The Existence of Hyperbolic Excitons*

J. HERMANSON+

Department of Physics and Institute for the Study of Metals

The University of Chicago, Chicago, Illinois

Abstract. Using a separable model, Duke and Segall have suggested that hyperbolic excitons are unstable and so cannot account for resonance structure in the optical spectra of insulators. Calculations based on a general dispersion model are presented which explicitly exhibit narrow resonances derived from saddle-point edges.

Two models have been proposed for the resonant structure frequently observed in the optical spectra of insulators above the direct absorption threshold. The first model[1,2] attributes the resonances to localized ("molecular") electron-hole excitations, and discusses the positions and multiplicities of the resonances by reference to atomic energy levels and the crystal point group (the group of $\underline{k} = \Gamma = 0$). Phillips[3,4] has proposed a second model which regards the resonances primarily as kinematic rather than atomic in origin and stresses their Wannier wave-packet character, which is strongly dependent on the crystalline energy bands. He suggests that resonances may be generated not only by thresholds but also by saddle-point edges in the electron-hole joint density of states; such edges usually arise from points $\underline{k}$ on Brillouin zone faces rather than at $\underline{k} = 0$.

Duke and Segall[5] have studied a model of saddle-point edges which does not contain such hyperbolic excitons. From this model they conclude that in general hyperbolic excitons do not exist. This Letter contains results which show that hyperbolic excitons do exist.

In Duke and Segall's model the saddle-point energy surfaces are approximated quadratically, and the potential energy of attraction between electron and hole is chosen so that the Schrodinger equation becomes separable. In this model no resonance can be even metastable, because with an attractive interaction a given wave-packet can always reduce its energy by concentrating in k-space along the axis with negative reduced mass (say k_3) and then letting $\langle k_3^2 \rangle \to \infty$. In a real crystal, of course, $\langle k_i^2 \rangle$ is always bounded by K_{BZ}^2 within a given band, where K_{BZ} is a typical Brillouin zone dimension. Moreover, large values of $\langle k_i^2 \rangle$, which correspond to small excitons, cannot be treated by a quadratic approximation to the energy surfaces near the saddle-point, because there are isoenergetic regions of k-space (e.g., between two equivalent saddle-points) where the expansion is invalid.

In spite of these objections, to show that hyperbolic excitons can exist a specific model is required. In this Letter we discuss the results of calculations which use a realistic band structure and an electron-hole potential which extends to second-neighbor atoms around the central cell. We begin by defining the resolvent

$$R(z) = (z - H)^{-1} \tag{1}$$

where $H = H_0 + V$ is the two-body Hamiltonian containing a free part H_0 and an interaction term V and z is a complex variable. Apart from unimportant factors the optical absorption coefficient for momentum-independent oscillator strength $f(\underline{k})$ is given by the spectral function[6]

$$\alpha(E) = \sum_{\nu} |F_{\nu}(0)|^2 \delta(E - E_{\nu 0}) \quad . \tag{2}$$

where F_{ν} is the envelope function in the Wannier representation of the $\nu^{\underline{th}}$ excited

state $|\nu\rangle$ and $E_{\nu 0}$ is the corresponding eigenvalue. In terms of the Wannier state $|0\rangle$ in which the electron and hole occupy the same lattice site, $F_\nu(0) = \langle 0|\nu\rangle$ and equation (2) may be written as

$$\alpha(E) = -\frac{1}{\pi} \mathrm{Im} \langle 0 | \left\{ \sum_\nu |\nu\rangle \frac{1}{E - E_{\nu 0} + i\hbar\eta^+} \langle \nu| \right\} |0\rangle \qquad (3)$$

$$= -\frac{1}{\pi} \mathrm{Im} \langle 0 | R(E + i\hbar\eta^+) | 0 \rangle$$

where $\eta^+ \longrightarrow 0^+$; in deriving (3) we have used the relation

$$\frac{1}{x + i\eta^+} = P\frac{1}{x} - i\pi\delta(x)$$

where P denotes the principle part.

To study the effect on α (E) of the electron-hole scattering term V we introduce the unperturbed resolvent $R_0(z) = (z - H_0)^{-1}$. In terms of R_0 we have the operator identity $R = (1 - R_0 V)^{-1} R_0$, and (3) may be written as

$$\alpha(E, V) = -\frac{1}{\pi} \mathrm{Im} \langle 0 | [1 - R_0 V]^{-1} R_0 | 0 \rangle \qquad (4)$$

The random phase approximation to the spectrum is obtained by setting V = 0; we find easily that α (E,0) = $n_0(E)$, the joint density of states for non-interacting pairs. In the presence of electron-hole coupling the spectrum is modified by the term $(1 - R_0 V)^{-1}$, which leads to resonances in α (E) at energies E_r which satisfy the secular equation

$$\det \| 1 - R_0(E_r + i\hbar\eta^+) V \| = 0. \qquad (5)$$

In general E_r is complex; the real part gives the location of the resonance in the

spectrum, and the imaginary part is a decay width arising from interactions with the continuum of scattering states.

Before proceeding further we remark that Callaway has already shown[7] that a contact interaction (interaction restricted to the central cell[8]) can lead to saddle-point resonances in the joint density of states $n(E)$, providing the strength g of the central cell interaction defined by $\langle 0|V|0\rangle = -g$ lies in a suitable range. Let us suppose that this is the case, so that the condition $(-g)I(E_r) = 1$ is satisfied for $E_0 < E_r < (E_0 + \Delta)$, where E_0 is the energy gap and Δ the bandwidth; $I(E)$ is the Hilbert transform of $n_0(E)$. Then we may expand $\alpha(E,g)$ near E_r to exhibit explicitly the resonance behavior. The result is

$$\alpha(E,g) = \frac{n_0(E_r)/[I'(E_r)g]^2}{(E-E_r)^2 + \pi^2[n_0(E_r)/I'(E_r)]^2} \qquad (6)$$

where we have assumed that $n_0(E)$ varies slowly compared to $I(E)$ for E near E_r. Equation (6) is a symmetric resonance centered about $E = E_r$ with half-width $\Gamma_r/2 = \pi n_0(E_r)/I'(E_r)$. Because Γ_r arises from resonance-continuum interactions it is small when n_0 is small near E_r. We have shown that if the contact interaction leads to resonances in $n(E)$ it also leads to resonances in $\alpha(E)$; in fact for this model $\alpha(E) = n(E)$. The latter result is an accidental consequence of the contact potential and does not hold for long-range interactions[9] (in insulators $V \sim \beta^{-1}$ for large electron-hole separations β). In general the factor $|F_\nu(0)|^2$ in (2) considerably enhances resonant structure in $n(E)$, for V is strong at the origin.

We have calculated the optical spectrum for a fcc crystal in which V is allowed to extend to second-neighbor lattice sites. The non-zero matrix elements of V in the Wannier representation are the central-cell term $\langle 0|V|0\rangle = -g$, the nearest-

neighbor term $\langle 1|V|1\rangle = -g$, and a second-neighbor term $\langle 2|V|2\rangle = -g/\sqrt{2}$. The form used for the energy bands is the nearest-neighbor tight-binding approximation

$$E(\text{valence}, \underline{k}) = \text{const} = 0$$

$$E(\text{conduction}, \underline{k}) = E_0 + 3 - \cos\frac{k_x a}{2}\cos\frac{k_y a}{2} - \cos\frac{k_y a}{2}\cos\frac{k_z a}{2} - \cos\frac{k_x a}{2}\cos\frac{k_z a}{2} \tag{7}$$

The optical spectrum was obtained from equation (4) for three values of the coupling strength: g = 0 (random phase approximation), g = 0.3 (weak coupling), and g = 1.2 (strong coupling); the results are given in Fig. 1. For g = 0 the spectral function is identical to $n_0(E)$, the joint density of states. As g is increased from zero the spectrum is shifted to the lower energy region as a smoother version of $n_0(E)$, until finally two resonances rise out of the continuum; for g = 1.2 (appropriate to solid Xe [10]) these states occur at $E_1 - E_0 = 1.45$ eV and $E_2 - E_0 = 2.10$ eV. The E_1 peak is a hyperbolic exciton, since, as suggested by the figure, it is derived from scattering states (g = 0) near the saddle-joint edge at 3 eV. Similarly the second peak appears to originate from pair states near 4 eV. Both resonances are metastable because of their degeneracy with a continuum, unlike the parabolic exciton resonances which lie in the gap, but both are narrow compared to the characteristic spacing of interband edges.

The short-range interaction considered here has the property that it leads to resonances only for g in a certain range. In real insulators the interaction is the long-range coulomb one, which produces bound states below a parabolic threshold for arbitrarily weak coupling. We have carried out extensive calculations to study the effect of the range of the interaction on the character of hyperbolic excitons. The results of these calculations will

be reported elsewhere.[10] Our basic conclusion is that the form of hyperbolic exciton resonances is even more sensitive to the range of the interaction than are the bound states. Because the problem for the former is intrinsically non-separable no convenient asymptotic approximation has been found which permits continuation of the inner solution (obtained from a truncated secular equation) to an analytic outer solution. However, our calculations, which have been carried out to 15 shells in the fcc lattice, for a band structure and interaction strength appropriate to Xe, do tend to confirm Phillip's explanation[11] of resonance structure in that crystal.

REFERENCES

* This work was supported in part by the National Aeronautics and Space Administration, United States Office of Naval Research, and Advance Research Projects Agency.

+ Present address: University of Illinois, Urbana, Illinois.

1. A. W. Overhauser, Phys. Rev. 101, 1702 (1956).
2. R. S. Knox and N. Inchauspe, Phys. Rev. 116, 1093 (1959).
3. J. C. Phillips, Phys. Rev. Letters 12, 142 (1964).
4. J. C. Phillips, Solid State Physics 18, 55 (1966).
5. C. B. Duke and B. Segall, Phys. Rev. Letters 17, 19 (1966).
6. R. J. Elliott, Phys. Rev. 108, 1384 (1957).
7. J. Callaway, J. Math. Phys. 5, 783 (1964).
8. G. F. Koster and J. C. Slater, Phys. Rev. 95, 1436 (1954).
9. J. Hermanson (to be published).
10. J. Hermanson (to be published in the Physical Review).
11. J. C. Phillips, Phys. Rev. 136, A1714 (1964).

FIGURE CAPTION

Fig. 1. Optical spectrum for model insulator calculated from equation (4), for various electron-hole coupling strengths g. The spectrum for g = 0 is identical to the unperturbed density of states $n_0(E)$.

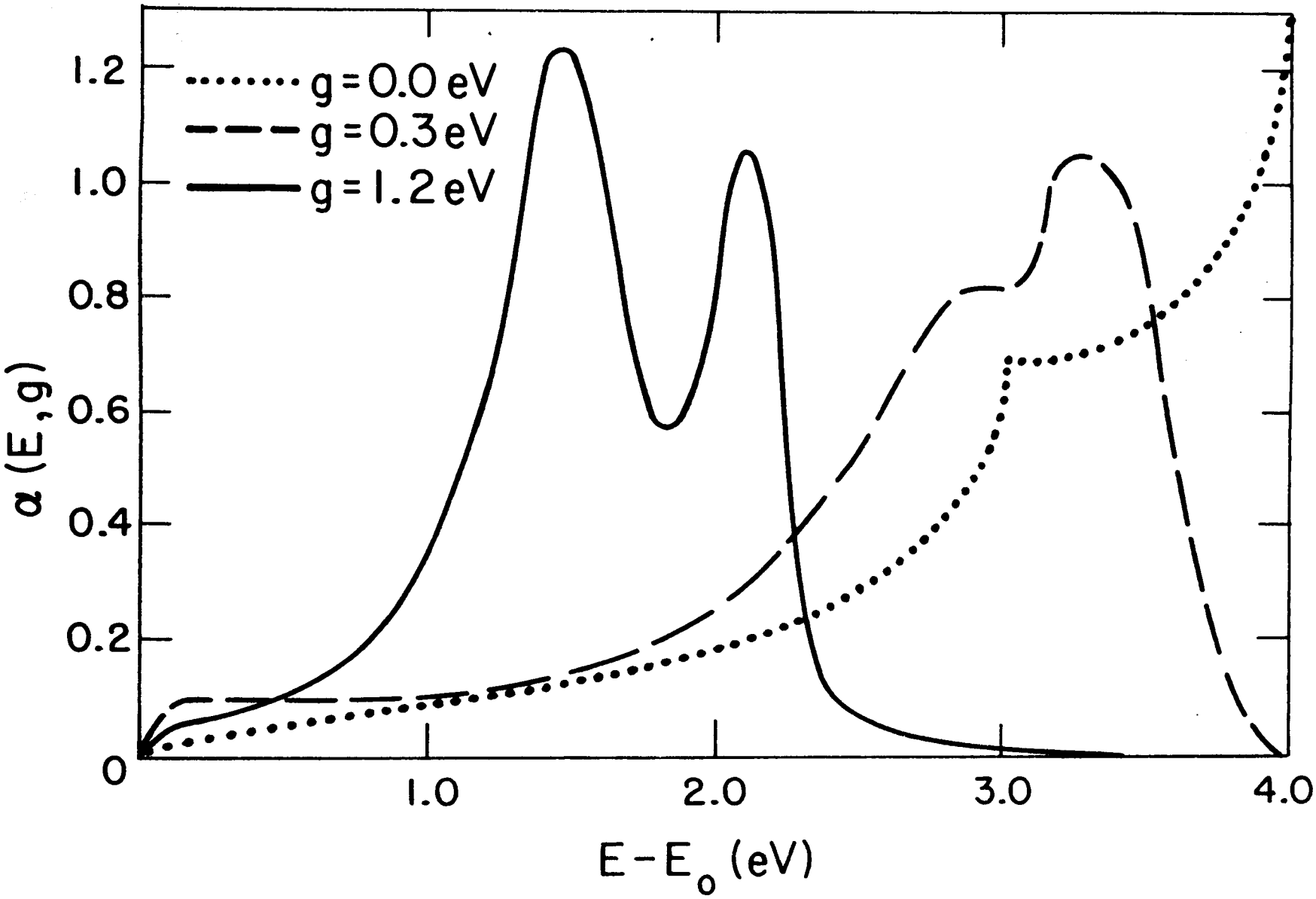

Fig. 1