Resonant Scattering of Polaritons as Composite Particles†

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To calculate correctly the scattering of light by phonons or impurities in a crystal, the true asymptotic scattering states of the coupled system of crystal plus light (polaritons) should be used. When the light frequency is close to one exciton or optical-phonon frequency, the polariton is entirely excitonlike, and the polariton scattering can, in the Born approximation, be related to exciton scattering properties. If the exciton itself interacts strongly with an imperfection in the crystal, it is not permissible to treat either the exciton scattering or the exciton-photon interaction as perturbations. This problem of resonant scattering of polaritons is solved for short-range exciton-impurity interactions. Radiative damping and spatial dispersion appear in this solution in a natural fashion. Giant oscillator strengths of bound-exciton transitions are likewise automatically obtained. The proper inclusion of radiative damping and spatial dispersion keeps all cross sections finite. The relation between the theory and experiments is briefly discussed.

I. INTRODUCTION

LIGHT whose frequency is very near a strong absorption band in a solid (e.g., near an exciton or optical-phonon resonance energy) couples strongly with a crystal. The polariton, a mixed mode of light and crystal polarization, is the true eigenmode of propagation in the crystal.[1] The Rayleigh, Raman, or Brillouin scattering of light in a crystal is most physically described as a scattering of a polariton by an impurity, optical phonon, or acoustic phonon and is often so described in theory.[2] For photon frequencies far away from any resonance, polaritons chiefly resemble renormalized photons, and elementary points of view about photon are useful. For photon frequencies near an exciton resonance (for example) polaritons are chiefly excitionlike, and it should be possible to use this feature of polaritons to express polariton scattering in terms of parameters relevant to the scattering of bare excitons from impurities or phonons.

This study is motivated by the growing number of experiments on the scattering of light near the fundamental exciton absorption resonance in semiconductors and insulators.[3,4] Our results provide a simple method of estimating cross sections and understanding energy dependences in that energy region where the strong coupling between light and matter makes the problem appear most difficult. In the present work, spatial dispersion and radiative damping each enter the theory in an elementary fashion. While the results of this paper can be (and some have been) obtained from more conventional points of view when the scattering is weak,[5] the conceptual simplification provided by the composite particle approach is considerable even in this case, and is essential for resonant scattering near exciton transitions.

In Sec. II, a model for the polariton with light very near an exciton frequency is set up, and its application is reviewed in a case in which the scattering can be treated in the Born approximation. In Sec. III, the model is applied to the case in which an impurity produces a resonant scattering (bound-exciton state). A giant oscillator strength and a complicated energy dependence of the cross section emerge. The results are discussed in comparison with experiments and other theories in Sec IV.

II. POLARITON SCATTERING IN THE BORN APPROXIMATION

The dielectric medium in which the polariton propagates is presumed to be characterized by a background dielectric constant ϵ_0 and a single resonant freuqency ω_0. For light frequencies close to ω_0, the precise origin of the background dielectric response is immaterial. If the dielectric resonance frequency $\omega_0(\mathbf{k})$ is also allowed to be wave-vector-dependent, the dielectric response of the medium in the absence of a scattering center is assumed to be of the form

$$\epsilon(\mathbf{k},\omega)=\epsilon_0+\frac{4\pi\beta}{1-\omega^2/\omega_0^2(\mathbf{k})}. \tag{1}$$

It will further be assumed that, for small k,

$$\omega_0^2(\mathbf{k})=\omega_0^2+\hbar k^2\omega_0/m. \tag{2}$$

This is not the most general form of small-$\mathbf{k}$ single-resonance dielectric response, even for a cubic crystal. For finite $\mathbf{k}$, ϵ_0 could have been a nondiagonal tensor, and the degeneracy in $\omega_0(\mathbf{k})$ could be split for $\mathbf{k}\neq 0$. To preserve algebraic and conceptual simplicity, such unnecessary complications will be ignored. The dielectric response then represents that due to an exciton or other quasiparticle having a dispersion relation (in the *absence* of a coupling to light)

$$E_{\mathbf{k}}=\hbar\omega_0(\mathbf{k}) \tag{3}$$

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[1] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), pp. 89–100.

[2] L. N. Ovander, Fiz. Tverd. Tela **3**, 2394 (1961); **5**, 21 (1963) [English transls.: Soviet Phys.—Solid State **3**, 1737 (1962); **5**, 13 (1963)].

[3] R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters **17**, 10 (1966).

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

[5] A. K. Ganguly and J. L. Birman, Phys. Rev. **162**, 806 (1967).

and mass m. Such a model has been successfully used for treating problems involving spatial dispersion.[5]

The polariton normal modes of wave propagation in such a medium can be treated either quantum-mechanically or classically. If we denote the quantum-mechanical exciton creation (annihilation) operators by $b_k^\dagger$ (b_k), and the photon operators by $a_k^\dagger$ (a_k), then the transformation from exciton and photon operators to polariton operators is[1]

$$\begin{aligned}
&\alpha_k^\dagger = c_{11}a_k^\dagger + c_{12}b_k^\dagger + c_{13}a_{-k} + c_{14}b_{-k}, \\
&c_{11} = \frac{(1-\omega/\omega_0)(ck/\omega_0+\omega/\omega_0)(1+\omega/\omega_0)}{2(ck\omega/\omega_0^2)^{1/2}[(1-\omega^2/\omega_0^2)^2+4\pi\beta/\epsilon_0]^{1/2}}, \\
&c_{12} = \frac{-i(\pi\beta/\epsilon_0)^{1/2}(1+\omega/\omega_0)}{(\omega/\omega_0)^{1/2}[(1-\omega^2/\omega_0^2)^2+4\pi\beta/\epsilon_0]^{1/2}}, \\
&c_{13} = c_{11}(ck/\omega_0-\omega/\omega_0)/(ck/\omega_0+\omega/\omega_0), \\
&c_{14} = c_{12}(1-\omega/\omega_0)/(1+\omega/\omega_0),
\end{aligned} \tag{4}$$

where $\alpha_k^\dagger$ is a creation operator for a polariton wave vector $\mathbf{k}$. The frequency ω of such a polariton is given by a solution of

$$\frac{c^2\mathbf{k}^2}{\omega^2} = 1 + \frac{4\pi\beta/\epsilon_0}{1-\omega^2/\omega_0^2}. \tag{5}$$

In these equations, c is the renormalized velocity of light $3\times10^{10}/\sqrt{\epsilon_0}$ cm/sec.

Let E_{lt} be the splitting between a longitudinal exciton and its corresponding transverse exciton. This energy can be expressed in terms of the already defined parameters by

$$E_{lt} \equiv \hbar\omega_{lt} = [(1+4\pi\beta/\epsilon_0)^{1/2}-1]\hbar\omega_0 \approx (2\pi\beta/\epsilon_0)\hbar\omega_0, \tag{6}$$

and is often directly measurable. In CdS, a typical seimconductor, this energy is about 0.002 eV for the lowest-energy exciton. For NaCl, the corresponding number is about 0.1 eV. Define a coupling energy

$$\hbar\omega_c \equiv E_c = (\hbar\omega_0 E_{lt})^{1/2}. \tag{7}$$

For photon energies $\hbar\omega$ such that $|\hbar\omega-\hbar\omega_0|$ is somewhat less than E_c, the transformation (4) becomes

$$c_{11}\approx 0, \quad c_{13}\approx 0, \quad c_{14}\approx 0, \quad c_{12}\approx 1, \quad \alpha_k^\dagger \approx b_k^\dagger. \tag{8}$$

In short, the polariton *wave function* in this energy region is virtually all excitonlike, although *its dispersion relation* need not be. We call this case the exciton limit.

A classical indication of why this is so is seen from an examination of the polariton dispersion relation. Letting the exciton mass be infinite for the moment, one can write the polariton dispersion relation approximately as

$$\frac{c^2\mathbf{k}^2}{\omega^2} \approx \epsilon_0 + \frac{2\pi\beta}{1-\omega/\omega_0} = \epsilon_0\left(1+\frac{\omega_{lt}}{\omega_0-\omega}\right). \tag{9}$$

For $|\omega_0-\omega| > 2\omega_{lt}$, the index of refraction is not dominated by the exciton. Yet the group velocity, approximately

$$v_g = \frac{1}{dk/d\omega} \approx \frac{c}{\sqrt{\epsilon_0}}\left[1+\frac{1}{2}\left(\frac{\omega_c}{\omega_0-\omega}\right)^2\right]^{-1}, \tag{10}$$

is dominated by the ω_c^2 term for all $|\omega-\omega_0| < \omega_c$, showing that the polariton is chiefly excitonlike. If is often not appreciated that the energy at which it becomes excitonlike (i.e., E_c) is far enough from that of the exciton resonance to be experimentally important.

Suppose some new perturbation is introduced into the Hamiltonian. The simplest such perturbation might be a weak, short-range electrostatic potential $V(r)$. If we ignore exciton-photon interactions, the differential scattering cross section for an exciton (of isotropic mass) scattering from state $|\mathbf{k}\rangle$ to state $|\mathbf{k}'\rangle$ can be evaluated in the Born approximation,[6] and is given by

$$\begin{aligned}
\frac{d\sigma}{d\Omega} &= \frac{1}{v_{ex}}|\langle\mathbf{k}|V(r)|\mathbf{k}'\rangle|\frac{k^2}{\pi\hbar}\frac{dk}{dE} \\
&= |\langle\mathbf{k}|V(r)\mathbf{k}'\rangle|^2\frac{k^2}{\pi\hbar^2}\frac{1}{v_{ex}^2},
\end{aligned} \tag{11}$$

where the matrix element of V is taken between initial and final states normalized to unit volume, and the conservation of energy demands $|\mathbf{k}| = |\mathbf{k}'|$. The velocity of the exciton is $v_{ex} = \hbar k/m$, and its energy is $E = h^2\mathbf{k}^2/2m$. Consider now the scattering of a polariton for which $|\omega-\omega_0| < \omega_c$ from the same impurity potential. Because the polariton wave function is essentially excitonlike, the matrix element is simply

$$\langle\text{polariton } \mathbf{k}|V(r)|\text{polariton } \mathbf{k}'\rangle = \langle\mathbf{k}|V(r)|\mathbf{k}'\rangle. \tag{12}$$

In the Born approximation (i.e., using Fermi's transition-rate "Golden rule"),[5] the differential scattering cross section for polariton $\mathbf{k}$ scattering to $\mathbf{k}'$ is

$$\begin{aligned}
\left(\frac{d\sigma}{d\Omega}\right)_{pol} &= \frac{1}{v_g}|\langle\mathbf{k}|V(r)|\mathbf{k}'\rangle|^2\frac{k^2}{\pi\hbar^2}\frac{dk}{dE} \\
&= |\langle\mathbf{k}|V(r)|\mathbf{k}'\rangle|^2\frac{k^2}{\pi\hbar^2}\frac{1}{v_g^2},
\end{aligned} \tag{13}$$

where E is the polariton energy and v_g is the polariton group velocity. Thus

$$\left(\frac{d\sigma}{d\Omega}\right)_{pol} = \left(\frac{d\sigma}{d\Omega}\right)_{ex}\left(\frac{v_{ex}}{v_g}\right)^2, \tag{14}$$

where all cross sections and velocities are evaluated for the same $\mathbf{k}$. This gives an immediate method of evaluating the polariton scattering cross section (i.e., the Rayleigh scattering of the impurity) for energies near the excition resonance, in terms of the bare-exciton scattering. Such a result is particularly useful when the bare-exciton scattering cross section can be estimated

[6] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).

from the appropriate magnitude and range of $V(r)$, the internal structure of the exciton, and the wave vector.

When ω is not too near ω_0, Eq. (10) is an adequate expression for v_g, and the dominant frequency dependence of the cross section is proportional to $(\omega-\omega_0)^{-4}$. When ω is very near ω_0, however, the $\mathbf{k}$ dependence of the exciton energy must be taken into account in evaluating the group velocity. Inspection of the polariton dispersion relation including a finite positive exciton mass (Fig. 1) shows that the group velocity of the polariton is always greater than that of the exciton of the same wave vector. When ω approaches very close to the exciton energy, $(v_{ex}/v_g)^2$ only goes to a limit of 1.0, not infinity. In this description there is no nonphysical divergence[4] in the polariton scattering cross section near the $\mathbf{k}=0$ exciton energy.

Inelastic scattering cross sections for polaritons—for example, near-resonance Raman scattering cross sections—can again be calculated in the Born approximation from the matrix elements for a similar pure exciton scattering process. In this case, the pure exciton inelastic process may often fail to conserve energy and therefore occur only as a virtual process. The matrix element for the the virtual process will still be well defined. If $|\langle\mathbf{k}|M|\mathbf{k}',\mathrm{ph}\rangle|$ is the Born-approximation matrix element for scattering a pure exciton from state $\mathbf{k}$ to state $\mathbf{k}'$ with the excitation of a phonon of frequency ω_{ph} (assumed $\mathbf{k}$-independent) and wave vector $\mathbf{k}'-\mathbf{k}$, the inelastic polariton differential scattering cross section is[7]

$$\frac{d\sigma}{d\Omega}=\frac{(k')^2}{\pi h^2 v_g v_g'}|\langle\mathbf{k}|M|\mathbf{k}',\mathrm{ph}\rangle|^2, \tag{15}$$

where v_g and v_g' are the group velocities of the polaritons of wave vector $\mathbf{k}$ and $\mathbf{k}'$, respectively. Conservation of energy requires $\omega(k')+\omega_{\mathrm{ph}}=\omega(k)$. For this inelastic (Raman Stokes) scattering, the dominant frequency dependence is $(\omega_0-\omega)^{-2}(\omega_0-\omega_p-\omega)^{-2}$. Again, if ω is too near a singularity, the group velocity including spatial dispersion only drops to the exciton velocity for the same k, and there is no divergence of the calculated cross section.

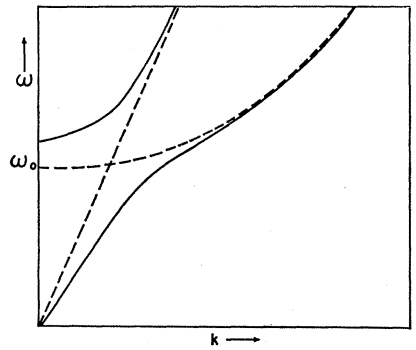

FIG. 1. Dispersion relation for bare excitons and bare light (dashed lines) and for polaritons (solid lines). The right-hand polarization curve has a greater slope for a given k than the bare-exciton curve.

[7] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), pp. 199–201 and 205–206.

When two exciton transitions lie close together, entirely similar methods can be applied once the polariton wave function has been written down. While in principle the general method can be extended to arbitrarily complicated situations and to energies far from resonances, such extensions yield little understanding beyond that available in terms of conventional nonlinear polarizabilities.

III. RESONANT POLARITON SCATTERING

Consider the same single-exciton model of a polariton for $|\omega-\omega_0|<\omega_c$. In this strong-coupling case, the polariton is the particle whose scattering must be calculated, as was done in the Born approximation in Sec. II. In the present section we consider the Rayleigh scattering of such a polariton from a strong, short-range potential. Such a potential cannot, of course, be treated in the Born approximation. Of particular interest is the case in which the potential is so strong that the exciton, if it were not coupled to light, would bind to the potential. The fundamental theoretical problem is that two kinds of coupling are simultaneously strong. Neither can be calculated as a perturbation.

The most direct method of attacking this problem is to construct a set of classical electromagnetic equations which have all the desired properties, and to examine their solution. Consider the classical field equations[4]

$$\nabla\times\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t},\quad \mathbf{B}=\mathbf{H},\quad \mathbf{D}=\mathbf{E}+4\pi\mathbf{P},$$
$$\nabla\times\mathbf{H}=-\frac{1}{c}\frac{\partial\mathbf{D}}{\partial t}, \tag{16}$$
$$\left(\frac{1}{\omega_0^2}\frac{\partial^2}{\partial t^2}-\frac{\hbar\nabla^2}{m\omega_0}+\frac{2U(r)}{\hbar\omega_0}+1\right)\mathbf{P}=\beta\mathbf{E},$$

where $U(r)$ is a "potential" of short range. If $\beta=0$, there is no coupling between the electromagnetic field and the polarization field. The polarization field equation with a harmonic time dependence $e^{i\omega t}$ then becomes

$$\left(-\frac{\hbar^2\nabla^2}{2m}+U(r)\right)\mathbf{P}(\mathbf{r})=\tfrac{1}{2}\hbar\omega_0\left(\frac{\omega^2}{\omega_0^2}-1\right)\mathbf{P}(\mathbf{r}). \tag{17}$$

If $U(r)$ has a form such that, as a potential in the Schrödinger equation, it yields a binding energy E_B, i.e.,

$$\left(-\frac{\hbar^2\nabla^2}{2m}+U(r)\right)\psi_B=-E_B\psi_B, \tag{18}$$

and if $E_B\ll\hbar\omega_0$, then Eq. (17) will have the same solution ψ_B for $\omega=\omega_0-E_B/\hbar$. Thus an appropriate choice of $U(r)$ will produce a shallow bound-state Schrödinger equation for the exciton in the absence of coupling

between the exciton and light. (In the classical theory, **P** plays a role rather like an exciton c.m. wave function.) Once again, we have not inserted all the tensorial complications possible, but have chosen the simplest set of equations consistent with the objective of examining a resonance situation. Because the photon and phonon "particles" of these classical fields are bosons and the basic equation is linear, second quantization of these equations is unnecessary.

B, **H**, and **D** can be immediately eliminated, and a solution harmonic in time presumed, yielding

$$(\text{grad div}-\nabla^2)\mathbf{E}=-\omega^2[\mathbf{E}+4\pi\mathbf{P}], \tag{19a}$$

$$\left[-\frac{\omega^2}{\omega_0^2}-\frac{\hbar^2}{m\omega_0}\nabla^2+\left(1+\frac{2V(r)}{\hbar\omega_0}\right)\right]\mathbf{P}=\beta\mathbf{P}. \tag{19b}$$

If light could be longitudinal as well as transverse, (19a) would lack the "grad div" term. If the "grad div" term were absent, the vector nature of Eq. (19) would be irrelevant, because both **P** and **E** would be constant vectors times a scalar function of position. Because there is much less algebra without the "grad div" term, we shall omit it.

Since this appears *extremely* arbitrary, a digression to explain the nature of the approximation is in order. The basic physics problem under investigation is simple. Two fields, A, and B are linearly coupled, and have a "level-crossing" form of dispersion relation like Fig. 1 for their composite normal mode. If, in the absence of coupling between fields, the field A had a bound state near the level-crossing energy, what will be the behavior of the scattering of the composite particle near this energy? This question is very similar whether the fields A and B are vector fields or scalar fields. The algebra is easier for the scalar-field case, while the exciton-photon problem is the vector case. The important basic physics is preserved on substituting the scalar problem for the vector one.

A few obvious minor differences result from this substitution. First, the scattering cross section for the simplest scalar problem is isotropic, while it is not for the simplest vector case. Second, the total cross section is too large by a factor of $\frac{3}{2}$, for our approximation adds a nonexistent longitudinal photon mode to the two transverse ones. Third, the approximation eliminates the energy difference between longitudinal and transverse excitons. It cannot, then, be expected to be useful for $\omega_0-\omega\lesssim\omega_{lt}$. (The usual models of excitons binding to impurities also neglect this difference.)

The equations which will be used are

$$\begin{aligned}\nabla^2\mathbf{E}&=\frac{\omega^2}{c^2}(\mathbf{E}+4\pi\mathbf{P}),\\ \left[\frac{\omega^2}{\omega_0^2}-\frac{\hbar^2\nabla^2}{m\omega_0}+\left(1+\frac{2V(r)}{\hbar\omega_0}\right)\right]\mathbf{P}&=\beta\mathbf{E},\end{aligned} \tag{20}$$

where

$$\begin{aligned}V(r)&=-V_0, \quad \text{for } r\leq a \ (V_0>0)\\ &=0, \quad \text{for } r>a.\end{aligned}$$

This latter is an arbitrary but simple form for $V(r)$. Strong, short-range potentials normally exhibit long-wavelength scattering which is characterized by a potential depth and range,[8] and is independent of details of the potential. The desired solution to (20) gives the scattering cross section for an incoming polariton. If the scattering center is sufficiently small, only the S-wave scattering will be important. The S-wave part of the angular momentum decomposition of (20) is

$$\begin{aligned}\frac{1}{r^2}\frac{d}{dr}r^2\frac{dE}{dr}&=\frac{\omega^2}{c^2}(E+4\pi P),\\ \left[\frac{\omega^2}{\omega_0^2}-\frac{\hbar^2}{m\omega_0}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}+\left(1+\frac{2V(r)}{\hbar\omega_0}\right)\right]P&=\beta E.\end{aligned} \tag{21}$$

The general solution to (21) for $\omega<\omega_0$ and $r>a$ is

$$\begin{aligned}E&=r^{-1}[(\cos\delta\sin kr-\sin\delta\cos kr)+(Ae^{-\kappa r}+Be^{\kappa r})],\\ P&=r^{-1}[\alpha(k,\omega)(\cos\delta\sin kr-\sin\delta\cos kr)\\ &\qquad+\alpha(i\kappa,\omega)(Ae^{-\kappa r}+Be^{\kappa r})],\end{aligned} \tag{22}$$

where k^2 and $(i\kappa)^2$ are the positive and negative roots, respectively, for k^2 in the dispersion relation

$$\frac{c^2k^2}{\omega^2}=\epsilon_0+\frac{4\pi\beta}{1-\omega^2/\omega_0^2+\hbar k^2/m\omega_0} \tag{23}$$

appropriate to the external region where $V(r)$ vanishes. The function $\alpha(k,\omega)$ is defined by

$$\alpha(k,\omega)\equiv\frac{\beta}{1-\omega^2/\omega_0^2+\hbar k^2/m\omega_0}. \tag{24}$$

In order that the wave function represent a scattering wave function, B must be chosen zero. The asymptotic solution for E for large r is then

$$r^{-1}(\cos\delta\sin kr-\sin\delta\cos kr). \tag{25}$$

This asymptotic form corresponds to the scattering of the polariton wave from the impurity, and δ is the S-wave phase shift. If all other phase shifts are negligible, the differential cross section will be isotropic, and the total cross section will be

$$\sigma_{\text{tot}}=(4\pi\sin^2\delta)/k^2. \tag{26}$$

The simplicity of the form (25) is due to the fact that ω is below ω_0, and only one mode of real wave number exists for such ω.

The general solution to (21) for $\omega<\omega_0$ but $r<a$ is

[8] See, e.g., M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley-Interscience, Inc., New York, 1964), pp. 286–294.

given by

$$E=r^{-1}[c_1 \sin k_1 r+c_3 \cos k_1 r+c_2 \sin k_2 r+c_4 \cos k_2 r],$$
$$P=r^{-1}[\alpha_v(k_1,\omega)(c_1 \sin k_1 r+c_3 \cos k_1 r)+\alpha_v(k_2,\omega)(c_2 \sin k_2 r+c_2 \cos k_2 r)], \quad (27)$$

where now k_1 and k_2 are the roots of

$$\frac{c^2k^2}{\omega^2}=\epsilon_0+4\pi\beta\left(1-\frac{\omega^2}{\omega_0{}^2}+\frac{\hbar k^2}{m\omega_0}-\frac{2V_0}{\hbar\omega_0}\right)^{-1}, \quad (28)$$

and $\alpha_v(k,\omega)$ is defined by

$$\alpha_v(k,\omega)=\beta\left(1-\frac{\omega^2}{\omega_0{}^2}+\frac{hk^2}{m\omega_0}-\frac{2V_0}{h\omega_0}\right)^{-1}. \quad (29)$$

The boundary condition that E, P and their first derivatives are continuous at the origin necessitates setting c_3 and c_4 equal to zero. For V_0 large enough to bind a particle, the two wave-number roots of (28) will both be real.

The over-all solution to the problem (within a multiplicative constant) is found by picking c_1, c_2, A, and δ such that P, E, and their first derivatives are continuous at $r=a$. The four simultaneous equations which must be solved for these variables (of which we are interested only in δ) are

$$c_1 \sin k_1 a+c_2 \sin k_2 a=\cos\delta \sin ka-\sin\delta \cos ka+Ae^{-\kappa a}, \quad (30a)$$

$$c_1 k_1 \cos k_1 a+c_2 k_2 \cos k_2 a=k \cos\delta \cos ka+k \sin\delta \sin ka-A\kappa e^{-\kappa a}, \quad (30b)$$

$$c_1\alpha_v(k_1,\omega) \sin k_1 a+c_2\alpha_v(k_2,\omega) \sin k_2 a=\alpha(k,\omega)(\cos\delta \sin ka-\sin\delta \cos ka)+A\alpha(i\kappa,\omega)e^{-\kappa a}, \quad (30c)$$

$$c_1 k_1\alpha_v(k_1,\omega) \cos ka+c_2 k_2\alpha_v(k_2,\omega)\cos k_2\alpha=\alpha(k,\omega)(k \cos\delta \cos ka+k \sin\delta \sin ka)-\kappa A\alpha(i\kappa,\omega)e^{-\kappa a}. \quad (30d)$$

The reader may write down the general solution for $\sin^2\delta$ if he wishes. The author restricts himself to a solution of (30) in the exciton limit for a short-range potential.

The effect of the deep short-range potential in (28) is to virtually decouple the electric and polarization fields within the potential well. This decoupling leads to $\alpha_v(k_1,\omega)\ll\alpha_v(k_2,\omega)$ on the left-hand side of (30c) and (30d). (For definiteness, we presume k_1 corresponds to the excitonlike mode, and k_2 to the lightlike mode.) c_2 can now be neglected in (30c) and (30d), and c_1 eliminated between them, yielding

$$-\gamma\equiv\frac{k_1 \cos k_1 a}{\sin k_1 a}=\frac{\alpha(k,\omega)(k \cos\delta \cos ka+k \sin\delta \sin ka)-\kappa A\alpha_v(i\kappa,\omega)e^{-\kappa a}}{\alpha(k,\omega)(\cos\delta \sin ka-\sin\delta \cos ka)+A\alpha_v(i\kappa,\omega)e^{-\kappa a}}. \quad (31)$$

It is convenient (but not essential) to use a short-range and deep potential, and to take $\gamma a\ll 1$. In this case, the ω dependence of γ can be neglected in the energy range of interest. The binding energy of the exciton to the impurity in the absence of coupling to light is then $E_B=\hbar^2\gamma^2/2m$. The mode (2) is essentially lightlike, and dominates the left-hand side of (30a) and (30b). When setting c_1 to zero and eliminating c_2 in these equations, it is convenient to realize that $k_1\alpha(k_1,\omega)\gg k_2\alpha(k_2,\omega)$. Thus

$$\frac{1}{a}=\frac{k \cos\delta \cos ka+k \sin\delta \sin ka-A\kappa e^{-\kappa a}}{\cos\delta \sin ka-\sin\delta \cos ka+Ae^{-\kappa a}}. \quad (32)$$

Equations (31) and (32) can be solved for $\cot\delta$. Since $ak<\kappa a\ll 1$, it is consistent to omit all higher powers of ka and κa in expanding the solution. The result is

$$\cot\delta=\frac{\alpha_v(i\kappa,\omega)}{\alpha(k,\omega)}\frac{\kappa-\gamma}{k} \quad (33)$$

or

$$\sigma=\frac{4\pi}{k^2}\sin^2\delta=\frac{4\pi}{k^2+(\kappa-\gamma)^2[\alpha_v(i\kappa,\omega)/\alpha(k,\omega)]^2}. \quad (34)$$

The approximate scattering cross section of Eq. (34) can be more directly obtained in the exciton limit by directly constructing the asymptotic scattering wave function. When all waves have 100% exciton component, a polariton wave function for an S wave of energy E can be written

$$\psi_E(r)=\int\frac{d^3k\,e^{ikr}}{E(k)-E}=\frac{1}{ir}\int_{-\infty}^{\infty}\frac{kdk(e^{ikr}-e^{-ikr})}{E(k)-E}, \quad (35)$$

where $E(k)$ is the (isotropic) polariton dispersion relation. This wave function will satisfy the polariton Schrödinger equation for $r>a$, where $V(r)$ vanishes. The solution obtained depends upon the path of integration.

For a free particle, or an exciton not interacting with light, having the dispersion relation

$$E^2(k)=E_0{}^2+E_0\hbar^2k^2/m, \quad (36)$$

there are two roots to the dispersion relation, at

$$k=\pm k_0\equiv\pm\left(\frac{m}{\hbar^2}\frac{E^2-E_0{}^2}{E_0}\right)^{1/2}\approx\pm\left(\frac{2m}{\hbar^2}(E-E_0)\right)^{1/2}.$$

The path of integration in Fig. 2(a) can be evaluated by residues; this is done by closing the contour in the upper- and lower-half plane for the factors e^{ikr} and e^{-ikr}, respectively. This integration then yields

$$\psi(r)=\frac{4\pi k_0}{r}e^{-ik_0r}\left[\left(\frac{dE}{dk}\right)_{-k_0}\right]^{-1}. \quad (37a)$$

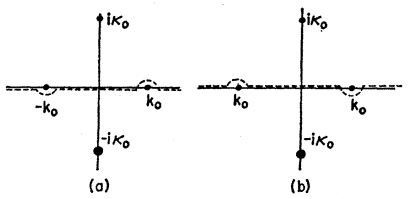

FIG. 2. Paths of integration (dashed lines) for the two solutions to the free-polariton or free-exciton equation.

The corresponding integration along path (b) yields

$$\frac{4\pi k_0}{r}e^{ik_0r}\left[\left(\frac{dE}{dk}\right)_{k_0}\right]^{-1}, \tag{37b}$$

the other solution to the free-particle wave equation.

The same procedure can be followed for the case in which $E(k)$ is the polariton dispersion relation. There are now, however, two pairs of solutions to the dispersion relation, one being real, at $\pm k_0$, and one being imagniary, at $\pm i\kappa$. The same integration can be carried out, the residues now yield for path (a)

$$\psi(r)\frac{4\pi}{r}=\left\{e^{-ik_0r}(-k_0)\left[\left(\frac{dE}{dk}\right)_{-k_0}\right]^{-1}+e^{-\kappa r}(+i\kappa)\left[\left(\frac{dE}{dk}\right)_{+i\kappa}\right]^{-1}\right\}, \tag{38a}$$

and for path (b)

$$\psi(r)=\frac{4\pi}{r}\left\{e^{+ik_0r}(+k_0)\left[\left(\frac{dE}{dk}\right)_{+k_0}\right]^{-1}+e^{-\kappa r}(+i\kappa)\left[\left(\frac{dE}{dk}\right)_{+i\kappa}\right]^{-1}\right\}. \tag{38b}$$

For energies closer to the exciton energy than the coupling energy but farther away from the exciton energy than E_{lt}, the solutions for the two polariton modes factor into the approximate dispersion relations

$$\begin{aligned} k_0&: \frac{c^2k^2}{\omega^2}\approx\epsilon_0+\frac{4\pi\beta}{1-\omega^2/\omega_0{}^2},\\ \kappa&: E(k)\approx\hbar\omega_0+\hbar^2k^2/2m. \end{aligned} \tag{39}$$

The derivative evaluated at k_0 can be written in terms of the group velocity of conventional "light." The two solutions are then

$$\begin{aligned} r^{-1}(e^{-ik_0r}+e^{-\kappa r}v_g m/k_0\hbar)&=\psi_1,\\ r^{-1}(e^{ik_0r}+e^{-\kappa r}v_g m/k_0\hbar)&=\psi_2. \end{aligned} \tag{40}$$

The exterior solution to ψ in the presence of a potential near the origin is

$$\psi_{\text{ext}}=\cos\delta\ \ (\psi_1-\psi_2)-\sin\delta\ \ (\psi_1+\psi_2).$$

A long distance from the origin, the wave function becomes

$$r^{-1}\sin(k_0r-\delta),$$

and the polariton scattering cross section will be the usual $4\pi k^{-2}\sin^2\delta$.

As before, let a deep, short-range potential be capable of binding an exciton in the absence of exciton-photon coupling. In the presence of such coupling, the deep potential decouples the exciton and photon parts within the potential. Within the potential well, the wave function begins excitonlike; it reaches the boundary of the potential with a slope/value ratio $-\gamma$, which as before is only weakly energy-dependent. The general solution can be joined to this slope/value ratio for only one value of $\cot\delta$, namely,

$$\cot\delta=\frac{\cos ka-k\sin ka+(v_g m/\hbar k)e^{-\kappa a}(\gamma-\kappa)}{\gamma\sin ka+k\cos ka}, \tag{41}$$

where we have replaced k_0 by the symbol k. By supposition, $ka<\kappa a\ll 1$. In this approximation,

$$\sigma=\frac{4\pi\sin^2\delta}{k^2}\frac{1}{k^2+(v_g m/\hbar k)(\gamma-\kappa)^2}. \tag{42}$$

Using the approximation (39) for the dispersion relations, $\alpha(i\kappa,\omega)$ can be evaluated from its definition [(24) and (23)]. For this complex wave vector, α is huge. ϵ_0 in (23) can then be neglected, leaving

$$\alpha(i\kappa,\omega)=-(1/4\pi)c^2\kappa^2/\omega^2. \tag{43}$$

Since, for the mode k, if spatial dispersion is not yet a major effect, α can be written

$$\alpha(k,\omega)=\frac{1}{4\pi}\frac{nc}{\omega v_g}\frac{\hbar\kappa^2}{m}, \tag{44}$$

the result (42) is equivalent to (34) in the vicinity of the resonance. The requirements that κa and ka be small are not essential to the method, but greatly shorten the algebra.

IV. DISCUSSION

A. "Theoretical" and "Experimental" Cross Sections

The cross sections which have been computed in Secs. II and III have been calculated for a crystal of infinite extent. The cross section is conceptually defined by beginning with a propagating polariton wave packet in the crystal, letting it scatter off an impurity, and examining the asymptotic form of the outgoing wave packet in the crystal. For frequencies below the first excition energy in a direct band-gap insulator, there is only one propagating (real wave-vector) polariton for a given polarization, and the relations between incoming and outgoing asymptotic forms are defined by a set of

phase shifts. At higher energies, where several propagating polaritons can exist for a given energy, the relation between the outgoing waves and an incoming wave is much more complicated.

When light whose quantum energy is less than that of the lowest-energy exciton is incident on a crystal, a reflected wave is produced outside the crystal, and surface polaritons (which decay exponentially in space) and a unique propagating polariton are produced inside the crystal. When there is no damping, the energy which goes into the one propagating polariton is the energy of the externally incident light minus the energy of the reflected light. In a non-birefringent crystal, an externally incident light beam of low frequency produces a unique polariton beam. No complicated boundary problem need be solved to obtain this correspondence. Similarly, a polariton internally incident on a surface produces a unique internally reflected polariton, surface polaritons, and a transmitted wave. Again, the reflectivity determines the relation between the magnitudes of the incident and transmitted beams.

When a few impurities are randomly placed in a crystal whose dimensions are large compared with the wavelength of light, most of the impurities will be located in the interior of the crystal, where the surface polaritons have neglibigle amplitude. These will scatter the polaritons as described in Secs. II and III, and the polaritons will reconvert to external photons at the boundary. A few impurities will be in the thin surface layer in which surface polaritons exist. These will have different scattering properties, and will produce a surface scattering. Since in typical scattering experiments the surface-exciton penetration depth is perhaps 100 Å and the crystals are 10^4–10^7 Å in thickness, the surface-impurity scattering is generally unimportant compared to the volume scattering. For volume-scattering considerations, it is unnecessary to solve the problem of impurity scattering in a crystal of finite volume.

For photon energies above the lowest exciton energies, the general considerations are more complicated because of the existence of several propagating polariton modes. Even in this case, for the consideration of volume-scattering effects the theory of the reflectivity connection relations (boundary condition) and the internal scattering problem can be separately solved. For this higher-energy case, it is usually true in experimental situations that one polariton is most nearly lightlike—propagates fastest and has the longest mean free path—and dominates the relation between internal and external waves for volume scattering.

B. Comparison with One-Level Model

The form of the scattering cross section in Eq. (34) resulting from the (approximate) solution to the square-well model has a scattering resonance at $\hbar\omega_{\rm res}=\hbar\omega_0-E_B$. Very near this resonance, the ω dependence of γ and k can be neglected, and the ω dependence of κ is adequately described by

$$\kappa=\gamma-\tfrac{1}{2}\kappa_0(\omega-\omega_{\rm res})/\omega_{\rm res}, \tag{45}$$

$$\kappa_0\equiv(2mE_B/\hbar^2)^{1/2}. \tag{46}$$

The scattering cross section as a function of frequency is

$$\sigma=4\pi\left[k^2+\kappa_0^2\left(\frac{v_g m}{\hbar k}\right)^2\frac{1}{4}\left(\frac{\hbar\omega-\hbar\omega_{\rm res}}{E_B}\right)^2\right]^{-1} \tag{47}$$

and has a resonance-energy half-width at half-maximum of

$$\Gamma=\hbar^2k^2\kappa_0/m^2v_g. \tag{48}$$

At resonance,

$$v_g=ncE_B^2/2\pi\beta\hbar^2\omega_0^2,$$

so that

$$\Gamma=4\pi\beta n\hbar\omega^4/c^3\kappa^3, \tag{49}$$

where n is the index of refraction at the resonant energy. The physical interpretation of a resonant Rayleigh cross section like (47) having such a width is that there is a "state" of electronic excitation at $\omega_{\rm res}$ having an optical decay rate of $2\Gamma/\hbar$. Small level shifts have been neglected; the resonance frequency $\omega_{\rm res}$ in our approximation is at the energy at which a real bound-exciton state would occur if exciton-photon coupling were neglected. The integrated absorption of the resonance is proportional to σ multiplied by density of scatterers.

Define the oscillator strength per an intrinsic exciton transition by

$$f_{\rm ex}=\left(\frac{N_0}{V}\right)^{-1}A\int\epsilon_i(\omega)d\omega, \tag{50}$$

where A is a normalizing constant, N_0/V is the number of unit cells divided by the crystal volume, $\epsilon_i(\omega)$ is the imaginary part of the dielectric function (neglecting spatial dispersion), and the integration is carried out over a single exciton line. The oscillator strength for a weak impurity absorption line (due to Rayleigh scattering) is

$$f=\left(\frac{N}{V}\right)^{-1}A\int_{\text{impurity line}}\epsilon_i(\omega)d\omega=A\frac{\omega n}{c}\int\sigma(\omega)d\omega, \tag{51}$$

where N/V is the number of impurities divided by the volume. The method of defining A depends somewhat on how the local fields are defined, but it is irrelevant for present purposes. Using (50) and (51), one obtains the relation

$$f=f_{\rm ex}8\pi(N_0/V)/\kappa^3. \tag{52}$$

This result is equivalent to the gaint oscillator strength result of Rashba and Gurgenishvili.[9] These workers calculated this same ratio in the case in which the photon-exciton coupling is weak. In the short-range-

[9] E. I. Rashba and G. E. Gurgenishvili, Fiz. Tverd. Tela 4, 1029 (1962) [English transl.: Soviet Phys.—Solid State 4, 759 (1962)].

potential approximation, the bound-state wave function can, for the calculation of oscillator strength, be approximated by

$$\psi=(2\kappa/4\pi)^{1/2}e^{-\kappa r}/r. \tag{53}$$

The fraction of $k=0$ exciton in this wave function is $8\pi/\kappa^3 V$, in agreement with (52). The strong- and weak-coupling models give the same result for the relation between the exciton and the impurity integrated absorptions. The relation between the decay rate and the integrated absorption contains in our solution the exciton contribution to the index of refraction, which is lacking in the weak-coupling model.

The most important difference between a one-level model, in which only the bound-exciton excited state is kept, and the present calculation occurs away from the resonant frequency. At a general energy, the contribution from continuum exciton intermediate states is as important as the contribution from the bound state. The method of Sec. III is equivalent to summing perturbation theory over all continuum states. The greatest difference between the one-excited-state model and the model assumed in Sec. III is that the former leads to a cross section of the form $\sigma\propto(E-E_{\rm res})^{-2}$ away from resonance, while the latter leads to a form

$$\sigma\propto[(E_{\rm res}+E_B-E)^{1/2}-(E_B)^{1/2}]^{-2}$$

away from resonance. There is a large difference between these two forms for energies such that $|E-E_{\rm res}|\sim E_B$.

C. Comparison with Experiment

There is at present one experiment which can be compared with the theory of Sec. III. Rayleigh scattering from spinless impurities in insulators has not been experimentally observed. Spin-flip Raman scattering from neutral donors in CdS has been observed.[4] If valence bands other than the top valance band in CdS are ignored, the spin-flip scattering is directly related to the Rayleigh cross section. By this means it is possible to obtain experimental results related to theory.

The binding energy of the exciton to a neutral donor impurity is about 0.007 eV. If the exciton total mass is presumed to be about one electron mass,[10] the decay constant κ for such a bound exciton is 4.5×10^6 cm^{-1}. Since the exciton Bohr radius is 27 Å, the idealizations of the exciton as a point particle and the well as a very-short-range potential are not very good. Solving the algebra of Eq. (41) for a well of finite width would better describe this experiment. The exciton-photon coupling strength for this lowest-energy exciton is 0.06 eV. The two photon energies used in the experiment lay 0.012 and 0.057 eV from the $k=0$ exciton energy. The exciton limit should be good for the former energy, but less so for the latter. Since the spin-orbit splitting of the valence band is only about 0.07 eV, the neglect of the other two nearby valence bands is an important omission for the lower-energy one of the two Raman-scattering experiments.

The absolute oscillator strength of the bound-exciton transition should be 12.5 if the value of κ calculated above and the value of the oscillator strength are substituted into (52). The agreement with the experimental value of 9, in view of the scale of the exciton, is fortuitous. The experimental absolute Raman-scattering cross section is an order of magnitude larger than the theoretical one. Experimental error may be a major source of this discrepancy error. Finally, the ratio between the Raman cross sections for light 0.005 and 0.050 eV below the bound-exciton transition is 1/130 in experiment, 1/100 for a one-level approximation, and 1/37 in Eq. (34). A correction to include a compensating spin-orbit-split band 0.070 eV to higher energies raises the estimate for Eq. (34) to 1/85.

The available comparisons between theory and experiment are not adequately precise. They could be considerably sharpened experimentally by doing experiments in a (preferably cubic) material of larger spin-orbit coupling (e.g., CdTe) and at more laser frequencies. On the theoretical side, it is possible to solve Eq. (30) without the short-range approximation and without the complete-exciton limit. The addition of a second exciton mode would still represent a feasible amount of algebra.[11]

D. Approach through Equation (35)

The approach to resonant scattering through Eq. (35) has the advantage of parametrizing an extrapolation away from the resonance when the nature of the binding of the exciton is complicated. Even when the potential is not of zero range, the asymptotic form (40) for the exciton wave function is valid well outside the potential region. Other forms of disturbance will fall off faster than $e^{-\kappa r}$. Thus, if an appropriate radius a is chosen, (41) is valid when the potential is not of short range, and even when the exciton may be distorted in a complicated fashion inside the potential well. The only additional complication is that when a is finite, γ also depends on the energy. The general problem of the variation of γ with energy is well understood in conventional scattering theory,[8] and the problem here is completely analogous.

[10] J. J. Hopfield and D. G. Thomas, Phys. Rev. **123**, 35 (1961).

[11] See E. Burstein, D. L. Mills, A. Pinczuk, and S. Ushioda, Phys. Rev. Letters **22**, 348 (1969).