infty dt \int (d\mathbf{k}) e^{+i[E-E(\mathbf{k})]t} e^{i\mathbf{k} \cdot \mathbf{R}_p}. \quad (\text{A3})$$

In (II), we mentioned that the Green's function when taken in this form could be used for the case where E lies outside of the band even though it was originally proposed for the case where E lies in the band. We can show that the form of the Green's function in Eq. (A3) is actually the same as the form in Eq. (A2) and therefore also Eq. (A1). Let us imagine that we replace the variable t , in Eq. (A2), by the complex variable $z = x + iy$. We may now do a contour integral along a contour which extends along the real axis from plus infinity to the origin, from thence up the imaginary axis to plus infinity, and finally we close the contour along a quarter of a circle at infinity which connects the real to the imaginary axis. Since $E > E(\mathbf{k})$ for all \mathbf{k} , the real part of the exponent in Eq. (A2) will be negative for all values of $x \neq 0$ on the contour we have chosen, since the contour is contained in the first quadrant. This means that the quantity,

$$\int (d\mathbf{k}) e^{-[E-E(\mathbf{k})]z} e^{i\mathbf{k} \cdot \mathbf{R}_p}, \quad (\text{A4})$$

will vanish at almost all points along the quarter of a circle at infinity since it has an infinite real negative part to the exponent. There is one point where it might not vanish. This is the point, which approaches infinity, which lies at the intersection of the quarter circle and the imaginary axis. There is no real part to the exponent at this point. We are saved by the fact that at this point

the oscillating nature of the exponential function for large values of complex exponent will cause the integration over \mathbf{k} to give a vanishing result in Eq. (A4). Thus we see that the contribution to the contour integral from the quarter circle will vanish. We are therefore left with the statement that

$$\int_0^\infty dt \int (d\mathbf{k}) e^{-[E-E(\mathbf{k})]x} e^{i\mathbf{k} \cdot \mathbf{R}_p} + i \int_0^\infty dy \int (d\mathbf{k}) e^{-i[E-E(\mathbf{k})]y} e^{i\mathbf{k} \cdot \mathbf{R}_p} \quad (\text{A5})$$

must be equal to $2\pi i$ times the sum of the residues within the contour. However, the quantity in Eq. (A4) has no poles within this contour. We integrate a finite quantity over the first Brillouin zone; therefore Eq. (A4) must be finite. This gives us the result that Eq. (A5) vanishes. From this fact, we conclude that Eq. (A2) is the same as Eq. (A3) by taking the complex conjugate of Eq. (A5) and replacing the variables of integration x and y by t .

We are now in a position to apply these results to the problem at hand. In the case of the simple cubic lattice with nearest neighbor interactions the integrations over reciprocal space can be carried out explicitly. In Sec. III of this paper the solution to the difference equations was given by Eq. (18). Applying the transition from Eq. (A1) to Eq. (A2) to this case we obtain the result,

$$U_{p,q,r} = \frac{V'(0)}{\pi^3} U(0) \int_0^\infty dt \int_0^\pi d\alpha_1 \int_0^\pi d\alpha_2 \int_0^\pi d\alpha_3 \\ \times \cos p\alpha_1 \cos q\alpha_2 \cos r\alpha_3 \\ \times e^{-[E' - \cos\alpha_1 - \cos\alpha_2 - \cos\alpha_3]t}. \quad (\text{A6})$$

Using the definitions of the Bessel functions of imaginary argument¹⁰ reduces this to

$$U_{p,q,r} = V'(0) U(0) \int_0^\infty e^{-E't} I_p(t) I_q(t) I_r(t) dt. \quad (\text{A7})$$

Equation (A5), when applied to this case, would give the result:

$$\frac{1}{i} \int_0^\infty dt e^{-iE't} J_p(t) J_q(t) J_r(t). \quad (\text{A8})$$

Here we have used the definition of the ordinary Bessel function to obtain the result. This form of the Greens' function is valid within as well as outside of the band. The form (A7) would, of course, be valid only outside of the band ($E' > 3$).

¹⁰ H. Jeffreys and B. E. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, Cambridge, 1950), p. 579.