In Fig. 5 for low fields $\nu_{iv} - \nu_{iv0} \propto E^2$ holds up to about 100 V/cm, where $\nu_{iv0}$ is the zero-field intervalley scattering frequency. At intermediate fields the $\nu_{iv} \propto E^{0.87}$. For a Maxwellian electron distribution $\nu_{iv} \propto E$ is expected for electron energies large compared to the phonon involved in intervalley scattering. The tendency toward saturation at high fields is probably associated with the breakdown of the assumption that the effect of intervalley scattering on the distribution function in a single valley can be neglected.

# Optical Absorption in the Presence of a Uniform Field*

K. Tharmalingam

*Princeton University, Princeton, New Jersey*

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Expressions for the absorption coefficient in the presence of a uniform field, of semiconductors and insulators for both allowed and forbidden transitions are derived. The results are expressed in terms of Airy functions, and the limiting cases examined indicate the tunneling mechanism as a possible explanation for the experimentally observed long-wavelength tails.

## 1. INTRODUCTION

INSULATING and semiconducting crystals, in the absence of any perturbations, are transparent below a certain photon energy above which the absorption rises rapidly. In practice, however, this edge exhibits a complicated structure often giving an exponential type tail in the long-wavelength region.[1] It has been suggested unsuccessfully that (a) the absence of perfect periodicity, and (b) the presence of impurity states in the forbidden band leads to absorption tails in the long-wavelength region.[2,3]

An alternative explanation of the above effect rests on the tunneling of electron states into the forbidden band due to band bending; such band bending in practice can occur at the surface of the crystal, due to the termination of periodicity, or in the bulk of the crystal.[4] Franz[5] considered the effect of a uniform field, on the absorption coefficient, by using the Houston[6] wave functions to calculate the matrix elements and his results were expressed partly in terms of an infinite series.

We have, in this paper, treated the states as stationary and thus adopted the standard procedure to calculate the matrix elements. The results, expressed in terms of the well-known Airy functions in Sec. 3, are, in fact, identical to those obtained by Franz for the case of allowed transitions. Our results, however, can be extended to the case of forbidden transitions giving the expected exponential type tail in the long-wavelength region. A brief discussion of the results, including the effect of binding between electron-hole pairs, is in Sec. 4, and the definition of absorption coefficient in Sec. 2.

## 2. THE ABSORPTION COEFFICIENT

The absorption coefficient $\alpha$ is defined by[7]

$$\alpha = \frac{4\pi^2 e^2}{ncm^2\omega} \sum_i |P_{if}|^2 \delta(E_f - E_i - \hbar\omega), \qquad (2.1)$$

where $E_i$, $E_f$ are the initial and final energies of the system interacting with photons of energy $\hbar\omega$. $n$ is the refractive index; $\hbar$ is the Planck's constant; $c$ is the velocity of light; and $e$, $m$ are charge and mass of an electron, respectively. The matrix element $P_{if}$ for electrons going from the initial state $i$ to the final state $f$ can be written as[8] (a) for allowed transitions

$$P_{if} = \Phi(0) C_0 \delta_{k_i, k_f}, \qquad (2.2)$$

and (b) for forbidden transitions

$$P_{if} = \hbar |\nabla_{r_q} \Phi(0)| C_1 \delta_{k_i, k_f}. \qquad (2.3)$$

In (2.2) and (2.3), $C_0, C_1$ involving the matrix elements between the periodic parts of the Bloch states at the band edges, are independent of the electron wave vector $\mathbf{k}$ with $C_0$ having the dimensions of momentum and $C_1$

* Supported in part by the U. S. Atomic Energy Commission.
[1] J. R. Dixon and J. M. Ellis, Phys. Rev. 123, 1560 (1961).
[2] D. L. Dexter, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p. 155.
[3] D. M. Eagles, J. Phys. Chem. Solids 16, 76 (1960).
[4] G. W. Mahlman, W. B. Nottingham, and J. C. Slater, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p. 489.
[5] W. Franz, Z. Naturforsch 13a, 484 (1958).
[6] W. V. Houston, Phys. Rev. 57, 184 (1940).

[7] J. Bardeen, F. J. Blatt, and L. H. Hall, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p. 146.
[8] R. J. Elliott, Phys. Rev. 108, 1384 (1957).

being a nondimensional constant. The $\delta$ function ensures momentum conservation, and $\mathbf{q}$ is the polarization vector of the photons with negligible momentum. $\Phi(r)$ is the solution of the two-particle Schrödinger equation with $r$ as the relative coordinate of the electron-hole pair. For a pair in the presence of a uniform field $F$ (in the $\mathbf{Z}$ direction) $\Phi(r)$ is obtained from

$$[(\hbar^2/2\mu)\nabla^2 + |e|FZ + E]\Phi(r) = 0, \qquad (2.4)$$

where $E$ is the sum of the electron and hole energies measured from their respective band edges, and $\mu$ the reduced mass is defined by

$$\frac{1}{\mu} = \frac{1}{m_0} + \frac{1}{m_h}, \qquad (2.5)$$

with $m_0$ and $m_h$ as the "effective masses" of the electrons and holes in the conduction and valence bands, respectively. We remark here that the inclusion of Coulomb binding, between the electron-hole pairs, in (2.4) would, in fact, describe the Stark effect of hydrogen-like atoms and a discussion of this is given in Sec. 4. We shall now consider the interband transitions in the absence of any such binding between the pairs.

## 3. INTERBAND TRANSITIONS

The exact solution of (2.4) can be written as[9]

$$\Phi(r) = A\frac{e^{i(k_x x + k_y y)}}{2\pi\hbar}\text{Ai}(-\xi), \qquad (3.1)$$

where

$$\xi = \left(Z + \frac{\epsilon}{|e|F}\right)\left(\frac{2\mu F|e|}{\hbar^2}\right)^{1/3}, \qquad (3.2)$$

with

$$\epsilon = E - (\hbar^2/2\mu)(k_x^2 + k_y^2). \qquad (3.3)$$

The normalization factor $A$ is given by

$$A = \frac{(2\mu)^{1/3}}{\pi^{1/2}(|e|F)^{1/6}\hbar^{2/3}}, \qquad (3.4)$$

and the Airy function $\text{Ai}(\beta)$ is defined by[9]

$$\text{Ai}(\beta) = \frac{1}{\sqrt{\pi}}\int_0^\infty \cos(\tfrac{1}{3}u^3 + \mu\beta)du. \qquad (3.5)$$

### (a) Allowed Transitions

From the above expressions we find that

$$\Phi(0) = \frac{1}{2\pi\hbar}\frac{(|e|F)^{1/2}}{\pi^{1/2}\hbar\theta_F}\text{Ai}\left(-\frac{\epsilon}{\hbar\theta_F}\right), \qquad (3.6)$$

where

$$\theta_F^3 = e^2 F^2/2\mu\hbar. \qquad (3.7)$$

[9] L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon Press Inc., New York, 1959), p. 170.

From (2.1), (2.2), and (3.6), replacing the sum by an integral in (2.1) and including a factor 2 for spin, we finally have the absorption coefficient in the presence of a uniform field, for allowed transitions given by

$$\alpha = R\theta_F^{1/2}\int_{(\omega_1-\omega)/\theta_F}^\infty |\text{Ai}(t)|^2 dt, \qquad (3.8)$$

where

$$R = \frac{2e^2C_0^2}{\hbar\omega cnm^2}\left(\frac{2\mu}{\hbar}\right)^{3/2}, \qquad (3.9)$$

and $\hbar\omega_1$ is the energy of the gap. Since the Airy function satisfies the differential equation

$$\frac{d^2\text{Ai}(t)}{dt^2} = t\,\text{Ai}(t), \qquad (3.10)$$

the last integral can be evaluated to give

$$\int_\beta^\infty |\text{Ai}(t)|^2 dt = -\beta|\text{Ai}(\beta)|^2 + |\text{Ai}'(\beta)|^2, \quad (3.11)$$

where prime denotes differentiation with respect to the argument. We remark here that $\alpha$ can also be expressed in terms of Bessel functions of order $1/3$.

It is instructive to study the limiting cases of $\alpha$, namely, (i) When $\omega > \omega_1$ and near the edge,

$$\alpha \simeq R\theta_F^{1/2}\left[\left(\frac{\omega-\omega_1}{\theta_F}\right)^{1/2} + \int_0^\infty |\text{Ai}(t)|^2 dt\right]$$

$$\to R(\omega-\omega_1)^{1/2} \quad \text{as} \quad F \to 0. \quad (3.12)$$

Hence, in the absence of field, and $\omega > \omega_1$, we get the familiar expression for $\alpha$ with the square root dependence[7] on the frequency (measured relative to the edge). (ii) When $\omega \ll \omega_1$, again using the known properties of Airy function, we obtain[10]

$$\alpha \approx R\frac{\theta_F^{3/2}}{8(\omega-\omega_1)}\exp\left[-\frac{4}{3}\left(\frac{\omega_1-\omega}{\theta_F}\right)^{3/2}\right], \quad (3.13)$$

thus giving us an exponential-type tail in the long-wavelength region. The trivial solution $\alpha \to 0$ as $F \to 0$ is satisfied by (3.13) and we remark here that (3.13) is identical to that obtained by Franz; in fact, his integral expression for $\alpha$ can, with change of variables, be reduced to (3.8).

### (b) Forbidden Transitions

$|\nabla_{r_q}\Phi(0)|$ can again be obtained from (3.1) and we now need to consider two separate cases:

(i) The polarization vector $\mathbf{q}\|\mathbf{F}$, in which case

$$\nabla_z\Phi(0) = \frac{1}{2\pi\hbar}\frac{(|e|F)^{3/2}}{\pi^{1/2}(\hbar\theta_F)^2}\text{Ai}'\left(-\frac{\epsilon}{\hbar\theta_F}\right); \quad (3.14)$$

[10] H. Jeffreys and B. S. Jeffreys, Methods of Mathematical Physics (Cambridge University Press, Cambridge, 1946), p. 508.

and (ii) $q \perp F$ (say $q \| x$), in which case

$$\nabla_x \Phi(0) = i k_x \Phi(0). \qquad (3.15)$$

An identical calculation to that for the case of allowed transitions yields from (2.1), (2.3), (3.14), and (3.15).

$$\alpha_{\|} = S \theta_F^{3/2} \int_{(\omega_1-\omega)/\theta_F}^{\infty} |Ai'(t)|^2 dt, \qquad (3.16)$$

$$\alpha_{\perp} = \frac{S}{2} \theta_F^{3/2} \int_{(\omega_1-\omega)/\theta_F}^{\infty} \left(t + \frac{\omega_1-\omega}{\theta_F}\right) |Ai(t)|^2 dt, \quad (3.17)$$

where

$$S = \frac{2e^2 C_1^2 \hbar}{\omega c n m^2} \left(\frac{2\mu}{\hbar}\right)^{5/2}. \qquad (3.18)$$

Again using the known properties of the Airy function it can be easily verified that

(i) when $\omega \ll \omega_1$,

$$\alpha_{\|,\perp} \to S \theta_F^{3/2} \exp\left[-\frac{4}{3}\left(\frac{\omega_1-\omega}{\theta_F}\right)^{3/2}\right]; \qquad (3.19)$$

and (ii) when $\omega > \omega_1$ and $F \to 0$,

$$\alpha_{\|,\perp} \to S(\omega-\omega_1)^{3/2}, \qquad (3.20)$$

thus giving us the familiar three-halves power law for forbidden transitions.[7] In the gap, however, we again have an exponential-type tail, given by (3.19), in the presence of a uniform field. We now proceed to consider the effect of Coulomb binding on the absorption coefficient, and a brief discussion of results.

## 4. DISCUSSION

It is interesting to note that both the allowed and forbidden transitions give an exponential-type tail in the long-wavelength region, this being an essential feature of the tunneling mechanism. Another striking observation is the dependence of the absorption coefficient on the field term $\theta_F$ having the dimension of frequency; in particular, at the edge ($\omega = \omega_1$) the absorption coefficient varies as $\theta_F^{1/2}$ for allowed transitions and as $\theta_F^{3/2}$ for forbidden transitions. The results of Sec. 3 can be extended to the case of slowly varying (in space) one-dimensional fields by integrating $\alpha$ over

the crystal. This and other more specific application of the present results, will be considered by Dr. Redfield in a forthcoming paper.

In the absence of the field the effect of Coulomb binding (namely, exciton absorption), on the absorption coefficient, has been considered by Elliot.[8] In the presence of the field no exact expression, for the absorption coefficient of bound pairs, is available. Approximate expressions for $\alpha$ in the two limiting cases of large- and small-orbit excitons can, however, be written.

(a) In the (near) continuum corresponding to ionized pair states where the Coulomb interaction still affects the motion, and is treated as a perturbation, we expect the absorption coefficient (when $\omega > \omega_1$) to be modified by the appropriate Sommerfeld factor $\Gamma$, i.e., $\alpha_{exciton}(\omega,\theta_F) \approx \Gamma\alpha(\omega,\theta_F)$. (For example, for allowed transitions[8] $\Gamma = \pi\lambda e^{\pi\lambda}/\sinh\pi\lambda$, where $\lambda = [E_I/\hbar(\omega-\omega_1)]^{1/2}$ and $E_I = \mu e^4/2\hbar^2\kappa^2$, $\kappa$ being the dielectric constant.)

(b) For the case of tight binding, the field term may be treated as a perturbation and the predominant effect of the field on the discrete hydrogenic spectrum is to give us the Stark shift.

The above approximation is evidently crude and a more detailed study is necessary, especially near the edge and in the long-wavelength region. Closely related to this problem is the absorption into empty impurity levels (in the gap) and was considered by Eagles[3] for the field free case. In the presence of a uniform field, a similar calculation indicates that Eagles' result is modulated by a factor

$$\beta^{-1/2} \int_{-\beta}^{\infty} |Ai(t)|^2 dt,$$

with $\beta = [(\hbar\omega - \hbar\omega_1 + E_I)/\hbar\theta_F]$, where for absorption into donor states, the reduced mass $\mu$ becomes $m_0$. This modulation factor leads to the presence of an exponential-type tail, for photon energies less than $(\hbar\omega_1 - E_I)$, again reflecting the features of tunneling.