Effective-Mass Approximation for Electrons in Crossed Electric and Magnetic Fields

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A criterion of applicability of the effective-mass approximation to the dynamics of a Bloch electron in crossed electric and magnetic fields is derived based on a treatment of Luttinger and Kohn. The requirements necessary for the diagonalizability of the Hamiltonian for an electron in a periodic crystal field in the presence of a perturbing magnetic field and an electric potential are examined. These requirements lead to a restriction on the ratio of the electric and magnetic fields. The validity of the effective-mass approximation is also considered for higher Landau states in a magnetic field as well as for lowest states of an impurity ion.

I. INTRODUCTION

THE effective-mass approximation (EMA) is a very useful tool for treating the dynamics of electrons in solids. After being developed by Luttinger and Kohn[1] it has been used to explain a great number of phenomena associated with the motion of electrons in perturbed periodic potentials, e.g., when in addition to the periodic potential of the crystal there is a perturbation caused either by external fields or by imperfections of the crystal. There are two main cases where the effective-mass approximation has been applied successfully for describing the dynamics of electrons in solids: (1) motion in the field of an impurity atom; and (2) motion in a constant magnetic field. Both cases were treated in detail by Luttinger and Kohn[1] who also showed when the effective-mass approximation is applicable to the lowest energy levels. For the lowest impurity level the orbit must be large enough so that the potential of the impurity does not change considerably in the vicinity of the orbit in a lattice unit cell. The same argument was applied to higher impurity levels[2] and it turned out that although the EMA cannot be applied to describe the ground state, it is nevertheless applicable to higher states. This is in agreement with the experimental results. The criterion of the smallness of the fractional change of the potential in a unit cell seems therefore to work very well for the impurity states. In the second case, the applicability of the effective mass approximation was proven for the ground state in any practically achievable magnetic field.[1] For high Landau levels this is no longer the case. As indicated by McLean,[3] the variation of the wave function for high Landau states becomes very rapid and the effective-mass approximation cannot be applied. Both the "gentleness" of the potential and the smoothness of the wave function are general conditions for the effective-mass approximation to be valid.

Apart from the two cases mentioned above, there is another configuration where the EMA has been used recently. This is the dynamics of an electron in crossed electric and magnetic fields.[4–6] Aronov[4] applied the EMA to the calculation of optical interband absorption and found that the energy gap of a semiconductor in crossed electric and magnetic fields decreases proportionally to $(E/H)^2$, where E is the electric field and H the magnetic field. No limitations are given as to when this variation of the energy gap with fields holds. It is evident that such an $(E/H)^2$ dependence cannot be valid when E/H becomes very large. This means that the results obtained from the EMA are incorrect in the limit of large E/H ratios and it is of interest to find out the limits on E/H in order for the EMA to be applicable. One could expect that if the EMA is valid for small E and for small H, it must be valid also for crossed fields providing both are small. We will show that this is not in general the case and that for the EMA to be valid, it is not enough for E and H to be sufficiently small but there must be a limitation on the ratio E/H as well. The general reason for this is the following: The crossed-field case is a particular example of the application of the EMA to a problem where more than one kind of perturbation is involved—in the above-mentioned case, that of electric and magnetic fields. Since the EMA follows in fact from a diagonalization procedure of the Hamiltonian, we must require the nondiagonal terms of a given perturbation to be small not only in comparison with the diagonal terms of the same perturbation but also to be small in comparison with the diagonal terms of the other kind of perturbation. This requirement leads to a limitation on the ratio of the perturbation. In general, if the diagonal parts of the perturbation are of a different order of magnitude, we must expect the EMA to be

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[1] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[2] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

[3] T. P. McLean, in *Proceedings of the International School of Physics "Enrico Fermi" Course*, edited by R. A. Smith (Academic Press Inc., New York, 1963), Vol. 22, p. 479.

[4] A. G. Aronov, Fiz. Tverd. Tela **5**, 552 (1963) [English transl.: Soviet Phys.—Solid State **5**, 402 (1963)].

[5] Q. H. F. Vrehen and B. Lax, Phys. Rev. Letters **12**, 471 (1964).

[6] Q. H. F. Vrehen, Phys. Rev. Letters **14**, 558 (1965).

inapplicable because it will then be impossible to eliminate all the nondiagonal elements.

II. APPLICABILITY OF THE EFFECTIVE-MASS APPROXIMATION

In many approximate theories the most difficult question to answer is when do these theories work. A similar situation exists for the EMA which has been used very often in solid-state theory, but only in very few cases has a justification of such a use been given. As mentioned in the Introduction, a criterion for the applicability of the EMA to the motion in the field of an impurity atom and to the motion in a constant magnetic field was derived before.[1-3] The limitations on the EMA for a more general perturbation potential, including the case where the perturbation is caused by different fields, will be obtained in this section. Our derivation will be based on the theory of Luttinger and Kohn,[1] which we review briefly now.

Let us start with Schrödinger's equation for an electron in a periodic potential $V(\mathbf{r})$, a constant magnetic field U in a Landau gauge, $A_x=-\mathcal{H}y$, $A_y=A_z=0$ (where $\mathbf{A}$ is the vector potential), and another perturbation $U(\mathbf{r})$ that can be caused, for example, by a constant electric field or an impurity atom:

$$\{(\mathbf{p}+(e/c)\mathbf{A})^2/2m+V(\mathbf{r})+U(\mathbf{r})\}\psi(\mathbf{r})=\epsilon\psi(\mathbf{r}). \quad (1)$$

Here, p is the momentum of the electron, e is the absolute value of the electron charge, c is the velocity of light, and m is the free-electron mass. In this special gauge, the Hamiltonian of Eq. (1) can be written as follows:

$$H=H_0-(\hbar s/m)yp_x+(\hbar^2s^2/2m)y^2+U(\mathbf{r}), \quad (2)$$

where H_0 is the Bloch Hamiltonian and $s=e\mathcal{H}/ch$. In the Kohn-Luttinger (KL) representation we have

$$\langle n\mathbf{k}|H|n'\mathbf{k}'\rangle=\Big[\Big(\epsilon_n+\frac{\hbar^2\mathbf{k}^2}{2m}\Big)\delta(\mathbf{k}-\mathbf{k}')-\frac{\hbar^2k_xs}{m}\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}-\frac{\hbar^2s^2}{2m}\frac{\partial^2\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'^2}\Big]\delta_{nn'}+\frac{1}{m}\Big[\hbar k_\alpha p_{nn'}{}^\alpha\delta(\mathbf{k}-\mathbf{k}')-\hbar sp_{nn'}{}^x\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}\Big]+\langle nk|U|n'k'\rangle. \quad (3)$$

In the last expression,

$$p_{nn'}{}^\alpha=\frac{(2\pi)^3}{\Omega}\int u_{n0}{}^*\Big(\frac{\hbar}{i}\nabla_\alpha\Big)u_{n'0}d\mathbf{r}, \quad (4)$$

where Ω is the volume of a unit cell and the integration is over a unit cell. The aim of the EMA is to eliminate elements nondiagonal in the band index n by applying a diagonalization procedure to the Hamiltonian [Eq. (3)]. There are in general three nondiagonal terms in Eq. (3): two with $p_{nn'}$ and possibly the matrix element of the perturbation potential $U(\mathbf{r})$. To carry out the diagonalization procedure one has first to require the fractional change of the perturbation potential $U(\mathbf{r})$ to be small over the dimension of a unit cell. This requirement makes U diagonal[1] and its matrix element will be

$$\langle n\mathbf{k}|U|n'\mathbf{k}'\rangle=U(\mathbf{k}-\mathbf{k}')\delta_{nn'}, \quad (5)$$

where

$$U(\mathbf{k})=(1/2\pi^3)\int U(\mathbf{r})\exp(-i\mathbf{kr})d\mathbf{r} \quad (6)$$

is the Fourier transform of $U(\mathbf{r})$. Having assumed that U is diagonal, we introduce the following notation for the different terms in the Hamiltonian [Eq. (3)]:

$$H=H_B{}^{(D)}+H_M{}^{(D)}+H_E{}^{(D)}+H_B{}^{(ND)}+H_M{}^{(ND)}=H^{(D)}+H^{(ND)}, \quad (7)$$

$$\langle n\mathbf{k}|H_B{}^{(D)}|n'\mathbf{k}'\rangle=(\epsilon_n(0)+\hbar^2k^2/2m)\delta_{nn'}\delta(\mathbf{k}-\mathbf{k}'), \quad (8)$$

$$\langle n\mathbf{k}|H_M{}^{(D)}|n'\mathbf{k}'\rangle=\Big[-\frac{\hbar^2sk_x}{m}\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}-\frac{\hbar^2s^2}{2m}\frac{\partial^2\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'^2}\Big]\delta_{nn'}, \quad (9)$$

$$\langle n\mathbf{k}|H_E{}^{(D)}|n'\mathbf{k}'\rangle=U(\mathbf{k}-\mathbf{k}')\delta_{nn'}, \quad (10)$$

$$\langle n\mathbf{k}|H_B{}^{(ND)}|n'\mathbf{k}'\rangle=\frac{1}{m}\hbar k_\alpha p_{nn'}{}^\alpha\delta(\mathbf{k}-\mathbf{k}'), \quad (11)$$

$$\langle n\mathbf{k}|H_M{}^{(ND)}|n'\mathbf{k}'\rangle=-\frac{1}{m}\hbar sp_{nn'}{}^x\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}. \quad (12)$$

The subscripts B, M, and E mean Bloch, magnetic and electric terms, respectively; the superscripts D and ND mean diagonal and nondiagonal terms; $\epsilon_n(0)$ is the energy at the extremal point of the zone. Now, to obtain the effective-mass Hamiltonian, one has to perform a canonical transformation in order to remove the nondiagonal elements to the lowest order. Since this was done in detail before,[1] we instead carry out this procedure symbolically and derive a general criterion of the applicability of the EMA. Let us apply an operator e^S of a canonical transformation to the Hamiltonian H in Eq. (7). Assuming that S is small we have

$$\bar{H}=e^{-S}He^S=H_B{}^{(D)}+H_M{}^{(D)}+H_E{}^{(D)}+H^{(ND)}+[H_B{}^{(D)},S]+[H_M{}^{(D)},S]+[H_E{}^{(D)},S]+[H^{(ND)},S]+\tfrac{1}{2}[[H_B{}^{(D)},S],S]+\text{higher order terms in } S. \quad (13)$$

To remove the interband terms $H^{(ND)}$ to the lowest order, one requires that $H^{(ND)}+[H_B{}^{(D)},S]=0$. From

this condition one can determine S, namely,

$$\langle n\mathbf{k}|S|n'\mathbf{k}'\rangle=-\frac{1}{m}\Big[\hbar k_\alpha p_{nn'}{}^\alpha\delta(\mathbf{k}-\mathbf{k}')-\hbar s p_{nn'}{}^x\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}\Big]\Big/\hbar\omega_{nn'},\quad n\neq n';$$
$$=0,\quad n=n', \tag{14}$$

where $\hbar\omega_{nn'}=\epsilon_n(0)-\epsilon_{n'}(0)$. Inserting the expression for S into Eq. (13), one finds:

$$\bar{H}=H_B{}^{(D)}+H_M{}^{(D)}+H_E{}^{(D)}-\tfrac{1}{2}[[H_B{}^{(D)},S],S]+[H_M{}^{(D)},S]+[H_E{}^{(D)},S]+\cdots. \tag{15}$$

The effective-mass Hamiltonian may be obtained from relation (15) provided that the two last terms can be neglected with respect to all the others. If there is only one kind of perturbation, say the magnetic field, then the term $[H_M{}^{(D)},S]$ can always be neglected with respect to $H_M{}^{(D)}$ because, as assumed, the matrix S is small. But when there are two perturbations, as in Eq. (15), one has to require both $[H_M{}^{(D)},S]$ and $[H_E{}^{(D)},S]$ to be smaller than the ones we keep in the effective Hamiltonian.

In order to compare terms, let us write down the effective-mass Hamiltonian:

$$H^*=H_B{}^{(D)*}+H_M{}^{(D)*}+H_E{}^{(D)}, \tag{16}$$

where

$$\langle n\mathbf{k}|H_B{}^{(D)*}|n'\mathbf{k}'\rangle=\Big[\epsilon_n(0)+\frac{1}{2}\Big(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_\alpha\partial k_\beta}\Big)_0 k_\alpha k_\beta\Big]\times\delta_{nn'}\delta(\mathbf{k}-\mathbf{k}'), \tag{17}$$

$$\langle n\mathbf{k}|H_M{}^{(D)*}|n'\mathbf{k}'\rangle=\Big\{\hbar^2 s\Big[k_\alpha\Big(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_\alpha\partial k_x}\Big)_0\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}+\frac{1}{2i}\Big(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_x\partial k_y}\Big)_0\delta(\mathbf{k}-\mathbf{k}')\Big]-\frac{\hbar^2 s^2}{2m}\frac{\partial^2\delta(\mathbf{k}-\mathbf{k})}{\partial k_y'^2}\Big\}\delta_{nn'}, \tag{18}$$

$$\langle n\mathbf{k}|H_E{}^{(D)}|n'\mathbf{k}'\rangle=U(\mathbf{k}-\mathbf{k}')\delta_{nn'}. \tag{19}$$

It is interesting to point out that the term $H_E{}^{(D)}$ was not changed by the diagonalization procedure. We can now state that for the EMA to be valid, it is necessary that both terms $[H_M{}^{(D)},S]$ and $[H_E{}^{(D)},S]$ be much smaller than the terms in the effective Hamiltonian [Eq. (16)]. As will be seen in the next section, this requirement leads to an applicability criterion of the EMA to the problem of crossed electric and magnetic fields.

From the effective Hamiltonian we can write down the equation for the functions in the new representation. Let us again write it in symbolic form:

$$(H_B{}^{(D)*}+H_M{}^{(D)*}+H_E{}^{(D)})B_n=\epsilon B_n, \tag{20}$$

where B_n is the wave function in the new representation and n is the band index which shows that Eq. (20) is written for the nth band. For finding the wave function in the coordinate representation, Luttinger and Kohn[1] define a function $F_n(\mathbf{r})$:

$$F_n(\mathbf{r})=\int\exp(i\mathbf{k}\mathbf{r})B_n(\mathbf{k})d\mathbf{k}, \tag{21}$$

where the integration is over the the first Brillouin zone. However, since Eq. (20) is valid only for small vectors $\mathbf{k}$ [the smallness of $\mathbf{k}$ is derived by the requirement that S in Eq. (14) is much less than 1], it is meaningful to deal with functions $F_n(\mathbf{r})$ that are given by Eq. (21) with an integration over small $\mathbf{k}$ only. Such functions do not vary appreciably over a unit cell and one gets the following equation for them[1]:

$$[\epsilon_n((1/i)\nabla+(e/\hbar c)\mathbf{A})+U(\mathbf{r})]F_n(\mathbf{r})=\epsilon F_n(\mathbf{r}), \tag{22}$$

where $\epsilon_n((1/i)\nabla+(e/\hbar c)\mathbf{A})$ is an expression that is obtained by expanding $\epsilon_n(\mathbf{k})$, the Bloch energy, up to quadratic terms, replacing $\mathbf{k}$ by $(1/i)\nabla+(e/\hbar c)\mathbf{A}$ and properly symmetrizing products of noncommuting operators. Equation (22) is called the effective-mass equation and it holds only for such solutions $F_n(\mathbf{r})$, the Fourier transform of which vanishes for all $\mathbf{k}$ that are outside the range of validity of Eq. (20). As we have already seen, in order to derive Eq. (20) we had to require the matrix S given by relation (14) to be much less than 1. This requirement leads to

$$(p_{nn'}{}^y/m\omega_{nn'})k_y\ll 1,\ (p_{nn'}{}^z/m\omega_{nn'})k_z\ll 1, \tag{23}$$

and

$$(p_{nn'}{}^x/m\omega_{nn'})(k_x-s(1/i)\partial/\partial k_y)\ll 1, \tag{24}$$

where the values k_y, k_z, and $(k_x-s\partial/i\partial k_y)$ are to be evaluated for the states which are given by the solutions of the effective mass Hamiltonian (16). Thus, for determining whether Eq. (22) is valid, we have to find whether its solution $F_n(\mathbf{r})$ can be written in the form (21) where the integration is only over those $\mathbf{k}$ that satisfy inequalities (23) and (24).

Let us now summarize the conditions for the applicability of the EMA.

1. The potential $U(\mathbf{r})$ has to be given by a diagonal matrix in the Kohn-Luttinger representation [Eq. (5)].
2. The terms $[H_M{}^{(D)},S]$ and $[H_E{}^{(D)},S]$ in Eq. (15) have to be small with respect to the terms in Eq. (16).
3. The solutions of the effective mass Eq. (22) describe the physical situation only if they can be given by a Fourier integral [Eq. (21)] with those $\mathbf{k}$ that satisfy Eqs. (23) and (24).

It is interesting that a condition on the solutions of Eq. (22) can also be formulated in a much simpler way

in terms of energies. To do this, let us note that the order of magnitude of $H_B^{(D)*}$ in Eq. (20) is $\epsilon_n(0)+\hbar^2k^2/2m^*$ and that for the EMA to be valid, the terms $H_M^{(D)*}$ and $H_E^{(D)}$ must be of the same order as $\hbar^2k^2/2m^*$ or smaller.[7] Thus the order of magnitude of $\epsilon-\epsilon_n(0)$, where ϵ is the eigenvalue of Eq. (20) is the same as $\hbar^2k^2/2m^*$ .We have, therefore, the following necessary condition: only these solutions of Eq. (22) are physical for which the eigenvalues satisfy the relation

$$\epsilon-\epsilon_n(0)\sim\hbar^2k^2/2m^*, \tag{25}$$

where $\sim$ means the same order of magnitude and $\mathbf{k}$ is limited by the relations (23) and (24).

III. APPLICATIONS

In this section the applicability of the EMA to the dynamics of a Bloch electron in different perturbing potentials is checked. Although our main concern is the problem of crossed electric and magnetic fields, we give also, for completeness, a short description of the cases of an impurity center and a constant magnetic field.

A. Impurity Centers

It was shown by KL[2] that the effective-mass formalism gives bad results for ground states of donor impurities in silicon. There are two reasons for this: (1) in the immediate vicinity of the donor atom the perturbing potential $V(\mathbf{r})$ changes from $-e^2/\kappa r$ to $-\Delta Ze^2/\kappa r$ (κ=dielectric constant) where ΔZ is the excess charge of the donor nucleus over that of Si; (2) in this region the fractional change of $V(\mathbf{r})$ in a typical lattice distance, a, is large. It is to be expected that the rapid variation of the potential results in a rapid variation of the wave function $F(r)$. In terms of Fourier transformation criterion [Eq. (21)] this should mean that we have to use too wide a range of $\mathbf{k}$ values to construct a solution within the limits of EMA. We shall now examine the problem in detail.

For an electron in a periodic potential perturbed by an impurity atom the Hamiltonian is

$$H=\mathbf{p}^2/2m+V(\mathbf{r})-e^2/\kappa r, \tag{26}$$

where for large distances from the nucleus the Coulomb potential is used. Let us check the three requirements necessary for the validity of EMA.

1. The Coulomb potential [$U=-e^2/\kappa r$ in Eq. (26)] can be given by a diagonal matrix in the KL representation if we are interested in regions sufficiently far from the nucleus.

2. The term $[U,S]$ may be neglected with respect to U provided the S matrix is small.

3. The effective-mass equation for a simple nondegenerate and spherical energy band takes the form

$$(-(\hbar^2/2m^*)\nabla^2-e^2/\kappa r)F(\mathbf{r})=\epsilon F(\mathbf{r}). \tag{27}$$

Luttinger and Kohn[1] estimated the k value for the ground state using the fact that for the lowest level $k\approx\Delta k$ and $r\approx\Delta r$; the uncertainty relation gives $k\sim1/a_B$, a_B denoting the effective Bohr radius. This method, however, cannot be used for higher states and we have to apply the relation (21). The hydrogen-like functions $F(\mathbf{r}/a_B)$ are given by[8]

$$F_{nlm}\left(\frac{r}{a_B}\right)=\int\exp\left((\mathbf{k}a_B)\frac{\mathbf{r}}{a_B}\right)\times P_{nl}(ka_B)Y_{lm}(\theta,\varphi)d^3(\mathbf{k}a_B). \tag{28}$$

The probability of finding the absolute value of the $\mathbf{k}$ vector between k and $k+dk$ is given by

$$|P_{nl}(ka_B)|^2(ka_B)^2d(ka_B), \tag{29}$$

where

$$P_{nl}(ka_B)=A_{nl}\frac{(ka_B)^l}{[n^2(ka_B)^2+1]^{l+2}}\times C_{n-l-1}^{l+1}\left[\frac{n^2(ka_B)^2-1}{n^2(ka_B)^2+1}\right]; \tag{30}$$

A_{nl} is a normalization constant, and C_N^ν is the Gegenbauer function. The probability [Eq. (29)] is steeply decreasing for $ka_B>1$. We can also use the well-known mean-value relation[8]

$$[\langle(ka_B)^2\rangle_{av}]^{1/2}=1/n \tag{31}$$

which is independent of l. This condition indicates that indeed values $ka_B>1$ are not of much importance, especially for l close to n.[9] In terms of Eq. (28) this means that we can construct all hydrogen-like functions $F(\mathbf{r})$ using $0\leq ka_B<1$. Now we can estimate whether these values are within the EMA limitations. We use the criterion $ka\approx0.1\ll1$.[10] Hence $ka_B\approx a_B/10a$. Table I gives values of parameters and approximate estimates for conduction bands of Si, Ge, and InSb.[11] It can be seen that for Si the EMA allows a maximal value of $ka_B\approx0.5$, which is not enough to construct the $1s$ hydrogen-like state. The situation is better for excited states because in order to construct, say, $2p$ states, it is enough to take $0\leq ka_B\leq\frac{1}{2}$ [Eq. (31)]. In Ge, the criterion allows for wider range of ka_B values to be used, however, one has to bear in mind that we have not taken into account the anisotropy of the conduction band near the minimum. This anisotropy makes the

[7] This statement again follows from a comparison of terms we keep in Eq. (16) with those we neglect. It is clear that in order to be able to neglect $[H_M^{(D)*},S]$ and $[H_E^{(D)},S]$ with respect to $H_B^{(D)*}$, the terms $H_M^{(D)*}$ and $H_E^{(D)}$ cannot be much larger than $H_B^{(D)*}$.

[8] H. L. Bethe and E. E. Salpeter, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXXV, Chap. 1, p. 125.

[9] For the ground state, the relation (31) gives just the estimate used by LK (Ref. 1).

[10] $p_{nn'}/m\omega_{nn'}\sim a$, where a is a typical lattice spacing.

[11] H. Ehrenreich, J. Appl. Phys. 32, 2155 (1961).

TABLE I. Values of parameters and approximate estimates for conduction bands of Si, Ge, and InSb. For Si and Ge, $1/m^*=2/m_t+1/m_l$ where m_t and m_l are transverse and longitudinal masses, respectively. In estimating $k_{\max}$ for InSb, $p_{nn'}/m\omega_{nn'}$ instead of a was used, since it gives a much stronger restriction. $p_{nn'}$ values were calculated using $2p_{nn'}^2/m=20$ eV for InSb and 28 eV for Ge (Ref. 11).

Material	Dielectric constant (κ)	Effective mass (m^*/m_0)	Effective Bohr radius a_B(Å)	Lattice constant a(Å)	$\frac{p_{nn'}}{m\omega_{nn'}}\times 10^8$ (cm)	Wave vector $k_{\max}$(cm^{-1})	$k_{\max}a_B$
Si	12	0.26	25	5.4		1.8×10^6	0.5
Ge	16	0.12	70	5.6	13.5	1.8×10^6	1.3
InSb	17	0.013	700	6.5	36	3×10^5	2.1

$F(\mathbf{r})$ functions strongly anisotropic and eventually wider range of ka_B values is necessary to construct these functions. For InSb, in spite of the stronger restrictions for k, the small effective mass results in a very large effective Bohr radius and even the lowest states can be obtained from Eq. (21) by use of $0\leq ka_B\leq 2$.

We shall notice that k values involved in $F_{nlm}(\mathbf{r})$ hydrogenic states can be estimated by using Eq. (25). For an impurity center we have

$$\hbar^2k^2/2m^*\approx(m^*e^4/2\hbar^2\kappa^2)(1/n^2) \tag{32}$$

which gives an estimate identical with Eq. (31).

B. External Magnetic Field

In the case when an electron is subjected to an homogeneous magnetic field the Hamiltonian takes the form [Eq. (2)] with the last term (the electrical potential) omitted. The diagonalization procedure for this Hamiltonian has been described before and the only nondiagonal elements are proportional to $p_{nn'}$. The first condition is therefore fulfilled and for checking the second requirement, let us write down the Hamiltonian after the diagonalization:

$$\bar{H}=H_B^{(D)*}+H_M^{(D)*}+(H_M^{(D)},S)+\cdots. \tag{33}$$

We have to estimate the order of magnitude of the last term in comparison with the first two. Assuming that S is small, we can neglect the third term with respect to the first two terms because as is known, the latter are of the same order of magnitude.

For checking the third condition, let us write the effective-mass Hamiltonian for an electron in a simple nondegenerate spherical energy band:

$$(1/2m^*)((\hbar/i)\nabla+(e/c)\mathbf{A})^2F(\mathbf{r})=\epsilon F(\mathbf{r}). \tag{34}$$

The solutions of Eq. (34) in the Landau gauge can be expressed by the well-known harmonic-oscillator functions. We shall determine those values of the $\mathbf{k}$ vector which are necessary to construct these solutions. Since the Fourier transforms of the harmonic-oscillator functions are again the oscillator functions, we have

$$F_n(\mathbf{r})=C_n\exp[i(k_xx+k_yy)]\int_{-\infty}^{+\infty}\exp[-(Lk_y)^2/2]\times H_n(Lk_y)\exp[ik_y(y-y_0)]dk_y, \tag{35}$$

where $F_n(\mathbf{r})$ are the wave functions describing the nth Landau level, C_n is a normalization constant, $H_n(x)$ the Hermite polynomials, $L=(\hbar c/e\mathfrak{H})^{1/2}$ is the first cyclotron radius and $y_0=L^2k_x$.

One can see that k_z is a good quantum number which can take any value. This means that we can construct functions $F_n(\mathbf{r})$ which are solutions of the effective-mass equation (35) as long as k_z fulfills the EMA requirement $k_zp_{nn'^z}/m\omega_{nn'}\ll1$. We know, moreover, that the function $\exp[-(Lk_y)^2/2]H_n(Lk_y)$ goes steeply to zero for $|k_yL|>(2n+1)^{1/2}$. In terms of Eq. (35) it means that we can construct the nth Landau state using k_y values such that

$$-(2n+1)^{1/2}\leq k_yL\leq+(2n+1)^{1/2}.$$

Since the EMA procedure requires $k_yp_{nn'^y}/m\omega_{nn'}\ll1$,

$$\text{or}\quad [(2n+1)^{1/2}/L](p_{nn'}/m\omega_{nn'})\ll1 \quad (2n+1)^{1/2}(a/L)\ll1. \tag{36}$$

The magnetic field strength gives the L value and the condition (36) determines which Landau states can be described for this field by the solutions of the effective-mass equation (34).[12] To check the requirement (24) we notice that in the coordinate representation it can be rewritten in the form

$$(p_{nn'^x}/m\omega_{nn'})(1/L^2)(y_0-y)\ll1, \tag{37}$$

where y_0 is the center of the cyclotron orbit and y_0-y is to be evaluated for a given Landau state. It is well known, however, that the radius of the magnetic orbit is $y-y\sim L(2n+1)^{1/2}$, and from (37) we obtain again the limitation (36). This is what one could expect, since the physical problem with the magnetic field along z direction is symmetrical in x and y.

For large magnetic fields (50–100 kG) the validity of EMA for electrons in the conduction band of Ge or Si is restricted to the first few Landau levels, whereas for the conduction band of InSb, using the $p_{nn'}/m\omega_{nn'}$ value given in Table I, the EMA can be used to describe the first few Landau levels for fields not exceeding 10 kG. In order to treat higher states it is necessary to

[12] For the lowest state we get $a/L\ll1$ which is just the LK estimate obtained by use of the uncertainty relation.

take into account terms of higher order in k in the effective Hamiltonian.[13,14]

The energy criterion [Eq. (25)] takes the form

$$\hbar^2k^2/2m^*\approx\hbar\omega_c(n+\tfrac{1}{2}) \tag{38}$$

which again gives $k\sim(2n+1)^{1/2}L^{-1}$.

C. Crossed Magnetic and Electric Fields

We consider now the case when an electron in a band is subjected to crossed external magnetic and electric fields. The magnetic field is directed as before along the z axis and the electric field along the y axis. Using the Landau gauge, we can write the Hamiltonian in the form

$$H=\mathbf{p}^2/2m+V(\mathbf{r})-(s/m)yp_x+(s^2/2m)y^2+eEy. \tag{39}$$

The electric-field term does not give any nondiagonal elements in the Kohn-Luttinger representation. Thus the diagonalization procedure can be carried out as usual and for the case of a nondegenerate spherical energy band [see Eqs. (7)–(12)] we get

$$\left[\frac{\hbar^2\mathbf{k}'^2}{2m^*}\delta(\mathbf{k}-\mathbf{k}')-\frac{\hbar^2k_x'}{m^*}\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}-\frac{\hbar^2s^2}{2m^*}\frac{\partial^2\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'^2}+eE\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}\right]\delta_{nn'}+(H_{\mathrm{M}}^{(\mathrm{D})},S)+(H_{\mathrm{E}}^{(\mathrm{D})},S)+\cdots. \tag{40}$$

Let us now estimate when it is possible to neglect the last two terms in Eq. (40). First, in order to neglect the terms $(H_{\mathrm{M}}^{(\mathrm{D})},S)$ and $(H_{\mathrm{E}}^{(\mathrm{D})},S)$ in comparison with the terms $H_{\mathrm{M}}^{(\mathrm{D})}$ and $H_{\mathrm{E}}^{(\mathrm{D})}$, respectively, we have to require $S\ll1$. This leads to inequalities (23) and (24). The values of k_y, k_z, and $(k_x-s\partial/i\partial k_y)$ are now to be evaluated for the solutions of the effective-mass equation (16) which in our case is

$$[(1/2m^*)(\mathbf{p}+(e/c)\mathbf{A})^2+e\mathbf{Er}]F(\mathbf{r})=\epsilon F(\mathbf{r}), \tag{41}$$

a free electron in crossed magnetic and electric fields with an effective mass replacing the free-electron mass.

The solutions of the problem in the gauge we used before are given by the harmonic-oscillator functions of the argument $(y-k_xL^2+m^*c^2E/e\mathfrak{H}\mathcal{C}^2)/L$. k_z and k_x are again the constants of motion. Using these solutions the requirement (24) can be estimated to give

$$\frac{p_{nn'}{}^x}{m\omega_{nn'}}\frac{1}{L^2}(L^2k_x-y)\sim\frac{p_{nn'}{}^x}{m\omega_{nn'}}\left[(2n+1)^{1/2}L^{-1}+\frac{m^*eE}{\hbar\mathfrak{H}\mathcal{C}}\right]\ll1; \tag{42}$$

using again $p_{nn'}{}^x/m\omega_{nn'}\sim a$, we get

$$(2n+1)^{\frac{1}{2}}a/L\ll1, \tag{43}$$

and

$$eEa/\hbar\omega_c\ll1, \tag{44}$$

where $\omega_c=e\mathfrak{H}\mathcal{C}/m^*c$ is the effective cyclotron frequency. In order to compare $(H_{\mathrm{E}}^{(\mathrm{D})},S)$ with the diagonal magnetic terms, we rearrange the terms in the diagonal part to give

$$\left[\frac{\hbar^2k_y'^2}{2m^*}+\frac{m\omega_c^2}{2}\left(\frac{1}{i}\frac{\partial}{\partial k_y'}-y_0\right)^2\right]\delta(\mathbf{k}-\mathbf{k}')\delta_{nn'}+\frac{\hbar^2k_z'^2}{2m^*}\delta(\mathbf{k}-\mathbf{k}')\delta_{nn'}+\left(\frac{eEk_x'}{\hbar\mathfrak{H}\mathcal{C}}-\frac{m^*c^2E^2}{2\mathfrak{H}\mathcal{C}^2}\right)\times\delta(\mathbf{k}-\mathbf{k}')\delta_{nn'}+(H_{\mathrm{M}}^{(\mathrm{D})},S)+(H_{\mathrm{E}}^{(\mathrm{D})},S)+\cdots, \tag{45}$$

where $y_0=L^2k_x'-m^*c^2E/e\mathfrak{H}\mathcal{C}^2$. Because k_x and k_z are the constants of motion, the second and third terms in Eq. (45) are also constants of motion and they do not determine the wave functions; they only shift the energy levels. It is sufficient therefore to require $(H_{\mathrm{E}}^{(\mathrm{D})},S)$ to be much smaller than the first diagonal term in Eq. (45). For the eigenvalues of the effective Hamiltonian [Eq. (45)] the first term gives $\hbar\omega_c(n+\frac{1}{2})$. We have therefore to require $(H_{\mathrm{E}}^{(\mathrm{D})},S)$ to be smaller than any Landau level, $[H_{\mathrm{E}}^{(\mathrm{D})},S]\ll\hbar\omega$. By use of Eqs. (23), (24), and (40) this again leads to requirements (43) and (44).

To check the third condition we notice that since k_z is a good quantum number the EMA may be used for quantum states such that $k_za\ll1$. To determine which k_y values are involved in constructing the solutions $F(\mathbf{r})$ for the crossed-field case we can use a procedure identical with that used for the magnetic-field case. The result is also identical and we obtain the restriction (36).

Thus we conclude that Eqs. (43) and (44) restrict the validity of the effective mass approximation in crossed magnetic and electric fields. If the electric field is very low, we can neglect all the terms containing the electric field and the solutions in crossed fields go smoothly into usual Landau solutions in a magnetic field.

The energy criterion [Eq. (25)] takes the form

$$\hbar^2k^2/2m^*\sim\hbar\omega_c(n+\tfrac{1}{2})+eEL^2k_x-m^*c^2E^2/2\mathfrak{H}\mathcal{C}^2+\hbar^2k_z^2/2m^*. \tag{46}$$

Solving for the order of magnitude of k we find

$$k\sim m^*eE/\hbar\mathfrak{H}\mathcal{C}\pm(2n+1)^{1/2}L^{-1}. \tag{47}$$

From the requirement $ka\ll1$ and from Eq. (47) we get $(2n+1)^{1/2}(a/L)\ll1$ [which is again Eq. (36)] and $eEa/\hbar\omega_c\ll1$ which gives the same restriction [Eq. (44)] on the applicability of the EMA to the situation in crossed magnetic and electric fields. It therefore

[13] T. Kjeldaas and W. Kohn, Phys. Rev. **105**, 806 (1957).
[14] Laura M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 90 (1958).

follows that the theory developed by Aronov[4] is correct only as far as the relations (43) and (44) are fulfilled.

In conclusion we would like to mention that in the measurements of the optical absorption in Ge in crossed fields by Vrehen and Lax[5,6] the light-hole–electron transitions can be described by the effective-mass approximation. Indeed, for $E\sim5\times10^4$ V/cm, $\mathcal{H}\sim10^5$ G, $a\sim5\times10^{-8}$ cm, $m^*\sim0.04m_0$, we have $eEa/\hbar\omega_c^*\sim0.1$. Heavy holes having the effective mass approximately 10 times larger than that of the light holes, cannot be described by EMA under the above experimental conditions.

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Diffusion of Copper and Gallium in Single Crystals of Zinc*

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The sectioning technique was used to study the diffusion of radioactive tracers in high-purity zinc single crystals. Diffusion both parallel and perpendicular to the hexagonal axis was measured. The diffusion of Cu^{64} was measured over the temperature range from about 338°C to 415°C with the results

$$D_{\parallel}=(2.22\pm0.57)\exp[-(29.53\pm0.29)\times10^3/RT]\ \text{cm}^2/\text{sec},$$
$$D_{\perp}=(2.00\pm0.54)\exp[-(29.92\pm0.30)\times10^3/RT]\ \text{cm}^2/\text{sec}.$$

The diffusion of Ga^{72} was measured over the range from about 240°C to 403°C with the results

$$D_{\parallel}=(0.016\pm0.001)\exp[-(18.40\pm0.06)\times10^3/RT]\ \text{cm}^2/\text{sec},$$
$$D_{\perp}=(0.018\pm0.001)\exp[-(18.15\pm0.08)\times10^3/RT]\ \text{cm}^2/\text{sec}.$$

Copper diffused at a rate faster than gold but slower than silver. As in silver and gold, $D_{\parallel}>D_{\perp}$; but the anisotropy was much smaller in Cu than in Ag or Au. The measured values of gallium fall somewhat below those for indium and show $D_{\perp}>D_{\parallel}$. The relative diffusion rates are qualitatively in accord with the predictions of LeClaire's theory of homovalent diffusion. The sign of anisotropy is explained in terms of the electrostatic interaction between the diffusing ion and the vacancy, and the reduced anisotropy of copper diffusion is interpreted as evidence of a size effect.

INTRODUCTION

IN the last few decades much effort has been expended in the study of impurity diffusion in order to develop a better understanding of the diffusion mechanisms. Considerable work has been reported in literature on impurity diffusion in cubic metals, particularly the noble metals, and the over-all pattern seems to be well understood on the basis of the screened interaction model proposed by Lazarus[1] and later modified by LeClaire.[2] There has been less information available on diffusion in anisotropic crystals which possess more than one rate of diffusion in the same lattice structure.

Experimental data on self-diffusion[3] and on the diffusion of indium, silver,[4] cadmium, and gold[5] impurities in noncubic divalent zinc single crystals are available. The general trend of the activation energies with the valence of the diffusing atom was found to be in qualitative accord with Lazarus' theory.

Following the approach of Lazarus, Ghate[6] developed the screened interaction model for impurity diffusion in zinc and calculated the difference ΔQ in the activation energies for impurity diffusion and self-diffusion. He considered the diffusion of both trivalent and monovalent impurities, parallel and perpendicular to the hexagonal axis. The results of this calculation check fairly well in the case of indium and gold but a considerable discrepancy exists for silver. The lack of quantitative agreement is probably due to the fact that the theory does not take into account the differences in the electronic constitution of the inner core of the diffusing and the host ions and their relative sizes. These factors do contribute to the diffusion parameters as is evident from the results of diffusion of homovalent

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[1] D. Lazarus, Phys. Rev. **93**, 973 (1954).
[2] A. D. LeClaire, Phil. Mag. **7**, 141 (1962).
[3] G. A. Shirn, E. S. Wajda, and H. B. Huntington, Acta Met. **1**, 513 (1953).
[4] J. H. Rosolowski, Phys. Rev. **124**, 1828 (1961).
[5] P. B. Ghate, Phys. Rev. **131**, 174 (1963).
[6] P. B. Ghate, Phys. Rev. **133**, A1167 (1964).