

Effect of Traps on Carrier Injection in Semiconductors*

H. Y. FAN

Purdue University, Lafayette, Indiana

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The effect of carrier traps on the behavior of a semiconductor with respect to injected carriers is analyzed. Two problems are considered: photoconductivity, and spread of excess carrier concentration under applied field. It is shown that trapped minority carriers, by causing an increase in majority carrier concentration, give rise to increased photoconductivity which may be nonlinear with light intensity and have a very long time constant. These conclusions are in agreement with recent experimental results. The drift of excess carriers is treated, neglecting diffusion. Expression is obtained for the time and space distribution of excess minority carriers, and the effect of traps on the apparent drift mobility is discussed.

IN a semiconductor, imperfections of the crystal may introduce in the forbidden energy gap discrete energy levels with localized wave functions. We may speak of these localized states as carrier traps. An increase in the number of electrons in these states gives trapped electrons whereas a decrease corresponds to trapped holes. Shockley and Read¹ have analyzed the hole-electron recombination rate resulting from the presence of such traps under constant perturbed electron distribution. The effect of the traps considered was that of an intermediate step for the transition of an electron from the conduction to the valence band. Recent investigations on photoconductivity^{2,3} and decay of injected carriers⁴ as well as experiments on drift mobility⁵ indicated the necessity of considering the effect of traps in these problems where the accumulation or depletion of trapped electrons or holes has to be considered. In general there may be several different types of imperfections, and an imperfection of each kind may give several discrete levels. However, under a given condition it may be that only one set of traps is effective. In the following we shall give an analysis of this simple case. The problem of photoconductivity will be considered first, where a uniformly irradiated region of the sample is sufficiently wide and the applied field is sufficiently low that we do not have to deal with spatial variations. Then the problem of injected carriers drifting under an applied field will be discussed.

PHOTOCONDUCTIVITY

Consider a semiconductor in which the radiation of a suitable wavelength excites electrons across the energy gap, producing hole-electron pairs. The resulting photoconductivity measured by the increase of conductivity is given by

$$\Delta\sigma = e(\mu_e\Delta n + \mu_h\Delta p), \quad (1)$$

where μ_e and μ_h are electron and hole mobilities, and n and p are electron and hole concentrations. Let n_t be

the concentration of electrons in the traps. When the electrons and holes deviate from their normal concentrations, n_t will also change from its normal value. We speak then of trapped electrons (Δn_t) or trapped holes ($\Delta p_t = -\Delta n_t$). Condition of electrical neutrality requires

$$\Delta n = \Delta p + \Delta p_t. \quad (2)$$

Although trapped electrons or holes do not participate in the conduction directly, their presence may change Δn and Δp , thus affecting $\Delta\sigma$.

Consider the rates of electron transition between the traps and the valence and conduction bands owing to the processes which establish thermal equilibrium. Excitation owing to the irradiation will be considered separately. Let R be the rate of transition per unit volume and let subscripts t , v , and c refer to traps, valence band, and conduction band, respectively. We can write

$$\begin{aligned} R_{tv} &= r_v n_t p, \\ R_{ct} &= r_c n(N - n_t), \end{aligned} \quad (3)$$

where N is the concentration of traps and r_c and r_v are coefficients which may depend on the temperature. According to the principle of detailed balance $R_{vt} = R_{tv}$ and $R_{tc} = R_{ct}$ in equilibrium. Furthermore, R_{vt} should be proportional to the concentration of vacant traps, and R_{tc} should be proportional to the concentration of electrons in the traps. Therefore,

$$\begin{aligned} R_{vt} &= r_v n_{t0} p_0 (N - n_t) / (N - n_{t0}) = r_v p_1 (N - n_t), \\ R_{tc} &= r_c n_0 (N - n_{t0}) n_t / n_{t0} = r_c n_1 n_t, \end{aligned} \quad (4)$$

subscript 0 referring to the normal condition. According to Fermi-Dirac statistics the ratio of empty to occupied traps is

$$(N - n_t) / n_t = \exp[(E_t - \zeta) / kT],$$

where E_t is the energy level of traps. Thus,

$$\begin{aligned} n_t &= n_0 \exp[(E_t - \zeta) / kT] \\ &= 2(2\pi m_e kT / h^2)^{3/2} \exp[(E_t - E_c) / kT], \\ p_t &= p_0 \exp[(\zeta - E_t) / kT] \\ &= 2(2\pi m_h kT / h^2)^{3/2} \exp[(E_v - E_t) / kT], \end{aligned} \quad (5)$$

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¹ W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).

² Gebbie, Nisenoff, and Fan, Phys. Rev. **91**, 230 (1953).

³ J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).

⁴ D. Navon and H. Y. Fan, Phys. Rev. **91**, 491 (1953).

⁵ R. Lawrence, Phys. Rev. **89**, 1295 (1953).

where E_c is the bottom energy of the conduction band and E_v is the top energy of the valence band. We see that p_1 and n_1 are equal to the hole and electron concentrations, respectively, when $\zeta = E_t$. The net rates of transition from the traps to the two bands are

$$\begin{aligned} R_{tv} - R_{vt} &= r_v [p n_t - p_1 (N - n_t)], \\ R_{tc} - R_{ct} &= r_c [n_1 n_t - n (N - n_t)]. \end{aligned} \quad (6)$$

Under thermal equilibrium both these rates are equal to zero.

(A) Steady State Under Continuous Irradiation

Under such conditions

$$(R_{tv} - R_{vt}) + (R_{tc} - R_{ct}) = 0. \quad (7)$$

It follows from (6) and (7) that the fraction of traps occupied by electrons is

$$\frac{n_t}{N} = \frac{r_c n + r_v p_1}{r_c (n + n_1) + r_v (p + p_1)}. \quad (8)$$

There is a continuous electron transition from the conduction band to the traps and from the traps to the valence band, given by

$$R_{ct} - R_{tc} = R_{tv} - R_{vt} = N r_c r_v \frac{n p - n_0 p_0}{r_c (n + n_1) + r_v (p + p_1)}. \quad (9)$$

This is the hole-electron recombination rate resulting from the existence of the traps in agreement with the formula derived by Shockley and Read. Introducing

$$\eta = r_c n_0 + r_v p_1, \quad \beta = r_c (n_0 + n_1) + r_v (p_0 + p_1), \quad (10)$$

we get

$$n_{t0}/N = \eta/\beta, \quad \frac{\Delta n_t}{N} = \frac{r_c (\beta - \eta) \Delta n - r_v \eta \Delta p}{\beta (\beta + r_c \Delta n + r_v \Delta p)}. \quad (11)$$

Experimentally we usually have $\Delta\sigma/\sigma_0 \ll 1$. Therefore, Δn and Δp are small compared to the normal concentration of majority carriers which is n_0 , assuming n -type samples; hence,

$$r_c \Delta n \ll \beta.$$

If $r_v \Delta p$ is also small compared to β , then Δn_t will vary linearly with Δn and Δp . It is found,² at least in germanium, that the part of photoconductivity resulting from traps saturates with increasing light intensity. This can be expected if $r_v \Delta p$ becomes large compared to β . Neglecting the terms containing $r_c \Delta n$, we get

$$\begin{aligned} -\Delta n_t/N &= (\eta/\beta) [\Delta p/(\beta/r_v) + \Delta p] \\ &= (n_{t0}/N) [\Delta p/(\beta/r_v) + \Delta p]. \end{aligned} \quad (12)$$

This approximation amounts to assuming

$$r_c \ll r_v. \quad (13)$$

For steady state under irradiation the number of electrons on the traps remains constant; therefore, Δp is determined by the rate (per unit volume) of hole-electron excitation, L , and recombination. If an excess hole has a definite rate $1/\tau_r$ of recombining with a conduction electron, then

$$\Delta p = L \tau_r. \quad (14)$$

Substituting (14) into (12), we get

$$\Delta p_t = -\Delta n_t = n_{t0} \frac{L}{\beta/r_v \tau_r + L}. \quad (15)$$

Thus we get, under irradiation trapped holes, minority carriers. Since Δp according to (14) is independent of the existence of traps, the trapped holes just cause a corresponding increase in Δn according to (2). Although the trapped minority carriers cannot conduct themselves, by increasing the excess of majority carriers they enhance the photoconductivity. Expression (14) is in agreement with observations on low temperature photoconductivity in germanium.² For small excitation intensity Δp_t is proportional to L . For high excitation intensities,

$$L > \beta/r_v \tau_r,$$

the trapped holes tend to saturate, approaching n_{t0} .

It has been suggested that hole-electron recombination is mainly determined by some traps present in the material.¹ It should be pointed out that if the traps considered here were also the traps determining recombination, then the photoconductivity should not show saturation. For, in that case, the recombination rate is given by (9) which should be equal to the excitation rate, L , under steady state

$$L = N r_c r_v \frac{n p - n_0 p_0}{\beta + r_c \Delta n + r_v \Delta p} \approx N r_c n_0 \frac{\Delta p}{\beta/r_v + \Delta p},$$

in view of $p_0 \ll n_0$ and $\Delta n \ll n_0$. Substituting into (12), we get

$$\Delta p_t = -\Delta n_t = (n_{t0}/r_c n_0 N) L.$$

The trapped holes, consequently the photoconductivity caused by them, are proportional to the light intensity.

For n -type material ζ should be close to the top of the energy gap. Therefore, we may expect $(\zeta - E_t) > 0$; consequently,

$$n_1 \ll n_0 \quad \text{and} \quad p_1 \gg p_0. \quad (16)$$

It follows then:

$$n_{t0}/N = \eta/\beta \sim 1, \quad \beta/r_v \approx p_1 + r_c n_0/r_v. \quad (17)$$

Now p_1 varies exponentially with $1/T$ according to (5). At the same time, for semiconductors with low impurity activation energy, such as germanium, the majority carrier concentration n_0 remains constant over a wide temperature range. Therefore, β/r_v will be determined by p_1 if the temperature is sufficiently high. With

increasing temperature, p_1 should eventually become so high as to make Δp_i negligible according to (12). This explains the experimental observation that the photoconductivity in germanium shows the effect of traps only at low temperatures but not at room temperature.² On the other hand, with decreasing temperature, p_1 will become so small that very low intensity, for example, background radiation, will saturate the traps. The effect of trapping will again not be observed. Thus the effect of any set of traps should be observable only in a limited temperature range. However, the term $r_e n_0 / r_v$, if not negligible, may extend the range of trapping effect to lower temperatures.

(B) Transient Condition

Let photoexcitation of hole-electron pairs begin at $t=0$ with constant rate L per unit volume. We shall assume that each excess hole has a definite rate $1/\tau_r$ of recombination with a conduction electron; τ_r may be called recombination lifetime. Furthermore, the holes also become trapped at a rate equal to the rate of decrease of electrons on the traps. The net rate of increase in hole concentration is then

$$dp/dt = L - \Delta p/\tau_r + dn_i/dt. \quad (18)$$

For the electrons on traps we find, by using (6),

$$\begin{aligned} -\frac{dn_i}{dt} &= (R_{tc} - R_{ci}) + (R_{tv} - R_{vt}) \\ &= -(r_e n + r_v p_1)N \\ &\quad + [r_e(n + n_i) + r_v(p_0 + p_1)]n_i + r_v n_i \Delta p. \end{aligned} \quad (19)$$

There is also an equation for the rate of change of conduction electrons. Thus we have a set of three simultaneous equations. However, for $\Delta n \ll n_0$, n can be approximately replaced by n_0 . Then we get in view of (10) and (11):

$$\begin{aligned} \frac{d(-\Delta n_i)}{dt} &= -\eta N + \beta n_i + r_v n_i \Delta p = \beta \Delta n_i + r_v n_i \Delta p \\ &= -(1/\tau_f)(-\Delta n_i) + (1/\tau_e n_{i0})n_i \Delta p, \end{aligned} \quad (20)$$

where we have introduced

$$1/\tau_f = \beta, \quad 1/\tau_e = r_v n_{i0}.$$

Since $(-\Delta n_i)$ is the concentration of trapped holes, we see that τ_f is the time required to release a trapped hole and τ_e is the time required to trap an excess free hole if there is normal concentration n_{i0} of electrons in the traps. Now we have only to deal with Eqs. (18) and (20) with two variables Δp and Δn_i . Still (20) has a nonlinear term, involving $n_i \Delta p$, which makes the solution difficult.

We shall first limit ourselves to low intensities of light: $L \ll \beta / r_v \tau_r$. According to (15), we have in this

case $-\Delta n_i \ll n_{i0}$. Putting $n_i/n_{i0} \sim 1$ in (20), we get by combining (18) and (20)

$$\begin{aligned} d^2 \Delta n_i / dt^2 + (1/\tau_r + 1/\tau_f + 1/\tau_e) d \Delta n_i / dt \\ + (1/\tau_r \tau_f) \Delta n_i + L/\tau_e = 0. \end{aligned} \quad (21)$$

For the boundary conditions at $t=0$,

$$\Delta n_i = 0, \quad d(\Delta n_i)/dt = 0,$$

the solution is

$$\begin{aligned} \Delta p_i = -\Delta n_i = L(\tau_r \tau_f / \tau_e) [1 - (\alpha_1 / \alpha_1 - \alpha_2) e^{-\alpha_2 t} \\ - (\alpha_2 / \alpha_1 - \alpha_2) e^{-\alpha_1 t}] \end{aligned} \quad (22)$$

for trapped holes, and

$$\begin{aligned} \Delta p = L \tau_r \{ 1 - [\alpha_1 / \alpha_1 - \alpha_2 (1 - \tau_f \alpha_2) e^{-\alpha_2 t} \\ - \alpha_2 / \alpha_1 - \alpha_2 (1 - \tau_f \alpha_1) e^{-\alpha_1 t}] \} \end{aligned} \quad (23)$$

for free holes, where

$$\begin{aligned} \alpha_{1,2} = (1/2)(1/\tau_r + 1/\tau_f + 1/\tau_e) \\ \pm [(1/4)(1/\tau_r + 1/\tau_f + 1/\tau_e)^2 - 1/\tau_r \tau_f]^{1/2}. \end{aligned} \quad (24)$$

In the decay process after the light is cut off we get, of course, only the transient terms.

Experimentally, when the trapping effect is observed, the decay of the photoconductivity lasts much longer than τ_r , the recombination lifetime.^{2,3} Since $\alpha_1 > 1/\tau_r$, this means

$$\alpha_2 \ll \alpha_1, \quad \text{or} \quad 1/\tau_r \tau_f \ll (1/4)(1/\tau_f + 1/\tau_r + 1/\tau_e)^2.$$

Therefore, $1/\tau_f \ll 1/\tau_r$ and/or $1/\tau_f \ll 1/\tau_e$. Expanding the square root in (24), we get

$$\begin{aligned} \alpha_1 = 1/\tau_r + 1/\tau_f + 1/\tau_e \approx 1/\tau_r + 1/\tau_e, \\ \alpha_2 = (1/\tau_r \tau_f) / (1/\tau_r + 1/\tau_f + 1/\tau_e) \approx \tau_e / \tau_f (\tau_r + \tau_e). \end{aligned} \quad (25)$$

The equation for the decay of free holes given by the transient part of (23) can be written

$$\begin{aligned} \Delta p = L \tau_r \tau_f / \tau_e [(\alpha_1 / \alpha_1 - \alpha_2) \tau_e \tau_r / \tau_f (\tau_e + \tau_r) e^{-\alpha_2 t} \\ + (\alpha_2 / \alpha_1 - \alpha_2) \tau_r + \tau_e / \tau_r e^{-\alpha_1 t}], \end{aligned}$$

and the decay of trapped holes is given by the transient part of (22). We see that the photoconductivity,

$$\Delta \sigma = e [(\mu_e + \mu_h) \Delta p + \mu_e \Delta p_i],$$

has a much larger slow component, with decay constant α_2 , as compared to the faster component with α_1 . The slow component is mainly the result of trapped holes. On the other hand, the free holes give the larger contribution to the fast component.

Consider now the case of high intensity of light: $L > \beta / r_v \tau_r$. According to (15) the steady state value of Δp_i in this case approaches the saturation value n_{i0} . Whereas the final value of Δp_i has a saturation limit, the rate of rise increases with increasing light intensity. Thus the trapped holes will be saturated faster with higher intensity. When the trapped holes are saturated, further build-up of free holes will proceed with time constant τ_r . On the other hand in the decay process the release of the trapped holes always ends

with the time constant $1/\alpha_2 > \tau_r$. Therefore, with high intensities of light the rise and decay of photoconductivity will become asymmetrical. This deduction is also in agreement with experimental observation.²

DRIFT OF INJECTED CARRIER UNDER APPLIED FIELD

We shall consider the one-dimensional problem. Furthermore, to get a simple solution bringing out the essential features of the problem, we shall neglect diffusion. We have then a specimen with an applied voltage giving a constant field E in the X direction. At a certain point, $x=0$, carriers are injected into the specimen. We are interested in the distribution of excess carriers in the specimen as function of time. The injection is assumed to be small so that Δn and Δp are small compared to the normal concentration of majority carriers n_0 . The variation of E will then also be small, and the continuity equation for holes gives

$$\begin{aligned} \partial \Delta p / \partial t &= -\text{div}(E\mu p) - \Delta p / \tau_r + \partial n_i / \partial t \\ &= -E\mu \partial \Delta p / \partial x - \Delta p / \tau_r + \partial n_i / \partial t. \end{aligned} \quad (26)$$

Assuming that hole-trapping does not approach saturation anywhere in the sample, we can use the same approximation in the expression of $\partial n_i / \partial t$ as in the analysis of transient photoconductivity. The differential equation for holes becomes

$$\begin{aligned} \partial^2 \Delta p / \partial x^2 + (1/\tau_r + 1/\tau_f + 1/\tau_i) \partial \Delta p / \partial t + E\mu \partial^2 \Delta p / \partial t \partial x \\ + E\mu / \tau_g \partial \Delta p / \partial x + 1/\tau_g \tau_r \Delta p = 0. \end{aligned} \quad (27)$$

Let the carrier be injected at $x=0$, beginning at $t=0$, keeping a constant hole concentration at this point. The boundary conditions are

$$\begin{aligned} t < 0: \quad \Delta p = 0 \quad \text{for any } x, \\ t \geq 0: \quad \Delta p = \Delta p_0 \quad \text{at } x = 0. \end{aligned} \quad (28)$$

The solution is

$$t \geq t_x: \quad \Delta p = P_x \left[1 + \int_0^\Delta e^{-(\tau_i/4t_x)\delta} \frac{I_1(\sqrt{\delta})}{2\sqrt{\delta}} d\delta \right], \quad (29)$$

$$t < t_x: \quad \Delta p = 0,$$

where

$$\begin{aligned} P_x &= \Delta p_0 \exp[-t_x(1/\tau_r + 1/\tau_i)], \\ t_x &= x/E\mu, \\ \Delta &= (4t_x/\tau_i) [(t - t_x)/\tau_g], \end{aligned} \quad (30)$$

and I_1 is the modified Bessel function. The time t_x is the transit time, the time required for the first injected carriers to reach the point x . Because we have neglected diffusion, the equation shows that at t_x there is an abrupt rise of excess holes from zero to P_x . The first holes arriving to give this abrupt rise decay during the transit time with the combined rates of recombination and trapping. The holes arriving later will be damped less and less as the accumulated trapped holes

approach equilibrium with the free holes. Equation (29) gives

$$\Delta p = \Delta p_0 \exp(-t_x/\tau_r) = P_x \exp(t_x/\tau_i) \quad (31)$$

at $t = \infty$, the traps having come to an equilibrium with the valence band. The holes decay on transit only by recombination, as we would expect. If t_x/τ_i is large, the initial rise of Δp is negligible compared to the final steady state value. For a given t_x/τ_i , the time required for Δp to approach the steady state value is directly proportional to τ_g and can be very long if τ_g is large. This is in contrast to the case without traps where Δp rises immediately to the steady state value at t_x except for the smearing due to diffusion.

Consider now a pulse of injection which is often used in experiments studying drift mobility. Instead of a step function, Δp_0 at the point of injection lasts only from $t=0$ to T , the duration of the pulse. Since the differential Eq. (27) is linear, the solution in this case is simply a superposition of two solutions: one given by (29) and the other having the same form, but with $(-\Delta P_0)$ replacing Δp_0 and $(t-T)$ replacing t . Thus,

$$\begin{aligned} t < t_x: \quad \Delta p &= 0, \\ t_x \leq t < t_x + T: \quad \Delta p &\text{ is given by (4),} \\ t \geq t_x + T: \quad \Delta p &= P_x \int_{\Delta_1}^\Delta e^{-(\tau_i/4t_x)\delta} \frac{I_1(\sqrt{\delta})}{2\sqrt{\delta}} d\delta, \end{aligned} \quad (32)$$

where

$$\Delta_1 = (4t_x/\tau_i) [(t - t_x + T)/\tau_g]$$

When the injection pulse is very short, the time variation of Δp at a given point x is very simple to calculate, e.g., for

$$\Delta - \Delta_1 = 4t_x T / \tau_i \tau_g \ll 1, \quad (33)$$

we can use for $t \geq (t_x + T)$, the approximation

$$\begin{aligned} \Delta p &= [(\Delta - \Delta_1) P_x I_1(\sqrt{\Delta}) / 2\sqrt{\Delta}] \exp[-(\tau_i/4t_x)\Delta] \\ &= (4t_x T / \tau_i \tau_g) P_x f(\Delta). \end{aligned} \quad (34)$$

Figure 1 gives the calculated curves of the function

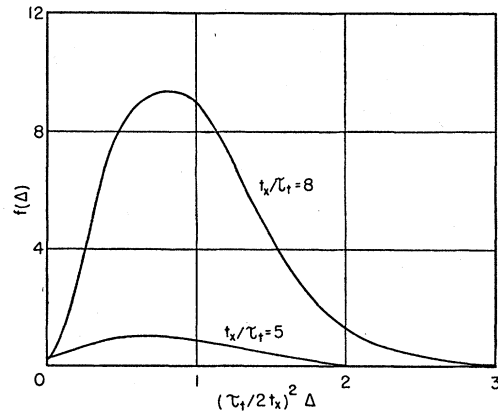


FIG. 1. Curves of the function $f(\Delta)$ plotted against $(\tau_i/2t_x)^2 \Delta$, for two values of the parameter t_x/τ_i .

$f(\Delta)$ plotted against $(\tau_i/2t_x)^2\Delta$ for two values of t_x/τ_i . Starting from $f(0)=0.25$ the curves go through a maximum which rapidly increases with increasing t_x/τ_i . Differentiating $f(\Delta)$, we find that at the maximum

$$(\sqrt{\Delta})I_1(\sqrt{\Delta})/I_2(\sqrt{\Delta})=2t_x/\tau_i.$$

The function on the left-hand side increases with Δ . It approaches 4 as $\Delta \rightarrow 0$. Therefore, $f(\Delta)$ has no maximum for $t_x/\tau_i < 2$. On the other hand, for large t_x/τ_i the value of Δ corresponding to the maximum of $f(\Delta)$ will be large and we have approximately

$$I_2(\sqrt{\Delta}) \sim I_1(\sqrt{\Delta}) \sim e^{\sqrt{\Delta}}/(2\pi\sqrt{\Delta})^{1/2}.$$

Therefore, the maximum of $f(\Delta)$ corresponds to

$$\sqrt{\Delta} \sim 2t_x/\tau_i. \quad (35)$$

Δ being related to t by (30), we find that the peak of pulse of excess free holes at distance x from the injection point occurs at

$$t = t_x(\tau_g + \tau_i)/\tau_i \quad (36)$$

and that the magnitude of the peak is

$$\Delta\phi_{\max} = [P_x/(4\pi)^{1/2}](T/\tau_g)(\tau_i/t_x)^{1/2}e^{t_x/\tau_i}. \quad (37)$$

For sufficiently large t_x/τ_i , the initial step in $\Delta\phi$, equal to P_x , will be negligible compared to the peak. $\Delta\phi$ will appear to rise gradually; and it will, therefore, be impractical to determine t_x from the first arrival of the pulse. The time corresponding to the easily observable maximum is given by (36). This result is easily understood. As τ_g is the average time required for releasing a trapped hole and τ_i is the average time required for trapping a free hole, $\tau_i/(\tau_i + \tau_g)$ is the fraction of time during which the hole remains free. Therefore, the time required for most of the holes to reach the collector is $(\tau_i + \tau_g)/\tau_i$ times longer than the transit time t_x in the absence of traps. The apparent drift mobility will be $\tau_i/(\tau_i + \tau_g)$ times the true mobility. Small apparent drift mobility has been reported for silicon³ and for germanium at low temperatures.⁵

Generalized Variational Equations for the Scattering of Electrons by Hydrogen Atoms*

M. M. GORDON AND J. G. JONES
Physics Department, University of Florida, Gainesville, Florida
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Generalized variational equations are derived for calculating the elastic and inelastic scattering amplitudes associated with the scattering of electrons by hydrogen atoms. The derivation of these equations is such that no unnecessary restrictions are imposed on possible trial wave functions. Two equivalent formulations are given: one involving the use of symmetrized wave functions; the other involving wave functions of the conventional (Mott and Massey) type. For trial wave functions consisting of only the incident wave (multiplied by a hydrogen eigenfunction), these variational equations yield the same results as are obtained by the approximations of Born and Oppenheimer. Various calculation procedures are discussed.

In an appendix, it is shown that the Hulthén variational equation for the scattering phases is a special case of the Kohn variational equation for the scattering amplitude.

I. INTRODUCTION

THE first development of a variational procedure for dealing with the scattering of electrons by hydrogen atoms was carried out by Huang.¹ His method is based on two assumptions: the wave function's asymptotic value contains only the incident and elastically scattered waves; only S -wave scattering takes place. By an extension of Hulthén's one-body scattering variational procedure, Huang thereby obtains a variational equation for determining the S -wave phase shifts. The calculation procedure based on the Hulthén-Huang variational equation was improved and extended

by Massey and Moiseiwitsch who carried out detailed calculations for the S -wave phases.² Where a comparison was possible, they found that the results of their variational methods, even for very simple trial functions, are in very good agreement with the results obtained previously by direct numerical integration of the wave equation. Erskine and Massey extended this work still further by calculating variationally the $1s \rightarrow 2s$ excitation cross section at low energies.³ Their method assumes that only S -wave scattering takes place and that a "distorted wave" approximation is valid. Moiseiwitsch has improved the variational method for dealing with the inelastic scattering processes.⁴ His procedure is based on two variational equations whose

* A brief report of this work and that of reference 8 was presented at the 1952 Thanksgiving Meeting of the American Physical Society [see Phys. Rev. **89**, 913 (1953)].

¹ S. S. Huang, Phys. Rev. **76**, 477 (1949). A variational procedure for the analogous nuclear problem, $n-d$ scattering, was developed by: W. Kohn, Phys. Rev. **74**, 1763 (1948), and M. Verde, Helv. Phys. Acta **22**, 339 (1949).

² H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A205**, 483 (1951).

³ G. A. Erskine and H. S. W. Massey, Proc. Roy. Soc. (London) **A212**, 521 (1952).

⁴ B. L. Moiseiwitsch, Phys. Rev. **82**, 753 (1951).