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APPROXIMATE TREATMENT OF EXCITON EFFECTS IN ELECTRIC FIELD MODULATION VIA THE SLATER-KOSTER INTERACTION

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Exciton effects on electric field modulation line shapes at general critical points are treated using a Slater-Koster contact interaction to approximate the Coulomb potential. This interaction produces a mixing of one-electron line shapes similar to that calculated for an unperturbed solid. By comparison with experiment, we show that exciton effects are present in the E_1 structure of low-temperature electroreflectance data of Ge.

The one-electron approximation, which neglects the electron-hole interaction, does not predict experimentally observed optical-modulation line shapes,[1-6] and hence does not provide a means of identifying the nature of the associated transitions. This has been shown explicitly for temperature,[3] stress,[4] and wavelength modulation,[5] where spectra are related to the energy derivative of the dielectric function of the unperturbed solid. Because of this simple connection, it is possible to utilize the Slater-Koster "contact" interaction[7,8] to approximate the Coulomb interaction at higher interband critical points. The purpose of this paper is to extend the contact exciton formalism to include additional perturbations which can be described in the effective-mass approximation (EMA). This extension allows the contact exciton interaction to be included in the theory of electric field modulation and enables for the first time an approximate theoretical treatment of excitonic effects at general critical points in electroreflectance. Predicted line shapes are found to be in good agreement with low-temperature electroreflectance spectra of M_1 critical points in Ge.[9]

In the EMA,[10] the dielectric function can be written in terms of either the relative coordinate excitation energies E_α as

$$\epsilon = \frac{Q}{\pi\omega^2}\sum_\alpha \frac{1}{E_\alpha - z}, \tag{1}$$

or a resolvent (lattice Green's function) G_0 as

$$\epsilon = \frac{Q}{\pi\omega^2}\lim_{\vec{R}_j,\vec{R}_{j'}\to 0}\langle \vec{R}_{j'}|G_0|\vec{R}_j\rangle, \tag{2}$$

where $G_0 = (H_0 - z)^{-1}$, $z = \hbar\omega + i\Gamma$, $Q = 4\pi^2 e^2 m^{-2} \times |\hat{\epsilon}\cdot\vec{P}|^2$, and $\vec{P}$ is the interband momentum matrix element (which is assumed constant for simplicity). The state $|\vec{R}_j\rangle$ is a Wannier function centered on the lattice site $\vec{R}_j$, and $|\alpha\rangle$ is an eigenstate of the relative-coordinate Hamiltonian H_0, such that $H_0|\alpha\rangle = E_\alpha|\alpha\rangle$. In the unperturbed one-electron picture, $|\alpha\rangle$ represents an electron-hole pair state expressed in terms of Bloch functions, and the envelope function $F_\alpha(0) = \langle 0|\alpha\rangle$ connecting Eq. (1) to Eq. (2) is identically 1. One can easily generalize Eq. (2) by noting that a perturbing field (e.g., a uniform electric field) requires new pair states $|\varphi\rangle$ to diagonalize the perturbed Hamiltonian $\tilde{H}_0 = H_0 + H_1$. The corresponding envelope functions $F_\varphi(0)$ are generally not equal to unity. These may be found either by expanding the new eigenstates $|\varphi\rangle$ in terms of the Wannier functions $|\vec{R}_j\rangle$, or by solving the EMA Schroedinger equation for them directly.[11]

We now consider in addition to H_1 a Slater-Koster contact potential V defined as

$$\langle \vec{R}_j|V|\vec{R}_{j'}\rangle = \tilde{g}\delta_{\vec{R}_j,0}\delta_{R_{j'},0}. \tag{3}$$

Following previous treatments[7,8] of the unperturbed Hamiltonian, the resolvent operator $\tilde{G}$ in-

cluding both the contact exciton and the perturbing field is

$$\tilde{G} = [H_0 + H_1 + V - z]^{-1}, \tag{4}$$

and

$$\tilde{G} = \tilde{G}_0 + \tilde{G}_0 V \tilde{G}, \tag{5}$$

where $\tilde{G}_0$ is the resolvent operator defined for $V = 0$. By taking Wannier-function matrix elements of both sides of Eq. (5), one obtains

$$\langle 0|\tilde{G}|0\rangle = \langle 0|\tilde{G}_0|0\rangle - \sum_{jj'} \langle 0|\tilde{G}_0|R_j\rangle \times \langle R_j|V|R_{j'}\rangle\langle R_{j'}|G|0\rangle, \tag{6}$$

and therefore, by Eq. (3),

$$\tilde{\epsilon} = \frac{\tilde{\epsilon}_0}{(1 + g\tilde{\epsilon}_0)}, \tag{7}$$

where we define g in terms of the strength factor $\tilde{g}$ as $g = \omega^2 Q^{-1}\tilde{g}$.

Equation (7) relates the interband dielectric function $\tilde{\epsilon}$ of a solid with electron-hole scattering approximated by a contact interaction, to the dielectric function $\tilde{\epsilon}_0$ of the solid with no direct electron-hole interaction but with an additional perturbation H_1 included. If the perturbation H_1 is small, so that $\tilde{\epsilon}_0$ is related to the dielectric function ϵ_0 of a completely unperturbed solid by a small quantity $\Delta\epsilon_0 = \tilde{\epsilon}_0 - \epsilon_0$, then by Eq. (7) the contact interaction V modifies the response $\Delta\epsilon_0$ in first order to

$$\Delta\epsilon = (1 + g\epsilon_0)^{-2}\Delta\epsilon_0. \tag{8}$$

Equation (8) is the main result of our paper. It extends previous calculations[7,8] of the effect of an electron-hole contact interaction on the unperturbed dielectric function to its effect on a perturbation response which can be obtained by various methods. Although the short-range "contact" interaction cannot be expected to reproduce the hydrogenic bound states characteristic of a long-range Coulomb potential,[11] its use does provide a reasonable description of the electron-hole continuum states. This approach is further justified by the fact that the experimental lifetime broadening above the absorption edge typically exceeds excition binding energies for all but very large gap materials,[12] and hence the detailed shape of the electron-hole potential is unimportant.[13]

We now apply the general result to electric-field modulation. It is apparent from Eq. (8) that the Slater-Koster interaction mixes the real and imaginary parts of $\Delta\epsilon_0$ such that a critical-point of type M_j appears as a mixture of types M_j and M_{j+1} in experimental line shapes. The parameter g in effect enables the phase of $\Delta\epsilon_0$ to vary in a systematic way. For $g \equiv 0$ a phase-change increment of $\frac{1}{2}\pi$ causes $\Delta\epsilon_0$ to change from M_j type to M_{j+1} type. For $g \neq 0$ the phase increment will be less than $\frac{1}{2}\pi$, resulting in an apparent mixture of line shapes. Figure 1 illustrates the progression of Franz-Keldysh line shapes which results from $\frac{1}{4}\pi$ increments of the phase of $\Delta\epsilon_0$, where $\Delta\epsilon_0$ is calculated for a uniform electric field oriented in a positive-mass direction. In Fig. 1, all energies are normalized to the characteristic energy $\hbar\theta = (e^2\mathcal{E}^2\hbar^2/2\mu)^{1/3}$, in order-of-magnitude agreement with experimental values. The smooth progression of M_0 toward M_2 line shapes, together with the shift and eventual inversion of the main peak, suggests that experimental line shapes themselves cannot uniquely determine the type of critical point without some information about the strength of the exciton interaction. In particular, the en-

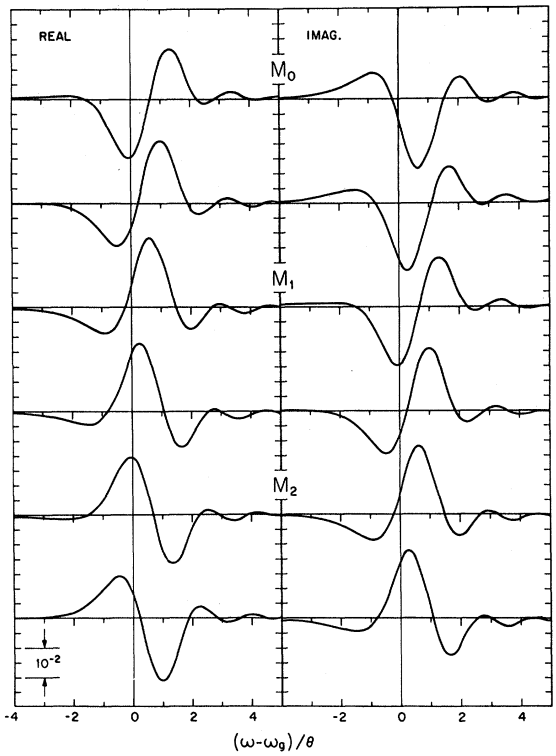

FIG. 1. The progression of Franz-Keldysh line shapes for $\frac{1}{4}\pi$ phase-angle increments, calculated for a uniform electric field oriented in a positive-mass direction. The lifetime broadening energy Γ for these curves is taken equal to $\hbar\theta$. For a field oriented in a negative-mass direction, the energy axis is reversed and the sequence relabeled (from top) M_1, M_2, and M_3.

ergy shift of the main structure is so large that a precise value of the energy gap cannot be determined by its usual assignment to the negative extremum of the line shape. We note that contact exciton line-shape mixing is qualitatively different from mixing due to inhomogeneous fields,[14] which shifts the phase in the opposite direction and in addition substantially broadens the fundamental line shapes.

Figure 2 shows the results of a detailed fit of Eq. (8) to the surface-barrier electroreflectance data of Nishino and Hamakawa, taken at 24°K using a heterojunction technique.[9] The sample doping and field strength are such that field-inhomogeneity effects are negligible.[15] In Fig. 2, the experimental data[9] are compared with the best-fit curve generated from known optical constants of Ge[16] using Eq. (8). Also shown is the curve calculated for no electron-hole interaction. A small constant zero offset was subtracted from the experimental data points and the two calculated curves were normalized to experiment at the maximum of the main positive peak. The asymptotic approximation[17] to the M_1 Franz-Keldysh line shapes[18] was used to calculate the theoretical curves (appropriate angles to the [111] direction of the electric field were included). It is obvious from Fig. 2 that including the contact exciton interaction significantly improves the fit as compared with the pure Franz-Keldysh line shape. The only adjustable parameters were the exciton interaction strength g, the energy gap

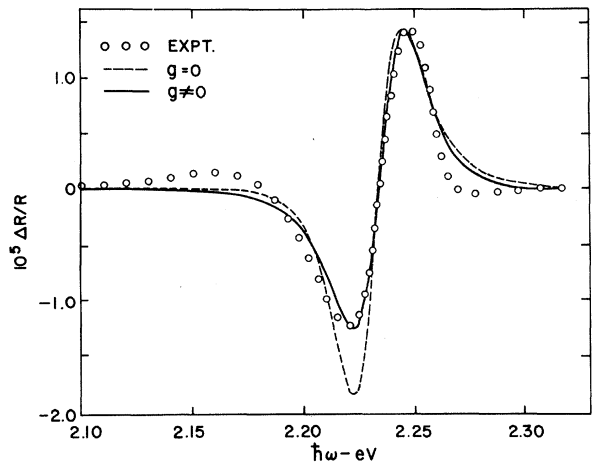

FIG. 2. A comparison of theoretical curves excluding (dashed curve) and including (solid curve) the electron-hole contact interaction, with the experimental data of Ref. 9, taken at 24°K with a field $\mathcal{E} = 1.5 \times 10^4$ V/cm. The curve for $g \neq 0$ represents ~20° phase advancement in $\Delta\epsilon_0$ of the 90° from an M_1 to an M_2 critical point.

E_g, and the lifetime broadening parameter Γ. The calculated curve with no interaction gives the values $E_g = 2.231 \pm 0.001$ eV and $\Gamma = 0.025 \pm 0.001$ eV, while the curve obtained by using Eq. (8) gives $E_g = 2.235 \pm 0.001$ eV, $\Gamma = 0.024 \pm 0.001$ eV, and $g = -0.007 \pm 0.001$.[19] In the asymptotic approximation,[17] the characteristic energy $\hbar\theta$ appears only as a scaling factor, but must satisfy the inequality

$$2\hbar\theta \leq \Gamma. \tag{9}$$

Using Eq. (9) and the experimental value of 1.5×10^4 V/cm for the applied field, a lower limit for the transverse reduced mass $\mu_\perp$ is $0.046 m_e$, in good agreement with the predictions of band-structure calculations.[20-22]

The good agreement in Fig. 2 between the experimental data and the curve calculated from Eq. (13) provides strong evidence that the simple contact exciton model adequately describes the effect of the Coulomb interaction upon the interband dielectric function above the absorption edge where the lifetime broadening is large. Further work to relate these results to energy-derivative line shapes obtained from stress or wavelength modulation experiments, in order to determine the possible existence of quasidegenerate M_0 and M_1 critical points, is in progress.

A complete discussion of the critical point(s) responsible for the E_1 structure in Ge is beyond the scope of this Letter. However, it is worthwhile to note that for our exciton model, an increase in the electron-hole coupling g would require the contribution of an M_0 critical point.[4] The cyclic relationship between the critical-point nature and the exciton coupling strength was first predicted by Toyozawa, et al.[7] for the zero-field dielectric function and confirmed experimentally using wavelength-modulated reflectance[5] and thermoreflectance.[3,23] Although we have chosen to fit a single M_1 critical point, as suggested by band-structure calculations,[20-22] this model for the density of states is not unique since the exciton strength is unknown. Hence a more detailed analysis of the E_1 transition must be postponed until additional evidence becomes available.

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INFLUENCE OF HIGHER-BAND INTERACTIONS ON EFFECTIVE MASS IN DOPED HgSe AND HgTe†

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We give a calculation of the electron–effective-mass dependence of the energy gap $E_g = |E_{\Gamma_6} - E_{\Gamma_8}|$ which includes the higher band interactions. We show that in high-concentration HgSe and HgTe, the effective mass increases with decreasing E_g.

In narrow-gap semiconductors, the $|E_{\Gamma_6} - E_{\Gamma_8}| = E_g$ energy gap can be significantly changed by either hydrostatic pressure or temperature. In a semiconductor with the grey-tin model of the band structure,[1] it is possible by these means to reduce this energy gap to zero and subsequently to produce a positive energy gap. Effective-mass changes accompany the changes in the energy gap; the effect is particularly strong in pure materials. Usually the data have been interpreted using Kane's three-band approximation. In his approximation, the effective mass m^* always decreases when E_g decreases.[2,3] We have calculated m^* vs E_g for the II-VI semiconductors HgSe and HgTe assuming a higher approximation which takes into account higher band interactions. It will be shown that in lightly doped samples the results in this approximation are in qualitative agreement with the three-band approximation. However, in heavily doped samples we find that the effect is opposite, that is, m^* increases with decreasing energy gap. This behavior seems to be quite general, the details (concentration at which the reversal takes place) being a function of the band parameters of the individual semiconductor.

We calculated m^* vs E_g for fixed electron concentrations; all other band parameters are assumed to be independent of E_g. Our results should be directly applicable to the analysis of effective-mass changes in doped material as a function of hydrostatic stress or temperature. We use Kane's equation in the form[4]

$$E = E' + \frac{\hbar^2 k^2}{2m_0} u + \frac{\hbar^2}{2m_0} v f_i(\vec{k}), \tag{1}$$

where

$$u = 1 + a^2 A' + b^2 M + c^2 L', \tag{2}$$

$$v = (b^2 - 2c^2)(L - M - N), \tag{3}$$

and

$$f_1(\vec{k}) = (k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^2. \tag{4}$$