Summing up these two processes, the total Hamiltonian for the mixing effect is expressed as

$$H'=\frac{A_0}{N'}\sum_{\mathrm{n,k,k'}} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_\mathrm{n}}\{(a^*_{\mathrm{k'}+}a_{\mathrm{k}+}-a^*_{\mathrm{k'}-}a_{\mathrm{k}-})S^z_\mathrm{n} + a^*_{\mathrm{k'}-}a_{\mathrm{k}+}S^+_\mathrm{n}+a^*_{\mathrm{k'}+}a_{\mathrm{k}-}S^-_\mathrm{n}\}, \quad \text{(A4)}$$

where

$$A_0=V_0^2\left\{\frac{1}{\epsilon_e^- - \epsilon_F}+\frac{1}{\epsilon_e^+ - \epsilon_F}\right\}, \quad \text{(A5)}$$

and

$$V_0^2=(4\pi)^{1/2}\int_0^\infty P(\mathbf{r})V_{sd}(\mathbf{r})j_0(r)r^2dr. \quad \text{(A6)}$$

Here, it is assumed that $V_{sd}(\mathbf{r})$ is spherical; $P(r)$ is the radial part of $\varphi_i(\mathbf{r})$; and j_0 is the zeroth-order spherical Bessel function.

The value A_0 in (A4) is positive. Comparing Eq. (A4) with Eq. (5) in Sec. IV, we may conclude that the mixing of the wave functions of conduction and localized electrons gives the negative contribution $-A_0$ to the exchange integral. Then the sign of the exchange integral J' is determined by the two competing effects, the direct-exchange integral, which is positive, and the effect of mixing, which is negative. Therefore a negative J' is possible if the effect of mixing is appreciably large. It is possible that this mixing effect for the *s-d* interaction in *n*-type InSb is very large, since the energy level of the localized state seems to exist not far from the Fermi level, as discussed in Sec. IV.

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Excitons in Degenerate Semiconductors

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The band-to-band optical absorption is calculated for a direct-band-gap semiconductor that has one band degenerate *n* or *p* type. The degenerate band is treated as a high-density Fermi gas. It is shown that exciton states, arising from the electron-hole Coulomb attraction, still affect the optical absorption. The calculations show that exciton states cause a logarithmic singularity in the absorption at the Burstein edge. This singularity is present at a moderate density of electrons or holes in the degenerate band, but it gradually disappears in the high-density limit. Lifetime broadening could make the logarithmic singularity difficult to observe at higher densities.

I. INTRODUCTION

VALENCE-band-to-conduction-band optical-absorption experiments have provided much information about insulating or lightly doped semiconductors. Of particular fruitfulness has been the study of exciton states, the electron-hole bound states which drastically alter the shape of the absorption edge in semiconductors where the lowest transition is direct. The present calculation is concerned with optical-absorption processes in direct-gap semiconductors which have one band sufficiently doped that it can be viewed as a degenerate electron gas at low temperatures. The case where the conduction band is doped is indicated in Fig. 1, where the transition of interest is from the heavy-hole band. The results of this calculation show that exciton effects, in the form of final-state electron-hole Coulomb scattering, still drastically affect the optical-absorption spectra. This seems to occur even in the limit that the conduction electrons can be viewed as a high-density electron gas.

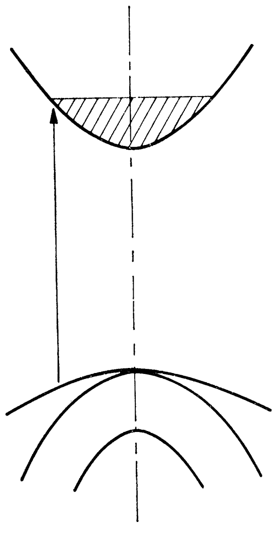

FIG. 1. Optical absorption in a semiconductor with a degenerate conduction band. The onset of optical absorption is at $\omega=E_G+p_F^2/2\nu$, where E_G is the energy gap, p_F is the electron Fermi momenta, and ν is the electron-hole reduced mass.

Elliott[1] showed that optical absorption in semiconductors should be viewed as the creation of an electron-hole pair. In his calculation for insulating semiconductors, the electron-hole Coulomb interaction was included by solving Schrödinger's equation for a hydrogen atom. The inclusion of these Wannier exciton states provided

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[1] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

an understanding of the fundamental absorption edge of insulating semiconductors.

We now consider semiconductors which are doped so that the conduction band becomes a degenerate electron gas. As the density of electrons in the conduction band is increased, these exciton effects should, in some fashion, go away. This question is attacked by viewing the conduction band as a high-density electron gas. The influence of the electron-hole Coulomb interaction on the optical absorption can then be investigated using the formalism of many-body theory.

This calculation shows that exciton effects on the optical absorption persist even into the regions where the conduction band is a high-density electron gas. Were it not for lifetime broadening, a real electron-hole bound state would exist. Its binding energy would be approximately

$$E_B=(2p_F^2/\nu)e^{-1/\Delta},$$

$$\Delta=\frac{1}{2\pi p_F a_B}\ln(1+4p_F^2/k_s^2),$$

$$a_B=\epsilon_0\hbar^2/e^2\nu,$$

where ν is the electron-hole reduced mass, p_F is the electron Fermi momentum, and k_s is the Fermi-Thomas screening wave vector. This bound state would appear in the optical absorption at a frequency $\hbar\omega=E_G+p_F^2/2\nu-E_B$, where E_G is the energy gap, and the usual absorption edge occurs at $E_G+p_F^2/2\nu$. Since the minimum energy an electron-hole pair can have is $E_G+p_F^2/2m_e$, the exciton state is metastable unless $E_B>p_F^2/2m_h$.

As will be shown in Sec. III, this bound state obeys a Schrödinger equation with a nonlocal interaction. The existence of the bound state is related to the exclusion-principle restrictions on the electron's scattering. The nature of the bound state is similar to the Cooper pair[2–4] state in the theory of superconductivity, because the properties of both states depend upon the sharpness of the Fermi surface.

The binding energy E_B vanishes as p_F becomes large. The exciton state gradually disappears in the high-density limit. Because the bound state is so near the Fermi energy, lifetime broadening eliminates the possibility of seeing a distinct line in the absorption spectra. When the lifetime broadening is small, an absorption resonance does appear at the Fermi energy. This resonance has a logarithmic character. The calculations of Sec. III demonstrate the nature of this resonance for various values of electron conduction-band density.

As indicated in Fig. 1, the onset of optical absorption is shifted to higher frequencies in degenerate materials because the absorption must lift the electron above the Fermi energy. This was first observed by Tanenbaum and Briggs.[5] This "Burstein shift" was immediately confirmed and explained by Burstein.[6] Successive optical experiments[7–13] have confirmed the model, although some tunneling data[14,15] indicate that the band may also shift rigidly down. All optical-absorption experiments in degenerate semiconductors have been confined to the low-energy absorption tail.

In order to see the exciton effects described below, the optical absorption has to be measured above the absorption edge. This is barely feasible in one quantum absorption because of the high absorption constant. But the measurements could be done by two-quantum absorption,[16,17] or else by one of the ac-optical measurements—piezoreflectance[18] or electroreflectance[19,20]—which also provide detailed information about ϵ_2.

II. ELECTRON AND HOLE ENERGIES

Before considering the Coulomb states of an electron-hole pair created optically, we consider the energies of each of them individually. The effects of electron-electron interaction have been widely studied. The energy of an electron in a degenerate conduction band was considered by Parmenter,[21] who examined the electron's interaction with a single impurity. This leads to a downward shift of the band.[22,23] The randomness of the impurity locations allows the possibility that they can be locally bunched, which leads to low-energy band tailing. This has been studied by Kane,[24] Bonch-Bruevich,[22] and recently by Lax and Halperin.[25]

A single hole in a degenerate electron gas is subject to the same interactions as the electron. Its energy is

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shifted from the multiple interactions with multiple impurities, because this raises, rather than lowers, the hole energy. But valence-band tailing does occur from hole interaction with phonons.

Another term which appears differently for the hole than for the electron is the hole exchange energy

$$\Sigma_x(k)=-\frac{1}{\beta}\sum_{q_n}\int\frac{d^3q}{(2\pi)^3}v(q)\frac{\mathcal{G}_h(\mathbf{k}+\mathbf{q})}{\epsilon(q)}\,.$$

When one does the sum over q_n, there results one term proportional to the number of holes $\eta_{Fh}(\mathbf{k}+\mathbf{q})$, and one term from the branch cuts of $\epsilon(q)$. For the electron's exchange energy, Wolff[23] noted that the η_{Fe} term is the most important, whereas, for the single hole, $\eta_{Fh}=0$. The contribution from the dielectric function is

$$\Sigma_x(k)=-\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{e^{\beta\omega}-1}\int\frac{d^3q}{(2\pi)^3}\times\frac{v(q)}{ik_n+\omega-\xi_{\mathbf{k}+\mathbf{q}}}\operatorname{Im}\frac{1}{\epsilon(q,\,\omega+i\delta)}\,.$$

The random-phase approximation is used for $\epsilon(q)$. Changing to the dimensionless variables $x=q/p_F$, $w=\cos\theta$, and $y=(\omega+x^2\mu)/2\mu x$, the cuts in $\epsilon(q,\omega)$ are analyzed as before.[26] The exchange energy becomes

$$\Sigma_x(k)=\frac{4}{\pi^2}E_{BD}\int_{-1}^{1}dw\left\{\int_{-1}^{1}dy(1-y^2)\int_{y+1}^{\infty}\times dx-\int_0^{\infty}dx\,x\int_{x-1}^{x/2}dy(2y-x)\right\}\times\frac{x^2}{(x^2+\gamma)^2}\frac{1}{(ik_n-\xi_k)/\mu+2xy-2Kxw-x\lambda}\,;\quad(1)$$

$$\gamma=k_s^2/p_F^2=0.6634r_{se}\,,$$

$$r_{se}=\left(\frac{3}{4\pi n_0}\right)^{1/3}\frac{e^2m_e}{\epsilon_0}\,,$$

$$\lambda=1+m_e/m_h\,,$$

$$K=km_e/p_Fm_h\,,$$

$$E_{BD}=e^4m_e/2\epsilon_0^2\hbar^2=\text{donor binding energy}.$$

In deriving this expression, the denominator $\epsilon_R^2+\epsilon_I^2$ in

$$\operatorname{Im}\frac{1}{\epsilon(q,\,\omega+i\delta)}=\frac{-\epsilon_I}{\epsilon_R^2+\epsilon_I^2}$$

is approximated by the Fermi-Thomas expression. The integral (1) was evaluated for the real part of $\sum_x(k)$ on the mass shell, $ik_n=\xi_k$. The results for $k=0$ are shown in Fig. 2. The exchange energy is negative and, except for the dependence upon r_{se}, of the order of the donor binding energy.

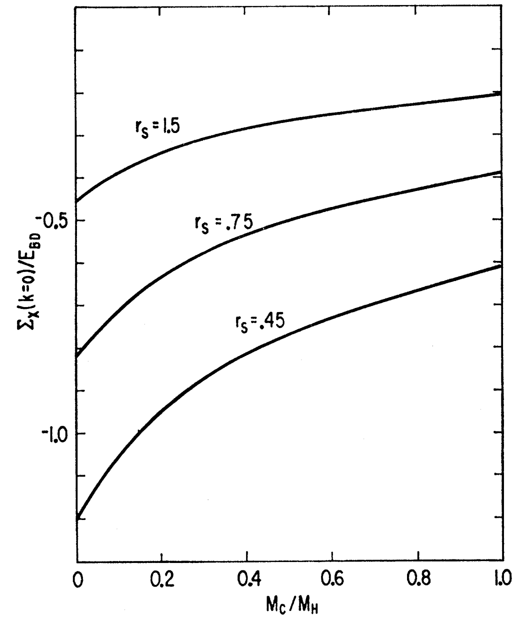

FIG. 2. The exchange energy of a $k=0$ hole in a degenerate n-type semiconductor. The energy scale is in units of a donor binding energy E_{BD}. The electron-density parameter r_s is defined in (1).

Additional calculations have been done on the wave-vector dependence of $\sum_x(k)$. For $m_e=m_n$, a plot of $\sum_x(k)$ versus k looks very similar to that for holes interacting with optical phonons. For low $k(k<p_F)$, the hole mass is increased. And, for $k>p_F$, $\sum_x(k)$ falls off rapidly as an inverse power of k. When the hole mass is heavier, $m_h>m_e$, the k dependence of $\sum_x(k)$ becomes less pronounced.

For the exciton calculations, the electron and hole bands are assumed to be parabolic. This is valid since most of the effects discussed above give rise to a band shift or a change in the effective mass. The omission of band tailing is allowable, since the present concern is with effects at and above the absorption edge.

III. OPTICAL ABSORPTION

Elliott[1] showed that it was proper to view the absorption as the optical creation of an electron-hole pair. In his calculation, the final-state Coulomb interaction between the electron and hole was included by solving the Schrödinger equation for a hydrogen atom. This simple procedure is no longer possible when the conduction band is degenerate. Because the electron's scattering is limited by the exclusion principle, the resulting Schrödinger equation is nonlocal. The present calculation is done using the diagrammatic methods of many-body theory.[3]

The optical absorption is related to a two-particle correlation function, which is evaluated using the Matsubara formulation.[3] Denoting electron operators

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[26] G. D. Mahan and C. B. Duke, Phys. Rev. 149, 705 (1966).

by $C_p{}^\dagger$, and hole operators by $d_k{}^\dagger$, this correlation function is, for allowed dipole transitions,

$$\pi(\mathbf{k},i\omega_n)=\frac{\alpha_0}{V}\sum_{\mathbf{p},\mathbf{p}'}\int_0^\beta d\tau\, e^{i\omega_n(\tau-\tau')}$$
$$\times\langle T_\tau C_\mathbf{p}(\tau)d_{\mathbf{k}-\mathbf{p}}(\tau)d^\dagger{}_{\mathbf{k}-\mathbf{p}'}(\tau')C_{p'}{}^\dagger\cdot(\tau')\rangle. \quad (2)$$

In the case of forbidden band-to-band dipole transition, one instead evaluates the current-current correlation function. The constant α_0 contains the square of the band-to-band matrix element and other factors. For optical absorption, we can immediately set the electron-hole center-of-mass wave vector $\mathbf{k}$ equal to zero. The electron and hole Green's functions are

$$\mathcal{G}_e(\mathbf{p})=\frac{1}{ip_n-\xi_{ep}},\quad \xi_{ep}=\epsilon_{ep}-\mu_e$$
$$\mathcal{G}_h(\mathbf{k})=\frac{1}{ik_n-\xi_{h\mathbf{k}}},\quad \xi_{h\mathbf{k}}=\epsilon_{h\mathbf{k}}-\mu_h.$$

After evaluating $\pi(i\omega_n)$, the retarded function $\pi_{\text{ret}}(\omega)$ is obtained by letting $i\omega\rightarrow\omega-E_G-\mu_e-\mu_h+i\delta$. The optical absorption is

$$A(\omega)=2\,\text{Im}\pi_{\text{ret}}(\omega). \quad (3)$$

In the absence of any electron-hole Coulomb scattering, the correlation function (2) becomes

$$\pi^{(0)}(i\omega_n)=\frac{\alpha_0}{\beta}\sum_{p_n}\int\frac{d^3p}{(2\pi)^3}\mathcal{G}_e(\mathbf{p},ip_n)\mathcal{G}_n(-\mathbf{p},\, i\omega_n-ip_n).$$

This diagram is shown in Fig. 3(a). Doing the Matsubara sum over p_n gives

$$\pi^{(0)}(i\omega_n)=-\alpha_0\int\frac{d^3p}{(2\pi)^3}\frac{[1-n_{Fe}(p)-n_{Fh}(p)]}{i\omega_n-\xi_{ep}-\xi_{hp}}.$$

It is assumed that the density of holes is negligible, $\eta_{Fh}=0$. Analytically continuing $i\omega_n\rightarrow\omega-E_G-\mu_e-\mu_h+i\delta$ gives the absorption, from (3),

$$A^{(0)}(\omega)=2\pi\alpha_0\int\frac{d^3p}{(2\pi)^3}(1-n_{Fe}(p))\delta(\omega-E_G-p^2/2\nu). \quad (4)$$

The result (4) is

$$A^{(0)}(\omega)=(\alpha_0/2\pi)(2\nu)^{3/2}(\omega-E_G)^{1/2}\theta(\omega-E_G-p_F{}^2/2\nu),$$
$$\begin{aligned}\theta(x)&=1 \qquad x>0 \qquad (5)\\ &=0 \qquad x<0.\end{aligned}$$

This is the standard result that the absorption is proportional to the square root of the energy above the band gap, and the electron's exclusion principle requires that $\omega>E_G+p_F{}^2/2\nu$.

The Coulomb interaction between the electron and hole alters the simple result (5). The Coulomb interaction is discussed using the Hamiltonian

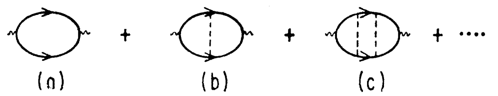

FIG. 3. The ladder diagrams which are summed in evaluating the correlation function (2). Figure 3(a) gives the absorption coefficient (5) in the absence of electron-hole Coulomb interactions. For insulating semiconductors, with negligible electron or hole concentration, the ladder diagrams give all the important terms for the electron-hole Coulomb interaction. For degenerate semiconductors, vertex corrections which are not ladder diagrams also contribute to electron-hole Coulomb scattering.

$$\mathcal{H}=\sum_p\xi_{e\mathbf{p}}C_\mathbf{p}{}^\dagger C_\mathbf{p}+\sum_k\xi_{h\mathbf{k}}d_\mathbf{k}{}^\dagger d_\mathbf{k}+\sum_{\mathbf{q},\mathbf{k},\mathbf{p}}V(q)C_{\mathbf{p}+\mathbf{q}}{}^\dagger C_\mathbf{p}d_{\mathbf{k}-\mathbf{q}}{}^\dagger d_\mathbf{k}.$$

Electron-electron interactions are included by screening the Coulomb interaction

$$V(q)=-4\pi e^2/[\epsilon_0(q^2+k_s{}^2)]. \quad (6)$$

The final-state Coulomb scattering[27] between the electron and hole is included by summing the ladder diagrams indicated in Fig. 3. For absorption in insulating crystals, where the conduction band is empty, the result obtained by summing these ladder diagrams is identical to Elliott's method of solving the hydrogenic Schrödinger equation. The equivalence of the two approaches is shown below. Other vertex corrections besides the ladder diagrams have a contribution which depends upon the density of electrons or holes. They give no contribution to the Elliott result for insulating semiconductors. Their contribution to the absorption in degenerate semiconductors is discussed in the next section.

The sum of the ladder diagrams is expressed as a vertex function

$$\pi(i\omega_n)=\alpha_0\int\frac{d^3p}{(2\pi)^3}\frac{1}{\beta}\sum_{p_n}\mathcal{G}_e(\mathbf{p},ip_n)$$
$$\times\mathcal{G}_h(\mathbf{p},\, i\omega_n-ip_n)\Gamma(\mathbf{p},i\omega_n), \quad (7)$$

$$\Gamma(\mathbf{p},i\omega_n)=1-\int\frac{d^3p'}{(2\pi)^3}V(\mathbf{p}-\mathbf{p}')\frac{1}{\beta}\sum_{p_{n'}}$$
$$\times\mathcal{G}_e(\mathbf{p}',ip_{n'})\mathcal{G}_h(\mathbf{p}',i\omega_n-ip_{n'})\Gamma(p',i\omega_n). \quad (8)$$

That $\Gamma(\mathbf{p},i\omega_n)$ does not depend upon p_n in (7) or (8) is a convenient result of the instantaneous nature of the Coulomb interaction. It also allows the Matsubara sums to be done immediately:

$$\pi(i\omega_n)=-\alpha_0\int\frac{d^3p}{(2\pi)^3}\frac{(1-n_{Fe}(p))\Gamma(\mathbf{p},i\omega_n)}{i\omega_n+\mu_e+\mu_h-p^2/2\nu}, \quad (7')$$

$$\Gamma(\mathbf{p},i\omega_n)=1+\int\frac{d^3p'}{(2\pi)^3}\frac{V(\mathbf{p}-\mathbf{p}')(1-n_{Fe}(\mathbf{p}'))\Gamma(\mathbf{p}',i\omega_n)}{i\omega_n+\mu_e+\mu_h-p'^2/2\nu}. \quad (8')$$

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[27] J. Gillespie, *Final State Interactions* (Holden-Day, Inc., San Francisco, 1964).

Rather than solve the integral equations for the $\mathbf{p}$ variable, it is easier to transform the equations to an $\mathbf{r}$ variable. Define

$$\pi(\mathbf{r},i\omega_n)=-\alpha_0\int\frac{d^3p}{(2\pi)^3}\frac{e^{i\mathbf{p}\cdot\mathbf{r}}(1-n_{Fe}(p))\Gamma(\mathbf{p},i\omega_n)}{i\omega_n+\mu_e+\mu_h-p^2/2\nu}. \quad (9)$$

The function (7′) is just the special case of $\pi(\mathbf{r},i\omega_n)$ as $r\to 0$. The vertex function (8′) can be written as

$$\Gamma(\mathbf{p},i\omega_n)=1-\alpha_0^{-1}\int d^3r'V(\mathbf{r}')\pi(\mathbf{r}',i\omega_n)e^{-i\mathbf{p}\cdot\mathbf{r}'}.$$

The function $\pi(\mathbf{r},i\omega_n)$ satisfies a differential equation with a nonlocal interaction. The kernel for this interaction is

$$K(\mathbf{r})=\int\frac{d^3p}{(2\pi)^3}e^{i\mathbf{p}\cdot\mathbf{r}}(1-n_{Fe}(p))$$
$$=\delta(\mathbf{r})+\frac{1}{2\pi^2r^3}[rp_F\cos rp_F-\sin rp_F],$$

and the equation is

$$\left[\frac{-\nabla^2}{2\nu}-i\omega_n-\mu_e-\mu_h\right]\pi(\mathbf{r},i\omega_n)+\int d^3r'V(\mathbf{r}')\pi(\mathbf{r}',i\omega_n)K(\mathbf{r}-\mathbf{r}')=\alpha_0K(\mathbf{r}). \quad (10)$$

The solution is obtained by first finding the exciton wave functions $\psi_\lambda(\mathbf{r})$ and eigenvalues E_λ from the equation

$$\frac{-\nabla^2}{2\nu}\psi_\lambda(\mathbf{r})+\int d^3r'V(\mathbf{r}')\psi_\lambda(\mathbf{r}')K(\mathbf{r}-\mathbf{r}')=E_\lambda\psi_\lambda(\mathbf{r}). \quad (11)$$

Outgoing wave boundary conditions should be used for $\psi_\lambda(\mathbf{r})$ when $E_\lambda>p_F^2/2\nu$. The solution to Eq. (10) is expressed in terms of the functions $\psi_\lambda(\mathbf{r})$:

$$\pi(\mathbf{r},i\omega_n)=\alpha_0\int d^3r'K(\mathbf{r}')\sum_\lambda\frac{\psi_\lambda^*(\mathbf{r}')\psi_\lambda(\mathbf{r})}{E_\lambda-i\omega_n-\mu_e-\mu_h}. \quad (12)$$

This equation can be immediately related to Elliott's result when the conduction band is empty. Setting $n_{Fe}=0$, then $K(\mathbf{r})=\delta(\mathbf{r})$, and (11) is just the hydrogenic Schrödinger equation. Using (3), the absorption is

$$A(\omega)=2\,\mathrm{Im}\pi_{\mathrm{ret}}(r=0,\ i\omega_n\to\omega-\mu_e-\mu_h+E_G+i\delta), \quad (13)$$

$$A(\omega)=2\pi\alpha_0\sum_\lambda|\psi_\lambda(0)|^2\delta(E_\lambda+E_G-\omega), \quad (14)$$

which is Elliott's result for optical absorption in insulating semiconductors.

The absorption is still given by (13) even when the conduction band is degenerate. When taking the imaginary part of the retarded Green's function in (13), the contributions from the imaginary part of the wave functions and $K(\mathbf{r})$ all cancel. This cancellation is shown below. For the degenerate case, the absorption is given by

$$A(\omega)=2\pi\alpha_0\int d^3r'K(\mathbf{r}')\sum_\lambda\psi_\lambda^*(\mathbf{r}')\psi_\lambda(0)\delta(E_G+E_\lambda-\omega). \quad (15)$$

In the Elliott result (14), the optical absorption is related to the square of the hydrogenic, relative wave function at the origin.[1,27] This gives the probability that the electron and hole are on the same lattice site. In the absorption for a degenerate conduction band, the electron-hole interaction is nonlocal. Correspondingly, the optical absorption is not just related to the exciton relative wave function at the origin. The result (15) shows that one must add in the parts of the wave function in space which are near $r=0$. This is an additional consequence of the nonlocal interaction.

The exciton Hamiltonian (11) is solved by the method developed by Noyes.[28–30] The Hamiltonian is changed into an integral equation.

$$\psi_\lambda(\mathbf{r})=\psi_\lambda^{(0)}(\mathbf{r})+\int d^3r'V(\mathbf{r}')\psi_\lambda(\mathbf{r}')\times\int\frac{d^3p}{(2\pi)^3}\frac{e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')}(1-n_{Fe}(p))}{E_\lambda-p^2/2\nu+i\delta}.$$

The equation for the exciton bound states, which have $E_\lambda<p_F^2/2\nu$, has the $\psi_\lambda^{(0)}$ term missing. For the exciton scattering states, which have $\gamma_\lambda>p_F^2/2\nu$, set $E_\lambda=k^2/2\nu$. Since the absorption depends upon $\psi_\lambda(\mathbf{r}=0)$, only the s-wave part of ψ_λ is needed, and this is called $\phi_0(k,r)$.

$$\phi_0(k,r)=j_0(kr)+\frac{4\nu}{\pi}\int_0^\infty r'^2dr'V(r')\phi_0(k,r')\times\int_{p_F}^\infty\frac{p^2dp\,j_0(pr)j_0(pr')}{k^2-p^2+i\delta}.$$

This is Fourier transformed

$$\phi_0(k,p)=\frac{2pk}{\pi}\int_0^\infty r^2dr\,j_0(pr)\phi_0(k,r),$$

which gives

$$\phi_0(k,p)=\delta(k-p)-\frac{2\nu e^2}{\pi\epsilon_0}\frac{1-n_{Fe}(p)}{k^2-p^2+i\delta}\times\int_0^\infty dp'\phi_0(k,p')Q_0\left(\frac{p'^2+p^2+k_s^2}{2pp'}\right). \quad (16)$$

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[28] H. P. Noyes, Phys. Rev. Letters **15**, 538 (1965).
[29] K. L. Kowalski, Phys. Rev. Letters **15**, 798 (1965).
[30] A. J. Layzer, Phys. Letters **13**, 121 (1964).

The generalized Legendre function[31] is

$$Q_0\left(\frac{p'^2+p^2+k_s^2}{2pp'}\right)=\tfrac{1}{2}\ln\frac{(p+p')^2+k_s^2}{(p-p')^2+k_s^2}.$$

This is abbreviated by $Q_0(p,p')$. The equation for higher partial waves $\phi_l(k,p)$ is given in terms of $Q_l(p,p')$. Noyes showed that the solution to (16) is[32]

$$\phi_0(k,p)=\delta(k-p)-\frac{2e^2\nu}{\pi\epsilon_0}\frac{(1-n_{Fe}(p))}{k^2-p^2+i\delta}t(k)f(k,p),$$

where

$$t(k)=(1+\Lambda_1(k))^{-1},$$

$$\Lambda_1(k)=\frac{2e^2\nu}{\pi\epsilon_0 Q_0(k,k)}\int_0^\infty dp\frac{(1-n_F(p))f(k,p)Q_0(k,p)}{k^2-p^2+i\delta}, \quad (17)$$

and $f(k,p)$ is generated by the equation

$$f(k,p)=Q_0(p,k)+\frac{2e^2\nu}{\pi\epsilon_0}\int_0^\infty dp'\frac{(1-n_{Fe}(p'))f(k,p')}{k^2-p'^2}$$
$$\times[Q_0(p,k)Q_0(k,p')-Q_0(p,p')Q_0(k,k)]/Q_0(k,k). \quad (18)$$

The function $f(k,p)$ is real, and for $k=p$ it is given by the first term of this equation. It is also necessary to define

$$\Lambda_2(k)=\frac{2e^2\nu}{\pi\epsilon_0 k}\int_0^\infty p\,dp\frac{(1-n_{Fe}(p))f(k,p)}{k^2-p^2+i\delta}. \quad (19)$$

Note that $\mathrm{Im}\Lambda_1(k)=\mathrm{Im}\Lambda_2(k)$. Now the exciton wave functions can be expressed in compact form. The wave function at $r=0$ is

$$\phi_0(k,r=0)=\frac{1}{k}\int_0^\infty pdp\,\phi_0(k,p)=1-\frac{\Lambda_2(k)}{1+\Lambda_1(k)}.$$

Similarly,

$$\int d^3r'K(\mathbf{r}')\psi_\lambda^*(\mathbf{r}')=(1-n_{Fe}(k))\left[1-\frac{\Lambda_2(k)^*}{1+\Lambda_1(k)^*}\right].$$

This last equation is just valid at zero temperature, and for the scattering states with $k>p_F$. Using the last two equations, the scattering states contribute to $\pi(r=0,i\omega_n)$ in (12) the amount

$$\pi_s(i\omega_n)=\frac{\alpha_0}{2\pi^2}\int_{p_F}^\infty\frac{k^2dk}{k^2/2\nu-i\omega_n-\mu_e-\mu_h}$$
$$\times\frac{[1+\Lambda_1(k)-\Lambda_2(k)]^2}{|1+\Lambda_1(k)|^2}.$$

The optical absorption from these continuum energy states is

$$A_s(\omega)=A^{(0)}(\omega)\frac{[1+\Lambda_1(k)-\Lambda_2(k)]^2}{|1+\Lambda_1(k)|^2}\Big|k=(2\nu(\omega-E_G))^{1/2}. \quad (20)$$

The functions $\Lambda_1(k)$ and $\Lambda_2(k)$ are defined in (17)–(19).

The other contributions to $\pi(i\omega_n)$ arise from the bound exciton states, which occur for $E_\lambda<p_F^2/2\nu$. For a bound exciton state of energy E_j, the absorption is just

$$A_j(\omega)=2\pi\alpha_0\int d^3r'K(\mathbf{r}')\psi_j(r')\psi_j(0)\delta(E_G+E_j-\omega).$$

The magnitude of the absorption of these bound states is determined by the wave functions $\psi_j(r)$. These can only be obtained by solving (11), which has not been done. However, it is easy to show that the wave function has a large extension in space, and that the relative charge density at large distances has an oscillatory component proportional to $\cos 2p_Fr$. The energies at which the bound states occur can be obtained from the poles of $t(k)$. This exciton binding energy $E_B=k_j^2/2\nu$ is found from

$$1+\Lambda_1(k_j)=0.$$

Since $\mathrm{Im}\Lambda_1(k)=0$ for $k_j<p_F$, this equation gives the bound-state poles at real energy. The binding energy for weakly bound states can be estimated by approximating $\Lambda_1(k)$ in (17):

$$\Lambda_1(k)\approx\frac{1}{\pi a_Bp_F}f(p_F,p_F)\ln\left|\frac{k-p_F}{k+p_F}\right|.$$

This gives a binding energy, measured relative to the Fermi energy, of

$$E_B=(2p_F^2/\nu)e^{-1/\Delta},$$
$$\Delta=1(/2\pi p_Fa_B)\ln(1+4p_F^2/k_s^2).$$

It is interesting to compare these bound exciton states with Cooper-pair states in superconductivity. Both sets of bound states exist because the sharpness of the Fermi surface limits the electron scattering. Yet the exciton binding energy decreases in the limit of high electronic density, while the superconducting gap usually increases. Also, the exciton pole is at a real frequency in the scattering amplitude, while the Cooper pole is at a complex frequency.

The two parameters which determine $\Lambda_1(k)$ and $\Lambda_2(k)$ are $2/\pi a_Bp_F$ and k_s^2/p_F^2. They can both be related to the parameter $r_s=r_{se}\nu/m_e$:

$$2/\pi a_Bp_F=0.3317r_s,$$
$$k_s^2/p_F^2=0.6634r_s(m_e/\nu).$$

In doing these numerical computations, we set $m_e/\nu=1$ in the expression for k_s^2/p_F^2. This should not cause

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[31] *Handbook of Mathematical Functions*, edited by M. Abromowitz and I. A. Stegun (National Bureau of Standards, Washington, D. C., 1964).

[32] The normalization of $f(k,p)$ has been changed from Noyes's definition in Ref. 28.

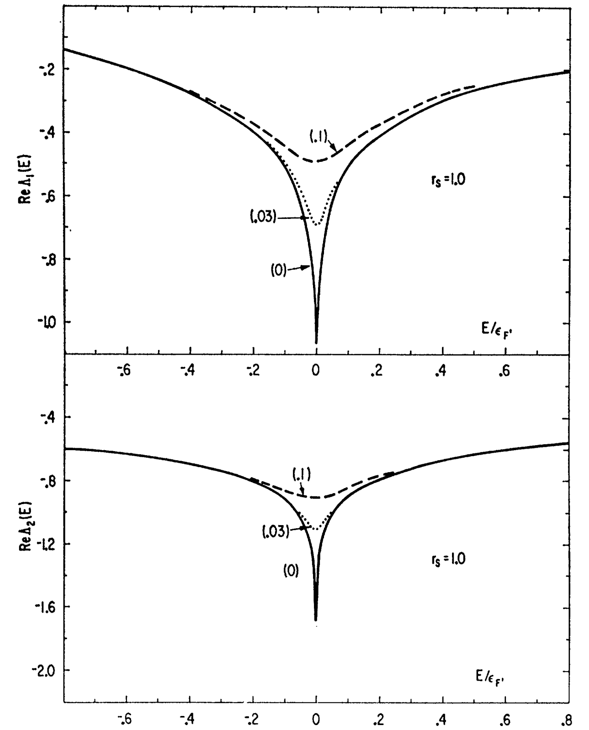

FIG. 4. The functions $\mathrm{Re}\Lambda_1(k)$ and $\mathrm{Re}\Lambda_2(k)$ plotted versus $E=k^2/2\nu-\epsilon'_F$, in units of ϵ_F', where $\epsilon_F'=p_F^2/2\nu$. The screening parameter $r_s=1$ is defined in (1). Various values of the damping parameter Γ are indicated in parentheses. Increased damping just rounds over the logarithmic singularities. The functions are defined in (17) and (19). They are dimensionless, so their value is given in absolute units. They were evaluated numerically, and just the leading term of $f(k,p)$ in (18) was used.

serious errors, since the screening parameter is always contained in a logarithmic functions. Besides, the approximation $m_e/\nu\approx 1$ is not far wrong for heavy holes. In evaluating $\Lambda_1(k)$ and $\Lambda_2(k)$, we approximate $f(k,p)$ by the leading term in (18). The higher order terms in (17) are of order $\sim 0.16r_s$, and are unimportant in the high-density limit $r_s\rightarrow 0$. Even at lower densities, the important logarithmic singularities involve $f(p_F,p_F)$, which is entirely given by the first term of (18). The p integrals in (17) and (19) were done numerically.

Finally, the finite lifetime of the hole must be included. The absorption process creates holes with wave vectors p_F, and here the hole lifetime is a significant parameter. Both the hole and electron lifetimes have been included in a phenomenological way by introducing an energy uncertainty $\Gamma p_F^2/2\nu$. The dimensionless constant Γ has been inserted in the equations by changing the logarithmic and step functions to

$$\ln|\Omega| \rightarrow \ln(\Omega^2+\Gamma^2)^{1/2},$$

$$1-N_{Fe}(k)=\theta(k/p_F)\rightarrow \tfrac{1}{2}+\frac{1}{\pi}\tan^{-1}\left(\frac{k^2-p_F^2}{p_F^2\Gamma}\right).$$

The effect of damping upon the functions $\mathrm{Re}\Lambda_1(k)$ and $\mathrm{Re}\Lambda_2(k)$ is shown in Fig. 4 for $r_s=1.0$. As expected, increasing Γ just rounds over the logarithmic singularities. The functions $\mathrm{Re}\Lambda_1(k)$ and $\mathrm{Re}\Lambda_2(k)$ increase in magnitude for larger r_s, and decrease with smaller r_s. The magnitude of $\mathrm{Re}\Lambda_2(k)$ is always larger than $\mathrm{Re}\Lambda_1(k)$. For $r_s<1$, and for a reasonable value of $\Gamma\sim 0.1$, no true

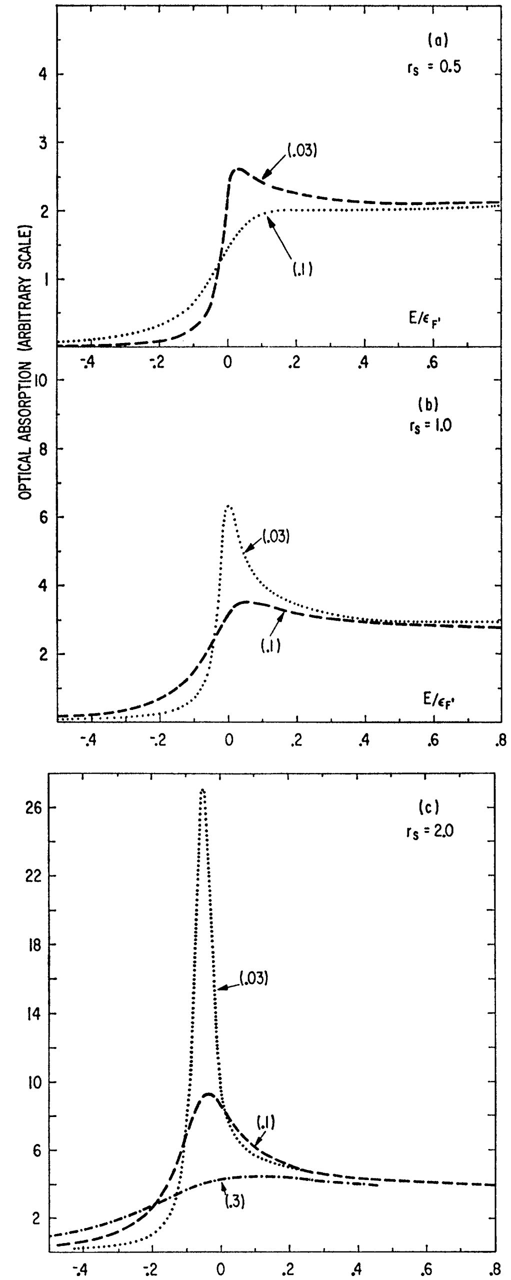

FIG. 5. The optical absorption calculated from (20) for three values of r_s and several values of Γ. The energy scale is measured from the Burstein edge at $\epsilon_F'=p_F^2/2\nu$ above the energy gap, and the energy is listed in units of ϵ_F'. The absorption is given in arbitrary units, but the same units were used for each value of r_s. Higher r_s raises the back shoulder (the flat trailing edge) of the absorption to a higher value. Exciton effects cause the logarithmic resonance at the Burstein edge. This resonance decreases for increasing electron density ($r_s\rightarrow 0$) or increasing Γ.

bound states exist, since $1+\mathrm{Re}\Lambda_1>0$. The resonances observed in the absorption refer to metastable states. It is not necessary to solve the bound-state problem in order to calculate the optical absorption. One can just use (20) with the damping constant included.

The optical absorption was evaluated using (20). The results for $r_s=0.5$, 1.0, and 2.0 are shown in Fig. 5. Different values of Γ are indicated in the figures. Energy is listed in units of $\epsilon_F'=p_F^2/2\nu$. The energy zero is ϵ_F' above the energy gap, which is the onset of the Burstein edge. At low densities ($r_s=2.0$), the exciton peak is quite noticeable, but it gradually disappears in the high-density limit $r_s\rightarrow 0$. Yet exciton effects are still noticeable at $r_s\simeq 1$, which is a high-density electron gas. Since n-type GaAs at 5×10^{17} doping corresponds to $r_s\simeq 1$, these effects should be observable in semiconductors.

IV. DISCUSSION

The calculations of the preceding section show that exciton effects alter the absorption edge of degenerate semiconductors. By viewing the absorption process as the optical creation of an electron-hole pair, the electron-hole Coulomb scattering was calculated in the final state. This scattering causes logarithmic singularities in the absorption spectra. These singularities decrease in intensity as $r_s\rightarrow 0$, which is the limit of high density.

The existence of real electron-hole bound states was also considered. Were it not for the electron and hole lifetimes, stable bound states would exist. Using a finite lifetime causes the bound states to become metastable, and smoothes over the logarithmic singularities in the absorption spectra. Of course, for a large enough damping constant, this structure in the absorption is sufficiently smoothed over that it is eliminated.

It is important to appreciate that the exciton problem is different in degenerate materials from that of an electron bound to an ionized donor. One usually solves the donor problem by considering a one-electron Schrödinger equation with a local potential. The finite hole mass prevents the exciton problem from being approximated in the same way, and leads to the nonlocal interaction. For example, when evaluating the electron's self-energy via Coulomb scattering from holes, one gets terms which are logarithmically divergent in the momentum integrals for energies near the Fermi surface. These divergences all cancel as $m_h\rightarrow\infty$, which corresponds to the donor problem. The occurrence of the logarithmic divergences for finite m_h are related to the existence of these weakly bound exciton states. As hole masses in III-V semiconductors tend to be small, even for heavy holes, it seems appropriate to use the formalism for finite m_h.

The only electron-hole scattering terms which were considered in the calculation were the ladder diagrams of Fig. 3. Other types of terms, which we call nonladder diagrams, will also affect the optical absorption. There is no possibility that these omitted terms will cancel the logarithmic singularity which results from the ladder diagrams. Just note that the diagram of Fig. 3(b) contributes a logarithmic singularity by itself: Since it is the only vertex correction in that order of coupling constant, it cannot be cancelled by any other diagram. The first nonladder diagram of interest is similar to Fig. 3(c), except that the two Coulomb lines are crossed—or it can be alternatively drawn so that the Coulomb lines are vertical while the electron line is looped. It also contributes a logarithmic singularity to the optical absorption, although there is one less power of the logarithm than from Fig. 3(c). That is, it contributes the same type of logarithmic singularity as Fig. 3(b), but the coupling constant is one higher power in r_s. This means that it is pointless to try to solve for $f(k,p)$ in (17) to a high power in r_s without, at the same time, including contributions from these nonladder diagrams. But the ladder diagrams are the most important contributions to the electron-hole interaction for $r_s<1$, and it is in this regime that the present results are valid.

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