Scattering of Electrons in Crystals in the Presence of Large Electric Fields

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By the calculation of transitions between states appropriate to electrons moving in a large uniform electric field superimposed on a periodic crystal field, it is shown the probabilities of scattering by lattice vibrations or imperfections are independent of the uniform field and are given by the usual expressions derived for zero field. This justifies the procedure of treating acceleration by the field and scattering as independent processes.

IN calculations of electrical conduction in solids it is usual to treat acceleration of electrons by the applied field and by scattering as independent processes. The probability of scattering is calculated for the case in which no electric field is present. A question may arise as to the validity of this procedure, particularly when the applied field is so large that the state of the electron changes considerably between collisions. We shall show that although the details of the transition processes may be altered by the electric field, the final expressions for the scattering probabilities are independent of the field.

According to the usual theory the probability per unit time of a transition from a state with crystal momentum $\mathbf{P}=\hbar\mathbf{k}$ to $\mathbf{P}'=\hbar\mathbf{k}'$ is:[1]

$$f(\mathbf{P},\mathbf{P}')=(2\pi/\hbar)|M(\mathbf{P},\mathbf{P}')|^2\delta(E(\mathbf{P})-E'(\mathbf{P}')), \quad (1)$$

where $M(\mathbf{P},\mathbf{P}')$ is the matrix element for the transition and $E(\mathbf{P})$ and $E'(\mathbf{P}')$ are the energies of the initial and final states, respectively. We shall suppose that $E'(\mathbf{P}')$ includes the energy $\hbar\omega$, of the phonon involved in the collision as well as the energy of the electron:

$$E'(\mathbf{P}')=E(\mathbf{P}')\pm\hbar\omega. \quad (2)$$

The upper sign corresponds to absorption and the lower to emission of the phonon.[2] It is convenient to introduce coordinates P_1', P_2', P_3', for $\mathbf{P}'$ such that $dP_2'dP_3'$ lies on the surface of constant energy, $E'(\mathbf{P}')=E(\mathbf{P})$, and dP_1' is normal to this surface. The over-all probability of scattering into $dP_2'dP_3'$ in time Δt is then

$$\rho dP_2'dP_3'\Delta t\int f(\mathbf{P},\mathbf{P}')dP_1'$$
$$=(2\pi/\hbar)|M(\mathbf{P},\mathbf{P}')|^2\rho dP_2'dP_3'\Delta t/(\partial E'/\partial P_1'), \quad (3)$$

where $\rho=h^{-3}$ is the density of states in momentum space. We shall show that (3) still applies when an electric field is present.

The wave equation for an electron influenced by a periodic crystal field, $V_0(\mathbf{r})$, an electric field which produces a force, $\mathbf{F}$, and an interaction operator, H_I, which gives the scattering, can be written as

$$[-(\hbar^2/2m)\Delta+V_0(\mathbf{r})-\mathbf{F}\cdot\mathbf{r}+H_I]\psi=i\hbar\partial\psi/\partial t. \quad (4)$$

We shall solve this equation by the method of variation of constants. The wave function is expanded in a series of functions, $\psi_P(\mathbf{r},t)$, described in Eq. (6), which are solutions of the equation for $H_I=0$ and the coefficients in the expansion are to be determined as functions of time:

$$\psi=\sum_{p'}a_{P'}(t)\psi_{P'}(\mathbf{r},t). \quad (5)$$

The treatment differs from the usual one in that the wave functions used in the expansion are appropriate to an applied electric field, $\mathbf{F}$, rather than for zero field. Such wave functions have been used by Houston[3] to discuss the probabilities of transitions between bands induced by the applied field.

Houston showed that

$$\psi_P(\mathbf{r},t)=U_{P+\lambda t}(\mathbf{r})\exp[(i/k)(\mathbf{P}+\mathbf{F}t)\cdot\mathbf{r}]$$
$$\times\exp\left[-(i/\hbar)\int^t E(\mathbf{P}+\mathbf{F}t')dt'\right] \quad (6)$$

is an approximate solution for an electron in a periodic field on which a uniform force, $\mathbf{F}$, is superimposed. This solution corresponds to a state with momentum increasing uniformly in time as suggested by the motion of a wave packet. The wave function and energy, $E(\mathbf{P})$, corresponding to $\mathbf{F}=0$ are those for zero applied field. The fact that (6) is not an exact solution of (4) with $H_I=0$ corresponds to the possibility of the electron making a transition from one Brillouin zone to another when $\mathbf{P}+\mathbf{F}t$ is near a zone boundary. This is the problem discussed by Houston.[3] Such transitions are important when the force $\mathbf{F}$ is so large that it produces a potential energy difference across one unit cell of the same order as the gap between energy bands. This corresponds to an electric field of the order of 10^7 volts/cm. We shall not be concerned with such large fields and shall neglect the differences between (6) and the exact solution of the time-dependent equation with $H_I=0$.

We are concerned with the effect of the interaction, H_I, which produces transitions between states with

[1] See, for example, F. Sietz, *The Modern Theory of Solids* (McGraw-Hill Book Co., Inc., New York, New York, 1940), p. 521 and following.

[2] If, as in impurity scattering, no phonon is involved, we may set $\hbar\omega=0$.

[3] W. V. Houston, Phys. Rev. **57**, 184 (1940).

different $\mathbf{P}$. Initially the electron is in the state $\mathbf{P}$, so that at $t=0$,

$$a_P(0)=1, \quad a_{P'}(0)=0, \quad \mathbf{P}'\neq\mathbf{P}. \tag{7}$$

The equation for $a_{P'}(t)$, obtained by substituting (4) into (3), multiplying by $\psi_{P'}(\mathbf{r},t)^*$ and integrating over space is:

$$i\hbar(da_{P'}/dt)=a_P(t)M(\mathbf{P},\mathbf{P}')$$
$$\times\exp\left[-(i/\hbar)\int_0^t(E(\mathbf{P}+\mathbf{F}t')-E'(\mathbf{P}'+\mathbf{F}t'))dt'\right], \tag{8}$$

where

$$M(\mathbf{P},\mathbf{P}')=\int\psi_{P'}{}^*H_I\psi_P dv. \tag{9}$$

In the derivation of (8) we have treated the $a_{P'}$ with $\mathbf{P}'\neq\mathbf{P}$ as small quantities and have neglected terms which contain both $a_{P'}$ and H_I.

In integrating (8) we shall suppose that the time interval involved is so short that $a_P(t)$ does not change appreciably and may be set equal to unity. We also suppose that the matrix element does not vary appreciably with time during the interval so that it can be treated as a constant. The range of validity of these assumptions shall be discussed later. The integral of (8) from $t=0$ to Δt is then

$$a_{P'}(t)=-(i/\hbar)M(\mathbf{P},\mathbf{P}')$$
$$\times\int_0^{\Delta t}\exp\left[-(i/\hbar)\int_0^t(E(\mathbf{P}+\mathbf{F}t')-E'(\mathbf{P}'+\mathbf{F}t')\right]dt'dt. \tag{10}$$

The exponential is a rapidly oscillating function which integrates to zero except when the rate of change of phase with respect to time vanishes. This latter condition corresponds to the requirement of conservation of energy:

$$E'(\mathbf{P}'+\mathbf{F}t)=E(\mathbf{P}+\mathbf{F}t). \tag{11}$$

The value of $a_{P'}(t)$ is negligibly small unless (11) is satisfied at some time during the interval $0\rightarrow\Delta t$.

To evaluate the integral when this condition is satisfied, we expand the argument of the exponential as a power series in t:

$$\int_0^t[E(\mathbf{P}+\mathbf{F}\tau)-E'(\mathbf{P}'+\mathbf{F}\tau)]d\tau=\alpha t+\tfrac{1}{2}\beta t^2+\cdots. \tag{12}$$

The coefficients have the values:

$$\alpha=E(\mathbf{P})-E'(\mathbf{P}'), \quad \beta=\mathbf{F}\cdot\mathrm{grad}_P(E)-\mathbf{F}\cdot\mathrm{grad}_{P'}E'. \tag{13}$$

If (11) is satisfied at $t=t_0$,

$$\alpha t+\tfrac{1}{2}\beta t^2=\tfrac{1}{2}\beta(t-t_0)^2-\tfrac{1}{2}\beta t_0^2. \tag{14}$$

With use of (12) and (14), Eq. (10) becomes:

$$a_{P'}(t)=-(i/\hbar)M(\mathbf{P},\mathbf{P}')\exp(i\beta t_0^2/2\hbar)$$
$$\times\int_0^{\Delta t}\exp[-i\beta(t-t_0)^2/2\hbar]dt. \tag{15}$$

The integral can be evaluated by the method of stationary phases. Thus if we assume that $\beta\Delta t^2/\hbar$ is a large number and that $0<t_0<\Delta t$, we can replaced the limits 0 and Δt by $-\infty$ and $+\infty$ without appreciable error. Since

$$\int_{-\infty}^{\infty}\exp(ix^2)dx=(1+i)(\pi/2)^{\frac{1}{2}}, \tag{16}$$

we obtain finally

$$|a_{P'}(t)|^2=2\pi|M(\mathbf{P},\mathbf{P}')|^2/|\beta|\hbar \text{ for } 0<t_0<\Delta t \tag{17}$$
$$=0 \text{ otherwise.}$$

We shall next show that the probability of scattering into a certain group of end states given by (17) reduces to the value given by (2). For this purpose we again use coordinates P_1', P_2', P_3' for $\mathbf{P}'$, defined so that $dP_2'dP_3'$ lies on a surface of constant energy. For given P_2', P_3', we suppose that P_{10}' is the value of P_1' which satisfies conservation of energy at $t=0$:

$$E'(P_{10}',P_2',P_3')=E(\mathbf{P}), \tag{18}$$

and that $P_{\Delta t}'\equiv(P_{1\Delta t}',P_2',P_3')$ is the value of $\mathbf{P}'$ which satisfies the equation at $t=\Delta t$:

$$E'(\mathbf{P}_{\Delta t}'+\mathbf{F}\Delta t)=E(\mathbf{P}+\mathbf{F}\Delta t). \tag{19}$$

Transitions are possible for those values of P_1' which lie between P_{10}' and $P_{1\Delta t}'$. The allowed range of values for P_1' for which (19) holds is denoted by

$$\Delta P_1'=P_{1\Delta t}'-P_{10}'. \tag{20}$$

Since Δt is assumed small, $\Delta P_1'$ can be evaluated by expanding both sides of (19) to terms linear in Δt. Using (18) and (20) this gives

$$\Delta P_1'(\partial E'/\partial P_1')+\Delta t\mathbf{F}\cdot\mathrm{grad}_{P'}E'=\Delta t\mathbf{F}\cdot\mathrm{grad}_P E. \tag{21}$$

Solving for $\Delta P_1'$, we find

$$|\Delta P_1'|=\Delta t|\mathbf{F}\cdot\mathrm{grad}_{P'}E'-\mathbf{F}\cdot\mathrm{grad}_P E|/(\partial E'/\partial P_1')$$
$$=\Delta t|\beta|/(\partial E'/\partial P'). \tag{22}$$

Since the probability of scattering is the same for each of the states in the range $|\Delta P_1'|dP_2'dP_3'$, the total probability of scattering into the range $dP_2'dP_3'$ in time Δt is:

$$\rho|a_{P'}(t)|^2|\Delta P_1'|dP_2'dP_3'$$
$$=2\pi\rho|M(\mathbf{P},\mathbf{P}')|^2|\Delta P_1'|dP_2'dP_3'/|\beta|\hbar. \tag{23}$$

With use of (22) for $|\Delta P_1'|$ this becomes

$$(2\pi/\hbar)|M(\mathbf{P},\mathbf{P}')|^2\rho dP_2'dP_3'\Delta t/(\partial E'/\partial P_1'), \tag{24}$$

which is identical with (2). Thus the scattering probabilities are independent of the field.

It remains to discuss the limits of validity of the approximation used in obtaining (2) and (24). Peierls[4] has discussed the applications of (1) and (2) to the theory of conductivity. These equations can be used when the relaxation time, τ, which is the average time between collisions, is sufficiently large so that

$$\tau\Delta E > h, \tag{25}$$

where ΔE is of the order of $\hbar\omega$. If (1) is to be integrated over the distribution function of the electrons, one may take the less stringent condition $\Delta E \sim k_0 T$. Thus (1) and (2) may be used if

$$\tau k_0 T > h. \tag{26}$$

The approximations made in the derivation of (17) and (24) are of a different nature since they depend on the magnitude of the electric field. In the derivation of (17) it was assumed that Δt is sufficiently large so that

$$\beta(\Delta t)^2 > h \tag{27}$$

and at the same time small enough so that $a_P(t)$ and $M(\mathbf{P}, \Delta')$ do not vary appreciably during the interval Δt. Taking $a_P(\Delta t) \sim 1$ implies that

$$\Delta t < \tau. \tag{28}$$

The constancy of the matrix element implies that the state of the electron does not change very much during Δt. Since the momentum changes by $\mathbf{F}\Delta t$, this implies that

$$\mathbf{F}\Delta t < \Delta\mathbf{P}, \tag{29}$$

where $\Delta\mathbf{P}$ is a momentum interval over which the matrix element is substantially constant.

[4] R. Peierls, Zeits. f. Physik **88**, 786 (1934); Helv. Phys. Acta, **7** 24 (1934).

The maximum allowed value of Δt is the smaller of the values determined by the limiting conditions (28) and (29). Condition (29) applies if the electric field is such that the momentum of the electron is changed by a large amount between collisions. Equation (28) applies if $\mathbf{F}\tau$ represents a relatively small change in momentum.

Equation (27) can be written in a somewhat different form by use of the definition (13) for β. It follows from (13) that

$$\beta\Delta t = \Delta E_{\Delta t}, \tag{30}$$

where $\Delta E_{\Delta t}$ is the change in energy of the electrons during Δt. Thus (27) can be written as

$$\Delta E_{\Delta t}\Delta t > h. \tag{31}$$

If (28) applies, (31) may be written

$$\Delta E_\tau \tau > h, \tag{32}$$

where ΔE_τ is now the energy change between collisions. This expression is similar to Peierls' conditions (25) and (26), but may be less stringent if the field, $\mathcal{E}$, is such that $\Delta E_\tau > k_0 T$. If (29) applies, (31) may be written

$$(\partial E/\partial P)(\Delta P)^2 > |eFh|. \tag{32}$$

This equation gives an upper limit for the electric field, but the limiting field is ordinarily quite large. For example, if we set $\partial E/\partial P \sim v \sim 10^7$ cm/sec. and $\Delta P \sim mv$, the limit is:

$$\mathcal{E} < m^2 v^3/eh \sim 2\times 10^3 \text{ e.s.v.} \sim 6\times 10^5 \text{ volts/cm.} \tag{33}$$

These arguments show that the usual expressions for scattering probabilities can be used ordinarily when an electric field is present, and, in fact, the range of validity of the expressions may be extended by the presence of an electric field.