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Perturbation-Theory Investigation of the Exciton Ground State of Cubic Semiconductors in a Magnetic Field

M. Altarelli*

Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

Nunzio O. Lipari

Xerox Corporation, Rochester Research Center, Webster, New York 14580

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The influence of the degeneracy and anisotropy of the valence band on the exciton ground state in the low-magnetic-field region is investigated. Using first- and second-order perturbation theory, simple analytical expressions are given for the Zeeman splittings and the diamagnetic shifts of the eightfold-degenerate ground state. Selection rules for optical transitions and their dependence on polarization are discussed. The results are compared with available experimental data.

I. INTRODUCTION

The relevance of excitonic transitions in the interpretation of magneto-optical experiments has long been recognized.¹ From the theoretical point of view, the problem of the exciton in a magnetic field presents great difficulties, owing to the complexity of the valence-band structure in cubic semiconductors. So far, all investigations either have neglected the electron-hole interaction while retaining the complexity of the band structure,² or have treated the Coulomb interaction assuming simple parabolic bands.³ The experimental results, however, show deviations from the predictions of these simplified approaches,⁴⁻⁷ thus pointing out the need for a more accurate theory.⁸

The purpose of the present work is to investigate the lowest direct exciton states of diamond and zinc-blende semiconductors in the low-field region, taking into account both the Coulomb interaction and the actual band structure near the fundamental edge. In fact, it has been recently shown⁹ that, in the absence of magnetic fields, the effects of the degeneracy and anisotropy of the va-

lence band can be treated quite accurately. In the following we will show that it is also possible to include the effects of a weak magnetic field by similar methods.

In Sec. II the problem is formulated and the solution is presented. In Sec. III the results are discussed and compared with available experimental data.

II. PERTURBATION ANALYSIS

If we assume the conduction and valence-band extrema to be at the Γ point, we can write the Hamiltonian for the relative electron-hole motion in a magnetic field as¹⁰

$$\mathcal{H}_{ex} = \mathcal{H}_e \left(\vec{p} + \frac{e}{c} \vec{A} \right) - \mathcal{H}_h \left(-\vec{p} + \frac{e}{c} \vec{A} \right) - \frac{e^2}{\epsilon r}, \quad (1)$$

where, following Luttinger,¹¹ we have defined

$$\mathcal{H}_e(\vec{k}) = (1/2m_e^*)k^2 + \mu^* \vec{\sigma} \cdot \vec{H}, \quad (2)$$

$$- \mathcal{H}_h(\vec{k}) = (1/m_0) \left[(\gamma_1 + \frac{5}{2}\gamma_2) \frac{1}{2} k^2 - \gamma_2 (k_x^2 J_x^2 + k_y^2 J_y^2 + k_z^2 J_z^2) \right]$$

$$\begin{aligned}
& -2\gamma_3 \{k_x k_y\} \{J_x J_y\} \\
& + \{k_y k_x\} \{J_y J_x\} + \{k_x k_x\} \{J_x J_x\} \\
& + (e/c) \kappa \vec{J} \cdot \vec{H} \\
& + (e/c) q (J_x^3 H_x + J_y^3 H_y + J_z^3 H_z). \quad (3)
\end{aligned}$$

Here, $\hbar=1$, J_x , J_y , and J_z are spin- $\frac{3}{2}$ matrices,¹¹ μ^* is the effective magnetic moment of the conduction electron,² $\{ab\} = \frac{1}{2} \{a, b\} = \frac{1}{2}(ab + ba)$, and all other quantities are defined by Luttinger. We choose for a constant magnetic field the gauge $\vec{A} = \frac{1}{2}(\vec{H} \times \vec{r})$. In Eq. (1) we have neglected, for simplicity, the very small effects due to the presence of the split-off valence band, to the electron-hole exchange interaction, and to the terms linear in \vec{p} which arise from the lack of inversion symmetry in zinc-blende materials. We now assume that the magnetic field is along the z direction, although the following analysis can similarly be carried out for any direction.

Equation (1) can be rewritten as follows:

$$\mathcal{H}_{\text{ex}} = \mathcal{H}_s + \mathcal{H}_d + \mathcal{H}_l + \mathcal{H}_q, \quad (4)$$

where \mathcal{H}_s and \mathcal{H}_d are defined in Ref. 9 and describe the exciton in the absence of a magnetic field; the subscripts s and d refer to the s - and d -like symmetry of \mathcal{H}_s and \mathcal{H}_d , respectively. \mathcal{H}_l and \mathcal{H}_q are, respectively, the linear and quadratic terms in \vec{H} :

$$\begin{aligned}
\mathcal{H}_l &= \frac{eH}{c} \left[\left(\frac{1}{2m_0^*} - \frac{\gamma_1}{2m_0} - \frac{5}{4\mu_1} \right) (xp_y - yp_x) \right. \\
& + \frac{1}{\mu_1} (xp_y J_y^2 - yp_x J_x^2) + \frac{1}{2\sqrt{3}\mu_2} [(xp_x - yp_y) \{J_x J_y\} \\
& + xp_z \{J_y J_z\} - yp_z \{J_x J_z\}] + \frac{1}{m_0} (\kappa J_z + q J_z^3)] + \mu^* \sigma_z H, \\
& \quad (5) \\
\mathcal{H}_q &= \frac{e^2 H^2}{4c^2} \left[\left(\frac{1}{2\mu_0} + \frac{5}{4\mu_1} \right) (x^2 + y^2) - \frac{1}{\mu_1} (y^2 J_x^2 + x^2 J_y^2) \right. \\
& \quad \left. + \frac{1}{\sqrt{3}\mu_2} xy \{J_x J_y\} \right], \quad (6)
\end{aligned}$$

where μ_0 , μ_1 , μ_2 are related to the Luttinger γ_1 , γ_2 , γ_3 parameters by the simple relationships

$$\begin{aligned}
\frac{1}{\mu_0} &= \frac{1}{m_0^*} + \frac{\gamma_1}{m_0}, \quad \frac{1}{\mu_1} = \frac{\gamma_2}{m_0}, \\
\frac{1}{\mu_2} &= 2\sqrt{3} \frac{\gamma_3}{m_0}.
\end{aligned}$$

It was previously shown⁹ that \mathcal{H}_d can always be treated as a small perturbation with respect to \mathcal{H}_s . Therefore, in the region of low magnetic fields, the Hamiltonian (4) can be investigated by considering $\mathcal{H}_d + \mathcal{H}_l + \mathcal{H}_q$ as a perturbation. In the present analysis we will include terms up to second order in the magnetic field and we will con-

sider only the exciton ground state.

In the absence of the magnetic field, the exciton ground state is eightfold degenerate (fourfold degenerate without spin). The magnetic field lifts this degeneracy and the perturbation shift of the i th level is given by

$$\begin{aligned}
\Delta E_i &= \langle i | \mathcal{H}_l | i \rangle + \langle i | \mathcal{H}_q | i \rangle + \sum_n \frac{|\langle i | \mathcal{H}_d | n \rangle|^2}{E_0 - E_n} \\
& + \sum_n \frac{|\langle i | \mathcal{H}_l | n \rangle|^2}{E_0 - E_n} + \sum_n \frac{\langle i | \mathcal{H}_d | n \rangle \langle n | \mathcal{H}_l | i \rangle + \text{c. c.}}{E_0 - E_n} \\
& \quad \pm \frac{1}{2} \mu^* H, \quad (7)
\end{aligned}$$

where the $(-)$ sign is understood for $i=1, \dots, 4$ ($i=5, \dots, 8$). The symbol \mathbf{S} means summation over discrete states and integration over continuum states.

From now on, we will use as units of energy and length, respectively,

$$R_0 = \mu_0 e^4 / 2 \hbar^2 \epsilon^2, \quad a_0 = \epsilon \hbar^2 / \mu_0 e^2.$$

We finally obtain

$$\begin{aligned}
E_1 &= -1 - \frac{4}{5} \phi S_1 + \left[(3\kappa + \frac{27}{4}q + \frac{1}{2}\bar{\mu}^*) \frac{\mu_0}{m_0} + \frac{8}{15} \left(\frac{\mu_0}{\mu_2} \right)^2 M \right] \gamma \\
& \quad + \left(\frac{1}{2} + \frac{1}{2} \frac{\mu_0}{\mu_1} - \frac{2}{5} \phi N \right) \gamma^2, \quad (8a)
\end{aligned}$$

$$\begin{aligned}
E_2 &= -1 - \frac{4}{5} \phi S_1 + \left[(\kappa + \frac{1}{4}q + \frac{1}{2}\bar{\mu}^*) \frac{\mu_0}{m_0} - \frac{8}{15} \left(\frac{\mu_0}{\mu_2} \right)^2 M \right] \gamma \\
& \quad + \left(\frac{1}{2} - \frac{1}{2} \frac{\mu_0}{\mu_1} - \frac{2}{5} \phi N \right) \gamma^2, \quad (8b)
\end{aligned}$$

$$\begin{aligned}
E_3 &= -1 - \frac{4}{5} \phi S_1 + \left[(-\kappa - \frac{1}{4}q + \frac{1}{2}\bar{\mu}^*) \frac{\mu_0}{m_0} + \frac{8}{15} \left(\frac{\mu_0}{\mu_2} \right)^2 M \right] \gamma \\
& \quad + \left(\frac{1}{2} - \frac{1}{2} \frac{\mu_0}{\mu_1} - \frac{2}{5} \phi N \right) \gamma^2, \quad (8c)
\end{aligned}$$

$$\begin{aligned}
E_4 &= -1 - \frac{4}{5} \phi S_1 + \left[(-3\kappa - \frac{27}{4}q + \frac{1}{2}\bar{\mu}^*) \frac{\mu_0}{m_0} \right. \\
& \quad \left. - \frac{8}{15} \left(\frac{\mu_0}{\mu_2} \right)^2 M \right] \gamma + \left(\frac{1}{2} + \frac{1}{2} \frac{\mu_0}{\mu_1} - \frac{2}{5} \phi N \right) \gamma^2, \quad (8d)
\end{aligned}$$

where $\bar{\mu}^*$ is the effective magnetic moment expressed in effective Bohr magnetons,

$$\phi = 8 (\mu_0/\mu_1)^2 + (\mu_0/\mu_2)^2; \quad (9)$$

$$\gamma = eH/2\mu_0 c R_0, \quad (10)$$

and

$$S_1 = 0.2246, \quad (11a)$$

$$M = 0.2812, \quad (11b)$$

$$N = 0.4687 \quad (11c)$$

TABLE I. Band parameters μ_0 , μ_1 , μ_2 from Ref. 12, effective Rydberg R_0 (meV) and magnetic field (kG) corresponding to $\gamma=0.4$ (see text).

	μ_0/m_0	μ_1/m_0	μ_2/m_0	R_0	H_{\max}
AlSb	0.017	0.990	0.165	2.32	2.69
GaP	0.099	1.02	0.174	10.95	75
GaAs	0.044	0.415	0.088	3.86	11.8
GaSb	0.029	0.248	0.055	1.73	3.5
InP	0.053	0.481	0.105	4.95	18.2
InAs	0.016	0.119	0.031	1.55	1.69
InSb	0.009	0.064	0.017	0.45	0.30
Ge	0.025	0.235	0.051	1.45	2.5
ZnS	0.164	1.33	0.265	33.92	384
ZnSe	0.092	0.806	0.173	16.46	104
ZnTe	0.108	0.935	0.176	14.34	107
CdTe	0.064	0.529	0.117	9.20	41

are dimensionless coefficients arising from the summations over intermediate states appearing in Eq. (7). The quantities M and N are defined and computed in the Appendix, in analogy with the calculation of S_1 , described in Ref. 9. The expressions corresponding to the $i=5, \dots, 8$ states are obtained from Eq. (6) by reversing the sign of the $\bar{\mu}^*$ term.

Equations (8) describe the Zeeman splitting and diamagnetic shift of the exciton ground state in the low-magnetic-field region, taking into account the complicated structure of the valence band. In Eq. (8a) and similarly for the other states, the second term represents the effect of the valence-band structure in the absence of a magnetic field. The third term, linear in H , describes the Zeeman splitting of the octuplet, symmetric with respect to the zero-field level. The last term describes the diamagnetic shift and is the sum of two contributions; the term $\frac{1}{2}\gamma^2$ is the familiar result of second-order perturbation theory for the hydrogen atom, and the remainder describes the corrections due to anisotropy. It is important to note that the latter is different for the various states, so that the Zeeman levels are shifted by unequal amounts.

The complete removal of the eightfold degeneracy of the exciton ground state by the magnetic field can be easily predicted by group-theoretical analysis, which, in addition, provides the symmetry of the various levels and the selection rules for optical transitions from the crystal ground state. As expected, the selection rules depend on the experimental configuration and on the polarization of the electromagnetic wave. In particular, in the Voigt configuration (i. e., for propagation perpendicular to \vec{H}) six of the eight transitions are allowed, two for $\vec{E}\parallel\vec{H}$ and four for $\vec{E}\perp\vec{H}$; in the Faraday configuration (i. e., for propagation along \vec{H})

four transitions are allowed, two for σ_+ and two for σ_- polarization.

III. DISCUSSION OF RESULTS AND CONCLUSIONS

Before comparison with experiment is attempted, it is important to investigate the range of validity of the perturbation treatment. In the simplified hydrogenic model of the exciton, where a variational calculation can also be performed, one sees³ that the perturbative treatment for the ground state is valid for values of γ about 0.4. Inspection of Eqs. (8) for all realistic values of the band parameters shows that the same is true in our case. In Table I we list the values H_{\max} of the magnetic field corresponding to this upper limit of $\gamma=0.4$ for various materials. One sees that these values vary from a few to several hundred kilogauss for different crystals. For most materials, however, the Zeeman splittings are very small in this region, and therefore very hard to resolve experimentally. It is to be expected then, that for a given experimental configuration and light polarization, instead of a well-resolved multiplet, a single absorption peak will be detected, centered roughly at an energy corresponding to the weighted average of the single components. As previously pointed out, the diamagnetic shifts are different for the various levels and, therefore, average energies for different polarizations can also differ from one another. In fact, relative transition probabilities to the Zeeman levels can be evaluated from the symmetry properties of the s - and p -like functions of the band extrema. A detailed analysis shows that the diamagnetic shifts Δ of the observable peaks for the various experimental configurations are given by

Voigt Configuration:

$$\vec{E}\parallel\vec{H}: \Delta = \left[\frac{1}{2} - \frac{2}{5}\phi N - \frac{1}{2}(\mu_0/\mu_1)\right]\gamma^2, \quad (12a)$$

$$\vec{E}\perp\vec{H}: \Delta = \left[\frac{1}{2} - \frac{2}{5}\phi N + \frac{1}{4}(\mu_0/\mu_1)\right]\gamma^2, \quad (12b)$$

Faraday Configuration:

$$\sigma_+, \sigma_-: \Delta = \left[\frac{1}{2} - \frac{2}{5}\phi N + \frac{1}{4}(\mu_0/\mu_1)\right]\gamma^2. \quad (12c)$$

In Table II the quantities Δ/γ^2 are listed for several semiconductors. The variation of these quantities from the hydrogenic value $\frac{1}{2}$, and their dependence on polarization, reflects the influence of the complexity of the band structure.

The detailed behavior of the lowest exciton absorption in a magnetic field has been observed in a few materials.⁴⁻⁷ In GaSb^{4,5} high-resolution measurements in low fields, within the range of validity of the present investigation, show the predicted polarization dependence of the diamagnetic shifts, and the observed splitting between the $\vec{E}\parallel\vec{H}$ and $\vec{E}\perp\vec{H}$ peaks is in semiquantitative agreement with Eq. (7). A more quantitative comparison would

TABLE II. Values of the dimensionless quantity Δ/γ^2 , defined in the text, for different configurations and polarizations. Column 1, Voigt configuration with $\vec{E} \parallel \vec{H}$; column 2, Voigt configuration with $\vec{E} \perp \vec{H}$ and Faraday configuration.

	$\vec{E} \parallel \vec{H}$	$\vec{E} \perp \vec{H}$
AlSb	0.489	0.502
GaP	0.376	0.449
GaAs	0.382	0.462
GaSb	0.366	0.455
InP	0.378	0.461
InSb	0.338	0.448
Ge	0.383	0.463
ZnS	0.344	0.437
ZnSe	0.371	0.456
ZnTe	0.353	0.439
CdTe	0.363	0.453

require experimental determination of the orientation of \vec{H} with respect to the crystal axes. For GaAs^{6,7} even though the experiments were performed for values H outside the range of the perturbation region, the results are in qualitative agreement with the present theory, in that the observed diamagnetic shift is smaller than predicted by the simple hydrogenic model, consistent with the results of our investigation.

It is important to point out that, to date, the band parameters for most semiconductors are not known with satisfactory accuracy. In fact, determinations by different investigators¹²⁻¹⁵ are at variance with one another and the numerical results obtained, although in over-all agreement, depend on the particular choice of the parameter values.

Finally, on the basis of the present knowledge, it would be highly desirable to provide a more accurate theoretical study for the intermediate- and high-field regions and, on the other hand, to perform detailed experiments in those materials where the perturbative analysis holds also for reasonably high fields.

Note added in proof. After submission of the manuscript, our attention was called upon a recent work by Rees,¹⁶ who considers the high-field region. This region will be the subject of a forthcoming publication. We are grateful to Professor F. Bassani for pointing out to us the results of Ref. 16.

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APPENDIX

In this appendix, we derive the expressions for the quantities M and N used in the text. In Ref. 9, it was shown that

$$\sum_n \frac{|\langle \hat{q} | \mathcal{H}_d | n \rangle|^2}{E_0 - E_n} = -\frac{4}{5} \phi(\mu_0, \mu_1, \mu_2) S_1, \quad (\text{A1})$$

where

$$S_1 = \sum_{n=3}^{\infty} \frac{|I_n|^2}{1 - 1/n^2} + \int_0^{\infty} dk \frac{|I_k|^2}{1 + k^2}, \quad (\text{A2})$$

with

$$I_n = \int_0^{\infty} R_{n2}(r) (r + r^2) e^{-r} dr. \quad (\text{A3})$$

Here $R_{nl}(r)$ are the normalized-hydrogenic-radial wave functions. I_k is defined by Eq. (A3) after replacing the lower index n by k .

Using a similar procedure, it is easy to show that

$$\sum_n \frac{|\langle \hat{q} | \mathcal{H}_t | n \rangle|^2}{E_0 - E_n} = -\frac{2}{5} \phi \gamma^2 N, \quad (\text{A4})$$

where

$$N = \sum_{n=3}^{\infty} \frac{|L_n|^2}{1 - 1/n^2} + \int_0^{\infty} dk \frac{|L_k|^2}{1 + k^2} \quad (\text{A5})$$

and

$$L_n = \int_0^{\infty} R_{n2}(r) r^3 e^{-r} dr. \quad (\text{A6})$$

L_k is defined by Eq. (A6) after replacing n with k ; γ and ϕ are defined in the text.

Similarly for the fifth term of the right-hand side of Eq. (7) we get

$$\sum_n \frac{(\langle 1 | \mathcal{H}_d | n \rangle \langle n | \mathcal{H}_t | 1 \rangle + \text{c. c.})}{E_0 - E_n} = \frac{8}{15} \left(\frac{\mu_1}{\mu_2} \right)^2 \gamma M, \quad (\text{A7})$$

where

$$M = \sum_{n=3}^{\infty} \frac{L_n I_n}{1 - 1/n^2} + \int_0^{\infty} dk \frac{L_k I_k}{1 + k^2}. \quad (\text{A8})$$

In analogy with the calculation for I_n and I_k in Ref. 9, we can write Eq. (A6) in a compact way suitable for computation. After straightforward calculations, one gets

$$L_n = \frac{8n^2}{n^2 - 1} [n(n^2 - 1)(n^2 - 4)]^{1/2} \left(\frac{n-1}{n+1} \right)^n, \quad (\text{A9})$$

$$L_k = \frac{1}{(1 - e^{-2\pi/k})^{1/2}} \frac{8}{(1 + k^2)^3} \times [k(1 + k^2)(1 + 4k^2)]^{1/2} e^{-(2/k) \arctan k}. \quad (\text{A10})$$

Using the above expressions, the quantities M and N can be computed to any degree of accuracy.

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Auger Theory at Defects—Application to States with Two Bound Particles in GaP

G. F. Neumark

Philips Laboratories, Briarcliff Manor, New York 10510

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Auger transitions at defects in semiconductors are investigated with the objectives of determining the wave-function influence, carry out interimpurity comparisons, and apply the results to defects in GaP. As an aid to this, it is shown that in indirect-gap semiconductors the Auger transition matrix can be factored, approximately, into a product of overlap integrals over the periodic parts of the wave functions and an interaction integral with the nonperiodic parts. This result simplifies calculations and moreover shows that interimpurity comparisons should be quite reliable. Specific calculations are carried out for systems with two bound particles. A He-type defect is used to examine the role of the bound-state wave function by use of several He Hylleraas-type functions; it is concluded that the effect of wave-function variation is minor. The He system is then compared with an excitonlike defect for interdefect comparison. The results are applied to defects in GaP, with halide impurities as prototypes for He-like defects, and the Zn-O complex for exciton defects. It is shown that the theoretical Auger probability of the complex agrees with experimental values. It is also shown that Cl is an appreciably stronger Auger center than Zn-O.

I. INTRODUCTION

Auger recombination at defect centers is an important and probably dominant nonradiative process¹ in semiconductor phosphors such as GaP. Various recent theoretical analyses of the problem have considered recombination at singly charged impurities,²⁻⁴ "exciton" centers⁴ (i. e., isoelectronic impurities and donor-acceptor nearest-neighbor pairs), some multiple-impurity complexes,⁵ and through impurity bands.⁶ However, there appears little in the way of reliability estimates in these treatments, nor comparisons between different defects. In fact, such comparisons are hindered by use of different types of wave functions in the various treatments: partly effective-mass-type envelope functions alone,³⁻⁵ partly effective-mass-type envelope functions plus the periodic parts,⁶ and partly a noneffective-mass approach with a localized p state for the hole of the exciton state.⁴ The objectives of the present paper are to (i) emphasize a systematic investigation of the role of the wave

functions, (ii) carry out this investigation mainly for defects with two bound particles, and thus simultaneously obtain results for this interesting case, and (iii) evaluate the theory for GaP, a material presently of high interest for luminescence applications.

For systematizing the wave-function role, we extend an analysis used by Landsberg and co-workers^{7,8} for band-to-band (nondefect) Auger processes. This approach splits the transition integral over the periodic and nonperiodic parts of the wave functions into a product of overlap integrals over the periodic parts of the wave function and an "interaction" integral over the nonperiodic parts. With use of effective-mass functions for impurities, an analogous result is obtained for defects in indirect-gap semiconductors. We shall refer to this treatment as the overlap integral approximation.

The use of systems with two bound particles (particle = electron or hole) has been chosen for several reasons. Partly, this case is of relatively high