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Theory of Scattering in Solids*

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The scattering of an electron by an imperfection in a lattice is set up in terms of a linear combination of the Wannier functions associated with the lattice. The difference equations which the coefficients of the Wannier functions satisfy are discussed in the light of simple examples. A Green's function formulation of the difference equations is then introduced which leads to the proper asymptotic behavior of the scattered wave. This approach avoids many of the unwarranted assumptions usually made in the discussion of scattering in solids.

I. INTRODUCTION

IN a previous paper, the author and J. C. Slater treated the problem of impurity levels in a solid.[1] [We shall refer to this paper as (I)]. In that paper we used a linear expansion of the impurity wave function in terms of the complete set of Wannier[2] functions for the unperturbed periodic solid. It was shown that the coefficients in this linear expansion satisfied a set of difference equations involving the perturbation to the Hamiltonian. A formalism was derived for solving this set of difference equations which had some desirable features. As will be seen in a later section of this paper, the formalism employed in (I) is best suited for the treatment of the bound states caused by the impurity within the solid. We shall present in this paper a modification of the method which will be better suited for use in discussing the unbound levels of the perturbed solid. The hope will be that by treating the rigorous set of difference equations we shall avoid some of the simplifying assumptions made in the usual treatments of scattering caused by imperfections in the perfect periodic lattice.[3]

These simplifying assumptions consist, in most cases, of replacing the rigorous difference equations by approximate differential equations. The differential equations derived in this way generally is a Schrödinger equation where the potential term is the potential of the imperfections and the effect of the band structure of the periodic lattice is condensed into an effective mass which replaces the electron mass in the Schrödinger equation. In many cases, this simplification is not justified and we would be much safer in using the difference equations for doing our scattering theory.

Following the methods of the previous paper (I), we shall first set up the general difference equations for the scattering problem, and then use them to solve a simple linear chain scattering problem in order to illustrate the use of the difference equations. The method of the last paper (I) will then be used to solve a simple three-dimensional scattering problem. A modification of this method will be seen, in light of this three-dimensional example, to be advantageous. This modification will allow us to derive an asymptotic form for the scattered wave.

II. DIFFERENCE EQUATIONS FOR THE SCATTERING PROBLEM IN A SOLID

We shall assume that the reader is familiar with the notations and contents of (I). We expand the solution to our perturbed Hamiltonian H_0+H_1 in terms of Wannier functions belonging to different bands and lattice sites,

$$\psi(\mathbf{r})=\sum(n)\sum(\mathbf{R}_j)U_n(\mathbf{R}_j)a_n(\mathbf{r}-\mathbf{R}_j). \quad (1)$$

The unknown coefficients $U_n(\mathbf{R}_j)$ can be shown to satisfy a set of difference equations,

$$\sum(m,\mathbf{R}_j)[\mathcal{E}_m(\mathbf{R}_i-\mathbf{R}_j)\delta_{nm}+V_{nm}(\mathbf{R}_i,\mathbf{R}_j)]U_m(\mathbf{R}_j)=EU_n(\mathbf{R}_i). \quad (2)$$

These equations are Eq. (8) of (I) and are no different whether we are doing bound perturbed states or the scattering problem. The difference between these problems comes in the choice of the energy E. If E lies in the band, we know that there are propagating solutions to the unperturbed problem. Since this is the case, for those difference equations beyond the point where the perturbation vanishes, it is possible to find solutions which extend out to infinity. We noted in (I) that for this case (E lying in a band) there would be a solution to our impurity problem for every energy in the bands.

Since this is the case we might pose the following problem. We wish to find the solution to our difference equations assuming that at very large distances from the perturbation the wave function consists of an incident unperturbed solution to our problem and outgoing waves. The unperturbed solutions to the periodic potential problem for energies lying in the band are the Bloch functions. When expressed in terms of solutions to the difference equations these are the functions $U(\mathbf{R}_j)=\exp(i\mathbf{k}\cdot\mathbf{R}_j)$, where $E(\mathbf{k})$ is equal to E, the energy at which the scattering takes place. We therefore look for

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[1] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

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

[3] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1949) and various other papers. The general method of replacing difference equations by differential equations is treated in reference 2 and in J. C. Slater, Phys. Rev. **76**, 1592 (1949).

solutions to the difference equations $[U(\mathbf{R}_j)]$ which consist of $\exp(i\mathbf{k}\cdot\mathbf{R}_j)$ plus some function of $\mathbf{R}_j$ which represents the outgoing scattered wave.

III. A SIMPLE LINEAR PROBLEM

In order to examine the case of impurity levels in the band, let us treat a simplified one-dimensional crystal. We will use the same example as we did in (I). This is the case of a linear chain with nearest neighbor interactions. The difference equations for this case take the form:

$$\mathcal{E}(0)U(p)+\mathcal{E}(1)[U(p+1)+U(p-1)]=EU(p), \quad (3)$$

$$\mathcal{E}(0)U(0)+\mathcal{E}(1)[U(1)+U(-1)] =[E-V(0)]U(0). \quad (4)$$

The impurity only has matrix elements between Wannier functions located at the central atom. In (I) the energy band for this case was shown to contain the energies,

$$E=\mathcal{E}(0)+2\mathcal{E}(1)\cos kR. \quad (5)$$

Following the method outlined in the last section, we will look for a solution to our impurity problem for an energy in the band which consists of an incoming wave and outgoing scattered waves. We know that the only solutions to our general difference equations (3) are $\exp(\pm ikRp)$. The solution to our scattering problem must be made up of linear combinations of these two functions. We let our incident wave be described by $\exp(-ikRp)$. The scattered waves are outgoing waves. We have, therefore, that for

$$p\geqslant 0:\quad U_p=\exp(-ikRp)+A\exp(ikRp); \quad (6)$$

$$p\leqslant 0:\quad U_p=\exp(-ikRp)+B\exp(-ikRp). \quad (7)$$

(For $p<0$ we could lump the two terms together since they both depend on p in the same manner, but writing the solution in this form is nearest to what is done in three dimensions.) The constants A and B which represent the reflected and part of the transmitted wave must be determined from the special Eq. (4). First we notice that in order for both solutions to give the same value at the origin, A must equal B. Substituting these solutions into Eq. (4) we arrive at the result that

$$[\mathcal{E}(0)+V(0)](1+A) +\mathcal{E}(1)[2\cos kR+2Ae^{ikR}]=E(1+A). \quad (8)$$

Expressing the cos in terms of the energy by use of (5), we can simplify this to yield

$$V(0)(1+A)+2A\mathcal{E}(1)e^{ikR}=[E-\mathcal{E}(0)]A. \quad (9)$$

This can be further simplified by use of (5), giving finally:

$$V(0)(1/A)=-i2\mathcal{E}(1)\sin kR-V(0). \quad (10)$$

This is the desired equation for A. If A is expressed in the form $R\exp(-i\phi)$, where R is positive and real, we can readily show that

$$R=\left(\frac{[2\mathcal{E}(1)]^2-E'^2}{V^2}+1\right)^{\frac{1}{2}}, \qquad \phi=\tan^{-1}\frac{\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}{V}, \quad (11)$$

where $E'=E-\mathcal{E}(0)$. We have now found the amplitude of the wave scattered from the impurity. [This result should be compared with (21) of (I).]

In this simple case, the solutions to the general difference equations (3) could be easily found. They consist solely of the propagating band solutions. In (I) we noted that even in more complex linear chain problems there are other solutions to the general difference equations (equations not involving the perturbation) for energies in the band besides the propagating ones. The presence of these additional nonpropagating solutions was what made the method used above impractical for more complex cases in (I). The same problem arises here.

The knowledge of the presence of these nonpropagating solutions for energies in the band allows us to say more of the nature of the scattered waves. If we demand that our scattered wave remains finite for large distances, the scattered wave must contain no behavior involving complex propagation constants $\mathbf{k}$, which gives rise to an exponential increase of $U(\mathbf{R}_j)$ with distance. Therefore that portion of the scattered wave which comes from the nonpropagating states ($\mathbf{k}$ complex or pure imaginary) must fall off exponentially with distance from the scattering center. This means, of course, that at very large distances, the scattered wave consists of only a linear combination of those states in the band which have the energy E of the incident wave. As we come close to the scattering center, there will be in addition to the asymptotic form a more rapidly varying dependence with distance which arises from the complex propagation constants which are solutions to the equations:

$$E(\mathbf{k})=E. \quad (12)$$

It would be convenient to ignore these complex propagation constants. We unfortunately are not at liberty to do so since they may form an important part of our scattering problem.

The presence of these nonpropagating parts of the scattered wave forms the essential difference between scattering in a solid and that in free space. In free space, the energy depends quadratically on the propagation constant $|\mathbf{k}|$. For positive energies (energies "in the band") there are only real propagation constants which are a solution to (12) and consequently there are no exponentially damped solutions to our unperturbed problem. In a solid, this is not the case. It may be true that scattering theory may be done in certain cases in a solid ignoring the nonpropagating solutions to the difference equations but this will involve a certain approximation. (For instance assuming that E depends on k quadratically.) It is safer not to make this assumption and deal directly with the difference equations trying to include all the propagating and nonpropagating solutions to the unperturbed equations.

IV. GREEN'S FUNCTION FORMULATION OF THE SCATTERING PROBLEM

We remember that in (I) we were able to avoid the knowledge of the nonpropagating solutions to our difference equations with the energy E by the use of what turned out to be equivalent to a Green's function formulation to the problem. We can use the same method used in that paper to solve the scattering problem. We notice that in Eq. (38) of (I) the quantity

$$\sum(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}/[E-E_m(\mathbf{k})] \tag{13}$$

plays the role of a Green's function giving the effect at the lattice site $\mathbf{R}_j$ of a disturbance at the lattice site $\mathbf{R}_l$ for the mth band. Let us try to make use of this same quantity to satisfy our difference equations for the scattering problem.

We imagine that we have an incident wave of energy E and propagation constant $\mathbf{k}$. Since we are doing the scattering problem, it is assumed that this energy is contained in one of the bands. Let us call this the qth band. By the general method indicated in Sec. II, we can try as our wave function a sum of the incident wave and outgoing waves.

$$U_m(\mathbf{R}_j)=\delta_{q,m}e^{i\mathbf{k}\cdot\mathbf{R}_j} +\sum(\mathbf{R}_l)c_m(\mathbf{R}_l)\sum(\mathbf{k})\frac{e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}}{E-E_m(\mathbf{k})}. \tag{14}$$

The only propagating parts to this solution come from the qth band and for those $\mathbf{k}$ values in that band which have the energy E. All other contributions to the sum over $\mathbf{k}$ for each band must contribute only to the nonpropagating part of the solution. The sum over $\mathbf{R}_l$ in (14) is to extend over only those lattice sites at which the perturbation does not vanish, that is, over those lattice sites for which $V_{nm}(\mathbf{R}_i,\mathbf{R}_j)$ is not zero. The unknown quantities $c_m(\mathbf{R}_l)$ are to be determined in order to satisfy the difference equations (2). We may substitute (14) into (2) in order to get the desired set of simultaneous equations for the c's.

$$\begin{aligned}\sum(m,\mathbf{R}_j)\{&[\mathcal{E}_m(\mathbf{R}_i-\mathbf{R}_j)-E\delta(\mathbf{R}_i-\mathbf{R}_j)]\delta_{n,m}\\ &\times\sum(\mathbf{R}_l)c_m(\mathbf{R}_l)K_{E,m}(\mathbf{R}_j-\mathbf{R}_l)\\ &+V_{n,m}(\mathbf{R}_i,\mathbf{R}_j)\sum(\mathbf{R}_l)c_m(\mathbf{R}_l)K_{E,m}(\mathbf{R}_j-\mathbf{R}_l)\}\\ &=-\sum(m,\mathbf{R}_j)V_{n,m}(\mathbf{R}_i,\mathbf{R}_j)\delta_{q,m}e^{i\mathbf{k}\cdot\mathbf{R}_j}.\end{aligned} \tag{15}$$

In Eq. (15) we have introduced the notation $K_{E,m}(\mathbf{R}_j-\mathbf{R}_l)$ for the kernel or Green's function of (13). We have also made one simplification by making use of the fact that the incident wave satisfies the equations with the perturbation set equal to zero.

A further simplification can be made in the first term inside the curly brackets in (15). There appears in this term the following:

$$\begin{aligned}\sum(\mathbf{R}_j)[\mathcal{E}_m(\mathbf{R}_i-\mathbf{R}_j)-E\delta(\mathbf{R}_i-\mathbf{R}_j)]K_{E,m}(\mathbf{R}_j-\mathbf{R}_l)\\ =\sum(\mathbf{k},\mathbf{R}_j)[\mathcal{E}_m(\mathbf{R}_i-\mathbf{R}_j)\\ -E\delta(\mathbf{R}_i-\mathbf{R}_j)]\frac{e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}}{E-E_m(\mathbf{k})}.\end{aligned} \tag{16}$$

Making use of the expansion of the energy $E_m(\mathbf{k})$ in a Fourier series,

$$E_m(k)=\sum(\mathbf{R}_s)\mathcal{E}(\mathbf{R}_s)e^{-i\mathbf{k}\cdot\mathbf{R}_s}, \tag{17}$$

we can eliminate the sum over $\mathbf{R}_j$, and arrive at the result that (16) equals

$$\sum(\mathbf{k})\frac{E_m(\mathbf{k})-E}{E-E_m(\mathbf{k})}e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_l)}=-N\delta(\mathbf{R}_i-\mathbf{R}_l). \tag{18}$$

We have made use of the well-known delta-function property of the sum over $\mathbf{k}$ of $\exp[i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_l)]$. Substituting this result back into (15), we find as the set of simultaneous equations for the c's,

$$\begin{aligned}\sum(m,\mathbf{R}_j,\mathbf{R}_l)[-N\delta(\mathbf{R}_i-\mathbf{R}_l)\delta_{n,m}\\ +V_{n,m}(\mathbf{R}_i,\mathbf{R}_j)K_{E,m}(\mathbf{R}_j-\mathbf{R}_l)]c_m(\mathbf{R}_l)\\ =-\sum(\mathbf{R}_j)V_{n,q}(\mathbf{R}_i,\mathbf{R}_j)e^{i\mathbf{k}\cdot\mathbf{R}_j}.\end{aligned} \tag{19}$$

We notice that the incident wave contributes the inhomogeneous term to these equations. We have therefore reduced the scattering problem to the solution of a set of linear simultaneous inhomogeneous equations for the c's. This set of equations extends over those bands and lattice sites for which the perturbation has nonvanishing matrix components. We have not shown this fact in a rigorous manner here but we could have carried out an argument similar to the one which we carried out in (I) in order to deduce the size of the secular equation rigorously.

There is, of course, another point which we glossed over in the foregoing derivation which we should discuss. We have correctly introduced the incident plane wave but we have not shown that the Green's function (13) corresponds to an outgoing wave. We know that the contribution to the wave function for other bands than the qth (the band in which the energy E lies) will contribute only an exponentially damped term from our experience in the last paper. The outgoing wave must therefore come from the qth band and in particular for those propagation vectors which give rise to the energy E. These are just the energies for which $E_q(\mathbf{k})=E$. This causes the denominator in (13) to vanish, giving rise to a singularity in the sum (or integral) over **k**. This is a familiar state of affairs. The manner in which we integrate around this singularity will determine whether our solution corresponds to incoming, outgoing, or standing waves. This is best illustrated by a simple example. This example will also tend to illustrate the difficulties involved in the method presented above and in a later section we shall show how these difficulties can be overcome by a modified definition of the Green's function.

Let us imagine that we have a situation where the energy falls near the bottom of a band which has its minimum near $\mathbf{k}=0$ and which is spherically symmetric about this point. If we choose the zero of energy at $\mathbf{k}=0$, the energy of the band can be expressed in the following form for small propagation vectors:

$$E=\alpha|\mathbf{k}|^2. \tag{20}$$

We now substitute this expression into the Green's function and assume that the principal contribution to the integral comes from the region around $k=0$. In this case we have that

$$K_E(\mathbf{R}_j-\mathbf{R}_l)=\int\frac{e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}}{E-\alpha|\mathbf{k}|^2}(d\mathbf{k}). \tag{21}$$

We can easily perform the integration over angles, giving us one of the spherical Bessel functions:

$$\begin{aligned}K_E(\mathbf{R}_j-\mathbf{R}_l)&=\int_0^\infty\frac{\{\sin k|\mathbf{R}_j-\mathbf{R}_l|\}2\pi k^2dk}{(E-\alpha k^2)k|R_j-R_l|}\\&=\int_{-\infty}^\infty\pi\frac{e^{ik|\mathbf{R}_j-\mathbf{R}_l|}kdk}{(E-\alpha k^2)|\mathbf{R}_j-\mathbf{R}_l|}.\end{aligned} \tag{22}$$

This is, of course, nothing more than the familiar Green's function for scattering in free space. We notice that this integral has simple poles at $k=\pm(E/\alpha)^{\frac{1}{2}}$ along the real axis. We can get a variety of Green's functions depending on how we choose to integrate around these singularities in the complex plane. We can arrive at the results (ignoring constant multipliers)

$$\begin{aligned}K_E(\mathbf{R}_j-\mathbf{R}_l)&\sim\frac{\sin[(E/\alpha)^{\frac{1}{2}}|\mathbf{R}_j-\mathbf{R}_l|]}{|\mathbf{R}_j-\mathbf{R}_l|}\\&\sim\frac{\cos[(E/\alpha)^{\frac{1}{2}}|\mathbf{R}_j-\mathbf{R}_l|]}{|\mathbf{R}_j-\mathbf{R}_l|}\\&\sim\frac{\exp[i(E/\alpha)^{\frac{1}{2}}|\mathbf{R}_j-\mathbf{R}_l|]}{|\mathbf{R}_j-\mathbf{R}_l|}\\&\sim\frac{\exp[-i(E/\alpha)^{\frac{1}{2}}|\mathbf{R}_j-\mathbf{R}_l|]}{|\mathbf{R}_j-\mathbf{R}_l|}.\end{aligned} \tag{23}$$

The first two represent standing waves and the third and fourth represent outgoing and incoming waves, respectively. Since we are looking for a Green's function which represents an outgoing wave, we would, of course, choose the third path of integration. We notice that (21) or (13) is not sufficient to determine the Green's function. In addition, a path of integration around the singularity must be specified.

In this simple example, the integration generating the Green's function could be reduced to a one-dimensional integration in the complex plane. In the case of more complicated dependence of $E(\mathbf{k})$ on **k**, this reduction to a one-dimensional integral may not be so trivial. In this event, we should have difficulty in knowing what we meant by choosing a path of integration which gave rise to an outgoing Green's function. In the next section, we shall give a method of overcoming this difficulty so that we shall more easily restrict ourselves to outgoing waves.

V. IMPROVED GREEN'S FUNCTION FORMULATION

In the last section, (13) was used as the Green's function for the solution of the difference equations which expressed the scattering problem in a periodic structure. In this section we shall introduce a Green's function which will also satisfy the perturbed difference equations; but in addition, have the advantage of giving explicitly outgoing waves.

Let us try as a Green's function the quantity

$$K_{E,m}(\mathbf{R}_j-\mathbf{R}_l)=(1/i)\sum(\mathbf{k})\times\int_0^\infty dt e^{i[E-E_m(\mathbf{k})]t}e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}. \tag{24}$$

The sum over **k** values once again goes over the first Brillouin zone. The integration over t can be carried out at once and, when evaluated at the lower limit, will give rise to the Green's function (13). The evaluation of the integral over t is of course ambiguous when evaluated at the upper limit. It will be seen however that this does not influence the validity of the use of this Green's function. We must now substitute this Green's function into the difference equations and see if we can solve them.

We assume once again that the form of the solution to the difference equations is given by

$$U_m(\mathbf{R}_j)=\delta_{q,m}e^{i\mathbf{k}\cdot\mathbf{R}_j}+\sum(\mathbf{R}_l)c_m(\mathbf{R}_l)\sum(\mathbf{k})K_{E,m}(\mathbf{R}_j-\mathbf{R}_l). \tag{25}$$

The energy E is assumed to lie in the qth band. The first term represents the incoming Bloch wave. The sum extends over only those lattice sites over which the perturbation extends. As before, we substitute (25) into (2). The proof that this form of the Green's function satisfies the difference equations runs exactly as the proof that (13) is a Green's function which allows us to satisfy the difference equations. We can make essentially the same simplification in the first term in the curly brackets in (15) that we did before. The only difference will come in (18). This relation will be replaced by

$$\sum(\mathbf{k})(1/i)\int_0^\infty dt[E_m(\mathbf{k})-E]e^{i[E-E_m(\mathbf{k})]t}e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}. \quad (26)$$

We shall now carry out the integral over t and replace the upper infinite limit by some large number A. This yields

$$\sum(\mathbf{k})(-1)\left\{\frac{E_m(\mathbf{k})-E}{E-E_m(\mathbf{k})}e^{i[E-E_m(\mathbf{k})]A}\right.$$
$$\left.-\frac{E_m(\mathbf{k})-E}{E-E_m(\mathbf{k})}\right\}e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}. \quad (27)$$

The first term in the summation we can make as small as we please by choosing A large enough. The rapid oscillation of the exponential will insure this. The second term is exactly the term which we had in (18). Thus we see that (26) will give the same value as (18) in the limit as A approaches infinity. That is, (26) will have the value $-N\delta(\mathbf{R}_i-\mathbf{R}_l)$. We are then justified in using the set of simultaneous equations (19) as the condition for the solution to the scattering problem. The only change that will take place is that we use the new definition (24) of the Green's function.

In order to complete the discussion of this Green's function, we must show that for large distances from the scattering center it represents an outgoing wave. The only term in (25) which contributes to the asymptotic form of the scattered wave is that portion of the wave function which comes from the qth band. The contribution from all other bands will give coefficients of the Wannier function which are exponentially damped. Let us therefore study $K_{E,q}(\mathbf{R}_n)$ for large $\mathbf{R}_n$. For convenience we shall drop the index q throughout the following remembering that we shall throughout be discussing the band in which the energy E lies. We have that

$$K(\mathbf{R}_n)=(1/i)\int(d\mathbf{k})$$
$$\times\int_0^\infty dt\exp\{i[E-E(\mathbf{k})]t+i\mathbf{k}\cdot\mathbf{R}_n\}. \quad (28)$$

Here we have assumed that we can replace the summation over $\mathbf{k}$ by an integral over the first Brillouin zone. $\mathbf{R}_n$ is assumed to be very large. This will cause rapid oscillations in the value of the exponential. We shall follow the method of stationary phases and assume that the principal contribution to the integral comes from that region where the variation of the exponent is small. This means that we shall set the gradient of the exponent in $\mathbf{k}$ space equal to zero as well as the derivative of the exponent with respect to t. This gives the conditions that

$$E=E(\mathbf{k})\,; \quad -[\nabla E(\mathbf{k})]t+\mathbf{R}_n=0. \quad (29)$$

The gradient in (29) is, of course, the gradient in $\mathbf{k}$ space. These equations determine the values of t and $\mathbf{k}$ around which the principal contributions to the integral (28) arise. The first of the two relations says that the contributions come from the surface of constant energy with energy E. This is not surprising since we know that the only propagating solutions of the difference equations with the energy E come from that portion of the energy band which has the energy E. The second of the relations embodied in (29) says that the portion of the constant energy surface which contributes to the integral is the portion near the point on this energy surface where the gradient is parallel to the vector $\mathbf{R}_n$. Let the values of the variables which satisfy these relations be $t=t_0$ and $\mathbf{k}=\mathbf{k}_0$. We can now introduce new variables which represent the change in the values of $\mathbf{k}$ and t as we depart from $\mathbf{k}_0$ and $t_0\cdot\mathbf{k}=\mathbf{k}_0+\boldsymbol{\kappa}$; $t=t_0+\tau$. We shall now carry out the integral (28) over the variables τ and $\boldsymbol{\kappa}$ allowing these to range from plus to minus infinity assuming that the major contribution comes from the region where these variables are zero.

We start by expanding the exponent in a Taylor series keeping only terms up to the second order. [We have already assured the vanishing of the first order terms by the conditions (29).]

$$[E-E(\mathbf{k})]t+\mathbf{k}\cdot\mathbf{R}_n$$
$$=\mathbf{k}_0\cdot\mathbf{R}_n-[\nabla E(\mathbf{k}_0)]\cdot\boldsymbol{\kappa}\tau-\tfrac{1}{2}t_0\left\{\frac{\partial^2E(\mathbf{k}_0)}{\partial\kappa_x{}^2}\kappa_x{}^2\right.$$
$$\left.+\frac{\partial^2E(\mathbf{k}_0)}{\partial\kappa_x\partial\kappa_y}\kappa_x\kappa_y+\cdots\frac{\partial^2E(\mathbf{k}_0)}{\partial\kappa_x{}^2}\kappa_z{}^2\right\}. \quad (30)$$

Substituting this into (28) gives

$$K(\mathbf{R}_n)\approx(1/i)e^{i\mathbf{k}_0\cdot\mathbf{R}_n}$$
$$\times\int\int_{-\infty}^{\infty}\int\int d\tau(d\boldsymbol{\kappa})e^{-i[E(\mathbf{k}_0)\cdot\boldsymbol{\kappa}]\tau}e^{-\frac{1}{2}t_0[\cdots]}. \quad (31)$$

The second brackets in the exponent contain the expression contained in the curly brackets in (30). We shall now choose a coordinate system for $\boldsymbol{\kappa}$ one coordinate of which is perpendicular to the $E(\mathbf{k})=E$ surface at the point $\mathbf{k}_0$ and therefore parallel to the gradient of $E(\mathbf{k})$ at this point. The coordinates in the plane tangent to the constant energy surface we shall orient in such a way that we eliminate all cross derivative terms between these two coordinates in (30). If we call the coordinate perpendicular to the constant energy surface κ_1 and the two coordinates in the plane tangent to the energy surface κ_2 and κ_3, then the integral over τ from minus to plus infinity will be equal to $[2\pi/|\nabla E(\mathbf{k}_0)|]\delta(\kappa_1)$. This means that in the integral over κ_1 we must set $\kappa_1=0$. The integral (31) is thereby reduced to

$$K(\mathbf{R}_n)\approx(1/i)\frac{2\pi}{|\nabla E(\mathbf{k}_0)|}e^{i\mathbf{k}_0\cdot\mathbf{R}_n}\int_{-\infty}^{\infty}d\kappa_2\int_{-\infty}^{\infty}d\kappa_3$$

$$\times\exp(-\tfrac{1}{2}it_0)\left\{\frac{\partial^2E(\mathbf{k}_0)}{\partial\kappa_2{}^2}\kappa_2{}^2+\frac{\partial^2E(\mathbf{k}_0)}{\partial\kappa_3{}^2}\kappa_3{}^2\right\}.\quad(32)$$

The integrals over κ_2 and κ_3 are elementary integrals. They are proportional to $\int_0^\infty(dx)\sin x^2=\frac{1}{2}(\pi/2)^{\frac{1}{2}}$. If we make use of this fact and substitute the value of t_0 which we obtain from (29), $[t_0=|R_n|/|\nabla E(\mathbf{k}_0)|]$, we obtain as a final result for the asymptotic form of the scattered wave:

$$K(\mathbf{R}_n)\approx-\frac{4\pi^2}{|\mathbf{R}_n|}e^{i\mathbf{k}_0\cdot\mathbf{R}_n}$$

$$\bigg/\left[\left(\frac{\partial^2E(\mathbf{k}_0)}{\partial\kappa_2{}^2}\right)\left(\frac{\partial^2E(\mathbf{k}_0)}{\partial\kappa_3{}^2}\right)\right]^{\frac{1}{2}}.\quad(33)$$

We have still to show that this corresponds to an outgoing wave. We can indicate this best by Fig. 1. In this figure we show a two-dimensional surface of constant energy. In addition, we show the vector $\mathbf{R}_n$. The vector $\mathbf{k}_0$ is determined by the points of tangency of planes perpendicular to the vector $\mathbf{R}_n$ with the surface of constant energy. This, of course, satisfies the condition that the gradient of $E(\mathbf{k})$ be parallel to $\mathbf{R}_n$, since the gradient is normal to the surface of constant energy. We notice at once that in general there will be two points where the gradient is parallel to $\mathbf{R}_n$. Only one of these values of $\mathbf{k}_0$ will satisfy the second of the conditions (29). The reason is that the value of $t(t_0)$ determined from this relation must be positive. This means that the vectors $\mathbf{R}_n$ and $\nabla E(\mathbf{k}_0)$ must point in the same direction as well as being parallel. As we can see from the diagram, this means that the dot product of $\mathbf{R}_n$ and $\mathbf{k}_0$ will be positive. This corresponds to an outgoing wave in (33). We can see at once that there could be a somewhat different situation. In the preceding discussion, we have assumed that the gradient of $E(\mathbf{k})$ points outward. The reverse situation might also occur. This would mean that a surface of slightly higher energy would lie inside the surface of constant energy which we have drawn. In this case, the dot product of $\mathbf{R}_n$ and $\mathbf{k}_0$ would be negative which would not correspond to an outgoing wave. This situation can be easily remedied however by taking the complex conjugate of the first exponential term in (24). This will replace the negative sign in (29) by a plus sign and we shall once again be forced to get outgoing waves. From this discussion, we can see what it is in the Green's function (24) which gives us the outgoing rather than the incoming waves. It is merely whether we take $e^{-i[E-E(\mathbf{k})]t}$ or $e^{+i[E-E(\mathbf{k})]t}$ in the Green's function (24).

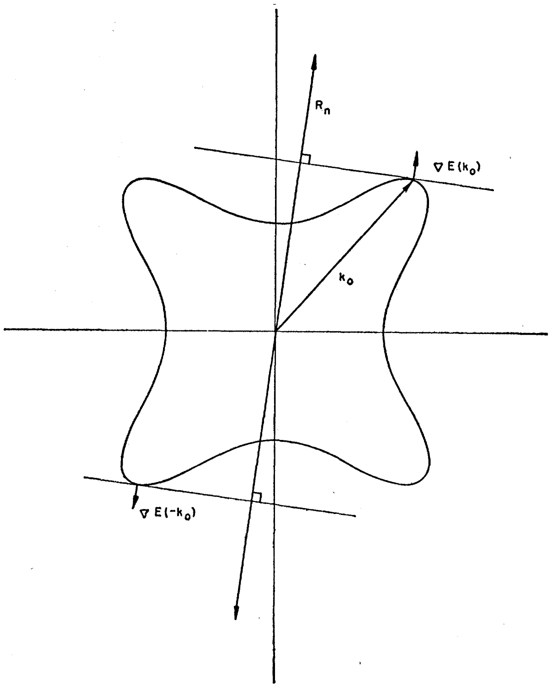

FIG. 1. A contour of constant energy (E) showing the relations between $\mathbf{k}_0$, the wave vector of the wave observed at $\mathbf{R}_n$ a point a large distance from the scattering center, and the vector representing the position of this lattice site ($\mathbf{R}_n$).

We see now what it is that corresponds to the third and fourth Green's functions in (23) (case of spherical energy surfaces). We can also see that if we take the real and imaginary parts of the Green's function (24) we shall get the first and second style Green's functions in (23). It is rather instructive to take the imaginary part of the Green's function (24) explicitly. The imaginary part of (24) is given by

$$\mathrm{Im}K(\mathbf{R}_n)=\tfrac{1}{2}\int_{-\infty}^{\infty}dt\int(d\mathbf{k})e^{it[E-E(\mathbf{k})]}e^{i\mathbf{k}\cdot\mathbf{R}_n}.\quad(34)$$

We have made use of the fact that $E(\mathbf{k})=E(-\mathbf{k})$. The integral over t just gives us a delta function,

$$\mathrm{Im}K(\mathbf{R}_n)=\pi\int d\mathbf{k}\delta(E-E(\mathbf{k}))e^{i\mathbf{k}\cdot\mathbf{R}_n}.\quad(35)$$

By introducing coordinate surfaces one of which is the surface of constant energy, we could actually carry out the integration over the delta function explicitly. This is quite straightforward and we shall not do this here. We shall content ourselves with pointing out that only propagating solutions of the unperturbed difference equations contribute to the imaginary part of the Green's function. This means that the imaginary part of (24) contributes only to the asymptotic form of the scattered wave. The remaining part of the asymptotic form comes from the real part of (24). This real part, in addition, is what makes up the rapidly varying exponentially damped part of the scattered wave which we mentioned at the end of Sec. III. We might also point out in this connection that in the event we were to use the present formalism to calculate bound states (this means that E does not lie in any energy band) our Green's function would have no imaginary part. This can be seen at once from (35); E cannot equal $E(\mathbf{k})$ and the integral over the delta function will give a vanishing result. This would be the case discussed in (I). Since we should not be discussing the scattering problem in this case we should have to eliminate the incoming wave on the right side of (19) and replace it by zero. The satisfaction of Eqs. (19) in this case would just lead to the eigenvalue condition (41) of (I). Thus we can see that the present formalism will give the same results as (I) for the bound states but has the advantage of being better suited for the discussion of the scattering problem.

VI. APPLICATION OF THE METHOD

We are now in a position to apply the method outline in the last section to the problems which we discussed in Secs. III and IV. In Sec. IV we derived the Green's function for the difference equations using (13) as the Green's function for the case $E=\alpha|\mathbf{k}|^2$. We could now derive the Green's function using the definition (24). This can be done in a straightforward manner which we shall not reproduce here. The integrations over $\mathbf{k}$ and t can be carried out; all the integrals which appear being well known. The result is that we get the third of the Green's functions in (23). This is correct since it is the one which corresponds to an outgoing wave. We also can derive the asymptotic form of the Green's function for this case using (33). It turns out, as one might expect, that we get the same result doing this as we get from (24). This is not surprising for in the case of a quadratic dependence of E on $\mathbf{k}$ the asymptotic form of the Green's function holds all the way in to small values of $\mathbf{R}_n$.

The other simplified case which we treated in this paper was the case of a linear chain with nearest neighbor interactions with an impurity which extends over only one lattice site. For this case (using the notation of Sec. III), Eq. (19) reduces to

$$[-N+V(0)K_E(0)]c(0)=-V(0). \tag{36}$$

The solution to the difference equations is given by

$$U_p=\exp(-ikRp)+c(0)K_E(p). \tag{37}$$

In order to solve Eq. (36) for $c(0)$, we must first evaluate (24) for this case,

$$K_E(p)=\frac{N}{2\pi}(1/i)\int_{-\pi}^{\pi}d\alpha\int_0^\infty dt \times\exp\{it[E'-2\mathcal{E}(1)\cos\alpha]\}e^{i\alpha p}. \tag{38}$$

Here we have replaced the sum over k by an integral over the first Brillouin zone and have introduced the notation $\alpha=kR$. The integral over α is just an integral representation for the Bessel function. Carrying out this integral gives

$$K_E(p)=\frac{N}{i}e^{+i\pi p/2}\int_0^\infty e^{itE'}J_p[-2\mathcal{E}(1)t]dt. \tag{39}$$

The integral over t is a special case of an integral discussed in Watson[4] and gives $p\geqslant 0$.

$$\begin{aligned}K_E(p)&=\frac{N}{i}e^{+i\pi p/2}\frac{1}{\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}\\&\quad\times\left\{\cos\left[p\sin^{-1}\left(\frac{E'}{2\mathcal{E}(1)}\right)\right]\right.\\&\quad\left.-i\sin\left[p\sin^{-1}\left(\frac{E'}{2\mathcal{E}(1)}\right)\right]\right\}\\&=\frac{Ne^{-i\pi p/2}(1/i)}{\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}\left\{\cos p\left(\frac{\pi}{2}-\alpha\right)\right.\\&\quad\left.-i\sin p\left(\frac{\pi}{2}-\alpha\right)\right\}=\frac{Ne^{+ip\alpha}}{i\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}\\&=\frac{Ne^{+ikRp}}{i\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}.\end{aligned} \tag{40}$$

For $p\leqslant 0$, following Watson, we get the result:

$$K_E(p)=\frac{-Ne^{-ikRp}}{i\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}. \tag{41}$$

We notice then that the Green's function does correspond to outgoing waves. We must now go on and determine the value of $c(0)$.

$$\begin{gathered}\left\{-N+\frac{V(0)Ni}{\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}\right\}c(0)=-V(0),\\ \frac{1}{c(0)}=+\frac{N}{V(0)}-\frac{Ni}{\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}}.\end{gathered} \tag{42}$$

If we multiply this relation by $1/K_E(0)$, we find that

$$\frac{1}{c(0)K_E(0)}=\frac{-i}{V(0)}\{[2\mathcal{E}(1)]^2-E'^2\}^{\frac{1}{2}}-1. \tag{43}$$

This is, however, just the same as the relation (10) if we identify $c(0)K_E(0)$ with A. If we make this identifica-

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[4] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1952), p. 405.

tion, the solution to the scattering problem will be given once again by (6) if we substitute the value of $c(0)$ into (37).

Thus we see that this method gives the same results as the direct solution of the difference equations for a simple case. The method also includes free electron scattering as we have seen earlier in this section. It is hoped that this method can be used to overcome some of the difficulties encountered in the direct solution of the difference equations without making the approximations inherent in replacing these difference equations by approximate differential equations.

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Calculation of Wave Functions in a Symmetrical Crystalline Field

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It is possible to calculate the splitting of the energy levels of an ion caused by a crystalline field of a certain symmetry in a more systematic way. Instead of solving the secular equation, certain algebraic quantities, i.e., the idempotent elements of the ring of the group, are introduced which contain all the information that can be obtained from the symmetry. This makes it possible to state, before other physical arguments are introduced, how many parameters enter a particular problem. In order to make the method easy to handle, some tables have been added, and a special case has been worked out.

I. BETHE-KRAMERS METHOD[1,2]

WHEN an ion is subject to the influence of a crystalline environment, the allowed rotations of the ion are considerably reduced in number. Instead of the full rotation group, we deal with a subgroup consisting of 24, or fewer, transformations. By picking those representation matrices which correspond to the elements of the subgroup, we obtain a representation of this subgroup. This representation is however, in general, reducible. Now Wigner's theorem[3] states that those wavefunctions which transform according to one irreducible representation belong to the same eigenvalue, and in order to apply this theorem to the finite group mentioned above, the representation has to be reduced.

Bethe[1] showed that, by means of the properties of the characters, one can determine how many and which irreducible representations are contained in the reducible one. He gave the answer for most of the subgroups which occur in practice; a supplement and a correction of one of Bethe's statements are given by Opechowski.[4] The actual computation of the wave functions is usually carried out by conventional procedures without the use of group theory. The secular matrix,

$$\langle m_l,l|V_{el}|m_l',l\rangle=\lambda\langle m_l|\delta|m_l'\rangle,$$

is calculated, and using the roots of its eigenvalue equation one tries to find the unitary matrix which diagonalizes the V_{el} matrix. Unfortunately, the eigenvalue equation is of degree $2l+1$, although sometimes a factorization into equations of the first and second degree can easily be found (e.g., a cubical field on an adapted coordinate system).

To summarize, we can say that no use is made in the usual method of our knowledge of the characters of the representation. This fact, as well as the simplification in the secular determinant often found at the end of the calculation, led us to look for a method in which the reduction is performed in a direct way. We found such a method in a paper by Schoeneberg.[5] Essentially the same method is used for permutation degeneracy by Heitler[6] and Serber.[7] Wigner[8] comes still closer to our problem in a treatment of proper vibrations of symmetrical systems, but in none of these are explicit results given for the transformation matrices which perform the reduction.

II. REDUCTION OF A REPRESENTATION BY IDEMPOTENT ELEMENTS

The reduction of a representation consists of: (a) looking for a unitary transformation T which brings all the representation matrices G_k into the "box-form," and (b) of considering these boxes as separate representations of the group $\mathfrak{G}$.

The essential idea of the method is that instead of first transforming by T and then considering the "boxes" separately, these two steps are taken in the reverse

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