QUANTUM MECHANICS OF COLLISION PROCESSES

I. SCATTERING OF PARTICLES IN A DEFINITE FORCE FIELD

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APPENDIX, ELECTRON DIFFRACTION

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BY A collision will be understood the interaction of two or more of the entities with which atomic physics is concerned under such conditions that before and after the collision they are widely separated in space but during the collision they are close together. The entities which may take part in collisions include electrons, protons, photons, atoms and molecules. If photons were to be considered the report would also need to treat of the entire problem of the interaction of radiation and matter. This is too much and so it is arbitrarily excluded. Certain other topics such as the Ramsauer effect, the collisions of two atoms and the polarization of the light emitted by atoms excited by an incident unidirectional electron beam are also left out of consideration. The report is thus intended simply to serve as an introduction to the simpler problems and to the method by which the more complicated problems are attacked.

§1. The Laws of Quantum Mechanics

The general principles of the theory are now available in a number of accounts. Of the elementary grade may be mentioned the articles of Kemble and of Kemble and Hill[1] in this journal, and the books of Condon and Morse,[2] Sommerfeld,[3] Frenkel,[4] deBroglie,[5] all of which cover approximately the same ground. More advanced are the books of Born and Jordan,[6] Weyl[7] and Dirac.[8] This last presents a general formulation of the theory in a form most suitable for our purposes so that reference to it will be the main source for fundamental ideas.

[1] Kemble and Hill, Rev. Mod. Phys. **1**, 157 (1929) and **2**, 1 (1930).
[2] Condon and Morse, Quantum Mechanics, New York, McGraw-Hill, 1929.
[3] Sommerfeld, Wave Mechanics, New York, E. P. Dutton, 1930.
[4] Frenkel, Einführung in die Wellenmechanik, Berlin, J. Springer, 1929.
[5] de Broglie, Introduction à l'étude de la mécanique ondulatoire, Paris, Hermann et Cie, 1930.
[6] Born and Jordan, Elementare Quantenmechanik, Berlin, J. Springer, 1930.
[7] Weyl, Gruppentheorie und Quantenmechanik, Leipzig, S. Hirzel, 1928.
[8] Dirac, Quantum Mechanics. Oxford University Press, 1930.

Although duplicating Dirac, it is perhaps worthwhile to preface the treatment of collision problems with a condensed statement of the fundamental ideas. Page references to Dirac follow the essential statements.

In the next few pages the principles of the theory will be set down in terms of the properties of certain abstract symbols, this corresponding to the purely symbolic treatment of vector analysis which is independent of any coordinate system. There follows the translation of the same ideas into a notation which makes reference explicitly to coordinate systems but where, of course, all the results must remain invariant under all the allowed changes of coordinate system. The latter method, of course, is more analogous to the spirit of tensor analysis as used in relativity theory while the former is the analogue of the treatment of vectors by Gibbs.

The state (p. 7) of a system is described by a quantity called ψ (not to be confused with Schrödinger's ψ-function) which is analogous to a vector in a space of many (perhaps an infinite number) of dimensions (p. 18).

In any given coordinate system the components of ψ may be complex numbers. Associated with each ψ will be a ϕ whose components in any coordinate system are the conjugate complex numbers to the components of ψ in that same coordinate system.

One can add two different ψ's to get another ψ. Similarly one can add two ϕ's to get a ϕ. But there is no place in the algebra for addition of a ϕ and a ψ.

A given state is thus described by a ψ and the associated ϕ. The symbol $\phi\psi$ is defined as the analogue of the scalar product of two vectors in vector analysis and is therefore an ordinary number (p. 21). One never multiplies two ψ's nor two ϕ's nor a ϕ and a ψ in the order $\psi\phi$, but always in the order $\phi\psi$. If ϕ_r, ψ_r, refer to one state and ϕ_s, ψ_s, refer to another, then the ordinary number $\phi_r\psi_s$ is the conjugate complex number to $\phi_s\psi_r$ and moreover $\phi_r\psi_r$ is real and positive.

In observing a system experimentally we build an apparatus on a macroscopic scale which acts on and is acted upon by the system by a certain set of operations, and a scale or pointer reading results. The essential feature of classical physics has been that we have expected to be able to formulate the laws of physics in terms of functional relations between the pointer-readings given by one set of observing apparatus and those given by the pointer-readings of another set, or of other sets. All of physics and exact natural science has proceeded along such lines hitherto. Quantum mechanics does not do this. This departure from the ordinary way in which mathematics is employed in natural science is so fundamental that it is at first hard to grasp. But once grasped the formalism of the theory is easily understood.

Any set of experimental apparatus and operations is therefore not going to appear in the theory simply as the source of certain pointer-readings which bear a direct functional relationship with other sets of pointer-readings. Instead it appears as a quantity of a more complicated sort about to be described. Thus we are dealing not merely with a new set of laws of nature but with an entirely new mathematical canvas on which to represent these laws. In this respect the quantum mechanics is a much more far-reaching advance than was the theory of relativity.

There are two parts to the study of the theory. One is the weaving of the new canvas of purely mathematical relations on which the picture of nature is to be painted. The other is the painting of the picture.

Any given set of experimental operations leading to numerical results of observation of the system, *i.e.* pointer-readings, will be called an observable (p. 25). In the mathematical framework an observable is considered as a quantity which acts on a ψ and converts it into another ψ. It is analogous to a tensor of the second rank or to the linear vector function of Gibbs (p. 26). Because of experimental difficulties we are not always able to observe the observables directly as pointer-readings and much of importance remains to be said on the side of the relation of observing apparatus to the observed system. But we pass over that. Thus most actual observations in atomic physics are quite indirect. Nevertheless we speak of ordinary classical concepts as observables, e.g. the position of an electron.

An observable in the mathematical theory is a rule for acting on any ψ and converting it into another ψ. If α denotes the observable, one has $\alpha\psi$ as another ψ and the α's are assumed to be linear so that $\alpha(\psi_1+\psi_2)=\alpha\psi_1+\alpha\psi_2$. Similarly an observable acting on a ϕ is written $\phi\alpha$ and the result is another ϕ. The sum of two observables, α_1 and α_2, is defined by $(\alpha_1+\alpha_2)\psi=\alpha_1\psi+\alpha_2\psi$, where ψ is arbitrary. The product of two observables is defined by $(\alpha_2\alpha_1)\psi=\alpha_2(\alpha_1\psi)$ and so in general $\alpha_2\alpha_1\neq\alpha_1\alpha_2$. One requires the assumption $\phi(\alpha\psi)=(\phi\alpha)\psi$ and hence such an expression can be written $\phi\alpha\psi$.

We now make the important physical postulate (p. 30) that a state ψ for which $\alpha\psi=a\psi$, where a is an ordinary number, is characterized by α having precisely the numerical value a. For a given state ϕ, ψ the quantity $\phi\alpha\psi$ is defined to be the average value of α in that state if the auxiliary condition, $\phi\psi=1$, is satisfied. This is an important notion: that there exist states in which an observable does not have a precise value but instead may have various values weighted with different probabilities so that many observations of α made on the same state will yield different values, leading to an average α characteristic of the state. $\phi\alpha\psi$ cannot be regarded as the value of α associated with that state because then if $\phi\alpha_1\psi$ is the value of α_1 and $\phi\alpha_2\psi$ that of α_2, we ought to have $(\phi\alpha_1\psi)(\phi\alpha_2\psi)$ equal to $\phi(\alpha_1\alpha_2)\psi$. But this is not the case, and this agrees with the ordinary behavior of averages where the average of the product of two quantities is not in general equal to the product of the averages (p. 32).

The conjugate complex of α, written $\bar{\alpha}$, is defined by its satisfying the equation

$$\phi_s\bar{\alpha}\psi_r = \overline{\phi_r\alpha\psi_s}, \tag{1.1}$$

where the two states r and s are arbitrary (p. 28).

An observable in general is not capable of assuming all values *precisely.* The values which it can take on are the ones for which the equation in ψ,

$$\alpha\psi = \alpha'\psi \tag{1.2}$$

where α' is an ordinary number, has solutions (p. 35). These are the allowed

values of α and may form a discrete set of numbers or a continuous set. Of course $\phi\alpha\psi$ can have any value between the least α' and the greatest. Weyl calls a state ψ satisfying this equation a pure state (reine Fall) for this observable. Dirac calls the allowed values eigenvalues and the ψ's which satisfy this equation eigen-ψ's of α and speaks of a given eigen-ψ belonging to an α' if it satisfies this equation with that particular α'. The eigen-ψ belonging to α' will be denoted by $\psi(\alpha')$. Similarly one has the eigen-ϕ associated with α' satisfying the equation

$$\phi\alpha = \alpha'\phi$$

and denoted by $\phi(\alpha')$ when desired.

Theorem:

$$\phi(\alpha')\psi(\alpha'') = 0, \text{ if } \alpha' \neq \alpha'', \tag{1.3}$$

i.e. the eigenstates are orthogonal.

Proof:

$$\begin{aligned} \phi(\alpha')\alpha\psi(\alpha'') &= \alpha''\phi(\alpha')\psi(\alpha'') && \text{(Since } \psi \text{ is an eigen-}\psi\text{)} \\ &= \alpha'\phi(\alpha')\psi(\alpha'') && \text{(Since } \phi \text{ is an eigen-}\phi\text{)} \end{aligned}$$

Therefore: $(\alpha'-\alpha'')\phi(\alpha')\psi(\alpha'')=0$, hence the theorem (p. 36).

Assume that any ψ can be expanded in terms of the eigen-ψ's of any observable. This amounts to assuming the whole of a kind of generalized Sturm-Liouville theory at one step; hence mathematicians will recognize that much needs to be filled in here by studying exactly what class of ψ's can be so expanded (p. 38). One may write the expansion coefficient of $\psi(\alpha')$ as $(\alpha'|)$, i.e.

$$\psi = \sum_{\alpha'} \psi(\alpha')(\alpha'|\,) \tag{1.4}$$

where the space to the right of $|$ can be used to put indices to distinguish the expansion coefficients of different ψ's with respect to the eigen-ψ's of α (p. 73). $(\alpha'|)$ is a function of α' which need be defined only for all the allowed values of α. From the orthogonality property of the eigen-ψ's just as with Fourier series, multiplying (1.4) by $\phi(\alpha')$,

$$(\alpha'|\,) = \phi(\alpha')\psi \tag{1.5}$$

provided $\phi(\alpha')\psi(\alpha')=1$. Similarly an arbitrary ϕ can be expanded,

$$\phi = \sum_{\alpha'} (|\,\alpha')\phi(\alpha'), \text{ with } (|\,\alpha') = \phi\psi(\alpha').$$

The set of eigenstates can be thought of as a set of unit orthogonal vectors in which case $(\alpha'|)$ becomes the components of ψ on the coordinate system formed by them, found by taking the scalar product of ψ with the appropriate eigenstate.[9]

[9] In the preceding, and in what follows, where the symbol $\sum_{\alpha'}$ is used, it is tacitly supposed that all the allowed values of α' form a discrete set. In many important cases the allowed values form a set that is wholly continuous or consists of discrete and continuous portions. In these cases generalizations of the above treatment are required which are analogous to Kemble I, p. 188. It is convenient to write the formulas as if only discrete values were involved with the understanding that the appropriate change has to be made where continuous sets present themselves. (Compare Dirac §25, p. 70).

Consider $\phi\alpha\psi$ when ϕ, ψ are so expanded, in terms of eigenstates of α. One has

$$\phi\alpha\psi = \left\{ \sum_{\alpha'} (\,|\,\alpha')\phi(\alpha')\alpha' \right\} \left\{ \sum_{\alpha''} \psi(\alpha'')(\alpha''\,|\,) \right\} = \sum_{\alpha'} \alpha' (\,|\,\alpha')(\alpha'\,|\,), \quad (1.6)$$

by the orthogonality property for the eigenstates. Here one has the average of α expressed as a sum of the allowed values of α, multiplied by weighting factors. Hence the interpretation of $(\,|\alpha')(\alpha'\,|\,)$ as the probability that α have the value α' in the state ϕ, ψ (p. 82). Since one has $(\,|\alpha') = \overline{(\alpha'\,|\,)}$ these probabilities are necessarily real and positive as they should be.

In case $\alpha\beta = \beta\alpha$, states may exist, $\psi(\alpha', \beta')$, which are simultaneous eigenstates of both α and β, so that

$$\alpha\psi(\alpha', \beta') = \alpha'\psi(\alpha', \beta')$$
$$\beta\psi(\alpha', \beta') = \beta'\psi(\alpha', \beta')$$

and similarly for the associated ϕ's (p. 44). To describe a system one may choose any set of commuting observables such that there is no other observable that is not a function[10] of them which commutes with all of them. Such a set is said to be complete (p. 47). It is convenient to denote all the members of a complete set by α for short, meaning thereby the ensemble $\alpha_1, \alpha_2, \cdots$.

Consider now an observable β which does not commute with all the members of the set α. Then generally an eigenstate of β will not be one of the set α. Suppose $\psi(\beta')$ belongs to β'. One can expand $\psi(\beta')$ in terms of the $\psi(\alpha')$ and get

$$\left.\begin{aligned} \psi(\beta') &= \sum_{\alpha'} \psi(\alpha')(\alpha'\,|\,\beta'). \\ \text{Similarly,} \quad \phi(\beta') &= \sum_{\alpha'} (\beta'\,|\,\alpha')\phi(\alpha'). \end{aligned}\right\} \quad (1.7)$$

Since the state belonging to β' is one in which β has precisely the value β' we have the result that

$$(\beta'\,|\,\alpha')(\alpha'\,|\,\beta') = (\alpha'\,|\,\beta')\overline{(\alpha'\,|\,\beta')} \quad (1.8)$$

is the probability that the observables $\alpha_1 \cdots \alpha_n$ have the values $\alpha_1' \cdots \alpha_n'$ when β is known to have precisely the value β' (p. 83).

Perhaps it will help the reader who is already familiar with Schrödinger's work to be told that a solution of Schrödinger's equation, as $\psi_W(x, y, z)$, in the Schrödinger notation, is a special case of this result where the positions x, y, z are the observables symbolized here by α and the total energy W is to be identified with β.

[10] A function of an observable α need be defined only for the allowed values of α since no other values of α have any significance in the theory (p. 39). γ is said to be a function of α if its value is specified for each allowed value of α. As to functions of several observables, these are only defined when the several observables appearing as arguments commute with each other, and are then defined similarly (p. 46).

Consider the action of β on an eigenstate of the α's. $\beta\psi(\alpha')$ will be another ψ and so can be expanded in terms of the eigenstates of the α's. For this we adopt the notation

$$\beta\psi(\alpha') = \sum_{\alpha''}\psi(\alpha'')(\alpha''\,|\,\beta\,|\,\alpha'). \tag{1.9}$$

The quantity β is thus described by the double array of coefficients $(\alpha''\,|\beta\,|\alpha')$ obtained when α'' and α' range independently over all the allowed values of the α's. This array of coefficients is called the matrix of β in the α scheme (p. 58 and p. 74).

If ψ is arbitrary it is given by $(\alpha'|)$ in the α scheme. Then $\beta\psi$ is

$$\beta\psi = \sum_{\alpha'}\beta\psi(\alpha')(\alpha'\,|\,) = \sum_{\alpha'\alpha''}\psi(\alpha'')(\alpha''\,|\,\beta\,|\,\alpha')(\alpha'\,|\,)$$

and therefore the component of $\beta\psi$ relative to the α'' eigenstate in the α scheme is

$$\phi(\alpha'')\beta\psi = \sum_{\alpha'}(\alpha''\,|\,\beta\,|\,\alpha')(\alpha'\,|\,), \tag{1.10}$$

by the orthogonality property.

In the α scheme the matrix of any one of the α's is especially simple: $\alpha_1\psi(\alpha')=\alpha_1'\psi(\alpha')$ and therefore $(\alpha''\,|\alpha_1\,|\alpha')=\alpha_1''\delta_{\alpha''\alpha'}$, where $\delta_{\alpha''\alpha'}=0$ if $\alpha''\neq\alpha'$ and equals 1 if $\alpha''=\alpha'$, and the α's have discrete values. This needs some special consideration for the case in which the allowed α values form a continuous set, but that will not be given here.

Suppose now β stands for another set of commuting observables. An arbitrary ψ will be given by

$$\psi = \sum_{\alpha'}\psi(\alpha')(\alpha'\,|\,).$$

One has further that

$$\psi(\alpha') = \sum_{\beta'}\psi(\beta')(\beta'\,|\,\alpha').$$

Hence

$$\psi = \sum_{\beta'\alpha'}\psi(\beta')(\beta'\,|\,\alpha')(\alpha'\,|\,) = \sum_{\beta'}\psi(\beta')(\beta'\,|\,).$$

So

$$(\beta'\,|\,) = \sum_{\alpha'}(\beta'\,|\,\alpha')(\alpha'\,|\,), \tag{1.11}$$

which gives the relation between the components of a ψ in two different coordinate systems.

Similarly one has, if γ is another observable,

$$\gamma\psi(\alpha'') = \sum_{\beta'\beta''}\psi(\beta')(\beta'\,|\,\gamma\,|\,\beta'')(\beta''\,|\,\alpha''),$$

$$\psi(\beta') = \sum_{\alpha'}\psi(\alpha')(\alpha'\,|\,\beta'),$$

so

$$\gamma\psi(\alpha'') = \sum_{\alpha'\beta'\beta''} \psi(\alpha')(\alpha' \mid \beta')(\beta' \mid \gamma \mid \beta'')(\beta'' \mid \alpha'').$$

But

$$\gamma\psi(\alpha'') = \sum_{\alpha'} \psi(\alpha')(\alpha' \mid \gamma \mid \alpha''),$$

so by the orthogonality property

$$(\alpha' \mid \gamma \mid \alpha'') = \sum_{\beta'\beta''} (\alpha' \mid \beta')(\beta' \mid \gamma \mid \beta'')(\beta'' \mid \alpha''), \tag{1.12}$$

which gives the rule for changing a matrix from one coordinate system, or scheme, to another.

The transformation functions $(\alpha' \mid \beta')$ satisfy certain identities since

$$(\alpha' \mid\ ) = \sum_{\beta'} (\alpha' \mid \beta')(\beta' \mid\ ) = \sum_{\beta'\alpha''} (\alpha' \mid \beta')(\beta' \mid \alpha'')(\alpha'' \mid\ ).$$

Hence, comparing coefficients, one must have

$$\left.\begin{aligned} \sum_{\beta'} (\alpha' \mid \beta')(\beta' \mid \alpha'') &= \delta_{\alpha'\alpha''}, \\ \text{and similarly} \qquad \sum_{\alpha'} (\beta' \mid \alpha')(\alpha' \mid \beta'') &= \delta_{\beta'\beta''}. \end{aligned}\right\} \tag{1.13}$$

This completes the statement of the formal rules.

This is the mathematical pattern in terms of which we seek to formulate the laws of atomic physics. The remainder of the theory consists in the recognition of the properties of the operators which are to represent various observables. To a particular mode of observation with certain apparatus is to be associated a certain operator. The laws of nature are not, as before, the functional relations between the numerical values given by certain experiments, but relations between the operators that stand for various modes of observation. The recognition of what operator is to be associated with each set of experimental operations has been carried out thus far partly by appeal to the correspondence principle (as with coordinate position and conjugate momentum) and partly by appeal to experiment (as with electron spin). Of course the correspondence principle itself is a broad generalization from experiment so the known relations between operators for physical quantities all spring from experiment. Essentially the laws are as follows (Dirac, Chap. VI):

The quantities $q_1 \cdots q_n$ which are analogous to Cartesian coordinates of particles are capable of taking on all values from $-\infty$ to $+\infty$. The quantities $p_1 \cdots p_n$ which are analogous to the Cartesian components of momentum similarly take all values from $-\infty$ to $+\infty$.

The quantities q and p satisfy the following quantum-theoretic laws of nature,

$$\begin{aligned} q_iq_j - q_jq_i &= 0 \\ p_ip_j - p_jp_i &= 0 \\ p_iq_j - q_jp_i &= (h/2\pi i)\delta_{ij}. \end{aligned} \tag{1.14}$$

Analogous to the total energy of the system is a Hamiltonian function H which is represented by the same functional form of the p's and q's as on the classical theory for the analogous classical dynamical system. The importance of H on the classical theory lay in the fact that through Hamilton's equations of motion it determined the time variation of the state. That continues to be its importance here, the dependence of the state ψ on the time being given by

$$-\frac{h}{2\pi i}\frac{\partial\psi}{\partial t} = H\psi. \tag{1.15}$$

The eigenstates for the Hamiltonian are stationary states in the sense that the probability that any quantity α have a value α' is independent of the time. One has for the eigenstate belonging to H',

$$H\psi = H'\psi,$$

and therefore the time dependence of such a ψ is,

$$\psi_t(H') = \psi_0(H')e^{-2\pi iH't/h}.$$

Similarly

$$\phi_t(H') = \phi_0(H')e^{+2\pi iH't/h}.$$

The average value of α is independent of the time in such a state.[11] The proof is as follows:

$$\phi_t(H')\alpha\psi_t(H') = \phi_0(H')e^{+2\pi iH't/h}\alpha\psi_0(H')e^{-2\pi iH't/h}$$

so that

$$\phi_t(H')\alpha\psi_t(H') = \phi_0(H')\alpha\psi_0(H'),$$

the time dependence having just cancelled out.

The place of Schrödinger's equation in this scheme (pp. 103, 104) is that it is a special case of the equation $\alpha\psi = a\psi$. Suppose we are dealing with a system which is specified by Cartesian coordinates and momenta $q_1p_1 \cdots q_np_n$. Then the coordinates $q_1 \cdots q_n$ form a complete set of commuting observables whose allowed values are all values from $-\infty$ to $+\infty$. Let $\psi(q')$ be the eigen-ψ belonging to the set of values $q_1' \cdots q_n'$. Then an eigen-ψ for the total energy can be written, as usual,

$$\psi(H') = \sum_{q'}\psi(q')(q' \mid H').$$

The equation $H\psi = H'\psi$ can then be written

$$\begin{aligned} H\psi(H') &= \sum_{q'}H\psi(q')(q' \mid H') \\ &= \sum_{q'q''}\psi(q'')(q'' \mid H \mid q')(q' \mid H') \\ &= \sum_{q''}H'\psi(q'')(q'' \mid H'). \end{aligned}$$

Hence, by the orthogonality property of the $\psi(q')$,

[11] If α does not involve the time explicitly.

$$\sum_{q'}(q''\,|\,H\,|\,q')(q'\,|\,H') = H'(q''\,|\,H').$$

Schrödinger's great discovery consisted in the observation that the operation on $(q'\,|H')$ which is represented by the left-hand side of the equation could be replaced by a differential operator, so that this equation became a differential equation for $(q\,|H')$.

The differential operator for H is to be found[12] by replacing each p by the corresponding $(h/2\pi i)(\partial/\partial q)$ in the classical expression for $H(p,q)$. The equation for $(q\,|H')$ is then the partial differential equation,

$$H\left\{\frac{h}{2\pi i}\frac{\partial}{\partial q},\ q\right\}(q\,|\,H') = H'(q\,|\,H'). \tag{1.16}$$

Hence the $\psi_W(q)$ of Schrödinger is to be identified with the $(q\,|H')$ of the present notation, where $W=H'$ and is an allowed energy level.

In fact, more generally, any quantity, such as angular momentum, which classically is expressed as a function of the q's and p's may be made into an operator for the q-scheme by writing $(h/2\pi i)(\partial/\partial q)$ for the corresponding p.

§2. One Dimensional Collisions

The best way to become familiar with the workings of the theory is by consideration of simple one-dimensional problems in which a particle moves under the influence of a potential energy function $V(x)$ so that the classical Hamiltonian is

$$H = \frac{1}{2\mu}p^2 + V(x). \qquad (\mu = \text{mass}).$$

It is of importance to know the behavior of the function $(x\,|H')$ which in Schrödinger's notation is the $\psi(x)$ belonging to the energy level H'.

In order to speak of a particle colliding with a force-field it is necessary to suppose that the forces become negligible at large distances from the origin. Hence, since the zero of V is arbitrary we suppose that $V\to 0$ as $x\to-\infty$ and $V\to V_0$ as $x\to+\infty$ and for definiteness suppose $V_0>0$.

The Schrödinger equation for $(x\,|H')$ is then

$$\left\{-\frac{h^2}{8\pi^2\mu}\frac{\partial^2}{\partial x^2} + V(x) - H'\right\}(x\,|\,H') = 0.$$

This has to be solved with the understanding that $(x\,|H')$ remains finite. (More accurately, so that $\int_a^b(H'\,|x)(x\,|H')dx$ is finite if $(b-a)$ is finite and such that $\int_a^b(H'\,|x)(x\,|H')dx/(b-a)$ is finite as $b\to\infty$ and $a\to-\infty$). By easy studies of this ordinary differential equation one can establish the following:

(a) H' not less than $V_{\min}$ where $V_{\min}$ is the absolute minimum of $V(x)$.

(b) If $V_{\min}<0$ then the allowed H' in the range $V_{\min}<H'<0$ form a dis-

[12] Compare Kemble I, Sec 4, "The Energy Operators."

crete set, and for these $\int_{-\infty}^{+\infty}(H'|x)(x|H')dx$ is finite and can therefore be set equal to unity by a proper normalization of $(x|H')$. Also $(x|H')$ is real so that

$$(H'|\ x) = (x|\ H').$$

(c) The allowed H' in the range $0<H'<V_0$ form a continuous set, i.e. all values are allowed. The $(x|H')$ is real and

$$\frac{1}{b-a}\int_a^b (H'|\ x)(x|\ H')dx$$

tends to a finite limit (not zero) for b fixed and $a\to-\infty$ and tends to zero for a fixed and $b\to+\infty$.

(d) For $H'>V_0$ all values are allowed and associated with each H' are two different $(x|H')$ which will be denoted by $(x|H',\ 1)$ and $(x|H',\ 2)$. Since an arbitrary linear combination $c_1(x|H',\ 1)+c_2(x|H',\ 2)$ is a solution of the Schrödinger equation one sees that $(x|H')$ is here to a certain extent indeterminate. For either solution one has

$$\frac{1}{b-a}\int_a^b (H'|\ x)(x|\ H')dx$$

equal to a finite limit for either $b\to+\infty$ or $a\to-\infty$ or both.

The states of class (b) correspond to the classical periodic vibratory motion inside the range of values of x in which $H'-V(x)>0$. In this range $(x|H')$ is an oscillatory function and in the range where $H'-V(x)<0$, it sinks asymptotically and without oscillations to zero roughly at the same rate as an exponential function. Since the particle has a negligible probability of being at infinity for these states they are not of interest for collision problems.

The states of class (c) correspond to the classical aperiodic motion in which a particle comes from $x=-\infty$ with kinetic energy H', goes as far as the least value of x for which $H'-V(x)=0$ and returns to $x=-\infty$ with kinetic energy H'. For them $(x|H')$ is an oscillatory function in the range from $-\infty$ to the least value of x for which $H'-V(x)=0$. For x greater than the greatest value of x for which $H'-V(x)=0$, the function sinks asymptotically to zero, roughly like an exponential function. A detailed consideration of its behavior between the least and greatest values of x for which $H'-V(x)=0$ reveals some striking and important phenomena in which quantum mechanics gives very different results from classical mechanics. The particle has some chance of penetrating to positions where, classically speaking, its potential energy alone is greater than its total energy.

The states of class (d) correspond to classical aperiodic motions, which classically are of quite different nature according as $H'>V_{\max}$ or $<V_{\max}$ where $V_{\max}$ is the absolute maximum of $V(x)$. In the former case one type of classical motion is that in which the particle comes from $x=-\infty$ with kinetic energy H' and goes, without ever changing its direction to $x=+\infty$ with

kinetic energy $H'-V_0$. The other type would be a similar motion carried out in the reverse direction. Similarly for $H'<V_{\max}$ one classical motion is approach from $x=-\infty$ to the least value of x for which $H'-V(x)=0$ and return to $x=-\infty$. The other is approach from $x=+\infty$ to the greatest value of x for which $H'-V(x)=0$ and return to $x=+\infty$. We shall see that in quantum mechanics the sign of $(H'-V_{\max})$ does not play the role of a sharp dividing line between two distinct classes of motions.

To remove the arbitrariness about the two $(x\,|H')$ in class (d) we will suppose that $(x\,|H',1)$ has been so chosen that it has the asymptotic form

$$(x\,|\,H',1)\rightarrow e^{ik_0x} \qquad \text{as } x\rightarrow+\infty$$

$$k_0=\frac{2\pi}{h}[2\mu(H'-V_0)]^{1/2},$$

and similarly $(x\,|H',2)$ will be taken so that

$$(x\,|\,H',2)\rightarrow e^{-ikx} \qquad \text{as } x\rightarrow-\infty.$$

$$k=\frac{2\pi}{h}(2\mu H')^{1/2}.$$

We shall see that this choice of $(x\,|H',1)$ and $(x\,|H',2)$ is a canonical one, the former corresponding to a state of affairs in which particles in the neighborhood of $x=+\infty$ are certainly moving from left to right, the second corresponding to a state in which the particle when in the neighborhood of $x=-\infty$ is certainly moving from right to left.

In accordance with that consequence of quantum mechanics known as Heisenberg's uncertainty principle[13] we cannot speak of a precise value of the momentum of a particle at a precisely given position (because p and x do not commute). But we can ask about the value of the momentum when the particle is at $x=\pm\infty$ because this virtually amounts to no restriction on the position of the particle. This point is akin to an approximation that is always made in optics which needs for its correction the theory of the resolving power of optical instruments. A light wave is strictly monochromatic only if it is of infinite extent both in the wave-front and perpendicular to it—and yet we admit only a small portion of the wave into the narrow slit of a spectroscope and continue to talk of it as essentially monochromatic! Since $(x\,|H',1)$ becomes for large x asymptotically the same as the wave function of a free particle of precisely known momentum, $(hk_0/2\pi)$, it is safe to interpret this as a state of the system in which the particle's momentum certainly has the value $+(hk_0/2\pi)$ when at $x=+\infty$. Similarly $(x\,|H',2)$ represents a state in which the particle's momentum certainly has the value $-(hk/2\pi)$ or $-(2\mu H')^{\frac{1}{2}}$ when at $x=-\infty$.

[13] Heisenberg's book, *The Physical Principles of the Quantum Theory*, published in July, 1930 by the University of Chicago Press gives a full account of this.

Another property of $(x|H')$ of which we now make use is that the asymptotic expansion of $(x|H', 1)$ as $x\rightarrow-\infty$ is of the form

$$(x|\,H', 1) \rightarrow A(H')e^{ikx} + B(H')e^{-ikx},$$

which means that $(x|H', 1)$ represents a state in which particles are coming from $x=-\infty$ with momentum, $+(hk/2\pi)$, in numbers proportional to $A(H')\overline{A}(H')$ and are going to $x=-\infty$ in numbers proportional to $B(H')\overline{B}(H')$ with momentum $-(hk/2\pi)$. Therefore we shall interpret $(x|H', 1)$ as a state of motion in which $A(H')\overline{A}(H')(hk/2\pi)$ particles come from $x=-\infty$ in unit time, and of these $hk_0/2\pi$ in unit time get through to $x=+\infty$ and $B(H')\overline{B}(H')(hk/2\pi)$ are reflected or scattered back to $x=-\infty$. What will happen to any particlar particle cannot be stated. Evidently for this view to be tenable one must have the sum of the numbers transmitted and scattered back equal to the number coming from $x=-\infty$. That this is true quite generally may be readily proven as follows.

We write down the Schrödinger equation for $(x|H')$ and for $(H'|x)$, its complex conjugate; multiply the former by $(H'|x)$ and the latter by $(x|H')$, substract and integrate with regard to x. The result is

$$(x|\,H')\frac{d}{dx}(H'|\,x) - (H'|\,x)\frac{d}{dx}(x|\,H') = \text{constant}.$$

Evaluating this expression for $x\rightarrow+\infty$ and for $x\rightarrow-\infty$ and equating the results we have the theorem of the conservation of the number of particles. (Compare Weyl, p. 63.)

We can thus define the probability of transmission as

$$\text{tr.} = k_0/kA(H')\overline{A}(H'),$$

and of reflection as

$$\text{ref.} = B(H')\overline{B}(H')/A(H')\overline{A}(H'),$$

where

$$\text{tr.} + \text{ref.} = 1,$$

as it should. The interpretation of $(x|H', 2)$ is exactly analogous, this representing a state of motion in which a particle coming from $x=+\infty$ has a chance of being reflected back and a chance of being transmitted to $x=-\infty$.

The interpretation of states of class (c) is now quite evident. Asymptotically for $x\rightarrow+\infty$ one has $(x|H')\rightarrow 0$ so that no particles move off to $x=+\infty$. For $x\rightarrow-\infty$, $(x|H')$ is asymptotically real and oscillatory so that the intensity of the incident and reflected beams are equal, as they should be.

The essential thing in the study of problems of the type of class (d) is to be able to compute $A(H')$, for from it the transmission and reflection probabilities can be obtained at once. This calls for a solution of Schrödinger's equation for the problem in question. As stated before, classically we have $\text{tr.}(H')=0$ for $H'<V_{\max}$ and $\text{tr.}(H')=1$, for $H'>V_{\max}$. This is replaced in quantum mechanics by a gradually changing function with the properties:

tr.$(H')\to 0$ for $H' << V_{\max}$ and tr.$(H')\to 1$ for $H' >> V_{\max}$. Instead of proving this in general, the main features of the theory will now be illustrated by working out a few cases where $V(x)$ has a mathematically tractable form.

Such cases are afforded by supposing $V(x)$ to be constant except for a finite number of finite discontinuities. For our Case I suppose $V(x)=0$, for $x<0$ and $V(x)=V_0$ for $x>0$. In this type of problem it is assumed that $(x\,|H')$ and $(d/dx)(x\,|H')$ are continuous at the discontinuities in $V(x)$. These assumptions were first made by Faxen and Holtsmark.[14] Of course, it is to be understood that no problems of real physical interest will show mathematical discontinuities in $V(x)$ and so boundary conditions are not needed for real problems. But if $V(x)$ changes by a considerable amount in a space small compared to a de Broglie wave-length, $2\pi/k$, we expect that the solution for such a case can be found by treating the change as an actual discontinuity with appropriately chosen boundary conditions. Faxen and Holtsmark's paper purports to show that these are the appropriate conditions in this sense. On this point see also H. A. Wilson, Phys. Rev. **35**, 948 (1930), Eckart, Phys. Rev. **35**, 1298 (1930) and Wilson, Phys. Rev. **35**, 1586 (1930).

For $0<H'<V_0$ one has,

$$x>0 \qquad (x\,|\,H') = e^{-k_0 x} \qquad k_0 = \frac{2\pi}{h}[2\mu(V_0 - H')]^{1/2},$$

$$x<0 \qquad (x\,|\,H') = Ae^{ikx} + \overline{A}e^{-ikx} \quad k = \frac{2\pi}{h}(2\mu H')^{1/2}$$

where, in order to have the required continuities:

$$Re(A) = \tfrac{1}{2}, \quad Im(A) = k_0/2k,$$

where $Re(A)$ and $Im(A)$ mean real and imaginary parts of A.

Hence there is some probability of being at places where $x>0$, which is impossible on classical mechanics. The total probability of x being between 0 and $+\infty$ is proportional to

$$\int_0^\infty e^{-2k_0 x}dx = 1/2k_0.$$

The probability of being in unit length at $x<0$ is proportional to

$$\lim_{a\to\infty}\frac{1}{a}\int_{-a}^{0}(H'\,|\,x)(x\,|\,H')dx = \frac{1}{2}[1 + (k_0/k)^2].$$

The ratio of these two quantities gives a kind of mean depth of penetration of the particle into the non-classical region. It is

$$1/k_0[1 + (k_0/k)^2].$$

It varies from 0 at $H'=0$, to ∞ as $H'\to V_0$.

For $H'=V_0$ the same treatment holds, if we write $k_0=0$. For $x>0$,

[14] Faxen and Holtsmark, Zeits. f. Physik **45**, 311 (1927).

$(x\,|H')=1$ and for $x<0$, $(x\,|H')=\cos kx$. This is a peculiar transition case since the flow at $x>0$ vanishes with k_0 but nevertheless the penetration is infinite.

For $H'>V_0$, we have

$$x>0 \quad (x\,|\,H',1)=e^{ik_0x} \quad k_0=\frac{2\pi}{h}[2\mu(H'-V_0)]^{1/2}$$

$$x<0 \quad (x\,|\,H',1)=Ae^{+ikx}+Be^{-ikx},\ k \text{ as before},$$

where, to satisfy the continuity requirements,

$$A=\tfrac{1}{2}(1+k_0/k),\quad B=\tfrac{1}{2}(1-k_0/k).$$

Hence the transmission and reflection probabilities are,

$$\text{tr.}=\frac{4k_0/k}{(1+k_0/k)^2},\quad \text{ref.}=\frac{(1-k_0/k)^2}{(1+k_0/k)^2}.$$

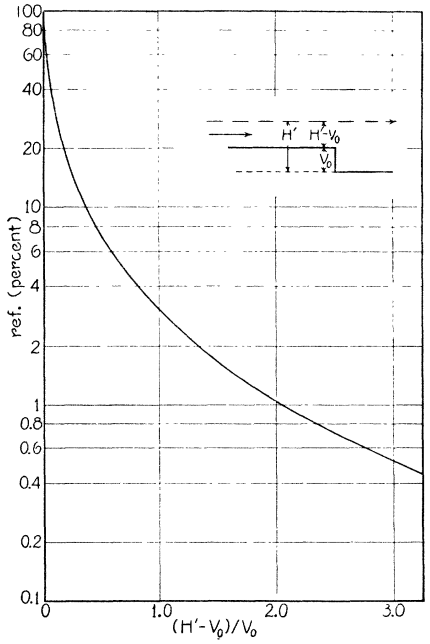

Fig. 1. Probability of reflection at a sudden drop in the potential energy.

Since tr.+ref.$=1$, it is sufficient to consider the dependence of tr. on H'. At $H'=V_0$, tr.$=0$, since $k_0=0$. At $H'=4V_0/3$, $k_0/k=\frac{1}{2}$ and tr.$=8/9$ so we see that the rise of tr. to the value unity is rapid when $(H'-V_0)$ becomes an appreciable fraction of V_0. By considering $(x\,|H',2)$ in the analogous way we may see that the probability of transmission in the right-to-left motion is zero for $H'=V_0$ but rapidly rises to unity for $H'>V_0$. In Figure 1 is plotted the logarithm of ref. against $(H'-V_0)/V_0$ for this case. One can see that the

particle approaches rapidly to its classical behavior as H' becomes appreciably larger than V_0.

Case II will be defined by $V(x)=0$, for $x<0$, $V(x)=V_1$ for $0<x<a$ and $V(x)=V_0$ for $a<x$ where $V_1>V_0$. For $H'<V_0$ we get certain reflection as in Case I but with a somewhat more complicated calculation of the mean depth of penetration. The result, it can easily be foreseen, will be a somewhat greater mean depth for a given V_1 than if V_0 were equal to V_1. We pass to $(x\,|H',\,1)$ for $V_0<H'<V_1$. We have

$$a<x \qquad (x\,|\,H',\,1)=e^{ik_0x} \qquad k_0 \text{ as before,}$$

$$0<x<a \qquad (x\,|\,H',\,1)=Ae^{k_1x}+Be^{-k_1x} \qquad k_1=\frac{2\pi}{h}[2\mu(V_1-H')]^{1/2}$$

$$x<0 \qquad (x\,|\,H',\,1)=Ce^{ikx}+De^{-ikx}, \qquad k \text{ as before,}$$

where the A, B, C and D are determined by the continuity requirements at $x=0$ and $x=a$. The results are,

$$A=\tfrac{1}{2}e^{-k_1a}(1+ik_0/k_1)e^{ik_0a}$$

$$B=\tfrac{1}{2}e^{k_1a}(1-ik_0/k_1)e^{ik_0a}.$$

$$C=\tfrac{1}{4}e^{ik_0a}[(1-ik_1/k)(1+ik_0/k_1)e^{-k_1a}+(1+ik_1/k)(1-ik_0/k_1)e^{+k_1a}]$$

$$D=\tfrac{1}{4}e^{ik_0a}[(1+ik_1/k)(1+ik_0/k_1)e^{-k_1a}+(1-ik_1/k)(1-ik_0/k_1)e^{+k_1a}],$$

the details being left to the reader. Hence the transmission coefficient is

$$\text{tr.}=k_0/kC\overline{C}=(8k_0/k)\{1+4k_0/k+k_0^2/k^2-k_0^2/k_1^2-k_1^2/k^2 + (1+k_0^2/k_1^2+k_1^2/k^2+k_0^2/k^2)\cosh 2k_1a\},$$

which is a somewhat complicated function of H'. If $2k_1a>>1$ the second term dominates the denominator and the transmission coefficient is small, of the order e^{-2k_1a}. Hence for a potential wall of finite height and finite thickness there is always some chance of penetration and escape to $x=+\infty$, contrary to classical mechanics. For $H'>V_1$, $(x\,|H',\,1)$ is of the same form except in the middle portion, where it is

$$0<x<a \qquad (x\,|\,H',\,1)=Ae^{ik_1x}+Be^{-ik_1x} \qquad k_1=\frac{2\pi}{h}[2\mu(H'-V_1)]^{1/2}.$$

This amounts merely to a substitution of ik_1 for k_1 in the preceding expressions. Hence the transmission coefficient now is

$$\text{tr.}=8(k_0/k)\left\{1+4\frac{k_0}{k}+\frac{k_0^2}{k^2}+\frac{k_0^2}{k_1^2}+\frac{k_1^2}{k^2}+\left(1-\frac{k_0^2}{k_1^2}-\frac{k_1^2}{k^2}+\frac{k_0^2}{k^2}\right)\cos 2k_1a\right\}^{-1}.$$

One observes that as $H'\to\infty$ the transmission probability tends to certainty but not monotonically because of the oscillations of the cosine term. This term is a maximum for $2k_1a=2n\pi$ where n is an integer, that is, when an integral

number of half de Broglie wave-lengths is contained in a (the wave-length corresponding to the classical momentum in the range 0 to a is meant). Because the other terms vary with H', the transmission minima or maxima will not come precisely at these values but only approximately so.

The behavior of tr. as a function of H'/V_1 is shown in Figure 2 where curves for three proportions of the wall are shown, for the case $V_0=0$.[15] The curves are labelled by the value of the ratio, $h^2/2\mu a^2 V_1$, which expresses completely the characteristics of the wall for this problem, being the ratio of the energy of a particle of de Broglie wave-length a to V_1.

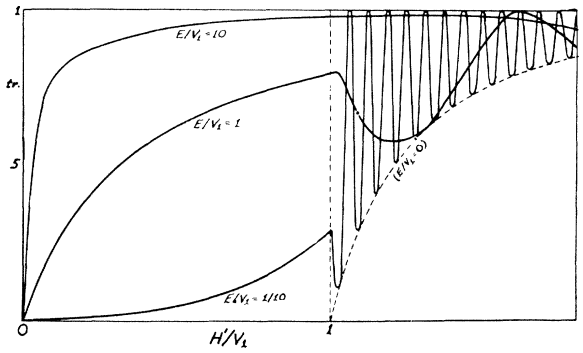

Fig. 2. Probability of transmission at a potential wall of height V_1. (E is the energy of a particle of de Broglie wave-length equal to the thickness of the wall.)

Case III will be defined by

$$\begin{aligned} V(x) &= 0 && x < 0 \\ &= V_1 && 0 < x < a \\ &= V_2 && a < x < b \\ &= V_0 && b < x \end{aligned}$$

where it is supposed that $V_1>0$, $V_2<V_1$, and $V_0>>V_1$. If $V_0>>V_1$ the penetration of the particles into $b<x$ may be neglected for $H'<<V_0$ and $(x\,|H')$ set equal to zero at $x=b$ for this case. We shall consider in detail only the case for which $V_2<H'<V_1$ as the other ranges of H' will present phenomena not differing essentially from the preceding cases. Since $(x\,|H')=0$ at $x=b$ one can write

$$\begin{aligned} a < x < b \quad (x\,|\,H') &= \sin k_2(x-b) && k_2 = \frac{2\pi}{h}[2\mu(H'-V_2)]^{1/2} \\ 0 < x < a &= Ae^{k_1 x} + Be^{-k_1 x} && k_1 \text{ as before} \\ x < 0 &= Ce^{ikx} + De^{-ikx} && k \text{ as before.} \end{aligned}$$

A, B, C, and D are determined by the continuity requirements as before, and $D=\overline{C}$. It is here somewhat more convenient to write

[15] Kindly prepared for this report by Professor J. E. Mack.

$$x < 0 \quad (x \mid H') = E \sin k(x - \delta).$$

One finds for E,

$$E^2 = (1 + k_1^2/k^2)(A^2 + B^2) + 2(1 - k_1^2/k^2)AB,$$

where

$$A = \frac{1}{2}\left[\frac{k_2}{k_1}\cos k_2(b - a) - \sin k_2(b - a)\right]e^{-k_1 a},$$

$$B = \frac{1}{2}\left[-\frac{k_2}{k_1}\cos k_2(b - a) - \sin k_2(b - a)\right]e^{+k_1 a}.$$

The probability of being in the range $a<x<b$ is $\int_a^b \sin^2 k_2(x-b)dx$ which is of the order of $\frac{1}{2}(b-a)$. The probability of being in unit length of the range $x<0$ is $\frac{1}{2}E^2$. Ordinarily, if $k_1a>>1$, then E^2 is a very large number because of the quantity B^2 in the formula for E^2, which makes E^2 of the order of e^{2k_1a} if the bracket in the formula for B is of the order of unity. For such energy levels one has the result that particles coming from $x=-\infty$ are reflected without appreciable penetration into the region $a<x<b$ which might have been expected by analogy with Case I. The important new result is that for values of H' such that

$$(k_2/k_1)\cos k_2(b - a) + \sin k_2(b - a)$$

is of the order of e^{-2k_1a}, then E^2 is very small, of the order e^{-2k_1a}, so that the probability of being in unit length in $x<0$ is almost vanishingly small compared with that in the region $a<x<b$. This means that, on the average, particles coming from $x=-\infty$ with such energies will not only penetrate into the region $a<x<b$ but will remain there a long time before going out to $x=-\infty$. It does not mean, of course, that *every* particle coming from $x=-\infty$ will penetrate into $a<x<b$. Some may be reflected in the region $0<x<a$; if there are such then the mean stay in $a<x<b$ of those that do penetrate must be correspondingly longer. There is no way of telling by means of the $(x\,|H')$ function *for a single energy level*[16] how many penetrate into $a<x<b$ and hence what the mean duration in this region is for those which penetrate. But we can set a lower limit on the mean duration. In a length $(b-a)$, where $x<0$ any one particle spends the time $2(b-a)/(2H'/\mu)^{\frac{1}{2}}$ since it traverses the distance twice, once going in and once coming out, with almost precisely the classical velocity. The time spent inside must bear the ratio to the time spent outside given by the relative values of $(H'\,|x)(x\,|H')$, which is E^2, hence the mean time spent inside by those that penetrate must be

$$T = \frac{2(b - a)}{(2H'/\mu)^{1/2}}(1/E^2),$$

if each particle penetrates, and longer if some do not.

[16] For elucidation of this point, see §6 of this report.

These three cases will suffice to illustrate some of the striking characteristics of the theory. Naturally results, semi-quantitatively the same, hold for $V(x)$ a continuous function of x of the same general shape as those considered here.[17] In particular, Case III illustrates the quantum theory of radioactive disintegration by alpha-particle emission in the form due to Gurney and Condon.[18] The theory was developed independently by Gamow[19] along somewhat different lines.

Approximation Methods

It is now clear how we have to interpret a rigorous solution for $(x\,|H')$ if one has been found for the particular potential energy curve $V(x)$ describing the problem. We next consider what approximate methods are available for finding $(x\,|H')$ when the rigorous solution cannot be obtained. Born has developed a method of successive approximations for this problem. For convenience let $u(x)$ stand for $(x\,|H',\ 1)$ and suppose $V(x)\to 0$ as $x\to\pm\infty$. We write

$$u(x) = e^{ikx} + u_1(kx) + u_2(kx) + \cdots$$

where $u_1, u_2, \cdots$ vanish for $x\to+\infty$ and are determined by the equations:

$$\begin{aligned} u_1'' + u_1 &= Ve^{i\xi}/H' \\ &\cdots\cdots\cdots \\ u_n'' + u_n &= Vu_{n-1}/H'. \end{aligned} \qquad (\xi = kx).$$

These simple equations can be solved with the condition, $u_n(\infty)=0$, the result being,

$$u_n(\xi) = \frac{1}{H'}\int_{\xi}^{\infty} u_{n-1}(\eta)V\left(\frac{\eta}{k}\right)\sin(\eta-\xi)d\eta.$$

For $x\to-\infty$ this gives,

$$u_n(\xi) = (i/2H')\left[e^{i\xi}\int_{\xi}^{\infty} u_{n-1}(\eta)V(\eta/k)e^{-i\eta}d\eta - e^{-i\xi}\int_{\xi}^{\infty} u_{n-1}(\eta)V(\eta/k)e^{i\eta}d\eta\right].$$

which becomes

$$u_n(\xi) = (i/2H')e^{i\xi}\int_{-\infty}^{+\infty} u_{n-1}(\eta)V(\eta/k)e^{-i\eta}d\eta - (i/2H')e^{-i\xi}\int_{-\infty}^{+\infty} u_{n-1}(\eta)V(\eta/k)e^{i\eta}d\eta,$$

so that asymptotically each $u_n(\xi)$ behaves like a sum of constant coefficients into $e^{i\xi}$ and $e^{-i\xi}$. Hence the sum of them behaves this way, hence the possi-

[17] An interesting example in treated by Eckart, Phys. Rev. **35**, 1303 (1930).
[18] Gurney and Condon, Phys. Rev. **33**, 127 (1929).
[19] Gamow, Zeits. f. Physik **51**, 204 (1928).

bility of making an interpretation of incident and reflected streams of particles as in the preceding paragraphs.

Born's[20] published convergence proof for the method is erroneous. Weyl has given a proof of convergence in his book[21] which imposes the restriction

$$k\int_{-\infty}^{+\infty}\left|\frac{V(x)}{H'}\right|dx < 1,$$

which for a given $V(x)$ can always be satisfied if H' is taken large enough. One can easily see that this restriction greatly narrows the range of important physical questions to which the method is applicable. It is therefore desirable to find a better form of the successive approximations method. Thus in Case II, if $V_0=0$, we have

$$k\int_{-\infty}^{+\infty}\left|\frac{V(x)}{H'}\right|dx = kaV_1/H' = (k_1aV_1/H')(k/k_1)$$

so that Born's method would not converge in the case where $H'<V_1$ and $K_1a>>1$, since $k/k_1\sim 1$, if Weyl's restriction is necessary.

In any approximation method one starts from a problem whose solution is rigorously known, and it is desirable to have this starting problem correspond as closely as possible to the one whose solution is sought. In Born's method the starting point problem is that of the absolutely free particle. Instead let us suppose $V(x)=V_0(x)+V_1(x)$ where $V_0(x)$ is the potential energy function of a problem whose rigorous solution is known and which is so chosen that $V_1(x)$ is small compared to $V_0(x)$ everywhere. The equation for $(x\,|H')$ can be written

$$\frac{d^2u}{d\xi^2}+[1-U_0(\xi)]u = U_1(\xi)u$$

where

$$k^2=\frac{8\pi^2\mu H'}{h^2},\quad \xi=kx,\quad U_0(\xi)=V_0(x)/H',\quad U_1(\xi)=V_1(x)/H',$$

and $u(\xi)$ is $(x\,|H')$. Let $u(\xi)$ be in particular $(x\,|H',1)$ and suppose that $u_a(\xi)$ is $(x\,|H',1)$ for the potential energy function $V_0(x)$ while $u_b(\xi)$ is any linearly independent solution of the Schrödinger equation for $u_a(\xi)$.

For $u(\xi)$ we write

$$u(\xi)=u_a(\xi)+u_1(\xi)+u_2(\xi)+\cdots$$

where the sum of all terms after the first must vanish for $\xi\to+\infty$. These terms will be determined as solutions of the equations,

$$\frac{d^2u_1}{d\xi^2}+(1-U_0(\xi))u_1 = U_1(\xi)u_a(\xi),$$
$$\cdots\cdots\cdots\cdots$$
$$\frac{d^2u_n}{d\xi^2}+(1-U_0(\xi))u_n = U_1(\xi)u_{n-1}.$$

[20] Born, Zeits. f. Physik **38**, 803 (1926).

[21] Weyl, Gruppentheorie und Quantenmechanik, p. 61.

Letting

$$D(\xi) = u_a(\xi)u_b'(\xi) - u_b(\xi)u_a'(\xi)$$

the solutions are found to be,

$$u_1(\xi) = \int_\xi^\infty K(\xi, \eta)U_1(\eta)u_a(\eta)d\eta$$

. . . . . .

$$u_n(\xi) = \int_\xi^\infty K(\xi, \eta)U_1(\eta)u_{n-1}(\eta)d\eta$$

where,

$$K(\xi, \eta) = [u_b(\xi)u_a(\eta) - u_a(\xi)u_b(\eta)]/D(\eta).$$

From this it is evident that $u(\xi)$ satisfies the integral equation

$$u(\xi) = \int_\xi^\infty K(\xi, \eta)U_1(\eta)u(\eta)d\eta.$$

This is a Volterra equation and the method of solving it here given is a standard one.

Dirac[22] has treated one-dimensional collisions by an approximate method, which is equivalent to the first order of Born's successive approximations, using the momentum representative of the states instead of the coordinate representative which characterizes the preceding treatment. The calculations are considerably complicated by the fact that the momentum representatives, $(p|)$, are discontinuous and involve the δ-function.

§3. Special One-Dimensional Calculations

Detailed evaluation of reflection and transmission coefficients for various one-dimensional potential energy walls have their chief application in the theory of thermionic emission of metals worked out by Nordheim and Fowler. According to the present ideas in the electron theory of metals, the free electrons behave like a gas at such a high density that the Fermi equation of state must be applied in discussing its properties.[23] At the boundary between metal and free space the potential energy of an electron increases by some 20 volts, as experiments on the diffraction of de Broglie waves show. (Appendix). Of those electrons which attain a velocity component normal to the surface whose energy equivalent is in excess of this amount only a certain fraction will actually escape because of the existence of a reflection coefficient at the wall, as was discussed in Sec. 2.

Nordheim and Fowler have shown that if I is the saturated electronic thermionic current then A in the formula

$$I = AT^2e^{-\chi/kT}$$

[22] Dirac, Zeits. f. Physik **44**, 585 (1927).

[23] Compare Darrow, Phys. Rev. Suppl. **1**, 115 and 123 (1929).

(T = absolute temperature, k = Boltzmann constant, χ = work function) is given by

$$A = \frac{2\pi mek^2}{h^3} g\bar{D}.$$

Here $g=2$ and is the weight factor brought in by the two spin orientations for each ordinary phase-space cell and $\bar{D}$ is a mean of the transmission coefficient for the surface potential energy function weighted according to the distribution of normal components of electronic translational energy. Therefore thermionic emission depends on the mean value of the transmission coefficient and hence on the form of the potential energy law in the neighborhood of the metal surface. This has given rise to the calculation of $\bar{D}$ for a number of special assumptions concerning the potential energy $V(x)$, where x is a coordinate running from metal to vacuum, normal to the metal-vacuum interface.

Nordheim[24] first worked out the case which is called Case II of Sec. 2 but made an algebraic error which was corrected by Fowler.[25] But Fowler's Fig. 2 is quite wrong in that it fails to show the interference effects in the transmission coefficient for the energies greater than the potential energy maximum. The correct form is that given by Fig. 2 of this report.

Nordheim[26] has also made the calculation for the case in which the square wall of our Case I, Sec. 2 is rounded off by the Schottky image force, to give a better approximation to actual conditions. He uses

$$V(x) = C - e^2/4x, \quad x > x_0$$
$$= 0 \qquad\qquad x < x_0$$

where x_0 is given by $e^2/4x_0 = C$. Naturally this makes the transmission coefficient a rather complicated function of the energy, W (called H' in Sec. 2). The important effect of rounding off the sharp discontinuity in V is that now the transmission coefficient does not tend to zero as $W \to C$, but takes on a limiting value 0.927 in case the particles are electrons and $C=12$ electron volts. Therefore the non-classical reflection when $W > C$ is almost inappreciable. Therefore the mean value $\bar{D}$ is close to unity so that with the weighting factor, $g=2$, the thermionic constant A comes out to be 120 amp./cm.^{2} Empirically A has a value nearer half of this.

The theory of A has had its ups and downs! The theoretical expression, omitting $g\bar{D}$, is due to Dushman and agrees with experimental values. The electron spin makes $g=2$ instead of assigning unit weight to each phase cell as implied in Dushman's derivation, but at first Fowler and Nordheim thought $\bar{D} \sim \frac{1}{2}$ so that the agreement of theory and experiment remained unimpaired. But now Nordheim's analysis shows that $\bar{D} \sim 1$ so theory gives a value about

[24] Nordheim, Zeits. f. Physik **46**, 833 (1928).
[25] Fowler, Proc. Roy. Soc. **A122**, 39 (1929).
[26] Nordheim, Proc. Roy. Soc. **A121**, 626 (1928).

twice too large. Fowler[27] has recently discussed several possible ways of removing this difficulty.

Georgeson[28] has worked out the transmission coefficient for the case in which the potential energy function is of the form given in Fig. 3. He finds for tr. for $W>B$

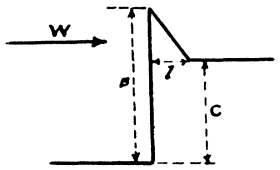

Fig. 3. Form of the potential energy function used by Georgeson.

$$\text{tr.} = \frac{4W^{1/2}(W-B)^{1/2}}{\{(W-B)^{1/2}+W^{1/2}\}^2-(BE/\sigma)\sin 2\lambda}$$

in which $F=(B-C)/l$, $\sigma=4k(W-C)^{3/2}$, $\lambda=(2k/3F)\{(W-C)^{3/2}-(W-B)^{3/2}\}$ and $k^2=8\pi^2\mu/h^2$, where μ is the mass of the particle.

For $W<B$ but not very near to C, he finds

$$\text{tr.} = \frac{4(B-W)^{1/2}W^{1/2}e^{-2Q}}{B+\dfrac{F}{k(B-W)^{1/2}}+\dfrac{F^2}{3k^2(B-W)^2}+\dfrac{1}{3^{1/2}}\dfrac{FW^{1/2}}{k(B-W)}},$$

in which

$$Q=\frac{2k}{3F}(B-W)^{3/2}.$$

Georgeson also works out special forms valid when $W\sim C$ and $W\sim B$. He gives three figures showing the transmission coefficient as a function of W for various values of B, C and l. These are probably only meant to show the

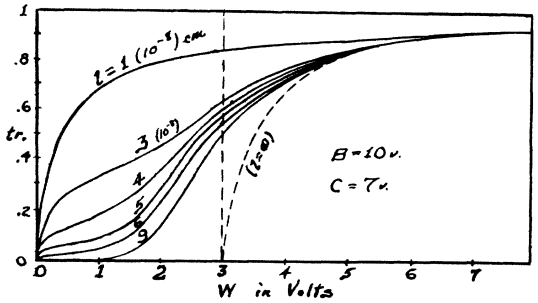

Fig. 4. Transmission probabilities for the potential barrier of Fig. 3.

general trend since they do not show the interference effects for $W>B$ which are implied by the sine term in the denominator. One of Georgeson's figures is reproduced in our Fig. 4.

[27] Fowler, Proc. Roy. Soc. **A122,** 36 (1929).

[28] Georgeson, Proc. Camb. Phil. Soc. **25,** 175 (1929).

Eckart [29] has published an interesting special case in which the penetration of electrons through a potential barrier that is without discontinuities in value or slope is worked out.

§4. Three-Dimensional Collisions

We shall suppose that a particle of mass μ free to move in three dimensions is acted on by a field of potential energy $V(x, y, z)$, which becomes rapidly equal to zero as $r=(x^2+y^2+z^2)^{\frac{1}{2}}\rightarrow\infty$. We have to study the possible stationary states of the motion for positive values of H' through the representative $(x, y, z\,|H')$ which for simplicity will be written $u(x, y, z)$. The essential difference between the three-dimensional and the one-dimensional case is that we now have an ∞^2 set of stationary states associated with each H' instead of two as in the one-dimensional problem. This is because there is now an ∞^2 continuum of directions of motion possible when far from the origin, instead of just two as in the one-dimensional case. It is imperative therefore that we have some means of classifying this wealth of solutions and that we have some knowledge of their properties.

This is best done in analogy with the one-dimensional problems by making a preliminary study of the $(x, y, z\,|H')$ for a free particle in three dimensions. Then $V=0$ everywhere and the equation for $(\boldsymbol{r}\,|H')$ is

$$\Delta(\boldsymbol{r}\,|\,H') + k^2(\boldsymbol{r}\,|\,H') = 0 \quad k^2 = \frac{8\pi^2\mu H'}{h^2}$$

of which a canonical form of solution is

$$(\boldsymbol{r}\,|\,H') = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

where $\boldsymbol{k}$ is any vector whose magnitude is k; hence this form implies an ∞^2 family of solutions. Since $H'=(h^2/8\pi^2\mu)k^2$ it is best to use the vector $\boldsymbol{k}$ to label the canonical form, i.e.,

$$(\boldsymbol{r}\,|\,k) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

This function is that of an infinitely extended plane wave and corresponds, according to Sec. 1, to a precisely given value of the linear momentum vector. The operator for the linear momentum, $\boldsymbol{p}$, is $(h/2\pi i)grad$ and this operator applied to $(\boldsymbol{r}\,|k)$ gives $(kh/2\pi)(\boldsymbol{r}\,|k)$; hence $(\boldsymbol{r}\,|k)$ is the representative of a state in which $\boldsymbol{p}$ has precisely the value $kh/2\pi$.

Since we are going to be concerned with the scattering of particles by a localized field of force it will also be of interest to learn the representatives of states in which the angular momentum about some fixed origin has a precise value. A set of solutions appropriate for answering this question is obtained by solving the Schrödinger equation in polar coordinates. The equation is known to have solutions of the type,

$$(\boldsymbol{r}\,|\,k, l, m) = \frac{R_l(kr)}{kr}\Theta_{lm}(\theta)\,\Phi_m(\phi).$$

[29] Eckart, Phys. Rev. **35**, 1303 (1930).

Here the factors Θ_{lm} and Φ_m are the normalized factors of a surface harmonic

$$\Theta_{lm}(\theta) = \left(\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right)^{1/2} \sin^{|m|}\theta \frac{d^{|m|}}{d(\cos\theta)^{|m|}} P_l(\cos\theta),$$

$$\Phi_m(\phi) = e^{im\phi}/(2\pi)^{1/2},$$

and $R_l(\xi)$ is a solution of the equation

$$\left(\frac{d^2}{d\xi^2} + 1 - \frac{l(l+1)}{\xi^2}\right) R_l(\xi) = 0, \quad (\xi = kr)$$

which vanishes at the origin. Functions which satisfy this equation arise in many problems of physics and many notations have been used for them (Watson, Bessel Functions, p. 55). We shall be interested in the general solution of this equation. It is of the form

$$y = c_1 e^{i\xi} f_l(-i\xi) + c_2 e^{-i\xi} f_l(+i\xi)$$

where $f_l(i\xi)$ is defined by the terminating series

$$f_l(i\xi) = \sum_{r=0}^{l} \frac{(l+r)!}{r!(l-r)!(2i\xi)^r}.$$

If the solution is to be finite at the origin one must have $c_2 = (-1)^{l+1}c_1$. We shall define $R_l(\xi)$ by the equation

$$R_l(\xi) = e^{i\xi} f_l(-i\xi) - (-1)^l e^{-i\xi} f_l(+i\xi).$$

With this definition one has the relation

$$R_l(\xi) = (+i)^{l+1}(2\pi\xi)^{1/2} J_{l+1/2}(\xi)$$

where $J_{l+\frac{1}{2}}(\xi)$ is the usual Bessel function of half an odd integer.

Since the operator for the component of angular momentum along the pole of a spherical polar coordinate system is $(h/2\pi i)(\partial/\partial\phi)$, one sees that in $(\boldsymbol{r}|k, l, m)$ we have a pure state for this component and that m labels the precise value of it in Bohr units $(h/2\pi)$. Similarly the operator for the squared resultant angular momentum is

$$-\left(\frac{h}{2\pi}\right)^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

so that it can be seen that $(\boldsymbol{r}|k, l, m)$ refers to a pure state for squared resultant angular momentum, the precise value being $l(l+1)(h/2\pi)^2$. The interpretation of k, as proportional to resultant linear momentum, we already know.

To find the distribution of angular momentum in the infinite unidirectional beam we must expand $(\boldsymbol{r}|k)$ in terms of the $(\boldsymbol{r}|k, l, m)$. Suppose the pole of the polar coordinates has the direction of k, then $k\cdot r = kr\cos\theta$ and the expansion desired is a well-known one,

$$e^{ikr\cos\theta} = (2\pi/kr)^{1/2}\sum_{l=0}^{\infty}(l+\tfrac{1}{2})i^l J_{l+1/2}(kr)P_l(\cos\theta)$$

or in our notation,

$$(\boldsymbol{r}\,|\,k) = -i\sum_{l=0}^{\infty}[2\pi(l+\tfrac{1}{2})]^{1/2}(\boldsymbol{r}\,|\,k, l, 0).$$

The absence of terms for $m \neq 0$ shows that the component of angular momentum in the direction of the beam is certainly zero, which corresponds with classical mechanics.

Let us now consider the scattering of particles by a spherically symmetric field of force. First we study the solutions of the equation for the motion of the particles,

$$\Delta u + \frac{8\pi^2\mu}{h^2}(H' - V(r))u = 0.$$

Since V is spherically symmetric this will have solutions of the form

$$u = \frac{R_l(kr)}{kr}\Theta_{lm}(\theta)\Phi_m(\phi)$$

where the angle factors are the same as for the free particle but $R_l(\xi)$ is a new function whose properties we need to study. It satisfies the equation

$$\left[\frac{d^2}{d\xi^2} + 1 - \frac{l(l+1)}{\xi^2} - U(\xi)\right]R_l(\xi) = 0.$$

in which $U(\xi) = V(\xi/k)/H'$. The boundary conditions on $R_l(\xi)$ are:

$$R_l(0) = 0, \text{ and } R_l(\infty), \text{ finite.}$$

It will now be supposed that for $\xi \to \infty$, we have $U(\xi) << l(l+1)/\xi^2$.

We observe that the equation for $R_l(\xi)$ is of the same form as that of a one-dimensional problem in which $U(\xi)$ is infinite for $\xi < 0$, if ξ is regarded as a coordinate which can range from $-\infty$ to $+\infty$. Hence by the arguments used in Sec. 2, there will be one solution associated with each positive value of H', which will be essentially real and which asymptotically will have the form,

$$R_l(\xi) \to A_l[e^{i(\xi-\gamma_l)} - (-1)^l e^{-i(\xi-\gamma_l)}], \qquad \xi \to \infty.$$

Here A is in general a complex number to be determined by normalization or other requirements and γ_l is a phase which is fully determined by the fact that $R_l(\xi)$ is the particular solution that vanishes for $\xi = 0$.

For a given H' there is thus the same wealth of solutions for the particle in the force field as for the free particle, namely $(2l+1)$ corresponding to the different values of m associated with each l, with l taking on all integral values from 0 to ∞. To find the scattering we proceed to build up a superposition of these fundamental solutions which will represent an incident plane wave plus outgoing waves only, at points far from the origin. To do this we have to choose the coefficients A_l in such a way that

$$A_l[e^{i(\xi-\gamma_l)} - (-1)^l e^{-i(\xi-\gamma_l)}] = [2\pi(l+\tfrac{1}{2})]^{1/2}(-i)[e^{i\xi} - (-1)^l e^{-i\xi}] + B_l e^{i\xi}.$$

The first term on the right is that needed to make up a plane wave, as shown by the expansion of $(\boldsymbol{r}|\boldsymbol{k})$ in terms of $(\boldsymbol{r}|k, l, m)$, while the second corresponds to outgoing waves. Hence, equating coefficients of $e^{i\xi}$ and $e^{-i\xi}$, we find

$$A_l = -i[2\pi(l+\tfrac{1}{2})]^{1/2} e^{-i\gamma_l}$$
$$B_l = -2[2\pi(l+\tfrac{1}{2})]^{1/2} e^{-i\gamma_l} \sin\gamma_l.$$

The solution with these values of A_l and $m=0$ is then

$$u = \sum_{l=0}^{\infty} (2\pi)^{-1/2} A_l (R_l(\xi)/\xi)\Theta_l(\theta)$$
$$\to e^{ikz} + \sum_{l=0}^{\infty} (2\pi)^{-1/2} B_l (e^{i\xi}/\xi)\Theta_l(\theta) \quad \text{for} \quad \xi \to \infty .$$

Hence at very large distances from the origin one has a unit intensity per unit volume of particles moving in the positive z-direction, and particles moving outward away from the origin. The number of outward moving particles in the volume element $r^2 \sin\theta dr d\theta d\phi$ is proportional to

$$\frac{e^{i\xi}e^{-i\xi}}{2\pi\xi^2} r^2 \sin\theta dr d\theta d\phi \left(\sum_l B_l\Theta_l\right)\left(\sum_l \overline{B}_l\Theta_l\right)$$
$$= \frac{1}{2\pi k^2} dr d\omega \left(\sum B_l\Theta_l\right)\left(\sum \overline{B}_l\Theta_l\right).$$

Hence the number crossing the surface element bounded by the differential of solid angle $d\omega$ in unit time is

$$v \cdot \frac{1}{2\pi k^2}\left(\sum B_l\Theta_l\right)\left(\sum \overline{B}_l\Theta_l\right) d\omega$$

where $v = (2H'/\mu)^{\frac{1}{2}}$.

The number of incident particles per unit normal cross-section area of beam per unit time is simply v. The ratio of the number going out in unit time in solid angle $d\omega$ to this is therefore a quantity of the dimensions of an area and is the cross-section of the incident beam needed to contribute the number of particles scattered off in the solid angle $d\omega$. One speaks therefore of the scattering power of the field of force in terms of this effective cross-section of the force field for producing the scattering in question. The coefficient $1/2\pi k^2$ can be written $\lambda^2/8\pi^3$ where λ is the de Broglie wave-length for the particle being scattered. The cross-section for scattering into the element of solid angle $d\omega$ is thus,

$$\alpha d\omega = \frac{\lambda^2}{8\pi^3}\left(\sum_l B_l\Theta_l\right)\left(\sum_l \overline{B}_l\Theta_l\right) d\omega.$$

The total cross-section for scattering in all directions is

$$\alpha = \int_0^{2\pi} \int_0^{\pi} \alpha_\theta d\theta d\phi = \frac{\lambda^2}{4\pi^2} \sum_l B_l \bar{B}_l$$

because of the orthogonality of the Θ_l for different l. Recalling the definition of B_l this can be written

$$\alpha = \frac{\lambda^2}{\pi} \sum_l (2l + 1) \sin^2 \gamma_l.$$

In the corresponding classical motion particles of momentum p whose line of motion at infinite distance passes at distance d from the origin would have angular momentum pd. The area of the beam in which the particles have angular momentum between l and $(l+1)$ Bohr units is therefore $\alpha_l = (2l+1)$ $\lambda^2/4\pi$ where $\lambda = h/p$. The scattering formula can thus be written

$$\alpha = 4 \sum_l \alpha_l \sin^2 \gamma_l,$$

to bring out the fact that each term in the summation is of the order of magnitude of a corresponding classical term.

For a particle of energy W and mass M the value of α_l in terms of the area, πa^2 of the first Bohr orbit in hydrogen, is given by

$$\alpha_l/\pi a^2 = (2l + 1)(R/W)(\mu/M)$$

in which R is the ionization energy of atomic hydrogen and μ is the mass of the electron.

The preceding calculation shows that the scattering arises essentially from the fact that the phases of the asymptotic solution in the force field are not the same as in the case when no forces act. The scattering power is thus referred back completely to the shift in phase of the wave function of the particle in the force field relative to that of the free particle. The convergence of the series for α is insured if $\sin\gamma_l \to 0$ sufficiently rapidly as $l \to \infty$. For large l the term $U(\xi)$ becomes negligible relative to $l(l+1)/\xi^2$ in the equation for $R_l(\xi)$ which tends to bring this about, but the exact criteria for the convergence are not known.

The foregoing rigorous theory calls for an exact solution for $R_l(\xi)$ or at least an exact calculation of the phase shifts, γ_l, relative to the free particle solutions. There are not very many functions $V(r)$ for which such an exact solution is possible. The Coulomb law, $V(r) \sim r^{-1}$, requires special treatment (Sec. 5) since it falls off less rapidly than the $l(l+1)/\xi^2$ term due to centrifugal force, whereas the preceding developments imply the opposite behavior. As in the one-dimensional case, various features of the theory can be illustrated by supposing $V(r)$ to consist of a finite number of constant portions connected by finite discontinuities. The calculations follow the pattern of the one-dimensional calculations with Bessel functions appearing in the former role of the exponential and trigonometric functions. This makes them considerably less susceptible to numerical treatment because the necessary tables of Bessel functions are not available.

Successive approximations method.

The method of successive approximations was extended to the three-dimensional case by Born in his original paper. One seeks a particular solution of

$$\Delta u + \frac{8\pi^2\mu}{h^2}(H' - V)u = 0$$

which at large distances from the origin consists of a plane wave and outgoing scattered waves. Writing $k^2 = 8\pi^2\mu H'/h^2$ one can write $\xi = kx$, $\eta = ky$, $\zeta = kz$ and $U(\xi, \eta, \zeta) = V/H'$ so the equation is

$$\Delta u + (1 - U(\xi,\eta,\zeta))u = 0$$

where now ξ, η, ζ are the independent variables in the Laplacian. We may write,

$$u = u_0 + u_1 + u_2 + \cdots$$

and find u_0, $u_1 \cdots$ etc. from the equations,

$$\begin{aligned} \Delta u_0 + u_0 &= 0 \\ \Delta u_1 + u_1 &= u_0 U \\ &\cdots \\ \Delta u_n + u_n &= u_{n-1} U. \\ &\cdots \end{aligned}$$

We may take u_0 to be the incident plane wave, $e^{i\zeta}$, and seek the particular solutions for u_1, u_2, $\cdots$ which represent outgoing waves only. Such a solution of the equation for u_n may be found, by an application of Green's theorem, to be

$$u_n(\xi, \eta, \zeta) = -\frac{1}{4\pi}\int u_{n-1}(\xi', \eta', \zeta')U(\xi', \eta', \zeta')\frac{\exp(i|\varrho - \varrho'|)}{|\varrho - \varrho'|}d\xi' d\eta' d\zeta',$$

where $\varrho = \xi i + \eta j + \zeta k$ and similarly for ϱ' and the integration extends over all space. Thus each u_n may be found, in particular u_1 being,

$$u_1(\xi, \eta, \zeta) = -\frac{1}{4\pi}\int e^{i\zeta'}U(\xi', \eta', \zeta')\frac{\exp(i|\varrho - \varrho'|)}{|\varrho - \varrho'|}d\xi' d\eta' d\zeta'.$$

Asymptotically for large ρ one has $|\varrho - \varrho'| = \rho - \rho'\cos\theta'$ where θ' is the angle between ϱ and ϱ', so that

$$u_n(\xi, \eta, \zeta) = -\frac{1}{4\pi}\frac{e^{i\rho}}{\rho}\int u_{n-1}(\xi', \eta', \zeta')U(\xi', \eta', \zeta')e^{-i\rho'\cos\theta'}d\xi' d\eta' d\zeta',$$

which is an outgoing wave, whose amplitude is a function of the direction of ϱ, which may be specified as usual by polar angles, θ, ϕ, the z-axis being the pole for which $\theta = 0$.

Hence, if the series converges, we have

$$u = e^{i\xi} + A(\theta, \phi)e^{i\rho}/\rho \quad \text{for} \quad \rho \to \infty,$$

where

$$A(\theta, \phi) = -\frac{1}{4\pi} \sum_{n=1}^{\infty} \int u_{n-1}(\xi', \eta', \zeta') U(\xi', \eta', \zeta') e^{-i\rho' \cos\theta'} d\xi' d\eta' d\zeta'.$$

$A(\theta, \phi)$ is thus theoretically known although the calculation of A accurately is not feasible. The interpretation is as before: the number of outward moving particles in a volume element at distance r in solid angle $d\omega$ is proportional to

$$\frac{A\overline{A}}{k^2} d\omega = \left(\frac{\lambda}{2\pi}\right)^2 A\overline{A} d\omega$$

where λ is the de Broglie wave-length. This is the effective area for scattering particles in the particular solid angle $d\omega$. The total area for scattering in all directions can then be obtained by integrating over all directions.

It may be remarked that the particular solution here found satisfies the integral equation

$$u(\xi, \eta, \zeta) = e^{i\xi} - \frac{1}{4\pi} \int u(\xi', \eta', \zeta') U(\xi', \eta', \zeta') \frac{\exp(i \left| \varrho - \varrho' \right|)}{\left| \varrho - \varrho' \right|} d\xi' d\eta' d\zeta',$$

so the question of convergence of the successive approximations process may be referred back to the theory of such an integral equation. It is remarkable that simply the first term in the series for $A(\theta, \phi)$ can give a fair approximation to the solution in many instances.

As in the one-dimensional case there are many interesting physical cases for which the method probably does not converge. It would be possible to modify it by basing the approximations on known rigorous solutions for a $V_0(r)$ approximating to the actual $V(r)$ as was done in detail for one dimension but the method has not been hitherto used in the literature. When applicable, the successive approximations method does not require $V(x, y, z)$ to be spherically symmetrical.

First approximation: Central force.

The formulas for the Born successive approximation method appear to be so different from those of the preceding rigorous theory that it is instructive to show the connection of Born's first approximation with the formula of page 69, where the scattering is related to the phase-shifts in the radial factor of $(r \left| H' \right.)$ relative to the corresponding representative for the free particle. We assume $U(\xi', \eta', \zeta')$ is a function of ρ' alone. For large ρ one has asymptotically $\left| \varrho - \varrho' \right| = \rho - \rho' \cos\omega$ where ω is the angle between ϱ and ϱ'. If θ, ϕ and θ', ϕ' give the directions of ϱ and ϱ' then

$$\cos\omega = \cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi - \phi')$$

For $u_1(\xi,\eta,\zeta)$ we have therefore,

$$-\frac{e^{i\rho}}{4\pi\rho}\int_0^\infty U(\rho')\rho'^2 d\rho' \int\int e^{i(\zeta'-\rho'\cos\omega)}\sin\theta' d\theta' d\phi'.$$

The integral over the unit $\theta'\phi'$ sphere may be evaluated by making use of the developments,

$$e^{i\zeta'} = (\pi/2)^{1/2}\sum_{l'=0}^{\infty}(+\,i)^{l'}(2l'+1)\rho'^{-1/2}J_{l'+1/2}(\rho')P_{l'}(\cos\theta')$$

$$e^{-i\rho'\cos\omega} = (\pi/2)^{1/2}\sum_{l=0}^{\infty}(-\,i)^{l}(2l+1)\rho'^{-1/2}J_{l+1/2}(\rho')P_{l}(\cos\omega).$$

Multiplying these two together term by term and integrating, all terms vanish in which two Legendre polynomials of differing l appear. For those of equal l, a well-known result (e.g. MacRobert, Spherical Harmonics, p. 137) gives,

$$\int\int P_l(\cos\omega)P_l(\cos\theta')\sin\theta' d\theta' d\phi' = \frac{4\pi}{2l+1}P_l(\cos\theta)$$

so the expression for $u_1(\xi,\eta,\zeta)$ for large ρ is

$$u_1(\xi,\eta,\zeta) = -\frac{\pi e^{i\rho}}{2\rho}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)\int_0^\infty U(\rho')J^2_{l+1/2}(\rho')\rho' d\rho'.$$

so that the amplitude $A(\theta,\phi)$ which determines the distribution in angle of the scattering is the coefficient of $e^{i\rho}/\rho$ in this equation. The first order scattering area, for all directions, is obtained by integrating $A\bar{A}$ over all directions giving a result which may be written, in order to bring out the correspondence with the rigorous theory,

$$\sum_{l=0}^{\infty}\alpha_l\left[\int_0^\infty U(\rho)\left((\pi/\rho)^{1/2}\,J_{l+1/2}(\rho)\right)^2\rho^2 d\rho\right]^2$$

where α_l is the cross-section for classical angular momentum between l and $l+1$ Bohr units as before. One sees therefore that the Born first approximation amounts to a particular approximation to the phase shifts γ_l which occur in the rigorous theory.

The theory for central force fields as developed here is due to Faxen and Holtsmark (Zeits. f. Physik. **45,** 307 (1927)). This comparison of the first approximation of Born's method with the exact theory has not been published before although Mott (Proc. Camb. Phil. Soc. **25,** 304 (1928)) has approached the problem in a similar manner.

§5. Scattering in a Coulomb Field

The scattering of a beam of particles moving in the field of a Coulombian force center is one of the problems which can be treated rigorously by quantum mechanics. When an attempt is made to apply Born's successive ap-

proximations method (Sec. 4) to this problem a divergent integral presents itself. Wentzel[30] first avoided this difficulty by supposing the potential energy to vary as e^{-kr}/r instead of $1/r$. This made the integrals converge even when k was set equal to zero *after* the calculation! The result was a formula for the total intensity and angular distribution of scattered particles agreeing with that of Rutherford which was based on classical dynamics. But Wentzel's calculation is an approximate one. Later Oppenheimer[31] also treated the problem by Born's method.

Mott[32] and Gordon[33] gave the first rigorous proofs that the exact quantum mechanical solution is exactly in accord with the classical Rutherford formula. Later Temple[34] provided a much simpler proof of the same fact.

The mathematical methods employed are rather advanced in any case so the details will not be considered here. The aim, as in Sec. 4, is to find a particular solution of Schrödinger's equation which corresponds to incident particles in a plane wave and outgoing particles only. The feature of this problem of special interest is that one cannot find a solution which behaves asymptotically like a plane wave. This is connected with the fact that the Coulomb field falls off so slowly as the distance increases.

Classically we consider the scattering of a stream of particles all of which are moving with velocity v parallel to the axis of x when at large distances from the force center. The trajectory of each particle is a hyperbola and those of all the particles form a family of hyperbolas. By the general laws of correspondence between classical and quantum mechanics the wave fronts of the Schrödinger wave function should approximate to the surfaces orthogonal to this family of trajectories. Although each hyperbola has an asymptote parallel to the x-axis, the orthogonal surfaces nevertheless are not plane, but instead become the surfaces given by

$$x - \frac{ZZ'e^2}{mv^2}\log(r - x) = \text{const.}$$

where $Z'e$ is the charge on the particles being scattered and m their mass while Ze is the charge on the force center. (Mott's Eq. (16), p. 546, reference 32, should have ϵ^2, not ϵ.) Therefore we must find a particular solution of the wave equation which consists asymptotically of waves having a wave front of this form plus outgoing waves only. Mott finds such a solution, its asymptotic expansion being

$$e^{i[x-\rho\log(r-x)]} + R\cdot\left(\frac{1}{r}\right)e^{i[r+\rho\log(r-x)+\alpha]}$$

in which the unit of length is so chosen that $2\pi\rho/h = 1$ and where, in the ordinary units of length,

[30] Wentzel, Zeits. f. Physik **40,** 590 (1927).
[31] Oppenheimer, Zeits. f. Physik **43,** 413 (1927).
[32] Mott, Proc. Roy. Soc. **A118,** 542 (1928).
[33] Gordon, Zeits. f. Physik **48,** 180 (1928).
[34] Temple, Proc. Roy. Soc. **A121,** 673 (1928).

$$R = \frac{ZZ'e^2}{2mv^2} \operatorname{cosec}^2 \frac{\theta}{2}.$$

α is a phase shift which is without effect on the intensity of the scattered particles. The intensity of scattered particles per unit incident intensity is then $R^2 d\omega$ where $d\omega$ is the differential of solid angle between θ and $\theta+d\theta$ so this gives the Rutherford formula exactly for all velocities of the incident particles and all angles of scattering.

Temple's contribution consists in the observation that this result may be obtained more simply if paraboloidal coordinates are used, as in the Stark effect of atomic hydrogen, instead of spherical polar coordinates.

§6. Non-stationary States. Wave-packet Methods

Thus far we have only worked with stationary states, i.e. states in which the total energy of the system has a precise value. Such states are *stationary* in the sense that the probabilities for them do not vary with time. The equations of motion for ψ and ϕ are

$$-\frac{h}{2\pi i}\frac{\partial \psi}{\partial t} = H\psi \text{ and } +\frac{h}{2\pi i}\frac{\partial \phi}{\partial t} = \phi H.$$

If ψ is an eigen-ψ of H so that $H\psi = H'\psi$, then the variation of ψ with time is given by

$$\psi_t = \psi_0 e^{-2\pi i H' t/h}.$$

Similarly,

$$\phi_t = \phi_0 e^{+2\pi i H' t/h},$$

which means that each component of ϕ and ψ varies according to these equations in any representation. Hence the product of any component of ϕ with the corresponding component of ψ, such as $(H'|\alpha')(\alpha'|H')$, which gives the probability that α have the value α' when H is known to have the value H', is independent of the time. All probabilities are therefore independent of time in the eigenstates of total energy.

Because of this fact we cannot follow the course of events in any situation by confining ourselves to states in which energy has a precise value. In this section, we shall consider therefore the way in which the course of events may be followed in a collision by employing non-stationary states. Any non-stationary state and its time variation are conveniently studied in terms of its H representative, $(H'|)_t$, at a particular time, t. Because of the fundamental equation of motion the different components, $(H'|)$, change at different rates and thus the resultant ψ changes in time. We have

$$\left(\frac{h}{2\pi i}\frac{\partial \psi}{\partial t} + H\psi\right) = \sum_{H'} \psi_0(H')\left[\frac{h}{2\pi i}\frac{\partial (H'|)}{\partial t} + H'(H'|)\right] = 0.$$

Hence by the orthogonality property of the $\psi_0(H')$ each bracketed coefficient must vanish. Therefore,

$$(H'|)_t = (H'|)_0 e^{-2\pi i H' t/h}$$
$$(|H')_t = (|H')_0 e^{+2\pi i H' t/h}.$$

Hence ψ at any time is given, in terms of the coordinate system formed by the eigen-ψ's of energy at the initial time, by the relation,

$$\psi_t = \sum_{H'} \psi_0(H')(H'|)_0 e^{-2\pi i H' t/h}.$$

Thus although the magnitudes of the various components of ψ do not change in this representation, their phases relative to each other do change, which is sufficient to make the probabilities vary with the time for dynamical quantities that do not commute with H.

In any other representation the time variation is more complicated. If at $t=0$ the state is described by $(\alpha'|)_0$, then the initial value of $(H'|)$ is, from equation (1.11),

$$(H'|)_0 = \sum_{\alpha''} (H'|\alpha'')(\alpha''|)_0$$

and at time t we have

$$(\alpha'|)_t = \sum_{H'} (\alpha'|H')(H'|)_t.$$

Hence

$$(\alpha'|)_t = \sum_{\alpha''} \left(\sum_{H'} (\alpha'|H') e^{-2\pi i H' t/h} (H'|\alpha'') \right) (\alpha''|)_0.$$

We observe that the quantity in the bracket is simply the matrix component, in the α-scheme, of the operator, $e^{-2\pi i H t/h}$, which contains the time parametrically. The variation of the state with the time is thus given by a linear operation performed on the initial representatives.

Some simple illustrations of the variation of the state in time have been worked out by Kennard and by Darwin.[35] They have considered the variation in time of $(\mathbf{r}|)$ for a particle in various simple fields of force, such as no forces, constant field, charge in uniform magnetic field, etc. They show that if initially $(\mathbf{r}|)_0$ represents a particle in the neighborhood of the position whose vector is $\mathbf{a}$, then the place of maximum probability will move quite closely according to classical laws. Generally speaking, the uncertainty in position of the particle increases with the time in accordance with the fact that a finite initial uncertainty in position implies an uncertainty in initial momentum and so the analogue is to a family of classical motions rather than to a particular one. Usually in classical mechanics the positions of particles tracing out such a family of motions become farther and farther apart. In exceptional cases, as in that of the harmonic oscillator, this does not happen.

Such calculations with non-stationary states are often described as wave-packet methods. This is connected with the fact that the representatives,

[35] Kennard, Zeits. f. Physik **44**, 326 (1927); Darwin, Proc. Roy. Soc. **117A**, 258 (1927).

$(\boldsymbol{r}|H')$, occurring in the formula for $(\boldsymbol{r}|)_t$ in terms of $(\boldsymbol{r}|)_0$ are the solutions of Schrödinger's "wave" equation, and the summation over H' involved is analogous to a superposition of various wave patterns to give a moving group of waves. This fact is a great help in actually working with the theory because it gives a quantum mechanical meaning to much of the classical diffraction and interference theory.[36] The first wave packet problem to be worked out was that of the harmonic oscillator, due to Schrödinger,[37] who showed that by superposing the $\psi(H')$ for various energy levels of the harmonic oscillator, the amplitudes and phases being properly chosen, a wave packet could be obtained in which the place of maximum probability density oscillated back and forth with a simple harmonic motion having the classical frequency. Debye[38] has attempted a general treatment of the motion of a wave packet representing a particle whose position is fairly accurately known in a general one-dimensional force field. Other investigations in this direction are those of Ehrenfest and of Ruark.[39] These studies are all based on the use of approximate solutions of Schrödinger's equation for $(\boldsymbol{r}|H')$ and content themselves with showing the approximate validity of the Newtonian laws of motion for the place of maximum probability density. It would be of interest to pursue the matter further, for example, to construct a wave packet enabling one to watch the probabilities while a particle is in the act of slipping through a potential wall where it wouldn't be allowed by classical mechanics.

We shall not present the details of any of the wave packet calculations as they have not played a great role in collision theory thus far. The main object in mentioning them is simply to indicate the nature of the calculations to be done if one cares to follow the course of a collision in time.

The standard form (recommended by its analytical simplicity and *not* having any connection with the appearance of the same function as an approximate representation of Bernoulli's theorem in classical probability theory) for representing a situation in which the particle is known to be in the neighborhood of the place whose position vector is $\boldsymbol{a}$, with an uncertainty measured by σ, and with a mean momentum, $\boldsymbol{p}_0$, is to take for $(\boldsymbol{r}|)$, the expression,

$$(\boldsymbol{r}|\,) = \pi^{-3/4}\sigma^{-3/2} \exp\left\{-(\boldsymbol{r}-\boldsymbol{a})^2/2\sigma^2 + 2\pi i \boldsymbol{p}_0\cdot\boldsymbol{r}/h\right\}$$

This is so normalized that the integral of $(\,|\boldsymbol{r})(\boldsymbol{r}|)$ over all space is unity. This is an expression which will be used in later sections. To start with such a state at $t=0$ and to trace its development as time goes on is the nearest thing that one can do in quantum mechanics to the corresponding process of finding the motion belonging to given initial conditions. One can, of course, use such an initial state no matter what the Hamiltonian governing the particle. But the subsequent change of $(\boldsymbol{r}|)_t$ will depend on the Hamiltonian because of the occurrence of the functions, $(\boldsymbol{r}|H')$, in the equation for the change of $(\boldsymbol{r}|)_t$ with time.

[36] Compare e.g., Slater, Phys. Rev. **31**, 895 (1928).
[37] Schrödinger, Naturwiss. **14**, 664 (1926); Markoff, A. Zeits. f. Physik **42**, 637 (1927).
[38] Debye, Phys. Zeits. **28**, 170 (1927).
[39] Ehrenfest, Zeits. f. Physik **45**, 455 (1927): Ruark. Phys. Rev. **32**, 1133 (1928).

The $(\boldsymbol{p}\,|\,)$ representative of this same state is readily found to be

$$(\boldsymbol{p}\,|\,) = \pi^{-3/4}\tau^{-3/2} \exp\left\{-(\boldsymbol{p}-\boldsymbol{p}_0)^2/2\tau^2 + 2\pi i\boldsymbol{a}\cdot(\boldsymbol{p}-\boldsymbol{p}_0)/h\right\}$$

where $\tau = h/2\pi\sigma$. This brings out clearly the fact that the mean momentum for the state is $\boldsymbol{p}_0$ and that the product of the uncertainties in position and momentum is equal to $h/2\pi$ for this state.

APPENDIX

SCATTERING BY A CRYSTAL LATTICE

By P. M. Morse

When we consider the behavior of electrons inside a crystal, we encounter a much more complex problem than any of the previous examples. Inside the crystal, atoms are arranged in a regular three dimensional geometric pattern. An electron is never free from the influence of one or another atom, but is continually battering its way through the lattice, disrupting some of the bound atomic electrons, changing atomic energies, in turn being temporarily held by an atom, and, again, absorbing some atomic energy. In order to deal with this complicated process we are forced to make several drastic simplifications.

In the first place the atoms are much heavier bodies than the wandering electron, and are only slightly disturbed from their equilibrium position by electronic impact; and so the nuclei will be considered as fixed at their equilibrium points. But this simplification is not enough, for each atom is too complicated a system in its interactions with the electrons for us to be able to deal with, and a whole lattice of atoms would be still more impossible to handle.

In other words we first consider the behavior of a single electron in the potential field caused by the fixed atoms; then consider the vibration of the crystal atoms when undisturbed by electronic motions; and lastly we must calculate the effect on these motions of the interaction between electron and vibrating atoms and between electron and electron by approximate perturbation methods. These interactions must be taken into account when we wish to discuss the crystal's electrical conductivity, or its magnetic or mechanical properties; but the interaction calculations are very involved, and in the scattering of electrons from crystals they presumably introduce only slight corrections, so we shall neglect them here.

The problem discussed in this section is therefore that of the behavior of an electron traversing a fixed, three-dimensionally periodic potential field. This has been attacked in a number of different ways, and a number of different approximate forms of the function $(x'\,|H'\,)$ have been used.

The simplest approximation is to consider the periodic potential variation as being negligible. In this case the crystal is merely a uniform depression in the potential, an amount $h^2V_0/8\pi^2\mu$ less than the potential outside. If the crystal is infinite in extent, the function $(r'\,|W'\,)$ for an electron of kinetic energy $h^2W/8\pi^2\mu$ is $e^{i(\boldsymbol{r}\cdot\boldsymbol{p})}$, where the magnitude of $\boldsymbol{p}$ is $(W)^{1/2}$ and its direction is in the direction of the electronic motion.

This rough approximation was used by Sommerfeld, Houston and others[40] to explain many phenomena of metallic conduction, etc. However this approximation cannot deal with such experiments as those of Davisson and Germer,[41] where electrons are shot from the outside at a crystal and are reflected from this surface. Since the electron stream can be represented as a plane wave of wave-length inversely proportional to the electronic momentum, we should expect strong reflection for certain wave-lengths, similar to the Bragg beams for x-rays. Davisson and Germer obtain such strong reflections. Since the solution mentioned above neglects the atom-grating entirely we cannot expect it to deal with such an experiment. To this order of approximation the crystal acts as a homogeneous medium of index of refraction $(1+V_0/E)^{1/2}$, where $h^2E/8\pi^2\mu$ is the electron's kinetic energy outside the crystal,[42] and the reflection from such media has been discussed in an earlier section.

Perhaps a better approximation can be obtained by approaching the problem from a different viewpoint. Instead of considering the electron as approximating a completely free electron, we can consider it as approximating an atomic electron.[43] Since the electrons are under the influence of the nuclear fields their behavior will be somewhat like that of an electron in an isolated atom, and the lower the electronic energy, the better is this approximation.

In other words, the crystal can be considered as a large molecule composed of similar atoms, and the electron behavior can be determined by methods used in discussing electrons in molecules.

For instance in the case of an electron in a diatomic molecule of similar atoms,[44] since the potential barrier between the two nuclei is finite, there is a possibility that an electron originally about one nucleus can get through to the other nucleus. Therefore in equilibrium conditions the function describing the electronic behavior will best be approximated by a linear combination of the wave function about one nucleus, Φ_1, and that about the other, Φ_2, i.e.,

$$(x' \mid W') = a\Phi_1 + b\Phi_2 = \Psi.$$

The values of a and b are determined by the average energy change due to the proximity of the two nuclei, by the usual methods of dealing with degenerate systems. If the perturbing energy V is the change in potential about one nucleus due to the proximity of the other, then the average energies used are

$$E_1 = \int \bar{\Phi}_1 V \Phi_1 dv = E_2; \quad E_{12} = \int \bar{\Phi}_1 V \Phi_2 dv = E_{21}$$

and the values of a and b are determined by the equations

[40] Pauli, Zeits. f. Physik **41**, 81 (1927); Sommerfeld, Houston, Eckart, Zeits. f. Physik **47**, 1 (1928); Houston, Zeits. f. Physik **48**, 449 (1928).

[41] Davisson and Germer, Proc. Nat. Acad. **14**, 619 (1928).

[42] Bethe, Naturwiss. **15**, 787 (1927).

[43] Heisenberg, Zeits. f. Physik **49**, 619 (1928); Bloch, Zeits. f. Physik **52**, 555 (1928); Slater, Phys. Rev. **35**, 509 (1930).

[44] Morse and Stueckelberg, Phys. Rev. **33**, 932 (1929).

$$(E_1 - E)a + E_{12}b = 0$$
$$E_{21}a + (E_2 - E)b = 0$$

where E is the difference between the atomic energy level and the corresponding molecular level. The secular determinant determining E from these equations is

$$(E_1 - E)^2 = E_{12}^2$$

and so $E = E_1 \pm E_{12}$. In other words the proximity of the two similar nuclei splits the single atomic level into two levels. The two wave functions corresponding to the two levels are

$$\Psi_1 = (\Phi_1 + \Phi_2)/2^{1/2}; \quad \Psi_2 = (\Phi_1 - \Phi_2)/2^{1/2}.$$

If now we build up a one-dimensional crystal by stringing N similar nuclei in a line an equal distance d_x apart, we find that the original atomic energy level is split up into N different levels, each level corresponding to one of the linear combinations

$$\Psi_n = \sum_{r=1}^{N} a_{nr}\Phi_r \qquad (n = 1, 2, \cdots, N)$$

where Φ_r is the atomic wave function about the r'th nucleus.

If the perturbation between adjacent nuclei only be considered, then the equations determining the a's will be the set

$$a_{n,r-1}E_{12} + (E_1 - E_n)a_{n,r} + E_{12}a_{n,r+1} = 0 \quad (r = 1, 2, \cdots, N)$$

similarly to the simple case above. A solution of the secular determinant arising from these equations shows that

$$E_n = E_1 - 2E_{12}\cos \pi n/(N + 1).$$

If the ratio between the successive coefficients is taken equal

$$a_{n2}/a_{n1} = a_{n3}/a_{n2} = \cdots = a_{nN}/a_{nN-1} = x_n.$$

Then each set of equations above becomes

$$x_n^2 + 2\cos\left[\pi n/(N + 1)\right] \cdot x_n + 1 = 0$$

or

$$x_n = \exp \pm \left[\pi in/(N + 1)\right]$$

and therefore

$$\Psi_n = \frac{1}{N^{1/2}} \sum_{r=1}^{N} \Phi_r \exp\left[\pi inr/(N + 1)\right] \qquad \text{(for the plus sign)}.$$

The value of Ψ_n near the r'th nucleus, i.e., when $x = rd_x$, if the origin be placed at the first nucleus, will be nearly entirely due to the term with Φ_r, since the Φ's become very small at distances from their nucleus greater than $d_x/2$. This means that the function Ψ_n can be quite closely approximated by the function

$$\exp\left[\pi inx/(N + 1)d_x\right] \cdot U(x)$$

where

$$U(x) = \sum_{r=1}^{N} \Phi_r / N^{1/2}$$

and is a function periodic in x with period d_x.

If the crystal is very large, N is large, and the quantity $n/2(N+1)$ can be considered as having a continuous range of possible values between zero and $1/2$, and if U be expanded into a Fourier series,

$$\Psi = \exp[ik_x\alpha/x] \sum_{l=-\infty}^{\infty} b_{xl} \exp[il\alpha x]$$

where $\alpha = 2\pi/d_x$, and where the value of k_x, the variable corresponding to $n/2(N+1)$, determines the particular wave function chosen. It is seen also that the original single atomic energy level is now spread into a continuous band of allowed levels, which may or may not be separated from the band corresponding to the next atomic level by a band of forbidden energies.

For small values of k_x the energy varies linearly with the square of k_x, and so $k_x\alpha$ is analogous to the p in the free electron function.

The discussion so far has been for but one dimension, but the generalization to three dimensions is obvious, and for a simple cubic, orthorhombic or tetragonal lattice the wave function is

$$\Psi = \exp i(k_x\alpha x + k_y\beta y + k_z\gamma z) \cdot \sum_{l,m,n=-\infty}^{\infty} B_{lmn} \exp i(l\alpha x + m\beta y + n\gamma z).$$

This can be considered as a free electron, multiplied by a Fourier series representing the distortion due to the presence of the nuclei.

This approximation is somewhat better than the first mentioned one, and Bloch[43] has obtained fairly good results for conductivity with it. However it is a good approximation only for the electrons with the lowest energies. For higher energies the atomic wave functions used in the function U are not particularly good approximations to the actual wave function, for the distortion due to the presence of the neighboring nuclei is relatively large.

Perhaps the best way to treat the problem is to attack it directly, by solving for the motion of an electron in the three-dimensionally periodic field of the nuclei.[45] This should give results which will approximate that of the free electron for high energies, and that of the Bloch combination of atomic electrons for low energies. And it should predict the results of Davisson and Germer.

Any three dimensionally periodic potential function can be represented by the Fourier series

$$V = \frac{h^2}{8\pi^2\mu} \sum_{l,m,n} A_{l,m,n} \exp[i(l\boldsymbol{\alpha}+m\boldsymbol{\beta}+n\boldsymbol{\gamma}) \cdot \boldsymbol{r}]$$

[45] Morse, Phys. Rev. **35**, 1310 (1930).

where the summation extends from minus to plus infinity for all three indices, and where the A's are chosen so that V is everywhere real. $\boldsymbol{r}$ is the vector distance from some origin, and $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are vectors parallel to each of the crystal axes (four would be needed for the hexagonal system, but the generalization is apparent), of lengths equal to 2π divided by the respective lattice spacings.

This potential function is inserted in the usual Schrödinger equation and the function $(r|H')$ is to be found which is finite, single valued and continuous over all space. The resulting equation is a generalized form of Hill's equation,[46] and solutions satisfying the boundary conditions can be found if the series $\Sigma A_{l,m,n}$ is absolutely convergent.

For a working example a cubic, tetragonal, or orthorhombic crystal will be assumed, and the potential function will be simplified into the form

$$V = -\frac{h^2}{8\pi^2\mu}\left[\sum_l \alpha^2 A_{x,l} e^{il\alpha x} + \sum_m \beta^2 A_{y,m} e^{im\beta y} + \sum_n \gamma^2 A_{z,n} e^{in\gamma z}\right]$$

where α, β and γ are the scalar magnitudes of $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$; and, to make the average energy equal to zero and V real, $A_{x,0} = A_{y,0} = A_{z,0} = 0$, and $A_{x,l} = A_{x,-l}$ etc. This form of potential function is not general enough to express every sort of lattice, but the electronic behavior in such a field will be sufficiently illustrative.

The resulting Schrödinger equation,

$$\Delta u - [W + \alpha^2 \sum A_{x,l} e^{il\alpha x} + \beta^2 \sum A_{y,m} e^{im\beta y} + \gamma^2 \sum A_{z,n} e^{in\gamma z}]u = 0$$

where u is the function $(x, y, z|H')$ and where W is $8\pi^2\mu/h^2$ times the electronic energy, can be broken up into three simple equations if $u = X(x) \cdot Y(y) \cdot Z(z)$. These equations are

$$\frac{d^2X}{dx^2} - (Wa^2 + \sum \alpha^2 A_{x,l} e^{il\alpha x}) X = 0$$

$$\frac{d^2Y}{dy^2} - (Wb^2 + \sum \beta^2 A_{y,m} e^{im\beta y}) Y = 0$$

$$\frac{d^2Z}{dz^2} - (Wc^2 + \sum \gamma^2 A_{z,n} e^{in\gamma z}) Z = 0$$

where $(a^2+b^2+c^2) = 1$. The resulting solution, u, represents a stream of electrons travelling with a velocity equal to $(h^2W/4\pi^2\mu^2)^{1/2}$ in the direction given by the direction cosines a, b and c.

Since these equations are similar, an investigation of one of them will indicate the solutions to all three. The solution[47] of the first equation is

[46] Whittaker and Watson, A Course of Modern Analysis, Cambridge Univerity Press (1915), Chapter 19. An approximate solution has been found by Peierls, Ann. d. Physik **4**, 121 (1930). Bethe, Ann. d. Physik **87**, 55 (1928) discussed the equation and obtained a number of the properties of the solution.

[47] Van der Pol and M. J. O. Strutt, Phil. Mag. **5**, 18 (1928).

$$X = \sum_{r=-\infty}^{\infty} B_{x,r} e^{i(k_x+r)\alpha x}$$

where the B's are determined by the equations

$$\left[\frac{Wa^2}{\alpha^2} - (k_x + r)^2\right] B_{x,r} + A_{x,l} B_{x,r-1} = 0 \quad (r = \cdots, -1, 0, 1, 2, \cdots)$$

and the constant k_x is determined by the equation

$$\sin^2(\pi k_x) = \Delta(0) \cdot \sin^2(\pi a (W)^{1/2}/\alpha)$$

where $\Delta(0)$ is the determinant

$$\begin{vmatrix}
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & 1 & \frac{-A_{x,1}}{16-W'} & \frac{-A_{x,2}}{16-W'} & \frac{-A_{x,3}}{16-W'} & \frac{-A_{x,4}}{16-W'} & \cdots \\
\cdots & \frac{-A_{x,1}}{4-W'} & 1 & \frac{-A_{x,1}}{4-W'} & \frac{-A_{x,2}}{4-W'} & \frac{-A_{x,3}}{4-W'} & \cdots \\
\cdots & \frac{-A_{x,2}}{1-W'} & \frac{-A_{x,1}}{1-W'} & 1 & \frac{-A_{x,1}}{1-W'} & \frac{-A_{x,2}}{1-W'} & \cdots \\
\cdots & \frac{-A_{x,3}}{-W'} & \frac{-A_{x,2}}{-W'} & \frac{-A_{x,1}}{-W'} & 1 & \frac{-A_{x,1}}{-W'} & \cdots \\
\cdots & \frac{-A_{x,4}}{1-W'} & \frac{-A_{x,3}}{1-W'} & \frac{-A_{x,2}}{1-W'} & \frac{-A_{x,1}}{1-W'} & 1 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots
\end{vmatrix}$$

where $W' = Wa^2/\alpha^2$.

This solution is finite everywhere in a crystal of infinite extent for all real values of k_x. A study[47] of the behavior of k_x for values of the A's of the same order of magnitude or less than W shows that k_x is only complex for values of a^2W close to the set of values $\alpha^2/4$, α^2, $9\alpha^2/4$, $4\alpha^2$, ... This indicates that for any given electronic energy, there are certain values of a, b and c, i.e., certain directions of electron motion inside the crystal, which are barred.

Notice that this form of wave function is of the Bloch form, and will equal his solution for low energy values. For high energy values, unless the k's are complex, only B_{x0} is large, and the solution is that of the free electron.

If the crystal is not infinite in extent, but is bounded by surfaces, then these directions will not be barred, for u can then be finite everywhere even for complex values of the k's. However the real exponential term due to the imaginary part of the k's will insure that the amplitude of u for these directions is negligible except near the surface of the crystal. This indicates that for a beam of electrons of energy and direction such that $a^2W = l^2\alpha^2/4$, $b^2W = m^2\beta^2/4$, and $c^2W = n^2\gamma^2/4$ (l, m, n integers) the electron wave will be damped out as it penetrates the crystal, and therefore such beams will be strongly reflected from the crystal surface. The above relations between the

energy and direction of strongly reflected beams and the grating constants are those defining the analogues of Laue beams in x-rays.

The relation between a^2W/α^2 and k_x can be represented by the equation

$$\frac{a^2W}{\alpha^2} = k_x^2 + f(k_x)$$

where f only has values appreciably different from zero when k_x is near $n\alpha/2$. The values of $f(k_x)$ are shown in Figs. 5 and 6 for two different forms of po-

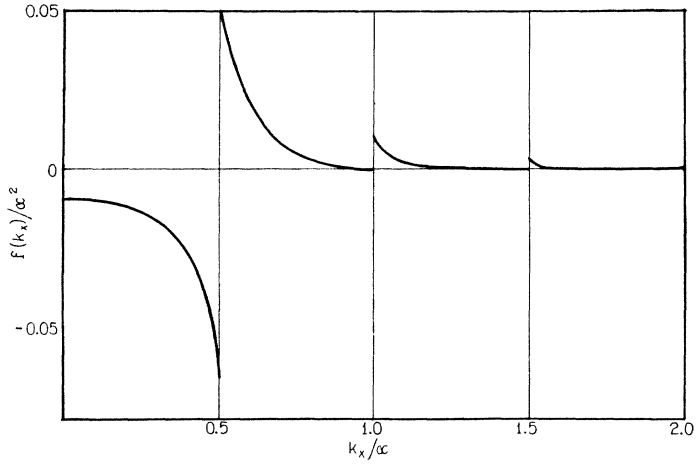

Fig. 5. Values of $f(k_x)/\alpha^2$ for the potential function $V=(h^2/8\pi^2\mu)(\cos \alpha x/2)$

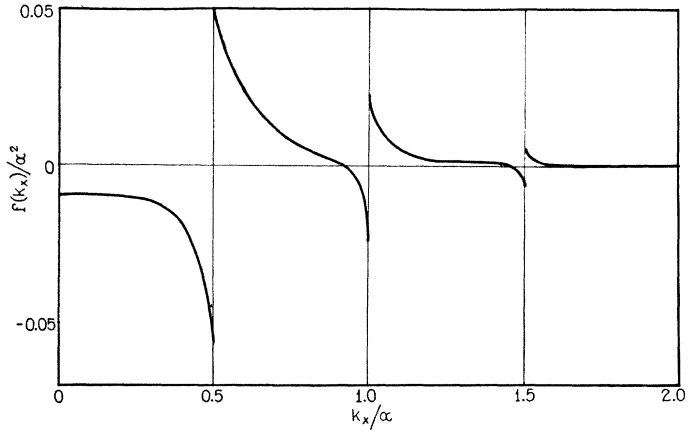

Fig. 6. Values of $f(k_x)/\alpha^2$ for the potential function $V=(h^2/8\pi^2\mu)$ [3 cos $(\alpha x)/4$ -3 cos$(2\alpha x)/10+$cos$(3\alpha x)/20$]

tential function, for real values of k_x. Note that the form of f when k_x is near $n/2$ is sensitive to changes in the form of V, and so if f is known, the general form of V can be estimated.

Thus we see immediately that some of the results of Davisson and Germer

and others are predicted. Their experiments have shown that an electron beam scatters from a crystal in a manner strikingly analogous to a beam of x-rays of wave-length equal to the de Broglie "wave-length" of the electron beam, if the crystal were considered to have an "index of refraction" equal to $[(E+V_0)/E]^{1/2}$, where E is the energy of the electron beam and V_0 is approximatily equal to the work function of the metal. We have already shown that electrons will be scattered from crystal surfaces in directions analogous to Laue beams, and we shall proceed to show that an application of the theory outlined above explains the other experimental results.

For simplicity, let the crystal surface be the plane, $x=0$, and let the space, x negative, be field-free. Since the average potential inside the crystal has been set equal to zero, and the average potential inside is less than that outside by the amount ϕ, where ϕ can be called the work function of the crystal, then the value of the constant potential in the space, x negative, will be ϕ.

The simplest case to consider is that of a beam of electrons falling normally on the surface: we wish to find the relative intensity of the beam reflected back on the primary beam as a function of the energy of the primary beam.

Since for the present we have ruled out electronic loss of energy by omitting the interaction between the electron and the nuclear vibration, we cannot deal with the electrons heterogeneously scattered with loss of energy: and since we are not for the present interested in the homogeneous scattering to the side, we can neglect the Y and Z factors, and impose the boundary conditions on the X factor alone.

Since the primary and reflected beams are in field-free space, use can be made of the results of section 2, and the function X will be

$$X_0 = Ce^{i(E)^{\frac{1}{2}}x} + De^{-i(E)^{\frac{1}{2}}x}$$

outside the crystal. E is $8\pi^2\mu/h^2$ times the electronic energy outside the crystal. Therefore the electronic energy inside the crystal will be $W=E+V_0$, where $V_0=8\pi^2\mu\phi/h^2$, and so the electron beam inside the crystal will be represented by the function

$$X_i = \sum_r B_{x,r}e^{i(k_x+r)\alpha x}.$$

At $x=0$ this must equal X_0 in slope and magnitude. The B's can be calculated for any assumed type of potential function, by the equations given previously, and so the two boundary conditions

$$C + D = \sum B_{x,r}$$

$$C - D = \sum \frac{\alpha(k_x + r)B_{x,r}}{(E)^{1/2}}$$

serve to determine C and D. The ratio $J=D\bar{D}/C\bar{C}$ will then be the relative intensity of the reflected beam. Analysis of the properties of the B's indicates that J will be unity for values of E which make k_x complex. Figure (7) shows

a simple form of potential function, and Figure (8) shows the values of J for different values of E. Actually, since a number of electrons are scattered heterogeneously in their passage through the crystal, the maximum values of J will not be unity, and since more electrons are so scattered at high energies than at low, these peaks will diminish in height for increasing E. Approximately, the energy E_n for each peak is given by the equation

$$E_n = \frac{n^2\alpha^2}{4} - V_0$$

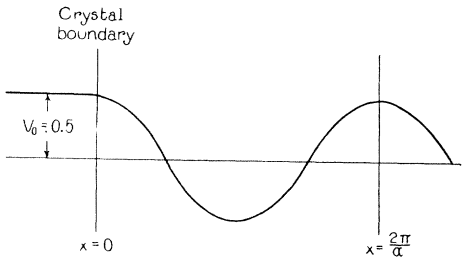

Fig. 7. Assumed form of potential energy function.

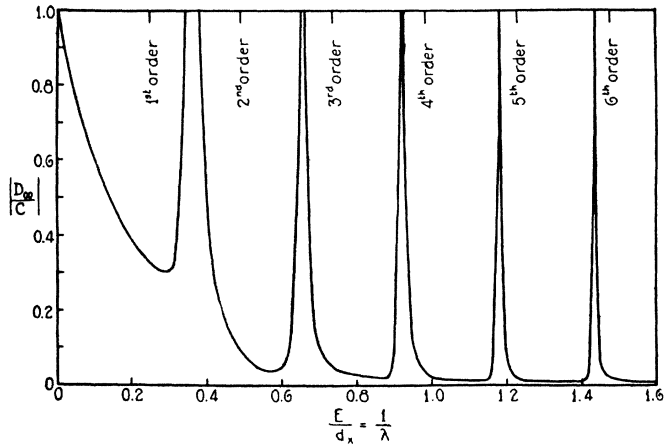

Fig. 8. Relative intensity of the regularly reflected beam as a function of the electronic wave number. The incident beam is normal to the 111 surface of a nickel crystal. Lines marked 1st order, etc., indicate positions of strong x-ray reflection for the same crystal.

which would be the values found for simple Bragg wave reinforcement if the crystal has an index of refraction equal to $[(E+V_0)/E]^{1/2}$.

The exact value of E_m is given by the equation

$$E_m + V_0 = \frac{n^2\alpha^2}{4} + \alpha^2 G_n$$

where G_n is a quantity, usually small compared to $\frac{1}{4}$, whose value depends on the surface conditions.

Thus the only information given by this exact treatment, additional to that given by the simpler Bragg theory, is that the difference between the energy values E_n and the values $n^2\alpha^2/4$ is not exactly V_0, but that this difference varies with change of surface conditions and with different n values. A glance at the experimental curves[48] shows that they bear out these additional refinements.

The case where the primary beam is in the x, y plane, and strikes the surface at an incident angle θ to the surface normal, corresponds to the usual Bragg method of x-ray analysis. In this case only the Z factor of the u function can be neglected. The function inside the crystal will be then

$$U_i = \sum_m B_{y,m} e^{i(k_y+m)\beta y} \cdot \sum_n B_{x,n} e^{i(k_x+n)\alpha x}$$

where k_x is a function of $W \cos\phi$ and k_y of $W \sin\phi$: that is, it represents an electron stream of energy $W=E+V_0$ travelling in the plane of incidence at an angle ϕ to the surface normal.

To satisfy the boundary conditions, which require that at $x=0$ the amplitude and normal gradient of the functions inside and outside the crystal be the same, the function outside must be

$$U_0 = C \exp\{i((E)^{1/2}\sin\theta y + (E)^{1/2}\cos\theta x)\} + \sum_r D_r \exp\{i[((E)^{1/2}\sin\theta + r\beta)y - (E - ((E)^{1/2}\sin\theta + r\beta)^2)^{1/2}x]\}$$

where $(E)^{1/2}\sin\theta = k_y\beta$. From the previous discussion we have seen that when k_y is not near $m/2$, then

$$\beta k_y = (W)^{1/2}\sin\phi \text{ approximately}$$

and since $\beta k_y = (E+V_0)^{1/2}\sin\theta$, this shows that the index of refraction, $\sin\theta/\sin\phi$, is approximately equal to $(E+V_0)^{1/2}/(E)^{1/2}$, except for values of E and θ such that k_y is near one of the values $m/2$.

A more correct relationship between E, θ, V_0 and ϕ is obtained by means of the equation for $g(k)$, and is

$$(E+V_0)\sin^2\phi = E\sin^2\theta + \beta^2\frac{((E)^{1/2}\sin\theta)}{\beta^{1/2}}$$

where g is only appreciably different from zero when $(E)^{1/2}\sin\theta$ is near one of the values $m\beta/2$.

The intensity of the regularly reflected beam can be found by equating the terms of U_0 and U_i, and $\partial U_0/\partial x_i$ and $\partial U_i/\partial x$ which have the y part of their exponential equal, at $x=0$. These equations reduce to

$$C + D_0 = B_{y,0}\sum_n B_{x,n}$$

$$C - D_0 = B_{y,0}\sum_n \frac{\alpha(k_x+n)B_{x,n}}{(E)^{1/2}\cos\theta}.$$

[48] Davisson and Germer, Proc. Nat. Acad. **14**, 622 (1928).

These equations are similar to those for the one dimensional case of normal incidence, and therefore the values of E and θ giving a strong regularly reflected beam are determined by the equation

$$(E_n + V_0) \cos^2 \theta_n = \frac{n^2\alpha^2}{4} + \alpha^2 G_n$$

where G_n is small and depends on the surface conditions. To relate this to θ, use is made of the previous equation, and we finally find that the values E_n and θ_n for a maximum regular reflection are given by

$$E_n \cos^2 \theta_n = \frac{n^2\alpha^2}{4} - V_0 + G_n + \beta^2 \frac{((E)^{1/2} \sin \theta)}{\rho} .$$

The Bragg analysis, for an external wave-length equal to $2\pi/(E)^{1/2}$ would give $E_n \cos^2 \theta = n^2\alpha^2/4$ for index of refraction unity, and $E_n \cos^2 \theta_n = (n^2\alpha^2/4) - V_0$ for index of refraction $[(E+V_0)/E]^{1/2}$.

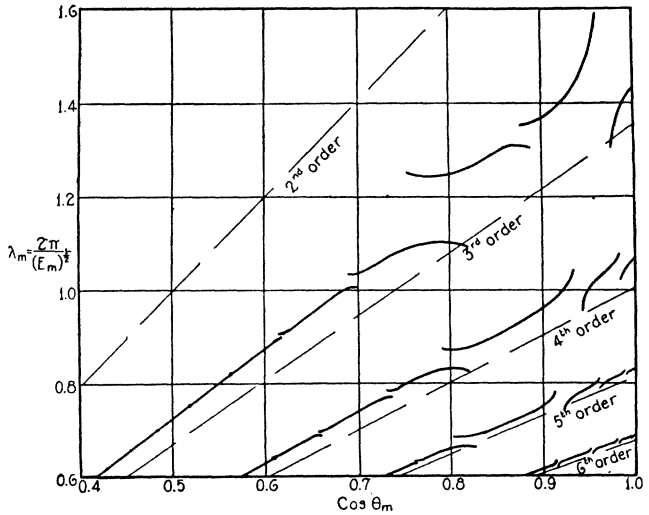

Fig. 9. Values of electronic wave number and angle of incidence of electron beam for strong regularly reflected beam. The cystal is nickel, the surface the 111 plane. Broken lines indicate positions of analogous x-ray reflection.

If $1/(E)_n^{1/2}$, which is proportional to the de Broglie wave-length of the electron beam, is plotted against cos θ_n for maximum regular reflection, the Bragg analysis would require straight lines all going through the origin, $1/(E)^{1/2} = 0$, cos $\theta = 0$. The curves required by the exact analysis above differ from the Bragg lines appreciably only when $(E)^{1/2} \sin \theta$ is near $m\beta/2$, i.e., when f is large.

A curve of values of $1/(E)_n^{1/2}$ and cos θ_n for maximum regularly reflected beams is given in Figure 9. The x and y parts of the potential function are taken to be simple sinusoidal variations, for simplicity. The dotted lines, marked 1st order, 2nd order, etc., are those given for index of refraction unity, and the curved lines give the correct relation. Note the "breaks" in the curves whenever $(E_n)^{1/2} \sin \theta_n$ equals $m\beta/2$.

Of course the shape of the curves near the breaks will be different for different forms of the potential function: but the breaks will always occur where $E_n \sin \theta_n = m\beta/2$.

A glance at the experimental curve[49] shows that such breaks are present, the most marked one near $(E_n)^{1/2} \sin \theta_n = 2.96$, and another near $(E_n)^{1/2} \sin \theta_n = 2.83$. The value of $\beta/2$ for this face of nickel and for the azimuth used is 1.46, so that the breaks occur at the proper places for $m = 2$.

Thus the simple examples we have worked out show that the analysis is not only capable of accounting for the general effects of electron scattering from crystal surfaces, but also of explaining the small peculiarities in the results. It appears probable that when the shape of the $1/(E_n)^{1/2}$, $\cos \theta_n$ curves are better known near the breaks it will be possible to make an empirical estimate of the form of the potential function inside a crystal.

[49] Davisson and Germer, Proc Nat. Acad. **14,** 624 (1928).