function of d only as per (2):

$$E_X = E_X|_{\text{Si}}(d/d_{\text{Si}})^{s_x} = \text{Vac.} - E_{X_5}. \tag{A4}$$

(5) The energy of the top of the valence band at the symmetry point L, the L_3 state, is midway between the values for Γ and X:

$$E_{L_3} = \tfrac{1}{2}(\text{I.P.} + E_{X_5}). \tag{A5}$$

(6) The splitting of the conduction-band X levels, X_1 and X_3, is proportional to C:

$$E_{X_3} - E_{X_1} = \text{const} \times C. \tag{A6}$$

(7) The perturbative effect of the d band on the s-like levels of greatest interest, $\Gamma_{1,c}$ and $L_{1,c}$, is expressed by decreasing the $E_0(\Gamma_{15,v} \rightarrow \Gamma_{1,c})$ and $E_1(L_{3,v} \rightarrow L_{1,c})$ energy gaps from the values indicated by (1) according to

$$E_i = [E_{i,h} - (D_{\text{av}} - 1)\Delta E_i][1 + (C/E_{i,h})^2]^{1/2}, \tag{A7}$$

where here $i = 0$, 1 and ΔE_i is a parameter which is a function of d only as per (2). The values of the 19 parameters of this formulation are shown in Table V. In Table VI, we give the empirically determined parameters used in this paper for the pure compounds from which the alloys are formed.

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Electroabsorption in Semiconductors: The Excitonic Absorption Edge

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Numerical calculations of the optical-absorption coefficient for direct, excitonic transitions in a uniform applied electric field are presented. The electron-hole scattering is treated within the effective-mass approximation and leads to an absorption coefficient which differs markedly in size and shape from the Franz-Keldysh absorption spectrum. A detailed numerical study of the shape of the absorption-edge spectrum at photon energies somewhat below the zero-field absorption threshold suggests that for small field strengths the dominant asymptotic form of the absorption coefficient is $\exp(-C_0|E-E_0'|/f)$, where $f = |e|Fa/R$ is the electric field strength in units of exciton Rydbergs per electron-exciton Bohr radius. This result contradicts the existing belief that the electron-hole interaction does not alter the asymptotic form of the Franz-Keldysh shape: $\exp(-C_0'|E-E_0'|^{3/2}/f)$. Physical arguments are presented to show why the exciton effects should be important. A discussion is presented of the interrelationships among the present treatment of electroabsorption and various one-electron, exciton, and many-body formalisms.

I. INTRODUCTION

IN 1958 Franz[1] and Keldysh[2] independently developed the theory of direct band-to-band optical transitions in semiconductors in a uniform applied electric field. The primary prediction of their theory, that the optical-absorption edge would broaden and shift toward lower energy in an electric field, was verified experimentally a year later by Böer, Hänsche, and Kummel[3] and others.[4] The introduction of modulation techniques by Seraphin[5] in 1964 greatly increased the interest in electroreflection and electroabsorption as diagnostic tools in analysis of the energy-band structure. This field has naturally expanded rapidly and comprehensive reviews of the experimental[6] and theoretical[7] developments are now becoming available.

It has long been recognized that the Franz-Keldysh theories and their extensions included no correlation

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* Research sponsored in part by the U. S. Air Force Office of Scientific Research under Contract No. AF49(638)1545.

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[5] B. O. Seraphin, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors*, edited by M. Hulin (Dunod Cie., Paris, 1964), p. 165.

[6] B. O. Seraphin, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. Beer (Academic Press Inc., New York, to be published), Vol. VI.

[7] D. E. Aspnes and N. Bottka, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. Beer (Academic Press Inc., New York, to be published), Vol. VI.

effects—not even the lowest-order effect of this type, for formation of excitons by the electron-hole interaction. Not until 1966, however, was it suggested that this excitonic influence is prominent in the electroabsorption spectra of semiconductors.[8] In this paper, we study the effects of excitons on the shape of the electroabsorption edge.

If one is willing to overlook small effects due to the sudden creation of the electron-hole pair, exchange, deviations from the effective-mass approximation and central-cell corrections (all of which are normally small in semiconductors), then the calculation of the electroabsorption (in the exciton approximation)[9] is formally equivalent to the solution of the Schrödinger equation for a hydrogen atom with a tensor mass in an extremely strong electric field. For the general tensor mass (i.e., at a general point in the conduction–valence-band structure), the Coulomb interaction renders the exact solution of this equation impossible. And the electron-hole scattering cannot be realistically treated as a small perturbation, even in zero applied field, since it severely perturbs the band-to-band density of states.[10] Here we consider only the case of a positive scalar mass (i.e., an M_0 critical point); and the hydrogenic equation reduces to the Stark-effect problem which has evaded complete solution since the early days of quantum mechanics.[11] In the case of the hydrogen atom, the binding energy is so large that experimentally realizable electric fields may be treated by perturbation theory to give useful *asymptotic* approximations to the wave functions and energy levels, even though the perturbation expansion necessarily *does not converge* to physically meaningful answers for any value of the field strength. In the case of the exciton, factors of effective mass and the square of the dielectric constant commonly reduce the binding energy by several orders of magnitude so that it is often *very small* compared with the change of electrostatic potential energy across the exciton for fields of, say, 10^5 V/cm. Hence any attempt to treat the problem of an exciton in an applied electric field must be essentially nonperturbative. A variational approach is likewise excluded, since the potential energy of an electron in a uniform electric field is unbounded below (or above); and the conventional WKBJ approximation is invalid for azimuthal quantum numbers such that $|m|\leq 1$.[12]

Duke was the first one to consider the effects of electron-hole scattering on electroabsorption,[12,13] and he based his treatment on an exact solution of the hydrogenlike problem for a model potential in parabolic coordinates (the accidental degeneracy associated with the Coulomb potential leads to separation of the Schrödinger equation in these coordinates). Ironically, in solving his model potential problem, he chose to work only with analytic functions and explicitly ruled out an exact numerical solution of the hydrogenic equations as impractical.[14] However, a numerical solution of the exact problem is made feasible by the very fact that the potential energy associated with the applied field is so large compared with the exciton binding energy.

With the recognition that we had available to us all the numerical machinery for solving the effective-mass equation,[15] we set about the task of doing so. Our motivation for attempting the solution came not only from an intent to study electroabsorption *per se*, but also from an interest in the lowest absorption edges in insulators and semiconductors and the relationship between Urbach's rule and the Franz-Keldysh effect.[16] During the early stages of this work, there appeared a paper in which Ralph had solved the effective-mass equation for excitons and had obtained the electroabsorption, concentrating on the spectral region near and above the lowest exciton peak.[17] Taking considerable advantage of Ralph's experience, we were able to calculate the shape of the electroabsorption edge well below the zero-field threshold. The numerical problems were considerably more difficult in this low-energy regime on account of the need to integrate through a high potential barrier where small numerical errors were rapidly amplified. Finally, we note that Blossey[18] has recently performed calculations similar to those of Ralph's and ours, from a slightly different viewpoint, and has included the exciton effects on electroabsorption near M_3 critical points (maxima) in the joint density of the conduction and the valence bands as well as the M_0 edges (minima) considered here.

In the remaining sections of this paper we shall present the physical basis and the results of our calculations. Section II deals with qualitative considerations; Sec. III is devoted to the formal theory of electroabsorption and includes a derivation of the Elliott formula for optical absorption from the viewpoint of modern linear-response theory. Section IV has a

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discussion of our numerical methods and results. Our conclusions are drawn in Sec. V and summarized in Sec. VI.

II. QUALITATIVE CONSIDERATIONS

There are two frequently used methods of calculating the optical absorption coefficient of a nonmetallic crystal. The first involves Fermi's Golden Rule for evaluating the probability per unit time for transitions between *stationary* states. In this method, one needs to know the matrix element of $\mathbf{A}\cdot\mathbf{p}$ between initial and final states and the density of final states (here $\mathbf{p}$ is the total momentum operator for the crystal and $\mathbf{A}$ is the vector potential associated with the light). The second method involves the evaluation of the time-dependent matrix elements of the current, or equivalently, the projection of the *time-dependent* photon-perturbed initial state on a time-dependent final state; that projection is then squared and appropriately Fourier transformed to give a frequency-dependent absorption coefficient.[19]

In a static-lattice, one-electron approximation and a two-band model, the initial and the final states (whether stationary or nonstationary) are electric field perturbed valence- and conduction-band states, respectively. The effects of the field $\mathbf{F}=F\hat{z}$ on each band may be calculated by solving either (i) the time-dependent Schrödinger equation for the nonstationary states or (ii) the time-independent Schrödinger equation for the stationary band states; in either case there remains the arbitrariness associated with the choice of gauge. The two most frequently used gauges are the time-dependent gauge[20] $\phi_0=0$, $\mathbf{A}_0=-c\mathbf{F}t$; and the time-independent gauge $\phi_0=\pm eFz$, $\mathbf{A}_0=0$ [the minus (plus) sign refers to the conduction (valence) band]. In the former gauge, one considers only nonstationary states and determines the time-dependent solutions of the one-band effective-mass equation

$$\frac{1}{2m^*}\left(\mathbf{p}-\frac{e}{c}\mathbf{A}_0\right)^2\psi(\mathbf{r},t)=i\hbar\frac{\partial\psi}{\partial t}(\mathbf{r},t)\,. \qquad (2.1)$$

These solutions are (neglecting the periodic part of the Bloch functions and normalized within a volume V)[21]

$$\psi_{\mathbf{k}}(\mathbf{r},t)=V^{-1/2}\exp i\{\mathbf{k}\cdot(\mathbf{r}-e\mathbf{F}t^2/2m^*) -[(\hbar^2k^2/2m^*)+e^2F^2t^2/6m^*)]t/\hbar\}\,. \qquad (2.2)$$

In the time-independent gauge, there are two widely used approaches. One is to solve the time-dependent equation

$$\left(\frac{p^2}{2m^*}-eFz\right)\psi(\mathbf{r},t)=i\hbar\frac{\partial\psi}{\partial t}(\mathbf{r},t) \qquad (2.3)$$

for the Houston functions[22]

$$\psi_{\mathbf{k}(t)}(\mathbf{r},t)=V^{-1/2}\exp i\left\{\mathbf{k}(t)\cdot\mathbf{r}-\int^t E[\mathbf{k}(t')]dt'\right\} \qquad (2.4)$$

with changing momentum and energy:

$$h\dot{\mathbf{k}}(t)=e\mathbf{F}/m^* \quad\text{and}\quad E(\mathbf{k})=\hbar^2k^2/2m^*. \qquad (2.5)$$

Another approach involves the solution of the eigenvalue problem

$$(p^2/2m^*-eFz)\psi(\mathbf{r},E)=E\psi(\mathbf{r},E) \qquad (2.6)$$

for the stationary-state plane-wave-modulated Airy functions[23]

$$\psi_{k_xk_y}(\mathbf{r},E)=V^{-5/12}(2\lambda\pi^2)^{1/4}\exp(ik_xx+ik_yy) \times\mathrm{Ai}\{\lambda z+[\lambda/eF][E-\hbar^2(k_x^2+k_y^2)/2m^*]\}\,, \qquad (2.7)$$

where $\lambda^3=2m^*|e|F/h^2$. The Houston and Airy functions are related to the functions calculated in the time-dependent gauge by gauge transformations; they are related to each other by a unitary (Fourier) transformation (as may be verified by examining the integral representation of the Airy function[24]).

Of the three pictures, the Houston picture is the most attractive physically, since the wave-functions represent electrons accelerating according to Newton's law $h\dot{\mathbf{k}}=e\mathbf{F}$ with steadily changing kinetic energy; the Houston picture is also easily generalized to nonparabolic energy bands providing a vivid classical picture of the electron or the hole as it oscillates back and forth through the bands with its effective mass changing.[25] The wave functions of the time-dependent gauge have constant crystal momentum but changing energy. The Airy functions bear less resemblance to the classical accelerated electron, but are the easiest to handle mathematically. Like the Houston functions, the Airy functions and their momentum-space counterparts (the crystal momentum representation)[26] can be generalized for use with nonparabolic bands. In this stationary-state Airy picture, the acceleration of the electron manifests itself as progressively more rapid oscillations in the wave function for large negative values of z. The

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[21] Of the two factors in the Bloch function, the field generally affects the plane-wave part considerably more, since the periodic part is atomiclike and therefore only weakly polarized by typical laboratory-strength fields.

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[23] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Ltd., London, 1958), p. 71.

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[25] For a more picturesque description of the dynamics of an electron in an applied field, see, e.g., J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, London, 1964), pp. 163–165.

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presence of a field is responsible for a tilting of the band edges in real space, with the band edges remaining parallel and separated *vertically* by the gap energy. Therefore the wave functions of the valence and the conduction-band states have exponentially decaying tails extending into the forbidden energy gap when the field is on. (If we define "momentum" by $p^2/2m^* - eFz = E$, this decaying tail corresponds to "imaginary momentum.") Thus it is possible for a light wave to induce a band-to-band transition with energy less than the gap energy. The local nature of the electromagnetic perturbation requires that the transition be vertical on a plot of energy versus position; that is, such a low-energy transition can occur only between the tail parts of the wave functions and hence its oscillator strength is smaller than the higher-energy band-to-band transitions. Therefore, in this picture the Franz-Keldysh effect may be viewed as a photon-assisted tunneling of an electron from the valence band to the conduction band,[27] the energy dependence of the transition probability being dominated by the band-to-band matrix element rather than by the density of states.

In contrast, if one uses nonstationary band states to calculate the transition (as in the Houston picture or in the time-dependent gauge), then the energy dependence comes from the effective density of states arising from the frequency Fourier decomposition of the time-dependent transition rate. The various pictures are, of course, connected by unitary transformations; or equivalently, the time-varying Bloch functions may be written as a superposition of wave functions whose tails extend into the forbidden gap (e.g., Airy functions) and vice versa.

However, none of these one-electron pictures is adequate for a discussion of electron-hole interactions and the formation of excitons. For this reason, concentrating on the fact that we are interested in the optical absorption below the zero-field threshold, we specialize the discussion to the case of two parabolic energy bands with minimum and maximum at the center of the Brillouin zone. The electron and hole masses are assumed to be scalar; with this approximation the transformation to center-of-mass and relative-motion coordinates is possible. Since the total charge of electron and hole is zero and the electric field is uniform, the center-of-mass motion reduces to the propagation of a free particle. The relative motion, however, will be uncorrelated free-particle-like only if the electron does not interact with the hole and if the applied electric field is zero (the field introduces correlations in the motions of the electron and hole in that it accelerates them in opposite directions). The electron-hole envelope wave function $U(\mathbf{r})$ describes the amplitude for finding the electron and the hole separated by the vector $\mathbf{r}$; that is, $|U(\mathbf{r})|^2$ is essentially the pair correlation function. To include electron-hole correlations in the optical-absorption cross section, one ought to (a) take the band-to-band cross section for optical transitions between plane-wave states (or Bloch states) which extend throughout the entire crystal, (b) multiply it by the probability $|U_\nu(0)|^2$ that the electron and hole are in the same unit cell, and (c) sum over all electron and hole wave vectors, and the states of relative motion ν.[9,28,29] In the case of no electron-hole scattering and zero electric field, the envelope function for relative motion is $U_{\mathbf{k}}(\mathbf{r}) = V^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}$; hence, we obtain the usual band-to-band transitions. For zero field, but with a Coulomb interaction, $U(\mathbf{r})$ becomes a hydrogenic wave function, and gives rise to the well-known hydrogenic absorption spectrum.[9,28,29] If the electric field is finite but the Coulomb interaction is turned off, $U(\mathbf{r})$ becomes a product of plane waves (propagating in the plane perpendicular to the field) times an Airy function (along the field).[30]

The case of interest here involves both the Coulomb interaction between the electron and the hole and the force exerted by the applied electric field. In the conventional gauge (rather than the time-dependent gauge), the Schrödinger equation for relative motion is

$$\left(\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{\epsilon r} - eFz\right)U_\nu(\mathbf{r}) = EU_\nu(\mathbf{r}), \qquad (2.8)$$

where μ is the exciton reduced mass ($\mu^{-1} = m_e^{-1} + m_h^{-1}$), ϵ is the (static) dielectric constant of the solid, $\mathbf{F}$ is the electric field and is taken to be in the z direction, e is the electronic charge ($e = -|e|$), $2\pi\hbar$ is Planck's constant, and $E=0$ corresponds to the gap energy E_g. The potential energy of relative motion as a function of position along the direction of the field is depicted schematically in Fig. 1. The straight line through open triangles is the potential due to the applied electric field; the Schrödinger equation for such a potential has a continuous eigenvalue spectrum with Airy functions as its solutions. Such functions oscillate in the far left half-plane ($z \ll 0$) and are exponentially damped in the far right half-plane ($z \gg 0$). The transition from oscillatory to damped behavior occurs at the classical turning point $z = -E/eF = E/|e|F$. Here E is the energy of the electron[31] measured relative to the zero-field gap energy ($E + E_g = \hbar\omega$ = photon energy). For this uniform field $U(z)$ is exponentially small for energies E less than

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[27] Zener tunneling may be thought of as a Franz-Keldysh absorption induced by a zero energy "static photon" associated with the interband perturbation of the effective-mass Hamiltonian. See C. Zener, Proc. Roy. Soc. (London) **145**, 523 (1934).

[28] R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5, pp. 37ff; pp. 119ff.

[29] T. P. McLean, in *Progress in Semiconductors*, edited by A. F. Gibson *et al.* (John Wiley & Sons, Inc., New York, 1961), Vol. 5, p. 54.

[30] K. Tharmalingam, Phys. Rev. **130**, 2204 (1963).

[31] We shall visualize this problem as the corresponding hydrogen-atom problem, often assuming that the hole is infinitely massive and the electron moves in its force field, although we are, in fact, discussing the *relative* motion of electron and hole.

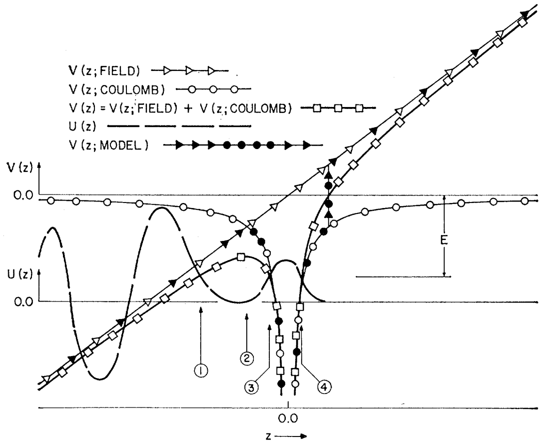

FIG. 1. The various potentials V (solid curves) and the envelope of the wave function U (broken curve) of relative motion as functions of the relative position of the electron and hold along the field direction. Open triangles and circles show the applied field and the Coulomb potential, respectively. Open squares show the exact potential of the combination. Circled positions 1, 3, and 4 are the classical turning points; position 2 is the local maximum of potential. The wave-function envelope shown is for the exact potential and for a state of energy E somewhat below this local maximum V (the classical ionization energy). The curve through the filled triangles and circles shows the spirit of the model potential used by Duke and Alferieff (Ref. 12).

the potential energy at the classical turning points; and, in particular, $U(0)$ is exponentially small for energies within the zero-field forbidden gap ($E<0$). This phenomenon is just the Franz-Keldysh effect discussed earlier in a one-electron picture.

The Coulomb interaction potential is the line through the open circles; the sum of it and the applied potential is denoted by open squares. The qualitative behavior of the wave function $U(z)$ (depicted for a value of E less than zero) is included in Fig. 1 as the broken curve: (i) It oscillates in the far left plane, (ii) crosses into the potential barrier at a classical turning point ① where $-e^2/\epsilon z-eFz=E$, (iii) is damped exponentially into the point ② where the potential barrier is a maximum $[z=-(|e|/\epsilon F)^{1/2}]$, (iv) *rises exponentially* until it crosses through the second classical turning point ③ ($-e^2/\epsilon z-eFz=E$), (v) remains relatively flat near $z=0$ (for an s-like state), (vi) crosses into the potential barrier in the right half-plane at ④ ($-e^2/\epsilon z-eFz=E$), and (vii) decays exponentially. The difference between the cases with electron-hole interaction and without is that steps (iv), (v), and (vi) above would be missing if the Coulomb term were turned off. Hence the Coulomb interaction (i) reduces the spatial decay rate of the wave function in the barrier (since the barrier is smaller), (ii) leads to an exponential *rise* in $U(\mathbf{r})$ as $\mathbf{r}$ approaches zero, and (iii) allows $U(\mathbf{r})$ to be totally undamped near the origin. Therefore we expect that the inclusion of the electron-hole Coulomb interaction will *exponentially* enhance $U(0)$ and the optical-absorption coefficient. In making these statements, we have tacitly assumed that the wave-function normalization is unaffected by the Coulomb interaction. This is true, in fact, because the potential energy associated with the electric field is unbounded below. Thus the wave function can be normalized only by confining the system to a large but finite box. In such a case the overwhelming contribution to the normalization comes from near the boundary of the box. Note also that the tunneling of the electron away from the hole makes the wave functions qualitatively different from the zero-field hydrogenic functions (no matter how small F is). It is this qualitative difference which is responsible for the divergence of perturbation theory. Observe also that the Coulomb interaction, on account of its long range, affects the *quantitative* behavior of the wave functions at large values of $|z|$. For example, the wave function undoubtedly approaches a logarithmically phase-shifted Airy function as z approaches negative infinity; much as Coulomb waves become logarithmically phase-shifted plane waves in the zero-field case.[32] However, in the asymptotic regions the solutions to Eq. (1) look *qualitatively* like Airy functions: For $z\rightarrow-\infty$, they have increasingly rapid oscillations (the momentum of the electron is increasing) which gradually diminish in amplitude (the current associated with the electron is finite).

The above considerations apply to the situation where the photon energy is such that $E<-(e^2/\epsilon|z|)+|e|Fz$ for some $z<0$; that is, energies such that the electron must tunnel through a barrier in order to get away from the hole. At higher energies the exciton is ionized by the applied field, but is still strongly affected by the Coulomb interaction. *Even though the exciton is ionized by the field it can still be responsible for a very strong and quite sharp line in the optical-absorption spectrum.* The reason for this is that the electron is in a resonancelike state in which it coherently bounces back and forth off the walls of the hole's potential, especially in the x and y directions, before it leaks out to infinity in the z direction. (Even if the energy is positive, so that there is no Coulomb potential wall in any direction, the electron once created near the hole will still have a desire to stay there since the classical forces are in that direction.) An exact *classical* criterion for the ionization of the nth ($n=1, 2, \ldots$) exciton of zero-field binding energy $E_n=-R/n^2=-|E_n|$ may be obtained by considering the energy required to get over the potential hump in Fig. 1. For an exciton of binding energy $E_n=-R/n^2$, this results in a critical field for ionization of $F_c=\epsilon E_n^2/4|e|^3$ (or, in terms of the exciton Rydberg R and radius a, $f_c\equiv|e|Fa/R=1/8n^4$). In general, quantum effects will result in an even smaller critical field since the field-perturbed levels will often shift to higher energies than the unperturbed $E_n=-R/n^2$, and tunneling will help the electron go through the

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[32] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Ltd., London, 1958), p. 419.

potential barrier. Note that even though ionization of the nth exciton occurs for fields stronger than $F_c = R/8n^4ea$, a discernible exciton peak remains in the absorption for fields an order of magnitude larger, as may be seen from both experimental[33] and theoretical[17,18,34] absorption spectra.

Duke and Alferieff have proposed a somewhat similar criterion for ionization based on calculations with their model potential.[12] Their calculations indicate that the exciton peaks disappear for field strengths giving values of f in excess of 0.30 and 0.10 for the $n=1$ and $n=2$ lines, respectively. The classical criterion indicates that ionization occurs at smaller values of f, namely, 0.125 and 0.0078, respectively. However, as we have emphasized, even though ionization may occur, well-defined but broad peaks will be shown to remain for fields as strong as $|e|Fa/R = f = 0.8$ and 0.2 for the first and the second exciton, respectively. The differences between Duke's and Alferieff's approximate results and the more exact answers can be attributed to their model potential. That potential is, we believe, also responsible for the prediction (which fails to agree with our numerical results) that the Coulomb interaction does not alter the shape of the low-energy Franz-Keldysh edge. The potential was formulated in parabolic coordinates

$$\xi = r + z, \tag{2.9a}$$

$$\zeta = r - z, \tag{2.9b}$$

in which the Schrödinger equation (2.8) separates so that the total effective potential energy becomes a sum of parts depending on the individual coordinates

$$\mathcal{V}_{\text{eff}}(\xi,\zeta) = \mathcal{V}_1(\xi) + \mathcal{V}_2(\zeta).$$

Duke and Alferieff chose $\mathcal{V}_1(\xi)$ to be purely Coulombic or purely uniform-field-like depending on whether ξ was less than or greater than a chosen parameter l; with a similar choice for $\mathcal{V}_2(\zeta)$. There is some inconsistency in this choice since, for example, $\mathcal{V}_2(\zeta)$ would be purely Coulombic everywhere along the positive z axis, while $\mathcal{V}_1(\xi)$ is Coulombic all along the negative z axis. Nevertheless, we have overlooked the topological complications of parabolic coordinates, and have illustrated what we believe the Duke and Alferieff potential was *meant to represent* by the curve through the filled circles and triangles in Fig. 1. It should be clear (as Duke and Alferieff emphasized) that such a potential generally underestimates the tunneling of the electron away from the hole and the linewidths as is indeed the case in Ref. 12. As those authors recognized, their potential also fails to provide an accurate description of the Stark shifts since it excludes the applied electric field from the region where the wave function is large, while excluding the Coulomb potential from the region where $|eFz|$ is large.

Before moving on to more formal topics, it is appropriate for us to say a few words about units and numbers. The natural units of energy and length for this problem are the exciton Rydberg R and the exciton Bohr radius a, respectively,

$$R = e^2/2\epsilon a, \quad a = \hbar^2\epsilon/\mu e^2.$$

In these units, the binding energy of the 1s exciton is -1. The field strength is therefore naturally written in terms of the dimensionless parameter

$$f = \frac{F}{(R/|e|a)} = 3.89\times10^{-10}\epsilon^3\left(\frac{m_0}{\mu}\right)^2 F \quad (F \text{ in V/cm}). \tag{2.10}$$

Note that f is the ratio of the potential energy drop of the field across the radius of the exciton to the exciton binding energy. In these units the relative-motion Schrödinger equation (2.8) becomes

$$(-\nabla^2 - 2/r + fz)U = EU,$$

where we have made the transcription to unitless quantities $(\boldsymbol{\nabla}, \mathbf{r}, z, F, E) \to (a^{-1}\nabla, \mathbf{r}a, za, fR/|e|a, ER)$. Although it might appear that for small f the electric field can be treated as a perturbation, it cannot as we have stressed above. Likewise for large f, it is not generally permissible to neglect the Coulomb interaction or to treat it as a perturbation. The reason is that the Coulomb potential is unbounded below, and hence can guarantee that any perturbation series expansion is either physically meaningless or divergent. A similar situation occurs in the case of exciton effects on the zero-field absorption, where the actual theoretical absorption spectrum only begins to quantitatively coincide with the spectrum calculated omitting the electron-hole interaction at photon energies in excess of 4000R above threshold.[29]

Finally, in Table I we present the values of f which correspond to a field of 10^4 V/cm for various semiconductors and insulators with the listed reduced masses and dielectric constants. Also tabulated are R and a. In the case of insulators, these numbers should not be taken too literally, since the exciton radius is of the order of a lattice constant, the Wannier model breaks down, and there is some question concerning whether the low- or high-frequency dielectric constant or some intermediate value should be used for ϵ.[35] Thus the listed values of R, a, and f may be off by factors as large as 4.0, 0.5, and 8.0, respectively. Also, we have generally assumed that the hole mass is infinite so that the exciton reduced mass is equal to the electron mass, and we have overlooked the distinction between

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[33] Q. H. F. Vrehen, Phys. Rev. **145**, 675 (1966).

[34] J. D. Dow, S. A. Newman, and B. Y. Lao (unpublished).

[35] W. B. Fowler, Phys. Rev. **151**, 657 (1966). See this reference for more accurate exciton binding energies in insulators.

TABLE I. Relevant properties of excitons. Values of the exciton Rydberg $R=m^*e^2/2\epsilon^2\hbar^2$ and radius $a=\hbar^2\epsilon/m^*e^2$ are calculated from the measured values given for the static dielectric constant ϵ and electron effective mass m^*/m. Calculated values of our dimensionless field strength $\bar{f}$ [see Eq. (2.10)] correspond to an applied field of 10^4 V/cm.

Substance	(m^*/m)[a]	ϵ[b]	R (eV)	a (Å)	$\bar{f}$
Ge (direct)	0.033[c]	16	0.0018	250	
C (diamond)	(1)	5.8[d]	0.40	3.1	0.00078
GaP	0.34[e]	10	0.044	16	0.036
GaAs	0.067[e]	12	0.0061	94	1.5
InSb	0.015[f]	18[g]	0.00067	620	93
CdS	0.20[h]	8.9[i]	0.035	23	0.065
ZnO	0.24[i]	7.9	0.053	17	0.033
ZnS	0.28[j]	8.3	0.055	16	0.028
ZnTe	0.15[k]	9.7	0.020	35	0.17
PbS	0.16[l]	170	0.000072	575	8000
Cu_2O	0.80[m]	10[n]	0.10	6.9	0.0070
AgCl	0.35[o]	9.5	0.052	14	0.028
AgBr	0.24[o]	11	0.029	23	0.080
TlCl	0.32[o]	38	0.0031	62	2.0
TlBr	(1)	31[p]	0.015	16	0.10
MgO	(1)	9.8[n]	0.14	5.2	0.0037
LiF	(1)	9.0[q]	0.16	4.8	0.0029
NaCl	(1)	5.9[q]	0.39	3.1	0.0008
KCl	0.50[o]	4.5	0.33	4.8	0.0014
RbCl	0.52[o]	4.6	0.33	4.7	0.0015
CsCl	(1)	7.2[q]	0.26	3.8	0.0015

[a] If no value of m^*/m was available, it was taken to be unity.
[b] Sources for m^*/m and ϵ are the same unless otherwise indicated.
[c] Y. Hamakawa *et al.* (Ref. 59).
[d] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio, 1967).
[e] O. Madelung, *Physics of III-V Compounds* (John Wiley & Sons, Inc., New York, 1964).
[f] E. D. Palik, R. Kaplan, B. W. Henvis, J. R. Stevenson, S. Iwasa, and E. Burstein, in *Proceedings of the Ninth International Conference on Physics of Semiconductors, Moscow* (Nauka, Leningrad, 1968).
[g] R. B. Sanderson, J. Phys. Chem. Solids **26**, 803 (1965).
[h] J. J. Hopfield and D. G. Thomas Phys. Rev. **122**, 35 (1961).
[i] B. Segall, in *Proceedings of the Conference on II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967).
[j] J. C. Miklosz and R. G. Wheeler, Phys. Rev. **153**, 913 (1967).
[k] D. T. F. Marple and M. Aven, in footnote i.
[l] P. T. Bailey, M. W. O'Brien, and S. Rabii, Phys. Rev. **179**, 735 (1969).
[m] Deduced from data in M. Grossmann, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum Press, Inc., New York, 1968).
[n] F. C. Brown, in footnote m.
[o] J. W. Hodby, J. A. Borders, F. C. Brown, and S. Foner, Phys. Rev. Letters **19**, 952 (1967).
[p] D. H. Martin, Advan. Phys. **14**, 39 (1965).
[q] R. S. Knox and K. J. Teegarden, in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968) Appendix A.

the bare band mass and the phonon-enhanced mass (the enhancement will generally only be significant in the alkali halides).

III. FORMALISM

In this section we derive Elliott's formula for the coefficient of optical absorption by excitons, using the language of linear-response theory.[36] We have kept the derivation concise, referring to readable presentations where necessary. In addition to defining notation, this section is meant to state the approximations leading to the Elliott formula and to establish the relationships between well-known formulas of semiconductor optics and the less familiar notation of many-body physics. In doing this, we wish to emphasize that the modern many-body techniques allow us to find formally exact expressions for the dielectric function $\epsilon(\omega)$ and provide us with elegant machinery for systematically performing perturbation expansions. In the final analysis, however, mathematical elegance is no substitute for physical insight.

In order to calculate the optical properties of semiconductors in a uniform electric field $\mathbf{F}$, we assume that a plane monochromatic homogeneous transverse wave (associated with incident photons plus transverse magnetic interactions)[37–39] is propagating through the medium of interest, with oscillating electric field

$$\mathbf{E}(\mathbf{r},t)=\mathrm{Re}\,\mathfrak{E}e^{i\mathfrak{k}\cdot\mathbf{r}-i\omega t}.$$

Here $\mathfrak{E}$ and $\mathfrak{k}$ are complex: $\mathfrak{E}=\mathbf{E}_1+i\mathbf{E}_2$ and $\mathfrak{k}=\mathbf{k}_1+i\mathbf{k}_2$, where $k_1=\eta'(\omega)\omega/c$ and $k_2=\kappa(\omega)\omega/c$ define the (real) index of refraction $\eta'(\omega)$ and the extinction coefficient $\kappa(\omega)$.[40] We further assume that the semiconductor is isotropic (e.g., has cubic symmetry) and linear, and is characterized in the classical crystal optics limit[41] by a frequency-dependent complex dielectric function $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$ and a magnetic permeability $\mu(\omega)$ (which we henceforth take to be unity since the magnetic susceptibility of semiconductors in the frequency region of interest here is typically negligible compared with unity). Maxwell's equations then lead to the basic dispersion relation

$$\begin{aligned}\mathfrak{k}\cdot\mathfrak{k}&=(\omega^2/c^2)\mu(\omega)\epsilon(\omega)\\&=(\omega^2/c^2)(\eta'+i\kappa)^2\simeq(\omega^2/c^2)\epsilon(\omega).\end{aligned}\tag{3.1}$$

The absorption coefficient $K(\omega)$, which is defined as the fractional decrease in the time-averaged power density per unit distance in the direction of photon propagation, is then easily expressed in terms of the extinction coefficient, or alternatively in terms of the index of refraction and the imaginary part of the dielectric function

$$K(\omega)=2\kappa(\omega)\omega/c=\omega\epsilon_2(\omega)/c\eta'(\omega).\tag{3.2}$$

This latter expression is the one which is most useful for quantum-mechanical calculations, since $\epsilon_2(\omega)$, as we shall see, is related to the current induced by the transverse field $\mathfrak{E}$. A knowledge of $\epsilon_2(\omega)$ for all frequencies, together with the dispersion relation

$$\epsilon_1(\omega)-1=\frac{1}{\pi}P\int_{-\infty}^{\infty}\frac{\epsilon_2(x)}{x-\omega}dx,\tag{3.3}$$

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[36] G. H. Wannier, *Statistical Physics* (John Wiley & Sons, Inc., New York, 1966), p. 492; R. J. Kubo, J. Phys. Soc. Japan **12**, 570 (1957); M. S. Green, J. Chem. Phys. **20**, 1281 (1952).

[37] We work throughout in the Coulomb gauge. Note that $\mathfrak{E}$ is the field *in the medium*. (See Refs. 38 and 39.)

[38] D. Pines and P. Nozieres, *The Theory of Quantum Liquids, 1: Normal Fermi Liquids* (W. A. Benjamin, Inc., New York, 1966), p. 251ff.

[39] H. Ehrenreich, in *Proceedings of the International School of Physics "Enrico Fermi" Course XXXIV, Varenna, 1965*, edited by J. Tauc (Academic Press Inc., New York, 1966), pp. 113–128.

[40] F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 5, pp. 300ff.

[41] V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Wiley-Interscience, Inc., New York, 1966).

determines $\epsilon_1(\omega)$ and hence the index of refraction and the other optical constants.

Thus we concentrate on the calculation of $\epsilon(\omega)$ and, in particular, the imaginary part $\epsilon_2(\omega)$. The dielectric function may be obtained quantum mechanically by calculating the induced dipole moment per unit volume to first order in the perturbing field $\mathfrak{E}$;

$$\langle\mathfrak{P}\rangle=(\epsilon-1)\mathfrak{E}/4\pi\,,$$

but modern practice, which we shall follow, is to calculate instead the complex conductivity[42] $\sigma(\omega)=-i\omega\epsilon/4\pi$ in terms of the induced transverse current density $\langle\mathbf{J}\rangle$ in the direction $\hat{\epsilon}$ of polarization of the photon

$$\begin{aligned}\langle\hat{\epsilon}\cdot\mathbf{J}(\mathbf{r},t)\rangle&=\mathrm{Re}\int\sigma(\mathbf{r},\mathbf{r}',\omega)\cdot\mathfrak{E}e^{i\mathfrak{k}\cdot\mathbf{r}'-i\omega t}\,d^3r'\\&=\mathrm{Re}-\frac{i\omega}{4\pi}\int\epsilon(\mathbf{r},\mathbf{r}',\omega)\cdot\mathfrak{E}e^{i\mathfrak{k}\cdot\mathbf{r}'-i\omega t}\,d^3r'.\qquad(3.4)\end{aligned}$$

In the classical crystal optics limit, we assume only a local response function $\epsilon(\omega)$ which is characteristic of the entire crystal. In order to obtain such a classical optical response function, we multiply Eq. (3.4) by $e^{-i\mathfrak{k}\cdot\mathbf{r}}$ and average it over the volume of the crystal.[43] It follows that

$$\epsilon(\omega)=\int\int e^{-i\mathfrak{k}\cdot\mathbf{r}}\epsilon(\mathbf{r},\mathbf{r}'\omega)e^{i\mathfrak{k}\cdot\mathbf{r}'}d^3r\quad d^3r'/V.\qquad(3.5)$$

The Hamiltonian for the semiconductor in the presence of both the photon field and the uniform applied field $\mathbf{F}=F\hat{z}$ is

$$H=\sum_i\frac{1}{2m_i}\left(\mathbf{p}_i-\frac{e_i}{c}\mathbf{A}(\mathbf{r}_i,t)\right)^2+\sum_{i<j}\frac{e_ie_j}{|\mathbf{r}_i-\mathbf{r}_j|}-\sum_i e_iFz_i,\qquad(3.6)$$

where the sums run over all particles, and e_i, m_i, $\mathbf{r}_i$, and $\mathbf{p}_i$ are the charge, mass, position operator, and momentum operator, respectively, of the ith particle. The Hamiltonian can be rewritten, omitting terms of order A^2, giving $H=H_0+V'$, where

$$V'=-\frac{1}{c}\int d^3r\,\mathbf{J}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r},t)\,,\qquad(3.7)$$

and H_0 is the Hamiltonian of the semiconductor in the presence of the static electric field but in the absence of the photon (i.e., for $\mathbf{A}\equiv0$), and $\mathbf{J}(\mathbf{r})$ is the current-density operator[44] for the crystal.

Observing that $\mathbf{E}=-c^{-1}\,\partial\mathbf{A}/\partial t$, [i.e., $\mathbf{A}(\mathbf{r},t)=\mathrm{Re}(c/i\omega)\mathfrak{E}\exp(i\mathfrak{k}\cdot\mathbf{r}-i\omega t)$], the perturbation becomes

$$V(t')=\mathrm{Re}\frac{i}{\omega}\int\mathbf{J}(\mathbf{r}')\cdot\mathfrak{E}e^{i\mathfrak{k}\cdot\mathbf{r}'-i\omega t'}d^3r'.\qquad(3.8)$$

Linear-response theory[36] gives the following result for the induced transverse current

$$\langle\hat{\epsilon}\cdot\mathbf{J}(\mathbf{r},t)\rangle=-\frac{i}{\hbar}\int_{-\infty}^{\infty}dt'\theta(t-t')\times\langle\langle[\hat{\epsilon}\cdot\mathbf{J}(\mathbf{r},t-t'),V'(t')]\rangle\rangle.\qquad(3.9)$$

Here $\langle\langle\cdots\rangle\rangle$ means the (canonical ensemble) expectation value in the ground state of the crystal in the absence of the photon, $\theta(t)$ is the unit step function, $\langle\cdots\rangle$ means the expectation value in the photon-perturbed ground state, and $[A,B]$ is the commutator of A and B. Comparison of Eqs. (3.4), (3.5), (3.8), and (3.9) yields

$$\epsilon(\omega)=-\frac{4\pi}{\omega^2V}\left(\frac{-i}{\hbar}\right)\int_{-\infty}^{\infty}dt\theta\,(t)e^{i(\omega+i0+)t}\int d^3r\int d^3r'\times\langle\langle[e^{-i\mathfrak{k}\cdot\mathbf{r}}\hat{\epsilon}\cdot\mathbf{J}(\mathbf{r},t),\,\hat{\epsilon}\cdot\mathbf{J}(\mathbf{r}',0)e^{i\mathfrak{k}\cdot\mathbf{r}'}]\rangle\rangle.\qquad(3.10)$$

Here $0+$ is a positive infinitesimal. This expression for $\epsilon(\omega)$, with the current operators expressed in second-quantized form, provides the basis for evaluating the optical properties from the two-particle Green's function.[45] Using the identity $(x+i0+)^{-1}=Px^{-1}-i\pi\delta(x)$, inserting a complete set of eigenstates $|n\rangle$ of H_0, we perform the time integrations in the usual fashion.[46] Assuming dipole transitions, and assuming the incident light beam is not significantly attenuated in one exciton mean free path, we arrive at the usual expression for the imaginary part of the dielectric function

$$\epsilon_2(\omega)=\frac{4\pi^2}{\omega^2V}\lim_{q\to0}\sum_n|\langle0|\,\hat{\epsilon}\cdot\mathfrak{J}(\mathbf{q})\,|n\rangle|^2\delta(\hbar\omega-\hbar\omega_{n0}).\qquad(3.11)$$

Here $\mathfrak{J}(\mathbf{q})$ is the Fourier transform of the current operator, $|0\rangle$ is the ground state of the crystal in the presence of the field $\mathbf{F}$, but not of the photon, and $\hbar\omega_{n0}$ is the excitation energy of the excited state $|n\rangle$.

We assume the crystal lattice to be fixed[47] and take the electronic states $|n\rangle$ to be exciton states of total

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[42] In optical calculations, the coefficient $\epsilon(\omega)+4\pi i\sigma(\omega)/\omega$, where the dielectric function $\epsilon(\omega)$ and the conductivity $\sigma(\omega)$ are both complex, often appears as a result of the indistinguishability of real and polarization currents at optical frequencies. We have resolved this ambiguity between real and polarization currents by *defining all* currents to be polarization currents, assuming $\sigma=0$ taking $\epsilon=\epsilon_1+i\epsilon_2$, and defining the "conductivity" in terms of ϵ as $-i\omega\epsilon/4\pi$.

[43] We neglect local-field effects, which should be small. See, e.g., N. Wiser, Phys. Rev. **129**, 62 (1963); S. L. Adler, *ibid.* **126**, 413 (1962); D. S. Falk, *ibid.* **118**, 62 (1960).

[44] J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964), p. 206.

[45] M. Porsch, Phys. Status Solidi **27**, 359 (1968); D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

[46] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), Chap. 21.

[47] The corrections for lattice distortion are typically very small except in the paraelectric perovskites. See, e.g., J. R. Brews, Phys. Rev. Letters **18**, 662 (1967).

momentum $\mathbf{K}$ and internal quantum numbers ν $|\mathbf{K}cv\nu\rangle$ formed by appropriate superposition of electron-hole pairs, with the weighting of each pair state determined by the electron-hole envelope function $U_{cv\nu\mathbf{K}}(\mathbf{R}^0)$:

$$|\mathbf{K}cv\nu\rangle = V^{1/2}N^{-1}\sum_{\mathbf{R}_{eh}0} U_{cv\nu\mathbf{K}}(\mathbf{R}^0{}_{eh}) \times \sum_{\mathbf{R}_h0} e^{i\mathbf{K}\cdot\mathbf{R}^0{}_h} c^+{}_{c\mathbf{R}_h{}^0+\mathbf{R}_{eh}{}^0} c_{v\mathbf{R}_h{}^0}|0\rangle. \quad (3.12)$$

Here N is the number of unit cells, the subscripts c, v refer to the (nondegenerate) conduction and valence bands from which the exciton is formed, and $c_{n\mathbf{R}^0}$ ($c_{n\mathbf{R}^0}{}^+$) destroys (creates) a Wannier state in band n centered at lattice site $\mathbf{R}^0$. The c's and c^+'s satisfy the usual fermion anticommutation rules, and we have omitted all spin indices. Introducing the second-quantized representation for the current operator, in terms of the one-electron matrix element $(i\mathbf{R}_i{}^0|e^{-i\mathbf{q}\cdot\mathbf{r}}\mathbf{p}|j\mathbf{R}_j{}^0)$ between Wannier states,

$$\mathfrak{J}(\mathbf{q}) = \sum_{\mathbf{R}_i{}^0,\,\mathbf{R}_j{}^0} \frac{e}{m}(i_i\mathbf{R}_i{}^0|e^{-i\mathbf{q}\cdot\mathbf{r}}\mathbf{p}|j\mathbf{R}_j{}^0) c^+{}_{i\mathbf{R}_i{}^0} c_{j\mathbf{R}_j{}^0}, \quad (3.13)$$

we obtain the current matrix element

$$\langle 0|\hat{\epsilon}\cdot\mathfrak{J}(\mathbf{q})|\mathbf{K}cv\nu\rangle = \frac{eV^{1/2}}{mN}\sum_{\mathbf{R}_{eh}{}^0} U_{cv\nu\mathbf{K}}(\mathbf{R}_{eh}{}^0) \times \sum_{\mathbf{R}_h{}^0} e^{i\mathbf{K}\cdot\mathbf{R}_h{}^0}(v,\mathbf{R}_h{}^0|e^{-i\mathbf{q}\cdot\mathbf{r}}\hat{\epsilon}\cdot\mathbf{p}|c,\mathbf{R}_h{}^0+\mathbf{R}_{eh}{}^0). \quad (3.14)$$

Since the single-particle momentum matrix element in Eq. (3.13) is to be evaluated using wave functions localized at sites $\mathbf{R}_h{}^0+\mathbf{R}_{eh}$, the dominant contribution to the current matrix element will occur when the valence and conduction Wannier functions occupy the same site ($\mathbf{R}_{eh}{}^0=0$) and have maximum overlap. An alternative, and more conventional expression for the current matrix element is obtained by introducing the single-particle Bloch states

$$|n\mathbf{k}\rangle = N^{-1/2}\sum_{\mathbf{R}_n{}^0} e^{-i\mathbf{k}\cdot\mathbf{R}_n{}^0}|n\mathbf{R}_n{}^0\rangle, \quad (3.15)$$

resulting in

$$\langle 0|\hat{\epsilon}\cdot\mathfrak{J}(\mathbf{q})|\mathbf{K}cv\nu\rangle = \frac{eV^{1/2}}{mN}\sum_{\mathbf{R}_{eh}{}^0} U_{cv\nu\mathbf{K}}(\mathbf{R}_{eh}{}^0) \times \sum_{\mathbf{k}}\langle v\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}\hat{\epsilon}\cdot\mathbf{p}|c\mathbf{k}+\mathbf{K}\rangle e^{-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_{eh}{}^0} \quad (3.16)$$

Concentrating on photon energies in the neighborhood of the threshold for "allowed" transitions,[48] we approximate the single-particle matrix element by its value at the minimum point ($\mathbf{k}_0=0$) in the difference between conduction and valence bands.[49] With this approximation, the sum over $\mathbf{k}$ in Eq. (3.16) can be performed, resulting in a δ function in $\mathbf{R}_{eh}{}^0$. The remaining expression for current matrix element may be inserted into Eq. (3.11) to give the imaginary part of the dielectric function:

$$\epsilon_2(\omega) = \frac{4\pi^2e^2}{\omega^2m^2}\lim_{\mathbf{K}\to 0,\mathbf{k}_0\to 0}|\langle v\mathbf{k}_0|e^{-i\mathbf{q}\cdot\mathbf{r}}\hat{\epsilon}\cdot\mathbf{p}|c\mathbf{k}_0+\mathbf{K}\rangle| \times\sum_{\nu}|U_{cv\nu\mathbf{K}}(0)|^2\delta(\hbar\omega-E_G-E_{cv\nu\mathbf{K}}), \quad (3.17)$$

and the Elliott formula for the "allowed" optical-absorption coefficient[9]:

$$K_{\mathrm{A}}(\omega) = \frac{4\pi^2e^2}{m^2c\eta'(\omega)\omega}|\langle v\mathbf{k}_0|\hat{\epsilon}\cdot\mathbf{p}|c\mathbf{k}_0\rangle|^2 \times\sum_{\nu}|U_{\nu}(0)|^2\delta(E-E_{\nu}). \quad (3.18)$$

Henceforth, we suppress the indices c, v, and $\mathbf{K}(=0)$, and let $E=\hbar\omega-E_g$.

There remains only the specification of the electron-hole envelope function $U(\mathbf{r})$. Noting that the exciton, on account of its small binding energy, is considerably more polarizable than a unit cell, we assume that the periodic parts of the Bloch states are unaltered by the applied field.[50] In this case, the wave equation for $U(\mathbf{r})$ reduces (in the Wannier continuum limit) to the hydrogenlike effective-mass equation[51,52]

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{\epsilon r}-eFz\right)U_{\nu}(\mathbf{r}) = EU_{\nu}(\mathbf{r}). \quad (3.19)$$

The label ν stands for energy E, azimuthal quantum number m, spin σ, and "parabolic eigenvalue" t. The function $U(\mathbf{r})$ is to be normalized to unity over the volume of the crystal.

IV. NUMERICAL CONSIDERATIONS

The calculation of the electroabsorption has been reduced to the solution of the effective-mass equation (3.19) (in dimensionless form):

$$(-\nabla^2-2/r+fz)U_{\nu}(\mathbf{r}) = EU_{\nu}(\mathbf{r}), \quad (4.1)$$

for the wave function at the origin and the density of states per unit energy. The introduction of parabolic

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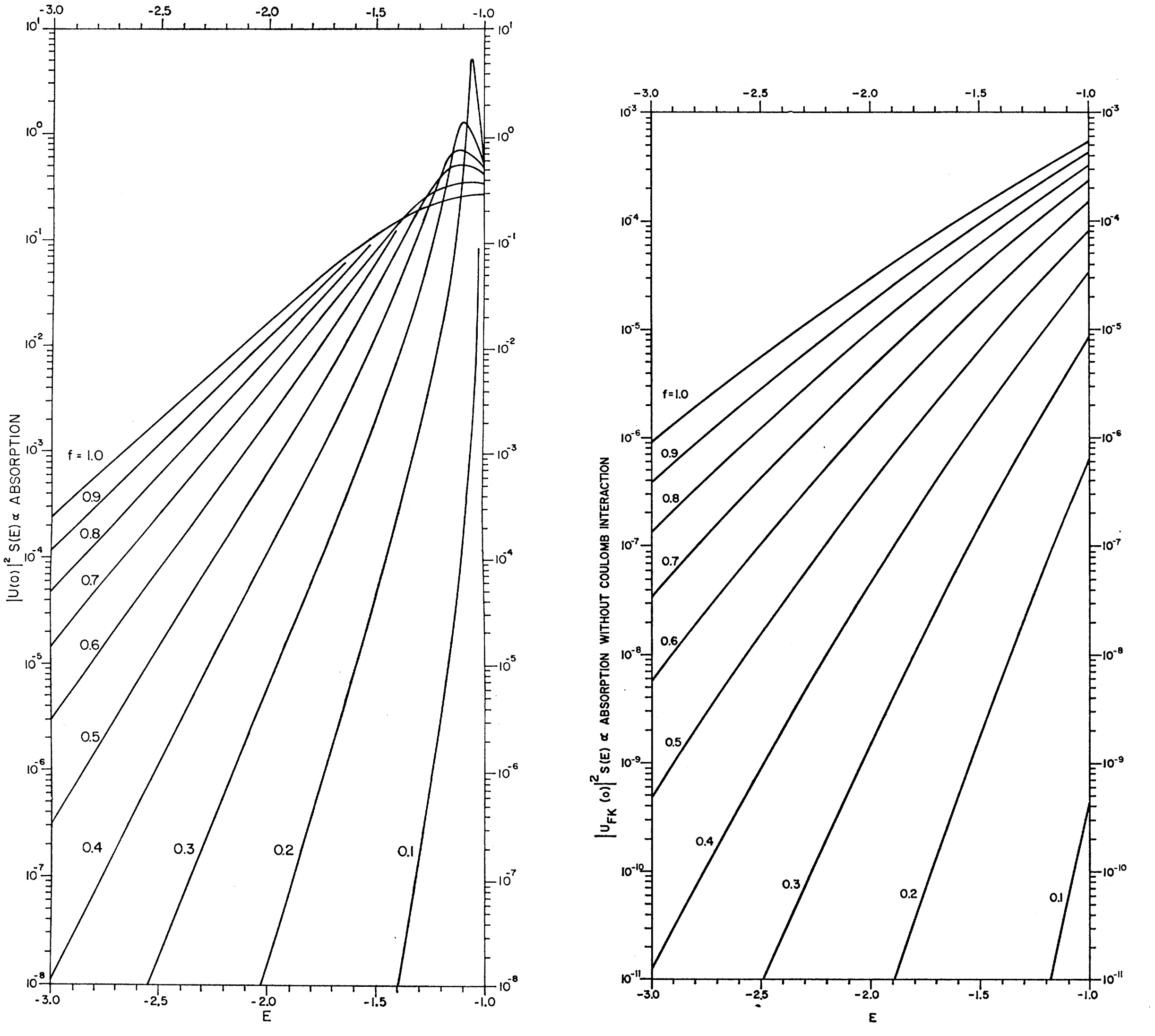
[48] R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5, p. 121.

[49] The relative error introduced by this approximation is of order a_L/a where a_L is the lattice constant and a is the exciton radius.

[50] Thus we neglect terms of order $R/\Delta E$, where ΔE is a typical interband energy separation and is typically of order 1 eV except in cases of nearly degenerate bands.

[51] L. J. Sham and T. M. Rice, Phys. Rev. **144**, 708 (1966); G. H. Wannier, *ibid.* **52**, 191 (1937).

[52] We neglect changes in the static dielectric function due to the applied field. See, e.g., V. M. Agranovich, Fiz. Tverd. Tela **8**, 2801 (1966) [English transl.: Soviet Phys.—Solid State **8**, 2239 (1966)].



(a) (b)

FIG. 2. (a) Spectral shape of the calculated absorption edges for different field strengths. Energy is measured from the energy gap in units of the binding energy of the unperturbed exciton. (b) Same as in (a) except the Coulomb interaction turned off, giving the Franz-Keldysh result. Note shift of vertical scale.

coordinates,[53]

$$\xi=r+z,\qquad \zeta=r-z,\qquad \phi=\phi,$$
$$x=(\xi\zeta)^{1/2}\cos\phi,\quad y=(\xi\zeta)^{1/2}\sin\phi,\quad z=\tfrac{1}{2}(\xi-\zeta),\tag{4.2}$$

allows the separation of the Eq. (4.1)[54] into

$$\chi_1''-V_1(\xi)\chi_1=0,\tag{4.3a}$$

$$\chi_2''-V_2(\zeta)\chi_2=0,\tag{4.3b}$$

where

$$U(\mathbf{r})=\frac{\chi_1(\xi)\chi_2(\zeta)}{(\xi\zeta)^{1/2}}e^{im\phi},\tag{4.4}$$

$$V_1(\xi)=-\left(\frac{1-m^2}{4\xi^2}+\frac{t}{\xi}+\tfrac{1}{4}E-\tfrac{1}{8}f\xi\right),\tag{4.5}$$

and

$$V_2(\zeta)=-\left(\frac{1-m^2}{4\zeta^2}+\frac{1-t}{\zeta}+\tfrac{1}{4}E+\tfrac{1}{8}f\zeta\right).\tag{4.6}$$

The quantity t is the separation parameter or "parabolic eigenvalue." Note that the "potential" $V_1(\xi)$ is positive as $\xi\to\infty$, so that $\chi_1(\xi)$ is exponentially decaying in

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[53] The notation here is the same as Ralph's (Ref. 17), except for a factor of 2 (for spin) which we have included. Note that the quantity we plot in Fig. 2 [$|U(0)|^2 S(E)$ for one spin] is the same as the one Ralph plots.

[54] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Ltd., London, 1958), p. 251.

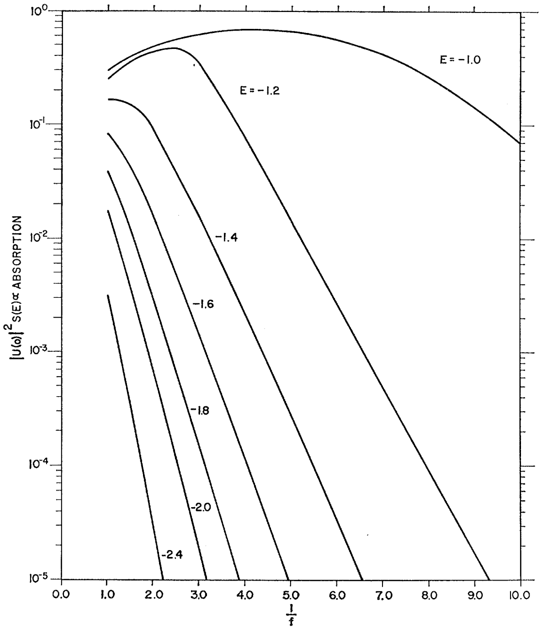

FIG. 3. Field dependence of the absorption coefficient at several spectral positions in the absorption edge. The electric field is measured in the dimensionless form defined in Eq. (2.10).

that region of space; hence the eigenvalue t will have an infinite number of discrete values t_n, where $n=0$, 1, 2 . . . is the number of nodes in $\chi_1(\xi)$. Similar consideration reveal that $\chi_2(\zeta)$ is oscillatory for large ζ. Hence the program for solving the Schrödinger equation is (a) fix E, specify n, and guess an approximate eigenvalue t_n; (b) numerically solve the quasi-Schrödinger equation (4.3a) determining the eigenvalue t_n and the normalized value of $\xi^{-1/2}\chi_1(\xi)$ as $\xi \rightarrow 0$; (c) integrate the second quasi-Schrödinger equation (4.3b) and obtain $\zeta^{-1/2}\chi_2(\zeta)$ as $\zeta \rightarrow 0$ and the density of states. Thus the eigenfunctions of the effective-mass equation may be labeled by four quantum numbers; the energy E, the eigenvalue t_n [n is the number of nodes in $\chi_1(\xi)$], the azimuthal quantum number m, and the spin σ.

[Note that for $m \neq 0$, $U(\mathbf{r} \rightarrow 0; E, n, t_n, m, \sigma)$ is zero and there is no contribution to the "allowed" absorption.] The details of the integration procedure may be found in Ralph's paper[17]; we have repeated the essential features in the Appendix for convenience. The resulting expression for the absorption coefficient for the case of "allowed" transitions is

$$K_{\mathrm{A}} = \frac{2\pi^2 e^2}{m^2 c \eta' \omega} 2|\langle c\mathbf{k}_0 | \hat{\epsilon}\cdot\mathbf{p} | v\mathbf{k}_0\rangle|^2 |U(0)|^2 S(E), \quad (4.7)$$

where, in the notation of the Appendix,

$$|U(0)|^2 S(E) = \frac{1}{Ra^3} \sum_n \left[A^2\pi^2 f^{1/2} \int_0^\infty \chi_{1-UN}{}^2(\xi)\xi^{-1} d\xi \right]^{-1}. \quad (4.8)$$

The numerical integration of Eq. (4.3) utilized Numerov's method,[55] with the eigenvalues t_n of Eq. (4.3a) determined by Cooley's correction formula.[56] Numerical errors were kept to a minimum by using an interval-doubling scheme which permitted utilization of a fine mesh where the wave functions varied rapidly and a coarser mesh in the regions where the functions χ_1 and χ_2 were smooth. In order to feel confident of our results, we (1) ran the computer program on two different computers with different hardware and software; (2) ran the program in both single- and double-precision arithmetic; and (3) "turned-off" the Coulomb interaction by replacing the $1-t$ in V_2 with $(-t)$. In cases (1) and (2) our results did not change, indicating that there was no random numerical error responsible for our answers. In case (3), we recovered the results of the Franz-Keldysh effect without the electron-hole interaction; this suggests that it is extremely unlikely that any significant systematic numerical error is present in our results.

The results of the calculations are presented in Figs. 2 and 3, where $|U(0)|^2 S(E)$, which is proportional to the absorption coefficient, is plotted as a function of energy E for various fields f and as a function $1/f$ for various values of E, respectively. For comparison's sake, we have included in Fig. 2(b) the corresponding values of $|U(0)|^2 S(E)$ calculated for the Franz-Keldysh effect (with no electron-hole interaction). Note that $E=-1.0$ is the binding energy of the unperturbed exciton and that f is the field strength in units of exciton Rydbergs per electron-exciton Bohr radius.

V. CONCLUSIONS

Two significant facts emerge from these calculations: (1) Well below the edge, the logarithm of the absorption coefficient varies very nearly *linearly* with the photon energy; and (2) below the zero-field absorption threshold, the absorption varies exponentially as $1/f$. That is, for small fields[57] and energies below the zero-field edge ($f \ll -E$), the absorption coefficient varies asymptotically as

$$K_A \sim \exp[-C_0 |E_0 - E| / f], \quad (5.1)$$

where C_0 and E_0 are constants. This directly contradicts a theorem of Duke and Alferieff[12] which states that in this limit the absorption coefficient reduces to the Franz-Keldysh coefficient

$$K_{A,FK} \sim \exp[-C_0' |E_0' - E|^{3/2} / f].$$

We should emphasize that the asymptotic form (5.1) has been deduced from numerical data, and therefore has in no rigorous sense been proven by us to be a

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general relationship. However, the energy dependence has been examined over 27 decades of absorption, and there seems to be only enough deviation from Eq. (5.1) to account for a multiplicative power of the energy—certainly no $\frac{3}{2}$ in place of unity in the exponent of $E-E_0$. The field dependence is based on somewhat more limited information, since we did not study extremely small fields. However, the field dependence seems to be the same as for the Franz-Keldysh effect, and attempts at least-squares fits to the field dependence of the calculated absorption seem to yield an exponent for f of minus unity within less than 5%.

The source of the difference between the Franz-Keldysh asymptotic form and the one obtained in this work seems to lie in the Coulomb interaction's reduction and distortion of the potential barrier through which the electron must tunnel in order to escape from the hole. The lowered potential barrier leads to an exponentially increased tunneling probability as described very qualitatively in Sec. II and Fig. 1. Concentrating on the fact that the Coulomb effects lie wholly in the Eq. (4.3b) for $\chi_2(\zeta)$, we plot the *unnormalized* wave functions $\chi_2(\zeta)$ for a typical set of values of E and f, both with and without the electron-hole interaction, in Fig. 4; the absolute values of the potentials $V_2(\zeta)$ are also plotted there. Observe that both wave functions have the same initial values and slopes at $\zeta=0$, but that the electron-hole interaction causes the Coulomb-perturbed function to be much flatter than its counterpart near $\zeta=0$. This is, of course, just the behavior which is required if $U(\mathbf{r})$ [which is proportional to $\zeta^{-1/2}\chi_2(\zeta)$] is to have a Coulomb-induced relative minimum near the point where the total potential barrier is a maximum. (The minimum condition is easily expressed in terms of the slope of the curve in Fig. 4 as $d\ln\chi_2/d\ln\zeta=\frac{1}{2}$.) In the absence of the Coulomb force, the potential $V_2(\zeta)$ is monotonic and $\zeta^{-1/2}\chi_2(\zeta)$ has no relative minimum near the origin; hence the χ_2 without Coulomb effects must rise more rapidly than the Coulomb-perturbed wave function. For intermediate values of the parabolic coordinate ζ, the Coulomb interaction continues to appreciably distort χ_2 from its free-particle value; but, as ζ increases beyond the potential barrier the two wave functions become more nearly proportional to each other. It is not until the electron has tunneled through the barrier and has been accelerated some distance by the applied field that its wave function begins to resemble the Coulomb-free wave function—and even then its phase is logarithmically different. The differences in the potentials $V_2(\zeta)$ with and without the electron-hole interaction are likewise strikingly large. All these facts seem to suggest that the electron-hole interaction markedly affects the small-field asymptotic form of the Franz-Keldysh absorption coefficient.

It is worth noting that the effect of electron-hole scattering seems to be to replace an energy to the $\frac{3}{2}$ power with an energy to the first power. Factors of the square root of the energy are somewhat characteristic of the Coulomb interaction, as for example in the case of field-free absorption where the interband transition is enhanced by the exciton factor

$$\kappa e^{\kappa}/\sinh\kappa,$$

where

$$\kappa=\pi(R/E)^{1/2}.$$

It is possible that Duke's and Alferieff's theorem is valid, but that our own calculations are not far enough into the asymptotic region ($f\ll -E$). In that case, we have shown that the electron-hole interaction does significantly alter the absorption shape for the physically relevant field strengths and energies studied here. However, it should be emphasized that the theorem of Ref. 12 was based on a model potential which we have critized above on physical grounds—and it may be that the theorem is invalid for a more realistic descrip-

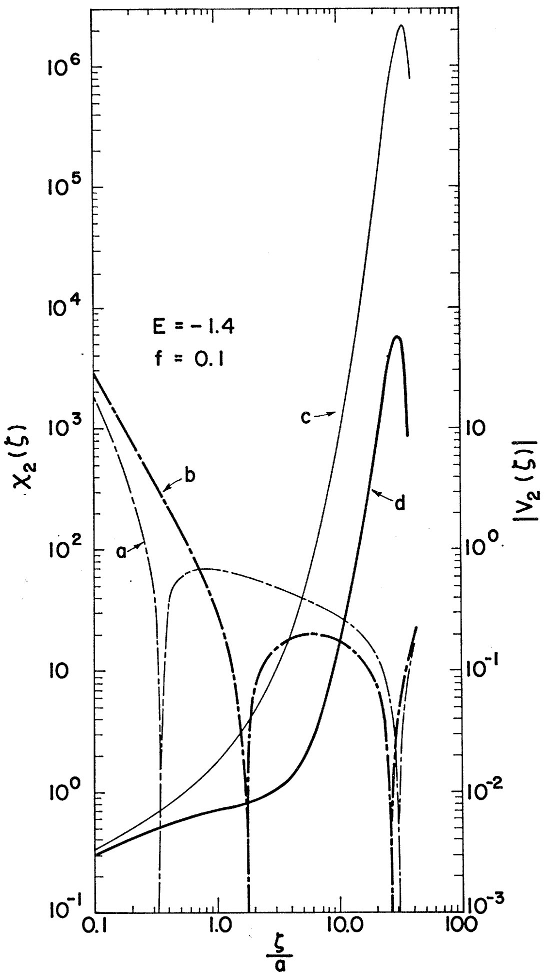

FIG. 4. The magnitudes of the potentials $V_2(\zeta)$ both (a) without the electron-hole interaction and (b) with the Coulomb term; and the corresponding wave functions $\chi_2(\zeta)$ calculated (c) without and (d) with the electron-hole interaction.

tion of the electron-hole scattering. Therefore we believe that it is appropriate that Duke's and Alferieff's theorem be reexamined theoretically.

VI. SUMMARY

In summary, we have shown numerically that the dominant asymptotic behavior of the logarithm of the optical-absorption coefficient (for $f \ll -E$) is very nearly linear in E/f, where E is the photon energy minus the band gap, and f is the applied field strength in units of exciton Rydbergs per electron-exciton Bohr radius. Results of calculations of the electroabsorption near and below the zero-field edge have been presented for intermediate field strengths characteristic of the fields generated by optical phonons in alkali halides. The calculations are presently being extended[34,58] to larger field strengths, higher energies, and forbidden and indirect transitions for the purpose of comparing with available electroabsorption data[59] and electroreflection experiments.[5,60]

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APPENDIX

The solution of the differential equations (4.3) for the wave function (4.4) begins with the specification of E, f, and m. (For the allowed transitions considered here, only $m=0$ contributes to the absorption.) An approximate value of t is specified; and the asymptotic form of $\chi_1(\xi)$ is determined by the WKBJ approximation. The Numerov integrator is then used to integrate inward until $\chi_1(\xi)$ has a relative maximum.[61] A similar outward integration is started at $\xi=0$ with a knowledge of the behavior of the (unnormalized) $\chi_1(\xi)$ near the origin

$$\chi_{1-UN}=\xi^{(|m|+1)/2}\left\{1-\frac{t\xi}{|m|+1}+O(\xi^2)\right\}. \tag{A1}$$

The two solutions are joined at the outer maximum and then each is rescaled so that χ_1 is continuous at the joining point and normalized to unity:

$$\int_0^\infty \frac{\chi_1^2(\xi)}{\xi}d\xi=1. \tag{A2}$$

The program then checks to see if the Numerov integration formula is suitably satisfied at the joining point; and adjusts t according to the Cooley formula, if necessary, and repeats the integration process until convergence is attained. For fixed E, f, and m, there are a countable infinity of values t_n for t, corresponding to the number n of nodes in χ_1. The value of t_n and the quantity

$$B(t_n,E)=\lim_{\xi\to 0}\frac{\chi_1(\xi)}{\xi^{(|m|+1)/2}} \tag{A3}$$

are then used as input, along with E, f, and m, for the solution of the equation for $\chi_2(\zeta)$. For the calculations presented here, only $n=0$, 1 led to significant contributions to the absorption.

The reason for the normalization (A2) is that the volume element in parabolic coordinates is

$$d^3r=\tfrac{1}{4}(\xi+\zeta)d\xi\, d\zeta\, d\phi, \tag{A4}$$

so that $U(\mathbf{r})$ is box normalized according to

$$\int |U(\mathbf{r})|^2\, d^3\mathbf{r} =1=\frac{1}{4}\int_0^{2\pi}d\phi\int_0^{L_1}d\xi\int_0^{L_2}d\zeta\frac{\chi_1^2(\xi)\chi_2^2(\zeta)}{\xi\zeta}(\xi+\zeta). \tag{A5}$$

At this point, we note that χ_1 is normalizable (since it decays exponentially as $\xi\to\infty$); while the asymptotic properties of Eq. (4.3) indicate that χ_2 approaches an (unnormalizable) Airy function, possibly phase shifted by a logarithmic amount δ, having the asymptotic form (A depends on E and t_n)

$$\chi_2(\zeta)\sim\frac{A}{(\frac{1}{2}\zeta+E/f)^{1/4}}\sin\left\{\frac{2}{3}f^{1/2}\left(\frac{E}{f}+\tfrac{1}{2}\zeta\right)^{3/2}+\delta\right\}. \tag{A6}$$

The most divergent contribution to the normalization integral (5) as $L_2\to\infty$ is

$$\tfrac{1}{2}\pi\int_0^\infty\frac{\chi_1^2(\xi)}{\xi}d\xi\int^{L_2}\chi_2^2(\zeta)d\zeta=1$$

$$=\tfrac{1}{2}\pi\int_0^\infty\frac{\chi_1^2(\xi)}{\xi}d\xi(2L_2)^{1/2}A^2. \tag{A7}$$

Here the lower limit on the ζ integration does not matter since all the contribution (in the limit $L_2\to\infty$) comes from the upper limit, permitting the evaluation of the integral using the asymptotic form (A6).

The coefficient A in Eq. (A6) is determined by solving the differential equation (4.3) for $\chi_2(\zeta)$, starting at $\zeta=0$ with the expansion for the unnormalized χ_2

$$\chi_{2-UN}(\zeta)=\zeta^{(|m|+1)/2}\left\{1+\frac{(1-t)\zeta}{|m|+1}+0(\zeta^2)\right\}, \tag{A8}$$

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and integrating outward using Numerov's method. For large ζ, the calculated function is fitted to the asymptotic form (A6) (with 0.5% accuracy) to determine A.

The allowed absorption coefficient is proportional to [see Eq. (3.18)]

$$\sum_{\nu}|U_\nu(0)|^2\delta(E-E_\nu)$$

$$=2\sum_{t,E'}\lim_{\xi\to0,\zeta\to0}\frac{|\chi_1(\xi;t_n,E')\chi_2(\xi;t_n,E')|^2}{\xi\zeta}\times\delta(E-E'),\quad\text{(A9)}$$

where the factor of 2 is included for spin. In order to convert the sum over E' to an integral, we determine the density of states $\rho(E)=dn/dE$ by requiring that the wave function χ_2 [Eq. (A6)] be zero at $\zeta=L_2$ [i.e., $\frac{2}{3}f^{1/2}(\frac{1}{2}L_2)^{3/2}\sim n\pi$],

$$\rho(E')=\frac{dn}{dE'}=\frac{1}{\pi}\frac{L_2{}^{1/2}}{2f}.\quad\text{(A10)}$$

The resulting allowed absorption coefficient is

$$K_A=\frac{4\pi^2e^2}{m^2c\eta'(\omega)\omega}\frac{2\sqrt{L_2}}{\pi(2f)^{1/2}}\times\sum\lim_{\xi\to0,\zeta\to0}\frac{|\chi_1(\xi;t_n,E)\chi_2(\zeta;t_n,E)|^2}{\xi\zeta}.\quad\text{(A11)}$$

If we follow Ralph and we do not normalize χ_1 and χ_2 according to Eqs. (A2) and (A7) but instead define "unnormalized" χ_{1-UN} and χ_{2-UN} by Eqs. (A1) and (A8), then we get Ralph's formula

$$K_A=[4\pi^2e^2/m^2c\eta'(\omega)\omega]2|U(0)|^2S(E),\quad\text{(A12)}$$

where

$$|U(0)|^2S(E)=\frac{1}{Ra^3}\sum_{n=0}^{\infty}\left(\pi^2f^{1/2}\int_0^\infty\frac{\chi_{1-UN}{}^2}{\xi}\times(\xi;t_n,E)d\xi A^2(t_n,E)\right)^{-1}.\quad\text{(A13)}$$

In Eqs. (A12) and (A13), we have restored cgs units, with the understanding that all quantities to the right of the summation in Eq. (A13) are unitless. Equation (A12) differs from Ralph's result by a factor of 2, presumably due to spin.

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X-Ray Scattering by Very Defective Lattices*

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There is evidence to indicate that some diffusely scattering substances are essentially highly defective lattices rather than made up of small domains diffracting incoherently with respect to each other. Equations have been derived for the diffraction profiles from such lattices; they are of a Cauchy type. Highly defective lattices are characterizable by a mean defect-free distance rather than a domain size. Several criteria are presented for distinguishing defect-broadening from domain or particle-size broadening, and procedures are outlined for the separation of strain and defect broadenings.

I. INTRODUCTION

DEFECTS in structures produce displacements in the positions of atoms. The effects of such displacements on the scattering intensities have been considered by several workers.[1–3] In the case of crystals, these treatments have been confined mostly to cases in which the concentration of defects is small. On the other hand, diffusely scattering substances are not treated as lattices containing a high defect concentration. Rather, they are commonly regarded as composed of small particles or crystallites or possessing some sort of a domain structure within the material such that the different domains diffract essentially incoherently with respect to one another.[4,5]

At least in carbons, the presence of small particles or crystallites having sizes indicated by the linewidths of their diffraction peaks is often not indicated by electron microscope observations[6–9] or small-angle x-ray scat-

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