MAY 15, 1937 PHYSICAL REVIEW VOLUME 51

Damped Electron Waves in Crystals

J. C. SLATER*
Institute for Advanced Study, Princeton, New Jersey

(Received March 24, 1937)

Electrons in solids, as in electron diffraction, suffer inelastic impacts if their energy is great enough to exceed the resonance energy of the atoms of the crystal, resulting in strong damping of the electron beams, with consequent broadening of the reflected peaks about the Bragg scattering angles, and reduction of the reflection coefficient. The problem is discussed mathematically, on the basis of the conventional theory of electron diffraction, by introducing an empirical damping constant in the form of a pure imaginary term in the potential. It is shown that such a constant leads to damped waves of the required sort, and the equations for energy and reflection coefficient are set up. The results are qualitatively of the sort necessary to explain the observations, though no marked asymmetry in the reflected peaks is predicted. Presumably the observed asymmetries arise, as Harding has suggested, from irregular spacings of the atomic planes near the surface. One interesting result of the theory is that the sharp distinction between allowed energy bands and forbidden gaps, which is found in the theory of undamped electrons in periodic lattices, is lost, for all waves are more or less damped.

1. INTRODUCTION

THE conventional theory of solids, developed particularly for metals, assumes as a first approximation that the electrons move in a periodic static potential field. The solution of this problem yields modulated wave functions, whose value is multiplied by a factor exp $(i\mathbf{k}\cdot\mathbf{R})$ in going from the neighborhood of one atom to a corresponding point in another unit cell, if $\mathbf{R}$ is the vector distance from one point to the other, $\mathbf{k}$ a constant. Such solutions exist for most energies, if the electron is in a high energy level, though there are certain gaps in the energy, in which only damped waves exist as solutions of the problem, one component of the vector $\mathbf{k}$ becoming pure imaginary. On account of these modulated solutions, it is generally supposed that electrons move freely through a crystal lattice, unless they happen to lie in the region of the energy gaps, in which case it is supposed that they are reflected from the crystal, accounting for the Bragg reflection in the problem of electron diffraction.

This naive picture, in which electrons either are freely transmitted or totally reflected, is, of course, far from agreeing with the experimental facts. The most conspicuous difference between electron and x-ray diffraction is the great extinction of electron beams in solids.[1] Furthermore, electrons not only fail to penetrate more than a few atomic layers, but the reflection coefficient at the Bragg angle is only of the order of one percent, instead of unity as the simple theory predicts, and the angular range over which there is reflection is of the order of ten times the range predicted by the simple theory. These are the sort of changes in reflection which would be expected if the electron wave were rapidly extinguished in the crystal. Such extinction is, of course, to be expected on general grounds. An electron moving through atoms in a gas will suffer only elastic collisions, with small loss of energy, if it has an energy smaller than the resonance energy of the atoms of the gas. At higher energies, however, it will suffer inelastic collisions, raising electrons of the gas atoms to higher energy, and losing energy itself. This results in a rapid extinction of beams of electrons of high energy, of a type not met with slow electrons. Of course, the electrons are not lost, only slowed down; but if we are considering only electrons of approximately the incident energy, we shall consider them lost to the beam. In a similar way, the conduction electrons in a metal can have only elastic impacts, losing a little energy to the lattice vibrations, but electrons with more than a few volts energy above the conduction levels can have inelastic impacts, losing part of their energy, raising conduction or x-ray electrons to excited energy levels in the lattice. This is observed experimentally; if electrons of a few hundred or more volts are shot

---

* On leave from the Massachusetts Institute of Technology, Cambridge, Massachusetts.

[1] For experimental information about electron diffraction, a useful reference is Beeching, *Electron Diffraction* (Methuen, London, 1936).

into a metal, two groups of secondary electrons are emitted: those which have lost a few volts, and happen to have their direction changed so that they emerge from the metal, and slow electrons, which have been raised from conduction levels by the collisions. The theory of such inelastic impacts has recently been discussed by Rudberg and the writer.[2]

A complete treatment of the inelastic damping of excited electron waves, along these lines, would be very complicated. In the present paper, we shall be content with a simpler task. We shall show that an empirical damping constant can be introduced, and that solutions of the wave mechanical problem including this damping give exponentially damped waves, of the sort to be expected intuitively. Furthermore, we shall set up the conditions for electron diffraction in the usual case, and shall show that the decreased reflection coefficient and broadened beam which are found experimentally are adequately described by the theory. We shall also find certain interesting consequences relating to the theory of metals. Thus, the distinction between the allowed and forbidden ranges of energy becomes lost when all waves are damped, and the discontinuities of energy which are such a characteristic feature of the theory with undamped waves become rapidly removed when even a small damping is introduced.

The dynamical theory of electron diffraction has been recently discussed by Harding,[3] using an extension of Darwin's method for x-ray diffraction, in which the scattering from each plane of atoms is considered separately. He attributes most of the broadening to irregularity of spacing of the few planes of atoms near the surface of the crystal, though he also considers absorption. Such an irregularity is undoubtedly responsible for many of the anomalies observed in electron diffraction, in particular for the asymmetry of beams, and Harding's method undoubtedly is the most practicable way of handling it. The object of the present paper is to point out, however, that the absorption can be treated by the conventional theory as well, with tolerably simple results, and to suggest that perhaps it has a more important role than Harding believes. Harding's statement, in particular, that absorption actually decreases the breadth of the beams, seems very questionable; the present theory indicates just the sort of broadening which we should expect on the basis of other types of damped waves with which we are familiar.

2. Damped Waves in a Region of Constant Potential

A damping constant can be formally introduced into Schrödinger's equation by the device of adding a pure imaginary term to the potential energy, just as in optics a pure imaginary term in the refractive index results in damping. In this section we shall ask how to handle such a term in a region of constant potential. That is, we shall consider the modified Schrödinger equation

$$-\nabla^2\psi+(U-iV)\psi=i\partial\psi/\partial t, \tag{1}$$

where U is the real potential, $-iV$ the damping term, both constants. The sign of the damping term is chosen so that it will result in disappearance rather than appearance of charge. The units in (1) are atomic units; that is, distances are measured in terms of the radius of the first Bohr orbit of hydrogen, energies in terms of the Rydberg energy, frequencies in terms of 2π times the Rydberg frequency. First we shall show that (1) really leads to a continuous disappearance of charge. To do this, we compute the time rate of change of the charge density $\psi^*\psi$, plus the divergence of the current density, which in these units is $i(\psi \text{ grad } \psi^*-\psi^* \text{ grad } \psi)$, and we shall show that the result is negative, rather than zero as it would be if the equation of continuity held. When we compute this quantity, we substitute from Eq. (1), and from the similar equation for the complex conjugate ψ^*, in which we note that the term iV must appear with positive rather than negative sign, and we find in an entirely conventional way

$$(\partial/\partial t)(\psi^*\psi)+\text{div } i(\psi \text{ grad } \psi^*-\psi^* \text{ grad } \psi) = -2V\psi^*\psi. \tag{2}$$

That is, the density represented by $\psi^*\psi$ is destroyed at a rate given by $-2V$ times the density itself. We should emphasize again, of course, that as we use the equation we shall be working only with electrons of a given energy, and by their destruction we mean merely their

---

[2] E. Rudberg and J. C. Slater, Phys. Rev. **50**, 150 (1936).

[3] J. W. Harding, Phil. Mag. **23**, 271 (1937).

inelastic scattering to another energy, so that they are removed from the particular energy beam we are considering.

Two types of solution of (1) are particularly important. In the first place, we can find solutions sinusoidal in space, but damped in time. Thus by substitution we see at once that

$$\psi = \exp(-Vt - iEt + i\mathbf{k}\cdot\mathbf{r}) \tag{3}$$

is a solution of the equation, where $\mathbf{k}$ is an arbitrary real vector, $\mathbf{r}$ the radius vector, provided

$$E = k^2 + U, \tag{4}$$

which in these units equals the kinetic energy (k^2, where $\mathbf{k}$ is essentially the momentum) plus the potential energy U. For this type of solution, the divergence of the current in (2) is zero, but if we form $\psi^*\psi$ we have $\exp(-2Vt)$, which obviously satisfies Eq. (2). The quantity $1/2V$ then plays the part of the relaxation time for the charge density, $1/V$ the relaxation time for the wave function. Such a solution would be appropriate, for instance, in a hypothetical problem in which electrons were raised to an excited state all through the interior of the volume by some sudden action, such as a sudden burst of x-rays or other radiation capable of penetrating the volume, and then were allowed to die down. We note that in such a case the damping constant does not affect the function of space at all, but only the time variation of the function.

The second type of solution is the one which concerns us in electron diffraction and similar problems. Here there is a steady state as far as time is concerned. Electrons are being fed into the crystal from the outside at a rate fast enough to balance their loss by inelastic impact, plus their reflection to the outside. We must then look for a solution which is purely exponential in time, but damped in space. Thus

$$\psi = \exp(-iEt - \boldsymbol{\alpha}\cdot\mathbf{r} + i\mathbf{k}\cdot\mathbf{r}), \tag{5}$$

where $\boldsymbol{\alpha}$, $\mathbf{k}$ are arbitrary vectors, is a solution of (1), provided

$$E = k^2 + U - \alpha^2 + 2i(\boldsymbol{\alpha}\cdot\mathbf{k}) - iV, \tag{6}$$

with a real E. Eq. (6) really involves two statements:

$$E = k^2 + U - \alpha^2, \tag{6a}$$

$$2(\boldsymbol{\alpha}\cdot\mathbf{k}) = V. \tag{6b}$$

Eq. (6b) determines the component of the damping vector $\boldsymbol{\alpha}$ in the direction of the propagation vector $\mathbf{k}$, but leaves its component at right angles undetermined, and (6a) determines the energy in terms of $\boldsymbol{\alpha}$ and $\mathbf{k}$. In any problem where a beam of electrons is entering a region over a plane surface, and is being damped inside, the direction of $\boldsymbol{\alpha}$ must of course be chosen normal to the surface, so that the boundary conditions with a beam of constant intensity outside can be satisfied. Equality of energy between the inside and outside beams must also be maintained, as well as equality of the tangential component of $\mathbf{k}$. These provide enough conditions to fix the vectors $\mathbf{k}$ and $\boldsymbol{\alpha}$ within the damping medium. It is to be noticed that even in a nonabsorbing medium, $V=0$, we can still have damped waves, as we know by the optical analogy of total reflection, but (6b) tells us that the damping must be at right angles to the propagation vector. Such waves have not been useful in electron theory, because electrons are bent toward the normal on entering a crystal, so that there is no total reflection at the surface between the crystal and air.

3. Damped Waves in a Periodic Potential Field

We now set up the problem of damped waves in a periodic potential field. We assume the same Schrödinger Eq. (1) as before, only now we assume that

$$U = \sum_{\mathbf{K}} W(\mathbf{K}) \exp -i(\mathbf{K}\cdot\mathbf{r}), \tag{7}$$

where the vectors $\mathbf{K}$ are the vectors in the reciprocal lattice corresponding to the crystal in question, and the W's are the Fourier coefficients of the potential. We continue to regard the damping term V as constant; but the results which we find hold without essential change if V is also a periodic function. Now we ask for a solution of (1) with the potential (7), in the form of a sinusoidal function of time, multiplied by a damped modulated function of position. That is, we try to find a solution

$$\psi = \exp(-iEt - \boldsymbol{\alpha}\cdot\mathbf{r} + i\mathbf{k}\cdot\mathbf{r})u(\mathbf{r}), \tag{8}$$

where $u(\mathbf{r})$, a periodic function of position, can be expanded as

$$u(\mathbf{r})=\sum_{\mathbf{K}}A_{\mathbf{K}}\exp i(\mathbf{K}\cdot\mathbf{r}). \qquad (9)$$

When the function (8) is substituted in the differential equation, we find the condition

$$\exp(-iEt-\boldsymbol{\alpha}\cdot\mathbf{r}+i\mathbf{k}\cdot\mathbf{r})\sum_{\mathbf{K}}\exp(i\mathbf{K}\cdot\mathbf{r})\sum_{\mathbf{K}'}C(KK')A_{\mathbf{K}'}=0, \qquad (10)$$

where

$$C(KK')=((\mathbf{k}+\mathbf{K})^2-\alpha^2+2i(\boldsymbol{\alpha}\cdot(\mathbf{k}+\mathbf{K}))-iV-E)\delta_{\mathbf{K},\mathbf{K}'}+W(\mathbf{K}'-\mathbf{K}). \qquad (11)$$

We can satisfy Eq. (10) by making the last summation equal to zero:

$$\sum_{\mathbf{K}'}C(KK')A_{\mathbf{K}'}=0, \text{ for each value of } \mathbf{K}. \qquad (12)$$

In order to satisfy this infinite set of simultaneous homogeneous linear equations, it is necessary as usual to make the determinant of coefficients $C(KK')$ equal to zero:

$$\Delta|C(KK')|=0. \qquad (13)$$

Eq. (13) provides a secular equation for E, to be solved subject to the condition that E is real. Just as in the case of constant potential, we have enough constants at our disposal to satisfy both conditions. Thus if $\mathbf{k}$ is determined, and the direction of the damping vector $\boldsymbol{\alpha}$ is fixed, we have two constants, the energy E and the magnitude of $\boldsymbol{\alpha}$, with which to satisfy the secular equation and the additional requirement that E be real. Or if, as in the electron diffraction case, the energy, the two components of $\mathbf{k}$ parallel to the surface of the crystal, and the direction of $\boldsymbol{\alpha}$ are determined, we have the normal component of $\mathbf{k}$ and the magnitude of $\boldsymbol{\alpha}$ at our disposal. In practice, the calculation seems to be simplest when $\mathbf{k}$ and the direction of $\boldsymbol{\alpha}$ are fixed, and E and the magnitude of $\boldsymbol{\alpha}$ are found by the equations.

We shall now consider the solution of the secular Eq. (13) in simple special cases. As in the conventional theory of electron diffraction, we shall assume that far from a Bragg reflection one term of the summation (9) is sufficient, and that near such a reflection two terms must be used. If only one term is to be used, the condition becomes at once

$$(\mathbf{k}+\mathbf{K})^2-\alpha^2+W(0)+2i(\boldsymbol{\alpha}\cdot(\mathbf{k}+\mathbf{K}))-iV-E=0,$$

exactly like Eq. (6) for the case of constant potential, which we have already discussed. We shall then concentrate on the case where two waves are to be used. To fix our attention on a definite problem, we shall take the reflecting planes parallel to the surface of the crystal, the case of regular reflection, though the treatment is carried out in an entirely analogous way in other cases. Then $\mathbf{K}$ is normal to the surface, pointing out of the crystal, and $\boldsymbol{\alpha}$ must be assumed normal, and pointing into the crystal. If $\mathbf{k}_n$ is the normal component of $\mathbf{k}$, pointing into the crystal, the secular equation then becomes

$$\begin{vmatrix} k^2-\alpha^2+W(0)+2i\boldsymbol{\alpha}\mathbf{k}_n-iV-E & W(\mathbf{K}) \\ W(\mathbf{K}) & k^2-\alpha^2+W(0)+2i\boldsymbol{\alpha}\mathbf{k}_n-iV-E-2\mathbf{k}_n|\mathbf{K}|+K^2-2i\boldsymbol{\alpha}|\mathbf{K}| \end{vmatrix}=0, \qquad (14)$$

where we have assumed the incident propagation vector to be $\mathbf{k}$, the reflected one $\mathbf{k}+\mathbf{K}$. We shall have Bragg reflection when $\mathbf{k}_n-|\mathbf{K}|/2=0$. Let us then let

$$\mathbf{k}_n-|\mathbf{K}|/2=\delta, \qquad (15)$$

where δ is a small quantity vanishing in the Bragg case. Expanding the determinant (14), and solving the quadratic, we then have

$$E=k^2-|\mathbf{K}|\delta+W(0)-\alpha^2+2i\boldsymbol{\alpha}\delta-iV \pm[W^2(\mathbf{K})-\alpha^2K^2+K^2\delta^2+2i\boldsymbol{\alpha}K^2\delta]^{\frac{1}{2}}. \qquad (16)$$

In practice, it is more convenient to express this in terms of the glancing angle of incidence θ. Then if $\mathbf{k}_t$ is the tangential component of $\mathbf{k}$, which by the boundary conditions must be equal inside and outside the crystal, we must have

$$E\cos^2\theta=\mathbf{k}_t^2. \qquad (17)$$

We then subtract $E\cos^2\theta$ from each side of (16), leaving $E\sin^2\theta$ on the left, and for the first two terms on the right $k^2-|\mathbf{K}|\delta-k_t^2=k_n^2-|\mathbf{K}|\delta=(\mathbf{K}/2)^2+\delta^2$. Eq. (16), with these changes, then becomes an equation for $E\sin^2\theta$. We still must impose the condition that E must be real. The radical in (16) is complex. Its imaginary term

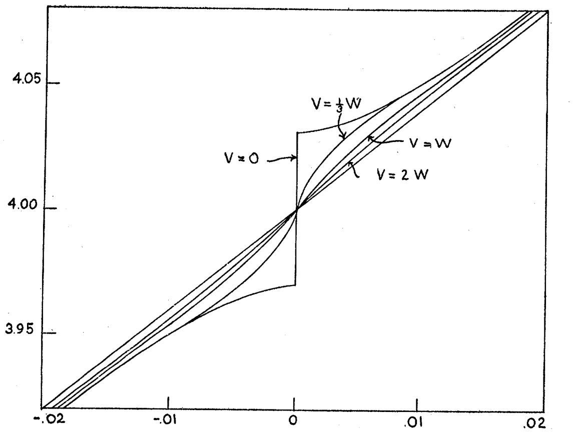

FIG. 1. $E\sin^2\theta$, component of energy normal to surface, as function of δ, component of momentum normal to surface, both in atomic units, for different values of V/W, the ratio of the damping constant to the energy perturbation between incident and reflected beams.

must cancel the other imaginary terms in the equation, and its real term alone is left to contribute to E. Thus we have

$$\pm[W^2(\mathbf{K})-\alpha^2K^2+K^2\delta^2+2i\boldsymbol{\alpha}K^2\delta]^{\frac{1}{2}} \\ =-2i\boldsymbol{\alpha}\delta+iV+f, \quad (18)$$

where f is the real part of the radical. We square both sides of (18), and equate real and imaginary parts separately. From the imaginary part we find

$$f=\boldsymbol{\alpha}K^2\delta/(V-2\boldsymbol{\alpha}\delta). \quad (19)$$

The real part gives a quadratic for $\boldsymbol{\alpha}$. Its solution is

$$\boldsymbol{\alpha}=-\frac{2\delta V}{K^2-4\delta^2} \\ \pm\left[\frac{W^2+V^2+K^2\delta^2-f^2}{K^2-4\delta^2}+\left\{\frac{2\delta V}{K^2-4\delta^2}\right\}^2\right]^{\frac{1}{2}}. \quad (20)$$

We could eliminate f between (19) and (20) to get an equation for the damping constant $\boldsymbol{\alpha}$, but the resulting equation is of the fourth degree and cannot be conveniently solved. It is much more practicable to solve Eqs. (19) and (20) simultaneously for f and $\boldsymbol{\alpha}$ by successive approximations, putting a trial value of $\boldsymbol{\alpha}$ in (19), computing a corrected $\boldsymbol{\alpha}$ from this f by (20), and repeating the process until the final value equals the initial one. With a little practice, this calculation proves to be very simple.

We note that Eq. (20) gives two solutions for $\boldsymbol{\alpha}$. One of these is in general positive and the other negative, and to get a wave which is damped as we go into the crystal we must take the positive root. This determines a single value for f, so that the double valued solution appearing in (16) is not really of physical significance. When we have found the appropriate value of f, we then find for the energy, from (16) and the changes made in that equation,

$$E\sin^2\theta=(K/2)^2+\delta^2+W(0)-\alpha^2+f. \quad (21)$$

Having found the energy, we can now use Eqs. (12) to find the reflection coefficient. Thus if A_0 is the incident amplitude, $A_{\mathbf{K}}$ the reflected amplitude, we have

$$A_0W(\mathbf{K})+A_{\mathbf{K}}(k^2-\alpha^2+W(0)+2i\boldsymbol{\alpha}\mathbf{k}_n \\ -iV-E-2\mathbf{k}_n|\mathbf{K}|+K^2-2i\boldsymbol{\alpha}|\mathbf{K}|)=0. \quad (22)$$

When we substitute for E, this becomes

$$A_0W(\mathbf{K})-A_{\mathbf{K}}(|\mathbf{K}|\delta+f \\ +i(V+\boldsymbol{\alpha}|\mathbf{K}|-2\boldsymbol{\alpha}\delta))=0. \quad (23)$$

From (23) we can then find the ratio $A_{\mathbf{K}}/A_0$ of reflected to incident amplitude, and squaring the magnitude of this we have the reflection coefficient

$$R=W^2(\mathbf{K})/((|\mathbf{K}|\delta+f)^2 \\ +(V+\boldsymbol{\alpha}|\mathbf{K}|-2\boldsymbol{\alpha}\delta)^2). \quad (24)$$

When V is of the same order of magnitude as W, numerical calculations must be made by the method we have sketched. If V^2 is large compared with W^2, however, W^2 can be neglected in the radical in (18), and the expressions simplify greatly. Eq. (18) then becomes

$$\pm|\mathbf{K}|(\delta+i\boldsymbol{\alpha})=-2i\boldsymbol{\alpha}+iV+f,$$

from which

$$f=\pm|\mathbf{K}|\delta, \quad \boldsymbol{\alpha}=V/(\pm|\mathbf{K}|+2\delta). \quad (25)$$

Eqs. (25) correspond to (19) and (20) in the general case. Since $|\mathbf{K}|$ is a large quantity, δ small, we see that to have $\boldsymbol{\alpha}$ positive we must choose the upper signs. Then the expression for the energy becomes

$$E\sin^2\theta=(|\mathbf{K}|/2+\delta)^2+W(0)-\alpha^2, \quad (26)$$

and the reflection coefficient is

$$R=(W/2)^2/((\mathbf{K}\delta)^2+(V\mathbf{K}/(\mathbf{K}+2\delta))^2). \quad (27)$$

For all ordinary cases, the line is narrow enough so that the ratio $\mathbf{K}/(\mathbf{K}+2\delta)$ can be replaced by unity. Then finally we have

$$R=(W/2)^2/((\mathbf{K}\delta)^2+V^2). \qquad (28)$$

The expression (28) is a typical resonance form of curve. The reflection coefficient at the maximum, $\delta=0$, is

$$\mathrm{R}_{\max}=(W/2V)^2, \qquad (29)$$

and the half-breadth, the difference of the two values of δ for which R has half its maximum value, is

$$\delta_2-\delta_1=2V/\mathbf{K}. \qquad (30)$$

It is more interesting to compare the breadth with the breadth which the totally reflecting region would have in the theory without damping. To do this, we must use $E\sin^2\theta$ rather than θ as independent variable. We find at once that

$$(E\sin^2\theta)_2-(E\sin^2\theta)_1=2V. \qquad (31)$$

The corresponding quantity for the totally reflecting region is $2W$. Hence the half-breadth with damping constant V is (V/W) times the width of this totally reflecting region. If the observed half-breadth is 10 times this theoretical totally reflecting breadth, then V is 10 times W, we are in the region where this approximation is valid, and the maximum reflection coefficient should be $(1/20)^2=1/400$, which is of the order of magnitude of the observed value. One has something of the impression, however, in comparing this theory with published statements of reflection coefficient and breadth, that for a given reflection coefficient the theory gives a somewhat narrower line than is observed. This would fit in with Harding's[3] theory that part of the broadening comes from irregularity of the lattice rather than absorption.

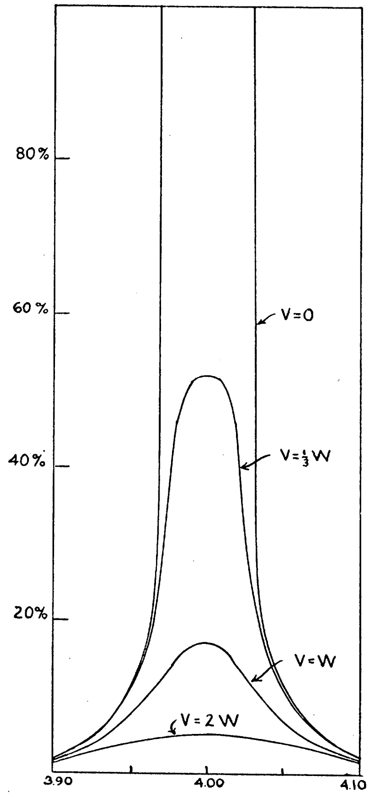

FIG. 3. Reflection coefficient of diffracted beam, as function of $E\sin^2\theta$. $E\sin^2\theta=4$ corresponds to the Bragg angle, $V=0$ corresponds to the case of no inelastic damping.

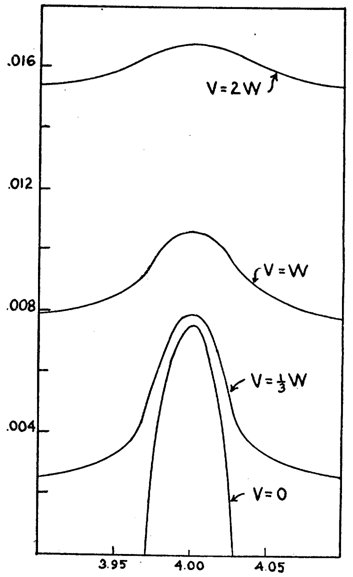

FIG. 2. Total damping constant α, arising from both inelastic and elastic impacts, as function of $E\sin^2\theta$.

To show the nature of the solution for smaller values of V/W, for which the approximations are not valid, numerical calculations have been made for a special case, shown in the figures. The values chosen were $K=4$ atomic units, $W=0.03$ atomic units, which are of the order of magnitude of constants actually encountered in the experiments. In Fig. 1 we plot $E\sin^2\theta$ as a function of δ, for several values of V/W. This is the sort of plot often made in the theory of metals, showing essentially the energy (or rather the component 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).

MAY 15, 1937 PHYSICAL REVIEW VOLUME 51

Wave Functions in a Periodic Potential

J. C. Slater*
Institute for Advanced Study, Princeton, New Jersey

(Received March 24, 1937)

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 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

---

* On leave from the Massachusetts Institute of Technology, Cambridge, Massachusetts.