Gauge-invariant energy variational principle applied to excitons in anisotropic semiconductors in high magnetic fields

Paul K. Kennedy* and Donald H. Kobe
Department of Physics, North Texas State University, Denton, Texas 76203
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A method for improving the trial wave function for a system in a magnetic field using the Rayleigh-Ritz energy variational principle is applied to anisotropic excitons. When the trial wave function is adapted to the gauge of the vector potential using a phase factor, a gauge-invariant variational energy is obtained, and the charge conservation equation is satisfied. The gauge-invariant variational method is used to obtain an upper bound to the ground-state energy of an exciton in the axially anisotropic semiconductors CdS and GaSe when magnetic fields in the megagauss range are applied. The variational calculations predict a measurable dependence of ground-state energy on field orientation.

I. INTRODUCTION

The Rayleigh-Ritz energy variational principle provides one of the best approximation methods for the solution of the Schrödinger equation for atoms and molecules in magnetic fields.[1–7] The energy operator involves the vector potential, the curl of which gives the magnetic field. Two significant difficulties arise, however, in applying the variational principle to such systems. First, the energy expectation value for an arbitrary trial wave function depends on the choice of the gauge of the vector potential. Second, charge conservation is found to be violated for an arbitrary choice of gauge when the current density is calculated from the trial wave function. These problems are serious and should be remedied.

In previous work[8] we have given a method for removing these difficulties by adapting the chosen trial wave function to the gauge of the vector potential using a phase factor. Use of a phase factor containing an arbitrary variational function to remove the gauge dependence was first suggested by Epstein,[9] but he gave no method for obtaining the phase factor in a general case. Epstein[9,10] also pointed out that the charge-conservation condition should be satisfied, but did not show how to obtain this condition in variational calculations. In our method[8] the trial wave function is multiplied by a phase factor and the energy is varied with respect to the variational phase function. The variation yields the condition for charge conservation. This condition provides a differential equation which can be solved to obtain the phase function that minimizes the energy.

The improved trial wave function obtained by using this phase function has a number of desirable properties. Because it is obtained using the charge-conservation condition, it satisfies this condition identically. The charge-conservation condition contains the vector potential, so the minimizing phase function depends on the gauge of the potential. The phase factor thus adapts the trial wave function to the gauge of the vector potential and removes the gauge dependence of the energy expectation value. The energy expectation value is also lower than the original energy expectation value, since the energy has been minimized with respect to an additional variational function.

The method has been applied previously to an anisotropic harmonic oscillator in a constant magnetic field.[8] In this paper it is applied to excitons (bound electron-hole pairs) in the axially anisotropic semiconductors CdS and GaSe in strong uniform magnetic fields. The variational upper bound to the ground-state energy in high magnetic fields is calculated as a function of field strength and orientation for GaSe excitons and excitons formed from the A-valence band of CdS.

The results of the gauge-invariant variational calculation give good agreement with the experimental data of Aldrich *et al.*[11] for GaSe excitons in high fields parallel to the crystal axis. The theory predicts a decrease in the ground-state energy of GaSe excitons and CdS A excitons as the field is shifted from parallel to perpendicular orientations with respect to the crystal axis. The superiority of the gauge-invariant method is demonstrated by comparison with energies obtained by a gauge-dependent approach. The effect of spin splitting on the exciton ground-state spectrum is also considered.

Numerous theoretical studies of the energy states of excitons in magnetic fields have been made both for isotropic[12–15] and anisotropic[11,16–18] semiconductors. Fritsche and Heidt[16] were the first to develop a formalism for computing the exciton spectrum of axially anisotropic semiconductors in high magnetic fields. They used the adiabatic approximation of Elliot and Loudon,[15] where the Coulomb attraction is neglected in the plane perpendicular to the field. Axially anisotropic excitons in high magnetic fields have also been treated in the adiabatic approximation by others.[11,17,18] No formalism has previously been developed, however, for treating excitons in totally anisotropic semiconductors in high magnetic fields. The formalism developed here may be applied to totally anisotropic semiconductors, does not neglect the Coulomb attraction in the plane perpendicular to the field, and gives ground-state energies for arbitrary field orientations. No previous calculation has been made of the variation of

ground-state energy with field angle for excitons in axially anisotropic semiconductors. Monozon and co-workers[17,18] have stated that the ground-state energy of excitons in uniaxial crystals varies with field angle; however, they do not state precisely how it varies or make computations. Most other studies have assumed that the field is aligned with the crystal axis.

In Sec. II the quasiparticle Hamiltonian for an exciton in a totally anisotropic semiconductor in a static magnetic field is derived. The gauge-invariant variational method is applied to this system in Sec. III and the quasiparticle current-conservation equation for the exciton is obtained. In Sec. IV a Gaussian trial wave function valid at high magnetic fields is shown to give a gauge-dependent energy expectation value. When the current-conservation condition is solved with this Gaussian trial wave function, the resulting improved trial wave function yields a gauge-invariant energy expectation value. The results of Sec. IV are specialized to the axially anisotropic case in Sec. V and applied to the axially anisotropic semiconductors GaSe and CdS. The conclusion is given in Sec. VI.

II. HAMILTONIAN FOR ANISOTROPIC EXCITONS

In this section the Hamiltonian is obtained for anisotropic excitons in nondegenerate semiconductors in a uniform strong magnetic field. After a brief description of the system, the single-particle effective Hamiltonian in relative coordinates is derived for the vector potential in an arbitrary gauge and then expressed in dimensionless units.

A. Exciton in a uniform magnetic field

The system consists of a single electron-hole pair created by a direct transition (direct exciton) in a semiconductor with anisotropic conduction and valence bands. The energy is calculated using the effective mass approximation for the exciton problem first given by Wannier.[19] The Wannier exciton may be pictured as an electron in a conduction band bound to a hole in a valence band.[20] The valence bands of the semiconductor are assumed to be nondegenerate in the magnetic field, when spin effects are neglected.[13] For nondegenerate valence bands a simple two-band model may be used.[21] The formalism is developed for a completely anisotropic semiconductor where the dielectric anisotropy is given by a diagonal dielectric tensor and the effective electron and hole masses are also diagonal tensors.[22]

A Cartesian coordinate system (x_1,x_2,x_3) which diagonalizes the dielectric and effective mass tensors is chosen.[23] A uniform magnetic field $\vec{B}$ is applied with a polar angle θ and an azimuthal angle ϕ. The field components may be written $\vec{B}=B\vec{C}$, where

$$\vec{C}=(C_1,\ C_2,\ C_3)$$
$$=(\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)\ . \tag{2.1}$$

The vector potential $\vec{A}$, the curl of which gives the magnetic induction field $\vec{B}$, is chosen to be in the mixed gauge[3] with components

$$A_i=(1-\xi_j)B_jx_k-x_j\xi_kB_k\ , \tag{2.2}$$

where (i,j,k) are cyclic permutations of (1,2,3) and the gauge parameters (ξ_1,ξ_2,ξ_3) are arbitrary real numbers. If $\xi_1=\xi_2=\xi_3=\frac{1}{2}$, the symmetric gauge is obtained, while if $\xi_1=\xi_2=\xi_3=0$ or 1, the two Landau gauges are obtained. The mixed gauge is chosen for generality and to demonstrate the gauge invariance of the method, since the gauge parameters act as indicators of gauge dependence in later results.

B. Hamiltonian

For a Wannier exciton in an anisotropic semiconductor in the presence of an external magnetic field, the minimally coupled Hamiltonian in Gaussian units is given by[16]

$$H(\vec{r}_e,\vec{r}_h)=\sum_{i=1}^{3}\left[\frac{1}{2m_{ei}}\left[-i\hbar\frac{\partial}{\partial x_{ei}}+\frac{e}{c}A_i(\vec{r}_e)\right]^2+\frac{1}{2m_{hi}}\left[-i\hbar\frac{\partial}{\partial x_{hi}}-\frac{e}{c}A_i(\vec{r}_h)\right]^2\right]$$
$$-e^2(K_1K_2K_3)^{-1/2}[K_1^{-1}(x_{e1}-x_{h1})^2+K_2^{-1}(x_{e2}-x_{h2})^2+K_3^{-1}(x_{e3}-x_{h3})^2]^{-1/2}\ , \tag{2.3}$$

where $\vec{r}_e=(x_{e1},x_{e2},x_{e3})$ and $\vec{r}_h=(x_{h1},x_{h2},x_{h3})$ are the displacement vectors of the electron and hole, respectively, A_i $(i=1,2,3)$ are the components of the vector potential, and $-e$ is the electronic charge. The elements of the diagonal electron and hole effective mass tensors are m_{ei} and m_{hi}, respectively, and K_i are the elements of the diagonal dielectric tensor. The Coulomb potential energy term in Eq. (2.3) is derived using Poisson's equation.[24] Exciton spin terms have been omitted in the Hamiltonian since they simply add a constant to the total energy and do not affect the variational calculations.[11] Spin effects are considered later. In the effective mass approximation, where the exciton dimension is large compared to the lattice constant, the effective Schrödinger equation is[16]

$$H(\vec{r}_e,\vec{r}_h)\Phi(\vec{r}_e,\vec{r}_h)=\epsilon\Phi(\vec{r}_e,\vec{r}_h)\ . \tag{2.4}$$

The envelope function $\Phi(\vec{r}_e,\vec{r}_h)$ describes the electron and hole motion on a scale large compared to atomic dimensions.[25]

The motion of the exciton can be expressed in relative

coordinates $\vec{r}=\vec{r}_e-\vec{r}_h=(x_1,x_2,x_3)$, and in center-of-mass coordinates $\vec{R}=(X_1,X_2,X_3)$, where

$$X_i=(m_{ei}x_{ei}+m_{hi}x_{hi})/(m_{ei}+m_{hi}) \quad (i=1,2,3) . \tag{2.5}$$

When Eq. (2.3) is written in terms of relative and center-of-mass coordinates, then because of the magnetic field the two motions of the exciton are coupled in the Hamiltonian in a complicated manner. In a magnetic field there is no way to separate them exactly.[26] An approximate separation may be achieved, however, if the center-of-mass motion is negligible in comparison to the relative motion. In this case Eq. (2.4) can be transformed into a one-particle (quasiparticle) Schrödinger equation for the relative motion in terms of reduced effective masses.

A partial decoupling of the center-of-mass and relative motions may be achieved using an envelope function of the form[16,26–28]

$$\Phi(\vec{r}_e,\vec{r}_h)=\exp[-ie\vec{A}(\vec{R})\cdot\vec{r}/\hbar c]\exp(i\vec{k}\cdot\vec{R})\psi(\vec{r}) , \tag{2.6}$$

where $\vec{A}(\vec{R})$ is the vector potential at the center of mass, $\vec{k}$ is the exciton wave vector, and $\psi(\vec{r})$ is the envelope function for the relative motion.[11,21] If Eq. (2.6) is used in Eq. (2.4), terms containing $\vec{A}(\vec{R})$ are removed.[26,27] There are still terms containing components of the exciton wave vector $\vec{k}$, however, which are the kinetic energy of the center of mass and coupling between the center of mass and relative motions in the field.[28] It is commonly assumed that the center of mass of the exciton is at rest ($\vec{k}=0$) (Refs. 11, 16, and 21) and calculations made in this approximation give satisfactory results when compared to experimental data.

When the center-of-mass terms are neglected, the single-particle effective Schrödinger equation for the relative motion can be written as

$$H(\vec{r})=\sum_{i=1}^{3}\left[\frac{1}{2\mu_i}\left[-i\hbar\frac{\partial}{\partial x_i}+\frac{e}{c}A_i(\overleftrightarrow{b}_i\cdot\vec{r})\right]^2+\frac{e^2}{2c^2M_i}[(\vec{B}\times\vec{r})_i^2-A_i^2(\vec{r})+A_i^2(\overleftrightarrow{a}_h\cdot\vec{r})+2A_i(\overleftrightarrow{a}_h\cdot\vec{r})A_i(\overleftrightarrow{a}_e\cdot\vec{r})+2A_i(\overleftrightarrow{a}_e\cdot\vec{r})]\right]+V(\vec{r}) . \tag{2.7}$$

The diagonal dyads

$$\overleftrightarrow{a}_h=\sum_{i=1}^{3}m'_{hi}\hat{x}_i\hat{x}_i , \tag{2.8}$$

$$\overleftrightarrow{a}_e=\sum_{i=1}^{3}-m'_{ei}\hat{x}_i\hat{x}_i , \tag{2.9}$$

and

$$\overleftrightarrow{b}_i=(\mu_i/m_{ei})\overleftrightarrow{a}_h+(\mu_i/m_{hi})\overleftrightarrow{a}_e \quad (i=1,2,3) , \tag{2.10}$$

are used to express some of the vector potential terms in weighted relative coordinates. The potential energy is

$$V(\vec{r})=-e^2(K_1K_2K_3)^{-1/2}\times[(x_1^2/K_1)+(x_2^2/K_2)+(x_3^2/K_3)]^{-1/2} . \tag{2.11}$$

The reduced effective masses ($i=1,2,3$) are

$$\mu_i^{-1}=m_{ei}^{-1}+m_{hi}^{-1} , \tag{2.12}$$

the total effective masses are

$$M_i=m_{ei}+m_{hi} , \tag{2.13}$$

and the dimensionless relative masses are

$$m'_{\alpha i}=m_{\alpha i}/M_i, \quad \alpha=e,h . \tag{2.14}$$

Equation (2.7) is the sum of the effective kinetic energy of the quasiparticle in the field in terms of the reduced effective masses μ_i which characterize the quasiparticle, a diamagnetic term which is proportional to the square of the field strength, and a Coulomb potential energy.

C. Dimensionless units

In order to find an upper bound to the exciton ground-state energy, the expectation value of Eq. (2.7) with respect to the trial wave function must be minimized with respect to the variational parameters. The energy expectation value of this system is too complicated to minimize analytically, so numerical methods are required. For convenience in numerical computation, dimensionless units of length and energy are used. First, however, it is necessary to define some constants of the system.

For the anisotropic exciton the effective Larmor frequency in Gaussian units is defined as[11,12]

$$\omega_L=eB/2\mu c , \tag{2.15}$$

the effective Bohr radius a_0 is

$$a_0=K\hbar^2/\mu e^2 , \tag{2.16}$$

and the effective rydberg $\mathscr{R}$ is

$$\mathscr{R}=\hbar^2/2\mu a_0^2=\mu e^4/2\hbar^2K^2 . \tag{2.17}$$

The geometrical mean of the anisotropic reduced effective mass is

$$\mu=(\mu_1\mu_2\mu_3)^{1/3} , \tag{2.18}$$

and the geometrical mean of the anisotropic dielectric constant is

$$K=(K_1K_2K_3)^{1/3} . \tag{2.19}$$

The relative reduced effective mass parameters ζ_i are defined as

$$\zeta_i=\mu/\mu_i \quad (i=1,2,3) . \tag{2.20}$$

A dimensionless magnetic field parameter is

$$\gamma=\hbar\omega_L/\mathscr{R}=(\hbar^3K^2/\mu^2e^3c)B , \tag{2.21}$$

where γ is proportional to the field magnitude B and thus gives a measure of the field strength.[3] The field components are given by $\vec{B}=B\vec{C}$ and Eq. (2.1).

When the constants defined above, the mixed gauge of Eq. (2.2), and Eqs. (2.8) and (2.1) are used in Eq. (2.7), the dimensionless Hamiltonian is

$$H(\vec{r})=\left[-\zeta_1\frac{\partial^2}{\partial x_1^2}+2i\gamma(T_1x_2+T_1'x_3)\frac{\partial}{\partial x_1}+\gamma^2(T_{12}x_3^2+T_{12}'x_1x_2)+(1\to2,2\to3,3\to1)+(1\to3,2\to1,3\to2)\right]$$
$$-2K^{-1/2}[(x_1^2/K_1)+(x_2^2/K_2)+(x_3^2/K_3)]^{-1/2} , \tag{2.22}$$

where energy is in units of the effective rydberg $\mathscr{R}$ and length is in units of the effective Bohr radius a_0. The dimensionless functions T_1, T_1', T_{12}, and T_{12}' are defined as

$$T_1=\mu C_3[(\beta_{123}/m_{e1})-(\eta_{213}/m_{h1})] , \tag{2.23}$$

$$T_1'=-\mu C_2[(\eta_{132}/m_{e1})-(\beta_{312}/m_{h1})] , \tag{2.24}$$

$$T_{12}'=-2\mu C_1C_2(\eta_{321}\beta_{312}m_{e3}^{-1}+\beta_{231}\eta_{132}m_{h3}^{-1}) , \tag{2.25}$$

and

$$T_{12}=\mu[C_2^2(\eta_{132}^2m_{e1}^{-1}+\beta_{312}^2m_{h1}^{-1})+C_1^2(\beta_{231}^2m_{e2}^{-1}+\eta_{321}^2m_{h2}^{-1})] , \tag{2.26}$$

where each of these equations gives two others through cyclic permutation of (1,2,3). Equations (2.23)–(2.26) are written in terms of the gauge-dependent dimensionless functions

$$\eta_{lmn}=(1-\xi_n)m_{hm}'+\xi_nm_{el}' \tag{2.27}$$

and

$$\beta_{lmn}=(1-\xi_n)m_{el}'+\xi_nm_{hm}' , \tag{2.28}$$

where (l,m,n) are cyclic permutations of (1,2,3).

The gauge-dependent Hamiltonian of Eq. (2.22) gives a gauge-dependent energy expectation value unless the trial wave function is adapted to the gauge of the vector potential. In the next section the gauge-invariant variational method is applied to the anisotropic exciton.

III. GAUGE-INVARIANT VARIATIONAL METHOD APPLIED TO ANISOTROPIC EXCITONS

When the Rayleigh-Ritz variational method is applied to a system in a static magnetic field, the energy obtained is an upper bound to the ground-state energy and depends on the gauge chosen for the vector potential in the energy operator. For an arbitrary choice of the trial wave function Ψ and an arbitrary gauge of vector potential $\vec{A}$, the divergence of the charge current density $\vec{J}$ does not in general vanish,

$$\vec{\nabla}\cdot\vec{J}\neq0 . \tag{3.1}$$

The charge-conservation condition for stationary states is therefore violated because the charge density $q|\Psi|^2$ is time independent. The gauge-invariant variational method[8] resolves these problems by multiplying the trial wave function by a phase factor. When the energy is minimized with respect to the variational function in the phase factor, the minimization condition yields the condition for charge conservation. The charge-conservation condition provides a differential equation which can be solved to obtain the phase function that minimizes the energy and adapts the trial wave function to the gauge of the vector potential. In this section the gauge-invariant variational method is applied to the anisotropic exciton system described in Sec. II which gives the charge-conservation equation for the quasiparticle.

An improved trial wave function Ψ' for the quasiparticle is obtained from the initial choice of trial wave function by multiplication by a phase factor

$$\Psi'=\exp(iq'\Lambda/\hbar c)\Psi , \tag{3.2}$$

where $\Lambda=\Lambda(\vec{r})$ is an arbitrary real variational function and q' is the effective quasiparticle charge ($q'=-e$). The expectation value of the quasiparticle Hamiltonian $H(\vec{r})$ calculated with respect to Ψ' is a functional of Λ:

$$E'=E[\Lambda]=\langle\exp(iq'\Lambda/\hbar c)\Psi|H\exp(iq'\Lambda/\hbar c)\Psi\rangle . \tag{3.3}$$

The variation of Eq. (3.3) with respect to Λ is

$$E[\Lambda+\delta\Lambda]-E[\Lambda]=\delta E[\Lambda]+\delta^2E[\Lambda]+\cdots , \tag{3.4}$$

where $\delta\Lambda(\vec{r})$ is an arbitrary real variation of $\Lambda(\vec{r})$. For an extremum in the energy it is necessary that the first variation vanish, $\delta E[\Lambda]=0$. For a minimum in the energy the second variation must be positive, $\delta^2E[\Lambda]>0$. The condition for an extremum is obtained in this section, while it has been shown elsewhere[8] that the extremum is indeed a minimum.

When the first variation of Eq. (3.3) is set equal to zero, the minimization condition is

$$\delta E[\Lambda]=-2q'(\hbar c)^{-1}\int d^3r\,\delta\Lambda(\vec{r})\mathrm{Im}\{\Psi'^*(\vec{r})H(\vec{r})\Psi'(\vec{r})\}=0 , \tag{3.5}$$

where Im denotes the imaginary part. To obtain Eq. (3.5) from Eq. (3.4) the exponential $\exp(iq\,\delta\Lambda/\hbar c)$ is expanded and only terms linear in $\delta\Lambda$ are retained. The Hermiticity of the energy operator is also used. Since $\delta\Lambda(\vec{r})$ is arbitrary, the only way for Eq. (3.5) to be satisfied is for the integrand to vanish,

$$\mathrm{Im}\{\Psi'^{*}H(\vec{r})\Psi'\}=0\ . \tag{3.6}$$

If the quasiparticle Hamiltonian $H(\vec{r})$ defined in Eq. (2.7) is used, then Eq. (3.6) becomes

$$\mathrm{Im}\{\Psi'^{*}[\vec{\Pi}\cdot\overleftrightarrow{\mu}^{-1}\cdot\vec{\Pi}]\Psi'\}=0\ . \tag{3.7}$$

The effective kinetic momentum $\vec{\Pi}$ of the quasiparticle in the magnetic field is

$$\vec{\Pi}=\sum_{i=1}^{3}\left[-i\hbar\frac{\partial}{\partial x_i}+\frac{e}{c}A_i(\overleftrightarrow{b}_i\cdot\vec{r})\right]\hat{x}_i\ . \tag{3.8}$$

From Eq. (3.8) it is clear that the quasiparticle effective charge $q'=-e$. The reciprocal of the reduced effective mass tensor is

$$\overleftrightarrow{\mu}^{-1}=\sum_{i=1}^{3}\mu_i^{-1}\hat{x}_i\hat{x}_i\ . \tag{3.9}$$

Equation (3.7) can be rewritten as

$$\mathrm{Im}\{-i\hbar\nabla\cdot[\Psi'^{*}\overleftrightarrow{\mu}^{-1}\cdot\vec{\Pi}\Psi']+(\vec{\Pi}\Psi')^{*}\cdot\overleftrightarrow{\mu}^{-1}\cdot(\vec{\Pi}\Psi')\}=0\ . \tag{3.10}$$

The last term in the curly brackets in Eq. (3.10) is real, so that Eq. (3.10) gives

$$\vec{\nabla}\cdot\vec{J}\,'=0\ . \tag{3.11}$$

The current density $\vec{J}\,'$ for the anisotropic exciton is

$$\vec{J}\,'=\mathrm{Re}\{\Psi'^{*}q'\overleftrightarrow{\mu}^{-1}\cdot\vec{\Pi}\Psi'\}\ , \tag{3.12}$$

where Re denotes the real part.

When Eq. (3.2) is inserted into Eq. (3.12), the result is

$$\vec{J}\,'=\vec{J}+\frac{q'^{2}}{\mu c}|\Psi|^{2}\sum_{i=1}^{3}\zeta_i\left[\frac{\partial\Lambda}{\partial x_i}\right]\hat{x}_i\ , \tag{3.13}$$

where μ is given by Eq. (2.18) and ζ_i $(i=1,2,3)$ are given by Eq. (2.20). The original current density $\vec{J}$ is given by

$$\vec{J}=\mathrm{Re}\{\Psi^{*}q'\overleftrightarrow{\mu}^{-1}\cdot\vec{\Pi}\Psi\}\ . \tag{3.14}$$

Equations (3.11) and (3.13) give the differential equation for the Λ which minimizes the energy,

$$\sum_{i=1}^{3}\zeta_i[\partial_i^{2}\Lambda+\rho^{-1}(\partial_i\rho)\partial_i\Lambda]=-\mu c(\vec{\nabla}\cdot\vec{J}\,)/q'\rho\ , \tag{3.15}$$

where $\partial_i=\partial/\partial x_i$ and the charge density is $\rho(\vec{r})=q'|\Psi(\vec{r})|^{2}$.

In the next section Eq. (3.15) is solved for a Gaussian wave function Ψ which is valid at high magnetic fields. The resulting improved trial wave function is shown to give a gauge-invariant energy expectation value.

IV. ENERGY EXPECTATION VALUE

In this section a Gaussian trial wave function is chosen which should describe the exciton ground state in high magnetic fields. When this trial wave function is used to calculate the expectation value of the energy operator, a gauge-dependent energy is obtained. The method of Sec. III is used to improve the trial wave function. When the energy is minimized with respect to the phase factor, the charge-conservation condition is obtained. When the equation of continuity is solved for the phase factor, which adapts this trial wave function to the gauge of the vector potential, the resulting improved trial wave function is shown to give a gauge-invariant energy expectation value.

A. Trial wave function for high magnetic field

The exciton is considered in the high-field limit where the magnetic field is sufficiently strong to make the field parameter $\gamma\geq 1$. Since an exciton is hydrogenic, a choice of trial wave function can be motivated by examining the case of the hydrogen atom in a high magnetic field.[1,2,13] The magnetic forces on the electron compress the orbitals in the direction perpendicular to the field and cause oscillations at a frequency comparable to the cyclotron frequency. Oscillations in the field direction are much slower. The ground-state wave function for a harmonic oscillator is a Gaussian function. Gaussian wave functions have been used as trial wave functions for the ground state of hydrogen atoms[1,2,29] and hydrogenic systems such as excitons[11] in high magnetic fields. A three-dimensional normalized Gaussian wave function

$$\Psi(\vec{r})=(8\alpha_1\alpha_2\alpha_3\pi^{-3})^{1/4}\exp(-\alpha_1x_1^{2}-\alpha_2x_2^{2}-\alpha_3x_3^{2}) \tag{4.1}$$

is therefore taken as the initial trial wave function, where $(\alpha_1,\alpha_2,\alpha_3)$ are real positive variational parameters.

B. Gauge-dependent energy expectation value

When the Gaussian wave function in Eq. (4.1) is used to calculate the expectation value of the dimensionless exciton Hamiltonian of Eq. (2.22) the result is

$$\begin{aligned}E&=\langle\Psi|H(\vec{r})\Psi\rangle\\&=\{\xi_1\alpha_1+\tfrac{1}{4}\gamma^{2}C_1^{2}[\chi_2\alpha_3^{-1}+\xi_1^{2}\chi_{32}\alpha_3^{-1}+\chi_3\alpha_2^{-1}+(1-\xi_1)^{2}\chi_{23}\alpha_2^{-1}]\\&\quad+(1\to2,\ 2\to3,\ 3\to1)+(1\to3,\ 2\to1,\ 3\to2)\}-(32\alpha_3/\pi\beta_3)^{1/2}\int_0^{1}du(au^{4}+bu^{2}+1)^{-1/2}\ ,\end{aligned} \tag{4.2}$$

in units of the rydberg in Eq. (2.17). This energy is gauge dependent since it contains the gauge parameters (ξ_1,ξ_2,ξ_3). The potential energy integral in Eq. (4.2) involves the parameters

$$a=-(\alpha_3/\beta_3)[(\alpha_1/\beta_1)^{-1}+(\alpha_2/\beta_2)^{-1}] +(\alpha_3/\beta_3)^2(\alpha_1/\beta_1)^{-1}(\alpha_2/\beta_2)^{-1}+1 \quad (4.3)$$

and

$$b=(\alpha_3/\beta_3)[(\alpha_1/\beta_1)^{-1}+(\alpha_2/\beta_2)^{-1}]-2\ , \quad (4.4)$$

where

$$\beta_i=K/K_i \quad (i=1,2,3)\ . \quad (4.5)$$

The parameters χ_i in Eq. (4.2) are

$$\chi_i=\mu/M_i \quad (i=1,2,3)\ , \quad (4.6)$$

where μ is defined in Eq. (2.18) and M_i is defined in Eq. (2.13). The parameter χ_{32} in Eq. (4.2) is

$$\chi_{32}=\mu(m_{h3}'^2 m_{e2}^{-1}+m_{e3}'^2 m_{h2}^{-1}-M_2^{-1})\ , \quad (4.7)$$

where $m_{\alpha i}'$ $(\alpha=e,h)$ $(i=1,2,3)$ is defined in Eq. (2.14), and χ_{23} is obtained by interchange of the indices 2 and 3. The constants χ_{13} and χ_{21} are obtained from Eq. (4.7) by cyclic permutation of (1,2,3). The energy expectation value E in Eq. (4.2) is the sum of a positive kinetic energy, a positive diamagnetic energy shift, and an attractive Coulomb potential energy. The diamagnetic term is proportional to γ^2 and thus is quadratic in the field magnitude B.[28]

C. Improved trial wave function

The energy expectation value of Eq. (4.2) is gauge dependent because the phase of the trial wave function $\Psi(\vec{r})$ in Eq. (4.1) is not adapted to the gauge of the vector potential in the energy operator. The adapting phase function can be obtained by inserting Eq. (4.1) into the quasiparticle charge-conservation condition in Eq. (3.14) and solving for the minimizing Λ. The solution is

$$\Lambda=-Bx_1x_2[(\alpha_1T_1+\alpha_2T_2')]/(\xi_1\alpha_1+\xi_2\alpha_2)] +(1\to2,\ 2\to3,\ 3\to1)+(1\to3,\ 2\to1,\ 3\to2)\ , \quad (4.8)$$

where the functions (T_1,T_2,T_3) and (T_1',T_2',T_3') are given by cyclic permutation of (1,2,3) in Eqs. (2.23) and (2.24), respectively. When Eqs. (4.8) and (4.1) are used in Eq. (3.2), the improved trial wave function is adapted to the gauge of the vector potential.

D. Gauge-invariant energy expectation value

When the improved trial wave function is used to calculate the energy expectation value, the result is

$$E'=\langle\Psi'\,|\,H(\vec{r})\Psi'\rangle =\{\xi_1\alpha_1+\tfrac{1}{4}\gamma^2C_1^2[\chi_2'\alpha_3^{-1}+\chi_3'\alpha_2^{-1}+\chi_{23}'(\alpha_2\zeta_2+\alpha_3\zeta_3)^{-1}] +(1\to2,\ 2\to3,\ 3\to1)+(1\to3,\ 2\to1,\ 3\to2)\}-(32\alpha_3/\pi\beta_3)^{1/2}\int_0^1 du(au^4+bu^2+1)^{-1/2}\ . \quad (4.9)$$

This energy is gauge invariant because it does not contain the gauge parameters (ξ_1,ξ_2,ξ_3). The parameters a and b in the potential energy integral are given in Eqs. (4.3) and (4.4). The parameters χ_i' are defined as

$$\chi_i'=\mu\mu_i/m_{ei}m_{hi} \quad (i=1,2,3)\ , \quad (4.10)$$

where μ is given in Eq. (2.18). The parameters χ_{23}' are defined as

$$\chi_{23}'=\mu^2(\mu_3/\mu_2)(m_{e2}'m_{h3}^{-1}-m_{h2}'m_{e3}^{-1})^2\ , \quad (4.11)$$

where $m_{\alpha i}'$ $(\alpha=e,h)$ $(i=1,2,3)$ is given in Eq. (2.14). The parameters χ_{31}' and χ_{12}' are obtained from Eq. (4.11) by cyclic permutation of (1,2,3). The energy in Eq. (4.9) consists of a positive kinetic energy term, a positive diamagnetic term proportional to γ^2, and an attractive Coulomb energy.

The energy in Eq. (4.9) is a function of the dielectric constants and effective masses. These parameters have been experimentally determined for the axially anisotropic semiconductors GaSe and CdS.[30–35] In Sec. V the results of Secs. II–IV are applied to these axially anisotropic semiconductors.

V. GROUND-STATE ENERGIES OF AXIALLY ANISOTROPIC EXCITONS

In this section the results of Sec. IV are specialized to the case of axially anisotropic semiconductors. The gauge-invariant energy expectation value is used to calculate the variational ground-state energies of GaSe excitons and CdS A excitons using numerical minimization. In order to check the validity of the trial wave function at high fields and of the values used for the material parameters of GaSe, the results of the theory are compared with the experimental data of Aldrich *et al.*[11] for GaSe excitons in high fields aligned with the crystal axis. The theoretical ground-state energies agree with experimental energies to within experimental error.

The ground-state energies of GaSe and CdS excitons are calculated for fields ranging from $\gamma=1.0$ to $\gamma=3.0$ as the angle of the field with the c axis varies from 0 to 90°. As a demonstration of how widely results can vary if the gauge-invariant approach is not used, the gauge-dependent energy expectation value of Eq. (4.2) is used to calculate the energy as a function of field angle for GaSe excitons with $\gamma=3.0$. The Landau and symmetric gauges are shown to give widely differing energies that are higher than the gauge-invariant energy.

A. Axially anisotropic semiconductors

Axially anisotropic crystals have a plane of rotational symmetry perpendicular to the crystal axis (c axis).[36] The dielectric tensor and effective mass tensors can be written in terms of components perpendicular ($\perp$) or parallel ($||$) to the c axis. If the x_3 axis is taken to be parallel to the c axis, the subscripts 1 and 2 can be replaced by $\perp$ and the subscript 3 can be replaced by $||$ for the dielectric constants, effective masses, and reduced effective masses.

Since the crystal has rotational symmetry about the x_3 axis, the field may be assumed to lie in the x_2-x_3 plane without loss of generality.[3] The projections of the unit vector in the magnetic field direction onto the axes are then $\vec{C}=(0, \sin\theta, \cos\theta)$, where the field is at an angle θ to the c axis. Only the squares of the field components enter the energy expectation value so allowing θ to vary from 0 to 90° covers all possible energies. The axially anisotropic excitons do not have rotational symmetry in the field unless the field is aligned with the crystal axis. Thus, for arbitrary field angles, the method of Sec. III is needed to adjust the trial wave function to the gauge of the vector potential.

An effective Larmor frequency ω_L, effective Bohr radius a_0, and effective rydberg are obtained from Eqs. (2.15)—(2.17), respectively, for the axially anisotropic case. Instead of K and μ as defined in Eqs. (2.18) and (2.19), respectively, with $K_1=K_2$ and $\mu_1=\mu_2$, it is conventional for axially anisotropic semiconductors to replace K with $(K_\perp K_{||})^{1/2}$ and μ with $\mu_\perp$ in Eqs. (2.15)—(2.17). The field parameter γ in Eq. (2.21) involves the same replacements for μ and K. The gauge-dependent energy E in Eq. (4.2) and the gauge-invariant energy E' in Eq. (4.9) can be obtained in terms of the new Larmor frequency, Bohr radius, and rydberg by making some replacements. The $\zeta_i=\mu/\mu_i$ is replaced by $\mu_\perp/\mu_i$. The μ in Eqs. (4.6), (4.7), (4.10), and (4.11) is replaced by $\mu_\perp$. The β_i in Eq. (4.5) is replaced by $K_\perp/K_i$, which occurs in Eqs. (4.2)—(4.4) and (4.9). With these replacements the energies in Eqs. (4.2) and (4.9) are expressed in terms of the new rydberg and lengths are expressed in terms of the new Bohr radius.

B. Material parameters

The material parameters of CdS and GaSe are discussed here and given in Table I. In a magnetic field CdS has three nondegenerate valence bands A, B, and C.[37] Parameters for excitons formed from the A-valence band, associated with the lowest-energy gap, have been determined by Seiler *et al.*[21] using two-photon magnetospectroscopy and by Hopfield and Thomas[33,38] using linear magnetooptical absorption. Effective masses and dielectric constants for CdS obtained from the above sources are listed in Table I. Parameters which characterize CdS A excitons, either obtained from the above sources or calculated from values given in them, are also listed in Table I. Values which are not referenced are calculated from referenced parameters. Uncertainties have been included when given in the references and used in calculated values.

Effective masses of direct excitons in GaAs have been determined by Ottaviani *et al.*[30] using transport measurements and results of magnetooptical absorption measurements at liquid-helium temperatures.[28,39] Parallel and perpendicular components of the dielectric tensor for GaSe have been measured by Leung *et al.*[31] Effective masses, dielectric constants, and exciton parameters for GaSe, obtained from the above sources or calculated from values given in them, are also listed in Table I. Although no uncertainties are given in Ref. 30, effective mass values of GaSe are uncertain to at least $\pm 10\%$, since the reduced effective masses used to calculate them have this degree of uncertainty.

TABLE I. Material parameters of CdS and GaSe excitons.

Parameter[a]	Definition[a]	GaSe value	CdS value[b]
$m_{e\perp}/m_0$		0.17[c]	0.210±0.003[e]
$m_{h\perp}/m_0$		0.8[c]	0.64±0.02[e]
$m_{e\|\|}/m_0$		0.3[c]	0.204±0.01[f]
$m_{h\|\|}/m_0$		0.2[c]	5.0[f]
$(K_\perp K_{\|\|})^{1/2}$		8.8[d]	8.9±0.2[e]
β	$K_\perp/K_{\|\|}$	1.34[d]	0.988±0.075[g]
$\mu_\perp/m_0$	$[m_0(m_{e\perp}^{-1}+m_{h\perp}^{-1})]^{-1}$	0.14	0.158±0.002[e]
$\mu_{\|\|}/m_0$	$[m_0(m_{e\|\|}^{-1}+m_{h\|\|}^{-1})]^{-1}$	0.12	0.196±0.010
ζ	$\mu_\perp/\mu_{\|\|}$	1.17	0.806±0.050
$\mathscr{R}$	$\mu_\perp e^4/2K_\perp K_{\|\|}\hbar^2$	24.5 meV	27.1±1.5 meV
a_0	$(K_\perp K_{\|\|})^{1/2}\hbar^2/\mu_\perp e^2$	33.3 Å	29.9±1.0 Å
B/γ	$c\mu_\perp^2 e^3/K_\perp K_{\|\|}\hbar^3$	59.3 T	74.0±5.0 T

[a]The symbol m_0 is the free electron mass.
[b]Values for CdS are for the A-valence band.
[c]From Ref. 30.
[d]From Ref. 31.
[e]From Ref. 21.
[f]From Ref. 33.
[g]From $\mu_\perp$, $\mu_{||}$, and $(\mu_\perp K_\perp)/(\mu_{||}K_{||})=0.797\pm0.013$ in Ref. 21

C. Energy minimization

The gauge-invariant energy expectation value of Eq. (4.9) expressed in the new dimensionless units of this section was numerically minimized with respect to the variational parameters $(\alpha_1,\alpha_2,\alpha_3)$. For a given set of material parameters, calculated energies are accurate to within $\pm 5\times 10^{-5}$ effective rydbergs. From Table I the effective exciton rydbergs are 24.5 meV for GaSe and 27.1 meV for CdS. These values give a computational error of less than ± 0.002 meV. Clearly, the primary source of error in the calculations is in the values used for the material parameters, especially for GaSe, where the uncertainties of the effective mass values are not specified in the references. The accuracy of these values and the validity of the trial wave function used can be checked by comparison with experimental measurements in high fields.

D. Comparison with experimental data for GaSe excitons

From Table I the high-field region ($\gamma > 1.0$) is roughly $B > 60$ T for GaSe excitons and $B > 74$ T for CdS A excitons. Although fields of up to 1000 T have been produced using explosive flux compression devices,[40] few exciton measurements have been made at these fields.

Aldrich *et al.*[11] have measured the energy spectrum of the ground state and the first two excited states of GaSe excitons for fields parallel to the c axis ($\theta=0°$) up to nearly 200 T. The optical exciton energies are the sum of the direct band-gap energy E_g and the exciton energy for the particular state considered.[28] The band-gap energy for GaSe at extremely low temperatures (1.7 K) was determined by Mooser and Schlüter[28] to be $E_g = 2129.6 \pm 0.05$ meV. If this value is subtracted from the optical energies, the experimental ground-state energies are obtained. These energies are plotted in Fig. 1. Magnetic fields range from 63 to 167 T. Because of difficulties in resolution due to diffraction fringes, the energies are only accurate to ± 20 cm^{-1} or roughly ± 2.5 meV.[41] For this reason the experimental data in Fig. 1 are given with error bars 5 meV wide. Theoretical values obtained from the variational calculations described in this section are given as solid dots. The large uncertainty in the experimental values makes it difficult to assess the accuracy of the variational calculations precisely. However, the agreement is within experimental error, which is excellent considering that such a simple trial wave function is used.

E. Energy as a function of field strength and orientation for GaSe and CdS excitons

The data taken by Aldrich *et al.*[11] are for fields parallel to the c axis ($\theta=0°$). Data for the perpendicular orientation have been taken for GaSe (Ref. 28) and CdS (Ref. 33) but only for $\gamma < 0.2$. No data have been taken for off-axis fields in the high-field limit. However, the theory can be used to predict the variation of energy with respect to field orientation for such fields.

Theoretical values for the ground-state energies for CdS A excitons and GaSe excitons were calculated for fields ranging from $\gamma = 1.0$ to $\gamma = 3.0$ and for angles from 0° to 90°. These energies are plotted as a function of field angle in Figs. 2 and 3, respectively. The energy for CdS excitons decreases for all values of γ as the field moves off axis. The decrease is larger for higher field values. For GaSe excitons the energy first rises above the on-axis value and then falls below it as the field angle continues to increase. The rise and fall is more pronounced for higher fields. The magnitude of the energy variation with angle is much smaller in GaSe than in CdS at comparable field strengths. The rise and fall of the GaSe exciton energies as the field moves off axis occurs because of competition between the increasingly positive diamagnetic term and the increasingly negative Coulomb term. For CdS excitons the decrease in the diamagnetic term and the increase in the Coulomb term both tend to reduce the energy.

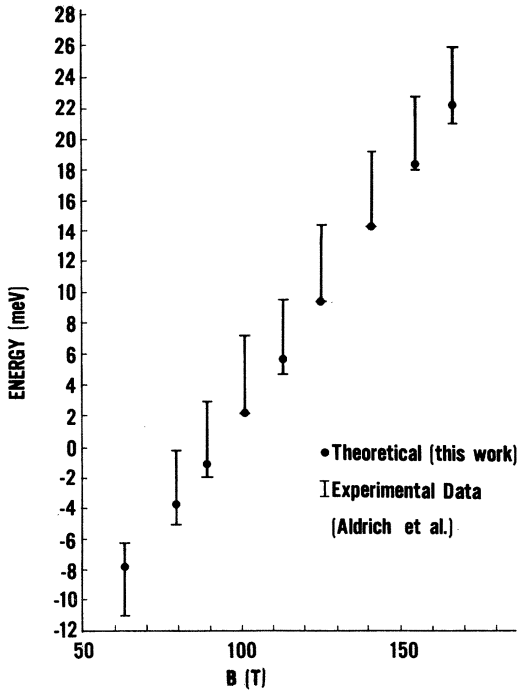

FIG. 1. Ground-state energies of GaSe excitons for fields parallel to the c axis ($\theta=0°$) as a function of the magnetic field. Error bars are experimental data from Ref. 11. Solid circles are theoretical values calculated using Eq. (4.9).

Experimental verifications of these results would be difficult because of the high fields needed and because of the accuracy required (experimental error was ± 2.5 meV in the data of Ref. 11). For GaSe excitons at $\gamma = 3.0$ ($B = 177.9$ T), there is a difference of only 3.5 meV between the maximum and minimum energies, which is too small to resolve using current techniques. For CdS excitons, however, a field of 200 T gives a shift of roughly 20 meV between parallel and perpendicular orientations. This shift could easily be resolved and the experiment could be simplified by measuring only the parallel and perpendicular orientations. Ground-state energies of GaSe excitons do have resolvable energy shifts at fields of 600 T and higher. Since fields of over 1000 T have been produced, measurement of energy shifts in GaSe at these fields is possible.

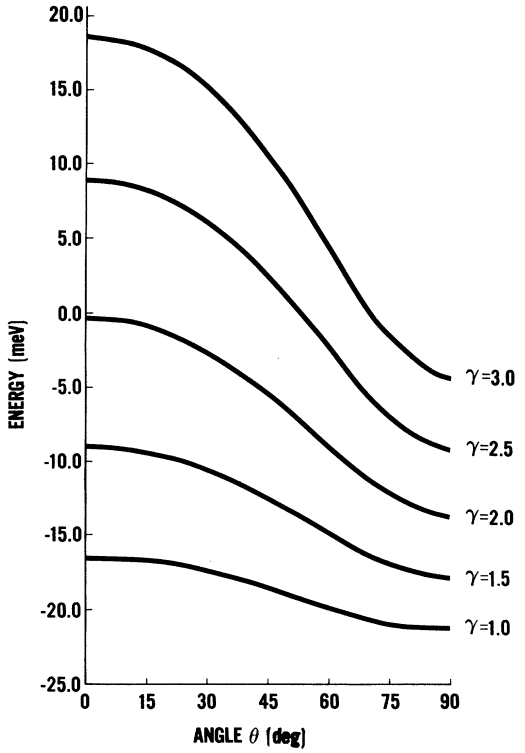

FIG. 2. Theoretical ground-state energies of CdS A excitons as a function of field angle θ at different magnetic fields. Magnetic fields in teslas are $\gamma \times 74.0$ T.

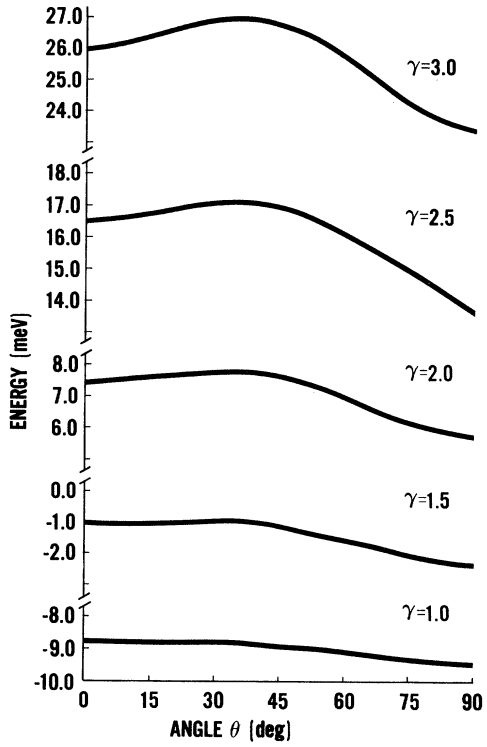

FIG. 3. Theoretical ground-state energies of GaSe excitons as a function of field angle at different magnetic fields. Magnetic fields in teslas are $\gamma \times 59.3$ T.

F. Gauge-dependent energies of GaSe excitons

In order to demonstrate how strongly results can vary using the gauge-dependent approach, calculations were made using the gauge-dependent exciton energy expectation value of Eq. (4.2) in the units of this section in the Landau ($\xi_1=\xi_2=\xi_3=1$) and symmetric ($\xi_1=\xi_2=\xi_3=\frac{1}{2}$) gauges. Gauge-dependent energies of GaSe excitons as a function of field angle for $\gamma=3.0$ are listed in Table II. The Landau- and symmetric-gauge values differ significantly, especially in the parallel orientation. Both sets of energies are higher than the gauge-invariant energies for $\gamma=3.0$, except for the symmetric gauge in the field-parallel case. In this case the system has cylindrical symmetry in the field and the real trial wave function is adapted to the symmetric gauge. The symmetric-gauge energies are close to the gauge-invariant energies for all angles because the GaSe exciton is only slightly anisotropic ($\zeta=\mu_\perp/\mu_{||}=1.17$). For strongly anisotropic excitons the symmetric gauge would not fit the symmetry of the system and the difference between gauge-invariant and symmetric-gauge values would be greater.

G. Exciton ground-state spin splitting

The energies calculated so far, using the minimally coupled Hamiltonian of Eq. (2.3), neglect the effects of exci-

TABLE II. Gauge-dependent ground-state energies of GaSe excitons. All energies are calculated for $\gamma=3.0$ ($B=177.9$ T) and are in units of meV.

θ (deg)	Symmetric gauge[a]	Landau gauge[b]	Gauge invariant[c]
0	25.97	34.79	25.97
15	26.36	35.10	26.35
30	26.95	35.31	26.90
45	26.91	34.23	26.78
60	25.89	31.35	25.71
75	24.30	27.29	24.19
90	23.42	24.86	23.41

[a]For the symmetric gauge $\xi_i=\frac{1}{2}$ in Eq. (4.2) with the units of Sec. V A.
[b]For the Landau gauge $\xi_i=1$ in Eq. (4.2) with the units of Sec. V A.
[c]The gauge-invariant energy is calculated from Eq. (4.9) with the units of Sec. V A.

ton spin on the ground-state-energy spectrum. For strong fields the effect of spin splitting is large and must be considered for completeness. The electron and the hole are both spin-$\frac{1}{2}$ particles. The $1s$ exciton level thus splits in a magnetic field into four nondegenerate spin states: a singlet of total spin $S=0$ corresponding to electron and hole spins antiparallel and three triplets of total spin $S=1$, where the component of total spin parallel to the field $S_B=+1, 0, -1$.[28] The variational calculation using Eq. (4.9) provides an upper bound to the lowest-energy state of the system for which spin contributions are zero. For the singlet and the middle triplet ($S_B=0$) there are no spin contributions to the energy and in CdS (Ref. 33) and GaSe (Ref. 28) the middle triplet is lower in energy than the singlet. Energies calculated previously are thus an upper bound to the middle triplet.

For fields parallel to the c axis ($B=B_z$) the upper and lower triplets can be computed by adding a spin term,[11,21]

$$H_s=g_z^* S_z(\gamma/2) , \tag{5.1}$$

to the Hamiltonian, where g_z^* is the effective g factor of the exciton for parallel fields and $S_z=\pm 1$ is the z component of total spin. This term has no coordinate dependence and therefore simply adds a constant to the variational energy obtained previously.

The effective g factor which determines the $1s$ triplet splitting in parallel fields has been measured for GaSe (Ref. 28) and CdS.[33] The spin splitting of GaSe and CdS $1s$ triplets has been calculated for on-axis fields. In experimental measurements it may be difficult to resolve the triplet splitting exactly. Aldrich *et al.*[22] were able to measure only the center of gravity of the ground-state triplets with any precision.[41] Since this energy corresponds to the energy of the middle triplet, with spin component $S_z=0$, the data agree very well with the variational upper bound to the $S_z=0$ level calculated neglecting spin effects. Since the g factor for fields at angle θ is not known in general, the precise spin splitting in off-axis fields is difficult to determine; however, the center of gravity of the spin-split triplets should have the values given by Figs. 2 and 3.

VI. CONCLUSION

A gauge-invariant energy variational method has been developed for application to systems in magnetic fields. The chosen trial wave function is adapted to the gauge of the vector potential using a phase factor, which produces gauge-invariant energies and ensures that the charge-conservation condition is satisfied.

The method is applied to excitons in the axially anisotropic semiconductors GaSe and CdS in the presence of a strong uniform magnetic field. The variational upper bound to the exciton ground-state energy is calculated as a function of field strength and orientation for GaSe excitons and excitons formed from the A-valence band of CdS. The results of the theory give good agreement with the experimental data of Aldrich *et al.*[11] for GaSe excitons in high magnetic fields parallel to the crystal axis. The theory predicts a decrease in the ground-state energy of CdS A excitons as the field is shifted from parallel to perpendicular orientation with respect to the crystal axis. For GaSe excitons the ground-state energy first rises above the on-axis value and then falls below it as the field shifts to the perpendicular orientation. The superiority of the gauge-invariant approach is demonstrated by the large variation of energy with respect to gauge when an unadapted trial wave function is used.

Experimental verification of the exciton calculations would be difficult because of the high magnetic fields needed and large experimental errors. For CdS excitons, however, the energy shifts are sufficiently large to be resolved at fields above 100 T. In addition to the high magnetic fields needed for verification, another restriction on application of the formalism for excitons and shallow donors is the need for prior knowledge of the material parameters. Other axially anisotropic nondegenerate semiconductors to which the formalism could be applied are Te (Ref. 42) and CdSe.[35,43]

The energy expressions for excitons can be specialized to the case of a shallow donor (an electron bound to a positively ionized donor impurity) by setting the effective hole mass equal to infinity.[20] In semiconductors with nondegenerate valence bands they could also be specialized to the case of shallow acceptors by setting the effective electron mass equal to infinity.

In conclusion, the improved trial wave function solves two problems associated with application of the variational method to systems in magnetic fields: gauge dependence and violation of charge conservation. It ensures charge conservation, a gauge-invariant energy, and the best upper bound to the ground-state energy consistent with the form of trial wave function chosen.

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*Present address: Rocketdyne Division, Rockwell International, 6633 Canoga Avenue, Canoga Park, CA 91304.

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