ready promotion to the conducting levels above the top Fermi level in the ground state. In graphite, which is the two-dimensional case for our system, there are one orbital and one valence electron per atom with three equivalent neighbors. For graphite it is clear both theoretically[9] and experimentally[7,10] that the two-dimensional metallic state exists. Thus, we see that for this system, at least, *bond resonance without vacant orbitals can produce the metallic state.* It is our theory that the new class of metals discussed here is the three-dimensional analog of the two-dimensional metal graphite. There are four orbitals and four valence electrons with four neighbors in the tetrahedral lattices of diamond, wurtzite, and sphalerite which on compression transform, according to Jamieson,[4] into the six-near-neighbor structure of metallic tin. Thus four bonds have to satisfy six atoms (the central atom contributes 4 valence electrons and each of the surrounding 6 atoms contributes 4/6 more for a total of 8, just adequate for four full bonds). The resonance state is possible because the Franck-Condon principle has been satisfied by the location of the atoms in equivalent positions, and, as a consequence, the full crystal is set into three-dimensional resonance such that the entire crystal becomes one molecule at least at the absolute zero of temperature. At finite temperatures the principle of strict symmetrical equivalence for neighbors will be violated by the lattice vibrations, and the resonance possibilities will be reduced because of the Franck-Condon principle; or in band theory language the scattering of conducting electrons will result.

The conduction act itself can be most clearly envisaged as the removal of an electron from the resonating molecule at one edge of the crystal at the cost of the ionization potential, the distribution of the resultant positive charge uniformly over the entire molecule because of the three-dimensional resonance, followed by the neutralization by acquisition of an electron at the opposite side of the crystal with the regaining of the energy corresponding to the ionization potential. In the presence of an electric field the positive charge obviously will not be completely uniformly distributed at any finite temperature because the relaxation time for the molecular lattice will necessarily be the time for the transport act in order that the charge be passed from anode to cathode, and this limitation in rate will cause a charge gradient to exist across the molecule. At the absolute zero of temperature this electrical resistance would appear to be zero.

Drickamer[3] and his co-workers have shown that, like true metals, the new compressed phases absorb light down to the lowest frequencies. This can be envisaged as being due to the close lying states in the crystal (molecule) corresponding to charge displacement from one end of the crystal to the other.

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Optical Absorption in an Electric Field

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The effect of an external electric field on the optical absorption associated with a direct transition between bands is studied. Expressions are given for the absorption constant for photon energies below and above the band gap. The formation of discrete levels in the presence of the electric field produces oscillations in the absorption.

THE influence of an electric field on the optical absorption of a semiconductor or insulator in the vicinity of an absorption edge has previously been studied by Franz[1] and by Keldysh.[2] These authors have shown that in the presence of a field, absorption occurs for photon energies lower than the ordinary band gap. This effect has been observed experimentally by Moss,[3] Williams,[4] Böer *et al.*,[5] and Vavilov and Britsyn.[6] In addition to the displacement of the edge, one expects to find oscillatory behavior of the absorption above the edge resulting from transitions between the discrete "Stark" levels produced in the band system by the external field.[7] This structure might be similar to that observed in the interband magneto-optical effect by Burstein *et al.*[8] and by Zwerdling *et al.*[9] The

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[8] E. Burstein, G. S. Picus, R. F. Wallis, and F. Blatt, Phys. Rev. **112**, 15 (1959).

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theoretical calculations of Franz and Keldysh do not predict such oscillations, and it was with the objective of determining whether oscillations should be expected that the present work was undertaken.

Our conclusion is that the absorption should contain an oscillatory component, both above and below the usual band gap. Although the amplitude of these oscillations will not be large for easily attainable field strengths, their observation would constitute strong evidence for the existence of discrete electronic levels in a uniform electric field.

This calculation is based on discussions of the theory of tunneling given by Kane[10] and Argyres.[11] We will use the notation of Argyres whenever possible.

In the presence of a uniform field of force, F, which is assumed to be in the x direction, and a periodic potential, the wave function of an electron may be written as

$$\phi_{\nu,n}(\mathbf{k}_\perp,\mathbf{r})=\sum\nolimits_{k_x} A_{\nu,n}(\mathbf{k})\psi_n(\mathbf{k},\mathbf{r}). \tag{1}$$

The $\psi_n(\mathbf{k},r)$ are Bloch functions for wave vector $\mathbf{k}$ and band index n. The $A_{\nu,n}$ are solutions of the equation

$$\left[E_n(\mathbf{k})-iF\frac{\partial}{\partial k_x}\right]A_{\nu,n}=W_{\nu,n}A_{\nu,n}. \tag{2}$$

In this equation $E_n(\mathbf{k})$ is the energy of the Bloch function $\psi_n(\mathbf{k})$ in the periodic potential plus the diagonal matrix element of the perturbing field, $-FX_{nn}(\mathbf{k})$. We will, however, neglect the latter quantity in the following.[12] It is assumed here, as in the calculations previously mentioned, that the direction of the electric field coincides with one of the reciprocal lattice vectors of the crystal. The solution of this equation is

$$A_{\nu,n}=\frac{1}{\kappa^{1/2}}\exp\left\{\frac{i}{F}\int_0^{k_x}[W_{\nu,n}-E_n(\mathbf{k}_\perp,k'_x)]dk_x'\right\}, \tag{3}$$

$$W_{\nu,n}=\frac{2\pi\nu F}{\kappa}+\frac{1}{\kappa}\int_{-\kappa/2}^{\kappa/2}E_n(\mathbf{k}_\perp,k_x)dk_x. \tag{4}$$

In these equations, $k_\perp$ stands for the components of the wave vector perpendicular to the field, κ is the width of the Brillouin zone in the x direction, and ν is an integer denoting the discrete "Stark" level. The entire effect of the electric field on the motion of the electron is not included in this calculation since there are off diagonal matrix elements of the Hamiltonian between states $\phi_{\nu,n}$ and $\phi_{\nu',n'}$ which must be included in a description of the phenomenon of tuneling. We will, however, neglect these quantities in this calculation.

To treat the problem of optical absorption, we suppose that an external time-dependent electromagnetic field described by a vector potential

$$\mathfrak{A}=\mathfrak{A}_0\boldsymbol{\varepsilon}e^{i(\mathbf{s}\cdot\mathbf{r}-\omega t)} \tag{5}$$

is incident on the system. The perturbation is

$$H'=(e/m)\mathfrak{A}\cdot\mathbf{p}. \tag{6}$$

In the calculation of the transition probability with the perturbation (6) we wish to avoid explicit use of the standard formula

$$W=(2\pi/\hbar)|H_{fi}'|^2\rho(E_f),$$

since this involves a density of states for a system which here contains discrete levels. We follow instead, the procedure of Argyres.[11] Let $\Psi(t)$ be the complete wave function for the perturbed system. This function can be expanded in terms of the functions ϕ:

$$\Psi(t)=\sum\nolimits_{n,\nu,\mathbf{k}_\perp} b_{\nu,n,\mathbf{k}_\perp}(t)\phi_{\nu,n}(\mathbf{k}_\perp,\mathbf{r}). \tag{7}$$

The probability that the system is in the state $\phi_{\nu,n}$ at time t if it was in $\phi_{\nu',n'}$ at $t=0$ is, to first order in the radiation field:

$$\begin{aligned}&|b_{\nu,n,\mathbf{k}_\perp}(t)|^2\\&\qquad=|M_{nn'}(\mathbf{k}_{\perp,\nu,\nu'})|^2\Omega(W_{\nu,n}-W_{\nu',n'}-\hbar\omega,\,t).\end{aligned} \tag{8}$$

It can easily be seen that the transverse components of the electron's wave vector are conserved. The function Ω is given by

$$\Omega(s,t)=(4/s^2)\sin^2(st/2). \tag{9}$$

The matrix element $M_{nn'}$ is given by

$$\begin{aligned}M_{nn'}&=\int\phi_{\nu,n}{}^*(\mathbf{k}_\perp,\mathbf{r})\frac{e\mathfrak{A}_0}{m}\boldsymbol{\varepsilon}\cdot\mathbf{p}\phi_{\nu',n'}(\mathbf{k}_\perp',\mathbf{r})d^3r,\\&=\frac{e\mathfrak{A}_0}{m}\int\int dk_xdk_x'A_{\nu,n}{}^*(\mathbf{k})A_{\nu'n'}(\mathbf{k}')\\&\qquad\times\int\psi_n{}^*(\mathbf{k},\mathbf{r})e^{i\mathbf{s}\cdot\mathbf{r}}\boldsymbol{\varepsilon}\cdot\mathbf{p}\psi_{n'}(\mathbf{k}',\mathbf{r})d^3r,\\&=\frac{e\mathfrak{A}_0}{m}\int_{-\kappa/2}^{\kappa/2}A_{\nu,n}{}^*(\mathbf{k})A_{\nu'n'}(\mathbf{k})\boldsymbol{\varepsilon}\cdot\mathbf{p}_{nn'}(\mathbf{k})dk_x.\end{aligned} \tag{10}$$

In order to obtain the last line of Eq. (10) we have made the standard approximations of radiation theory in which the momentum of the photon is neglected. The quantity $\mathbf{p}_{nn'}$ is the usual interband optical matrix element.

The number of electrons per unit volume and time which make transitions between band n' and band n is given by

$$w_{nn'}=\frac{1}{t}\frac{2}{L_x}\sum_{\nu,\nu'}\int\frac{d\mathbf{k}_\perp}{(2\pi)^2}|b_{\nu,n,\mathbf{k}_\perp}|^2. \tag{11}$$

In this equation, L_x, a macroscopic quantity, is the length of the specimen in the x direction. The factor

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[10] E. O. Kane, J. Phys. Chem. Solids **12**, 181 (1959).

[11] P. N. Argyres, Phys. Rev. **126**, 1386 (1962).

[12] The principal effect of this term is to produce an additional shift in the band edge linear in the field, in addition to the spreading into the gap described in Eq. (23).

of two takes account of spin. When the function Ω is placed inside the integral in (11), it may be interpreted as being proportional to a delta function for large times. Then we have

$$w_{nn'}=\frac{2}{L_x}\frac{2\pi}{\hbar}\sum_{\nu,\nu'}\int\frac{d\mathbf{k}_\perp}{(2\pi)^2}|M_{nn'}|^2 \times\delta(W_{\nu,n}-W_{\nu',n'}-\hbar\omega). \quad (12)$$

The sum over ν and ν' can be expressed in terms of a single sum and an integral through a relation employed by Argyres.[11] For a function $f(x)$, possessing a Fourier transform

$$\frac{1}{L_x}\sum_{\nu,\nu'}f(\nu-\nu')=\frac{\kappa}{2\pi}\sum_{l=-\infty}^{\infty}\int_{-\infty}^{\infty}f(x)e^{2\pi ilx}dx. \quad (13)$$

The matrix elements and the delta function depend on ν, ν' in the combination $\nu-\nu'$:

$$M_{nn'}=\frac{e\mathfrak{A}_0}{m\kappa}\int_{-\kappa/2}^{\kappa/2}\boldsymbol{\varepsilon}\cdot\mathbf{p}_{nn'}\exp\left\{\frac{i}{F}\int_0^{k_x}\left[\frac{2\pi F}{\kappa}(\nu'-\nu) +\Delta_{n'n}+E_{nn'}\right]dk_x'\right\}dk_x,$$

where

$$\Delta_{n'n}=\frac{1}{\kappa}\int_{-\kappa/2}^{\kappa/2}E_{n'n}dk_x;\quad E_{n'n}=E_{n'}-E_n.$$

Hence,

$$w_{nn'}=\frac{2\kappa}{\hbar}\sum_{l=-\infty}^{\infty}\int\frac{d\mathbf{k}_\perp}{(2\pi)^2}\int dx|M_{nn'}|^2 \times\delta\left(\frac{2\pi F}{\kappa}x+\Delta_{nn'}-\hbar\omega\right)e^{2\pi ilx},$$

$$=\frac{\kappa^2}{\pi F\hbar}\left\{\int\frac{d\mathbf{k}_\perp}{(2\pi)^2}|M_{nn'}(x_0)|^2 +2\sum_{l=1}^{\infty}\int\frac{d\mathbf{k}_\perp}{(2\pi)^2}|M_{nn'}(x_0)|^2\cos(2\pi lx_0),\right. \quad (14)$$

in which $x_0=(\kappa/2\pi F)(\Delta_{nn'}-\hbar\omega)$.

It is necessary now to evaluate $M_{nn'}$. We will first make the standard assumption that, for an allowed transition, the momentum matrix element $\mathbf{p}_{nn'}$ is independent of $\mathbf{k}$. We must also make assumptions concerning the band structure. Our concern here is with direct transitions. Two bands centered at $\mathbf{k}=0$ are considered, both in the effective mass approximation. One band has negative; the other, positive curvature. We have

$$E_{nn'}=E_g+\hbar^2k^2/2\mu, \quad (15)$$

with μ the reduced mass for the two bands: $\mu^{-1}=m_n^{-1}+m_{n'}^{-1}$. E_g is the energy gap at $\mathbf{k}=0$.

$$M_{nn'}=\frac{e\mathfrak{A}_0}{m}(\boldsymbol{\varepsilon}\cdot\mathbf{p}_{nn'}) \times\int_{-\kappa/2}^{\kappa/2}\exp\left[\frac{i}{F}\int_0^{k_x}\left(E_g-\hbar\omega+\frac{\hbar^2k'^2}{2\mu}\right)dk_x'\right]dk_x$$

$$=\frac{e\mathfrak{A}_0}{m}(\boldsymbol{\varepsilon}\cdot\mathbf{p}_{nn'})\int_{-\kappa/2}^{\kappa/2}\exp\left[i\left(\sigma k_x+\frac{k_x^3}{3\beta}\right)\right]dk_x,$$

where

$$\sigma=\frac{1}{F}\left(E_g-\hbar\omega+\frac{\hbar^2k^2}{2\mu}\right);\quad \beta=\frac{2\mu F}{\hbar^2}. \quad (16)$$

The limits of integration may be extended to ± ∞ when F is small. The integral then gives

$$M_{nn'}=\frac{2\pi e\mathfrak{A}_0\beta^{1/3}}{m\kappa}(\boldsymbol{\varepsilon}\cdot\mathbf{p}_{nn'})\ \mathrm{Ai}(\sigma\beta^{1/3}). \quad (17)$$

In this equation Ai is the Airy integral, defined by[13]

$$\mathrm{Ai}(z)=\frac{1}{\pi}\int_0^\infty\cos(sz+\tfrac{1}{3}s^3)ds.$$

This result must be substituted into Eq. (14) for the transition probability. There are two cases to be considered. If σ is positive, $\hbar\omega<E_g+\hbar^2k^2/2\mu$, for small fields we may employ the asymptotic expansion of the Airy integral

$$\mathrm{Ai}(z)\approx(1/2\pi^{1/2}z^{1/4})\exp(-\tfrac{2}{3}z^{3/2}). \quad (18)$$

On the other hand, if σ is negative, we use

$$\mathrm{Ai}(-z)=(1/\pi^{1/2}z^{1/4})\sin(\tfrac{2}{3}z^{3/2}+\tfrac{1}{4}\pi). \quad (19)$$

Let us first consider the case in which σ is positive. Then

$$w_{nn'}=\frac{e^2\mathfrak{A}_0^2\beta^{1/2}}{4\pi^2m^2F\hbar}|\boldsymbol{\varepsilon}\cdot\mathbf{p}_{nn'}|^2\left\{\int d\mathbf{k}_\perp\frac{\exp[-\frac{4}{3}\sigma^{3/2}\beta^{1/2}]}{\sigma^{1/2}} +2\sum_{l=1}^{\infty}\int d\mathbf{k}_\perp\frac{\exp[\frac{4}{3}\sigma^{3/2}\beta^{1/2}]}{\sigma^{1/2}}\cos\left[\frac{\kappa l}{F}(\Delta_{nn'}-\hbar\omega)\right]\right\}. \quad (20)$$

In the case of small fields, it is again legitimate to extend the limits of integration to infinity. Furthermore, we may expand $\sigma^{3/2}$.

$$\sigma^{3/2}\beta^{1/2}=\frac{1}{F}\left(\frac{2\mu}{\hbar^2}\right)^{1/2}\left[(E_g-\hbar\omega)^{3/2} +\tfrac{3}{2}(E_g-\hbar\omega)^{1/2}\frac{\hbar^2k^2}{2\mu}+\cdots\right].$$

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[13] H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, New York, 1950), p. 508.

The $\sigma^{1/2}$ in the denominator may be approximated by neglecting k^2 altogether. We recall that the absorption coefficient, α, is related to the transition probability by the formula

$$\alpha = 2\hbar w_{nn'}/\omega n\epsilon_0 c\mathfrak{A}_0^2. \tag{21}$$

Finally, we note that $\Delta_{nn'}$ is given by[14]

$$\Delta_{nn'} = E_g + \frac{\hbar^2 k^2}{2\mu} + \Delta_0,$$

where

$$\Delta_0 = \frac{1}{\kappa}\int_{-\kappa/2}^{\kappa/2}\left(E_{nn'} - E_g - \frac{\hbar^2 k^2}{2\mu}\right)dk_x. \tag{22}$$

We finally obtain after a straightforward calculation

$$\alpha = K\frac{\mu F}{4\omega(E_g - \hbar\omega)}\exp\left[-\left(\frac{E_g - \hbar\omega}{E_0}\right)^{3/2}\right]f(\omega), \tag{23}$$

where

$$K = 2e^2|\boldsymbol{\varepsilon}\cdot p_{nn'}|^2/\pi m^2\hbar^2 n\epsilon_0 c, \tag{24}$$

$$E_0^{3/2} = 3\hbar F/4(2\mu)^{1/2}, \tag{25}$$

and

$$f(\omega) = 1 + 4\sum_{l=1}^{\infty}\frac{[2\mu(E_g - \hbar\omega)]^{1/2}}{8\mu(E_g - \hbar\omega) + \hbar^2\kappa^2 l^2}$$
$$\times\left\{2[2\mu(E_g - \hbar\omega)]^{1/2}\cos\left[\frac{\kappa l}{F}(\hbar\omega - E_g - \Delta_0)\right]\right.$$
$$\left. + \hbar\kappa l\sin\left[\frac{\kappa l}{F}(\hbar\omega - E_g - \Delta_0)\right]\right\}. \tag{26}$$

The absorption edge is not sharp in the presence of the field, but rather falls off exponentially into the gap. The absorption in the gap is governed by the quantity E_0 which appears in the exponential. It is seen that E_0 is proportional to $F^{2/3}$, so we may say qualitatively that the spreading out of the absorption edge is proportional to the two-thirds power of the applied field. This spread is not large for fields of reasonable magnitude. When evaluated with numbers appropriate to GaAs, E_0 turns out to be approximately 10^{-2} eV for a field (internal) of the order of 10^6 V/m.

The summation term in (26) is periodic, repeating each time $\hbar\omega$ increases by $2\pi\kappa/F$. This quantity is just the Stark level splitting. Hence, we see that, as expected, the absorption has a component which a periodic with the period of the separation between the Stark levels. The amplitude of this term will be, however, relatively small. Normally we will expect $\hbar^2\kappa^2/2\mu \gg (E_g - \hbar\omega)$. In this case, the coefficient of the oscillatory term is $4[2\mu(E_g - \hbar\omega)/\hbar^2\kappa^2]^{1/2}$. It may be possible, however, to observe these oscillations, although they are rapidly damped.

The apparent singularity in α when $\hbar\omega = E_g$ is a consequence of the failure of the approximations made in the integration, and is not to be taken seriously.

It is also of interest to examine the absorption coefficient for photon energies greater than the band gap. In this case, there is a region of $k_\perp$ in which σ is negative. In this region, it is necessary to use the approximation (19) for the Airy function. We define a quantity R^2 by

$$R^2 = (2\mu/\hbar^2)(\hbar\omega - E_g). \tag{27}$$

For negative σ, we put $k_\perp{}^2 = R^2 - q^2$. For positive σ, we set $k_\perp{}^2 = R^2 + q'^2$. Then we obtain for α:

$$\alpha = K\left(\frac{4\mu}{\omega}\right)\left\{\int_0^R \sin^2(\tfrac{2}{3}\gamma q^3 + \tfrac{1}{4}\pi)dq + \tfrac{1}{4}\int_0^\infty e^{-4\gamma q^3/3}dq\right.$$
$$+ 2\sum_{l=1}^{\infty}\left[\int_0^R \sin^2(\tfrac{2}{3}\gamma q^3 + \tfrac{1}{4}\pi)\cos[\gamma\kappa l(q^2 - \delta^2)]dq\right.$$
$$\left.\left. + \tfrac{1}{4}\int_0^\infty e^{-4\gamma q^3/3}\cos[\gamma\kappa l(q'^2 + \delta^2)]dq\right]\right\}, \tag{28}$$

in which $\gamma = \beta^{-1} = \hbar^2/2\mu F$ and $\delta^2 = (2\mu/\hbar^2)\Delta_0$. This may be written as

$$\alpha = K\frac{(2\mu)^{3/2}}{\hbar\omega}(\hbar\omega - E_g)^{1/2}g(\omega), \tag{29}$$

where

$$g(\omega) = 1 + \frac{1}{R}\int_0^R \sin(\tfrac{4}{3}\gamma q^3)dq + \frac{1}{2R}\int_0^\infty e^{-4\gamma q^3/3}dq$$
$$+ \frac{2}{R}\sum_{l=1}^{\infty}\left\{\int_0^R [1 + \sin(\tfrac{4}{3}\gamma q^3)]\cos[\gamma\kappa l(q^2 - \delta^2)]dq\right.$$
$$\left. + \int_0^\infty e^{-4\gamma q^3/3}\cos[\gamma\kappa l(q^2 + \delta^2)]dq\right\}. \tag{30}$$

These integrals may be evaluated approximately in the limit of small fields with the aid of the additional assumption that $\kappa \gg R > 0$, which is valid for energies moderately close to the normal band edge. We obtain

$$g(\omega) = 1 + \left(\frac{3}{4\gamma}\right)^{1/3}\frac{\Gamma(4/3)}{R} - \frac{1}{4\gamma R^3}\cos(\tfrac{4}{3}\gamma R^3)$$
$$+ \sum_{l=1}^{\infty}\left\{(2\pi)^{1/2}\frac{\cos(\gamma\kappa l\delta^2)}{(\gamma\kappa l)^{1/2}R} + \frac{1}{\gamma\kappa l R^2}\right.$$
$$\left.\times[1 + \sin(\tfrac{4}{3}\gamma R^3)]\sin[\gamma\kappa l(R^2 - \delta^2)]\right\}. \tag{31}$$

The leading term in the absorption is just the usual

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[14] In the effective mass approximation, $\Delta_0 = \hbar^2\kappa^2/24$. The effective mass approximation may, however, fail badly in the calculation of $\Delta_{nn'}$, since this involves an integral across the entire Brillouin zone. In the following, we will regard it as an adjustable parameter.

absorption resulting from a direct transition between bands. The absorption constant for this process is

$$\alpha = (K(2\mu)^{3/2}/\hbar\omega)(\hbar\omega - E_g)^{1/2}.$$

The remaining terms in $g(\omega)$ contain the effect of the electric field. Since γ is inversely proportional to the field, the absorption increases as the field increases, as has been observed experimentally.[3–6] There are two oscillatory components in the absorption as a function of energy. The larger of these involves

$$\cos(\tfrac{4}{3}\gamma R^3) = \cos[(\hbar\omega - E_g)/E_0]^{3/2},$$

where E_0 is given by (25). The cosine repeats itself when $\hbar\omega$ changes by (approximately)

$$\Delta(\hbar\omega) = \tfrac{4}{3}\pi[E_0^{3/2}/(\hbar\omega - E_g)^{1/2}]. \qquad (32)$$

Therefore, this term tends to produce oscillations of decreasing period and amplitude as energy increases for constant field. The other oscillatory term in (31) is similar to that found in (26), and has the periodicity of the Stark level separation.

The first term in the summation in (31) gives rise to a periodicity of the absorption as a function of field strength for fixed energy of a different sort. Whenever the quantity γ changes by $\Delta\gamma$ such that

$$\Delta\gamma = 2\pi/\kappa\delta^2, \qquad (33)$$

the cosine in this term returns to its original value. The quantity $\Delta\gamma$ is approximately related to a change ΔF in the field by $\Delta\gamma = \hbar^2\Delta F/2\mu F^2$.

We conclude with some comments relating to the approximations employed in the calculation and to the possibility of experimental observation of these effects. Aside from the usual approximation of energy-band theory and of first order time-dependent perturbation theory, the principal computational approximation is the use of the effective mass formula for the energy difference between bands, Eq. (15). The latter should be considerably more accurate in the present work than in the theory of tunneling since only relatively small values of $F\sigma$ are important in the evaluation of the essential integrals. The existence of oscillations resulting from the Stark levels follows from Eq. (14) without any additional approximation. The only quantity in the calculation which is particularly sensitive to the effective mass approximation is δ^2 which determines the phase of the oscillations. The long-period oscillation (third term of Eq. 31) is the consequence of putting a finite upper limit on the integral of an oscillatory function, thus this oscillation is reasonably independent of the approximations. Use of Kane's reduced Hamiltonian[10] would enable us to take account of the departures of the conduction and valence bands from parabolic form but would not enable a more accurate determination of δ^2 since the latter quantity involves an integral over the entire Brillouin zone. The improvement in accuracy resulting from the use of this Hamiltonian would seem to be less significant than in the theory of tunneling, and would produce a more complicated mathematical problem.

It should be noted, in considering possible experimental observations of these oscillations, that the situation is not particularly favorable in tunnel diodes, since the potential drop across the junction is insufficient to produce two turning points in the classical description of the electron's motion. It is probably better to use an external electric field, as has been done in the experiments previously cited. For instance, Williams was able to maintain a potential difference of approximately 100 V across a thin layer in a sample of CdS.[4] For the purpose of making order of magnitude estimates of these effects, we will however, consider gallium arsenide. This material is available in a form with quite high resistivity so that it might be suitable for experimental investigations.

Assume that a field $\mathcal{E} = F/e = 5\times10^7$ V/m is present inside the material, directed along a [111] crystal axis. The Stark splitting amounts to 0.016 eV. This is appreciably larger than KT at liquid nitrogen temperatures and below. Let us consider an energy region approximately 0.15 eV above the normal band edge. Then $\gamma R^3 = 1.2$, and the principal effect of the field is to increase the absorption by a factor of about 5/3. [However, the relatively small value of γR^3 implies that additional terms in the expansion of the integrals in (30) should be considered in any detailed analysis of potential experimental results.] The quantity $(\gamma\kappa R^2)^{-1}[1+\sin(\tfrac{4}{3}\gamma R^3)]$ which determines the amplitude of the oscillations due to the Stark levels has the value 0.036. It might be possible to observe these oscillations at low temperatures if the resolution is good.

If we estimate δ^2 in the effective mass approximation, we find that for this field strength the oscillations predicted by (33) occur at intervals of 3×10^4 V/m. As the effective mass approximation presumably overestimates δ^2, the oscillations should be somewhat more widely spaced than is predicted here. Since $R^2 \ll \delta^2$, the second summation term has essentially the same periodicity in field strength, although the phase is different.