

# Calculation of the effective mass of an electron in a periodic field near the edge of an energy band

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It is shown that the integral of the current density over any section of the unit cell of a crystal vanishes for any wave vector  $\mathbf{k}_0$  at which the energy has an extremum as a function of the wave vector  $\mathbf{k}$  (even though the current density itself does not vanish), provided the wave vector is neither a reciprocal-lattice vector nor lies midway between reciprocal-lattice vectors. A method is presented for calculating the effective mass near the edge of an energy band. Unlike the familiar method in which perturbation theory is used to calculate quantities to the second order in  $\mathbf{k}-\mathbf{k}_0$ , which requires that the energy eigenfunctions and eigenvalues for all the bands be known at  $\mathbf{k}=\mathbf{k}_0$ , the proposed method requires the solution of only one eigenvalue equation—the one for the edge of the band of interest. In addition, there is an inhomogeneous equation to be solved; a particular solution of this equation is indicated, and this considerably simplifies the problem. The effective mass is expressed in terms of an integral of the wave functions. In the Wigner-Seitz approximation the problem reduces to the solution of two or three second-order ordinary linear homogeneous differential equations. The eigenvalue need be determined for only one of these equations. In the one-dimensional case the eigenvalue problem to be solved involves only a single ordinary differential equation; i.e., only one wave function need be known, the effective mass being given in terms of it by a simple formula [Eq. (25) in the text]. To illustrate the method the effective mass is calculated in the Wigner-Seitz approximation for compressed hydrogen, and in the one-dimensional case a quasichlassical expression is derived for the effective mass and the width of the energy band in terms of the quasichlassical momentum in the classically inaccessible region.

The initial approximation in the theory of solids may be taken as that in which quasifree electrons move in the crystal periodic field formed by the fields of the nuclei of the lattice atoms and the self-consistent field of the electrons. A periodic solution of the Thomas-Fermi equation (with or without corrections) may be employed to represent this field. The solution of the Hartree-Fock equations, or even the simple Hartree equations, involves a great deal of computational work.

The solution of the Schrödinger equation for an electron in the periodic field of the crystal can be written as a Bloch function<sup>[1,2]</sup>

$$\psi_{n,\mathbf{k}} = \varphi_{n,\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (1)$$

where  $\varphi_{n,\mathbf{k}}$  is a periodic function with the periods of the crystal lattice and  $\mathbf{k}$  is defined to within an arbitrary additive reciprocal-lattice vector. Hence the energy eigenvalue  $E_n(\mathbf{k})$  is a periodic function of  $\mathbf{k}$  with the periods of the reciprocal lattice.

In the presence of external fields that vary slowly in space and time, the quasimomentum  $\hbar\mathbf{k}$  of the electron varies just as would the momentum of a free "quasiparticle" under the action of the same force, but with the reciprocal effective mass tensor defined as

$$\left(\frac{1}{m^*}\right)_{rs} = \frac{\partial^2 E_n(\mathbf{k})}{\hbar^2 \partial k_r \partial k_s}. \quad (2)$$

The effective mass near the edges of the energy bands, i.e., near the extrema of the  $E_n(\mathbf{k})$ , play an important part in semiconductors, and sometimes in metals and dielectrics. In such a case it is not entirely necessary to find the complete function  $E_n(\mathbf{k})$ . If we write  $\mathbf{k} = \mathbf{k}_0 + \mathbf{q}$  ( $\mathbf{k}_0$  is the point at which  $E_n(\mathbf{k})$  has an extremum), we have

$$\psi_{n,\mathbf{k}} = \psi'_{n,\mathbf{k}} e^{i\mathbf{q}\cdot\mathbf{r}}, \quad qa \ll 1, \quad (3)$$

where  $a$  is of the order of a lattice period and  $\psi'_{n,\mathbf{k}}$  satisfies the equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi'_{n,\mathbf{k}} + U(\mathbf{r}) \psi'_{n,\mathbf{k}} - \frac{i\hbar^2}{m} (\mathbf{q} \cdot \nabla) \psi'_{n,\mathbf{k}} = \left( E_n(\mathbf{k}) - \frac{\hbar^2 q^2}{2m} \right) \psi'_{n,\mathbf{k}}.$$

By treating the third term as a perturbation, we can in principle find  $E_n(\mathbf{k})$  near  $\mathbf{k} = \mathbf{k}_0$  in the usual way (the so-called  $\mathbf{k} \cdot \mathbf{p}$  method):

$$E_n(\mathbf{k}_0 + \mathbf{q}) = E_n(\mathbf{k}_0) + \frac{\hbar^2 q^2}{2m} - \sum_{n' \neq n} \frac{\hbar^4}{m^2} \frac{|(\mathbf{q} \cdot \nabla)_{n',n}|^2}{E_n(\mathbf{k}_0) - E_{n'}(\mathbf{k}_0)}$$

and then one can evaluate the reciprocal effective mass tensor (2). In order to do this, however, we must find  $E_n(\mathbf{k}_0)$  and  $\psi_{n,\mathbf{k}_0}$  for all values of  $n$  in order to calculate the matrix elements  $(\mathbf{q} \cdot \nabla)_{n',n}$ , and this is practically impossible. Cases in which there are groups of comparatively few degenerate or almost degenerate levels  $E_n(\mathbf{k}_0)$  would be exceptions.

It would seem more reasonable to express  $E_n(\mathbf{k}_0 + \mathbf{q})$  in terms of a correction to the function  $\psi'_{n,\mathbf{k}}$  determined from the expansion

$$\psi'_{n,\mathbf{k}} = \psi_{n,\mathbf{k}_0} + iqa \chi_{n,\mathbf{k}_0} + \dots, \quad (4)$$

where the function  $\chi_{n,\mathbf{k}_0}$  is determined from the inhomogeneous equation

$$-\frac{\hbar^2}{2m} \nabla^2 \chi_{n,\mathbf{k}_0} + (U(\mathbf{r}) - E_n(\mathbf{k}_0)) \chi_{n,\mathbf{k}_0} = \frac{\hbar^2}{ma} \frac{\partial \psi_{n,\mathbf{k}_0}}{\partial z} \quad (5)$$

(the  $z$  axis is chosen here in the direction of the vector  $\mathbf{q}$ ). We have

$$E_n(\mathbf{k}_0 + \mathbf{q}) = E_n(\mathbf{k}_0) + \frac{\hbar^2}{2m} q^2 \left( 1 - 2a \int \chi_{n,\mathbf{k}_0} \frac{\partial \psi_{n,\mathbf{k}_0}}{\partial z} d\tau \right),$$

where  $d\tau$  is a volume element. By following this path one will obtain a different formula for  $E_n(\mathbf{k}_0 + \mathbf{q})$ .

For any periodic field,  $E_n$  has an extremum at  $\mathbf{k}_0 = 0$ . If the value of  $\mathbf{k}_0$  corresponding to an extremum of  $E(\mathbf{k})$  can be expressed in terms of integral or half-integral reciprocal-lattice basis vectors, the corresponding wave function will be real, and hence the corresponding current density at any point will vanish. If  $\mathbf{k}_0$  does not satisfy this condition,  $\psi_{n,\mathbf{k}_0}$  will be complex

and the current density will not vanish. Such values of  $\mathbf{k}_0$  occur, for example, in silicon and germanium<sup>[3]</sup>. It will be shown below that even in this case the states for which  $E(\mathbf{k})$  is extremal do not contribute to the current through the crystal, since the integral of the current density over the section (or the volume) of a cell vanishes.

The main purpose of this paper is to propose a different method for calculating the effective mass near an extremum of  $E_n(\mathbf{k})$  which, unlike the preceding methods, does not require the functions  $\psi_{n,\mathbf{k}_0}$  and  $E_n(\mathbf{k}_0)$  to be evaluated for other values of  $n$ .

## CURRENT DENSITY AT $\mathbf{k} = \mathbf{k}_0$ . EFFECTIVE MASS FORMULA

If we write the Schrödinger equation for  $\psi_{\mathbf{k}_0}^*$  and  $\psi_{\mathbf{k}_0+\mathbf{q}}$  ( $q$  is small), multiply the first of these equations by  $\psi_{\mathbf{k}_0+\mathbf{q}}$  and the second by  $\psi_{\mathbf{k}_0}^*$ , subtract one from the other, and so on, we obtain

$$E(\mathbf{k}) - E(\mathbf{k}_0) = \frac{\hbar^2}{2m} \int \nabla (\psi_{\mathbf{k}_0}^* \nabla \psi_{\mathbf{k}_0+\mathbf{q}} - \psi_{\mathbf{k}_0+\mathbf{q}} \nabla \psi_{\mathbf{k}_0}^*) d\tau \times \left[ \int \psi_{\mathbf{k}_0+\mathbf{q}} \psi_{\mathbf{k}_0}^* d\tau \right]^{-1} = \frac{\hbar^2}{2m} \oint (\psi_{\mathbf{k}_0}^* \nabla \psi_{\mathbf{k}_0+\mathbf{q}} - \psi_{\mathbf{k}_0+\mathbf{q}} \nabla \psi_{\mathbf{k}_0}^*) ds \left[ \int \psi_{\mathbf{k}_0+\mathbf{q}} \psi_{\mathbf{k}_0}^* d\tau \right]^{-1}. \quad (6)$$

Here the  $d\tau$  integration is taken over the volume of a unit (or primitive) cell, and the  $ds$  integration over the closed surface bounding that cell. We drop the subscript  $n$  throughout because here and in what follows we shall be concerned only with quantities pertaining to a single band.

Further, as in Eq. (3) we write  $\psi_{\mathbf{k}_0+\mathbf{q}} = \psi_{\mathbf{k}_0} + \mathbf{q} e^{i\mathbf{q}\cdot\mathbf{r}}$  and expand as in (4):  $\psi'_{\mathbf{k}_0+\mathbf{q}} = \psi_{\mathbf{k}_0} + i\mathbf{q}a\chi_{\mathbf{k}_0} + \dots$ . The reason for introducing  $\psi'_{\mathbf{k}_0+\mathbf{q}}$  is that, by virtue of (1), bilinear combinations of the form  $\psi'_{\mathbf{k}_0+\mathbf{q}} \hat{L} \psi_{\mathbf{k}_0}^*$ , where  $\hat{L}$  is an arbitrary local linear operator, do not contain the factor  $\exp\{i\mathbf{k}_0 \cdot \mathbf{r}\}$ ; they can be expressed in terms of  $\varphi_{\mathbf{k}_0}^*$  and  $\varphi_{\mathbf{k}_0+\mathbf{q}}$  and therefore have the period of the lattice. The same can be said of the quantities  $\chi_{\mathbf{k}_0} \hat{L} \psi_{\mathbf{k}_0}^*$ . After making these substitutions we obtain

$$E(\mathbf{k}_0+\mathbf{q}) - E(\mathbf{k}_0) = \frac{\hbar^2}{2m} \left\{ \oint e^{i\mathbf{q}\cdot\mathbf{r}} \left[ (\psi_{\mathbf{k}_0}^* \nabla \psi_{\mathbf{k}_0} - \psi_{\mathbf{k}_0} \nabla \psi_{\mathbf{k}_0}^*) + i\mathbf{q}a \left( \psi^* \nabla \chi_{\mathbf{k}_0} - \chi_{\mathbf{k}_0} \nabla \psi_{\mathbf{k}_0}^* + \frac{q}{qa} |\psi_{\mathbf{k}_0}|^2 \right) + qa\varphi_{\mathbf{k}_0}^* \right] ds \right\} \left( \int \psi_{\mathbf{k}_0+\mathbf{q}} \psi_{\mathbf{k}_0}^* d\tau \right)^{-1}. \quad (7)$$

All the terms in the brackets have the period of the lattice, and since they are vectors, the integral over the closed surface of the cell would vanish if it were not for the factor  $\exp(i\mathbf{q}\cdot\mathbf{r})$ .

Since in Eq. (7) we are interested only in terms of the order of  $(qa)^2$ , we can drop the last term at once on the basis of what was just said. Only the first term makes a contribution of the order of  $qa$  to the numerator of (7). However, since  $E(\mathbf{k})$  has an extremum at  $\mathbf{k} = \mathbf{k}_0$  by hypothesis, expansion (7) should begin with a term proportional to  $q^2$ . From this it follows that

$$\oint e^{i\mathbf{q}\cdot\mathbf{r}} (\psi_{\mathbf{k}_0}^* \nabla \psi_{\mathbf{k}_0} - \psi_{\mathbf{k}_0} \nabla \psi_{\mathbf{k}_0}^*) ds = e^{i\mathbf{q}\cdot\mathbf{a}} (e^{i\mathbf{q}\cdot\mathbf{a}} - 1) \int (\psi_{\mathbf{k}_0}^* \nabla \psi_{\mathbf{k}_0} - \psi_{\mathbf{k}_0} \nabla \psi_{\mathbf{k}_0}^*) ds = 0;$$

here  $a$  is the distance between opposite faces of the cell,  $\mathbf{q}$  is a vector normal to these faces, and the last integral is taken over any section of the cell parallel

to these faces. Thus, even though the current density  $\mathbf{j}$  does not vanish in general, the integral of

$$\mathbf{j} = \hbar (\psi_{\mathbf{k}_0}^* \nabla \psi_{\mathbf{k}_0} - \psi_{\mathbf{k}_0} \nabla \psi_{\mathbf{k}_0}^*) / im$$

over any surface of the cell does vanish. States with  $\mathbf{k} = \mathbf{k}_0$  do not contribute to the total current through the crystal.

There remains only the second term of (7), which is proportional to  $q^2$  and gives the effective reciprocal mass tensor:

$$q^2 (m^*)^{-1} = m^{-1} \oint e^{i\mathbf{q}\cdot\mathbf{r}} i\mathbf{q}a \left( \psi_{\mathbf{k}_0}^* \nabla \chi_{\mathbf{k}_0} - \chi_{\mathbf{k}_0} \nabla \psi_{\mathbf{k}_0}^* + \frac{q}{qa} |\psi_{\mathbf{k}_0}|^2 \right) ds \left( \int |\psi_{\mathbf{k}_0}|^2 d\tau \right)^{-1}. \quad (8)$$

The expression in parentheses in (8) must necessarily be periodic on the entire surface. This may be an arbitrarily translated Bragg cell, a unit cell, or (in the case of like atoms and a simple fcc or bcc lattice) a Wigner-Seitz cell.

In view of the fact that the closed integral in (8) would vanish without the exponential factor  $\exp(i\mathbf{q} \cdot \mathbf{r})$ , we can write (8) in the form

$$(m^*)^{-1} = m^{-1} \oint a \frac{q\mathbf{r}}{a} \left[ \psi_{\mathbf{k}_0}^* \nabla \chi_{\mathbf{k}_0} - \chi_{\mathbf{k}_0} \nabla \psi_{\mathbf{k}_0}^* + \frac{q}{qa} |\psi_{\mathbf{k}_0}|^2 \right] ds \left( \int |\psi_{\mathbf{k}_0}|^2 d\tau \right)^{-1}. \quad (8a)$$

If we take  $\mathbf{q}$  perpendicular to some face of the unit or primitive cell, take the  $z$  axis in the direction of  $\mathbf{q}$ , and take  $a$  as the distance between opposite faces, we obtain

$$(m^*)^{-1} = m^{-1} a^2 \int \left( \psi^* \frac{\partial \chi}{\partial z} - \chi \frac{\partial \psi^*}{\partial z} + a^{-1} |\psi|^2 \right) dx dy \left( \int |\psi|^2 dx dy dz \right)^{-1}. \quad (9)$$

Here and below all the wave functions are those for  $\mathbf{k} = \mathbf{k}_0$ , so we omit the subscript  $\mathbf{k}_0$ . The surface integral in (9) can be taken on any section of the cell perpendicular to  $\mathbf{q}$ , i.e., to the  $z$  axis, since the integrand in the numerator is independent of  $z$ .

According to (5), the solution for  $\chi$  can be expressed in the form

$$\chi = -z\psi/a + \tilde{\psi}. \quad (10)$$

The first term in (10) is a particular solution of (5) and does not satisfy the periodicity condition. The term  $\tilde{\psi}$  in (10) is a solution of the homogeneous Schrödinger equation that is linearly independent of  $\psi$ , increases linearly with  $z$  on the average, and is periodic in the directions of the  $x$  and  $y$  axes. If we substitute (10) into (9) we get

$$(m^*)^{-1} = m^{-1} a^2 \int \left( \psi^* \frac{\partial \tilde{\psi}}{\partial z} - \tilde{\psi} \frac{\partial \psi^*}{\partial z} \right) dx dy \left( \int |\psi|^2 dx dy dz \right)^{-1}, \quad (11)$$

since (9) vanishes for the particular solution for  $\chi$  in (10) and  $\tilde{\psi}$  is so chosen as to change by the amount  $\psi$  at equivalent points of the cell when  $z$  changes by  $a$  with a shift in  $x$  and  $y$  corresponding to the shape of the cell.

When the Wigner-Seitz cell is used, the periodic function  $\varphi$  must satisfy the requirement that the normal derivative at the boundary of the cell must vanish, i.e., that  $\varphi$  have the same value on both sides of the cell. If  $\psi$  is real, then it must satisfy this condition. The periodicity condition may also be satisfied by requiring that  $\psi = 0$  at the boundaries of the cell. The Schrödinger equation assures that the derivatives will be continuous.

It is a good approximation to replace the Wigner-Seitz cell by a sphere centered on an atom and having

a volume equal to the volume per atom of the crystal. The radius  $R$  of the sphere would be  $(\frac{3}{16}\pi)^{1/3}a \approx 0.39a$  for an fcc lattice and  $(\frac{3}{8}\pi)^{1/3}a$  for a bcc lattice, where  $a$  is the length of an edge of the (unit) cell of the cubic lattice. In this case if  $\psi$  is real we have either  $\partial\psi/\partial r = 0$  or  $\psi = 0$  at  $r = R$ .

The form of the particular solution of Eq. (5) for the function  $\chi$  remains the same. Hence if the potential is spherically symmetric and we write

$$\psi = S_l(r)P_l(\cos\theta), \quad (12)$$

then, setting  $a = R$  in (10), we obtain

$$\chi = -\frac{z}{R}\psi + \tilde{\psi} = -\frac{r}{R}S_l(r) \left[ \frac{l+1}{2l+1}P_{l+1}(\cos\theta) + \frac{l}{2l+1}P_{l-1}(\cos\theta) \right] + \tilde{S}_{l+1}(r)P_{l+1}(\cos\theta) + \tilde{S}_{l-1}(r)P_{l-1}(\cos\theta), \quad (13)$$

where  $\tilde{S}$  (like  $S$ ) satisfies the equation

$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2(r\tilde{S}_l)}{\partial r^2} + \left( U(r) + \frac{L(L+1)\hbar^2}{2mr^2} \right) \tilde{S}_l = E(k_0)\tilde{S}_l. \quad (14)$$

Thus, in order to satisfy the periodicity condition for  $\chi$  at  $r = R$  one must solve one (if  $l = 0$ ) or two equations (14) under the condition that  $rS(r) \rightarrow 0$  as  $r \rightarrow 0$  with a known value of  $E(k_0)$  and one equation (14) for the eigenvalue for  $S_l(r)$ . If we substitute (12) and (13) into (8a) for these cases and perform the angular integrations in the numerator and denominator, we obtain

$$(m^*)^{-1} = m^{-1}R^3 \left[ S_l \left( \frac{l+1}{2l+3}S'_{l+1} - \frac{l}{2l-1}S'_{l-1} \right) - \left( \frac{l+1}{2l+3}S_{l+1} + \frac{l}{2l-1}S_{l-1} \right) S' \right] \left( \int_0^R S_l^2(r)r^2 dr \right)^{-1}. \quad (15)$$

Here all the values of  $S$  and  $\tilde{S}$  (except in the integrand) as well as their derivatives with respect to  $r$  (indicated by primes) are taken at  $r = R$ . This will also be the case in what follows.

Since the periodicity condition requires that either  $S_l = 0$  or  $S'_l = 0$ , only one of the terms in parentheses within the brackets in Eq. (15) will differ from zero. The function  $\chi$  has the symmetry of  $\partial\psi/\partial z$ . Consequently, if we consider states with  $S'_l = 0$ , we can obtain  $\tilde{S}$  from Eq. (13) together with the condition that  $\chi(R) = 0$ :

$$\tilde{S}_{l+1} = \frac{l+1}{2l+1}S_l, \quad \tilde{S}_{l-1} = \frac{l}{2l+1}S_l, \quad (r=R); \quad (16a)$$

if we consider states with  $S_l = 0$ , however, we have  $\partial\chi/\partial r = 0$  at  $r \approx R$  and obtain

$$\tilde{S}'_{l+1} = \frac{l+1}{2l+1}S'_l, \quad \tilde{S}'_{l-1} = \frac{l}{2l+1}S'_l, \quad (r=R) \quad (16b)$$

Later we shall examine some specific examples.

## "COMPRESSED HYDROGEN"

Let us assume that the hydrogen is so strongly compressed that its molecular structure is quite destroyed and its atoms form a bcc lattice, as do alkali metal atoms, or perhaps an fcc lattice (in the Wigner-Seitz approximation, when the Wigner-Seitz cell is replaced by a sphere, it does not matter which). In this case the length of an edge of the cubic unit cell is of the order of an angstrom or less. In what follows we shall use atomic units ( $\hbar = m = e^2 = 1$ ) and write

$$g = rS(r). \quad (17)$$

This example is intended as an illustration only, so we consider only the first Brillouin zone, i.e.,  $k_0 = 0$ , and take the "wave function" for  $k = 0$  in the form

$$g(r) = e^{\beta r} - e^{-(2+\beta)r}. \quad (18)$$

This wave function corresponds to an assumed "self-consistent field of electrons" and a proton with the potential

$$U(r) = -2(1+\beta)[e^{2(1+\beta)r} - 1]^{-1}. \quad (19)$$

This is a Hulthén potential, which reduces to the Coulomb potential of the proton for small  $r$  and falls off exponentially as though screened by electrons for large  $r$ :  $U(r) \approx -2(1+\beta) \cdot \exp\{-2(1+\beta)r\}$  for  $2(1+\beta)r \gg 1$ .

However, a more accurate representation of the degree of screening is given by the "force"

$$-dU/dr = -(1+\beta)^2 \text{sh}^{-2}(1+\beta)r. \quad (19a)$$

According to the periodicity condition we must have  $S'_l = 0$ , and this gives  $dg/dr = g(R)/R$  for  $r = R$ , or

$$1 - \beta R = (1 + 2R + \beta R) e^{-2(1+\beta)R}. \quad (20)$$

From this equation we find that  $\beta R \rightarrow \sqrt{3R}$  as  $R \rightarrow 0$ ,  $\beta R = 0.79$  at  $R = 0.5$ ,  $\beta R = 0.916$  at  $R = 1$ , and  $\beta R \rightarrow 1$  as  $R \rightarrow \infty$ . The kinetic energy at  $r = R$  is equal to  $2(1+\beta)[\exp\{2(1+\beta)R\} - 1]^{-1} - \beta^2/2$ ; it is always negative.

Since  $l = 0$  in this case, we have to solve one of Eqs. (14)—for  $l = 1$ . It turns out that with good accuracy  $\tilde{S} = Ar$  in the region  $r \leq R$  (the coefficient  $A$  is somewhat larger for  $r \ll R$  than for  $r \approx R$ ). The coefficient  $A$  is determined from (16a):

$$A = S/R = (e^{2R} - e^{-(2+\beta)R})R^{-2}. \quad (21)$$

On substituting all this into Eq. (15) and interchanging the numerator and denominator, we obtain

$$m^* = \frac{3m}{R} \left[ \frac{e^{2\beta R} - 1}{2\beta} - 1 + e^{-2R} + \frac{1 - e^{-2(2+\beta)R}}{2(2+\beta)} \right] [e^{\beta R} - e^{-(2+\beta)R}]^{-2}. \quad (22)$$

Numerically, we find that  $m^* = 1.09$  for  $R = 1$  and  $m^* = 1.053$  for  $R = 0.5$ . We note that the potential in the vicinity of  $R \approx 1$  is very small:  $U(1) = 0.085$ , while the force, which should vanish, is equal to 0.33 in place of unity. The kinetic energy for  $R = 1$  is negative and equal to  $-0.34$  at the point  $r = R$ .

According to Eq. (22),  $m^* \rightarrow 1$  as  $R \rightarrow 0$  and  $m^* \rightarrow 1.3$  for  $R \gg 1$ . Of course the latter result cannot correspond to reality, since a Mott transformation should take place as  $R$  increases somewhat beyond unity, as a result of which the electrons find themselves in the field of an unscreened proton and the wave function (18) must be replaced by a hydrogen wave function  $g(r) = re^{-r}$  (i.e., a metal-to-dielectric phase transformation takes place).

## ONE-DIMENSIONAL CASE (A MODEL CRYSTAL WITH SEPARABLE VARIABLES)

Let  $\psi$  be represented in the form

$$\psi = \xi(x)\eta(y)\zeta(z). \quad (23)$$

The best function of this type can be obtained from a variational principle. Each of the functions  $\xi$ ,  $\eta$ , and  $\zeta$  satisfies a corresponding Schrödinger equation, and the function  $\psi$ , their product, satisfies a Schrödinger equation in which the true potential is replaced by a potential consisting of the sum of the potentials occurring in the one-dimensional Schrödinger equations for the separate functions  $\xi$ ,  $\eta$ , and  $\zeta$ . Then the second

linearly independent solution of the Schrödinger equation for  $\psi = \xi\eta\zeta$ , which occurs in (10) and (11) and makes  $\chi$  periodic, is expressed analytically in terms of  $\psi$  as follows:

$$\psi = \psi \int_0^z \psi^{-2} dz' \left( \int_0^z \psi^{-2} dz' \right)^{-1} = \xi(x)\eta(y)\zeta(z) \int_0^z \zeta^{-2} dz' \left( \int_0^z \zeta^{-2} dz' \right)^{-1}; \quad (24)$$

here  $a$  is the period in the direction of the  $z$  axis.

Substituting (24) into (11) and taking the reciprocal, we obtain the following expression for the effective mass in the direction of the  $z$  axis:

$$m^* = ma^{-2} \left[ \int_0^a \psi^{-2} dz \right]^{-1} \int_0^a \psi^2 dx dy dz = ma^{-2} \int_0^a \zeta^{-2} dz \int_0^a \zeta^2 dz. \quad (25)$$

Here  $\psi$  is necessarily real, since in view of what was said above about the current density,  $E(\mathbf{k})$  can have an extremum only for  $k_a = 0$  or  $k_a = \pi$ . In the one-dimensional case, the current necessarily vanishes at an extremum of  $E(\mathbf{k})$ .

Unfortunately, Eq. (25), as first written, is accurate only when  $U(\mathbf{r}) = U_{xy}(x, y) + U_z(z)$ . In particular, if the potential is small enough for perturbation theory to be applicable we obtain

$$m^* = m \left( 1 + \sum_k 16m^2 \hbar^{-4} |U_{g0}|^2 g_x^2 g_y^2 + \dots \right). \quad (26a)$$

for the lowest state ( $\psi = 1 + \dots$ ). From Eq. (25) (as first written), however, we obtain:

$$m^* = m \left( 1 + \sum_k 16m^2 \hbar^{-4} |U_{g0}|^2 g^{-4} + \dots \right). \quad (26b)$$

It is easy to see that Eqs. (26a) and (26b) are equivalent provided  $U(\mathbf{r}) = U_{xy}(x, y) + U_z(z)$  ( $U_{g0}$  is a Fourier component of the potential  $U(\mathbf{r})$ ,  $g$  being a reciprocal-lattice vector). If the variable  $z$  in the potential is separable and  $g_z = 0$ , only the Fourier components  $U_{g0}$  of the potential for which  $g^2 = g_x^2 + g_y^2$ , i.e.,  $g_x^2 = g_y^2 = 0$ , will differ from zero. At the same time, it is evident that (26a) and (26b) do not differ much from one another, so that in the general case it is basically only the first terms in expansion (26a) that are important. (The perturbation-theory proof of the necessity of (25) was suggested by A. M. Dykhne.)

In (25),  $\zeta^2$  may vanish as  $(z - z_p)^2 + O(z - z_p)^4$  (there are no terms in  $(z - z_p)^3$  because of Schrödinger's equation). The contour in the complex  $z$  plane for the first integral may pass either above or below the point  $z_p$  where  $\zeta^2$  vanishes—it does not matter which. Thus, if the integration is not performed analytically, we have

$$\int_0^a \zeta^{-2} dz = \int_0^{z_1-\epsilon_1} + \int_{z_1+\epsilon_1}^{z_2-\epsilon_2} + \dots + \int_{z_{n-1}+\epsilon_{n-1}}^{z_n-\epsilon_n} + \int_{z_n+\epsilon_n}^a \zeta^{-2} dz - \frac{2}{\zeta_1'^2 \epsilon_1} - \frac{2}{\zeta_2'^2 \epsilon_2} - \dots - \frac{2}{\zeta_{n-1}'^2 \epsilon_{n-1}} - \frac{2}{\zeta_n'^2 \epsilon_n}; \quad \zeta_p''' \epsilon_p^2 \ll \zeta_p', \quad (27)$$

for numerical integration along the real axis, where the points  $z_p = z_1, z_2, \dots, z_{n-1}, z_n$  are the values of  $z$  at which  $\zeta$  vanishes,  $\zeta_p'$  and  $\zeta_p''$  are the corresponding derivatives of  $\zeta$  with respect to  $z$  at these points, and the smallness of the segments  $\epsilon_p$  is specified in (27).

For the Kronig-Penney model, Eq. (25) gives the result at once since all the integrals are elementary. The result agrees with the ordinary result, which is obtained in a much more cumbersome manner but which yields the complete function  $E(\mathbf{k})$  and not merely its

values near the extrema. The same can be said of the case in which the quasiclassical formulas are applicable.

For simplicity let us suppose that there are just two regions in a single lattice period  $a$ : the region  $0 < z < b$ , in which  $p^2 \equiv 2m\hbar^{-2}(E - U(z)) > 0$  ( $p$  is the quasiclassical momentum divided by  $\hbar$ ), and the region  $b < z < a$ , in which  $p^2 < 0$ . We assume that the condition for the applicability of the quasiclassical approximation holds in both regions (except at the "turning points", and not merely because  $2m\hbar^{-2}a^2 U(z)$  varies slowly).  $E$  is determined by the Bohr-Sommerfeld quantum condition in the classically accessible region:

$$\int_0^a p dz = \int_0^b [2m\hbar^{-2}(E - U(z))]^{1/2} dz \approx \left( n + \frac{1}{2} \right) \pi; \quad n=1, 2, 3, \dots \quad (28)$$

In the classically accessible region we have

$$\zeta = |p|^{-1/2} \sin \left( \int_0^z p dz + \frac{\pi}{4} \right). \quad (29)$$

In the classically inaccessible region, where  $E - U(z) < 0$ , the solution of the Schrödinger equation for  $\zeta$  can be continued in two ways so as to be periodic:

$$\zeta = (-1)^n |p|^{-1/2} \exp \left\{ -\frac{1}{2} \int_0^a |p| dz \right\} \text{ch} \left( \int_0^z |p| dz - \frac{1}{2} \int_0^a |p| dz \right) \quad (30a)$$

or

$$\zeta = (-1)^{n+1} |p|^{-1/2} \exp \left\{ -\frac{1}{2} \int_0^a |p| dz \right\} \text{sh} \left( \int_0^z |p| dz - \frac{1}{2} \int_0^a |p| dz \right). \quad (30b)$$

It is assumed that  $n \gg 1$  in (28), and further, that

$$\int_0^a |p| dz \gg 1.$$

One of the solutions (29), (30) for  $\zeta$ , depending on  $n$ , changes sign on passing through the period  $a$ . This corresponds to an extremum of  $E(\mathbf{k})$  at  $k_a = \pi$ . States (30a) and (30b) differ from the nearest state with  $k = 0$  by the energy

$$\Delta E = \frac{2\hbar^2}{m} \exp \left\{ -\int_0^a |p| dz \right\} \left( \int_0^b |p|^{-1} dz \right)^{-1}, \quad (31)$$

as can be proved by calculating the Jacobian and integrating over a period as is done in problem 3 in Landau and Lifshitz's book<sup>[4]</sup> (p. 213).

Now it does not seem difficult to calculate the effective mass from Eq. (25), since the first integral in that equation can be easily evaluated, and in the second (normalizing) integral, we can, as usual, replace  $\sin^2 \dots$  by its average value 0.5 and integrate over the classically accessible region. We obtain

$$m^* = ma^{-2} \left[ 2 + (-1)^n \exp \left\{ \int_0^a |p| dz \right\} 2 \text{th} \left( \frac{1}{2} \int_0^a |p| dz \right) \right] \int_0^b \frac{dz}{2p} \approx (-1)^n \exp \left\{ \int_0^a |p| dz \right\} ma^{-2} \int_0^b \frac{dz}{2p} \quad (32)$$

and the same result with the opposite sign for the second solution (30). Formulas (31) and (32) are consistent with the relation  $E(\mathbf{k}) = E(0) + (\frac{1}{2}) \Delta E(1 - \cos ka)$ , which is obtained in the complete solution<sup>[5]</sup>. In the case of the quasiclassical solution with no inaccessible region the effective mass vanishes in the approximation under consideration, as in an "empty" lattice (except for the first zone).

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