represents, can therefore be rotated by these fields, in particular to a direction perpendicular to the scattering plane considered, so that the magnetic diffraction vanishes. Short-range ordering, being transient and dependent on shorter-range exchange interactions between nearby atoms, is substantially independent of applied fields. Thus just above T_c, the instantaneous pattern of spins is one of small regions in which spins are partly aligned, but not subject to re-orientation by a magnetic field. The diffuse diffraction peak is then independent of applied fields.

These conclusions are largely qualitative and likely to be general for various magnetic materials. More quantitative results on the interatomic magnetic coupling may be expected from more detailed studies of the shape, intensity, and temperature dependence of the diffuse magnetic peak for particular cases.

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Wave Functions for Impurity Levels*†

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The calculation of impurity levels in crystals is set up in terms of a linear combination of Wannier functions. The coefficients of this linear combination are shown to satisfy a set of difference equations. These difference equations are solved for two simple linear chain impurity problems. The difficulties encountered in solving the difference equations are explored on the basis of these examples and a general method of solving difference equations arising from impurity calculations is presented. This method seems to have advantages over previous methods of solving the impurity problem in crystals.

I. INTRODUCTION

THE customary approach to treating the effect of a perturbation on a perfect periodic lattice consists of expanding the perturbed wave function in terms of the wave functions of the unperturbed crystal. In almost all cases a one-electron approximation is used and instead of expanding the wave function in terms of the Bloch functions of the crystal, the complete set of Wannier functions[1] is used. These functions have the desirable property of being localized. This makes them most convenient for discussing a localized perturbation and the localized states arising from this perturbation. If the matrix of the total perturbed Hamiltonian is set up using the Wannier functions as a basis, it will be shown that coefficients of the Wannier functions in the expansion of the perturbed wave function satisfy a set of difference equations. One common way of treating these difference equations is to convert them to an approximate differential equation.[1,2] In this paper, we shall attempt to deal with the difference equations directly and shall present a general procedure for solving them in the hope of avoiding the assumptions and approximations involved in using the differential equation approximation. We shall first set up the difference equations involved in the impurity calculation and discuss some simplified cases. These simple examples illustrate with little calculation points which are typical of more realistic impurity calculations. The methods used to solve these simple problems will be seen to be inadequate to solve more complex problems. We shall then give a method for solving the difference equations which overcomes some of the difficulties illustrated by our simple impurity calculations.

II. A DIFFERENCE EQUATION FOR THE PERTURBED CRYSTAL

We describe our unperturbed crystal in terms of a one-electron Hamiltonian H_0. The eigenfunctions of this unperturbed Hamiltonian are $u_{n,\mathbf{k}}(\mathbf{r})$. n denotes the band to which this Bloch function belongs and $\mathbf{k}$ is the propagation vector such that when the wave function is translated through $\mathbf{R}_n$ (one of the primitive translations of the crystal) the Bloch function is multiplied by $\exp(i\mathbf{k}\cdot\mathbf{R}_n)$. The energy of these Bloch functions is denoted by $E_n(\mathbf{k})$. From these Bloch functions one can define the Wannier functions for a given band:

$$a_n(\mathbf{r}-\mathbf{R}_n)=N^{-\frac{1}{2}}\sum(\mathbf{k})u_{n,\mathbf{k}}(\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{R}_n). \quad (1)$$

(N is the number of primitive translations in the

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† G. F. Koster and J. C. Slater, Letter to the Editor under same title in Phys. Rev. **94**, 1392 (1954). M. Lax, this issue [Phys. Rev. **94**, 1391 (1954)].

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[1] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

[2] J. C. Slater, Phys. Rev. **76**, 1592 (1949), and various other papers. See however, for instance, P. Feuer, Phys. Rev. **88**, 92 (1952), in which the difference equations are treated directly.

macrocrystal over which periodic boundary conditions are defined.) It has been shown that the Wannier functions associated with a given band satisfy a set of simultaneous differential equations,[3]

$$H_0 a_n(\mathbf{r}-\mathbf{R}_j)=\sum(\mathbf{R}_i)\mathcal{E}_n(\mathbf{R}_i-\mathbf{R}_j)a_n(\mathbf{r}-\mathbf{R}_i), \quad (2)$$

where the $\mathcal{E}_n(\mathbf{R}_l)$ are the coefficients of the energy of the Bloch waves in its Fourier decomposition, and

$$E_n(\mathbf{k})=\sum(\mathbf{R}_l)\mathcal{E}_n(\mathbf{R}_l)\exp(-i\mathbf{k}\cdot\mathbf{R}_l). \quad (3)$$

These Fourier components of energy are also given by

$$\mathcal{E}_n(\mathbf{R}_l)=\int a_n^*(\mathbf{r})H_0 a_n(\mathbf{r}-\mathbf{R}_l)dv. \quad (4)$$

This can most easily be seen by multiplying Eq. (2) by $a_n^*(\mathbf{r})$ and integrating over all space using the orthogonality properties of the Wannier functions,

$$\int a_n^*(\mathbf{r}-\mathbf{R}_j)a_m(\mathbf{r}-\mathbf{R}_l)dv=\delta_{nm}\delta_{jl}. \quad (5)$$

We now have defined sufficient notation to describe our impurity problem in terms of Wannier functions. We wish to find the eigenfunctions associated with the Hamiltonian H_0+H_1. H_1 is the perturbation to our unperturbed Hamiltonian H_0. The perturbed wave function is described in terms of the complete set of Wannier functions

$$\psi(\mathbf{r})=\sum(n)\sum(\mathbf{R}_j)U_n(\mathbf{R}_j)a_n(\mathbf{r}-\mathbf{R}_j). \quad (6)$$

The unknown coefficients $U_n(\mathbf{R}_j)$ and the energy of the perturbed state are determined by the condition that

$$(H_0+H_1)\psi=E\psi. \quad (7)$$

Multiplying both sides of this equation by $a_m^*(\mathbf{r}-\mathbf{R}_i)$ and using the properties of the Wannier function given above, we are led to the simultaneous equations:

$$\sum(m,\mathbf{R}_j)[\mathcal{E}_n(\mathbf{R}_i-\mathbf{R}_j)\delta_{nm}+V_{nm}(\mathbf{R}_i,\mathbf{R}_j)]U_m(\mathbf{R}_j)=EU_n(\mathbf{R}_i). \quad (8)$$

Here

$$V_{nm}(\mathbf{R}_i,\mathbf{R}_j)=\int a_n^*(\mathbf{r}-\mathbf{R}_i)H_1 a_m(\mathbf{r}-\mathbf{R}_j)dv. \quad (9)$$

The solution of these difference equations gives us the solution to our perturbed periodic potential problem. We notice that if we let our perturbation go to zero we are left with the equation

$$\sum(\mathbf{R}_j)[\mathcal{E}_n(\mathbf{R}_i-\mathbf{R}_j)]U_n(\mathbf{R}_j)=EU_n(\mathbf{R}_i),$$

which can be solved by letting $U_n(\mathbf{R}_j)=\exp(i\mathbf{k}\cdot\mathbf{R}_j)$. This gives as the energy

$$E_n(\mathbf{k})=\sum(\mathbf{R}_s)\exp(-i\mathbf{k}\cdot\mathbf{R}_s)\mathcal{E}_n(\mathbf{R}_s), \quad (10)$$

which is correct.

The differential equation approach to this set of difference equations arises from considering the coefficients $U_n(\mathbf{R}_i)$ as a continuous function of some variable $\mathbf{r}$. It is then noted that if $\mathbf{k}$ is replaced by $\mathbf{p}/\hbar$ where $\mathbf{p}$ is a pseudo-momentum, and if $\mathbf{p}$ is then replaced by $-i\hbar\nabla$ (where ∇ acts on $\mathbf{r}$) in the usual quantum-mechanical manner, that

$$E_n(\mathbf{p}/\hbar)f(\mathbf{r})=\sum(\mathbf{R}_m)\mathcal{E}_n(\mathbf{R}_m)f(\mathbf{r}-\mathbf{R}_m),$$

where f is any function. If we in addition restrict ourselves to one band and make the additional assumption that $V(\mathbf{R}_i,\mathbf{R}_j)=\delta_{ij}V(\mathbf{r})$ where $\mathbf{R}_i$ is replaced by the continuous variable $\mathbf{r}$, we can rewrite Eq. (8) to be

$$E(-i\nabla)U(\mathbf{r})+V(\mathbf{r})U(\mathbf{r})=EU(\mathbf{r}), \quad (11)$$

which is like an ordinary Schrödinger equation. We notice that if $V(\mathbf{r})$ vanishes, $U(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})$ is a solution to this equation giving the energy (10). In the event that $V(\mathbf{r})$ does not vanish, $E(\mathbf{k})$ is usually expanded about its minimum up to terms of the second order in k which converts Eq. (11) into a second-order differential equation. If we call $\mathbf{k}_0$ the point where the minimum of $E(\mathbf{k})$ lies, it is convenient to rewrite $U(\mathbf{r})$ as $W(\mathbf{r})\exp(i\mathbf{k}_0\cdot\mathbf{r})$. The exponential function takes out the rapidly varying part of $U(\mathbf{r})$ leaving $W(\mathbf{r})$ to be smoothly varying. If this is done and a rotation of the axes in ordinary space is performed to remove the cross second derivatives in the expansion of $E(\mathbf{k})$, Eq. (11) can be written, up to terms of the second order, as

$$-\frac{\hbar^2}{8\pi^2}\left(\frac{1}{m_x}\frac{\partial^2W}{\partial x^2}+\frac{1}{m_y}\frac{\partial^2W}{\partial y^2}+\frac{1}{m_z}\frac{\partial^2W}{\partial z^2}\right)+[E_0+V(\mathbf{r})]W=EW, \quad (12)$$

where

$$m_x=\hbar^2\bigg/\frac{\partial^2E}{\partial k_x{}^2}, \text{ etc.,}\quad E_0=E(\mathbf{k}_0).$$

This is the form which the impurity problem takes in most treatments of impurities in semiconductors. Additional assumptions are also made in this case, namely: that $m_x=m_y=m_z$ and that $V(\mathbf{r})$ is a Coulomb potentiar in a dielectric medium. In the case of germanium, for instance, with a dielectric constant in the neighborhood of 16 and effective masses of the order of half the electron mass, this leads to wave functions extended over a good many angstroms, with energies which are a very small fraction of a volt.

These widely extended wave functions, which can be formed by solution of (12), allow us to examine the justification of the assumption that third and higher derivatives can be neglected in the expansion of $E(\mathbf{k})$ in Eq. (11). The energy, as we know, can be expanded in a Fourier series and ordinarily the first few terms of this series are the important ones. Thus we see that the successive derivatives of $E(\mathbf{k})$ with respect to k will be in the ratio of the powers of $\mathbf{R}_j$, the lattice spacing. If the function W is falling off like an exponential $\exp(-ar)$, as

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[3] G. F. Koster, Phys. Rev. 89, 67 (1953).

we should have for a hydrogen-like case, the successive derivatives will be in the ratio of powers of a, inversely proportional to the linear dimensions of the wave function. In other words, we may expect the terms in (11) in successively higher derivatives of W to fall off in the ratio of the lattice spacing to the linear dimensions of the wave function. If the wave function extends over many lattice spacings, as in the case of germanium, we may expect successive terms to get rapidly smaller, so that the reduction of the equation to the Schrödinger form is legitimate. On the other hand, if it does not extend out very far, as is the more usual case in a material of smaller dielectric constant, it is not legitimate to neglect higher derivatives. In such a case, we can try to retain additional terms in (11), but it is much better and more straightforward to return to the difference equation and try to solve this directly. The writers suspect that the number of actual cases where the approach by means of the differential equation is justified is very limited, and that in most cases we are on much firmer ground to use the difference equation. The differential equation may, however, be useful in pointing out the general form of the solution to be expected.

In order to familiarize ourselves with the methods of treating the difference equations directly, we shall in the next section solve the difference equations in a one-dimensional case. Even though these one-dimensional crystals are not met with in nature, the mathematics involved gives us insight into the more complex three-dimensional cases.

III. A ONE-DIMENSIONAL IMPURITY CALCULATION

In this section, we treat the effects of a perturbation on a one-dimensional crystal of equally spaced atoms. We further restrict ourselves to a single band describable in terms of a Wannier function which has reflection symmetry with respect to a plane passing through the atom about which the Wannier function is located. In this case, the difference equation (8) can be written in the form

$$\sum(q)[\mathcal{E}(p-q)+V(p,q)]U(q)=EU(q). \qquad (13)$$

The index p denotes the pth atom in the chain. The simplest case of an impurity in a linear chain is the case where the Wannier functions only have nearest-neighbor interactions and the impurity only extends over one lattice site. The first of these restrictions means that $\mathcal{E}(p)=0$ for $p>1$. The second of these assumptions means that $V(p,q)$ is zero unless both p and q are equal to zero. In this case, our difference equations (13) can be rewritten

$$\begin{aligned}&\mathcal{E}(0)U(p)+\mathcal{E}(1)[U(p+1)+U(p-1)]\\&\qquad\qquad=EU(p);\quad p\geqslant 1,\\&\mathcal{E}(0)U(0)+\mathcal{E}(1)[U(1)+U(-1)]\\&\qquad\qquad=[E-V(0)]U(0);\quad p=0.\end{aligned} \qquad (14)$$

The usual way to solve the general equations in (14) (the first set) is to make the assumption that $U(q)=b^{\pm q}$. If we substitute this into the first of Eqs. (14) we see that this is indeed a solution provided that

$$\mathcal{E}(0)+\mathcal{E}(1)[b+1/b]=E. \qquad (15)$$

If we let $b=\exp(ikR)$, where R is the lattice spacing the condition (15) becomes

$$\mathcal{E}(0)+2\mathcal{E}(1)\cos kR=E. \qquad (16)$$

We note that in this relation k may be either real or complex. In fact, we can at once say that if E is such that $|[E-\mathcal{E}(0)]/2\mathcal{E}(1)|>1$ then k must be pure imaginary. If the inequality is in the other direction, then k is pure real. We recognize the latter case as the states lying in the band. These are of course the states for which the coefficients of the Wannier function are all of unit absolute value, or the propagating states. The states where k is pure imaginary are those for which the coefficients of the Wannier function increase exponentially for either large positive or negative values of p.

We are now left with the necessity of solving the second of Eqs. (14). Let us set up periodic boundary conditions such that $U(p+2N)=U(p)$, and start by discussing the case where our energy falls in the band (k pure real). We notice at once because of the symmetry of the problem that our solutions must be either symmetric or antisymmetric about the central atom. In the first case $U(p)=U(-p)$; in the second $U(p)=-U(-p)$. For the antisymmetric state, the wave function has a node at the origin and therefore our perturbed problem just reduces to the unperturbed problem. This can most easily be seen by putting the condition of antisymmetry into the difference equations and noticing that the effect of the perturbation disappears completely from the equation. For this case we take as the solution $U(p)=\sin(kRp)$, which satisfies the boundary conditions provided that $kRN=n\pi$. [Sin(kRp) is of course a linear combination of our two solutions b^{+p} and b^{-p}.] We see that there are $N-1$ antisymmetric solutions.

The most convenient form in which to take the solution of the symmetric states is in the form $\cos[kR(p-N)]$. This form of the solution automatically satisfies the boundary condition at $p=N$. The energy is given at once by Eq. (16). Substituting this form of the solution in Eq. (14) for $p=0$ we arrive at the condition

$$-\tan(kRN)\sin(kR)=V(0)/2\mathcal{E}(1). \qquad (17)$$

In arriving at this condition, we have made use of the fact that E is given by Eq. (16). There are N solutions of this symmetric type. We can solve Eq. (17) graphically by plotting the left side as a function of k, and finding the k's for which this equals $V(0)/2\mathcal{E}(1)$. A plot of this function for $N=6$ as a function of kR, is given in Fig. 1. We see that the axis of abscissas cuts this curve in seven places. For the other horizontal lines, where there are only six intersections the missing state is a state for an imaginary value of k. This state gives a total of $N+1$ symmetric states and $N-1$ antisymmetric states giving

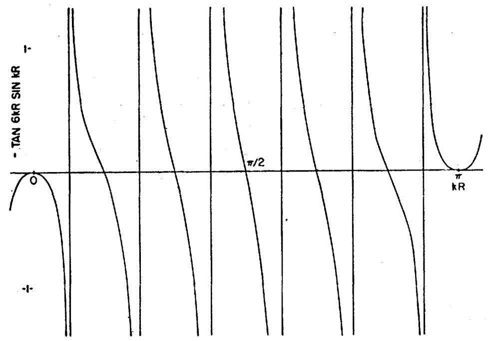

FIG. 1. Function $-\tan(kRN)\sin(kR)$, for $N=6$.

in total the required $2N$ states. We shall now go on and study in detail the state corresponding to the imaginary value of k.

If k is imaginary, then let us denote ik by γ. This is the case where E is such that it lies outside of the band. In this case, our solution to the difference equation is given by $\exp(\pm\gamma pR)$. The coefficients of our Wannier functions are thus seen to increase exponentially in one direction. We could proceed as before setting up a bound state which satisfies our periodic boundary conditions, but for large N it can be easily shown that proceeding in this manner gives the same result as demanding that our wave function go to zero for p infinite. If this is the case then the solution to the first of Eqs. (14) is taken as $U(p)=U(-p)=\exp(-\gamma Rp)$. We have of course the condition from the first of Eqs. (14) that

$$E=\mathcal{E}(0)+2\mathcal{E}(1)\cosh(\gamma R). \tag{18}$$

In order to satisfy the second of Eqs. (14), we must satisfy $\sinh(\gamma R)=V(0)/2\mathcal{E}(1)$. This determines a value of γ corresponding to a given value of $V(0)$. With this value of γ, the energy is given by Eq. (18). We can, of course, substitute for the cosh in terms of the sinh and get the relation that

$$E=\mathcal{E}(0)+2\mathcal{E}(1)\{1+[V(0)/2\mathcal{E}(1)]^2\}^{\frac{1}{2}}. \tag{19}$$

This shows that for small values of the perturbing potential the bound state leaves the band quadratically in $V(0)$.

In all the preceding discussion, we have tacitly assumed that the sign of the perturbation is the same as the sign of the nearest-neighbor interaction. This means that the bound state pushes out of the band at the point where $E=\mathcal{E}(0)+2\mathcal{E}(1)$. If the signs of the perturbing potential and the nearest-neighbor interaction are different then the bound state will push out of the band at the point where $E=\mathcal{E}(0)-2\mathcal{E}(1)$. In this case, it can easily be seen that the solution to the difference equation is given by $(-1)^p\exp(-\gamma Rp)$. The energy of the bound state is then given by Eq. (19) where the plus sign outside of the square root is replaced by a minus sign.

We have now accounted for our $2N$ states. We have one bound state, $N-1$ antisymmetric states in the band, and N symmetric states in the band. In Fig. 2 we plot the energies of these states for the case $N=6$ as a function of the perturbing potential. We have also included for comparison the energies of the antisymmetric states which are not affected by the perturbation. The interesting thing to notice is the way in which each of the energy levels within the band is displaced by the perturbation, only far enough to approach the mid-point between neighboring antisymmetric states, with the exception of the limiting state which becomes detached from the band, and forms the separate impurity state which we have discussed earlier. The case which we have shown is that of positive $\mathcal{E}(1)$, in which case it is the top of the band where the separate level appears for positive $V(0)$. We have shown the case for a small N value; but if N is very large, it is clear that the displacements of all levels but the one which becomes detached from the band will be negligible.

We have seen that a single energy level pushes away from the energy band under the action of the perturbation $V(0)$, and that its wave function falls off exponentially as we go away from the perturbing atom. As $V(0)$ becomes very large compared to the band width, the exponential fall off becomes very rapid, though it is small for small $V(0)$. At this point we can give an elementary check of the procedure of the preceding section, in which the difference equation was replaced by a differential equation. We start with the energy expression (16) and replace k in it by the operator $-id/dx$. We then use this operator to set up a differential equation. In this case, this leads to

$$\mathcal{E}(0)W(x)+2\mathcal{E}(1)\left[W+\frac{1}{2!}R^2\frac{d^2W}{dx^2}+\frac{1}{4!}R^4\frac{d^4W}{dx^4}+\cdots\right]+V(x)W(x)=EW(x), \tag{20}$$

where $V(x)$ is the perturbative potential, which is zero except when x is zero, so that except when x is zero we can omit the term in V. The simplified Schrödinger equation corresponding to (12) is obtained by omitting

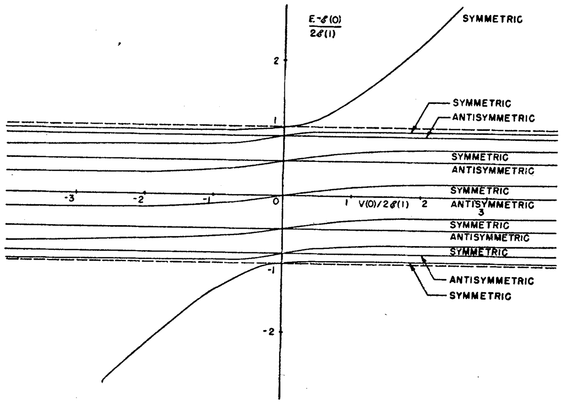

FIG. 2. Energy of perturbed energy levels, as a function of perturbative energy.

everything beyond the second derivative in (20). Now we can, in this simple case, solve either the approximate or the exact problem by assuming $W=\exp(-\gamma x)$, the only difference being in the relation which we find between γ and E. If we substitute this expression in (20), we find a solution of the exact equation if

$$E=\mathcal{E}(0)+2\mathcal{E}(1)[1+(\gamma R)^2/2!+(\gamma R)^4/4!+\cdots]$$
$$=\mathcal{E}(0)+2\mathcal{E}(1)\cosh\gamma R,$$

in agreement with (18). If on the contrary we neglect fourth and higher derivatives, we have $E=\mathcal{E}(0)+2\mathcal{E}(1)[1+(\gamma R)^2/2!]$ which is a satisfactory approximation only if $(\gamma R)^2$ is small in comparison to unity. This is the case in which the wave function $\exp(-\gamma x)$ falls off by only a small amount in the distance R, which agrees with the condition for the applicability of the second-order differential equation in the last section. If the perturbation is greater, so that the wave function falls off more rapidly, and the extra level is further from the band, the second-order differential equation is inapplicable, and we must use the difference equation, or the differential equation of infinite order, which is of course rigorously equivalent to it.

Before leaving this simple example it is informing to look at the states within the band in a somewhat different manner. For the symmetric states in the band, we can take a solution of the form $U(p)=U(-p)=\cos(kRp-\alpha)$. (We are no longer using periodic boundary conditions here.) If we do this, once again the energy is given by (16) and Eq. (14) gives a condition on α,

$$\tan\alpha=-V(0)/[2\mathcal{E}(1)\sin kR]. \quad (21)$$

This is instructive because it shows us that in the band there is a perturbed state corresponding to every energy in the band. The perturbation only has the effect of determining the phase factor α. We could of course do scattering theory in the band which would be closely related to this phase angle α. We can also notice that as $V(0)$ becomes infinite the phase angle approaches $\pi/2$. In this case, the symmetric state in the band approaches zero at the perturbed site. This means that whereas the perturbed states in the band avoid the impurity site the bound state which pulls out of the band becomes concentrated about the impurity site. We can see that this must be so in a very fundamental manner.

Let us consider the case of periodic boundary conditions. We are building up wave functions as linear combinations of the $2N$ Wannier functions on the atoms of the fundamental period. These Wannier functions are an orthonormal set of functions, as are the final linear combinations, so that the $U(p)$'s, which are the transformation coefficients from one set of functions to the other, form a unitary matrix. This is a matrix with $2N$ rows and columns: we have $2N$ energy levels, and $2N$ p's. If we now form the sum of the quantities $U^*(p)U(p)$, for a given p value, summed over the $2N$ energy levels, we know on account of the unitary property that this sum must be unity. Let us carry out this sum for $p=0$ corresponding to the impurity atom. For the separated state, with large perturbative potential $V(0)$, we know that the wave function will fall off as $\exp(-\gamma Rp)$ where γ is very large, so that the coefficients $U(p)$ will be very small for $p\neq 0$. Since the wave function must be normalized, we must have the sum of $U^*(p)U(p)$ over p, for a given energy level, equal to unity, which means that the contributions to the sum for $p\neq 0$ are very small, the term for $p=0$ must be very nearly equal to unity. We now return to our statement that the sum of $U^*(p)U(p)$ over all levels, for a fixed p must equal unity. For $p=0$, we have just seen that the contributions from all other levels must be very small, showing that with a large perturbation, the wave functions of the states in the band avoid the perturbing atom almost completely. This general type of proof is important, for it can be used in more complicated cases, where we cannot get explicit solutions.

We can introduce further complications into this one-dimensional impurity problem. It is possible to introduce next nearest neighbor interactions into the problem and still find solutions. We shall do this and introduce a perturbation which, once again, only extends over one lattice site. For this case the difference equations become

$$[\mathcal{E}(0)-E]U(p)+\mathcal{E}(1)[U(p+1)+U(p-1)]$$
$$+\mathcal{E}(2)[U(p+2)+U(p-2)]=0, \quad (22)$$

for p greater than zero and

$$[\mathcal{E}(0)+V(0)-E]U(0)+\mathcal{E}(1)[U(1)+U(-1)]$$
$$+\mathcal{E}(2)[U(2)+U(-2)]=0, \quad (23)$$

for p equals zero. By substitution of a propagating solution we find that the energy band is given by

$$E(k)=\mathcal{E}(0)+2\mathcal{E}(1)\cos(kR)+2\mathcal{E}(2)\cos(2kR). \quad (24)$$

It is informing to choose the parameters in this energy expression so that the minimum of the energy falls away from $k=0$. In order to do this, it is necessary that $|\mathcal{E}(2)|>|\mathcal{E}(1)|/4$. Figure 3 shows a plot of the energy as a function of k in this case. It should be emphasized that this is an imaginary problem since it is well known that the minimum of the energy for a one-dimensional crystal cannot fall away from either the center or the edges of the first Brillouin zone.[4] However, it is possible for the minimum of the band to come at an arbitrary point in the Brillouin zone for three-dimensional crystals. Because of the importance of this case in the theory of semiconductors, we thought it profitable to follow through this imaginary one-dimensional case in order to study the mathematics involved.

We follow the same method that we used in the nearest-neighbor example to solve this difference equation. We make the substitution $U(p)=b^p$. When this is

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[4] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 406.

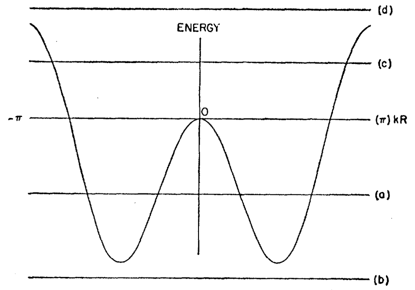

FIG. 3. Energy *vs* kR, for second-nearest neighbor interaction.

substituted into Eq. (22) we obtain an equation for b

$$[\mathcal{E}(0)-E]+\mathcal{E}(1)[b+b^{-1}]+\mathcal{E}(2)[b^2+b^{-2}]=0. \quad (25)$$

This is an equation of the fourth order in b. From its form we notice that if b is a solution to this equation so is b^{-1}. Since all complex roots of this equation must occur with their complex conjugates, b^* must also be a solution. This means of course that if b is taken in the form $\exp(ikR)$ then if k is complex all four roots are related by being all possible combinations of the complex conjugate and the inverse. By making the substitution $c=b+b^{-1}$, Eq. (25) can be reduced to an equation of the second order:

$$\mathcal{E}(2)(c^2-2)+\mathcal{E}(1)c+\mathcal{E}(0)-E=0. \quad (26)$$

By studying the solution of this equation as a function of the energy E, it is possible to determine whether k in $b=\exp(ikR)$ is real, complex, or pure imaginary. For the energy (d) in Fig. 3, k has two values both of which are pure imaginary. For the energy (c) k has two values, one pure real and the other pure imaginary. The energy (b) gives k two values both real. Finally for the energy (a) there is a complex value of the propagation constant. We will not discuss all of these cases in detail, but shall focus our attention on the case (a), since this is the case that corresponds to a bound state coming out of the bottom of the energy band.

Our solution to the difference equations will be some linear combination of the four solutions to Eq. (25). The constants in this linear combination are to be determined by the special Eq. (23). [The solution of (25) insures the solution of (22).] We can as before make use of the symmetry or antisymmetry of the solution to the difference equation to simplify our work. This will once again tell us that for the antisymmetric solution the effect of the perturbation vanishes. This means that the antisymmetric states in the band are unperturbed. For the bound state [case (a)], we need only study the symmetric solution. If we make the assumption of symmetry in Eqs. (22) and (23), we find that these two special equations are to be satisfied

$$[\mathcal{E}(0)+V(0)-E]U(0)+2\mathcal{E}(1)U(1)+2\mathcal{E}(2)U(2)=0, \quad (27)$$

$$[\mathcal{E}(0)-E]U(1)+\mathcal{E}(1)[U(2)+U(0)]+\mathcal{E}(2)[U(3)+U(1)]=0. \quad (28)$$

For the case (a), we therefore take the solution of our difference equation in the form

$$U(-p)=U(p)=e^{-\gamma p}(Ae^{i\kappa p}+A^*e^{-i\kappa p}), \quad (29)$$

where A and A^* are the unknown constants to be determined and $k=\kappa+i\gamma$. The energy is of course given by (25) and takes the form

$$E=2\mathcal{E}(1)\cos\kappa\cosh\gamma+2\mathcal{E}(2)\cos 2\kappa\cosh 2\gamma. \quad (30)$$

We are in the position where we have just enough constants to solve the pair of Eqs. (27) and (28). (The boundary conditions which are assumed here are that the wave function go to zero at infinity.) The mathematics of finding the energy as a function of the perturbation $V(0)$ is rather tedious and the results will be described instead of worked out in detail. For small perturbations, the bound state pulls out of the bottom of the band quadratically with the perturbation. As the perturbation increases the energy finally becomes linear with the perturbation. This is of course similar to the nearest-neighbor case worked out above. For small values of the perturbation the imaginary part of k is nearly zero and the real part is very nearly equal to k_0, the value of the propagation constant at the minimum of the band. As the strength of the perturbation increases the magnitude of the imaginary part increases, which means that the solution to the difference equation falls off more rapidly with distance from the central atom. We have the case where the wave function of the bound state becomes more localized. This means, in turn that the remaining states in the band avoid the impurity.

For a perturbation of the opposite sign to that which pulls a state out of the bottom of the band, a bound state will appear at the top of the band. This is the case (d). In this case, there are solutions to the difference equations with propagation constants which are pure imaginary. The solution of the difference equation which satisfies the special equation at the origin will consist of a linear combination of two terms both of which fall off exponentially with the distance from the origin. The two coefficients in this linear combination are determined by the two Eqs. (27) and (28). This state pulls out of the top of the band quadratically with the perturbation. The remaining two cases (b) and (c) are unbound impurity states in the band. The case (b) is the case of two real propagation constants and could be treated by the method of phase shifts introduced in the case of nearest-neighbor interactions. In this case there would be two phase shifts, one for each propagation constant. The case (c) is the case where there are two propagation constants; one pure real and the other pure imaginary. This means that the solution to our difference equation would consist of two terms one of which is a propagating term extending out to infinity coming from the ordinary band state. The other term is an exponentially damped term which dies out at infinity. Once again the special Eqs. (27) and (28) can be used to determine the unknown coefficients in this linear combination.

It is important to note, for this case, that even though we are in the band it is not legitimate to throw away the exponentially damped part of the solution to the difference equation and only consider the ordinary energy band state. The additional root to the Eq. (25) must be taken into account in addition to the propagating solution which makes up the ordinary Bloch state. This is an additional feature of the case of next-nearest neighbor interactions which was missing in the simple case of nearest-neighbor interactions. In the case of nearest-neighbor interactions, the only solutions to the analogous equation to (25) were the ordinary energy band solutions. Whereas this additional complication can be taken into account in the case of next-nearest neighbor interactions, we may imagine cases where it is necessary to take into account interactions with more distant neighbors. If we must do this the equation we get analogous to (25) will be of order twice the order of neighbors taken into account. It can readily be seen that the solution of this equation will become very difficult because of its high order. This factor is what makes the method we have been using to solve our difference equations in these simple cases inapplicable when it comes to more complex cases. In the next section, we shall try to formulate a method which does not have this drawback.

IV. A GENERAL METHOD OF TREATING DIFFERENCE EQUATIONS

In treating the impurity problem for more dimensions we might try to proceed as we did in the last paragraph. If we were to do this we would again have general and special equations arising from Eq. (8). The general equations would consist of the unperturbed equations which would be valid outside of the region where the perturbation acts. We would try to find solutions to these general equations of the form $\exp(i\mathbf{k}\cdot\mathbf{R}_n)$. Upon substituting this into the general equation we would get Eq. (9). Now however E is not restricted to be in the band nor is $\mathbf{k}$ restricted to be real. We must find all possible solutions to this equation solving for $\mathbf{k}$ as a function of E. This includes the exponentially damped solutions we ordinarily throw away while searching for the energy bands. After having found these general solutions to our unperturbed difference equations we must form linear combinations of solutions of a given energy so as to satisfy the special difference equations which involve the perturbation. We put in enough adjustable linear coefficients to be able to satisfy these special equations. This would lead to a set of simultaneous equations in the unknown coefficients. The number of equations would be of the order of the number of lattice sites over which the perturbing potential acts. As was mentioned in the last section we can see at once the great drawback of this method. It is in the finding of all the propagation constants which give rise to the energy E when substituted in Eq. (9) which forms the stumbling block. We saw that even in the case of higher-order interactions in the linear chain this could be a difficult task. In the case of a three-dimensional crystal where our propagation constant will have three components it seems hopeless.

If we reject this approach, we might think that we could treat our difference equations (8) simply as a set of linear equations, the determinant of the unknown coefficients $U(\mathbf{R}_n)$ being set equal to zero in order to determine the eigenvalues. The order of this secular equation in this case would be of the order of the number of lattice sites we choose to include in our crystal. This would in general far exceed the region over which the perturbation acts, since we know that the solution to the difference equations extends beyond the region of the perturbation. This approach might be quite hopeful in the case where we were looking for a highly localized bound state which falls off near the perturbed region. In the case where we have no reason to believe that our perturbed wave function is so localized, this approach would give rise to a prohibitively large secular equation. What would be desirable would be to deal only with the states which are the propagating energy-band states and still only be forced to solve a set of simultaneous equations no larger than the number of sites over which the impurity acts. We shall now show that this can be done by expanding our perturbed wave function in terms of the known Bloch functions.

We try to solve our perturbed problem by a linear combination of Bloch functions from various bands,

$$\psi(\mathbf{r})=\sum(n,\mathbf{k}')f_n(\mathbf{k}')u_{n,\mathbf{k}'}(\mathbf{r}), \tag{31}$$

where the Bloch functions are the eigenfunctions corresponding to our unperturbed Hamiltonian,

$$H_0u_{n,\mathbf{k}}(\mathbf{r})=E_n(\mathbf{k})u_{n,\mathbf{k}}(\mathbf{r}). \tag{32}$$

We wish to solve the problem

$$(H_0+H_1)\psi=E\psi. \tag{33}$$

Substituting (31) into (33), multiplying by $u_{m,\mathbf{k}}(\mathbf{r})$, integrating, and using the properties of the Bloch functions we arrive at the result that

$$f_m(\mathbf{k})[E_m(\mathbf{k})-E]+\sum(n,\mathbf{k}')V_{n,m}(\mathbf{k},\mathbf{k}')f_n(\mathbf{k}')=0, \tag{34}$$

where

$$V_{n,m}(\mathbf{k},\mathbf{k}')=\int u_{n,\mathbf{k}}^*(\mathbf{r})H_1u_{m,\mathbf{k}'}(\mathbf{r})dv. \tag{35}$$

It can easily be seen using the definition of $V_{n,m}(\mathbf{R}_i,\mathbf{R}_j)$ that (35) can be rewritten as

$$V_{n,m}(\mathbf{k},\mathbf{k}')=(1/N)\sum(\mathbf{R}_i,\mathbf{R}_j)V_{n,m}(\mathbf{R}_i,\mathbf{R}_j)e^{-i\mathbf{k}\cdot\mathbf{R}_i}e^{i\mathbf{k}'\cdot\mathbf{R}_j}. \tag{36}$$

Substituting (36) into (34) we arrive at the equation

$$f_m(\mathbf{k})+\frac{1}{N}\sum(n,\mathbf{R}_i,\mathbf{R}_j)\frac{e^{-i\mathbf{k}\cdot\mathbf{R}_i}V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)}{E_m(\mathbf{k})-E}\times\sum(\mathbf{k}')e^{i\mathbf{k}'\cdot\mathbf{R}_j}f_n(\mathbf{k}')=0, \quad (37)$$

where we have divided by $E_m(\mathbf{k})-E$. We now multiply both sides of this equation by $\exp(i\mathbf{k}\cdot\mathbf{R}_p)$ and sum over the values of $\mathbf{k}$ in the first Brillouin zone,

$$U_m(\mathbf{R}_p)+\frac{1}{N}\sum(n,\mathbf{R}_i,\mathbf{R}_j,\mathbf{k})\times\frac{e^{i\mathbf{k}\cdot(\mathbf{R}_p-\mathbf{R}_i)}}{E_m(\mathbf{k})-E}V_{mn}(\mathbf{R}_i,\mathbf{R}_j)U_n(\mathbf{R}_j)=0. \quad (38)$$

We have, in this equation, made use of the fact that the transformation between the coefficients of the Wannier function and those of the Bloch functions are given by

$$U_m(\mathbf{R}_p)=N^{-\frac{1}{2}}\sum(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}_p}f_m(\mathbf{k}). \quad (39)$$

This constitutes a set of simultaneous equations between the coefficients of the Wannier functions. We notice that there are as many equations as the number of lattice sites in the crystal times the number of bands under consideration. In order to satisfy this set of simultaneous linear homogeneous equations, the determinant of the coefficients must vanish. There is a simplifying feature to this determinant. Let us put those U's for which the perturbation has nonvanishing matrix elements in the earliest part of the determinant. If this is done, the determinant has the form in Fig. 4 where the shaded region is a region of nonvanishing elements and the unshaded region is the region which has vanishing elements except for the indicated 1's. We can see at once that all that is necessary for the vanishing of the determinant is the vanishing of the upper left-hand corner which is enclosed by the heavy lines. This is a determinant of size equal to the number of lattice sites over which the perturbation extends multiplied by the number of bands between which it has matrix elements. This is the form in which we propose to do the impurity calculations. We see that all that is necessary is a knowledge of the energy as a function of k for the energy-band solutions. The size of the determinant to be solved is limited to the size of region over which the effect of the impurity is felt.

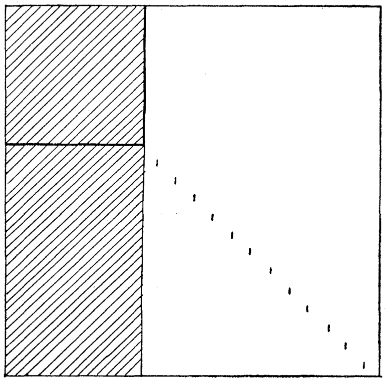

FIG. 4. Schematic diagram of secular equation used to solve the impurity problem.

We can now state in words what is involved if this formalism is used in an impurity calculation. We must first find the quantities

$$\sum(\mathbf{k})\frac{e^{i\mathbf{k}\cdot\mathbf{R}_l}}{E_m(\mathbf{k})-E} \quad (40)$$

as a function of the energy. This summation may be replaced by an integration over the first Brillouin zone if the allowed $\mathbf{k}$ values are dense. We must then solve the set of simultaneous equations (38) for those U's for which there are corresponding nonvanishing matrix components of the perturbation. This involves the vanishing of the determinant

$$\left|\delta_{m,n}\delta_{p,j}+\frac{1}{N}\sum(\mathbf{R}_i,\mathbf{k})\frac{e^{i\mathbf{k}\cdot(\mathbf{R}_p-\mathbf{R}_i)}}{E_m(\mathbf{k})-E}V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)\right|=0. \quad (41)$$

If we are looking for a bound state, the values of E for which this determinant vanishes are the energies of the bound states. For an energy for which this determinant vanishes we solve the set of simultaneous equations for the U's for which there are nonvanishing matrix elements of the perturbation. Having found these values of the U's the remaining values, outside of the region of the impurity, are given in terms of those within the region by (38). It is clear from the formalism that this method is very similar to a Green's function method of solving differential equations. Here we have a Green's function solution to the difference equation, the quantity (40) acting as the Green's function. This can be arrived at by considering the Green's function solution to the differential equation, as is shown in Appendix (1).

It is instructive to solve as an example the case in which we consider only one band and limit the effect of the impurity to one site. $[V(\mathbf{R}_i,\mathbf{R}_j)=\delta_{i,0}\delta_{j,0}\times V(0)]$. Equation (38) becomes

$$U(\mathbf{R}_p)=\frac{1}{N}V(0)\left[\sum(\mathbf{k})\frac{e^{i\mathbf{k}\cdot\mathbf{R}_p}}{E-E(\mathbf{k})}\right]U(0). \quad (42)$$

The determinant (41) in this case has only one row and one column and gives directly the energy as a function of the perturbation,

$$(V(0)/N)\sum(\mathbf{k})\frac{1}{E-E(\mathbf{k})}=1. \quad (43)$$

To show the power of this method, we shall use it to discuss the one-dimensional chain with nearest-neighbor interaction. For the one-dimensional case, we know that

$E(k)=\mathcal{E}(0)+2\mathcal{E}(1)\cos kR$. We must then evaluate the sum $\sum(k)1/[E-E(k)]$ in (43). In the case we are dealing with the discrete state, so that E lies outside the unperturbed band, we can convert this sum into an integral without trouble. We find that kR goes by equal steps from $-\pi$ to π or from 0 to 2π, there being N intervals. That is, we can replace $\sum(k)$ by $N/2\pi\int_0^{2\pi} d(kR)$. Thus (43) reduces to

$$[V(0)/N][N/2\pi] \times\int_0^{2\pi}[E-\mathcal{E}(0)-2\mathcal{E}(1)\cos\alpha]^{-1}d\alpha=1. \quad (44)$$

This can be integrated by elementary means, and gives

$$V(0)/\{[E-\mathcal{E}(0)]^2-[2\mathcal{E}(1)]^2\}^{\frac{1}{2}}=1. \quad (45)$$

When we solve (45) for the energy E, the result is identical with (19) which we obtained by straightforward solution of the difference equations. The integral in (42) can also be evaluated simply and gives the proper exponential falling off of the solution.

This solution of the problem of the single lattice site impurity which is embodied in Eqs. (42) and (43) also gives us additional insight into the solution of the problem with a more general impurity. In the case of a more general impurity, Eq. (38) instructs us to sum up the effects of single lattice site impurities at the various lattice sites over which the perturbation extends in order to get the total effect of the impurity. This most clearly illustrates the Green's function nature of our solution.

In simple cases, we can use (42) to obtain results about the wave function in an analytic way. Thus, let us consider the problem of a three-dimensional lattice, in which the energy $E(\mathbf{k})$ can be expanded about a minimum or maximum energy which we take to come at $k=0$, in a power series starting with the terms $a(k_x^2+k_y^2+k_z^2)$, where $a=h^2/8\pi^2m$, m being the effective mass. Let us have a perturbation at the atom at the origin, such that the discrete level lies at an energy E, below the bottom of the band (and hence negative if the bottom of the band is at zero energy). Then $E-E(k)$ can be approximated by $E-a(k_x^2+k_y^2+k_z^2)$, which is numerically small near $k=0$, but increases rapidly as we go away from this point. The significant contributions to the sum or the integral in (42) will then come from small values of k, and we shall not make serious errors if we integrate, not merely over the unit cell in k space, but out to infinity. The quantity $1/[E-E(k)]$ will depend only on the magnitude of k, to the approximation we are using, so that in carrying out the integration over k we may first average over angles, in which case the exponential $e^{i\mathbf{k}\cdot\mathbf{R}_p}$ can be replaced by the spherical Bessel function $\sin(kR_p)/(kR_p)$, where k and R_p stand for the magnitudes of the vectors. Thus the sum in (42) becomes proportional to

$$\int_0^\infty \frac{2\pi k^2\sin(kR_p)}{(E-ak^2)kR_p}dk=\frac{\pi^2}{aR_p}e^{-\gamma R_p}, \quad (46)$$

where $\gamma=(-E/a)^{\frac{1}{2}}=(2\pi/h)(-2mE)^{\frac{1}{2}}$. But this simply tells us that the quantity $U(R_p)$ is proportional to $e^{-\gamma R_p}/R_p$. This turns out to be the same result which would be obtained from the differential equation approach to the difference equations even down to the value of γ we have obtained.

We can, in other words, reproduce the results of the free electron approximation for the wave function very easily; but at the same time we have the machinery for easily improving the approximation. We merely have to investigate the change in the sum or the integral in (42) or (38) when we take a better approximation to the energy $E(\mathbf{k})$. In the limit, as we have very large perturbation, so that the energy E departs widely from the energy band, the constant term in the Fourier representation will outweigh any of the other terms; this means that $U(\mathbf{R}_p)$ is much larger for $\mathbf{R}_p=0$, or on the perturbing atom, than on any other lattice site, as we know should be the case from our earlier qualitative discussion. But it would be an easy thing, with any given function $E(\mathbf{k})$, to obtain numerical values for the other components, of the other $U(\mathbf{R}_p)$'s, to any desired degree of approximation. By (42) or (38), we have reduced the problem of any lattice with a single perturbing or many perturbing atoms to quadratures, and as more examples are worked out, the wave functions and energy levels of the discrete states in such problems can be completely investigated.

In all of the treatment above, we have assumed that we have the exact energy bands and Bloch functions. That is, we have assumed that we have already found the eigenfunctions of our unperturbed Hamiltonian. The finding of the exact eigenfunctions for the periodic potential problem is a task in itself. In many cases the exact eigenfunctions of the periodic potential problem are approximated by a linear combination of Bloch functions made up of linear combinations of atomic orbitals.[5] If this is the case, the unperturbed part of the Hamiltonian has matrix elements between the Bloch combinations of the atomic orbitals. Sometimes the perturbing part of the Hamiltonian has matrix elements which are better known between the original set of atomic orbitals rather than in terms of the Wannier functions. For these reasons it is profitable to find a formulation of the impurity problem which does not make the assumption that the eigenfunctions of the unperturbed Hamiltonian have been found.

We imagine that we have some set of mutually orthogonal atomic orbitals $\phi_n(\mathbf{r}-\mathbf{R}_i)$. From these we define Bloch functions

$$u_{n,\,\mathbf{k}}(\mathbf{r})=N^{-\frac{1}{2}}\sum(\mathbf{R}_i)e^{i\mathbf{k}\cdot\mathbf{R}_i}\phi_n(\mathbf{r}-\mathbf{R}_i). \quad (47)$$

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[5] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

With respect to these, we assume that our unperturbed Hamiltonian has matrix elements given by

$$H_{n,m}(\mathbf{k})=\int u_{n,\mathbf{k}}{}^*(\mathbf{r})H_0u_{m,\mathbf{k}}(\mathbf{r})dv. \tag{48}$$

We now proceed as we did in Eqs. (31) through (36). Every definition involving the Wannier functions is replaced by a corresponding one involving the ϕ's. Instead of Eq. (37) we arrive at the result that

$$\begin{aligned}\sum(m)f_m(\mathbf{k})[H_{m,n}(\mathbf{k})-E]&\\ +\frac{1}{N}\sum(s,\mathbf{R}_i,\mathbf{R}_j)e^{-i\mathbf{k}\cdot\mathbf{R}_i}V_{n,s}(\mathbf{R}_i,\mathbf{R}_j)&\\ \times\sum(\mathbf{k}')e^{i\mathbf{k}'\cdot\mathbf{R}_j}f_s(\mathbf{k}')=0.&\end{aligned} \tag{49}$$

If E is outside of the bands, it is possible to define an inverse to the matrix $H_{n,m}(\mathbf{k})-E$. Let us call this inverse $A_{p,n}(\mathbf{k})$. If we multiply Eq. (49) by $A_{p,n}(\mathbf{k})$, sum over n, and make use of the properties of the inverse of a matrix, we arrive at the result that

$$\begin{aligned}f_p(\mathbf{k})+\frac{1}{N}\sum(n,s,\mathbf{R}_i,\mathbf{R}_j)e^{-i\mathbf{k}\cdot\mathbf{R}_i}A_{p,n}(\mathbf{k})V_{n,s}(\mathbf{R}_i,\mathbf{R}_j)&\\ \times\sum(\mathbf{k}')e^{i\mathbf{k}'\cdot\mathbf{R}_j}f_s(\mathbf{k}')=0.&\end{aligned} \tag{50}$$

We can as before multiply by $e^{i\mathbf{k}\cdot\mathbf{R}_l}$ and sum over $\mathbf{k}$:

$$\begin{aligned}U_p(\mathbf{R}_l)+\frac{1}{N}\sum(n,s,\mathbf{R}_i,\mathbf{R}_j)V_{n,s}(\mathbf{R}_i,\mathbf{R}_j)&\\ \times[\sum(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_i)}A_{p,n}(\mathbf{k})]U_s(\mathbf{R}_j).&\end{aligned} \tag{51}$$

Here of course the U's are the coefficients of the ϕ's. In order to satisfy this set of equations, by the same argument as in the case of the Wannier functions, we must have the determinant of the coefficients vanish. This can once again be reduced to a determinant where the indices only go over those lattice sites and atomic orbitals which have nonvanishing matrix elements of the perturbation. In this case the determinant which vanishes is the following:

$$\left|\begin{aligned}\delta_{p,s}\delta_{l,j}+\frac{1}{N}\sum(n,\mathbf{R}_i)V_{n,s}(\mathbf{R}_i,\mathbf{R}_j)&\\ \times[\sum(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_i)}A_{p,n}(\mathbf{k})]&\end{aligned}\right|=0. \tag{52}$$

We notice that in this formulation it is the inverse of the matrix $H_{n,m}(\mathbf{k})-E$ which has the same role as $1/[E_n(\mathbf{k})-E]$. It might be mentioned in passing that both Eqs. (52) and (41) will be considerably reduced in size by considering the symmetry of the perturbed state which is desired.

APPENDIX

We could also solve for the impurity levels by a Green's function applied to the differential equation. In order to find the Green's function $G(\mathbf{r},\mathbf{r}')$ for the unperturbed Hamiltonian, we must solve the equation

$$(H_0-E)G(\mathbf{r},\mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}'). \tag{A1}$$

It is well known that the solution to this inhomogeneous differential equation is given in terms of the eigenstates of the unperturbed Hamiltonian by

$$G(\mathbf{r},\mathbf{r}')=\sum(n,\mathbf{k})\frac{u_{n,\mathbf{k}}{}^*(\mathbf{r}')u_{n,\mathbf{k}}(\mathbf{r})}{E_n(\mathbf{k})-E}. \tag{A2}$$

We can then express the solution to the perturbed Hamiltonian with energy E,

$$(H_0+H_1)\psi=E\psi, \tag{A3}$$

in the form of an integral equation:

$$\begin{aligned}\psi(\mathbf{r}')&=\int\psi(\mathbf{r})H_1G(\mathbf{r},\mathbf{r}')d\tau\\ &=\int\psi(\mathbf{r})H_1\sum(n,\mathbf{k})\frac{u_{n,\mathbf{k}}{}^*(\mathbf{r}')u_{n,\mathbf{k}}(\mathbf{r})}{E_n(\mathbf{k})-E}.\end{aligned} \tag{A4}$$

If we let $\psi(\mathbf{r})=\sum(l,\mathbf{R}_i)U_l(\mathbf{R}_i)a_l(\mathbf{r}-\mathbf{R}_i)$ and let $u_{n,\mathbf{k}}(\mathbf{r})=N^{-\frac{1}{2}}\sum e^{i\mathbf{k}\cdot\mathbf{R}_j}a_n(\mathbf{r}-\mathbf{R}_j)$ we can substitute these expressions in (A4) and multiply by $a_m{}^*(\mathbf{r}'-\mathbf{R}_p)$ and integrate over all space to give the result that

$$\begin{aligned}U_m(\mathbf{R}_p)+\frac{1}{N}\sum(n,\mathbf{R}_i,\mathbf{R}_j,\mathbf{k})&\\ \times\frac{e^{i\mathbf{k}\cdot(\mathbf{R}_p-\mathbf{R}_i)}}{E_m(\mathbf{k})-E}V_{m,n}(\mathbf{R}_i,\mathbf{R}_j)U_n(\mathbf{R}_j)=0.&\end{aligned} \tag{A5}$$

This is of course identical with the result in Eq. (38).