

# EFFECTIVE MASS APPROXIMATION FOR EXCITONS\*

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**Abstract**—The effective mass approximation for degenerate electronic energy bands is applied to the interaction of electrons and holes in an insulator. It is shown that bound exciton states result from this treatment. The exciton Hamiltonian is of the form derived previously for impurity-state problems. The criterion for the validity of the effective mass approximation is that the lowest state be bound with an energy  $<0.2$  eV. Corrections to the approximation to account for the effective magnetic moments of the electron and hole are indicated. Selection rules and line widths for optical excitation of excitons are discussed. The question of the existence of positronium in crystalline solids is also considered.

## 1. INTRODUCTION

IT was FRENKEL<sup>(1)</sup> who first proposed the existence of nonconducting excited electronic states in insulators. His original idea was that individual atoms in a solid could be excited and this excitation would travel in a particle-like fashion through the solid. These packets of excitation are termed excitons. The exciton concept has been used to explain certain optical absorption lines observed in pure solids.

Two distinctly different treatments for the exciton problem have been formulated, each with its own range of applicability. In ionic or molecular crystals an atomic orbital approach along the lines first proposed by FRENKEL<sup>(2)</sup> and extended recently by OVERHAUSER<sup>(3)</sup> and others<sup>(4)</sup> gives the more exact solution for the lowest bound exciton states. This treatment involves formulating exciton wave functions from atomic orbitals of the atoms at the crystal lattice sites. The original Frenkel proposal considered linear combinations of functions representing individual atoms in the crystal being excited (i.e. a combination of electron and hole at the same lattice site). The formation of functions representing an electron excited to an atomic orbital on a nearest-neighbor atom (electron and hole on nearest neighbors) has been discussed most recently by OVERHAUSER.<sup>(3)</sup> Further extensions to

include electrons excited to next nearest neighbors, etc. may easily be made using the techniques outlined in Ref. (3). The atomic orbital approach, however, leads in general only to a qualitative picture of the overall exciton spectrum. For weakly bound exciton states the necessity of including large contributions from the highly excited atomic orbital functions (i.e. states representing electrons and holes widely separated) makes even this qualitative treatment impractical.

An alternate treatment using the effective mass approximation for the exciton problem was first given by WANNIER.<sup>(5)</sup> His proposal for an exciton can be most clearly pictured as an electron in a conduction band being bound to a hole in a valence band. The validity of the effective mass approximation depends on having the interaction potential slowly varying over the dimensions of a unit cell; i.e., the exciton dimension is large compared to the lattice constant. This formulation of the perturbed periodic potential has been used quite extensively for impurity-state problems in semiconductors.<sup>(6, 7)</sup>

Recently, absorption bands, which may correspond to excitons as treated by an effective mass approximation, have been seen in  $\text{Cu}_2\text{O}$ ,<sup>(8, 9)</sup>  $\text{CdS}$ ,<sup>(10)</sup>  $\text{HgI}_2$ ,  $\text{PbI}_2$ , and  $\text{CdI}_2$ .<sup>(11)</sup>  $\text{Cu}_2\text{O}$ , cubic in structure, exhibits a hydrogenic spectrum which indicates that the simple spherical energy band model would be applicable to the valence and conduction-band extrema. The energy surfaces at band extrema for nondegenerate positions in the Brillouin

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zone, however, are in general elliptical in nature. The center of the zone in cubic structures is one of the few cases where spherical surfaces may occur. The possibility of degenerate extrema is also to be considered in the general formulation of an effective mass approximation for excitons. In addition to the gross features of the spectrum in  $\text{Cu}_2\text{O}$ , GROSS *et al.*<sup>(8)</sup> have observed fine structure and Zeeman splittings of a few of the exciton levels. Therefore, a discussion of the effects expected from the effective magnetic moments of the hole and electron forming the exciton is also required. With the development of these considerations in mind, one may then re-examine the optical absorption data in solids. The correct interpretation of exciton spectra may provide a useful tool in determining the electronic band structure in some insulators.

In this paper the effective mass approximation for excitons is extended to include degeneracies at the energy band extrema arbitrarily located within the Brillouin zone. The Hamiltonian which gives the exciton spectrum at the exciton-band extrema is derived, and the energy eigenvalues are discussed for a few examples. A perturbation theory treatment is formulated which gives the effective mass of the exciton band near the band minimum. This perturbation theory is similar to that for electronic energy bands.<sup>(12)</sup> A discussion of the failure of the effective mass formulation of the problem for tightly bound excitons, e.g. in ionic crystals,<sup>(3)</sup> is given. The selection rules for optical excitation of excitons are treated and reasons given for the absence of exciton absorption lines in certain semiconductors. Finally, the similarity between the exciton and positronium in solids is briefly considered.

## 2. DEVELOPMENT OF THE EXCITON HAMILTONIAN

In developing the effective mass theory for excitons we shall first treat the case of two spherical energy surfaces. Though the solution of this problem for nondegenerate energy surfaces is well known, the treatment given here is more readily extended to the more general case than is the usual formulation. In an effective mass approximation the Hamiltonian is:

$$H = -\frac{\hbar^2}{2m_e} \nabla_{r_e}^2 - \frac{\hbar^2}{2m_h} \nabla_{r_h}^2 - \frac{e^2}{\epsilon|r_e - r_h|}, \quad (1)$$

where  $m_e$  and  $m_h$  are the electron and hole effective masses,  $r_e$  and  $r_h$  are their respective co-ordinates, and  $\epsilon$  is the dielectric constant of the crystal. Making the co-ordinate transformation\*

$$\begin{aligned} R &= \frac{1}{2}(r_e + r_h) \\ r &= r_e - r_h, \end{aligned} \quad (2)$$

the Hamiltonian may be written

$$H = -\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{\epsilon r} \quad (3)$$

$$-\frac{\hbar^2}{2} \left( \frac{1}{m_e} - \frac{1}{m_h} \right) \nabla_r \cdot \nabla_R - \frac{\hbar^2}{2\mu} \nabla_R^2$$

where  $\mu = m_e m_h (m_e + m_h)^{-1}$  is the reduced mass. The operator  $\nabla_R$  commutes with the Hamiltonian, hence the eigenfunctions may be taken in the form

$$\Psi = e^{i\mathbf{K} \cdot \mathbf{R}} \psi(r), \quad (4)$$

where  $\mathbf{K}$  is the wave vector for the exciton and satisfies the equation

$$\left\{ -\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{\epsilon r} - \frac{\hbar^2}{2} i \left( \frac{1}{m_e} - \frac{1}{m_h} \right) \mathbf{K} \cdot \nabla_r + \frac{\hbar^2}{2\mu} \mathbf{K}^2 \right\} \psi(r) = E\psi(r). \quad (5)$$

The dispersion relation for the exciton band may now be found using perturbation theory for the  $\mathbf{K} \cdot \nabla_r$  term. This procedure is completely analogous to the perturbation theory treatment<sup>(13)</sup> for electronic energy bands. The unperturbed Hamiltonian

$$H^0 = -\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{\epsilon r} \quad (6)$$

has energy eigenvalues

$$E_n^0 = -\frac{\mu e^4}{2\hbar^2 \epsilon^2} \frac{1}{n^2} \quad (7)$$

and hydrogenic eigenfunctions  $\phi_n$ . Thus the excitons at the center of the zone have a hydrogenic spectrum given by eq. (7). For small values of  $\mathbf{K}$ , a perturbation expansion to terms in  $\mathbf{K}^2$  gives

\* The Jacobian of the transformation is unity, hence,  $\int F(r_e, r_h) dx_e dx_h = \int F(\frac{1}{2}\mathbf{r} + \mathbf{R}, -\frac{1}{2}\mathbf{r} + \mathbf{R}) d\mathbf{r} d\mathbf{R}$

$$E_n(\mathbf{K}) = E_n^\circ + \frac{\hbar^2 K^2}{2\mu} + \frac{\hbar^2}{4} \left( \frac{1}{m_e} - \frac{1}{m_h} \right)^2 \sum_{n'}' \frac{(\phi_n | \mathbf{K} \cdot \mathbf{p} | \phi_{n'}) (\phi_{n'} | \mathbf{K} \cdot \mathbf{p} | \phi_n)}{E_n^\circ - E_{n'}^\circ}, \quad (8)$$

where  $\mathbf{p} = -i\hbar\nabla_r$ .  
Using the  $f$ -sum rule,

$$\frac{2}{\mu} \sum_n' \frac{(\phi_n | p_\alpha | \phi_{n'}) (\phi_{n'} | p_\beta | \phi_n)}{E_n^\circ - E_{n'}^\circ} = -\delta_{\alpha\beta}. \quad (9)$$

Eq. (8) yields

$$E_n(\mathbf{K}) = E_n^\circ + \frac{1}{2} \hbar^2 (m_e + m_h)^{-1} K^2. \quad (10)$$

This result could have been obtained immediately if the transformation to the center of mass coordinates

$$\begin{aligned} R_{C.M.} &= (m_e + m_h)^{-1} (m_e \mathbf{r}_e + m_h \mathbf{r}_h) \\ \mathbf{r} &= \mathbf{r}_e - \mathbf{r}_h \end{aligned} \quad (11)$$

had been made instead of the transformation (2). However, a center of mass transformation cannot be defined for excitons formed from degenerate bands. Eq. (10) shows that all excitons have the same mass independent of the hydrogenic state in which they are excited. The wave function associated with the exciton is

$$\Psi_{ex} = \sum_{k_l, k_h} \Psi_{k_l, k_h}^{(\kappa, n)} \psi_{k_l}(r_l) \psi_{k_h}(r_h) \quad (12)$$

where  $\psi_{k_l}$  and  $\psi_{k_h}$  are the Bloch functions associated with the conduction and valence bands and  $\Psi_{k_l, k_h}^{(\kappa, n)}$  is the Fourier transform of  $\Psi$ .

We now proceed to the more general formulation using essentially the same steps as have been outlined above. Consider the conduction and valence electron extrema given by solutions of the secular determinants

$$\begin{aligned} ||H_{ij}^e - E_e \delta_{ij}|| &= 0 \\ ||H_{ij}^h - E_h \delta_{ij}|| &= 0, \end{aligned} \quad (13)$$

where the matrix elements  $H_{ij}^e$  and  $H_{ij}^h$  are of the general quadratic forms in the momenta:

$$\begin{aligned} H_{ij}^e &= \sum_{\alpha\beta} D_{ij}^{e\alpha\beta} (p_e - p_e^\circ)_\alpha (p_e - p_e^\circ)_\beta \\ H_{ij}^h &= \sum_{\alpha\beta} D_{ij}^{h\alpha\beta} (p_h - p_h^\circ)_\alpha (p_h - p_h^\circ)_\beta. \end{aligned} \quad (14)$$

The energy band extrema for conduction and valence bands occur at  $\mathbf{p}_e^\circ$  and  $\mathbf{p}_h^\circ$  respectively. In an effective mass approximation, the exciton Hamiltonian is

$$\begin{aligned} H_{ii', jj'} &= H_{ij}^e \delta_{i'j'} + \delta_{ij} H_{i'j'}^h \\ &+ V(|\mathbf{r}_e - \mathbf{r}_h|) \delta_{ij} \delta_{i'j'}, \end{aligned} \quad (15)$$

which in matrix form is written

$$\begin{aligned} \mathcal{H} &= \mathcal{H}^e(\mathbf{p}_e - \mathbf{p}_e^\circ) + \mathcal{H}^h(\mathbf{p}_h - \mathbf{p}_h^\circ) \\ &+ \mathcal{V}(|\mathbf{r}_e - \mathbf{r}_h|). \end{aligned} \quad (16)$$

Making the co-ordinate transformation (2), the Hamiltonian (16) becomes

$$\begin{aligned} \mathcal{H} &= \mathcal{H}^e(\mathbf{p} + \frac{1}{2}\mathbf{P} - \mathbf{p}_e^\circ) + \mathcal{H}^h(-\mathbf{p} + \frac{1}{2}\mathbf{P} - \mathbf{p}_h^\circ) \\ &+ \mathcal{V}(r), \end{aligned} \quad (17)$$

where  $\mathbf{p}$  and  $\mathbf{P}$  are the momenta conjugate to  $\mathbf{r}$  and  $\mathbf{R}$  respectively. The commutativity of  $\nabla_{\mathbf{r}}$  with the Hamiltonian (17) once again allows one to look for eigenfunctions of the form

$$\Psi = e^{i\mathbf{K} \cdot \mathbf{R}}(\mathbf{r}), \quad (18)$$

where  $\mathbf{K}$  is the exciton wave vector, and  $\Psi(\mathbf{r})$  satisfies the matrix equation

$$\bar{\mathcal{H}}(\Psi(\mathbf{r})) = E\Psi(\mathbf{r}), \quad (19)$$

where

$$\begin{aligned} \bar{\mathcal{H}} &= \mathcal{H}^e(\mathbf{p} + \frac{1}{2}\hbar\mathbf{K} - \mathbf{p}_e^\circ) \\ &+ \mathcal{H}^h(-\mathbf{p} + \frac{1}{2}\hbar\mathbf{K} - \mathbf{p}_h^\circ) + \mathcal{V}(r). \end{aligned} \quad (20)$$

In a crystal co-ordinate representation the Wannier equation (19) may be written as

$$\bar{\mathcal{H}}'\Psi'(\mathbf{r}) = E\Psi'(\mathbf{r}), \quad (21)$$

where

$$\Psi'(\mathbf{r}) = \exp\{\frac{1}{2}i(\hbar)^{-1}(\mathbf{p}_h^\circ - \mathbf{p}_e^\circ) \cdot \mathbf{r}\} \Psi(\mathbf{r}), \quad (22)$$

$$\begin{aligned} \bar{\mathcal{H}}' &= \mathcal{H}^e(-i\hbar\nabla_r + \frac{1}{2}\hbar\boldsymbol{\kappa}) \\ &+ \mathcal{H}^h(-i\hbar\nabla_r - \frac{1}{2}\hbar\boldsymbol{\kappa}) + \mathcal{V}(r), \end{aligned} \quad (23)$$

and

$$\hbar\mathbf{K} = \mathbf{p}_e^\circ + \mathbf{p}_h^\circ + \hbar\boldsymbol{\kappa}. \quad (24)$$

Eq. (22) represents a simple displacement of the origin in wave vector space to  $(2\hbar)^{-1}(\mathbf{p}_e^\circ - \mathbf{p}_h^\circ)$ . The matrices  $\mathcal{H}^e$  and  $\mathcal{H}^h$  are second order in  $\mathbf{p}$  and

may be written in terms of a matrix of effective mass tensors as

$$\mathcal{H}^e(\mathbf{p}) = \frac{1}{2} \sum_{\alpha\beta} \left( \frac{1}{\mathbf{m}_e} \right)_{\alpha\beta} p_\alpha p_\beta \quad (25)$$

$$\mathcal{H}^h(\mathbf{p}) = \frac{1}{2} \sum_{\alpha\beta} \left( \frac{1}{\mathbf{m}_h} \right)_{\alpha\beta} p_\alpha p_\beta.$$

Substitution of (25) into (23) yields the exciton Hamiltonian in a convenient crystal co-ordinate representation,

$$\begin{aligned} \overline{\mathcal{H}}' = \mathcal{H}^0 - \frac{1}{2}i\hbar^2 \sum_{\alpha\beta} \kappa_\alpha \frac{\partial}{\partial r_\beta} \left( \frac{1}{\mathbf{m}_e} - \frac{1}{\mathbf{m}_h} \right)_{\alpha\beta} + \\ + \frac{1}{8}\hbar^2 \sum_{\alpha\beta} \kappa_\alpha \kappa_\beta \left( \frac{1}{\mathbf{m}_e} + \frac{1}{\mathbf{m}_h} \right)_{\alpha\beta} \end{aligned} \quad (26)$$

where

$$\mathcal{H}^0 = \mathcal{H}^e(-i\hbar\nabla_r) + \mathcal{H}^h(-i\hbar\nabla_r) + \mathcal{V}^0(r). \quad (27)$$

### 3. EXCITON-BAND STRUCTURE

The exciton spectrum at  $\kappa = 0$  will be given by the solutions of the Wannier equation

$$H^0 \varphi_n = E_n^0 \varphi_n. \quad (28)$$

The dispersion relation for the exciton band in the neighborhood will be calculated using the term

$$\mathcal{H}' = -\frac{1}{2}i\hbar^2 \sum_{\alpha\beta} \kappa_\alpha \frac{\partial}{\partial r_\beta} \left( \frac{1}{\mathbf{m}_e} - \frac{1}{\mathbf{m}_h} \right)_{\alpha\beta} \quad (29)$$

as a perturbation. The eigenfunctions of (28) have either even or odd parity, since the inversion operator commutes with the Hamiltonian independent of whether the crystal is itself invariant under inversion. Hence all first-order terms in the perturbation vanish. The exciton band will accordingly have a critical point at  $\kappa = 0$ . The classification of the critical point as maxima, minima, saddle points, etc., will depend in general on the magnitude and sign of the terms in the matrix of effective mass tensors. An exciton of wave vector  $\mathbf{K}$  is formed from electron and hole-wave packets with wave vectors  $\mathbf{k}_e$  and  $\mathbf{k}_h$  respectively such that

$$\mathbf{K} = \mathbf{k}_e + \mathbf{k}_h. \quad (30)$$

If  $\mathbf{K}^0 = \mathbf{k}_e^0 + \mathbf{k}_h^0$  represents an extremum, an approximate criterion that it will be a minimum is that all  $\mathbf{k}_e$  and  $\mathbf{k}_h$  satisfying eq. (30) and in the neighborhood  $\mathbf{k}_e^0$  and  $\mathbf{k}_h^0$  represent larger energy differences between the electronic energy bands than the difference at  $\mathbf{k}_e^0$  and  $\mathbf{k}_h^0$ , i.e.

$$|E_e(\mathbf{k}_e) - E_h(\mathbf{k}_h)| > |E_e(\mathbf{k}_e^0) - E_h(\mathbf{k}_h^0)|, \quad (31)$$

where  $E_e(\mathbf{k})$  and  $E_h(\mathbf{k})$  are solutions of the secular determinants (13).

Unfortunately an exact solution of the Wannier eq. (28) can only be obtained for spherical energy surfaces (see eq. 7). However, if the components in the matrices of effective mass tensors ( $1/\mathbf{m}_e$ ) and ( $1/\mathbf{m}_h$ ) are known, one may compute the exciton spectrum by a suitable variational calculation. The impurity state problem discussed extensively by KOHN and LUTTINGER<sup>(14)</sup> may be considered as a special case of the exciton Hamiltonian (27). For example, if one allows the electron mass to become infinite, the acceptor state Hamiltonian results. Similarly the donor-state problem is obtained if one sets the hole mass equal to infinity. The impurity-state spectrum calculated by KOHN and LUTTINGER<sup>(14)</sup> for donors in Si represents a particular example of the sort of exciton spectrum which one would obtain from nondegenerate ellipsoidal energy surfaces. KOHN and SCHECHTER<sup>(15)</sup> have applied a variational calculation to the more complex problem arising in the case of degenerate-band impurity-state problems. This Hamiltonian is similar to that for an exciton formed from a degenerate valence band and a spherical-conduction band. Exciton spectra for other combinations of degenerate bands can be obtained by variational procedures similar to those cited above.

A generalization of the *f*-sum rule for the Hamiltonian (27) useful for the application of perturbation theory will now be derived. The commutator of  $r_\nu$  and  $H^0$  is

$$\begin{aligned} [r_\nu, H^0] &= -\frac{1}{2} \sum_{\alpha\beta} [p_\alpha p_\beta, r_\nu] \left( \frac{1}{\mathbf{m}_e} + \frac{1}{\mathbf{m}_h} \right)_{\alpha\beta} \\ &= i\hbar \sum_{\alpha} p_\alpha \left( \frac{1}{\mathbf{m}_e} + \frac{1}{\mathbf{m}_h} \right)_{\alpha\beta}. \end{aligned} \quad (32)$$

Taking the matrix element of this commutator, we get the expression

$$\begin{aligned}
& (\varphi_n | r_\gamma | \varphi_{n'}) \\
&= -i\hbar \sum_{\alpha} \frac{(\varphi_n | p_{\alpha} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)_{\alpha\gamma} | \varphi_{n'})}{E_n^{\circ} - E_{n'}^{\circ}} \quad (33)
\end{aligned}$$

which, when substituted into the matrix elements of the commutator

$$[p_{\beta}, r_{\gamma}] = -i\hbar \delta_{\beta\gamma}, \quad (34)$$

$$\begin{aligned}
& \sum_{n'} [(\varphi_n | p_{\beta} | \varphi_{n'}) (\varphi_{n'} | r_{\gamma} | \varphi_n) - \\
& - (\varphi_n | r_{\gamma} | \varphi_{n'}) (\varphi_{n'} | p_{\beta} | \varphi_n)] = -i\hbar \delta_{\beta\gamma}, \quad (35)
\end{aligned}$$

gives the generalized  $f$ -sum rule

$$\begin{aligned}
& \sum_{\alpha, n'} (E_n^{\circ} - E_{n'}^{\circ})^{-1} \left\{ (\varphi_n | p_{\beta} | \varphi_{n'}) \times \right. \\
& \quad \times \left( \varphi_{n'} | p_{\alpha} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)_{\alpha\gamma} | \varphi_n \right) + \\
& \quad \left. + \left( \varphi_n | p_{\alpha} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)_{\alpha\gamma} | \varphi_{n'} \right) (\varphi_{n'} | p_{\beta} | \varphi_n) \right\} \\
&= -\delta_{\beta\gamma}. \quad (36)
\end{aligned}$$

Applying second-order perturbation theory to the Hamiltonian (27) using the term (29) as a perturbation, gives the energy of the  $n$ th exciton level as

$$\begin{aligned}
E_n(\mathbf{x}) &= E_n^{\circ} + \\
&+ \frac{1}{2} \hbar^2 \sum_{\alpha\beta} \mathbf{x}_{\alpha} \mathbf{x}_{\beta} \left( \varphi_n | \left( \frac{1}{m_e} + \frac{1}{m_h} \right)_{\alpha\beta} | \varphi_n \right) + \\
&+ \frac{1}{2} \hbar^2 \sum_{\substack{\alpha\alpha' \\ \beta\beta' \\ n}} \mathbf{x}_{\alpha} \mathbf{x}_{\alpha'} (E_n^{\circ} - E_{n'}^{\circ})^{-1} \times \\
&\quad \times \left( \varphi_n | p_{\beta} \left( \frac{1}{m_e} - \frac{1}{m_h} \right)_{\alpha\beta} | \varphi_{n'} \right) \times \\
&\quad \times \left( \varphi_{n'} | p_{\beta'} \left( \frac{1}{m_e} - \frac{1}{m_h} \right)_{\alpha'\beta'} | \varphi_n \right). \quad (37)
\end{aligned}$$

For the most general type of degenerate bands, the  $f$ -sum rule (36) is of limited help in carrying out the summation (37). However, in a few specific examples, eq. (37) can be summed exactly using (36), and even when the more general case cannot

be done exactly, the procedure may be used to get an approximate expression for the exciton dispersion relation. For the general case the dispersion relation for the exciton bands will depend on the quantum state and degeneracy of the exciton.

The exciton eigenfunctions at the band extrema are

$$\Psi_{e\alpha}^{\circ} = \sum_{k_1 k_h j j'} \Psi_{k_1 k_h j j'}^{(\kappa, n)} \psi_{k_1 j}(\mathbf{r}_1) \psi_{k_h j'}(\mathbf{r}_k) \quad (38)$$

where  $\psi_{k_1 j}$  and  $\psi_{k_h j'}$  are the Bloch functions of the degenerate conduction and valence bands respectively; the subscripts label the wave vectors at the extrema and the degenerate states; and  $\Psi_{k_1 k_h j j'}^{(\kappa, n)}$  is the Fourier transform of 18. Two subscripts are needed to label the elements of the column matrix  $\Psi$ , as the Hamiltonian (15) is the direct product of the subspaces for electrons and holes.

In addition to the gross features of the exciton spectrum obtained by solving eq. (28), the levels may show structure. Experimental observations of GROSS *et al.*<sup>(8)</sup> on  $\text{Cu}_2\text{O}$  indicate that at low temperatures the lifting of some degeneracies may indeed occur. The level splittings may arise from magnetic-moment interactions or from higher-order terms in the effective mass approximation. The higher-order terms will tend to mix degenerate minima if these should be present, thus splitting the exciton band degeneracies.

We shall discuss first the exciton fine structure. Provided the spin-orbit interaction is weak, an effective particle moving in a magnetic field has a magnetic moment<sup>(18, 19)</sup> associated with it of

$$\boldsymbol{\mu} = \frac{K' e \hbar}{2c} \mathcal{J} \quad (39)$$

where  $\mathcal{J}$  is the angular momentum matrix associated with the particular degeneracy being considered.  $K'$  is a constant which differs from  $1/m$  ( $m$  is the free electron mass) if there is any orbital angular momentum mixed into the states at the extrema. For the special case of the two-fold degenerate  $p^{\dagger}$  states in cubic symmetry,  $K' \simeq 1/m^*$ . The Zeeman splitting of exciton levels given by SAMOILOVICH and KORENBLIT<sup>(20)</sup> assumed  $K' = 1/m^*$  and hence this treatment needs slight modification to cover the more general case. The fine structure interaction will consist of the dipole-dipole interaction

$$\mathcal{H}_d = \left(\frac{e\hbar}{2c}\right)^2 K_e' K_h' \left\{ \frac{r^2 \mathbf{J}_e \cdot \mathbf{J}_h - 3(\mathbf{J}_e \cdot \mathbf{r})(\mathbf{J}_h \cdot \mathbf{r})}{r^5} \right\} \quad (40)$$

as well as the contact term

$$\mathcal{H}_c = -\frac{8\pi}{3} \left(\frac{e\hbar}{2c}\right)^2 K_e' K_h' \mathbf{J}_e \cdot \mathbf{J}_h \delta(\mathbf{r}), \quad (41)$$

where the direct products of the vector components of the angular-momentum matrices occur. Under conditions of spherical symmetry, the dipole-dipole interaction vanishes, but the contact term will still give a fine structure splitting to the level. For two spherical energy surfaces the ground states are split into singlet and triplet states, with the singlet state being lower in energy. This problem is completely analogous to that of positronium in free space.

#### 4. DISCUSSION

By far the most serious restriction imposed on the effective mass approximation is the requirement that the interacting potential vary slowly over the lattice spacing. The ground-state binding energy of the exciton,  $E_1^0$  is of the order of  $e^2/(2e\bar{a})$ , where  $\bar{a}$  is a measure of the dimensions of the exciton. For the potential to be slowly varying we require  $\bar{a} >$  lattice constant, or  $|E_1^0| < \sim 0.2eV$ . Hence, in ionic crystals where the observed optical exciton transitions correspond to energies  $\sim 0.2eV$ , one would expect the atomic orbital approximation to be valid. On the other hand, in covalent semiconductors and insulators of large dielectric constant, one expects the effective mass approach outlined above to be the more correct. Even in those cases where the effective mass approximation is applicable, higher-order corrections to the approximation will be effective in splitting some of the remaining degeneracy. For example, if the energy extrema are ellipsoids, the higher-order corrections will mix exciton states formed from the various ellipsoids. This type of correction to the effective mass approximation has been discussed extensively by KOHN and LUTTINGER<sup>(14)</sup> in connection with the impurity-state problem for donors in Si and Ge. In the general case, the exciton state at the exciton band minima will have zero group velocity, and hence the correction terms will have the crystallographic sym-

metry of the lattice. The splittings are indicated in the usual group theoretical way by reducing the direct product representation of the wave functions (38) into the representations of the crystallographic point symmetry group. The effect of these correction terms on states different from  $\mathbf{K} = 0$  will be that of scattering excitons among the nearly degenerate bands, i.e.  $\mathbf{K}$  is no longer a good quantum number. This scattering might be the most effective for producing singlet-triplet-state conversion of excitons formed from spherical electronic-energy surfaces, provided the correction terms are sufficiently large.

It was mentioned in the introduction that optical excitation of the excitonic energy levels is presumably observable experimentally. The selection rule for direct optical transitions is that only transitions to the  $\mathbf{K} = 0$  exciton state are possible. This is easily seen since in the filled valence band (the initial state) the wave vectors sum to zero. The absorbed photon contributes a negligible amount of momentum, so that the final exciton state must be at  $\mathbf{K} \simeq 0$ . Indirect transitions to exciton states at general points in the Brillouin occur by the simultaneous absorption of a photon and emission of a phonon. However, the photon frequency is not unique due to the spread in possible values of the final exciton state, and hence no sharp absorption line spectrum would be observed. The indirect transitions to exciton states would contribute a low energy tail to the absorption curve similar to that discussed by HALL, BARDEEN, and BLATT<sup>(21)</sup> for indirect transitions to electronic levels. A more careful analysis of absorption coefficients would presumably show an additional low-energy tail due to indirect exciton transitions in cases where indirect electronic transitions are observed.

One source of line width for the optical excitation of excitons is indirect transitions to states  $\mathbf{K} \simeq 0$  through simultaneous absorption or induced emission of thermal phonons. The line width expected from this mechanism is  $\sim kT$  which corresponds to the temperature dependence and order of magnitude of the line widths observed in the absorption spectra in  $\text{Cu}_2\text{O}$ , CdS, etc.

The simplest band structure conceivable in non-cubic substances consists of nondegenerate ellipsoidal extrema. This case may be solved either by the perturbation treatment using the generalized  $f$ -sum rule or by a center of mass transformation.

The perturbation calculation will be presented here as a further illustration of the approach. If the symmetry is such that in a given co-ordinate system in wave vector space all effective mass tensors are diagonal (e.g.  $\langle 100 \rangle$  ellipsoids may all be diagonalized in the same co-ordinate system, however  $\langle 111 \rangle$  ellipsoids will not all be so diagonalized), then

$$\begin{aligned} \left(\frac{1}{m_e}\right)_{\alpha\beta} &= \frac{1}{m_{e\alpha\beta}} \delta_{\alpha\beta} \\ \left(\frac{1}{m_h}\right)_{\alpha\beta} &= \frac{1}{m_{h\alpha\beta}} \delta_{\alpha\beta} \end{aligned} \quad (42)$$

and eq. (36) becomes

$$2\left(\frac{1}{m_e} + \frac{1}{m_h}\right)_{\gamma\gamma} \sum_{n'}' \frac{(\varphi_n | p_\beta | \varphi_{n'}) (\varphi_{n'} | p_\gamma | \varphi_n)}{E_n^\circ - E_{n'}^\circ} = -\delta_{\beta\gamma}. \quad (43)$$

Eq. (37) may be summed by use of eq. (43) to give

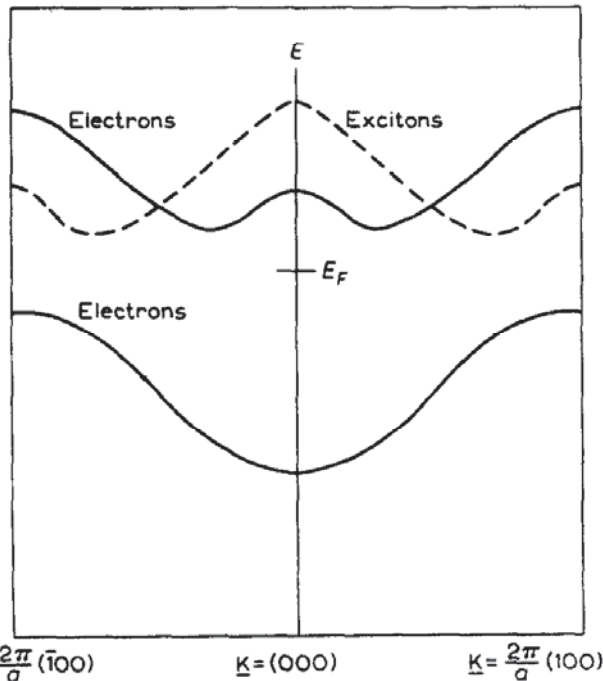


FIG. 1. Schematic drawing of electron- and exciton-band structure in a Brillouin zone with nondegenerate ellipsoidal energy extrema. The exciton-band minima occur at points in the zone which are the sum of the values of the wave vector at the electron and hole extrema. The Fermi energy,  $E_F$ , is situated such that the filled lower band represents the ground state of the system. The single exciton band is really an infinite manifold of nearly degenerate levels.

$$E_n(\mathbf{x}) = E_n^\circ + \frac{1}{2} \hbar^2 \sum_{\alpha} \mathbf{x}_{\alpha}^2 (m_{e\alpha\alpha} + m_{h\alpha\alpha})^{-1}. \quad (44)$$

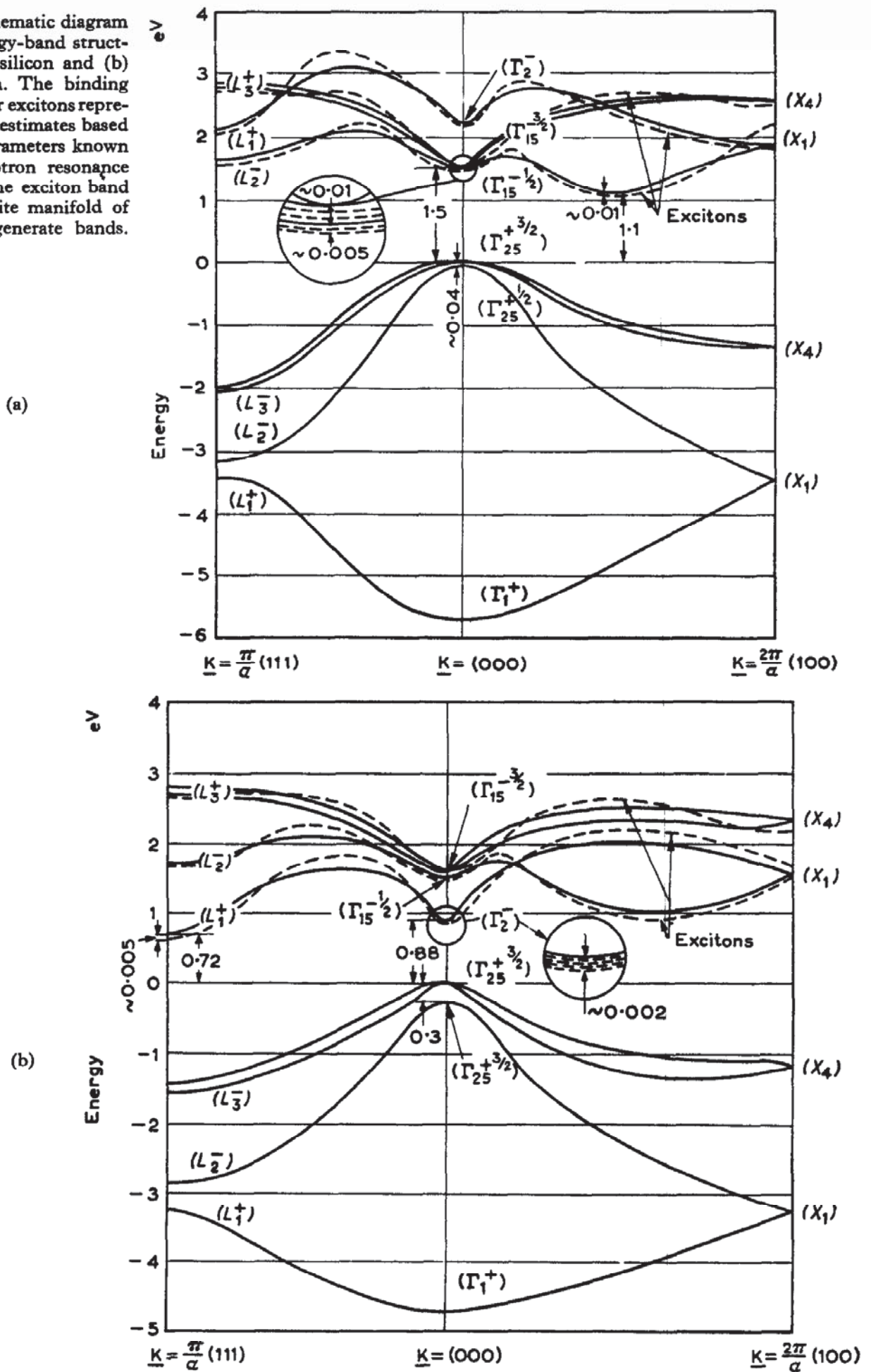
The exciton-band structure in noncubic substances such as CdS may be of the type given by eq. (44). Fig. 1 shows a highly schematic sketch of the exciton-band structure for a case where the electronic extrema are simple ellipsoids at general positions in the Brillouin zone. The single band, labelled excitons, is in reality a manifold of closely spaced bands.

Only order of magnitude calculations have so far been made for the more complicated degeneracies such as those exhibited in the valence-band structure in silicon and germanium. The calculations may, however, often be simplified by the following observation. If one is dealing with a degenerate band valence band and a nondegenerate conduction of light mass, then the non-diagonal terms may be treated as small perturbations. From the known band structure in silicon and germanium<sup>(16)</sup> order of magnitude estimates have been made for the lowest exciton levels at various minima in the exciton band. A rough estimate of the exciton band structure in Si and Ge is shown in Fig. 2. Estimates of effective masses for excited states<sup>(17)</sup> were made, based on matrix elements calculated from cyclotron resonance data. These excited state masses have been used in approximating the exciton band structure. The single bands, marked excitons, are once more manifolds of closely spaced levels.

In the interpretation of optical measurements on insulating crystals any observed structure at the absorption-band edge which lies in a region much less than 0.2 eV away from the band edge may be the result of exciton or impurity levels derivable within the effective mass approximation. The distinction between exciton and impurity levels can in principle be made by controlled doping of the crystal. For most of the spectra observed so far, this distinction has not been carefully made. The accurate interpretation of the spectra may yield information about the form and degeneracy of the conduction and valence-electron band structure. In addition, experimental information on the Zeeman splitting may help to identify band degeneracies and to establish the effective magnetic moments of the conduction and valence electrons.

The close analogy between the exciton and positronium suggests that the question of the existence

FIG. 2. Schematic diagram of the energy-band structure in (a) silicon and (b) germanium. The binding energies for excitons represent rough estimates based on the parameters known from cyclotron resonance results. The exciton band is an infinite manifold of nearly degenerate bands.





of positronium in insulating solids might be closely related to the considerations which we have discussed. A positron will be weakly bound in the solid, since the largest part of its wave function is confined to the large slowly varying regions of potential between ions. Weak binding implies that the positron effective mass is approximately that of a free electron. The formation of positronium implies that a thermalized positron binds a conduction electron. The only effect of the positron on a filled band is a polarization of the atomic core states. The binding which results from positronium formation in insulating crystals will in most cases be  $\sim 0.2$  eV. The excitation to a conduction band will in general require more energy than is available from positronium formation. Hence, the existence of positronium in an insulator would thus appear energetically unfavourable. In an amorphous solid where voids are available in which a positron may bind an electron closely, the free-space binding energy of positronium (6.8 eV) is available to extract an electron from a valence band and form positronium. In semiconductors one may have electrons available in the conduction band by thermal excitation or by doping. Here one can always decrease the energy of the system by forming positronium. However, the capture time associated with a positive charge in a semiconductor ( $\sim 1\mu$  sec) is much longer than the decay time of positrons in solids. Hence, it seems unlikely that positronium will form even in this event. These speculations are consistent with the experimental observations of BELL and GRAHAM<sup>(22)</sup> and TALEGDI<sup>(23)</sup> who could detect the typical free-space positronium decay only in amorphous solids.

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