# Electric-Field Effects on Optical Absorption near Thresholds in Solids*

DAVID E. ASPNES
*Materials Research Laboratory and Department of Electrical Engineering, University of Illinois, Urbana, Illinois*

(Received 21 February 1966)

The weak-field effective-mass-approximation calculations of the absorption coefficient in the presence of an electric field for direct and indirect transitions at a normal ($M_0$) threshold are extended to an arbitrary orientation of the electric field in an anisotropic solid. To do this, a systematic method of evaluating density-of-states integrals arising in the electroabsorption or Franz-Keldysh effect is presented. Certain integrals obtained in prior calculations at the $M_0$ threshold which have not been previously evaluated are given in closed form. This method is also used to derive the change in absorption coefficient, $\Delta\alpha(\mathcal{E})$, occuring at the saddle-point edges $M_1$ and $M_2$, as well as the edge $M_3$, for an arbitrary field direction in an anisotropic solid. It is shown that there is a direct correlation between $\Delta\alpha(\mathcal{E})$ for the $M_0$ and $M_3$ edges, and also for the $M_1$ and $M_2$ thresholds. Reduced masses of opposite signs, as in the $M_1$ and $M_2$ edges, give rise to two branches in $\Delta\alpha(\mathcal{E})$.

## INTRODUCTION

SINCE the initial calculations of Franz[1] and Keldysh,[2] there has been much experimental and theoretical interest in the effect of an electric field on the absorption of light in a semiconductor or insulator in the vicinity of normal ($M_0$) absorption edges. Tharmalingam[3] and Callaway[4] have given the field-dependent optical absorption for direct transitions, and the theory for the field-dependent absorption via indirect transitions has been done by Penchina,[5] Chester and Fritsche,[6] and Yacoby.[7] These calculations have been tested by direct measurement of the change in optical absorption $\Delta\alpha$ resulting from the application of an electric field[8,9] and by measurement of the field-induced change in reflectivity,[10–12] which can be related to $\Delta\alpha$ through the Kramers-Kronig relations.[13] Used as a tool, the electroabsorption effect has resulted in a much greater understanding of the optical properties and band structure of germanium- and zinc-blende-type structures at energies above the fundamental edge.[14]

In the weak-field approximations of Tharmalingam[3] and Penchina[5] for the direct- and indirect-transition optical absorption at an $M_0$ edge, solution of the equation of an electron-hole pair in the presence of a uniform electric field is required. This solution is the Airy function.[15] As Elliott shows, the evaluation of the absorption coefficient reduces to the problem of evaluating sums over initial and final states of a matrix element weighted by the probability of finding the electron and hole at the same point of space,[16] which in turn reduces to the evaluation of integrals involving Airy functions. We will present a systematic method of evaluating these integrals and will apply this method in extending the solutions in the weak-field approximation at the $M_0$ edge to an arbitrary orientation of the electric field in an anisotropic solid.

Optical absorption increases markedly not only at $M_0$ edges, but also for photon energies near any critical point of the band structure, defined by $\nabla_k(E_C-E_V)=0$, which results in a singularity in the joint density of states.[17] Band-structure calculations show that higher lying critical points may be saddle points of type $M_1$ and $M_2$, where one or two of the three reduced masses are negative, or the point $M_3$, where all three are negative.[18] There is experimental evidence of saddle-point transitions in electroreflectance measurements.[10,11] The electroabsorption theory for the edges $M_1$, $M_2$, and $M_3$ will be derived in this paper by an application of the method of evaluating Airy function integrals. The change in absorption coefficient associated with each of these critical points will be given as a function of the direction of the electric field. We first define the problem, then derive the necessary mathematical relations which are applied to obtain the electro-absorption results.

## A. ELECTRO-ABSORPTION AT CRITICAL POINTS

In the effective-mass approximation, the constant-energy surfaces near the energy minima of the con-

* This research was supported by the Advanced Research Projects Agency under Contract SD-131 and by the Rome Air Development Command.

1 W. Franz, Z. Naturforsch. **13**, 484 (1958).
2 L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. **34**, 1138 (1958) [English transl.: Soviet Phys.—JETP **7**, 788 (1958)].
3 K. Tharmalingam, Phys. Rev. **130**, 2204 (1963).
4 J. Callaway, Phys. Rev. **130**, 549 (1963); **134**, A998 (1964).
5 C. M. Penchina, Phys. Rev. **138**, A924 (1965).
6 M. Chester and L. Fritsche, Phys. Rev. **139**, A518 (1965).
7 Y. Yacoby, Phys. Rev. **140**, A263 (1965).
8 A. Frova, P. Handler, F. A. Germano, and D. E. Aspnes, Phys. Rev. **145**, 575 (1966).
9 A. Frova and P. Handler, Phys. Rev. **137**, A1857 (1965).
10 K. L. Shaklee, F. H. Pollak, and M. Cardona, Phys. Rev. Letters **15**, 883 (1965).
11 B. O. Seraphin, Phys. Rev. **140**, A1716 (1965).
12 B. O. Seraphin and N. Bottka, Phys. Rev. **139**, A560 (1965)
13 F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 299; Phys. Rev. **133**, A1653 (1964).
14 J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 55.
15 L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Pergamon Press, Inc., New York, 1959), pp. 70–71, 491.
16 R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
17 L. Van Hove, Phys. Rev. **89**, 1184 (1953).
18 D. Brust, Phys. Rev. **134**, A1337 (1964).

duction band can be approximated as quadratic surfaces having three axes of symmetry, each with an effective mass which can be designated as $m_{ex}$, $m_{ey}$, and $m_{ez}$. For the normal $M_0$ edge, these masses are usually all positive, and the corresponding quadratic surface of positive curvatures is an ellipsoid. We consider the hole masses in the valence band along these symmetry axes to be $m_{hx}$, $m_{hy}$, and $m_{hz}$, respectively. In relative coordinates of an electron-hole pair, the reduced masses

$$m_i^* = m_{ei}m_{hi}/(m_{ei}+m_{hi}), \tag{A1}$$

for each coordinate $r_i = x$, $y$, or $z$, enter. The applied electric field $\boldsymbol{\mathcal{E}}$ is broken up into components $\mathcal{E}_x$, $\mathcal{E}_y$, and $\mathcal{E}_z$ along these three major axes.

To be consistent with Brust,[18] we describe the edges by the following sign conventions for the reduced masses:

$M_0$: $m_x^*$, $m_y^*$, $m_z^*$ positive,

$M_1$: $m_x^*$, $m_y^*$ positive, $m_z^*$ negative,

$M_2$: $m_z^*$ positive, $m_x^*$, $m_y^*$ negative,

$M_3$: $m_x^*$, $m_y^*$, $m_z^*$ negative.

Throughout the calculations, we will consider the quantities $\mu_x$, $\mu_y$, and $\mu_z$ to represent the magnitudes of the reduced masses $m_x^*$, $m_y^*$, and $m_z^*$, and will explicitly introduce the negative signs of the negative reduced masses into the integrals which represent the sums over densities of states. The signed quantities $m_i^*$ will be used in setting up these integrals.

The derivation of the direct edge electroabsorption will essentially parallel that of Tharmalingam.[3] Using the results of Bardeen, Blatt, and Hall,[19] and Elliott[16] for the absorption coefficient, we find for direct transitions

$$\alpha = \frac{4\pi^2 e^2}{ncm^2\omega}\sum_i C_0^2|\phi(0)|^2\delta(E_f - E_i - \hbar\omega), \tag{A2}$$

where $C_0^2$ contains the matrix elements of the interaction, the sum is over all states in relative coordinates, and $\phi(r)$ is the properly normalized solution of the relative-coordinate Hamiltonian

$$\left\{\frac{\hbar^2}{2m_x^*}\frac{\partial^2}{\partial x^2}+\frac{\hbar^2}{2m_y^*}\frac{\partial^2}{\partial y^2}+\frac{\hbar^2}{2m_z^*}\frac{\partial^2}{\partial z^2} + e\boldsymbol{\mathcal{E}}\cdot\mathbf{r}+E\right\}\phi(\mathbf{r})=0, \tag{A3}$$

in the usual approximation which neglects the Coulomb interaction between the hole and electron. Eq. (A3) has the exact solution[15]

$$\phi(\mathbf{r}) = C_xC_yC_z\,\mathrm{Ai}(-\xi_x)\,\mathrm{Ai}(-\xi_y)\,\mathrm{Ai}(-\xi_z), \tag{A4}$$

where $\mathrm{Ai}(x)$ is the Airy function, to be discussed in Sec. B, and if we define

$$\varphi_i^3 = e^2\mathcal{E}_i^2/2\hbar m_i^* \tag{A5}$$

for each coordinate $r_i = x$, $y$, or $z$, then

$$\xi_i = \epsilon_i/\hbar\varphi_i + r_i\hbar^{-2/3}(2m_i^* e\mathcal{E}_i)^{1/3}, \tag{A6}$$

where $\epsilon_i$ is the energy associated with the solution for the coordinate $r_i$. Obviously

$$E = \epsilon_x + \epsilon_y + \epsilon_z. \tag{A7}$$

The constants $C_i$, which give a delta-function normalization with respect to the energy integral over each $\epsilon_i$, are given by

$$C_i = N(e|\mathcal{E}_i|)^{1/2}/\pi\hbar\varphi_i, \tag{A8}$$

which is shown in Sec. B. $N$ is the normalization constant of the Airy function defined in Eq. (B2a). The sum in Eq. (A2) may be converted directly into integrals over $\epsilon_x$, $\epsilon_y$, and $\epsilon_z$ using the constants $C_x$, $C_y$, and $C_z$, obtaining after substituting for $|\phi(0)|^2$

$$\alpha(\boldsymbol{\mathcal{E}}) = \frac{4e^5C_0^2|\mathcal{E}_x\mathcal{E}_y\mathcal{E}_z|N^6}{ncm^2\omega\pi^4\hbar^6\varphi_x^2\varphi_y^2\varphi_z^2}\int_{-\infty}^{\infty} d\epsilon_x d\epsilon_y d\epsilon_z \times\left[\mathrm{Ai}^2\!\left(\frac{-\epsilon_x}{\hbar\varphi_x}\right)\mathrm{Ai}^2\!\left(\frac{-\epsilon_y}{\hbar\varphi_y}\right)\mathrm{Ai}^2\!\left(\frac{-\epsilon_z}{\hbar\varphi_z}\right) \times\delta(E_g+\epsilon_x+\epsilon_y+\epsilon_z-\hbar\omega)\right], \tag{A9}$$

where $\mathrm{Ai}^2(x) \equiv [\mathrm{Ai}(x)]^2$. This is the integral which must be evaluated to give $\alpha(\boldsymbol{\mathcal{E}})$ from which the experimentally measurable change in absorption coefficient

$$\Delta\alpha(\boldsymbol{\mathcal{E}}) = \alpha(\boldsymbol{\mathcal{E}}) - \lim_{|\boldsymbol{\mathcal{E}}|\to 0}\alpha(\boldsymbol{\mathcal{E}}) \tag{A10}$$

will be calculated. As expected, the sign (direction) of the field along any major axis does not enter as can be seen from Eqs. (A5) and (A9). Moreover, the sign of the reduced mass, which enters through $\varphi_i$ by Eq. (A5), will not affect the prefactor of Eq. (A9), but only the arguments of the squares of the Airy functions. We will now introduce the signs of the reduced mass explicitly by defining for each coordinate

$$\theta_i^3 = |\varphi_i|^3 = e^2\mathcal{E}_i^2/2\hbar\mu_i, \tag{A11}$$

which is consistent with Tharmalingam's notation, his work involving only positive reduced masses.

If we multiply Eq. (A9) by two to include spin degeneracy, define the quantity

$$R = \frac{2e^2C_0^2}{\hbar\omega ncm^2}\left(\frac{8\mu_x\mu_y\mu_z}{\hbar^3}\right)^{1/2}, \tag{A12}$$

which includes the density-of-states factor, and explicitly include the sign of the reduced mass according

[19] J. Bardeen, F. J. Blatt, and L. H. Hall, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p. 146.

to the sign convention given earlier, we find Eq. (A9) takes the following forms for each of the critical points:

$$M_0:\quad \alpha_0(\mathcal{E})=\frac{4RN^6}{\pi^4\hbar^2(\theta_x\theta_y\theta_z)^{1/2}}\int_{-\infty}^{\infty}d\epsilon_x d\epsilon_y d\epsilon_z\left[\mathrm{Ai}^2\left(\frac{-\epsilon_x}{\hbar\theta_x}\right)\mathrm{Ai}^2\left(\frac{-\epsilon_y}{\hbar\theta_y}\right)\mathrm{Ai}^2\left(\frac{-\epsilon_z}{\hbar\theta_z}\right)\delta(E_g-\hbar\omega+\epsilon_x+\epsilon_y+\epsilon_z)\right], \quad \text{(A13a)}$$

$$M_1:\quad \alpha_1(\mathcal{E})=\frac{4RN^6}{\pi^4\hbar^2(\theta_x\theta_y\theta_z)^{1/2}}\int_{-\infty}^{\infty}d\epsilon_x d\epsilon_y d\epsilon_z\left[\mathrm{Ai}^2\left(\frac{-\epsilon_x}{\hbar\theta_x}\right)\mathrm{Ai}^2\left(\frac{-\epsilon_y}{\hbar\theta_y}\right)\mathrm{Ai}^2\left(\frac{+\epsilon_z}{\hbar\theta_z}\right)\delta(E_g-\hbar\omega+\epsilon_x+\epsilon_y+\epsilon_z)\right], \quad \text{(A13b)}$$

$$M_2:\quad \alpha_2(\mathcal{E})=\frac{4RN^6}{\pi^4\hbar^2(\theta_x\theta_y\theta_z)^{1/2}}\int_{-\infty}^{\infty}d\epsilon_x d\epsilon_y d\epsilon_z\left[\mathrm{Ai}^2\left(\frac{+\epsilon_x}{\hbar\theta_x}\right)\mathrm{Ai}^2\left(\frac{+\epsilon_y}{\hbar\theta_y}\right)\mathrm{Ai}^2\left(\frac{-\epsilon_z}{\hbar\theta_z}\right)\delta(E_g-\hbar\omega+\epsilon_x+\epsilon_y+\epsilon_z)\right], \quad \text{(A13c)}$$

$$M_3:\quad \alpha_3(\mathcal{E})=\frac{4RN^6}{\pi^4\hbar^2(\theta_x\theta_y\theta_z)^{1/2}}\int_{-\infty}^{\infty}d\epsilon_x d\epsilon_y d\epsilon_z\left[\mathrm{Ai}^2\left(\frac{+\epsilon_x}{\hbar\theta_x}\right)\mathrm{Ai}^2\left(\frac{+\epsilon_y}{\hbar\theta_y}\right)\mathrm{Ai}^2\left(\frac{+\epsilon_z}{\hbar\theta_z}\right)\delta(E_g-\hbar\omega+\epsilon_x+\epsilon_y+\epsilon_z)\right], \quad \text{(A13d)}$$

in which all constants are positive.

We now show that there is a direct relationship between $\alpha_0(\mathcal{E})$ and $\alpha_3(\mathcal{E})$, and also between $\alpha_1(\mathcal{E})$ and $\alpha_2(\mathcal{E})$. Suppose we replace $\epsilon_x$, $\epsilon_y$, and $\epsilon_z$ in Eq. (A13d) with $-\epsilon_x$, $-\epsilon_y$, and $-\epsilon_z$. The result is

$$\alpha_3(\mathcal{E})=\frac{4RN^6}{\pi^4\hbar^2(\theta_x\theta_y\theta_z)^{1/2}}\int_{-\infty}^{\infty}d\epsilon_x d\epsilon_y d\epsilon_z \times\mathrm{Ai}^2\left(\frac{-\epsilon_x}{\hbar\theta_x}\right)\mathrm{Ai}^2\left(\frac{-\epsilon_y}{\hbar\theta_y}\right)\mathrm{Ai}^2\left(\frac{-\epsilon_z}{\hbar\theta_z}\right)\times\delta(E_g-\hbar\omega-\epsilon_x-\epsilon_y-\epsilon_z). \quad \text{(A14)}$$

Since the delta function is an even function we may multiply its argument by $-1$. But the resulting expression is precisely $\alpha_0(\mathcal{E})$ given by Eq. (A13a) with $(E_g-\hbar\omega)$ replaced with $(\hbar\omega-E_g)$. Therefore, we have shown

$$\alpha_0(\mathcal{E},-(E_g-\hbar\omega))=\alpha_3(\mathcal{E},(E_g-\hbar\omega)), \quad \text{(A15a)}$$

$$\alpha_1(\mathcal{E},-(E_g-\hbar\omega))=\alpha_2(\mathcal{E},(E_g-\hbar\omega)), \quad \text{(A15b)}$$

the latter following from a parallel treatment. We need therefore obtain only $\alpha_0(\mathcal{E})$ and $\alpha_1(\mathcal{E})$ and the problem is solved for all four critical points.

In order to proceed further, it is necessary to derive relationships which can be used to evaluate the integrals of Eqs. (A13). These will be derived in Sec. B, and applied and the results discussed in Secs. C, D, and E.

## B. MATHEMATICAL RELATIONS

The defining equation of the Airy functions is[20]

$$\frac{d^2F(x)}{dx^2}=xF(x), \quad \text{(B1)}$$

where $F(x)$ is either $\mathrm{Ai}(x)$ or $\mathrm{Bi}(x)$, the solutions regular and irregular at infinity, respectively. The integral representations are[21]

$$\mathrm{Ai}(x)=\frac{1}{N}\int_0^{\infty}ds\cos[\tfrac{1}{3}s^3+xs], \quad \text{(B2a)}$$

$$=\frac{1}{2N}\int_{-\infty}^{\infty}ds\, e^{is^3/3+ixs}, \quad \text{(B2b)}$$

$$\mathrm{Bi}(x)=\frac{1}{N}\int_0^{\infty}ds\left[e^{-s^3/3+xs}-\sin(\tfrac{1}{3}s^3+xs)\right], \quad \text{(B2c)}$$

where the normalization constant $N$ is usually taken as $\pi^{1/2}$ or $\pi$. It will be left as $N$ in the following so the results will be applicable to either normalization, since both are used in the literature.[22]

In order to evaluate most phase-space integrals, it will be necessary to derive the integral representation of $\mathrm{Ai}^2(x)$ and examine the differential equation

$$\frac{d^3F(x)}{dx^3}=4x\frac{dF(x)}{dx}+2F(x), \quad \text{(B3)}$$

which has the three linearly independent solutions $F(x)=\mathrm{Ai}^2(x)$, $\mathrm{Ai}(x)\,\mathrm{Bi}(x)$, and $\mathrm{Bi}^2(x)$.[23] By Eq. (B2b)

$$\mathrm{Ai}^2(x)=\frac{1}{4N^2}\int_{-\infty}^{\infty}ds\,dt\,e^{is^3/3+it^3/3+ix(s+t)}. \quad \text{(B4)}$$

If new variables $\alpha$, $\gamma$ are defined as $\alpha=\frac{1}{2}(t-s)$ and $\gamma=t+s$, both of which range from minus to plus infinity, the double integral of Eq. (B4) is converted into a form in which the integral over $\alpha$ can be done explicitly, giving

$$\mathrm{Ai}^2(x)=\frac{\sqrt{\pi}}{2N^2}\int_0^{\infty}\frac{d\gamma}{\sqrt{\gamma}}\cos[\tfrac{1}{12}\gamma^3+x\gamma+\tfrac{1}{4}\pi]. \quad \text{(B5)}$$

[20] H. A. Antosiewicz, in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964), Appl. Math. Ser. **55**, p. 446.

[21] Reference 20, p. 447.

[22] The *Handbook of Mathematical Functions* uses the normalization $N=\pi$. The $N=\sqrt{\pi}$ normalization is used by Landau and Lifschitz (Ref. 15) and has been used in the previous weak-field approximation electro-absorption work, for instance, Refs. 3 and 5.

[23] Reference 20, p. 448.

The representations given by Eqs. (B2) and (B5) are improper integrals and care is required in interchanging orders of differentiation and integration when these operations are performed on the representations, e.g., it is not possible to equate $(d^3/dx^3)\,\mathrm{Ai}^2(x)$ to the third derivative of the integral in Eq. (B5) obtained by interchanging orders of integration and differentiation:

$$-\frac{\sqrt{\pi}}{2N^2}\int_0^\infty d\gamma\,\gamma^{5/2}\sin[\tfrac{1}{12}\gamma^3+x\gamma+\tfrac{1}{4}\pi]$$

and thus show directly that Eq. (B5) is a solution of Eq. (B3). Equation (B5) is however, a solution in the sense that

$$\mathrm{Ai}^2(x)=\lim_{\delta\to 0+}\int_0^\infty\frac{d\gamma}{\sqrt{\gamma}}e^{-\delta[(1/12)\gamma^3+x\gamma+\pi/4]}\times\cos[\tfrac{1}{12}\gamma^3+x\gamma+\tfrac{1}{4}\pi]\quad(\mathrm{B6})$$

is a solution, as can be easily shown. The limit is taken following the differentiations.

Equation (B6) is a solution of Eq. (B3) for any constant phase $\theta$ replacing $\frac{1}{4}\pi$ in the cosine argument, therefore the integral

$$F(x)=\frac{\sqrt{\pi}}{2N^2}\int_0^\infty\frac{d\gamma}{\sqrt{\gamma}}\sin[\tfrac{1}{12}\gamma^3+x\gamma+\tfrac{1}{4}\pi]\quad(\mathrm{B7})$$

must also be a solution of Eq. (B3), or

$$\frac{\sqrt{\pi}}{2N^2}\int_0^\infty\frac{d\gamma}{\sqrt{\gamma}}\sin[\tfrac{1}{12}\gamma^3+x\gamma+\tfrac{1}{4}\pi]=c_0\,\mathrm{Ai}^2(x)+c_1\,\mathrm{Ai}(x)\,\mathrm{Bi}(x)+c_2\,\mathrm{Bi}^2(x)\,,\quad(\mathrm{B8})$$

where $c_0$, $c_1$, and $c_2$ are constants. To evaluate these, we obtain the asymptotic expansion of the integral for large positive $x$. A contour integration over the rays $z=r$ and $z=re^{\pm i(\pi/6)}$ gives

$$\frac{\sqrt{\pi}}{2N^2}\int_0^\infty\frac{d\gamma}{\sqrt{\gamma}}\sin[\tfrac{1}{12}\gamma^3+x\gamma+\tfrac{1}{4}\pi]=\frac{\sqrt{\pi}}{2N^2}\int_0^\infty\frac{dt}{\sqrt{t}}e^{-(1/12)t^3-(1/2)xt}\sin[\tfrac{1}{2}\sqrt{3}xt+\tfrac{1}{3}\pi]\quad(\mathrm{B9a})$$

$$\sim\frac{\sqrt{\pi}}{2N^2}\int_0^\infty\frac{dt}{\sqrt{t}}e^{-(1/2)xt}\sin[\tfrac{1}{2}\sqrt{3}xt+\tfrac{1}{3}\pi]=\frac{\pi}{2N^2}x^{-1/2}.\quad(\mathrm{B9b})$$

Since $\mathrm{Bi}^2(x)\sim(\pi/N^2)x^{-1/2}e^{2\zeta}$, $\mathrm{Ai}(x)\,\mathrm{Bi}(x)\sim(\pi/2N^2)x^{-1/2}$, and $\mathrm{Ai}^2(x)\sim(\pi/4N^2)x^{-1/2}e^{-2\zeta}$, where $\zeta=\frac{2}{3}x^{3/2}$,[24] we have immediately $c_2=0$ and $c_1=1$. Evaluating Eq. (B8) at $x=0$ gives $c_0=0$, hence

$$\frac{\sqrt{\pi}}{2N^2}\int_0^\infty\frac{d\gamma}{\sqrt{\gamma}}\sin[\tfrac{1}{12}\gamma^3+x\gamma+\tfrac{1}{4}\pi]=\mathrm{Ai}(x)\,\mathrm{Bi}(x).\quad(\mathrm{B10})$$

[24] Reference 20, pp. 448–449.

We next consider integrals of the form $I(x)=\int_0^\infty dt\,t^n\times F(t+x)$, where $F(y)$ is any of the functions $\mathrm{Ai}(y)$, $\mathrm{Ai}'(y)$, or $\mathrm{Ai}_1(y)$, where $\mathrm{Ai}'(y)=(d/dy)\,\mathrm{Ai}(y)$ and $\mathrm{Ai}_1(y)=\int_y^\infty dt\,\mathrm{Ai}(t)$. The corresponding integrals containing Bi functions are all divergent. Integrands of the form of products of polynomials and Airy functions can be expressed as sums of integrals of this type, and certain results will be useful in evaluating integrals containing products of Airy functions, derivatives, or integrals. We first obtain a reduction formula for these integrals.

Since for $n>0$

$$\int_0^\infty dt\,t^n\,\mathrm{Ai}'(t+x)=-n\int_0^\infty dt\,t^{n-1}\,\mathrm{Ai}(t+x)\quad(\mathrm{B11a})$$

$$=\frac{d}{dx}\int_0^\infty dt\,t^n\,\mathrm{Ai}(t+x)\,,\quad(\mathrm{B11b})$$

and for $n>-1$

$$\int_0^\infty dt\,t^n\,\mathrm{Ai}_1(t+x)=\frac{1}{n+1}\int_0^\infty dt\,t^{n+1}\,\mathrm{Ai}(t+x)\quad(\mathrm{B12a})$$

$$=\int_x^\infty dx\int_0^\infty dt\,t^n\,\mathrm{Ai}(t+x)\,,\quad(\mathrm{B12b})$$

it is sufficient to consider integrals of the form $\int_0^\infty dt\,t^n\,\mathrm{Ai}(t+x)$. From Eq. (B1) it follows immediately that

$$\int_0^\infty dt\,t^n\,\mathrm{Ai}(t+x)=\int_0^\infty dt\,t^{n-1}\frac{d^2}{dt^2}\mathrm{Ai}(t+x)-x\int_0^\infty dt\,t^{n-1}\,\mathrm{Ai}(t+x)\quad(\mathrm{B13a})$$

$$=\left[\frac{d^2}{dx^2}-x\right]\int_0^\infty dt\,t^{n-1}\,\mathrm{Ai}(t+x)\,,\quad(\mathrm{B13b})$$

where, in Eq. (B13b), $[(d^2/dx^2)-x]$ is an operator upon the resulting function of $x$. Equations (B13) reduce the power of $t$ by 1, ending when the exponent $n$ of $t$ lies in the range $0\geqslant n>-1$. The interchange of integration and differentiation can be justified without difficulty.

Equations (B11b), (B12b), and (B13b) are useful when the reduced integrals can be expressed in closed form, obviously the case when $n$ is an integer. Here, reduction eventually yields a derivative, integrable immediately, an integral $\int_0^\infty dt\,\mathrm{Ai}(t+x)$ which is equal to $\mathrm{Ai}_1(x)$, or yields

$$\int_0^\infty dt\,\mathrm{Ai}_1(t+x)=-\mathrm{Ai}'(x)-x\,\mathrm{Ai}_1(x)\,,\quad(\mathrm{B14})$$

which follows from Eqs. (B12a) and (B13a). It is interesting to note that Eq. (B14) is equivalent to

$$\int dx \int_x^\infty dt\, \mathrm{Ai}(t) = x\, \mathrm{Ai}_1(x) + \mathrm{Ai}'(x) \qquad \text{(B15)}$$

so all repeated integrals of $\mathrm{Ai}(x)$ can be expressed in terms of $\mathrm{Ai}(x)$, $\mathrm{Ai}'(x)$, or $\mathrm{Ai}_1(x)$ multiplied by polynomials in $x$.

The integrals can also be evaluated explicitly when $n$ is half-integral. Repeated application of Eqs. (B13) will eventually yield the integrals

$$\int_0^\infty dt\, t^{-1/2}\, \mathrm{Ai}_1(t+x)\,, \quad \int_0^\infty dt\, t^{-1/2}\, \mathrm{Ai}(t+x)\,,$$

or

$$\int_0^\infty dt\, t^{-1/2}\, \mathrm{Ai}'(t+x)\,.$$

By Eq. (B2a)

$$\int_0^\infty \frac{dt}{\sqrt{t}} \mathrm{Ai}(t+x) = \frac{1}{N}\int_0^\infty \frac{dt}{\sqrt{t}} \int_0^\infty du \cos[\tfrac{1}{3}u^3 + xu + tu] \qquad \text{(B16a)}$$

$$= \frac{\sqrt{\pi}}{N}\int_0^\infty \frac{du}{\sqrt{u}} \cos[\tfrac{1}{3}u^3 + xu + \tfrac{1}{4}\pi]\,, \qquad \text{(B16b)}$$

which by comparison with Eq. (B5) shows that

$$\int_0^\infty \frac{dt}{\sqrt{t}} \mathrm{Ai}(t+x) = \kappa N\, \mathrm{Ai}^2(x/\kappa)\,, \qquad \text{(B17)}$$

where the constant $\kappa = 2^{2/3}$. The same evaluation method together with a comparison of the result to Eq. (B10) yields

$$\int_0^\infty \frac{dt}{\sqrt{t}} \mathrm{Ai}(x-t) = \kappa N\, \mathrm{Ai}(x/\kappa)\, \mathrm{Bi}(x/\kappa)\,. \qquad \text{(B18)}$$

Equation (B17) and (B18) give the very useful integral representations

$$\mathrm{Ai}^2(x) = \frac{1}{\kappa N}\int_0^\infty \frac{dt}{\sqrt{t}} \mathrm{Ai}(t+\kappa x)\,, \qquad \text{(B19a)}$$

$$\mathrm{Ai}(x)\, \mathrm{Bi}(x) = \frac{1}{\kappa N}\int_0^\infty \frac{dt}{\sqrt{t}} \mathrm{Ai}(\kappa x - t)\,, \qquad \text{(B19b)}$$

where $\kappa = 2^{2/3}$ and the normalization constant $N$ is defined in Eqs. (B2). The integrals in Eqs. (B19) can be shown to be solutions of Eq. (B3).

From Eq. (B17) we obtain by differentiating and integrating with respect to $x$

$$\int_0^\infty \frac{dt}{\sqrt{t}} \mathrm{Ai}'(t+x) = 2N\, \mathrm{Ai}(x/\kappa)\, \mathrm{Ai}'(x/\kappa) \qquad \text{(B20a)}$$

$$\int_0^\infty \frac{dt}{\sqrt{t}} \mathrm{Ai}_1(t+x) = \kappa^2 N\{\mathrm{Ai}'^2(x/\kappa) - (x/\kappa)\, \mathrm{Ai}^2(x/\kappa)\}\,. \qquad \text{(B20b)}$$

Equation (B20b) is derived with the help of

$$\int^t du\, \mathrm{Ai}^2(u) = t\, \mathrm{Ai}^2(t) - \mathrm{Ai}'^2(t)\,, \qquad \text{(B21)}$$

which follows from Eq. (B1); for future reference we write the analogous relation

$$\int^t du\, \mathrm{Ai}(u)\, \mathrm{Bi}(u) = t\, \mathrm{Ai}(t)\, \mathrm{Bi}(t) - \mathrm{Ai}'(t)\, \mathrm{Bi}'(t)\,. \qquad \text{(B22)}$$

A similar treatment can be given integrals of the form $\int_0^\infty dt\, t^n F(t+x) G(t+x)$, where $F(u)$ and $G(u)$ represent $\mathrm{Ai}(u)$, $\mathrm{Ai}'(u)$, or $\mathrm{Ai}_1(u)$. These integrals arise in density-of-states integrations and usually involve only the products $\mathrm{Ai}^2(u)$, $\mathrm{Ai}(u)\,\mathrm{Ai}'(u)$, and $\mathrm{Ai}'^2(u)$. Integrals containing one of these three products will always reduce into each other, so we restrict attention to them.

As before, the most general integral of this form is $\int_0^\infty dt\, t^n\, \mathrm{Ai}^2(t+x)$, since the relations

$$\mathrm{Ai}(x)\, \mathrm{Ai}'(x) = \frac{1}{2}\frac{d}{dx} \mathrm{Ai}^2(x)\,, \qquad \text{(B23a)}$$

$$\mathrm{Ai}'^2(x) = \frac{1}{2}\frac{d^2}{dx^2} \mathrm{Ai}^2(x) - x\, \mathrm{Ai}^2(x)\,, \qquad \text{(B23b)}$$

enable integrals over the products $\mathrm{Ai}(x)\,\mathrm{Ai}'(x)$ and $\mathrm{Ai}'^2(x)$ to be expressed as integrals over $\mathrm{Ai}^2(x)$.

The reduction relations corresponding to Eqs. (B13) are

$$\int_0^\infty dt\, t^n\, \mathrm{Ai}^2(t+x) = \frac{n}{2(2n+1)}\int_0^\infty dt\, t^{n-1} \frac{d^2}{dt^2} \mathrm{Ai}^2(t+x) - \frac{2xn}{2n+1}\int_0^\infty dt\, t^{n-1}\, \mathrm{Ai}^2(t+x) \qquad \text{(B24a)}$$

$$= \frac{n}{2n+1}\left[\frac{1}{2}\frac{d^2}{dx^2} - 2x\right]\int_0^\infty dt\, t^{n-1}\, \mathrm{Ai}^2(t+x)\,, \qquad \text{(B24b)}$$

valid for $n > 0$. Equation (B24b) is useful if the resulting integrals can be expressed in closed form, which occurs if $n$ is integral or half-integral. An immediate application of Eqs. (B23b) and (B24b) for integer $n$ is found in the evaluation of the integral derived by Tharmalingam[3] for the electro-absorption $\alpha$ for direct first-forbidden transitions in an isotropic medium where the electric-field and light-propagation vector are parallel:

$$\alpha(\boldsymbol{\varepsilon}\|\hat{z})\propto\int_0^\infty dt\,\mathrm{Ai}'^2(t+x)$$

$$=-\tfrac{1}{2}\,\mathrm{Ai}'^2(x)-\int_0^\infty dt\,(t+x)\,\mathrm{Ai}^2(t+x) \quad \text{(B25a)}$$

$$=-\tfrac{2}{3}\,\mathrm{Ai}(x)\,\mathrm{Ai}'(x)+\tfrac{1}{3}x^2\,\mathrm{Ai}^2(x)-\tfrac{1}{3}x\,\mathrm{Ai}'^2(x). \quad \text{(B25b)}$$

The expression for $x$ and the proportionality coefficient can be found in Ref. 3. The method of extending this result for arbitrarily oriented electric-field and light-propagation vectors will be presented in Sec. C.

Integrals involving half-integer values of $n$ can be reduced to integrals which may be evaluated with Eqs. (B5) or (B17). Since it can be shown that for any function $F(x)$

$$\int_0^\infty \frac{du}{\sqrt{u}}\int_0^\infty \frac{dt}{\sqrt{t}}F(u+t)=\pi\int_0^\infty dr\,F(r), \quad \text{(B26)}$$

we have from Eq. (B19a) for $n=-\frac{1}{2}$

$$\int_0^\infty \frac{du}{\sqrt{u}}\mathrm{Ai}^2(u+x)=\int_0^\infty \frac{du}{\sqrt{u}}\int_0^\infty \frac{dt}{\sqrt{t}}\frac{1}{\kappa N}\times\mathrm{Ai}(t+\kappa u+\kappa x)$$

$$=(\pi/2N)\,\mathrm{Ai}_1(\kappa x), \quad \text{(B27)}$$

where $\kappa=2^{2/3}$ and $N$ is defined in Eq. (B2a). From this we have

$$\int_0^\infty \frac{dt}{\sqrt{t}}\mathrm{Ai}(t+x)\,\mathrm{Ai}'(t+x)=-(\pi\kappa/4N)\,\mathrm{Ai}(\kappa x), \quad \text{(B28a)}$$

$$\int_0^\infty \frac{dt}{\sqrt{t}}\mathrm{Ai}'^2(t+x)=-(\pi/4N\kappa)[3\,\mathrm{Ai}'(\kappa x)+\kappa x\,\mathrm{Ai}_1(\kappa x)], \quad \text{(B28b)}$$

the last from Eqs. (B27) and (B23b).

As an example of the use of these equations, we evaluate the integral derived by Penchina[5] and by Chester and Fritsche,[6] which is proportional to the optical absorption $\alpha$ resulting from indirect allowed transitions in the presence of an electric field parallel to a symmetry axis of the reduced-mass ellipsoid at an $M_0$ edge:

$$\alpha_{\mathrm{ind}}\propto I(V_0)=\int_{V_0}^\infty dy\,(y-V_0)^{1/2}\int_y^\infty dt\,\mathrm{Ai}^2(t). \quad \text{(B29)}$$

Using Eq. (B21) and changing variables gives

$$I(V_0)=-\int_0^\infty du\,u^{1/2}[(u+V_0)\,\mathrm{Ai}^2(u+V_0)-\mathrm{Ai}'^2(u+V_0)]. \quad \text{(B30)}$$

We now use Eq. (B23b) to replace the term $\mathrm{Ai}'^2(u+V_0)$, then use the reduction relation, Eq. (B24b), to get integrals into one of the forms of Eqs. (B27) and (B28). After some algebra we obtain

$$I(V_0)=(\pi/8\kappa^2N)[\mathrm{Ai}(r)+r\,\mathrm{Ai}'(r)+r^2\,\mathrm{Ai}_1(r)], \quad \text{(B31)}$$

where $r=\kappa V_0$. The function bracketed in Eq. (B31) is, incidentally, the third repeated integral of $\mathrm{Ai}(r)$ with respect to $r$. These results will be extended in Sec. C to fields oriented in an arbitrary direction.

Integrals of the form $\int_0^\infty dt\,t^n\,\mathrm{Ai}_1(t+x)F(t+x)$, where $F(u)$ is $\mathrm{Ai}(u)$, $\mathrm{Ai}'(u)$, or $\mathrm{Ai}_1(u)$, apparently arise only rarely in physical situations and can usually be avoided. They will not be discussed except to point out that a parallel treatment can be given using

$$\int^t dt\,\mathrm{Ai}_1^2(t)=t\,\mathrm{Ai}_1^2(t)+2\,\mathrm{Ai}'(t)\,\mathrm{Ai}_1(t)+\mathrm{Ai}^2(t) \quad \text{(B32)}$$

to obtain the reduction relations. These integrals reduce in general to integrals containing all possible double products of $\mathrm{Ai}(x)$, $\mathrm{Ai}'(x)$, and $\mathrm{Ai}_1(x)$, as a result of the term $\mathrm{Ai}^2(t)$ in Eq. (B32).

Although all integrals necessary for evaluating density-of-states sums for the electro-absorption effect have now been derived, it is convenient to examine two special integrals which occur frequently. First, by Eq. (B2b)

$$\int_{-\infty}^\infty dt\,\mathrm{Ai}(t+x)\,\mathrm{Ai}(\alpha t+y)$$

$$=\frac{\pi}{2N^2}\int_{-\infty}^\infty ds\,e^{i(1/3)s^3[1-\alpha^3]}e^{is[y-\alpha x]} \quad \text{(B33a)}$$

$$=(\pi^2/N^2)\delta(y-x) \quad \text{if } \alpha=1 \quad \text{(B33b)}$$

$$=\frac{\pi}{N(1-\alpha^3)^{1/3}}\mathrm{Ai}\left(\frac{y-\alpha x}{(1-\alpha^3)^{1/3}}\right) \quad \text{if } \alpha<1 \quad \text{(B33c)}$$

$$=\frac{\pi}{N(\alpha^3-1)^{1/3}}\mathrm{Ai}\left(\frac{\alpha x-y}{(\alpha^3-1)^{1/3}}\right) \quad \text{if } \alpha>1, \quad \text{(B33d)}$$

the last two coming from a comparison of Eq. (B33a), for $\alpha\neq0$, with Eq. (B2b). Equation (B33b) merely expresses the fact that the Airy functions are orthogonal over the real axis, a result of their being eigenfunctions of a Hermitian operator.

Using Eqs. (B33) and the integral representation

(B19a), we find

$$\int_{-\infty}^{\infty} dt\, \mathrm{Ai}^2(t+x)\,\mathrm{Ai}^2(y-\alpha t) = \frac{\pi}{2N^2\sqrt{\alpha}} \int_0^{\infty} \frac{du}{\sqrt{u}}\, \mathrm{Ai}^2\left(u+\frac{\alpha x+y}{(1+\alpha^3)^{1/3}}\right) \quad \text{(B34a)}$$

$$= \frac{\pi^2}{4N^3\sqrt{\alpha}}\, \mathrm{Ai}_1\left(\frac{\kappa(\alpha x+y)}{(1+\alpha^3)^{1/3}}\right), \quad \text{(B34b)}$$

if $\alpha>0$. The integral diverges for $\alpha\leqslant 0$ as a consequence of the asymptotic form of $\mathrm{Ai}^2(x)$ for large negative $x$.

Equation (B33b) can be used to obtain the normalization coefficient $C_i$ of Eq. (A8) as follows. We define $C_i$ so that the wave function $\phi(\mathbf{r})$ of Eq. (A4) gives the delta function over energy for each coordinate. Since the integrations are separable, consider only the $x$ coordinate. We require

$$\delta(\epsilon_{x1}-\epsilon_{x2}) = C_x^2 \int_{-\infty}^{\infty} dx\, \mathrm{Ai}\left(\frac{-\epsilon_{x1}}{\hbar\varphi_x}+x\left(\frac{2m_x{}^*e\mathcal{E}_x}{\hbar^2}\right)^{1/3}\right) \times \mathrm{Ai}\left(\frac{-\epsilon_{x2}}{\hbar\varphi_x}+x\left(\frac{2m_x{}^*e\mathcal{E}_x}{\hbar^2}\right)^{1/3}\right) \quad \text{(B35a)}$$

$$= C_x^2\left(\frac{\hbar^2}{2m_x{}^*e|\mathcal{E}_x|}\right)^{1/3} \int_{-\infty}^{\infty} dx\, \mathrm{Ai}\left(x-\frac{\epsilon_{x1}}{\hbar\varphi_x}\right) \times \mathrm{Ai}\left(x-\frac{\epsilon_{x2}}{\hbar\varphi_x}\right), \quad \text{(B35b)}$$

which, by Eqs. (B33b) and (A5) leads to

$$C_x^2 = N^2 e|\mathcal{E}_x|/\pi^2\hbar^2\varphi_x^2, \quad \text{(B36)}$$

as given in Eq. (A8).

This completes the mathematical preliminaries, and the results will now be applied to Eqs. (A13) of Sec. A.

## C. ELECTRO-ABSORPTION AT NORMAL THRESHOLDS

The mathematical relations developed in Sec. B will first be used to evaluate the electro-absorption for the $M_0$ and $M_3$ thresholds, since these are less complicated than the results for the $M_1$ and $M_2$ edges, which have reduced masses of both signs present. To evaluate Eq. (A13a), we first integrate over $\epsilon_x$ to eliminate the delta function. By changing variables, the result can be written as

$$\alpha_0(\boldsymbol{\mathcal{E}}) = \frac{4RN^6(\theta_y\theta_z)^{1/2}}{\pi^4\hbar^2\sqrt{\theta_x}} \times \int_{-\infty}^{\infty} drds\, \mathrm{Ai}^2\left(\frac{E_g-\hbar\omega}{\hbar\theta_x}-\frac{\theta_y}{\theta_x}r-\frac{\theta_z}{\theta_x}s\right) \times \mathrm{Ai}^2(r)\,\mathrm{Ai}^2(s), \quad \text{(C1)}$$

which can be integrated using Eq. (B34a) [this is preferable to using the form in Eq. (B34b) which would give an integral over a product containing $\mathrm{Ai}_1(x)$]. A second application of Eq. (B34a) and another change of variable gives

$$\alpha_0(\boldsymbol{\mathcal{E}}) = \frac{RN^2}{\pi^2}(\theta_x{}^3+\theta_y{}^3)^{1/6} \times \int_0^{\infty} \frac{dudt}{(ut)^{1/2}}\, \mathrm{Ai}^2\left(t+u\frac{(\theta_x{}^3+\theta_y{}^3)^{1/3}}{\theta_0}+\frac{E_g-\hbar\omega}{\hbar\theta_0}\right), \quad \text{(C2)}$$

where

$$\theta_0{}^3 = \theta_x{}^3+\theta_y{}^3+\theta_z{}^3. \quad \text{(C3)}$$

We change variable again and apply Eqs. (B26) and (B21) to give the result describing direct-transition electro-absorption at an $M_0$ threshold:

$$\alpha_0(\boldsymbol{\mathcal{E}}) = (N^2/\pi)R\theta_0{}^{1/2}\{\mathrm{Ai}'^2(\eta)-\eta\,\mathrm{Ai}^2(\eta)\}, \quad \text{(C4a)}$$

where

$$\eta = (E_g-\hbar\omega)/\hbar\theta_0. \quad \text{(C4b)}$$

Equations (C4) have exactly the same form as the result for an isotropic solid.[3] $R$ is the anisotropic generalization of Tharmalingam's constant $R$ and is given in Eq. (A12). $\theta_0$ in Eq. (C3) is the generalization of Tharmalingam's $\theta$, obtained simply by redefining the isotropic reduced mass $\mu$ to be

$$\frac{1}{\mu_0} = \frac{1}{|\boldsymbol{\mathcal{E}}|^2}\left[\frac{\mathcal{E}_x{}^2}{\mu_x}+\frac{\mathcal{E}_y{}^2}{\mu_y}+\frac{\mathcal{E}_z{}^2}{\mu_z}\right], \quad \text{(C5)}$$

so that, by Eqs. (C3) and (A11)

$$\theta_0{}^3 = e^2|\boldsymbol{\mathcal{E}}|^2/2\mu_0\hbar. \quad \text{(C6)}$$

Therefore, the anisotropy and field direction enter only in that the effective mass used in $\theta_0$ is the effective mass in the direction of the electric field, i.e.,

$$\frac{1}{\mu_0} = \frac{1}{\hbar^2}\frac{\partial^2}{\partial k_{\mathrm{rel}\|}{}^2}E(\mathbf{k}_{\mathrm{rel}}), \quad \text{(C7)}$$

where $k_{\mathrm{rel}\|}$ is the component of the wave vector conjugate to the relative coordinate $\mathbf{r}$ in the direction of the field $\boldsymbol{\mathcal{E}}$. Although there appears to be a dependence on the normalization constant $N$, there actually is no dependence since this constant merely cancels the normalization constant implicit in the Airy functions, to give one value for the expression regardless of the normalization used.

The experimentally measured change in absorption coefficient defined in Eq. (A10) is obtained from Eq. (C4) using the asymptotic forms[24] for $x\to\infty$

$$x\,\mathrm{Ai}^2(x) \sim (\pi/4N^2)x^{1/2}e^{-(4/3)x} \sim \mathrm{Ai}'^2(x), \quad \text{(C8a)}$$

$$x\,\mathrm{Ai}^2(-x) \sim (\pi/N^2)(-x)^{1/2}\sin^2\left(\tfrac{2}{3}(-x)^{3/2}+\tfrac{1}{4}\pi\right), \quad \text{(C8b)}$$

$$\mathrm{Ai}'^2(-x) \sim (\pi/N^2)(-x)^{1/2}\cos^2\left(\tfrac{2}{3}(-x)^{3/2}+\tfrac{1}{4}\pi\right), \quad \text{(C8c)}$$

for a normalization constant $N$. Thus

$$\Delta\alpha_0(\mathcal{E}) = R\theta_0^{1/2}\{(N^2/\pi)[\mathrm{Ai}'^2(\eta) - \eta\,\mathrm{Ai}^2(\eta)] - (\sqrt{-\eta})H(-\eta)\}, \quad \text{(C9)}$$

where $H(x)$ is the unit step function, equal to one for positive $x$ and zero for negative $x$. $N$ has disappeared in the $\alpha_0(0)$ term as required. $\eta$ is given by Eq. (C4b), and we note that the zero-field-limit term of Eq. (C9) is completely independent of $\theta_0$ and therefore of the reduced mass which is dependent on the field direction, since the $\theta_0^{1/2}$ in the prefactor cancels the $\sqrt{\theta_0}$ in the denominator of $\sqrt{-\eta}$. This is required since the zero-field term cannot depend on the direction of the field of zero magnitude.

The bracketed function in Eq. (C9) is plotted in Fig. 1 as a function of $\eta$. By Eq. (C4b), increasing $\hbar\omega$ is read to the left, so the oscillations in $\Delta\alpha_0(\mathcal{E})$ occur above threshold. Since this curve has been discussed elsewhere,[3,25] we do not mention it further.

By Eq. (A15a), the value of $\Delta\alpha_3(\mathcal{E})$ at the $M_3$ threshold is given by Eq. (C9) with $\eta$ replaced by $-\eta$ which is expected physically because as the energy of the incident photons is increased the (finite) surface area in $k$ space to which transitions can be made decreases for an $M_3$ edge and increases for an $M_0$ edge. Increasing $\hbar\omega$ is read to the right, so the oscillations in $\Delta\alpha_3(\mathcal{E})$ occur below threshold.

[*Note added in proof.* The expressions for $\Delta\alpha(\mathcal{E})$ are based on the approximation that the index of refraction $n$ is constant. This is a good approximation only for the $M_0$ edge; for higher absorption thresholds the variation $n$ with field must be taken into account. The quantity $R$ defined in Eq. (A12) is therefore field dependent and differs in the finite-field and zero-field expressions for $\alpha$ at any threshold. Unless this dependence is evaluated, incorrect expressions for $\Delta\alpha$ are obtained. This difficulty can be avoided by using the imaginary part of the dielectric constant, $\epsilon_2 = (nc/\omega)\alpha$, which is independent of $n$. The relations obtained are correct for $\Delta\epsilon_2 = (nc/\omega)\Delta\alpha$. The author is indebted to M. Cardona for pointing out this error.]

Having the electro-absorption for direct transitions to the $M_0$ threshold, it is a straightforward matter to generalize Penchina's results[5] for the anisotropic solid with the field aligned with a symmetry axis, to an arbitrarily oriented field. From Bardeen, Blatt, and Hall,[19] using Penchina's notation,

$$\alpha_{\mathrm{ind}\pm}(\mathcal{E}) = \sum_{if} \frac{4\pi^2 e^2}{ncm^2\omega} C^2|\phi(0)|^2(n_{\kappa0} + \tfrac{1}{2} \pm \tfrac{1}{2}) \times \delta(E_F - E_i - \hbar\omega \pm h\nu_{\kappa0}), \quad \text{(C10)}$$

where $\phi(\mathbf{r})$ is the solution, Eq. (A4), of Eq. (A3). The upper and lower signs refer to the emission and absorption of phonons of energy $h\nu_{\kappa0}$, respectively. The inclusion of phonons gives another degree of freedom;

[25] B. O. Seraphin and N. Bottka, Phys. Rev. **145**, 628 (1966).

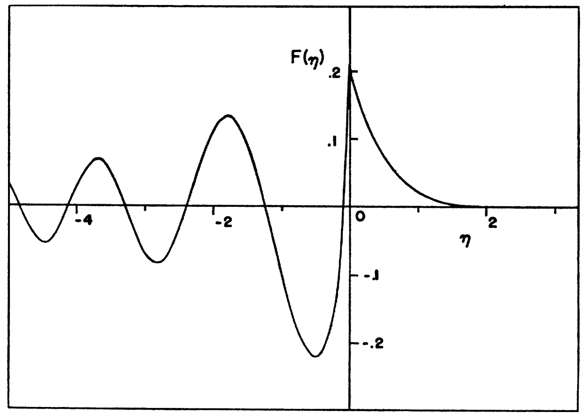


FIG. 1. The electro-absorption function $F(\eta)$ versus $\eta$ given in Eq. (E1e) which describes electro-absorption at $M_0$ and $M_3$ edges, and for parallel-type orientations of the electric field for the saddle-point thresholds $M_1$ and $M_2$.

whereas for the direct absorption, momentum conservation requires that the center-of-mass momentum and therefore the center-of-mass energy $E_{\mathrm{cm}}$ be zero, the energy is now shared between relative and center-of-mass coordinates. Rather than sum over hole and electron states, we sum over relative and center-of-mass wave vectors

$$k_{\mathrm{rel}\ i} = \frac{m_{hi}(K_{ei} - K_{0i}) - m_{ei}K_{hi}}{m_{hi} + m_{ei}}, \quad \text{(C11a)}$$

$$K_{\mathrm{cm}\ i} = (K_{ei} - K_{0i}) + K_{hi}, \quad \text{(C11b)}$$

where $\mathbf{K}_0$ represents the position of the conduction-band minimum.

The sum over relative wave vector is essentially $\alpha_0(\mathcal{E})$ given by Eqs. (C4), but must be modified in the following way. The energy argument of the delta function now includes $E_{\mathrm{cm}}$ and $h\nu_{\kappa0}$; this change is accomplished by the replacement

$$\hbar\omega \to \hbar\omega - E_{\mathrm{cm}} \mp h\nu_{\kappa0} \quad \text{(C12)}$$

in Eq. (C4b). The matrix element is now $C^2(\eta_{\kappa0} + \tfrac{1}{2} \pm \tfrac{1}{2})$ instead of $C_0^2$, and the sum over center-of-mass states can be expressed as the properly normalized integral

$$\sum_{\mathrm{cm}} \to \frac{(2M_xM_yM_z)^{1/2}}{2\pi^2\hbar^3} \int_0^\infty E_{\mathrm{cm}}^{1/2} dE_{\mathrm{cm}}, \quad \text{(C13)}$$

where $M_i = m_{ei} + m_{hi}$ for the coordinates $x$, $y$, and $z$. Therefore

$$\alpha_{\mathrm{ind}\pm}(\mathcal{E}) = W\hbar^2\theta_0^2 \frac{4N^2}{\pi^2} \int_0^\infty d\left(\frac{E_{\mathrm{cm}}}{\hbar\theta_0}\right)\left(\frac{E_{\mathrm{cm}}}{\hbar\theta_0}\right)^{1/2} \times \left[\int_{(E_g \pm h\nu_{\kappa0} - \hbar\omega)/\hbar\theta_0 + E_{\mathrm{cm}}/\hbar\theta_0}^{\infty} dt\, \mathrm{Ai}^2(t)\right], \quad \text{(C14)}$$

where $\theta_0$ is defined in Eq. (C6) and

$$W=\frac{e^2C^2(n_{\kappa 0}+\frac{1}{2}\pm\frac{1}{2})}{\pi ncm^2\omega\hbar^6}(m_{ex}m_{ey}m_{ez}m_{hx}m_{hy}m_{hz})^{1/2}. \quad (C15)$$

The factor of 2 for spin degeneracy has been included in $W$. The double integral of Eq. (C14) is the $I(V_0)$ integral given in closed form by Eqs. (B29) to (B31) with

$$V_0=(E_g\pm h\nu_{\kappa 0}-\hbar\omega)/\hbar\theta_0, \quad (C16)$$

so

$$\alpha_{\text{ind}_\pm}(\mathcal{E})=\frac{W\hbar^2\theta_0^2N}{2\pi\kappa^2}[\text{Ai}(r)+r\,\text{Ai}'(r)+r^2\,\text{Ai}_1(r)], \quad (C17)$$

where $r=\kappa V_0$, $\kappa=2^{2/3}$, and $N$ is the normalization constant of the Airy functions. The experimentally measured difference between finite-field and zero-field absorption is

$$\Delta\alpha_{\text{ind}_\pm}(\mathcal{E})=\frac{W\hbar^2\theta_0^2}{2\kappa^2}\left\{\frac{N}{\pi}[\text{Ai}(r)+r\,\text{Ai}'(r)+r^2\,\text{Ai}_1(r)] -r^2H(-r)\right\}, \quad (C18)$$

and $H(x)$ is the unit step function. Again, the field direction only enters through the reduced mass, this being the reduced mass in the direction of the field, given by Eq. (C5). The absorption coefficient for indirect transitions in the presence of an electric field along a symmetry axis has been discussed elsewhere[5,8]; since the solution for an arbitrarily oriented field differs only in the effective mass, no further discussion will be given.

The relations of Sec. B may also be used to calculate the absorption coefficient for direct first-forbidden transitions at an $M_0$ threshold. The resulting equations are quite complex, depending both on the orientation of the electric field with respect to the symmetry axes of the reduced- mass ellipsoid and the direction of the propagation vector of the light, because the function $|\phi(0)|^2$ in Eq. (A2) must be replaced by $|\hbar\hat{q}\cdot\nabla_{\mathbf{r}}\phi(\mathbf{r})|_{r=0}{}^2$ where $\hat{q}$ is the unit vector in the direction of the incident light.[19] We obtain a series of integrals like that of Eq. (A13a) over various combinations of $\text{Ai}(x)\,\text{Ai}'(x)$ (cross terms) or $\text{Ai}'^2(x)$ (diagonal terms of $|\hbar\hat{q}\cdot\nabla\phi|^2$). We mention that Eqs. (B34) can be extended to evaluate the cross term integrals by appropriate differentiation with respect to $x$ or $y$, or both. For diagonal terms, the function $\text{Ai}'^2(x)$ can be replaced by means of the identity of Eq. (B23b) at the expense of introducing a first power of the integration variable. This can be reduced with the relation

$$\int_{-\infty}^{\infty}dt\,t\,\text{Ai}^2(t+x)\,\text{Ai}^2(y-\alpha t) =\frac{\partial}{\partial\alpha}\int_y^{\infty}dy\int_{-\infty}^{\infty}dt\,\text{Ai}^2(t+x)\,\text{Ai}^2(y-\alpha t), \quad (C19)$$

for $\alpha>0$, giving

$$\int_{-\infty}^{\infty}dt\,\text{Ai}'^2(t+x)\,\text{Ai}^2(y-\alpha t) =\left[\frac{1}{2}\frac{d^2}{dx^2}-x+\frac{\partial}{\partial\alpha}\int_y^{\infty}dy\right]\frac{\pi^2}{4N^3\sqrt{\alpha}} \times\text{Ai}_1\left(\frac{\kappa(\alpha x+y)}{(1+\alpha^2)^{1/3}}\right), \quad (C20)$$

by Eq. (B34b), from which the direct first-forbidden absorption for electric-field and light-propagation vectors in arbitrary directions may be calculated.

## D. ELECTRO-ABSORPTION AT SADDLE-POINT THRESHOLDS

We next examine the absorption at the $M_1$ and $M_2$ saddle-point thresholds, which have reduced masses of both signs. The electro-absorption integral Eq. (A13b), will be evaluated similarly to the $M_0$ integral. By performing the integration over $\epsilon_x$ to eliminate the delta function and changing variables to

$$t=-\epsilon_y/\hbar\theta_y, \quad r=-\epsilon_z/\hbar\theta_z, \quad (D1)$$

we have

$$\alpha_1(\mathcal{E})=\frac{4RN^6(\theta_y\theta_z)^{1/2}}{\pi^4\sqrt{\theta_x}}\int_{-\infty}^{\infty}drdt\,\text{Ai}^2(t)\,\text{Ai}^2(r) \times\text{Ai}^2\left(\frac{E_g-\hbar\omega}{\hbar\theta_x}+\frac{\theta_z}{\theta_x}r-\frac{\theta_y}{\theta_x}t\right), \quad (D2)$$

which is divergent as a result of the integration over the variable $r$; $\theta_x$ and $\theta_z$ both being positive quantities. We may, however, isolate this divergence to a limit of an integral in the following way. Since $\theta_x$ and $\theta_y$ are positive, the integral over $t$ converges, and its value is given by Eq. (B34b):

$$\alpha_1(\mathcal{E})=\frac{RN^3\theta_z^{1/2}}{\pi^2}\int_{-\infty}^{\infty}dr\,\text{Ai}^2(r)\int_{\kappa[(E_g-\hbar\omega)/\hbar\theta_x+(\theta_z/\theta_x)r](1+\theta_y^2/\theta_x^2)^{-1/3}}^{\infty}du\,\text{Ai}(u) \quad (D3a)$$

$$=\frac{RN^3\theta_z^{1/2}}{\pi^2}\int_{\kappa[E_g-\hbar\omega]/\hbar\theta}^{\infty}du\int_{-\infty}^{\infty}dr\,\text{Ai}^2(r)\,\text{Ai}\left(u+\kappa\frac{\theta_z}{\theta}r\right), \quad (D3b)$$

where

$$\theta^3=\theta_x^3+\theta_y^3. \tag{D4}$$

The divergence is now contained in the upper limit of the integral over $u$, the integral over $r$ being finite.

By Eq. (B19a) this expression is equal to

$$\alpha_1(\boldsymbol{\mathcal{E}})=\frac{RN^2\theta_z^{1/2}}{\kappa^2\pi^2}\int_{\kappa(E_g-\hbar\omega)/\hbar\theta}^{\infty}du\int_0^{\infty}\frac{dt}{\sqrt{t}}\times\int_{-\infty}^{\infty}d\xi\,\mathrm{Ai}(t+\xi)\,\mathrm{Ai}\left(u+\frac{\theta_z}{\theta}\xi\right), \tag{D5}$$

which should, by Eqs. (B33), exhibit two branches depending on whether $\theta_z$ is greater or less than $\theta$. From Eq. (A11), an alternative statement of this condition is that the branch obtained depends on whether $\mathcal{E}_z^2/\mu_z$ is greater or less than $\mathcal{E}_x^2/\mu_x+\mathcal{E}_y^2/\mu_y$. All quantities $\mu$ are magnitudes, and $\mu_z$ is the magnitude of the reduced mass of odd sign (negative for $M_1$ and positive for $M_2$).

Suppose first $\theta=\theta_z$. By Eq. (B33b),

$$\alpha_1(\boldsymbol{\mathcal{E}})=\frac{R\theta_z^{1/2}}{\kappa^2}\lim_{D\to\infty}\int_{\max\{0,\kappa(E_g-\hbar\omega)/\hbar\theta_z\}}^{D}\frac{dt}{\sqrt{t}} \tag{D6a}$$

$$=\frac{2R\theta_z^{1/2}}{\kappa^2}\lim_{D\to\infty}\sqrt{D}-R\theta_z^{1/2}s_0^{1/2}H(s_0), \tag{D6b}$$

where

$$s_0=(E_g-\hbar\omega)/\hbar\theta_z, \tag{D6c}$$

and $H(x)$ is the unit step function.

The absorption coefficient is infinite, but the experimentally measurable difference between zero- and finite-field absorption is not infinite. Equation (D6b) is completely independent of the applied field both for $E_g\geqslant\hbar\omega$ and $E_g\leqslant\hbar\omega$ if we assume the limit $D\to\infty$ is taken before the limit $\boldsymbol{\mathcal{E}}\to 0$; hence

$$\Delta\alpha_1(\boldsymbol{\mathcal{E}})=0, \tag{D7a}$$

if

$$\theta_z=\theta;\quad\left(\frac{\mathcal{E}_z^2}{\mu_z}=\frac{\mathcal{E}_x^2}{\mu_x}+\frac{\mathcal{E}_y^2}{\mu_y}\right). \tag{D7b}$$

If $\theta_z^3>\theta_x^3+\theta_y^3$, that is, the field is more nearly parallel the reduced mass of odd sign, Eq. (B33d) together with Eq. (B17) applied to Eq. (D5) yields

$$\alpha_{1P}(\boldsymbol{\mathcal{E}})=R\theta_{1P}^{1/2}\frac{N^2}{\pi}\int_{-\infty}^{(\hbar\omega-E_g)/\hbar\theta_{1P}}du\,\mathrm{Ai}^2(u), \tag{D8a}$$

where

$$\theta_{1P}^3=\theta_z^3-\theta_x^3-\theta_y^3;\quad\left(\frac{\mathcal{E}_z^2}{\mu_z}>\frac{\mathcal{E}_x^2}{\mu_x}+\frac{\mathcal{E}_y^2}{\mu_y}\right), \tag{D8b}$$

or, if we define a reduced mass

$$\frac{1}{\mu_{1P}}=\frac{1}{|\boldsymbol{\mathcal{E}}|^2}\left[\frac{\mathcal{E}_z^2}{\mu_z}-\frac{\mathcal{E}_x^2}{\mu_x}-\frac{\mathcal{E}_y^2}{\mu_y}\right]>0, \tag{D9a}$$

then

$$\theta_{1P}^3=e^2|\boldsymbol{\mathcal{E}}|^2/2\mu_1\hbar. \tag{D9b}$$

The absorption is infinite as a result of the lower limit. The difference between the finite-field and zero-field absorptions is again finite, and is

$$\Delta\alpha_{1P}(\boldsymbol{\mathcal{E}})=R\theta_{1P}^{1/2}\left\{\frac{N^2}{\pi}[\eta\,\mathrm{Ai}^2(\eta)-\mathrm{Ai}'^2(\eta)]+(\sqrt{-\eta})H(-\eta)\right\}, \tag{D10a}$$

where $\theta_{1P}$ is given in Eqs. (D9) and

$$\eta=(\hbar\omega-E_g)/\hbar\theta_{1P}. \tag{D10b}$$

The bracketed function is just the negative of the bracketed function of Eq. (C9) which is plotted in Fig. 1. Increasing $\hbar\omega$ is read to the right, so for fields of orientation given by Eq. (D8b), the oscillations appear below threshold at an $M_1$ critical point.

For the electric field completely parallel to the negative reduced mass ($\theta=0$) this result reduces to Phillip's duality theorem[26]: The change in absorption coefficient is the negative of the change for an ordinary ($M_0$) edge in direct transitions with the sign of the energy reversed. The effect of moving the field orientation away from the negative mass axis is the same as decreasing the magnitude of the field while keeping it parallel to the negative reduced mass; the field effectively goes to zero when the condition of Eq. (D7b) is satisfied. It is assumed in the above derivation that the limit of zero field is taken after allowing the integral limit to approach infinity, so the infinite limits of $\alpha_{1P}(\boldsymbol{\mathcal{E}})$ and $\alpha_{1P}(0)$ cancel identically.

If $\theta>\theta_z$ so the field is primarily transverse with respect to the negative mass axis, Eq. (D5) must be evaluated with Eq. (B33c) followed by Eq. (B18), giving the result

$$\alpha_{1T}(\boldsymbol{\mathcal{E}})=R\theta_{1T}^{1/2}\frac{N^2}{\pi}\int_{(E_g-\hbar\omega)/\hbar\theta_{1T}}^{\infty}du\,\mathrm{Ai}(u)\,\mathrm{Bi}(u), \tag{D11a}$$

where

$$\theta_{1T}^3=\theta_x^3+\theta_y^3-\theta_z^3;\quad\left(\frac{\mathcal{E}_x^2}{\mu_x}+\frac{\mathcal{E}_y^2}{\mu_y}>\frac{\mathcal{E}_z^2}{\mu_z}\right), \tag{D11b}$$

or, if we define a reduced mass

$$\frac{1}{\mu_{1T}}=\frac{1}{|\boldsymbol{\mathcal{E}}|^2}\left[\frac{\mathcal{E}_x^2}{\mu_x}+\frac{\mathcal{E}_y^2}{\mu_y}-\frac{\mathcal{E}_z^2}{\mu_z}\right]>0, \tag{D12a}$$

then

$$\theta_{1T}^3=e^2|\boldsymbol{\mathcal{E}}|^2/2\mu_{1T}\hbar. \tag{D12b}$$

---

[26] J. C. Phillips and B. O. Seraphin, Phys. Rev. Letters **15**, 107 (1965); J. C. Phillips, in Proceedings of the International School of Physics "Enrico Fermi," 1966 [Nuovo Cimento Suppl. (to be published)].

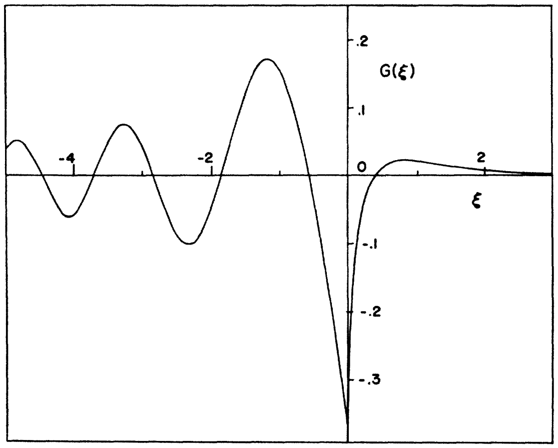


FIG. 2. The electro-absorption function $G(\xi)$ versus $\xi$ given in Eq. (E1f) which describes electro-absorption at $M_1$ and $M_2$ saddle-point thresholds for transverse-type orientations of the electric field.

The finite difference between finite- and zero-field absorptions is

$$\Delta\alpha_{1T}(\mathbf{\mathcal{E}})=R\theta_{1T}^{1/2}\left\{\frac{N^2}{\pi}[\mathrm{Ai}'(\xi)\,\mathrm{Bi}'(\xi)-\xi\,\mathrm{Ai}(\xi)\,\mathrm{Bi}(\xi)]+(\surd\xi)H(\xi)\right\},\tag{D13a}$$

where $\theta_{1T}$ is defined in Eqs. (D12) and

$$\xi=(E_g-\hbar\omega)/\hbar\theta_{1T}.\tag{D13b}$$

The bracketed function of Eq. (D11a) is plotted as a function of variable $\xi$ in Fig. 2. The oscillations now occur for energies greater than the threshold $E_g$, in contrast to the case of the field more nearly parallel the mass of negative sign at the same edge. The tail of $\Delta\alpha_{1T}(\mathbf{\mathcal{E}})$ extending below threshold falls off much more slowly. The result is dependent on the cancellation of the infinities for zero- and finite-field absorptions, as before.

We note that although there are two branches for the electro-absorption at an $M_1$ critical point, given by Eqs. (D10) and (D13), the zero-field limits of the two branches are identical, as they must be since the field can then have no effect on the absorption.

By Eq. (A15b), we can immediately extend all results for the $M_1$ threshold to the $M_2$ threshold by changing the sign of $(E_g-\hbar\omega)$ wherever it occurs in the equations for the $M_1$ threshold. Thus, for field orientations more parallel, the axis of the reduced mass of odd sign, the positive mass for an $M_2$ critical point, $\Delta\alpha_{2p}(\mathbf{\mathcal{E}})$ is given by Eq. (D10a) with $\eta$ replaced with $-\eta$. The oscillations occur above threshold as for the $M_0$ edge. For orientations more of a transverse nature as defined in Eq. (D12b), the solution is that of Eqs. (D13) with $\xi$ replaced by $-\xi$, i.e., Fig. 2 with the abscissa reversed and the oscillations now occurring below threshold.

The behavior of $\Delta\alpha(\mathbf{\mathcal{E}})$ as a function of the direction of the applied electric field for saddle points is quite curious in that two branches having a different functional dependence on $(E_g-\hbar\omega)/\hbar\theta$ are obtained which do not mix: either one or the other, but not both, occur for any given field direction. This is consistent, however, with the results obtained for the normal thresholds, since the reduced mass to be used in the calculations is still just the reduced mass in the direction of the electric field. Since the reduced mass in the parallel orientation is negative and the transverse orientation positive in the $M_1$ edge, for example, the effective mass in the field direction

$$\frac{1}{m_1^*}=\frac{1}{|\mathbf{\mathcal{E}}|^2}\left[\frac{\mathcal{E}_x^2}{\mu_x}+\frac{\mathcal{E}_y^2}{\mu_y}-\frac{\mathcal{E}_z^2}{\mu_z}\right]\tag{D14}$$

must become infinite and change sign as the field direction is swung from parallel to transverse orientations. This is also shown by Eq. (C7), for in going from the region of negative to positive curvature at the saddle point, one must necessarily go through a line of zero curvature where the reduced mass is infinite and changes sign. The apparent violation of the superposition principle, in that one might expect both parallel and transverse effects to appear for intermediate field orientations, is actually due to the qualitative difference caused by having reduced masses of opposite signs and does not represent the true superposition of the component fields at all.

## E. DISCUSSION

Electro-absorption for direct transitions to the $M_0$, $M_1$, $M_2$, and $M_3$ thresholds can be described completely as one of the functions

$$\Delta\alpha(\mathbf{\mathcal{E}})=\pm R\theta^{1/2}F(\eta),\tag{E1a}$$

$$\Delta\alpha(\mathbf{\mathcal{E}})=\pm R\theta^{1/2}G(\xi),\tag{E1b}$$

where

$$R=\frac{2e^2C_0^2}{\hbar\omega ncm^2}\left(\frac{8\mu_x\mu_y\mu_z}{h^3}\right)^{1/2},\tag{E1c}$$

$$\theta^3=\frac{e^2|\mathbf{\mathcal{E}}|^2}{2\mu\hbar},\tag{E1d}$$

$$F(\eta)=\frac{N^2}{\pi}[\mathrm{Ai}'^2(\eta)-\eta\,\mathrm{Ai}^2(\eta)]-(-\eta)^{1/2}H(-\eta),\tag{E1e}$$

$$G(\xi)=\frac{N^2}{\pi}[\mathrm{Ai}'(\xi)\,\mathrm{Bi}'(\xi)-\xi\,\mathrm{Ai}(\xi)\,\mathrm{Bi}(\xi)]+(\xi)^{1/2}H(\xi).\tag{E1f}$$

TABLE I. A summary of the electro-absorption results. The definition of the various critical points with respect to the signs of the reduced masses is given following Eq. (A1). The quantities $\mu_i$ in the table represent the magnitudes of these masses. The remaining quantities are defined in Eqs. (E1). $F(\eta)$ and $G(\xi)$ are universal curves plotted in Figs. 1 and 2, respectively.

| Threshold | $\Delta\alpha(\mathcal{E})$ | $\eta, \xi$ | $\mu$ |
|---|---|---|---|
| $M_0$ | $R\theta^{1/2}F(\eta)$ | $\eta=\dfrac{E_g-\hbar\omega}{\hbar\theta}$ | $\dfrac{1}{\mu}=\dfrac{1}{\lvert\mathcal{E}\rvert^2}\left[\dfrac{\mathcal{E}_x^2}{\mu_x}+\dfrac{\mathcal{E}_y^2}{\mu_y}+\dfrac{\mathcal{E}_z^2}{\mu_z}\right]$ |
| $M_1$, parallel | $-R\theta^{1/2}F(\eta)$ | $\eta=\dfrac{\hbar\omega-E_g}{\hbar\theta}$ | $\dfrac{1}{\mu}=\dfrac{1}{\lvert\mathcal{E}\rvert^2}\left[\dfrac{\mathcal{E}_z^2}{\mu_z}-\dfrac{\mathcal{E}_x^2}{\mu_x}-\dfrac{\mathcal{E}_y^2}{\mu_y}\right]>0$ |
| $M_1$, transverse | $R\theta^{1/2}G(\xi)$ | $\xi=\dfrac{E_g-\hbar\omega}{\hbar\theta}$ | $\dfrac{1}{\mu}=\dfrac{1}{\lvert\mathcal{E}\rvert^2}\left[\dfrac{\mathcal{E}_x^2}{\mu_x}+\dfrac{\mathcal{E}_y^2}{\mu_y}-\dfrac{\mathcal{E}_z^2}{\mu_z}\right]>0$ |
| $M_2$, parallel | $-R\theta^{1/2}F(\eta)$ | $\eta=\dfrac{E_g-\hbar\omega}{\hbar\theta}$ | $\dfrac{1}{\mu}=\dfrac{1}{\lvert\mathcal{E}\rvert^2}\left[\dfrac{\mathcal{E}_z^2}{\mu_z}-\dfrac{\mathcal{E}_x^2}{\mu_x}-\dfrac{\mathcal{E}_y^2}{\mu_y}\right]>0$ |
| $M_2$, transverse | $R\theta^{1/2}G(\xi)$ | $\xi=\dfrac{\hbar\omega-E_g}{\hbar\theta}$ | $\dfrac{1}{\mu}=\dfrac{1}{\lvert\mathcal{E}\rvert^2}\left[\dfrac{\mathcal{E}_x^2}{\mu_x}+\dfrac{\mathcal{E}_y^2}{\mu_y}-\dfrac{\mathcal{E}_z^2}{\mu_z}\right]>0$ |
| $M_3$ | $R\theta^{1/2}F(\eta)$ | $\eta=\dfrac{\hbar\omega-E_g}{\hbar\theta}$ | $\dfrac{1}{\mu}=\dfrac{1}{\lvert\mathcal{E}\rvert^2}\left[\dfrac{\mathcal{E}_x^2}{\mu_x}+\dfrac{\mathcal{E}_y^2}{\mu_y}+\dfrac{\mathcal{E}_z^2}{\mu_z}\right]$ |

$H(x)$ is the unit step function, and $N$ is the normalization of the Airy function defined in Eq. (B2). The above expressions are independent of the normalization $N$, since the explicit $N$ merely cancels the implicit $N$ in the Airy-function normalization resulting in one value of the functions regardless of normalization used. The results are summarized by giving the defining equations for $\Delta\alpha(\mathcal{E})$ and $\mu$ for each of the critical points in Table I. The functions $F(\eta)$ and $G(\xi)$ are plotted in Figs. 1 and 2, respectively.

It should be noted that the calculations have been done assuming one conduction-band minimum throughout, and that to extend the results to a practical case, such as indirect $M_0$ transitions to the lowest conduction-band minima in silicon and germanium, it is necessary to sum over all such minima. Also, all possible valence bands from which the transition can occur must be included.

The most serious approximation made for the calculations, particularly for saddle points, is perhaps the extension of the integration to infinity in the energy integrals, which represent a nonphysical situation of quadratic energy bands extending to infinite energy. The integrals should be cut off at a finite value of the energy, and this cutoff should be done in Eqs. (A13), the initial expressions for $\alpha(\mathcal{E})$, rather than in the final expressions since the latter would still give divergences for fields approaching zero. It seems reasonable to assume that the calculated changes in absorption, $\Delta\alpha(\mathcal{E})$, are probably uncertain by amounts equal to the value of $\Delta\alpha(\mathcal{E})$ when $(E_g-\hbar\omega)$ is equal to the cutoff energy on the least convergent (oscillatory) side.

A second approximation is the neglect of the Coulomb-attraction term between the hole and electron in Eq. (A3). For a discussion of the effect of this term for an isotropic reduced mass at an $M_0$ threshold, see Ref. 27.

It would be interesting to check the saddle-point results experimentally by observing electro-reflectance as a function of field orientation. As a result of the probable breakdown of the theory at large energies, it may not be possible to observe the long tail in $\Delta\alpha_{1T}(\mathcal{E})$ and $\Delta\alpha_{2T}(\mathcal{E})$ below and above threshold, respectively, although proper orientation to obtain a large reduced mass would help. It should be easy to see the large negative and positive peaks in $\Delta\alpha_{1T}(\mathcal{E})$ just above the threshold. Since no two thresholds have the same electro-absorption response, it should be possible to use the results given in Table I to identify higher lying direct transitions.

### F. CONCLUSION

A systematic method of evaluating the density-of-states integrals arising in electro-absorption has been presented, and the results applied to normal ($M_0$) direct and indirect transitions, and to direct transitions near $M_1$, $M_2$, and $M_3$ critical points. The change in absorption upon application of an electric field has been shown to depend on the orientation of the electric field only through the magnitude and sign of the reduced mass for direct allowed transitions at all edges. The results derived previously for $M_0$ transitions[3,5] are applicable for arbitrary field orientations provided the reduced mass is calculated accordingly.

The $M_1$ and $M_2$ saddle-point electro-absorption effects have two distinct branches, depending on whether the field is more parallel or transverse to the symmetry axis of the reduced mass of odd sign. For orientations more parallel the change in absorption

[27] C. B. Duke, Phys. Rev. Letters **15**, 625 (1965); C. B. Duke and M. E. Alferieff, Phys. Rev. **145**, 583 (1966).

resulting from the field is similar to that in a normal edge. If the field is more transverse, a branch of different functional form appears and the oscillations in $\Delta\alpha_T(\mathcal{E})$ occur on the opposite side of the threshold. The $M_3$ threshold electro-absorption is similar to that of the $M_0$ edge. Since all edges have different $\Delta\alpha(\mathcal{E})$ dependences on field orientation and photon energy, it should be possible to identify the nature of higher lying direct optical transitions on the basis of the measurement of the electro-absorption effect.


## ACKNOWLEDGMENT

I wish to thank Professor Paul Handler for pointing out the immediate interest in the electro-absorption effect at saddle-point thresholds, and for a critical reading of the manuscript.


PHYSICAL REVIEW VOLUME 147, NUMBER 2 15 JULY 1966

# Coupling between $H^-$ Localized Modes and Rare-Earth Ion Electronic States in Rare-Earth Trifluorides*

G. D. JONES AND R. A. SATTEN
*Physics Department, University of California, Los Angeles, California*
(Received 11 February 1966)

Crystals of $LaF_3$, $CeF_3$, $PrF_3$, and $NdF_3$ doped with hydrogen and deuterium have been studied spectroscopically. Two strong polarized fundamentals and their combinations have been observed in the infrared for both $H^-$ and $D^-$. The fundamentals appear also polarized in the vibronic spectrum of doped $NdF_3$ coupled to several electronic transitions. Extra electronic lines appearing only in the doped crystals occur on the long-wavelength side of the usual rare-earth electronic transitions. From frequency differences, these extra levels are the parent states for the local mode vibronic transitions. The displacement of the extra electronic lines from the usual electronic transitions is mainly due to a changed crystalline field and covalency arising from the replacement of F by H, and is greater at higher levels. In addition the extra electronic levels have slightly different frequencies for hydrogenated and deuterated crystals. This isotope shift depends in both magnitude and sign on the particular electronic level and ranges from 0.5 $cm^{-1}$ (for transitions to $^4F_{3/2}$) to $-2.0$ $cm^{-1}$ (for transitions to $^4F_{7/2}$). This effect is accounted for by a large difference in zero-point amplitude for $H^-$ and $D^-$ localized modes which, through the electron-vibration interaction, perturbs each electronic level to a different extent.

## INTRODUCTION

THE infrared absorption due to localized modes of $H^-$ defects in crystals[1–4] as well as the electronic transitions of the $U$ center in the ultraviolet[5] are well known. Because the concentrations of $H^-$ attainable in certain ionic crystals in which the $H^-$ replaces the anion are relatively large (of the order of 0.01%) it is possible to study the coupling of the localized $H^-$ ion vibrations with the electronic states of rare-earth ions in crystals. Our study is concerned with such coupling for localized $H^-$ and $D^-$ modes in rare-earth trifluorides, chiefly $NdF_3$.

The coupling is manifested in several ways: (1) as a shift in the electronic levels of the rare-earth ion in the changed environment due to the $H^-$, (2) as an isotope effect for these shifted lines, and (3) as vibronic transitions involving the absorption of a photon by the rare-earth ion accompanied by the creation of one localized phonon. We also present the results of polarized low-temperature infrared absorption by the $H^-$ and $D^-$ localized vibrations.

The rare-earth trifluorides are experimentally suitable for our studies because of the readiness with which they can be heavily doped with hydrogen and so display observable optical effects. However, they suffer from certain difficulties which limit the extent one can at present push the theoretical analysis of the results. Various studies involving rare-earth trifluorides suffer from a lack of agreement as to the crystal structure. Two slightly different crystal structures have been proposed for $LaF_3$ from x-ray analysis, one involving two molecules per unit cell with the rare-earth ions at $D_{3h}$ sites,[6] and the other involving six molecules per unit cell with rare-earth ions at $C_{2v}$ sites.[7] Nuclear magnetic resonance studies[8] on pure $LaF_3$ single crystals have recently shown that there are six magnetically different La sites with site symmetry either $C_s$ or $C_{2h}$, and based on these results a third crystal structure has

* Some of the results of this paper were presented at the September 1965 meeting of the Americal Physical Society. See APS Bulletin 10, 686 (1965).
[1] G. Schaefer, J. Phys. Chem. Solids 12, 233 (1960).
[2] B. Fritz, J. Phys. Chem. Solids 23, 375 (1962).
[3] B. Fritz, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965).
[4] R. J. Elliott, W. Hayes, G. D. Jones, H. F. Macdonald, and C. T. Sennett, Proc. Roy. Soc. (London) A289, 1 (1965).
[5] R. W. Pohl, Proc. Phys. Soc. (London) 49, 3 (1937).
[6] K. Schlyter, Arkiv Kemi 5, 73 (1952).
[7] I. Oftedal, Z. Krist. 72, 239 (1929); 78, 462 (1931).
[8] L. O. Andersson and W. G. Proctor (to be published).