Effective-mass theory of resonant Raman scattering by semiconductor donors

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We derive the Raman scattering cross section for transitions between states of a shallow semiconductor donor within a one-electron effective-mass theory that uses the $\mathbf{\Pi}\cdot\mathbf{A}$ interaction to second order. For interband enhanced scattering, we show that the cross section is given by the product of the (free-) conduction-band-electron cross section and a form factor which depends upon the donor wave functions. We show that within one-electron theory the cross section has a truncated resonance at the band gap, even in the absence of lifetime broadening, but that the absolute cross section is quite huge, particularly for light-mass (narrow-gap) semiconductors. The results of this theory, together with the availability of tunable lasers resonant with semiconductor band gaps, point to the possibility for novel tunable far-infrared sources, and the use of light scattering as a sensitive analytical tool for characterizing impurities in semiconductors.

I. INTRODUCTION

Raman scattering has been extensively employed to study vibrational modes, including those of crystalline lattices.[1] Scattering by shallow electronic impurity states in crystals has been much less studied because small (uncompensated) concentrations are required to avoid overlap (and Stark) broadening, and this makes Raman efficiencies small.

Raman scattering between electronic impurity levels in a crystal was first proposed by Elliot and Loudon[2] and first observed by Hougen and Singh[3] in rare-earth crystals. Semiconductor impurity levels were first studied by Henry *et al.*,[4] while Wright and Mooradian[5] made the first observations of shallow-donor scattering. The latter were also the first to compute the cross section of the $1s$ manifold valley-orbit transition. Most experimental studies of spin-conserving shallow-donor Raman scattering have been confined to such transitions.[6]

The first discovery of shallow-donor orbital transitions *between* rather than *within* hydrogenic shells was made by Henry and Nassau[7] who observed the Lyman-α transitions of CdS donors using the near-band-gap—resonant 4880-Å argon-laser line. Until the present decade, this remained the only such report, when Ulbrich *et al.*[8] reported intershell Raman scattering from CdTe donors when band-gap resonance is approached, inferring remarkably large cross sections.

To explain the large efficiencies claimed for such intershell Raman processes, workers are currently appealing to sophisticated theories, such as those involving excitonic polaritons.[8,9] They are presumably doing this because simple existing one-electron theory considering interband resonance predicts cross sections that are too small. In part, this is because the simple calculation has not been done correctly. The existing calculation[10] obtains a very small, if nonzero, intershell transition cross section by misapplying the completeness relation. In the present paper we seek to present a correct treatment of all single-valley shallow-donor Raman scattering processes within the limitations of an approximate, but comprehensive theory.

II. BASIC ASSUMPTIONS

We compute the light-scattering cross section, employing the notation of Yafet,[11] within one-electron theory via the Fermi golden rule, obtaining our perturbed Hamiltonian from the minimal substitution

$$H=\sum_i\left[\frac{P_i^2}{2m}+V(\mathbf{r}_i)+\frac{\hbar}{4m^2c^2}[\nabla V(\mathbf{r}_i)\times\mathbf{p}_i\cdot\boldsymbol{\sigma}_i]+H'+H''\right], \tag{1}$$

where

$$H'=\sum_i\frac{e}{mc}\mathbf{\Pi}_i\cdot\mathbf{A}(\mathbf{r}_i)\,,$$

$$\mathbf{\Pi}_i\equiv\mathbf{p}_i+\frac{\hbar}{4mc^2}[\boldsymbol{\sigma}_i\times\nabla V(\mathbf{r}_i)]\,,$$

$$H''=\sum_i\frac{e^2}{2mc^2}\mathbf{A}^2(r_i)\,,$$

$$\mathbf{A}(r)=\left[\frac{2\pi\hbar c^2}{v}\right]^{1/2}\times\sum_q\sum_\lambda\frac{1}{(\omega_q)^{1/2}}(\hat{\epsilon}_\lambda a_{q\lambda}e^{i\mathbf{q}\cdot\mathbf{r}}+\hat{\epsilon}_\lambda^* a_{q\lambda}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}})\,,$$

and $V(\mathbf{r})$ is the self-consistent crystal potential. To obtain light scattering we must "apply" $\mathbf{A}$ at least twice. In the present paper we apply H' in second-order theory and neglect the first-order contribution of H''. It is argued[11] that, roughly speaking, for free electrons, the term due to H' is smaller than that due to H'' by a factor of β. For electrons in shallow-donor states, the reduced *envelope*

velocity β is approximately α/ϵ_0. However, only the H' term shows a potentially resonant denominator, and since this limit is in our main concern, we neglect the H'' term in all the calculations of the present paper.

The differential Born-approximation cross section for one electron is then given by

$$d\sigma=\frac{1}{c/V}\frac{2\pi}{\hbar}\sum_F\left|\sum_N\frac{\langle F\,|\,H'\,|\,N\rangle\langle N\,|\,H'\,|\,I\rangle}{E_I-E_N}\right|^2 \times\delta(E_F-E_I)\,, \tag{2}$$

where c/V is the incident photon flux. In effecting the calculation of matrix elements for (2), we approximate that $\mathbf{A}(\mathbf{r})$ does not vary over the unit cell, i.e., $A(\mathbf{r})\rightarrow A(\mathbf{R})$ for a unit cell at $\mathbf{R}$. We take the simplest possible model for our semiconductor. We make the one-electron approximation. We assume both the crystal and donor sites possess inversion symmetry and that the band structure is described by two single-valley bands with scalar (spherical) masses, separated by a direct gap we choose to place at $k^*=0$ for convenience. We first assume the limited region of $\mathbf{k}$ space in which we are interested is sufficiently close to the band extremum ($k^*=0$) that we can replace the Bloch functions by the corresponding Kohn-Luttinger functions, i.e.,

$$\psi_{n,\mathbf{k},s}(\mathbf{r},\sigma)\equiv u_{n,\mathbf{k},s}(\mathbf{r},\sigma)\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \approx u_{n,\mathbf{k}^*,s}(\mathbf{r},\sigma)\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}}\,,$$

and, moreover, assume that the plane-wave part of the Kohn-Luttinger function is constant over a unit cell at $\mathbf{R}$:

$$\psi_{n,\mathbf{k},s}(\mathbf{r},\sigma)\rightarrow u_{n,\mathbf{k}^*,s}(\mathbf{r},\sigma)\frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{\sqrt{V}}\,, \tag{3}$$

noting the orthogonality of $\{u_{n,\mathbf{k}^*,s}(\mathbf{r},\sigma),\forall n\}$ over a unit cell. Later we introduce less simplified assumptions (Sec. IV).

We assume that the presence of a donor is adequately modeled within one-band effective-mass theory, i.e., that we write the bound-donor wave functions as

$$\psi_{Nlm}^{n,\mathbf{k}^*s}(\mathbf{r},\sigma)=u_{n,\mathbf{k}^*,s}(\mathbf{r},\sigma)\phi_{Nlm}(\mathbf{R})\,, \tag{4}$$

where ϕ is constant over any unit cell within the accuracy of the theory. We take the zero of energy as the conduction-band bottom: $E_{CB}(k^*)=0$. We use the shorthand $u_{CB}(\mathbf{r})$, $u_{VB}(\mathbf{r})$ to denote the periodic parts of the Kohn-Luttinger states of the conduction band and valence band, respectively. Within these assumptions[12] there are three types of intermediate states $|\,N\rangle$ which contribute in (2).

(1) *Interband states.* These are the valence-band states. We assume the presence of the donor negligibly perturbs them from the form (3).

(2) *Bound intraband states.* These are bound states of the donor other than the initial and final states and are of the form (4).

(3) *Free intraband states.* These are the "scattering" states of the donor (the conduction band) and are only poorly modeled by a form such as (3), as difficulties with donor photoionization theories which use even better wave functions reveal.[13]

In computing matrix elements for (2), we exploit the special form of the wave functions (3) and (4). The slowly-varying parts of (3) and (4), viz., $e^{i\mathbf{k}\cdot\mathbf{R}}/\sqrt{V}$ and $\phi_{Nlm}(\mathbf{R})$, respectively, are denoted collectively by $S(\mathbf{R})$. The general matrix element evaluates within our assumptions as

$$\begin{aligned}\int u_i^*(\mathbf{r})S_i^*(\mathbf{R})\{\mathbf{\Pi}\cdot[\mathbf{A}(\mathbf{R})\rightarrow\mathbf{A}_0e^{\pm i\mathbf{q}\cdot\mathbf{R}}]\}u_j(\mathbf{r})S_j(\mathbf{R})d^3R&\\ =\delta_{ij}\int S_i^*(\mathbf{R})\frac{\hbar}{i}\nabla_{\mathbf{R}}\cdot\mathbf{A}_0e^{\pm i\mathbf{q}\cdot\mathbf{R}}S_j(\mathbf{R})d^3R&\\ +(1-\delta_{ij})\frac{1}{\Omega}\int_\Omega u_i^*(\mathbf{r})\mathbf{\Pi}_{\mathbf{r}}\cdot\mathbf{A}_0u_j(\mathbf{r})d^3r&\\ \times\int S_i^*(\mathbf{R})e^{\pm i\mathbf{q}\cdot\mathbf{R}}S_j(\mathbf{R})d^3R\,,&\end{aligned} \tag{5}$$

where Ω is the unit cell volume and $\{i,j\}$ each refer to either the conduction band (CB) or valence band (VB). We now apply this result to each of the three intermediate-state resonances cases numbered above.

III. INTERBAND RESONANCE

We first remark on the nature of the resonant intermediate states for the interband enhanced scattering. Two types of interband intermediate states, A and B, might occur in principle.

A. This process involves only a single electron. The first application of $\mathbf{\Pi}\cdot\mathbf{A}$ takes the electron out of the initial donor state, putting it into an empty valence-band state. The second application of $\mathbf{\Pi}\cdot\mathbf{A}$ then takes the same electron and places it into the final donor state.

B. In this process two electrons are involved. First, $\mathbf{\Pi}\cdot\mathbf{A}$ takes an electron from a filled valence-band state, placing it into the final donor state. Then, $\mathbf{\Pi}\cdot\mathbf{A}$ takes the original donor electron and annihilates the valence-band hole created in the first step.

For a given valence-band state, only one of A or B is permitted, depending upon whether it is originally empty or occupied, respectively. Fortunately, it can be shown that the two processes have identical scattering amplitudes,[14] except for electron-electron interactions in the intermediate state. For scattering between (localized) donor states, these corrections are potentially quite important. However, for simplicity of exposition, we calculate cross sections completely within the one-electron approximation and then verbally address the qualitative effects many electron corrections have on the relevant type of process for full valence bands, type B.

We intend to show that the cross section for donor Raman scattering is closely related to that for (free-) conduction-band electron scattering and so we begin by rederiving the latter in a form similar to that used by Wolff.[15]

Case 0: Interband-intermediate-state conduction-band-electron scattering.

The quantum efficiency (not power flow) cross section is given by

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_{\rm Th}}{8\pi/3}\left[\frac{\omega_s}{\omega_l}\right]\left|M_0\equiv\sum_{\rm VB}\frac{\langle {\rm CB}'\,|\,\Pi\cdot\hat{\epsilon}_l\,e^{+i\mathbf{q}_l\cdot\mathbf{R}}\,|\,{\rm VB}\rangle\langle {\rm VB}\,|\,\Pi\cdot\hat{\epsilon}_s^*\,e^{-i\mathbf{q}_s\cdot\mathbf{R}}\,|\,{\rm CB}\rangle}{m\,(E_{\rm CB}-E_{\rm VB}-\hbar\omega_s)}\right|^2+\cdots\ . \tag{6}$$

The ellipses include an antiresonant sum, which we neglect, where $\sigma_{\rm Th}=(8\pi/3)r_{\rm cl}^2$ is the Thompson cross section, $r_{\rm cl}=e^2/mc^2$ is the classical electron radius, m is the free-electron mass, l refers to the incoming (laser) photon, and s refers to the scattered photon. The dimensionless term M_0 is given within the two-band model by

$$M_0=\frac{\hat{\epsilon}_l\cdot\Pi_{\rm CB,VB}\Pi_{\rm VB,CB}\cdot\hat{\epsilon}_s^*\,\delta^{\rm KR}(\mathbf{k}_f-\mathbf{q}_l-\mathbf{k}_{\rm VB})\delta^{\rm KR}(\mathbf{k}_i-\mathbf{q}_s-\mathbf{k}_{\rm VB})}{m\,[E_{\rm CB}(\mathbf{k}_i)-E_{\rm VB}(\mathbf{k}_{\rm VB})-\hbar\omega_s]}\ , \tag{7}$$

with

$$\Pi_{\rm CB,VB}\equiv\frac{1}{\Omega}\int_\Omega d^3r\,u_{\rm CB}^*(\mathbf{r})\Pi u_{\rm VB}(\mathbf{r})\ ,$$

$$\Pi_{\rm VB,CB}\equiv\frac{1}{\Omega}\,d^3r\,u_{\rm VB}^*(\mathbf{r})\Pi u_{\rm CB}(\mathbf{r})\ .$$

The tensor $\Pi_{\rm CB,VB}\Pi_{\rm VB,CB}$ can be broken into symmetric and antisymmetric parts which can be evaluated with the use of the identity $(\mathbf{a}\times\mathbf{b})\cdot(\mathbf{c}\times\mathbf{d})=\mathbf{a}\cdot(\mathbf{cd}-\mathbf{dc})\cdot\mathbf{b}$, and within the two-band model, in terms of the conduction-band inertial[16] $m_{\rm CB}$ and spin[27] $m_{\rm CB}^{\rm spin}$ masses, giving

$$M_0=\frac{PE_{\rm gap}}{R_{k_i,k_{\rm VB}}}\delta^{\rm KR}(\mathbf{k}_f-\mathbf{q}_l-\mathbf{k}_{VB})\delta^{\rm KR}(\mathbf{k}_i-\mathbf{q}_s-\mathbf{k}_{\rm VB})\ , \tag{8}$$

with

$$E_{\rm gap}\equiv E_{\rm CB}(k=0)-E_{\rm VB}(k=0)\ ,$$

and

$$R_{k_i,k_{\rm VB}}\equiv E_{\rm CB}(k_i)-E_{\rm VB}(k_{\rm VB})-\hbar\omega_s$$

is the resonance factor,

$$P\equiv\langle\chi_f\,|\,\chi_i\rangle\frac{\hat{\epsilon}_l\cdot\hat{\epsilon}_s^*}{2}\left[\frac{m}{m_{\rm CB}}-1\right]_{\rm partial}$$
$$+i\langle\chi_f\,|\,\sigma\,|\,\chi_i\rangle\cdot\left[\frac{\hat{\epsilon}_l\times\hat{\epsilon}_s^*}{2}\right]\left[\frac{m}{m_{\rm CB}^{\rm spin}}-1\right]_{\rm partial}$$

is the polarization factor, where σ is the spin-$\frac{1}{2}$ operator, and $|\chi_i\rangle$ and $|\chi_f\rangle$ are the initial and final spinor states and, of course,

$$\hbar ck_f+E_{\rm CB}(k_f)=\hbar ck_i+E_{\rm CB}(k_i)\ .$$

This result preserves all the important physical features of more realistic one-electron band models,[11,18] including the possibility of both spin-flip and spin-conserving processes.

We observe that since $\beta\ll1$ for electrons near the conduction-band edge, the scattering is quasielastic. Note that the cross section diverges when $E_{\rm CB}(k_i)-E_{\rm VB}(k_{\rm VB})\to\hbar\omega_s$. In reality, energy-broadening effects limit the divergence, which we can represent by adding $i\hbar\Gamma$ to $R_{k_i,k_{\rm VB}}$ in (8). We point out that in this quasielastic interband-enhanced free-electron scattering is the Raman dissipative process corresponding to[19] the degenerate four-wave mixing recently studied in InSb.[20] This mixing indeed showed huge enhancements as band-gap resonance is achieved.

In this paper the integrated Raman scattering cross section of a donor can be written as

$$\frac{d\sigma}{d\Omega}=\frac{\sigma_{\rm Th}}{8\pi/3}\left[\frac{\omega_s}{\omega_l}\right]|\,M_1+M_2+M_3\,|^2\ . \tag{9}$$

Below, we calculate each of the potentially resonant dimensionless partial amplitudes, M_1, M_2, and M_3, in cases 1, 2, and 3, respectively.

Case 1: Interband intermediate-state donor scattering.

We now consider scattering between donor states. The calculation proceeds much as for the (free-) conduction-band electrons, but now the slowly varying envelope integrals differ:

$$M_1\equiv\sum_{k_{\rm VB}}\frac{PE_{\rm gap}}{R_{\phi_i}+\hbar^2k_{\rm VB}^2/2m_{\rm VB}}\int\phi_f^*(\mathbf{R})e^{+i\mathbf{q}_l\cdot\mathbf{R}'}\frac{e^{i\mathbf{k}_{\rm VB}\cdot\mathbf{R}'}}{\sqrt{V}}d^3R'\int\frac{e^{-i\mathbf{k}_{\rm VB}\cdot\mathbf{R}}}{\sqrt{V}}e^{-i\mathbf{q}_s\cdot\mathbf{R}}\phi_i(\mathbf{R})d^3R\ , \tag{10}$$

with

$$R_{\phi_i}\equiv E_{\rm gap}+(E_{\phi_i}<0)-\hbar\omega_s\ ,$$

where E_{ϕ_i} is the binding energy of the initial donor state with respect to the conduction band.

We proceed by doing the $k_{\rm VB}$ integral $I_{k_{\rm VB}}$ first:

$$I_{k_{\rm VB}}\equiv\sum_{k_{\rm VB}}\frac{e^{i\mathbf{k}_{\rm VB}\cdot(\mathbf{R}'-\mathbf{R})}}{V(R_{\phi_i}+\hbar^2k_{\rm VB}^2/2m_{\rm VB})}$$
$$=\frac{1}{(2\pi)^3}\int d^3k\frac{e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}}{R_{\phi_i}+\hbar^2k^2}\ . \tag{11}$$

It is possible to do the integral in general, but we find it useful to first consider the limit of close to, but distinct from, band-gap resonance:

$$\frac{\hbar^2}{2m_{\rm VB}}\left[\frac{2\pi}{a_B}\right]^2\lesssim R_{\phi_i}\ll E_{\rm gap}\ ,$$

where a_B is the donor effective Bohr radius.

We expand the denominator approximately as

$$\frac{1}{R_{\phi_i}+\hbar^2k^2/2m_{\rm VB}}\approx\frac{1}{R_{\phi_i}}\left[1-\frac{\hbar^2k^2}{2m_{\rm VB}R_{\phi_i}}\right] \tag{12}$$

to evaluate

$$I_{k_{\rm VB}} \approx \frac{1}{R_{\phi_i}} \left[1 + \frac{\hbar^2 \nabla^2_{\mathbf{R}-\mathbf{R}'}}{2m_{\rm VB} R_{\phi_i}} \right] \delta^3(\mathbf{R}-\mathbf{R}') , \tag{13}$$

$$M_1 = \frac{PE_{\rm gap}}{R_{\phi_i}} \left[\int d^3R\, \phi_f^*(\mathbf{R}) e^{i(\mathbf{q}_l - \mathbf{q}_s)\cdot\mathbf{R}} \phi_i(\mathbf{R}) + \frac{\hbar^2}{2m_{\rm VB} R_{\phi_i}} \int\int d^3R\, d^3R' \phi_f^*(\mathbf{R}') e^{+i\mathbf{q}_l\cdot\mathbf{R}} \times [\nabla^2_{\mathbf{R}-\mathbf{R}'} \delta^3(\mathbf{R}-\mathbf{R}')] \phi_i(\mathbf{R}) e^{-i\mathbf{q}_s\cdot\mathbf{R}} \right] . \tag{14}$$

The second integral can be evaluated by changing variables from $\mathbf{R},\mathbf{R}'$ to $\mathbf{X}\equiv\mathbf{R}-\mathbf{R}',\mathbf{R}'$ and applying Green's theorem[21] in $\mathbf{X}$ space. The final result is

$$M_1 = \frac{PE_{\rm gap}}{R_{\phi_i}} S_{fi} , \tag{15}$$

where the form factor S_{fi} is given by

$$S_{fi} \equiv \int d^3R\, \phi_f^*(\mathbf{R}) e^{i(\mathbf{q}_l - \mathbf{q}_s)\cdot\mathbf{R}} \phi_i(\mathbf{R}) + \frac{\hbar^2}{2m_{\rm VB} R_{\phi_i}} \int d^3R\, \phi_f^*(\mathbf{R}) e^{i(\mathbf{q}_l - \mathbf{q}_s)\cdot\mathbf{R}} \times (\nabla_R - i\mathbf{q}_s)^2 \phi_i(\mathbf{R}) . \tag{16}$$

We see that the off-resonant interband-enhanced scattering cross section for donors is essentially that obtained for (free-) conduction-band electrons times the modulus squared of the form factor S_{fi}. The form factor gives the selection rules for the effective mass envelope of the orbital donor wave function.

First, let us neglect the photon momenta, $\mathbf{q}_l$ and $\mathbf{q}_s$. Orbital angular momentum (l,m) is preserved. In the present off-resonance limit, the second term in S_{fi} is generally smaller than a nonvanishing first term. The first term requires the initial and final wave functions overlap, which is equivalent to requiring they be identical if nondegenerate, as they are eigenfunctions of a common Hamiltonian. Thus, away from resonance, the only strong transition is within the $(1s)$ ground-state shell (i.e., spin-flip scattering), and its cross section is identically the same for bound and itinerant electrons. We write M_1 as

$$\lim_{q\to 0} M_1 = \frac{PE_{\rm gap}}{R_{\phi_i}} S_{fi} ,$$

where

$$S_{fi} = \left[\delta_{fi} + \frac{m_{\rm CB}}{m_{\rm VB}} \frac{R_y}{R_{\phi_i}} I_{fi}^{(1)} \right] \delta^{\rm KR}_{l_f,l_i} \delta^{\rm KR}_{m_f,m_i} , \tag{17}$$

with $I_{fi}^{(1)}$ a pure number of order unity and R_y the donor effective Rydberg. When we no longer neglect $\mathbf{q}_l$ and $\mathbf{q}_s$, we break orbital-angular-momentum conservation, with the scattering amplitude scaling[22] roughly as $(qa_B)^{\Delta l}$. These results justify the intuitive parity arguments first presented by Henry and Nassau.[7] Note that the enhanced cross section continues some distance above the band gap, but that Raman efficiency will suffer quite substantially from reductions in scattering volume as band-gap resonance is approached from below.

The general calculation of Eq. (11) gives

$$I_{k_{\rm VB}} = \frac{2m_{\rm VB}}{\hbar^2} \frac{Y_1}{4\pi |\mathbf{R}-\mathbf{R}'|} , \tag{18}$$

with $Y_1 = \exp[-(2m_{\rm VB} R_{\phi_i}/\hbar^2)^{1/2} |\mathbf{R}-\mathbf{R}'|]$, a dimensionless factor which approaches unity at resonance $(R_{\phi_i}=0)$. We have

$$M_1 = PE_{\rm gap} \frac{m_{\rm VB}}{2\pi\hbar^2} \int\int \frac{\phi_f^*(\mathbf{R}') e^{+i\mathbf{q}_l\cdot\mathbf{R}'} Y_1 e^{-i\mathbf{q}_s\cdot\mathbf{R}} \phi_i(\mathbf{R})}{|\mathbf{R}-\mathbf{R}'|} \times d^3R\, d^3R' = \frac{PE_{\rm gap}}{R_y} \frac{m_{\rm VB}}{m_{\rm CB}} \frac{I_{fi}^{(2)}}{4\pi} , \tag{19}$$

with $I_{fi}^{(2)}$ a pure number of order unity. Once again, scattering amplitude scales roughly as $(qa_B)^{\Delta l}$. For backscattering in an optically dense semiconductor the scaling parameter qa_B can be quite large. Even for the relatively small donor in CdS, $\lambda_{\rm free}\sim 5000$ Å, $a_B\sim 25$ Å, $n\sim 2.5$, and so

$$q_{\rm BS} a_B = 2 \frac{2\pi}{\lambda_{\rm free}} n a_B = 0.16 . \tag{20}$$

Crystal momentum is a good quantum number for the valence band. Since the donor envelope has no singularities in momentum space, the cross-section band-gap resonance [Eq. (17)] is truncated [Eq. (19)], even in the absence of broadening mechanisms, in contrast to the case of (free-) conduction-band electron scattering [Eq. (8)]. Comparing Eqs. (17) and (19), we see the effective "spatial localization" resonance broadening is approximately $\hbar\Gamma = R_y(m_{\rm CB}/m_{\rm VB})$, much larger than true energy-broadening contributions. The cross-section proportionality to $m_{\rm VB}^2$ arises because a more dispersionless valence band allows us to "approach resonance" more closely for a given donor wave-function size in $\mathbf{k}$ space. (This qualitative feature is in *accidental* agreement with a similar conclusion regarding the cross section based on entirely *different* considerations.[9])

As mentioned earlier, electron-electron interactions in the intermediate state modify these calculations. Both matrix elements and energy denominators are modified in important and complicated ways.

In the course of studying spin-flip Raman scattering between the $1s$ states of the CdS donor, Thomas and Hopfield[23] were the first to consider such issues. Like us, they

hypothesized the large, band-gap-resonance-enhanced cross section could be computed with the use of the expression of Eq. (2). However, they imagined the dominant intermediate state in their experiment was not the one-electron interband continuum we have used, but a discrete state: a complex, in its ground state, consisting of an exciton bound to the originally unmolested donor. Magneto-optic studies[24] of such three-particle complexes have shown that it is appropriate to think of the two electrons as occupying Kramer's conjugate states, thereby quenching their paramagnetism, with the valence-band hole orbiting nearby. If we for the moment neglect "configuration interaction" considerations (allowing admixtures of more than a single Slater determinant for a given bound-exciton eigenstate), the ground state can be said to consist of a pair of $1s$ donor electrons, as in the singlet D^- state, with a Bloch state hole, consistent with the spin-flip scattering model. Thomas and Hopfield *measured* the matrix element and energy denominator in Eq. (2) for this intermediate state and found the calculated cross section in acceptable agreement with their measured absolute cross section.

Adequately far from band-gap resonance, the one-electron theory of the present paper gives a result for the $1s$ spin-flip Raman cross section equal to that of Thomas and Hopfield under the transcription

$$i\langle\chi_f\,|\,\boldsymbol{\sigma}\,|\,\chi_i\rangle\cdot(\hat{\epsilon}_l\times\hat{\epsilon}_s^*)\left[\frac{m}{m_{\rm CB}^{\rm spin}}-1\right]\rightarrow f\cos\theta\ ,$$

where θ is the angle between the c axis and magnetic field and f is the measured oscillator strength ($\approx 9\pm 2$) relevant for the conditions under which the experiment was done. (In our simple isotropic band model we do not reproduce the completely anisotropic inverse-spin mass-defect contribution of the A valence band, $\vec{\mathscr{C}}-\vec{1}$, where $\mathscr{C}=(1/m_{\rm CB}^{\rm spin})_A^{ij}$ in the experiment under discussion). Note that it would seem that, for the small 40-cm^{-1} resonant denominator of the spin-flip experiment, the use of Eq. (19) rather than (17) might appear to be more correct. However, as the thoughtful reader has already realized, neither is correct. By introducing a *bound* intermediate state with a *discrete* rather than continuum spectrum, the many-electron interaction qualitatively changes the nature of the band-gap resonance, frustrating the divergence truncation predicted by the one-electron theory. Additionally, here it leads to matrix elements that turn out to be rather larger than predicted by using the one-electron continuum. (A two-band model for CdS in which the valence-band degeneracy is broken and the conduction-band mass is assumed to be 0.2 predicts that A-gap scattering should show an oscillator strength F of about unity.)

Similar considerations would be expected to apply to orbital donor scattering. Recently, this was suggested[25] by Yu (and then clarified[9] by Yu and Falicov). For $1s\rightarrow 2s$ scattering, for example, one would expect an excited bound-exciton state analogous to $D^-(1s,2s)$ (Ref. 9) to be the intermediate state of greatest (but not sole) importance. Limited studies of excited bound-exciton states have been done.[7,26]

Unfortunately, however, we remain largely ignorant of what the wave functions of bound excitons look like: "An exciton bound to a neutral donor . . . can be reduced to a four-body problem in the effective-mass approximation. General analytical solutions for this system are not possible, and the complicated dynamical structure must be approximated in order to *make progress* in understanding the observed *trends* in binding energies and other properties."[27] (Emphasis is ours.)

It is doubtful, therefore, that useful *ab initio* calculations of the important bound-exciton momentum matrix elements will be made. Moreover, they probably cannot even be measured, as they are between pairs of excited states of the crystal. For now, the present interband one-electron calculation, while overly conservative in cross-section divergence, provides a theoretical framework on which to expand. Additionally, a simple extension would prove most accurate when applied to considering the amplitude contributions of higher-lying (i.e., empty) bands (as long as adequate account is taken of its impurity states, of course).

Notwithstanding the difficulties discussed, we can use the present one-electron theory to numerically evaluate a lower bound on the band-gap resonance spin-conserving cross section.

Taking $\omega_s\approx\omega_l$, $m_{\rm CB}/m\ll 1$, $\hat{\epsilon}_l\cdot\hat{\epsilon}_s^*=1$, and $I_{fi}^{(2)}\sim 1$,

$$\frac{d\sigma}{d\Omega}\approx\frac{\sigma_{\rm Th}}{8\pi/3}\left[\frac{(m/m_{\rm CB})E_{\rm gap}/2}{R_y}\frac{m_{\rm VB}}{m_{\rm CB}}\frac{1}{4\pi}\right]^2$$
$$=\frac{\sigma_{\rm Th}}{8\pi/3}\left[\frac{E_{\rm gap}\epsilon_0^2}{8\pi R_y{}^H}\frac{m_{\rm VB}}{m}\left[\frac{m}{m_{\rm CB}}\right]^3\right]^2\ , \qquad (21)$$

where $R_y{}^H$ is the hydrogen-atom Rydberg. Over the range $30<n^4<440$, the empirical Moss rule[28,29] applies to semiconductors:

$$77\ {\rm eV}\approx n^4E_{\rm gap}=\epsilon_\infty^2E_{\rm gap}\approx\epsilon_0^2E_{\rm gap}\ , \qquad (22)$$

which gives us a reduced integral one-electron cross section of

$$F\equiv\frac{d\sigma/d\Omega}{\sigma_{\rm Th}}=0.006\left[\frac{m_{\rm VB}}{m}\left[\frac{m}{m_{\rm CB}}\right]^3\frac{E_{\rm gap}\epsilon_0^2}{77\ {\rm eV}}\right]^2$$
$$\approx 0.006\left[\frac{m_{\rm VB}}{m}\left[\frac{m}{m_{\rm CB}}\right]^3\right]^2\ . \qquad (23)$$

The figure of merit F is greatly increased by any small decrease in conduction-band mass, so that we expect especially large cross sections in narrow-gap materials, which have very small masses [except when exciton binding is too weak (quenching the influential exciton enhancement of cross-section) or donor and/or bound exciton linewidths are excessively broad due to the presence of destabilizing chemical and thermal lattice defects]. In Table I we tabulate the actual results for four typical semiconductors.[29] There are two important technological consequences of such large donor cross sections:

(1) The Raman gain of transition is proportional to the

TABLE I. Results for four semiconductors.

Material	m_{VB}/m	m_{CB}/m	ϵ_0	E_{gap} (eV)	F
CdS	>0.7	0.20	8.9	2.58	>324
CdSe	>0.4	0.13	10.6	1.85	>1449
GaAs	0.5	0.07	12	1.52	103K
InSb	0.18	0.0133	18	0.235	34M

ratio of the integrated cross section and the linewidth. Huge cross sections imply large gains despite considerable linewidths. This suggests the possibility of various band-gap radiation-pumped, far-infrared sources based on the donor Raman interaction.[30] A large gain is essential because excessive pump powers photoionize the neutral donors[31,32] on which a device would be based. Perhaps a ternary III-V injection laser might ultimately pump a nondegenerate GaAs device medium. Such a source would be tunable, as applied fields could significantly vary the transition energies of the donor. Note that both Raman gain and donor tunability are larger the smaller the semiconductor band gap.

(2) Laser Raman scattering is spatially resolving down to micron dimensions. Resonant scattering is a potentially powerful tool to diagnose the presence and distribution of residual donors for improving the purification of new semiconductor materials.[8]

IV. INTRABAND RESONANCE

In cases (2) and (3) we consider only intraband intermediate states, which should be accurately calculated within one-electron theory, unlike case (1). However, an added complication here is that the simplified wave functions discussed in Sec. II are inadequate to produce results correct even in lowest order.

Within effective-mass theory, the wave function is given by the convolution of the envelope function, $S_i(\mathbf{R})$, and the Wannier function for the appropriate band, $W_n(\mathbf{R})$. The Wannier functions are simply unitary transformations of the Bloch functions:

$$W_n(\mathbf{r}-\mathbf{R}',\sigma)=\frac{1}{\sqrt{N}}\sum_{\mathbf{k},s} e^{-i\mathbf{k}\cdot\mathbf{R}'}\psi^{\text{Bloch}}_{n,\mathbf{k},s}(\mathbf{r},\theta) ,$$

where

$$\psi^{\text{Bloch}}_{n,\mathbf{k},s}=u_{n,\mathbf{k},s}(\mathbf{r},\sigma)\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} .$$

Neglecting spin variables, the convolution can then be written as

$$\psi_{i,n}(\mathbf{r})=\sum_{\mathbf{R}'} S_{i,n}(\mathbf{R}')W_n(\mathbf{r}-\mathbf{R}) ,$$

$$=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}'} u_{n,\mathbf{k}'}(\mathbf{r})e^{i\mathbf{k}'\cdot\mathbf{r}}\mathcal{S}_{i,n}(\mathbf{k}') , \tag{24}$$

where

$$\mathcal{S}_{i,n}(\mathbf{k}')=\sum_{\mathbf{R}'} S_{i,n}(\mathbf{R}')e^{-i\mathbf{k}'\cdot\mathbf{R}'} .$$

Since $S_{i,n}(\mathbf{R}')$ is a slowly varying function, $\mathcal{S}_{i,n}(\mathbf{k}')$ is large only near $\mathbf{k}'=\mathbf{0}$, whence our approximations (3) and (4). However, in computing intraband-enhanced scattering, we cannot make this approximation. We must go beyond using

$$u_{n,\mathbf{k}'}(\mathbf{r})\rightarrow u_{n,k^*}(\mathbf{r})$$

in (24) above, using $\mathbf{k}\cdot\mathbf{p}$ perturbation theory[39] to obtain

$$u_{n,\mathbf{k}'}(\mathbf{r})\rightarrow u_{n,\mathbf{k}^*}(\mathbf{r})+\frac{1}{i}\sum_{n'\neq n} u_{n',\mathbf{k}^*}\mathbf{a}_{nn'}\cdot\nabla_{\mathbf{r}} ,$$

with $\mathbf{a}_{nn'}$ as defined in the Appendix.

Case 2: Bound-intraband intermediate-state donor scattering.

Considering potential resonances from bound donor states $\{\Phi_I\}$, including only terms potentially resonant for scattering from the donor ground state (excited-state-originating scattering is a trivial extension with little new physics), we obtain

$$M_2=\left[\frac{m}{m_{CB}}\right]^2\sum_I\left[\int d^3R'\,\phi_f^*(\mathbf{R}')\mathbf{P}_{\mathbf{R}'}\cdot\hat{\epsilon}_s^* e^{-i\mathbf{q}_s\cdot\mathbf{R}}\phi_I(\mathbf{R}')\frac{\int d^3R\,\phi_I^*(\mathbf{R})\mathbf{P}_{\mathbf{R}}\cdot\hat{\epsilon}_l e^{+i\mathbf{q}_l\cdot\mathbf{R}}\phi_i(\mathbf{R})}{m(E_{\phi_i}-E_{\phi_i}+\hbar\omega_l)}\right] , \tag{25}$$

$$M_2=\frac{m}{m_{CB}}R_y\sum_I\frac{\hat{\epsilon}_s\cdot\overleftrightarrow{\mathbf{I}}^{(3)}_{fIi}(\mathbf{q}_s,\mathbf{q}_l)\cdot\hat{\epsilon}_l}{E_{\phi_i}-E_{\phi_i}+\hbar\omega_l}\langle\chi_f\,|\,\chi_i\rangle , \tag{26}$$

where $\overleftrightarrow{\mathbf{I}}^{(3)}_{fIi}$ is a dimensionless tensor of order unity.

In computing the amplitude M_2, we derived prefixes of m/m_{CB} due to the existence of $\mathbf{a}_{nn'}\neq\mathbf{0}$ terms in the wave functions used. This amplitude is in agreement with earlier studies.[5,32] The result is of the form obtained for scattering by an atom in free space. Conservation of spin emerges because interband-coupling tensors only appear symmetrically. In the absence of damping, the cross section shows a divergence when the laser photon energy approaches the energy spacing of the initial and an intermediate donor state. Unfortunately, near-resonant excitation will tend to be accompanied by photo (thermal) ionization of the donor. Note that interband-enhanced scattering requires the use of exotic far-infrared lasers.

Neglecting the photon momenta $\mathbf{q}_l$ and $\mathbf{q}_s$, we can use the fact that

$$P=m\frac{[\mathbf{R},H_D]}{i\hbar} , \tag{27}$$

where

$$H_D=-\frac{\hbar^2}{2m_{CB}}\nabla^2_{\mathbf{R}}+\frac{e^2}{\epsilon_0\,|\,\mathbf{R}}$$

(the donor effective-mass Hamiltonian), to change the integrals in (25) to matrix elements of $\mathbf{R}$. It is then obvious that $\Delta l=(\Delta l_0\equiv 0,\pm 2)$. This rule is broken to include

$\Delta l = \Delta l_0 \pm \Delta l_1$ with a scattering amplitude that scales as $(qa_B)^{\Delta l_1}$.

Case 3: Free-intraband intermediate-state donor scattering.

Considering only donor scattering states for intermediate states, we have, again omitting antiresonant terms,

$$M_3 = \left[\frac{m}{m_{\rm CB}}\right]^2 \sum_{k_{\rm CB}} \left[\int\int d^3r'\, d^3r\, \phi_f^*(\mathbf{R}')\mathbf{P}_{\mathbf{R}'}\cdot\hat{\epsilon}_s e^{-i\mathbf{q}_s\cdot\mathbf{R}'} \frac{e^{i\mathbf{k}_{\rm CB}(\mathbf{r}'-\mathbf{r})}}{V} \frac{\mathbf{P}_{\mathbf{R}}\cdot\hat{\epsilon}_l\, e^{+i\mathbf{q}_l\cdot\mathbf{R}}\phi_i(\mathbf{R})}{m(E_{\phi_i} - \hbar^2 k_{\rm CB}^2/2m_{\rm CB} + \hbar\omega_l)} \right] \tag{28}$$

to evaluate

$$M_3 = \left[\frac{m}{m_{\rm CB}}\right]^2 \frac{1}{m} \int d^3R\, d^3R'\, \phi_f^*(\mathbf{R}')\mathbf{P}_{\mathbf{R}'}\cdot\hat{\epsilon}_s^* e^{-i\mathbf{q}_s\cdot\mathbf{R}} \frac{-m_{\rm CB} Y_2}{2\pi\hbar^2 |\mathbf{R}-\mathbf{R}'|} \mathbf{P}_{\mathbf{R}}\cdot\hat{\epsilon}_l\, e^{+i\mathbf{q}_l\cdot\mathbf{R}}\phi_l(\mathbf{R}') , \tag{29}$$

with

$$Y_2 = \exp\{-[2m_{\rm CB}(-E_{\phi_i} - \hbar\omega_l)/\hbar^2]^{1/2} |\mathbf{R}-\mathbf{R}'|\}$$

a dimensionless factor which approaches unity at "resonance" ($\hbar\omega_l = -E_{\phi_i}$). We have

$$M_3 = \left[\frac{m}{m_{\rm CB}}\right]^2 \frac{1}{m} \hat{\epsilon}_s^* \cdot \overleftrightarrow{\mathbf{I}}_{fi}^{(4)} \cdot \hat{\epsilon}_l \langle \chi_f | \chi_i \rangle , \tag{30}$$

where $\overleftrightarrow{\mathbf{I}}_{fi}^{(4)}$ is a dimensionless tensor of order unity. The same selection rules regarding spin and orbital angular momentum derived for case (2) apply here in case (3). Again, observe the absence of any divergence in the cross section because the donor wave functions are delocalized in **k** space.

V. SUMMARY

We have shown that a straightforward application of the Fermi golden rule employing the $\mathbf{\Pi}\cdot\mathbf{A}$ perturbation in second order to a very simple one-electron two-band single-valley effective-mass model of a semiconductor predicts Raman scattering between all the bound spin and orbital states of a shallow donor. We have examined intermediate states in the valence band, the conduction-band continuum, and other bound donor states. Within one-electron theory, only the last of these three types of states leads to a divergent cross section in the absence of damping. However, excitonic corrections to the interband amplitude contribution also show similar divergences. Only the interband process need not conserve donor spin.[12] To lowest order in (qa_B), donor envelope orbital angular momentum is conserved by the interband term, and changed by $\Delta l = \pm 2$ or not at all by intraband terms. Intraband scattering is analogous to scattering from an isolated hydrogen atom. The large interband cross sections we predict have important technological consequences for the development of far-infrared sources and the refinement and characterization of new semiconductor materials.

VI. FUTURE WORK

We have already remarked on the need to consider many-electron effects more carefully, and further to note the usefulness of doing the calculations for the case of nonzero applied external (electric or magnetic) field. Additional work is indicated by relaxing one or more of our assumptions. One should carefully reconsider the A^2 term in first order. As many semiconductors and/or donor sites lack inversion symmetry, one should reexamine our parity arguments, as well as allow for zone-center effective Hamiltonian terms linear in wave vector. The important case of multivalley donors, as in silicon,[5] is not addressed by the present theory. One would expect significant differences from fundamental edge enhanced transitions.[33] As we have noted, even simple complications such as mass anisotropies can have serious consequences for selection rules.[23] Calculations for Lyman (and other) transitions of acceptor states[34] should also be undertaken.

We emphasize that the present treatment has ignored the interaction of the light with the crystal as a whole. As a first approximation, we can account for this by replacing $1/(\omega_q)^{1/2}$ in Eq. (1) by $1/(\omega_q\mu\epsilon)^{1/2}$ (Ref. 35). However, near dielectric resonances (such as excitons) this procedure is inadequate. Proper account must be taken of polariton effects[36] and calculations relevant to impurity-state Raman scattering have been undertaken.[8,37,38] A notable feature of excitonic polariton effects is the possibility for enhanced momentum transfer in the resonance region. While exciton and polariton effects will modify the details of the theory presented here, the present computation has the merit of being exact within the simplified model it employs, which hopefully makes it of use in guiding the development or more sophisticated treatments in the future, as well as motivating systematic experimental studies of momentum and polarization selection rules.

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APPENDIX

The completeness of the Bloch functions permit an exact solution to the one-electron Coulombic defect problem, which we assume adequately represents the shallow-donor problem.

This exact solution sums contributions from all bands:

$$\psi_i(\mathbf{r})=\sum_n \psi_{i,n}(\mathbf{r}) , \tag{A1}$$

with $\psi_{i,n}(\mathbf{r})$ as defined in (24). Effective-mass theory assumes that the contributions from all but one band are negligible for any $\psi_i(\mathbf{r})$.

The essence of effective-mass theory[39] is that the slowly varying envelope, $S_{i,n}(\mathbf{R}')$ in (24), obeys the simple relationship

$$\left[-\frac{\hbar^2}{2}\nabla\cdot\overleftrightarrow{\mathscr{C}}^*\cdot\nabla+\delta V(\mathbf{R})-E_{i,n}\right]S_{i,n}(\mathbf{R}')=0 , \tag{A2}$$

where $\overleftrightarrow{\mathscr{C}}^*=(1/m^*)^{ij}$ and $\delta V(\mathbf{R})$ is the variation of the self-consistent crystal potential from the form from which the Bloch functions are derived.

Near a bound extremum, $\mathbf{k}^*$, $\mathbf{k}\cdot\mathbf{p}$ perturbation theory[39] can be used to derive the periodic part of the Bloch function, $\{u_{n,\mathbf{k}^*}(\mathbf{r})\}$, $\{E_n(k^*)\}$. The first-order correction yields the result

$$u_{n,\mathbf{k}'}\approx u_{n,\mathbf{k}^*}+\sum_{n'\neq n} u_{n',\mathbf{k}^*}\mathbf{a}_{nn'}\cdot\mathbf{k} , \tag{A3}$$

where

$$\mathbf{a}_{nn'}=\frac{\hbar^2}{m}\frac{\int u^*_{n',k^*}\nabla u_{n,k^*}d^3r}{E_n(k^*)-E_{n'}(k^*)} .$$

While this term is small, of order

$$|\,\mathbf{a}_{nn'}\,|\sim a_B^*(n)\left[\frac{R_y^*(n)}{E_{\text{gap}}}\right]^{1/2}$$

in our two-band model, it cannot be neglected in the intraband-mediated scattering treatment of Sec. IV. There we exploit the form of (24) to write the $\mathbf{k}$ in (A3) as $(1/i)\nabla$. For the interband-mediated treatment of Sec. III, such complications can be neglected.

[1]W. Hayes and R. Loudon, *Scattering of Light by Crystals* (Wiley, New York, 1978).

[2]R. J. Elliott and R. Loudon, Phys. Lett. **3**, 189 (1963).

[3]J. T. Hougen and S. Singh, Phys. Rev. Lett. **10**, 406 (1963).

[4]C. H. Henry, J. J. Hopfield, and L. C. Luther, Phys. Rev. Lett. **17**, 1178 (1966).

[5]G. B. Wright and A. Mooradian, Phys. Rev. Lett. **18**, 608 (1967). We regret the omission of detail in the calculations of the paper above and find the stated results equivocal.

[6]*Proceedings of the Third International Conference on Light Scattering in Solids,* edited by M. Balkanski *et al.* (Flammarion, Paris, 1976).

[7]C. H. Henry and K. Nassau, Phys. Rev. B **2**, 997 (1970).

[8]R. G. Ulbrich, N. V. Hieu, and C. Weisbuch, Phys. Rev. Lett. **46**, 53 (1981).

[9]P. Y. Yu and L. M. Falicov, Phys. Rev. B **24**, 1144 (1981).

[10]P. J. Colwell and M. V. Klein, Phys. Rev. B **6**, 498 (1972). The completeness relation does not justify the steps between Eqs. (10) and (11) of the paper above, even in the event of a single dominant intermediate state.

[11]Y. Yafet, in *New Developments in Semiconductors,* edited by P. R. Wallace, R. Harris, and M. J. Zuckermann (Noordhoff, Leyden, 1973).

[12]In particular, more sophisticated wave functions are needed to do even the simplest calculation of intraband-enhanced scattering. In Sec. IV and the Appendix we discuss the more general wave functions.

[13]S. T. Pantelides, Rev. Mod. Phys. **50**, 797 (1978).

[14]W. Heitler, *The Quantum Theory of Radiation* (Oxford, Clarendon, 1954).

[15]P. A. Wolff, in *Nonlinear Optics,* edited by P. G. Harper and B. S. Wherrett (Academic, New York, 1977).

[16]J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1976), p. 250.

[17]L. M. Roth, Phys. Rev. **118**, 1534 (1960).

[18]D. C. Hamilton and A. L. McWhorter, in *Light Scattering Spectra of Solids,* edited by G. B. Wright (Springer, New York, 1969).

[19]H. Mahr, in *Quantum Electronics: A Treatise,* edited by H. Rabin and C. L. Tang (Academic, New York, 1975).

[20]D. A. B. Miller, S. D. Smith, and B. S. Wherrett, Opt. Commun. **35**, 221 (1980).

[21]J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), p. 15.

[22]E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge, Cambridge, 1957), p. 176.

[23]D. G. Thomas and J. J. Hopfield, Phys. Rev. **175**, 1021 (1968).

[24]D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

[25]P. Y. Yu, Phys. Rev. B **20**, 5286 (1979).

[26]Studies of bound exciton excited states in CdS were summarized in D. Munz and M. H. Pilkuhn [Solid State Commun. **36**, 205 (1980)].

[27]D. C. Herbert, J. Phys. C **10**, 3327 (1977). Another theoretical review of bound excitons is given by U. Schroder, in *Festkörperprobleme XIII,* edited by H. J. Queisser (Vieweg, Braunschweig, BRD, 1973).

[28]M. Kurik, Phys. Lett. **24**, A742 (1967).

[29]J. I. Pankove, *Optical Processes in Semiconductors* (Prentice-Hall, Englewood Cliffs, N.J., 1971), p. 89. Appendix II of this paper supplies the values used in the table in the text. The careful reader has of course noted that $(m/m_{\text{CB}})^3$ in Eq. (23) is better rendered as $(m/m_{\text{CB}})^2(m/m_{\text{CB}}-1)_{\text{VB}}$, where the subscript VB refers to the actual $\mathbf{k}\cdot\mathbf{p}$ theory contribution of the valence band to $(m/m_{\text{CB}})-1$. However, as the two-band model is itself inadequate for the materials cited, the additional error of the present approximation is not noteworthy.

[30]Y. R. Shen, Appl. Phys. Lett. **23**, 516 (1973).

[31]S. Chaudhuri, Phys. Rev. B **26**, 6593 (1982).

[32]C. K. N. Patel and Y. Yafet, Appl. Phys. Lett. **34**, 318 (1979). Intraband scattering is implicitly derived in this paper using a treatment analogous to that of G. Weinreich [*Solids* (Wiley, New York, 1965), Sec. 9.10].

[33]J. F. Scott, T. C. Damen, R. C. C. Leite, and W. T. Silfvast, Solid State Commun. **7**, 953 (1969).

[34]J. F. Scott, F. Habbal, J. H. Nicola, D. J. Tos, and S. Nakashima, Phys. Rev. B **19**, 3053 (1979).

[35]D. Marcuse, *Engineering Quantum Electrodynamics* (Harcourt, Brace, and World, New York, 1970), pp. 68 and 69.

[36]Barker and R. Loudon, Rev. Mod. Phys. **44**, 18 (1972).

[37]J. J. Hopfield, Phys. Rev. **182**, 945 (1969).

[38]N. Baan, N. V. Hieu, N. Toanthang, and N. Aiviet, J. Phys. (Paris) **41**, 1067 (1980).

[39]J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, 1972), pp. 172ff and 118.