

the logarithmic derivative at the nuclear surface and thus the phase shifts. Assuming the radius $R=r_0A^{\frac{1}{3}}$, $r_0=1.48\times 10^{-13}$ cm, and $V_0=20$ Mev the phase shifts given by this theory are

$$\begin{aligned}\Delta 0 &= (-0.367 + 0.178i), \\ \Delta 1 &= (-0.209 + 0.128i), \\ \Delta 2 &= (-0.069 + 0.062i).\end{aligned}$$

By introducing the above values into Eq. (1), a theoretical angular distribution for the elastic scattering of 6.5-Mev protons from copper was determined. This distribution is shown by the solid curve in Fig. 5. The distribution does not differ appreciably from those calculated by Shapiro⁷ for 7.35 Mev using the same parameters. Decreasing r_0 to 1.35 or increasing V_0 to 28 Mev does not greatly alter the shape of the distribution.

Comparing the theoretical distribution with the experimental, one finds very little agreement. The maximum at 45 degrees and the rapid decrease in the cross

section at large angles which appear in the experimental distribution are not present in the theoretical one. The appearance of a minimum in both curves constitutes the only real agreement.

One may therefore conclude that: (1) definite nuclear effects are present in the elastic scattering of 6.5-Mev protons by copper; (2) the observed distribution cannot be fitted using only real phase shifts, implying that appreciable nuclear absorption takes place; and (3) the Feshbach-Weisskopf theory does not appear to describe adequately the interaction of a 6.5-Mev proton with a copper nucleus.

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Transition Probability for Photoelectric Emission from Semiconductors*

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An adaptation of Makinson's theory of photoelectric emission from metals is used to treat simple one- and three-dimensional semiconductor models. The probability of excitation from a state of initial energy ϵ lying near ϵ_0 , the top of an occupied band, is found proportional to $\epsilon_0 - \epsilon$. Thus, the transition probability vanishes at the top of the band. For a density of states having the normal form, $n \sim (\epsilon_0 - \epsilon)^{\frac{1}{2}}$, the energy distribution of the emitted electrons contains a factor $(\epsilon_0 - \epsilon)^{\frac{3}{2}}$ and is thus concave upward near the band edge.

For certain simple surfaces, the photoelectric threshold may be high because transitions requiring low energy are forbidden. It is pointed out that this feature is an idealization probably not found

for real surfaces having the usual inevitable irregularities. In a qualitative discussion, more realistic cases are mentioned. It is suggested that the results retain the form derived above, although the high threshold energy disappears.

An energy distribution proportional to $(\epsilon_0 - \epsilon)^{\frac{3}{2}}$ near the band edge is in good agreement with previous experimental results on Te and other monatomic semiconductors. With the graphical methods of analysis previously applied to data on these materials, the point of view taken above permits more definite location of the edges of occupied bands. Improved estimates of upper limits to the density of occupied surface levels are then possible.

I. INTRODUCTION

RECENT experiments indicate that the external photoelectric effect can give useful information on the electronic energy structure of solids.¹ There is interest in certain monatomic semiconductors and semimetals, for which photoelectric data are available in the form of a product $n(\epsilon) \cdot s(\nu, \epsilon)$. Here the quantity of interest is n , the density of electronic energy states expressed as a function of the energy ϵ ; s is a photoelectric excitation probability which may be a function

of both ϵ and the frequency ν .² In the absence of theoretical information, it has not been possible to isolate n without making questionable assumptions about the form of s . This paper attempts to improve this situation by showing that in certain idealized cases s is proportional to $\epsilon_0 - \epsilon$ in the vicinity of ϵ_0 , the top of the occupied energy band. These restricted conclusions are then qualitatively extended to more complicated and realistic situations.

There have been many attempts to develop a satisfactory theory of the external photoelectric effect at surfaces of simple metals.³ A recent and elegant treatment of the problem has been given by Makinson.⁴ His

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¹ Apker, Taft, and Dickey, Phys. Rev. **76**, 270 (1949), and foregoing papers.

² Apker, Taft, and Dickey, Phys. Rev. **74**, 1462 (1948).

³ For a review and recent theory, see K. Mitchell, Proc. Roy. Soc. (London) **146**, 442 (1934).

⁴ R. E. B. Makinson, Phys. Rev. **75**, 1908 (1949).

approach may be summarized briefly as follows: Free-electron wave functions of the metal are perturbed by light falling on the surface. This interaction gives rise to an excited state described by a wave function consisting of plane waves propagating away from the surface in both directions. Thus, the volume photoelectric effect³ is excluded. An auxiliary wave function is introduced for mathematical convenience, and simple manipulation yields the amplitude of the excited wave moving away from the metal into the vacuum. The resulting contribution to the photocurrent arising from the electrons that were initially in an infinitesimal region of momentum space $d\mathbf{k}$ is

$$dJ \propto E(\mathbf{k}, \nu) D(r) d\mathbf{k}. \quad (1)$$

Here E is an excitation probability involving the initial and auxiliary wave functions, the x component of the vector potential (the x direction is the surface normal), and the wavelength of the excited wave in the metal. D is the transmission coefficient of the surface barrier for the photoelectrons in question, which have a wavelength $2\pi/r$ in the vacuum. One of the most valuable features of Makinson's work is the separability of E and D in a general way. For real surfaces, it is practically always conceded that $D=1$ when escape is energetically possible.⁵

After some modification, this theory for metals may be applied to simple models of semiconductors. The free-electron wave functions must be replaced by functions appropriate to the periodic potential in the emitter. This will be done here for initial states. The effect of the periodic field on the excited electrons is considered briefly in the subsequent paper.

The optical properties of nonmetals are more complex than those of simple metals, since the light wave is affected in a different way in the important region near the surface. For the free-electron model used by Makinson,⁶ it was possible to assume that the action of the incident light involved no appreciable absorption by the electron system. More complicated effects may occur in nonmetals and some real metals since absorption is important in the spectral regions involved.⁷ Detailed consideration of optical phenomena must depend, then, on the particular substance investigated. The present paper attacks an aspect of the emission problem which, we believe, is not influenced in character by these details. The following crude point of view is, therefore, adopted: The dielectric constant is assumed to change abruptly at the surface to a positive value, and the three components of the electric vector are assumed to behave as in Makinson's work.⁸ The absolute magnitude of the result will not be significant.

⁵ C. Herring and M. H. Nichols, *Revs. Modern Phys.* **21**, 245 (1949).

⁶ R. E. B. Makinson, *Proc. Roy. Soc. (London)* **162**, 367 (1937).

⁷ See, for example, W. H. Brattain and H. B. Briggs, *Phys. Rev.* **75**, 1705 (1949), for data on Ge.

⁸ R. F. Miller, *J. Opt. Soc. Am.* **10**, 621 (1925) has shown that the real part of the dielectric constant is of the order of +3 at the pertinent frequency in Te, a material of interest here.

However, the dependence of the excitation probability on initial energy should not be greatly affected.

II. AN EXAMPLE IN ONE DIMENSION

For purposes of illustration, we first consider the behavior of electrons at the surface of an idealized one-dimensional crystal.⁹ In the region $x < 0$, we assume a periodic potential with an average value that is negative. Taking the surface at $x=0$, we set the constant potential in the region $x > 0$ equal to zero. In the periodic field, we choose two superposed Bloch running wave functions in the form

$$\varphi_k(x) = u_k(x) \exp(-ikx) + Au_k^*(x) \exp(+ikx), \quad x < 0, \quad (2)$$

to describe electrons of negative total energy. At $x=0$, this must be matched to the function

$$\varphi_k(x) = B \exp(-px), \quad x > 0. \quad (3)$$

We find

$$A = c(-p + ik - d)/(p + ik + d^*), \quad (4)$$

$$B = u_k(0)(+2ik - d + d^*)/(p + d^* + ik), \quad (5)$$

where

$$c = u_k(0)/u_k^*(0), \quad d = u_k'(0)/u_k(0).$$

When the potential inside the crystal is constant, u_k is constant, $c=1$, and $d=0$. In this case, we have the familiar Sommerfeld model of a metal. Equations (4) and (5) then express two well-known results: (1) the standing plane waves describing the free electrons inside the metal have very closely a node at $x=0$ when k is small; (2) the coefficient B which measured the amplitude of the wave function in the vicinity of the surface is proportional to k .

Mitchell³ and Makinson⁴ have shown that this same proportionality to k appears in the matrix element M for photoelectric emission from the state k in a Sommerfeld metal. Thus, in Eq. (1) Makinson's excitation function E becomes proportional to $M^2 \propto k^2$, which is proportional in turn to the kinetic energy of the metallic electrons in question; hence E vanishes linearly with kinetic energy at the bottom of the Fermi band. (The k vector of the light wave is neglected as small in this treatment.)

Except in one instance, a similar argument may be applied to the more complex case of electrons in a potential that is periodic rather than constant. We consider electrons near the top of an occupied band in a semiconductor. We take k to be the wave number vector of the "hole" (or of the envelope of the Bloch wave function). It can be shown by perturbation methods¹⁰ that in this case

$$u_k(x) = u_0(x) + ikv(x), \quad (6)$$

⁹ We are indebted to Professor H. Bethe for generalizing this argument.

¹⁰ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 352; J. Bardeen, *J. Chem. Phys.* **6**, 367 (1938).

where $u_0(x)$ is the wave function for the state at the top of the band. The question arises as to how far into the band the perturbation treatment is valid. For one case, at least,¹¹ it appears to have a sufficiently wide range of validity to be of interest here.

We may apply (6) in (5) and find that B is proportional to k except for one rare case. This occurs when the surface is so located that

$$-2p = d^* + d = 2u_0'(0)/u_0(0),$$

where terms of order k^2 are neglected in the last expression. Then $A = c$ and $B = 2u_0'(0)$, which is not proportional to k . At the surface, a resonance occurs between the modulational (short wavelength) part of the interior wave function and the damped exterior wave. A node in the envelope of the Bloch function is no longer required in the neighborhood of the surface. Because of the highly special surface condition required to produce this phenomenon, we shall look upon it as an artificiality and shall not consider it further here.

Except for the rare case above, then, the amplitude of the wave function at the surface of our periodic one-dimensional crystal behaves in the same way as that at the surface of a Sommerfeld free-electron metal. In place of the wave vector of the free electron in the metal, we substitute the wave vector k of the "hole" corresponding to the state in question near the top of the occupied zone in the periodic structure. We find that the amplitude of the damped part of the wave function outside the crystal surface (as measured by the constant B) is proportional to k .¹²

We may now apply Makinson's technique in an approximate way and calculate the transition probability for photoelectric emission from this one-dimensional system. For simplicity, we neglect the effect of the periodic field on the wave functions of the excited states and treat these electrons as practically free inside the crystal. Thus, we may use excited wave functions θ_k and auxiliary functions χ_r identical with Makinson's [see Eqs. (4) and (5), reference 4]. The part of the integral in Makinson's Eq. (6) which lies outside the metal involves the damped wave function. It is, therefore, proportion to B and so to k . Inside the metal, the wave function can be written

$$\varphi_k = [(1+A) \cos kx - i(1-A) \sin kx] u_0(x) + [(1+A) \sin kx + i(1-A) \cos kx] kv(x). \quad (7)$$

When integrated with a traveling wave, which is slightly damped as it goes into the metal, $\sin kx \cdot u_0(x)$ gives a contribution proportional to k . From Eq. (4) it can be seen that $(1+A)$ varies as k . It follows, therefore,

¹¹ P. M. Morse, Phys. Rev. **35**, 1310 (1930). This point is most clearly displayed in Morse's Fig. 5, which shows the Fourier coefficients for the functions that we symbolize here by u . At the top of the lowest zone, a relation like (6) holds over the range in which the quantities b_0, b_{-1} , involving Morse's first two Fourier coefficients, are linear in k .

¹² A proportionality of this type for "almost-free" electrons in a one-dimensional periodic structure was first proposed, to our knowledge, in unpublished work by H. Brooks.

that the part of the matrix integral arising from the region inside the metal is also proportional to k . Hence, the excitation function E in Makinson's Eq. (8) is proportional to k^2 .

On the basis of this application of Makinson's methods, we conclude that the transition probability for photoelectric emission from a state near the top of an occupied zone in our one-dimensional crystal is proportional to the energy of the hole formed by the transition. In the symbols used here (and in reference 2), the probability is proportional to $\epsilon_0 - \epsilon$, where ϵ_0 is the energy at the top of the band and ϵ is the energy of the state in question.¹³

III. THREE-DIMENSIONAL CASES

Consideration of real semiconductors involves problems that are necessarily three-dimensional. (In the foregoing section, any mention of the density of states would have been pointless because momenta parallel to the surface were either excluded or treated like those of free electrons.) Though the variety of possible situations is large and the detailed analysis is complex, it is possible to show that the character of the result in Sec. II is preserved in passing from the one- to the three-dimensional crystal.

The surface of the semiconductor is taken to be the plane $x=0$. Inside the crystal the wave function has the form

$$\phi_k(\mathbf{r}) = \exp[-i(k_x x + \mathbf{k}_\rho \cdot \boldsymbol{\rho})] u_k(+, \mathbf{r}) + A \exp[i(k_x x - \mathbf{k}_\rho \cdot \boldsymbol{\rho})] u_k(-, \mathbf{r}) + S(\mathbf{r}), \quad (8)$$

where $\boldsymbol{\rho}$ is the component of \mathbf{r} parallel to the surface plane, i.e., $\rho = (y^2 + z^2)^{1/2}$. The quantities \mathbf{k}_ρ and k_x are the components of the wave number vector of the hole respectively parallel and perpendicular to the surface. The three-dimensional analog of Eq. (6) is

$$u_k(\pm, \mathbf{r}) = u_0(\mathbf{r}) + i\mathbf{k}(\pm) \cdot \mathbf{v}(\mathbf{r}), \quad (9)$$

where $\mathbf{k}(\pm) = \mathbf{k}_\rho \pm k_x$, and is valid for a limited range at the top of the band.

In Eq. (8), the last term, $S(\mathbf{r})$ is a surface-type function possessing the periodicity of the surface but falling off rapidly toward the interior of the semiconductor. The introduction of this function is important to fit boundary conditions. It can be expanded as a series of functions all corresponding to the same energy as the wave function in the volume:

$$S(\mathbf{r}) = \sum_m S_m(x) \exp[-i(\mathbf{k}_\rho + \mathbf{K}_\rho + \mathbf{K}_m) \cdot \boldsymbol{\rho}]. \quad (10)$$

Here \mathbf{K}_ρ refers to the ρ -components of the free-electron \mathbf{k} for the state at the top of the band. The \mathbf{K}_m are the translation vectors of the two-dimensional space reciprocal to the semiconductor surface. The $S_m(x)$ decrease rapidly as a function of x going into the solid.

¹³ This result differs from that assumed by V. Weisskopf and L. Apker, Phys. Rev. **60**, 170 (1941) and from that tacitly assumed by E. U. Condon, Phys. Rev. **54**, 1089 (1938).

Outside the metal, the wave function has the form

$$\phi(\mathbf{r}) = \sum_n s_n \exp[-p_n x - i(\mathbf{K}_p + \mathbf{K}_n) \cdot \boldsymbol{\rho}], \quad (11)$$

where the \mathbf{K}_m are the same set of vectors as the \mathbf{K}_m . The s_n and the p_n are constants.

One method for determining a finite number of the constants S_m and s_n would be to satisfy boundary conditions for a continuous wave function and a continuous normal derivative at a finite number of points on the surface. In general, a straightforward procedure would be to work with a number of inhomogeneous, linear equations equal to the number of unknown quantities. One could obtain a solution for A , the s_n , and the S_m . However, it is more illuminating for our purpose to consider $(1+A)$ as an unknown and to solve our equations in terms of $(1-A)$. From the form of Eqs. (7) and (9), it is apparent that wherever $(1-A)$ appears it will be multiplied by k_x . It therefore follows in our solution that $(1+A)$, the s_n and the S_m will all be proportional to k_x , if our set of linear equations is linearly independent. The possibility of linear dependence has been noted already in our one-dimensional example. There this contingency appeared as a resonance effect, when a particular relationship between the wave functions inside and outside the surface was satisfied. Except when this occurs, the important amplitudes in the wave function are proportional to k_x in three dimensions as well as in one.

In passing, we note the following fundamental difference between this situation and that for a simple metal. An electron occupying an energy state inside a Sommerfeld metal has a definite momentum parallel to the surface. It appears externally as a photoelectron with this same momentum, since there is no binding in the surface plane. Simple wave functions describe the electron adequately on both sides of the surface and match at the interface. On the other hand, an electron in a three-dimensional crystal does not have a definite momentum parallel to the surface. Rather, it possesses a distribution of momenta (all leading to the same reduced momentum) determined by the crystal potential. The individual terms in the initial wave function outside the surface [see Eq. (11)], however, are associated with respectively distinct momenta, and each has a different damping constant perpendicular to the surface. A series of these simple functions must be used to match the internal wave function. Likewise, for the excited functions, for each traveling wave representing a freed photoelectron a series of functions inside the metal are needed for boundary fitting. All these functions will have the same reduced momentum parallel to the surface.

One of us has extended Makinson's treatment to the case of the periodic potential¹⁴ in three dimensions by using the expressions for the unexcited wave function ϕ_k [see Eqs. (8)–(11), inclusive], the excited wave func-

tion θ_k , and the auxiliary wave function χ_r appropriate to the periodic field.

On the basis of this work, we have come to the following conclusions:

(1) The matrix element M is proportional to k_x , and the transition probability is proportional to k_x^2 as in the one-dimensional case.

(2) For certain simple surfaces, important transitions may be forbidden. As an example, we may consider the (100) surface of a simple cubic crystal. The lowest Brillouin zone for such a structure is a cube in free-electron k space with sides at $k_x, k_y, k_z = K/2$, where $2\pi/K = a$, the lattice constant. The states of highest energy in this zone lie at the corners of the cube. Thus, $k_y \cong k_z \cong K/2$. Now the periodicity of the simple (100) surface is such that the crystal may absorb only momenta $s\hbar K$ in the y and z directions, where s has integral values. Thus, transitions from initial states near the band edge to final states having zero or very small momentum parallel to the surface are not permitted, since a momentum transfer of the type $\hbar K/2$ would be required. In the extension of Makinson's Eq. (5a) to three dimensions, the integrations over y and z automatically impose these restrictions.

Hence, the photoelectrons must emerge from the surface with y and z momentum components at least as large as $\hbar K/2$ and with a corresponding amount of kinetic energy. This means that the photoelectric threshold energy will be greatly increased, because this kinetic energy might otherwise be available in the x direction to overcome the surface barrier. This situation is, thus, quite different from that involving a simple metal, in which all of the initial energy may be used to overcome the surface barrier and for which photoelectrons consequently emerge with zero kinetic energy when ejected by quanta having the threshold energy.

These restrictions on the momentum parallel to the surface depend on the presence of a highly regular and especially simple surface structure. They probably would not appear in practice, therefore, since real surfaces do not possess such perfect configurations. Thus, a slight deviation from a (100) surface orientation immediately introduces periodicity on a much larger scale. This permits the absorption by the crystal of smaller quantities of momentum. A final state with y and z momenta very close to zero may, thereby, be permitted. Obviously, the probability of this kind of process may vary widely for different types of surfaces.

If the momentum restrictions described above for a simple surface should actually exist, they would be simple to detect experimentally, since only photoelectrons with kinetic energies of several electron volts would be emitted. Thus, a concentric-sphere phototube would show saturated currents even with large retarding fields. This would be difficult to overlook. It is not surprising, however, that it has not been observed. Apart from the ideal surfaces and special zone struc-

¹⁴ See the following article for details of this treatment, H. B. Huntington, Phys. Rev. 89, 357 (1952).

tures required, other influences such as electron interactions could mask the effect. We note further that forbidden transitions do not arise when the state of highest energy lies at the center of the zone (in a reduced-zone scheme).

To obtain the excitation probability $s(\nu, \epsilon)$ mentioned in the introduction,² we must integrate the transition probability in k space over the shell of constant energy ϵ . In the case of our simple cubic crystal, for instance, this shell is composed of small spherical octants centered at the corners of the cubical zone.¹⁵ After excitation, the electrons in the crystal occupy relatively small portions of a much larger spherical shell centered at the origin in free-electron k space. (At this point, we neglect the zone structure in the case of these higher energies.) A fraction of these excited electrons can emerge as photoelectrons. If we consider values of $h\nu$ appreciably larger than the threshold energy $h\nu_0$ required for emission from the state ϵ_0 at the top of the band, the value of this emergent fraction will be a slowly varying function of ϵ near ϵ_0 . (It will drop to zero when $\epsilon_0 - \epsilon = h(\nu - \nu_0)$.)

Thus, the energy distribution of the photoelectrons from initial states near the band edge is dominated by only two rapidly varying factors. One is the density of states, which goes to zero like $(\epsilon_0 - \epsilon)^{1/2}$. The other is the excitation probability $s(\nu, \epsilon)$ which is proportional to $\epsilon_0 - \epsilon$. We conclude that the energy distribution goes to zero like $(\epsilon_0 - \epsilon)^{3/2}$.

In the graphical method of analysis used in reference 2, this result leads to a value $\frac{3}{2}$ for the parameter m .¹⁶

IV. DISCUSSION OF THE RESULT

In this paper we have used a highly simplified approach to a very complex problem. We have neglected the detailed behavior of optical phenomena and the effect of zone structure on excited states, in the belief that the character of the result would in general not be affected. From this viewpoint, we shall proceed at once to direct comparison with experiment.

The result obtained here is in good agreement with available data on Te, since it arrives theoretically at the $\frac{3}{2}$ power dependence on energy shown by the function $N/E \sim n(\epsilon)s(\nu, \epsilon)$ for this element.² (The same

¹⁵ As pointed out by W. Shockley, Phys. Rev. **78**, 177 (1950), equal-energy surfaces need not be spherical in general.

¹⁶ An assumption made in using this method was that an excited electron had a probability of escape which varied linearly with the kinetic energy E of the external photoelectron. This is a reasonable first approximation when the excited electrons are uniformly distributed over a spherical shell in free-electron k space. If the shell is only partially occupied, as in the present case, the escape probability may exhibit structure. Then higher powers of E may become more important. This, however, does not affect the conclusions of this paper.

dependence is shown by the high energy portion of the energy distribution N .)

There is a further possibility that the very small tail found on the energy distributions for Te is due to thermal lattice vibrations¹⁷ (see Figs. 4 and 5, reference 2). If such be the case, we have interpretations of all the effects observed for Te. This requires that the upper limit estimated for the density of surface levels on Te in reference 2 be revised downward by an order of magnitude. There is no need to postulate superposed energy distributions from patches with different Fermi levels. This was done, in the previous work, for the case in which the transition probability was tentatively assumed to be independent of energy. The patch phenomenon or surface levels might still be of some importance for Ge and B. For these materials, the experimental results were less clear-cut than for Te. The energy distributions were roughly parabolic in form at higher energies. From the present point of view, however, these other effects need only explain the difference between the exponents 2 and $\frac{3}{2}$ instead of that between 2 and $\frac{1}{2}$ as formerly. Thus, the high estimated surface-state densities associated in reference 2 with exponents m smaller than $\frac{3}{2}$ are not required.

Finally, we note that the data on the function N/E for As, Sb, and Bi¹ can be interpreted more satisfactorily as overlapping $\frac{3}{2}$ power characteristics than as $\frac{1}{2}$ power characteristics. The behavior shown by each of these elements arises because the occupied band overlaps the conduction band. If the band edges have the normal form, one expects the density $n(\epsilon)$ of occupied states to show a sharp minimum slightly below the top of the occupied region and near the lower edge of the conduction band. The photoelectric data on the product $n(\epsilon) \cdot s(\nu, \epsilon) \sim N/E$ did not show such a behavior, although a plateau was observed in the case of Sb. If the transition probability s has the form suggested in this paper, the product sn for a semimetal is composed of two $\frac{3}{2}$ power characteristics. These overlap and produce a composite characteristic without a sharp minimum. This interpretation is in better agreement with the observations than is the assumption of a transition probability independent of energy.

We are indebted to Dr. R. E. B. Makinson for the privilege of reading his recent paper before publication and for supplying a copy of the thesis on which it was based. We wish to thank Professor H. Bethe for valuable discussions, particularly of the material given in Sec. III. We are grateful to Dr. Harvey Brooks for his unflagging interest and critical comments, and to Dr. Malcolm Hebb for many illuminating conversations.

¹⁷ W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950).