connected with motion normal to the surface) as a function of the component of the **k** vector normal to the surface, in the neighborhood of Bragg reflection. We see that as soon as the damping is introduced, the discontinuity in energy disappears, and is replaced by a gradual transition from one branch of the curve to the other, very rapidly approaching a smooth curve as V/W becomes large. The reason why the energy perturbations become small is clear: they arise from interactions between the incident and diffracted beams, which are of equal magnitude at the Bragg angle in the undamped case. In the damped case, the diffracted beam is of much smaller intensity, and has much less effect on the energy. It is also plain why there is no discontinuity: there is damping for every value of the energy, and the wave functions are no longer separated into two different groups, the damped and the undamped ones. This becomes clear in Fig. 2, where we plot the damping constant α as a function of $E \sin^2 \theta$, for various values of V/W. For the case $V=0$, the damping constant goes to zero at the edges of the energy gap, but for $V \neq 0$ the damping merely decreases to a somewhat smaller value as we depart from the

conditions for Bragg reflection. Finally in Fig. 3 we plot the reflection coefficient, as a function of $E \sin^2 \theta$, for different values of V/W. It will be noted that increasing V, for a given W, always decreases the reflection, but the decrease is so much greater in the middle of the range than at the edges that the effect is to broaden the range. This is entirely analogous to the effect of damping on absorption bands in optics.

In closing, it should be pointed out that damped solutions of the type we have described, while they are appropriate for problems of electron diffraction and other problems in which electrons enter a crystal from outside, would not be suitable for discussing such problems as x-ray absorption, where the electrons are produced within the crystal. In particular, Kronig[4] has discussed the fine structure of x-ray absorption edges in terms of the energy gaps between bands. The present argument does not affect that use of the theory of energy gaps, and it should not be thought that the fact that we find that the gaps disappear indicates a difficulty with Kronig's theory.

[4] R. DeL. Kronig, Zeits. f. Physik **70**, 317 (1931); **15**, 191 (1932); **75**, 468 (1932).

Wave Functions in a Periodic Potential

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A new method for approximating the solutions of the problem of the motion of an electron in a periodic potential, as a crystal lattice, is suggested. The potential is supposed to be spherically symmetrical within spheres surrounding the atoms, constant outside. The wave function is expanded in spherical harmonics and radial solutions of the wave equation within the spheres, and in plane waves outside the spheres, joining continuously at the surface. A single unperturbed function consists of a single plane wave outside the spheres, together with the necessary spherical functions within the spheres. The matrix components of energy are set up between these unperturbed functions, and the secular equation set up. This equation involves the energy explicitly, and also implicitly through the ratio of the slope of the various radial functions to the functions themselves at the surfaces of the spheres, and must be solved numerically. It is hoped that the method will be useful for comparatively low energy excited electrons, for which the usual method of expansion in plane waves converges too slowly.

INTRODUCTION

THE first step in the solution of the wave mechanical problem of the motions of electrons in a crystal is to replace the other

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electrons by a static distribution of charge, and to treat the motion of one electron in this static, periodic potential field. The potential is of a particular sort: Near each nucleus, it approaches the potential near the corresponding atom as it would be if isolated from its neighbors, the

potential energy of an electron becoming negatively infinite as the nucleus is approached. The potential is spherically symmetrical around a nucleus. Between atoms, the potential varies much less rapidly, making a continuous joining with the potentials near the various nuclei. It involves no great inaccuracy to idealize this potential in the following way: we assume spheres surrounding the various nuclei, the sphere around the nth nucleus having a radius R_n (these radii will naturally be equal if the atoms are all alike). We suppose that within each sphere, the potential is spherically symmetrical, so that within the nth sphere it may be taken to be $U_n(|r-r_n|)$, where r is the radius vector to an arbitrary point, r_n the radius vector to the nth nucleus. Outside all the spheres, we suppose the potential to be constant, and to get continuity of the potential we assume that each of the potentials U_n reduces to this constant value at the radius R_n. In particular, to simplify matters, we shall adjust the zero of potential so that the constant region between atoms is at zero potential. The present paper is devoted to a general formulation of the solution of such a boundary value problem, on the assumption that the atoms are arranged in a regular crystal, and to methods of approximating to the solution.

We seek a solution of energy E. Within any one of the spheres, the wave equation is one of spherical symmetry. Then it can be solved quite rigorously by well-known methods. We separate variables in spherical coordinates with respect to the nucleus. If these coordinates are $|r-r_n|$, θ, ϕ, the wave function is

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{lm} P_l^{|m|}(\cos \theta) \exp (im\phi) u_{nl}(|r-r_n|). \quad (1)$$

Here u_{nl} satisfies the equation

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{du_{nl}}{dr}\right)+\left(\frac{l(l+1)}{r^2}+U_n\right)u_{nl}=Eu_{nl}. \quad (2)$$

The radial function u_{nl} of course depends on the energy E as a parameter, but we shall not indicate that in the notation, since it is understood throughout. There are two independent solutions of (2) for any energy value E. Of these, one is regular at the origin, the other regular at infinity, the two coinciding for the characteristic

values of E. Since in general we are not dealing with characteristic values of E, and since we are interested in the interior of the sphere, we choose the functions regular at the origin. Then any series of the form (1), with arbitrary coefficients A_{lm}, satisfies the differential equation within the sphere.

Of course, outside the sphere, and up to the shortest distance $|r-r_n|$ at which the radius touches the sphere of another atom, so that the problem is still spherically symmetrical, we can still use a solution of type (1). For larger distances than this, however, the problem ceases to be spherically symmetrical, and (1) is no longer a solution. We must then seek a different type of solution which will hold in the region between the spheres. It is known that a general solution of the whole problem is provided by a series of plane waves,

$$\sum_{k} v(\mathbf{k}) \exp (i\mathbf{k}\cdot r), \quad (3)$$

where only certain discrete wave vectors $\mathbf{k}$ are to be used. These vectors are to be defined as follows. We start with a certain vector $\mathbf{k}_0$, which is arbitrary. Then we may add to this any one of the infinite number of vectors $\mathbf{K}_i$ of the reciprocal lattice.[1] The series (3) is then a solution of the wave equation everywhere, if the $v(\mathbf{k})$'s satisfy the difference equations

$$(\mathbf{k}_0+\mathbf{K}_i)^2 v(\mathbf{k}_0+\mathbf{K}_i)+\sum_{\mathbf{K}_j} W(\mathbf{K}_j)v(\mathbf{k}_0+\mathbf{K}_i+\mathbf{K}_j)$$
$$=Ev(\mathbf{k}_0+\mathbf{K}_i). \quad (4)$$

Here, as elsewhere in this paper, it is assumed that atomic units are used (energies measured in units of the Rydberg energy, distances in terms of the radius of the Bohr hydrogen orbit, so that the energy of a free electron whose wave function is $\exp (i\mathbf{k}\cdot r)$ is k^2). The matrix component $W(\mathbf{K}_j)$ is the matrix component of the potential energy between the wave functions in question, normalized in such a way that $W(0)$ is the average potential energy through the cell,

[1] For references to this and other points, the reader may consult Mott and Jones, *Properties of Metals and Alloys* (Oxford, 1936); Fröhlich, *Elektronentheorie der Metalle* (Berlin, 1936), as well as the older reviews, by Sommerfeld and Bethe, in the *Handbuch der Physik*, second edition, Vol. 24 (1933), and by J. C. Slater, Rev. Mod. Phys. 6, 209 (1933). Numerous references to special papers can be found in the books and articles mentioned above.

or through the crystal. That is, $W(\mathbf{K}_j)$ is the integral of the potential energy, times

$$\exp\ (i(-\mathbf{k}_0-\mathbf{K}_i+\mathbf{k}_0+\mathbf{K}_i+\mathbf{K}_j)\cdot r)=\exp\ (i\mathbf{K}_j\cdot r),$$

throughout the cell, divided by the volume of the cell. If the volume of the cell is Ω, we then have

$$W(\mathbf{K}_j)=\frac{1}{\Omega}\sum_n \exp\ (i\mathbf{K}_j\cdot r_n)F_n(\mathbf{K}_j),\qquad(5)$$

where the summation is over the atoms of a single cell, and where

$$F_n(\mathbf{K}_j)=\int U_n(|r-r_n|)\exp\ (i\mathbf{K}_j\cdot|r-r_n|)d\tau,\quad(6)$$

where the integral is over the volume of the nth sphere. By expanding the exponential, it can be at once shown that

$$F_n(\mathbf{K}_j)=4\pi\int_0^{R_n} r^2 U_n(r)\frac{\sin\ (|\mathbf{K}_j|r)}{|\mathbf{K}_j|r}dr.\quad(7)$$

It has been customary to discuss electron diffraction on the assumption that the matrix component $W(\mathbf{K}_j)$ was the one responsible for the process in which a wave of wave number $\mathbf{k}_0+\mathbf{K}_i$ in the crystal changed over to a wave of wave number $\mathbf{k}_0+\mathbf{K}_i+\mathbf{K}_j$, by Bragg reflection from the planes normal to $\mathbf{K}_j$. The Eq. (5) then expresses this quantity in a way analogous to the x-ray structure factor, and (7) gives the form factor of the nth atom, analogous to the x-ray form factor. The equations (4) are then analogous to the equations in the dynamical theory of x-ray diffraction,[2] and are the ones which must be solved if we wish to set up the whole solution for a diffracted beam.

It might be asked, since (3) gives a complete solution of our present problem, why is it necessary to go further? The answer is that the series (3) converges very slowly. The wave function in the neighborhood of a nucleus corresponds to a rapidly moving electron, and it changes phase in very short distances, corresponding to short wave-lengths. Thus in the series (3), we must have appreciable coefficients of the terms even of very high $\mathbf{k}$ values, such

that k^2 for these terms is comparable with the energy of the x-ray terms of the atom. Attempts to solve the difference Eq. (4) directly, made by the writer and Dr. Millman, as well as similar attempts made by others, have convinced us that the use of this series is impractical for obtaining wave functions and energy levels of low energy electrons, valuable though it is for the proof of general theorems and for high energy electrons. In spite of the objections to the use of (3) for practical purposes, still the whole wave function can be expanded in such a series of plane waves, and in particular the part of the function outside the atomic spheres can be so expanded. We shall then assume that the wave function is expanded in series (3) outside the spheres, and in the series (1) inside the spheres. We shall do this in the following way. We set up separate unperturbed functions, each equal to a plane wave outside the spheres, and to a series of type (1) inside the spheres, joining continuously on the surface of the spheres. Then we write the whole solution as a linear combination of such unperturbed functions, determining the coefficients essentially by perturbation theory. But now we may hope that the series represented by this linear combination will converge much more rapidly than the series (3). For the lack of convergence of (3), as we have mentioned, arises from the difficulty of expanding the wave function near the nucleus in plane waves. In our method, the wave function near the nucleus is automatically taken care of, and only the outer part, which really does not depart much from a plane wave anyway, is left to be expanded. Each of our functions can be regarded as an expansion in terms of plane waves, containing all the terms necessary to describe the function near the nucleus, but with correct phase relations so that it reduces to a single plane wave outside the spheres. We shall now proceed with the mathematical formulation of these waves, and shall set up the matrix components of energy between them and the resulting secular equation for determining the energy.

MATHEMATICAL FORMULATION OF THE PROBLEM

Let ψ_i be a function which equals $\exp\ (i\mathbf{k}_i\cdot r)$ outside the various spheres, and which joins

[2] See for instance M. von Laue, Ergeb. d. Exakt. Naturwiss. **10**, 133 (1931); also *Die Interferenzen von Röntgen- und Elektronenstrahlen* (Berlin, 1935).

continuously at the surface of each sphere onto a solution of the central field problem, corresponding to the energy E, within that sphere. By a well-known expansion, the exponential $\exp(i\mathbf{k}_i \cdot r)$ can be expanded in spherical coordinates about any point. In particular we expand about the nucleus of the nth atom, at r_n. Then we have

$$\exp(i\mathbf{k}_i \cdot r) = \exp(i\mathbf{k}_i \cdot r_n) \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (2l+1)i^l$$

$$\times j_l(k_i|r-r_n|) \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\cos\theta)$$

$$\times P_l^{|m|}(\cos\theta_i) \exp im(\phi-\phi_i). \quad (8)$$

Here $(|r-r_n|)$, θ, ϕ are polar coordinates about r_n as a pole, and θ_i, ϕ_i are polar coordinates giving the direction of the wave normal $\mathbf{k}_i$. The functions $j_l(kr)$ are spherical Bessel functions,[3] satisfying the differential equation

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dj_l}{dr}\right) + \frac{l(l+1)}{r^2}j_l = k^2 j_l. \quad (9)$$

They are finite or zero at the origin, and are so normalized that

$$\lim_{z=0} j_l(z) = \frac{z^l}{1\cdot3\cdot5\cdots(2l+1)}. \quad (10)$$

By comparing terms, we can then at once determine the coefficients A_{lm} of the expansion (1) of the function inside the sphere, so as to make the function continuous at the surface of the sphere. We at once find that inside the sphere we have

$$\psi_i = \exp(i\mathbf{k}_i \cdot r_n) \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (2l+1)i^l \frac{j_l(k_iR_n)}{u_{nl}(R_n)}$$

$$\times u_{nl}(|r-r_n|) \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\cos\theta)$$

$$\times P_l^{|m|}(\cos\theta_i) \exp im(\phi-\phi_i). \quad (11)$$

The value (11) inside the sphere at r_n, together with the expression $\exp(i\mathbf{k}_i \cdot r)$ outside all the spheres, determines the function ψ_i completely.

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[3] For a collection of formulas and tables regarding these functions, see P. M. Morse, *Vibration and Sound* (New York, 1936), pp. 246, 247, 335.

Having formulated our various unperturbed wave functions, we must set up the perturbation problem between them. We assume that the exact solution of our problem is expressed as a series

$$\sum_i v_i \psi_i, \quad (12)$$

where the v_i's are constants. Then by the general methods of quantum mechanics the series (12) will be a solution of the problem if the equations

$$\sum_j (H-E)_{ij} v_j = 0 \quad (13)$$

are satisfied for all values of i. Here H is the energy operator, E the characteristic energy, and

$$(H-E)_{ij} = \int \psi_i^*(H-E)\psi_j d\tau, \quad (14)$$

the matrix component of the operator $H-E$ between the two states in question. In order to satisfy the Eq. (13), we must as usual have the determinant of coefficients $(H-E)_{ij}$ equal to zero. We now compute these matrix components.

We must notice one point at the outset. Though our function ψ_i is everywhere continuous, its first derivative is in general not continuous at the surfaces of the various spheres, where the functions join. We may regard the object of our perturbation problem to be the setting up of a combination of functions which not only is continuous but has a continuous slope. But now the kinetic energy operator demands special treatment for a function with discontinuous slope. Two forms of integral are often seen for computing the kinetic energy. The more common one is $\int \psi_i^*(-\nabla^2)\psi_j d\tau$, but the other and more fundamental one is $\int \text{grad } \psi_i^* \cdot \text{grad } \psi_j d\tau$. Ordinarily one can show by integration by parts that one equals the other, but if the function has anywhere a discontinuous slope, they are no longer equal, but differ by a surface integral over the surface of discontinuity. In this case the second, more fundamental form is the correct one, as it is the one which directly enters the variation principle from which Schrödinger's equation is derived. If there is any doubt about this question, it can be easily shown that using the first formula we must add a surface integral, for a discontinuous first derivative amounts to

an infinite second derivative on the surface, and integrates to a finite contribution over the surface. This contribution can be found by a limiting process in which the change of slope occurs in smaller and smaller ranges of variable. We shall use the opposite treatment, however, as being more fundamental, starting with the second integral, but eventually reducing part of our result to a surface integral over the surface of discontinuity.

If U is the potential energy, equal to U_n within the nth sphere, and zero outside the spheres, we then have

$$(H-E)_{ij} = \int (\text{grad } \psi_i^* \cdot \text{grad } \psi_j$$
$$+ (U-E)\psi_i^*\psi_j)d\tau. \quad (15)$$

We shall carry out the integration in two parts: first over the region outside the spheres, then over the spheres. Outside the spheres, $\psi_i = \exp i(\mathbf{k}_i \cdot \mathbf{r})$, $U=0$. Then grad $\psi_i^* \cdot$ grad ψ_j $= (\mathbf{k}_i \cdot \mathbf{k}_j) \exp i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}$. To find the integral outside the spheres, we integrate over the whole space, and subtract the integral over the spheres. It is easily shown that the integral over each cell will be equal, so that we shall carry out all our integrations just over a single cell, which is assumed to be of volume Ω. Furthermore, to get agreement with (5), we shall divide our integrals by Ω, so that they will represent averages over the volume. Now the relation between the vectors $\mathbf{k}_i$ and $\mathbf{k}_j$ is such that $\exp i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}$ integrates to zero over the cell unless $i=j$. Thus we have

$$\frac{1}{\Omega} \int_{\text{cell}} (\text{grad } \psi_i^* \cdot \psi_j - E\psi_i^*\psi_j)d\tau$$
$$= (\mathbf{k}_i \cdot \mathbf{k}_j - E)\delta_{ij}, \quad (16)$$

where $\delta_{ij}=1$ if $i=j$, 0 if $i \neq j$. Within the nth sphere, we have the contribution

$$\frac{1}{\Omega}(\mathbf{k}_i \cdot \mathbf{k}_j - E) \exp i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}_n$$

$$\times \int_{\text{sphere}} \exp i(\mathbf{k}_j - \mathbf{k}_i) \cdot (\mathbf{r} - \mathbf{r}_n)d\tau$$

$$= (\mathbf{k}_i \cdot \mathbf{k}_j - E) \exp i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}_n$$

$$\times \frac{4\pi R_n^2}{\Omega} \frac{j_1(|\mathbf{k}_j - \mathbf{k}_i| R_n)}{|\mathbf{k}_j - \mathbf{k}_i|}. \quad (17)$$

The terms (17) are to be subtracted from (16) to get the whole contribution to $(H-E)_{ij}$ from the region outside the spheres.

Next we must find the contributions to $(H-E)_{ij}$ from the interiors of the spheres. In this case it is more convenient to integrate (15) by parts according to Green's theorem, obtaining for the nth sphere

$$\frac{1}{\Omega} \int \psi_i^*(-\nabla^2 + U_n - E)\psi_j d\tau$$

$$+ \int \psi_i^*(\partial \psi_j/\partial n)dS, \quad (18)$$

where n is the outer normal in the surface integral. The volume integral vanishes on account of (2). For the surface integral, we use the form (11) for the functions, differentiate the radial part of ψ_j with respect to r, and integrate over the angles, obtaining

$$\exp i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}_n \frac{4\pi R_n^2}{\Omega} \sum_{l=0}^{\infty} (2l+1)P_l(\cos \theta_{ij})$$

$$\times j_l(k_i R_n) j_l(k_j R_n) u_{nl}'(R_n)/u_{nl}(R_n). \quad (19)$$

We must now combine (16), (17), and (19), obtaining

$$(H-E)_{ij} = (\mathbf{k}_i \cdot \mathbf{k}_j - E)\delta_{ij}$$

$$+ \frac{1}{\Omega} \sum_n \exp i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}_n F_{nij},$$

where

$$F_{nij} = 4\pi R_n^2 \left\{ -(\mathbf{k}_i \cdot \mathbf{k}_j - E) \frac{j_1(|\mathbf{k}_j - \mathbf{k}_i| R_n)}{|\mathbf{k}_j - \mathbf{k}_i|} \right.$$

$$+ \sum_{l=0}^{\infty} (2l+1)P_l(\cos \theta_{ij}) j_l(k_i R_n) j_l(k_j R_n)$$

$$\left. \times u_{nl}'(R_n)/u_{nl}(R_n) \right\}. \quad (20)$$

The resemblance to Eqs. (5) and (6) is plain; F_{nij} plays the part of a form factor in the present theory, in place of the expression $F_n(K_j)$ of (6) and (7).

Having set up the matrix components $(H-E)_{ij}$ in (20), we must next solve the secular equation $\Delta|(H-E)_{ij}| = 0$. Of course, we cannot solve this exactly, and we must look for methods of approximation. It is a more difficult secular

equation than one usually meets. In the first place, the functions are not orthogonal, so that as we see from (20) the energy E appears explicitly in the nondiagonal terms. But worse than this, the energy appears implicitly in the expressions $u_{nl}'(R_n)/u_{nl}(R_n)$, which depend on the energy, and which appear both in diagonal and in nondiagonal terms. The only practical method of handling the determinant under the circumstances would seem to be to compute and plot it as a function of E, and find the intersections with the axis graphically. Rather than using the determinant as it stands, it would be more convenient to use a well-known device, and divide all elements of the ith row by the diagonal term $(H-E)_{ii}$. Then the diagonal terms of the new determinant are unity, and the nondiagonal elements are very large for those particular rows for which $(H-E)_{ii}$ is very small, while they are small in other cases. To a first approximation, then, we can consider only the particular rows for which $(H-E)_{ii}$ is small, and the expansion of the determinant becomes very simple. Further approximations can be made by expanding in power series in the small terms. This method amounts to applying a perturbation theory in which we treat the few states whose unperturbed energy is near the energy we are interested in by the perturbation method for degenerate systems, and treat more distant states by the power series method. It should make it possible to get a satisfactory approximation to the whole shape of the curve, and to find its zeros, to a fair approximation, though with considerable labor. The determinant plotted as a function of E will have many intersections with the axis, and may be expected to have roughly the form of a tangent curve, but of course with many local variations. A separate calculation, of course, must be made for each value of the momentum $\mathbf{k}_0$ (that is, at each point of the first or reduced Brillouin zone in $\mathbf{k}$ space). At certain points in this zone there will be symmetry properties which will allow us at once to factor the determinant, so that as

with other methods of approximation it will be easier to get the solution in directions having simple symmetry properties than in arbitrary directions.

In conclusion, we may suggest the cases where this method is likely to be particularly useful. These will obviously be the cases where one term of our series is itself a fairly good approximation, so that the correction terms are small. That is, they are the cases where the real wave function outside the spheres is very close to a single plane wave. Such cases are known to exist for the conduction levels of the alkali metals.[4] The method of Wigner and Seitz, as applied by the author to this case, is satisfactory for the conduction levels themselves, but has been shown by Shockley[5] to become very bad for levels even a few volts above the occupied levels. This is natural, for that method assumes an expansion throughout the whole cell in a very few spherical harmonics. But as we see from (8), a whole series of spherical harmonics is needed to expand a plane wave, and the higher terms become important for rather low energies, so that if we break off the series after a few terms, as the earlier method does, the results will be very inaccurate except for very low energies. The present method, however, with its infinite series of spherical harmonics, would not have this difficulty. It is not unlikely that if it were applied to the case of the alkalies, it would show that the excited levels for some distance up are much more like free electrons than the calculations mentioned in reference 4 would indicate, so that it would form a good approximation for this case. It is to be hoped, however, that the present method of approximation will have a wider range of application than this, for it should in principle suffice for finding any energy levels, and the reasons we have suggested in proposing it lead one to hope that it will be practical in its actual application.

[4] For application to sodium, see J. C. Slater, Phys. Rev. 45, 794 (1934).
[5] W. Shockley, Phys. Rev. 51, 379 (1937).