A GAUGE-INVARIANT ENERGY VARIATIONAL PRINCIPLE:
APPLICATION TO ANISOTROPIC EXCITONS
IN HIGH MAGNETIC FIELDS

DISSERTATION

Presented to the Graduate Council of the
North Texas State University in Partial
Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

Paul K. Kennedy, M. S.
Denton, Texas
December, 1983

A new method is developed for treating atoms and molecules in a magnetic field in a gauge-invariant way using the Rayleigh-Ritz energy variational principle. The energy operator depends on the vector potential which must be chosen in some gauge. In order to adapt the trial wave function to the gauge of the vector potential, the trial wave function can be multiplied by a phase factor which depends on the spatial coordinates. When the energy expectation value is minimized with respect to the phase function, the equation for charge conservation for stationary states is obtained. This equation can be solved for the phase function, and the solution used in the energy expectation value to obtain a gauge-invariant energy. The method is applicable to all quantum mechanical systems for which the variational principle can be applied. It ensures satisfaction of the charge conservation condition, a gauge-invariant energy, and the best upper bound to the ground-state energy which can be obtained for the form of trial wave function chosen.
The method is first illustrated by applying it to an anisotropic harmonic oscillator in a constant magnetic field. Then it is applied to shallow donors and excitons in the axially anisotropic semiconductors GaSe and CdS in the presence of a uniform strong magnetic field. The results of the variational calculation for the ground-state energy using a Gaussian trial wave function give good agreement with experimental values for the ground-state energies of GaSe excitons in high magnetic fields parallel to the crystal axis. The ground-state energies of GaSe excitons, CdS A-excitons, and shallow donors in CdS and GaSe are calculated for fields not aligned with the crystal axis. As the polar angle changes from 0 to 90 degrees, the ground-state energy of the GaSe exciton first rises above the on-axis value and then falls below it. The ground-state energies of the CdS A-exciton and the GaSe shallow donor decrease with increasing polar angle. The CdS shallow donor is a nearly isotropic system whose ground-state energy has little dependence on field orientation.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. GAUGE-IN Variant ENERGY VARIATIONAL METHOD FOR SYSTEMS IN MAGNETIC FIELDS</td>
<td>8</td>
</tr>
<tr>
<td>Difficulties with the Variational Method for Systems in Magnetic Fields</td>
<td></td>
</tr>
<tr>
<td>Improved Trial Wave Function</td>
<td></td>
</tr>
<tr>
<td>Many Particle Systems</td>
<td></td>
</tr>
<tr>
<td>Application to Systems With and Without Rotational Symmetry in the Field</td>
<td></td>
</tr>
<tr>
<td>III. ANISOTROPIC HARMONIC OSCILLATOR IN A UNIFORM MAGNETIC FIELD</td>
<td>19</td>
</tr>
<tr>
<td>Energy Operator</td>
<td></td>
</tr>
<tr>
<td>Standard Variational Treatment</td>
<td></td>
</tr>
<tr>
<td>Gauge-Dependent Energy Expectation Value</td>
<td></td>
</tr>
<tr>
<td>Violation of Charge Conservation</td>
<td></td>
</tr>
<tr>
<td>Gauge-Invariant Treatment</td>
<td></td>
</tr>
<tr>
<td>Improved Trial Wave Function</td>
<td></td>
</tr>
<tr>
<td>Gauge-Invariant Energy Expectation Value</td>
<td></td>
</tr>
<tr>
<td>Energy Minimization</td>
<td></td>
</tr>
<tr>
<td>Dimensionless Units</td>
<td></td>
</tr>
<tr>
<td>Variational Ground-State Energy</td>
<td></td>
</tr>
<tr>
<td>Magnetic Field Along a Principal Axis</td>
<td></td>
</tr>
<tr>
<td>Minimum Ground-State Energy</td>
<td></td>
</tr>
<tr>
<td>Exact Ground-State Energy</td>
<td></td>
</tr>
<tr>
<td>IV. ANISOTROPIC SHALLOW DONORS IN A UNIFORM STRONG MAGNETIC FIELD</td>
<td>33</td>
</tr>
<tr>
<td>Topic</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Donor Impurity in a Uniform Magnetic Field</td>
<td></td>
</tr>
<tr>
<td>Dimensionless Units</td>
<td></td>
</tr>
<tr>
<td>Improved Trial Wave Function</td>
<td></td>
</tr>
<tr>
<td>High Field Trial Wave Function</td>
<td></td>
</tr>
<tr>
<td>Charge Conservation Equation for the Anisotropic Electron</td>
<td></td>
</tr>
<tr>
<td>Gauge-Invariant Energy Expectation Value</td>
<td></td>
</tr>
<tr>
<td>V. ANISOTROPIC EXCITONS IN A UNIFORM STRONG MAGNETIC FIELD</td>
<td>42</td>
</tr>
<tr>
<td>Exciton in a Uniform Magnetic Field</td>
<td></td>
</tr>
<tr>
<td>Separation of the Center-of-Mass and Relative Motions</td>
<td></td>
</tr>
<tr>
<td>Single-Particle Effective Hamiltonian in Relative Coordinates</td>
<td></td>
</tr>
<tr>
<td>Dimensionless Units</td>
<td></td>
</tr>
<tr>
<td>Improved Trial Wave Function</td>
<td></td>
</tr>
<tr>
<td>High Field Trial Wave Function</td>
<td></td>
</tr>
<tr>
<td>Charge Conservation Equation for the Anisotropic Exciton</td>
<td></td>
</tr>
<tr>
<td>Gauge-Invariant Energy Expectation Value</td>
<td></td>
</tr>
<tr>
<td>Gauge-Dependent Energy Expectation Value</td>
<td></td>
</tr>
<tr>
<td>VI. EXCITONS AND SHALLOW DONORS IN AXIALLY ANISOTROPIC CRYSTALS</td>
<td>59</td>
</tr>
<tr>
<td>Axially Anisotropic Crystals</td>
<td></td>
</tr>
<tr>
<td>Axially Anisotropic Excitons</td>
<td></td>
</tr>
<tr>
<td>Gauge-Invariant Energy Expectation Value</td>
<td></td>
</tr>
<tr>
<td>Gauge-Dependent Energy Expectation Value</td>
<td></td>
</tr>
<tr>
<td>Axially Anisotropic Shallow Donors</td>
<td></td>
</tr>
<tr>
<td>Material Parameters of CdS</td>
<td></td>
</tr>
<tr>
<td>Material Parameters of GaSe</td>
<td></td>
</tr>
<tr>
<td>VII. GROUND-STATE ENERGIES OF AXIALLY ANISOTROPIC EXCITONS AND SHALLOW DONORS</td>
<td>68</td>
</tr>
<tr>
<td>Energy Minimization</td>
<td></td>
</tr>
<tr>
<td>Comparison with Experimental Data for GaSe Excitons</td>
<td></td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS—Continued

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy as a Function of Field Strength and Orientation for GaSe and CdS Excitons</td>
</tr>
<tr>
<td>Interpretation of Results</td>
</tr>
<tr>
<td>Possibility of Experimental Verification</td>
</tr>
<tr>
<td>Gauge-Dependent Energies of GaSe Excitons for the Landau and Symmetric Gauges</td>
</tr>
<tr>
<td>Exciton Ground-State Spin Splitting</td>
</tr>
<tr>
<td>Energy as a Function of Field Strength and Orientation for GaSe and CdS Shallow Donors</td>
</tr>
<tr>
<td>VIII. CONCLUSION</td>
</tr>
<tr>
<td>Appendix</td>
</tr>
<tr>
<td>A. THE EXTREMUM IS A MINIMUM</td>
</tr>
<tr>
<td>B. CURRENT DENSITY AND CHARGE CONSERVATION EQUATION FOR MANY-PARTICLE SYSTEMS</td>
</tr>
<tr>
<td>C. DERIVATION OF THE GAUGE-DEPENDENT ENERGY EXPECTATION VALUE FOR THE ANISOTROPIC OSCILLATOR</td>
</tr>
<tr>
<td>D. JUSTIFICATION FOR VARYING THE ENERGY WITH RESPECT TO GAUGE PARAMETERS</td>
</tr>
<tr>
<td>E. SOLUTION OF THE CHARGE CONSERVATION EQUATION FOR THE ANISOTROPIC OSCILLATOR</td>
</tr>
<tr>
<td>F. DERIVATION OF THE GAUGE-InVARIANT ENERGY EXPECTATION VALUE FOR THE ANISOTROPIC OSCILLATOR</td>
</tr>
<tr>
<td>G. COMPUTER PROGRAM</td>
</tr>
<tr>
<td>H. POTENTIAL ENERGY OF A HYDROGENIC SYSTEM IN A TOTALLY ANISOTROPIC SEMICONDUCTOR</td>
</tr>
<tr>
<td>I. DERIVATION OF THE DIMENSIONLESS HAMILTONIAN FOR THE ANISOTROPIC SHALLOW DONOR</td>
</tr>
<tr>
<td>TABLE OF CONTENTS--Continued</td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td>J. CHARGE CONSERVATION EQUATION FOR THE ANISOTROPIC ELECTRON .......................... 114</td>
</tr>
<tr>
<td>K. GAUGE-INvariant ENERGY EXPECTATION VALUE FOR ANISOTROPIC SHALLOW DONORS ............ 119</td>
</tr>
<tr>
<td>L. POTENTIAL ENERGY INTEGRAL ............................................... 124</td>
</tr>
<tr>
<td>M. PARTIAL DECOUPLING OF THE CENTER-OF-MASS AND RELATIVE MOTIONS OF THE EXCITON. ... 128</td>
</tr>
<tr>
<td>N. SINGLE-PARTICLE EFFECTIVE HAMILTONIAN FOR THE EXCITION ............................. 135</td>
</tr>
<tr>
<td>O. DERIVATION OF THE DIMENSIONLESS HAMILTONIAN FOR THE ANISOTROPIC EXCITION .......... 139</td>
</tr>
<tr>
<td>P. CHARGE CONSERVATION EQUATION FOR THE ANISOTROPIC EXCITON .......................... 143</td>
</tr>
<tr>
<td>Q. GAUGE-INvariant ENERGY EXPECTATION VALUE FOR ANISOTROPIC EXCITONS ................. 149</td>
</tr>
<tr>
<td>R. GAUGE-DEPENDENT ENERGY EXPECTATION VALUE FOR ANISOTROPIC EXCITONS ............... 156</td>
</tr>
<tr>
<td>S. EFFECTIVE BOHR MAGNETON OF THE EXCITON FOR ARBITRARY FIELDS ........................ 159</td>
</tr>
<tr>
<td>REFERENCES AND NOTES .............................................................. 179</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table | Page
---|---
I. Ground-State Energies of the Anisotropic Harmonic Oscillator | 160
II. Material Parameters of Cadmium Sulfide and Gallium Selenide Excitons | 161
III. Material Parameters of Cadmium Sulfide and Gallium Selenide Shallow Donors | 163
IV. Theoretical Ground-State Energies of Cadmium Sulfide A-Excitons | 164
V. Theoretical Ground-State Energies of Gallium Selenide Excitons | 165
VI. Ultra-High Field Ground-State Energies of Gallium Selenide Excitons | 166
VII. Gauge-Dependent Ground-State Energies of Gallium Selenide Excitons | 167
VIII. Theoretical Ground-State Energies of Gallium Selenide Shallow Donors | 168
IX. Theoretical Ground-State Energies of Cadmium Sulfide Shallow Donors | 169
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Theoretical Ground-State Energies of the Anisotropic Harmonic Oscillator</td>
<td>170</td>
</tr>
<tr>
<td>2.</td>
<td>Ground-State Energies of GaSe Excitons for Fields Parallel to the Crystal Axis</td>
<td>171</td>
</tr>
<tr>
<td>3.</td>
<td>Theoretical Ground-State Energies of CdS A-Excitons</td>
<td>172</td>
</tr>
<tr>
<td>4.</td>
<td>Theoretical Ground-State Energies of GaSe Excitons</td>
<td>173</td>
</tr>
<tr>
<td>5.</td>
<td>Variation of Ground-State Energy with Field Angle for CdS A-Excitons</td>
<td>174</td>
</tr>
<tr>
<td>6.</td>
<td>Variation of Ground-State Energy with Field Angle for GaSe Excitons</td>
<td>175</td>
</tr>
<tr>
<td>7.</td>
<td>Gauge-Dependent Ground-State Energies of GaSe Excitons</td>
<td>176</td>
</tr>
<tr>
<td>8.</td>
<td>Spin Splitting of the Exciton Ground-State for GaSe and CdS in On-Axis Fields</td>
<td>177</td>
</tr>
<tr>
<td>9.</td>
<td>Theoretical Ground-State Energies of GaSe Shallow Donors</td>
<td>178</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

For atoms and molecules in magnetic fields the Schrödinger equation generally cannot be solved exactly. Although perturbation and variational perturbation methods are often used, the Rayleigh-Ritz energy variational principle provides one of the best approximation methods for intermediate or strong fields. Since the vector potential enters the energy operator, some choice of gauge must be made. When a trial wave function is chosen, the energy expectation value generally depends on the choice of the gauge of the potentials. When the current density is calculated from the trial wave function, charge conservation is also found to be violated for an arbitrary choice of gauge. Since quantum mechanics is gauge invariant and charge is conserved, these defects of the energy variational method are serious. The remedy of these defects is given in this work.

A method is developed for improving the chosen trial wave function so that the energy expectation value is gauge invariant and charge is conserved. For a given vector potential and trial wave function, the trial wave function can be multiplied by a phase factor in which the phase depends on the spatial coordinates. When the energy is varied with
respect to the phase function, the condition for charge conservation is obtained. 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 problem of gauge invariance in variational calculations has been previously addressed by Epstein\textsuperscript{16,17} who suggested the use of a phase factor containing an arbitrary variational function to remove gauge dependence.\textsuperscript{17} This procedure was described as obtaining an "optimal gauge" for use with a certain trial wave function or set of wave functions. No equation for obtaining the phase factor in a general case was given. Epstein\textsuperscript{16,17} also pointed out that a trial wave function should satisfy the current conservation condition, but the difficulty here lies in a priori finding
such a wave function. In the method proposed here any trial wave function may first be chosen and then adapted to the gauge of the vector potential so that it simultaneously satisfies the current conservation condition and yields the lowest energy possible for all gauge-equivalent wave functions. This energy is independent of the gauge chosen for the vector potential in the energy operator.

The method is general and can in principle be applied to any system. In this work it is applied to three systems where the differential equation for the minimizing phase function can be solved analytically. First, as a simple example, it is applied to an anisotropic harmonic oscillator in a constant magnetic field. The energy expectation value is calculated using both the standard variational approach, with an unadapted trial wave function, and the gauge-invariant approach. When an unadapted trial wave function is used, the energy expectation value is gauge dependent and charge is not conserved. When the improved trial wave function is used, the energy expectation value is gauge invariant and charge is conserved. When the energy expectation values are numerically minimized, the gauge-dependent energy expectation value is shown to give a different variation of ground-state energy with respect to field orientation for different choices of gauge. The ground-state energies for all gauges are higher than the gauge-invariant energies at the same fields. When the field is along a principal axis
of the oscillator, the gauge invariant method gives the exact solution for the ground-state.

Second, the method is applied to two hydrogenic systems: electron-hole pairs (excitons) and electrons bound to positively ionized donor impurities (shallow donors) in anisotropic semiconductors in a strong uniform magnetic field. For the sake of generality, the theory is first developed for excitons and shallow donors in totally anisotropic semiconductors. The effective mass approximation for hydrogenic systems in semiconductors first developed by Wannier is used. The theory is then specialized to the axially anisotropic case for application to the axially anisotropic semiconductors GaSe and CdS.

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 and CdS shallow donors, GaSe excitons, and excitons formed from the A-valence band of CdS. The variational energies are calculated by numerical minimization of the gauge-invariant energy expectation value. Material parameters of GaSe used in the calculation are obtained from Ottaviani, et al., and Leung, et al. Material parameters of CdS are obtained from Hopfield and Thomas and Seiler, et al.

The results of the gauge-invariant variational calculation give good agreement with the experimental data of Aldrich, et al., for GaSe excitons in high fields parallel
to the crystal axis. The theory predicts a decrease in the ground-state energy of GaSe excitons, GaSe shallow donors, and CdS A-excitons as the field is shifted from parallel to perpendicular orientations with respect to the crystal axis. Shallow donors in CdS are nearly isotropic; therefore, their energies have little dependence on field orientation. 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 and shallow donors in magnetic fields have been made both for isotropic\(^24-29\) and anisotropic\(^23,30-34\) semiconductors. Fritsche and Heidt\(^30\) 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 Elliott and Loudon,\(^29\) 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.\(^23,31,32\) No formalism has previously been developed, however, for treating excitons and shallow donors in totally anisotropic semiconductors in high magnetic fields. The formalism developed in this work 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 computation has been made of the variation of ground-state energy with field angle for exitons and shallow donors in axially anisotropic semiconductors. Monozon and coworkers\textsuperscript{31,32} 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. Finally, no gauge-invariant variational formalism has previously been developed or applied.

In Chapter II the method for obtaining gauge-invariant variational results by adapting the trial wave function to the gauge of the vector potential is developed. In Chapter III an anisotropic harmonic oscillator in a uniform magnetic field is treated as a simple example to compare the standard and gauge-invariant variational approaches. The gauge-invariant method is used in Chapters IV and V to derive the gauge-invariant energy expectation value for shallow donors and excitons, respectively, in totally anisotropic semiconductors in a strong magnetic field. In Chapter VI the results of Chapters IV and V are specialized to the axially anisotropic case. In Chapter VII the ground-state energies of shallow donors and excitons in GaSe and CdS are calculated. The calculations are compared with the experimental data of Aldrich, \textit{et al.},\textsuperscript{23} for GaSe excitons and with the results
of a gauge-dependent method. Finally, Chapter VIII summarizes the results and gives the conclusions.
CHAPTER II

GAUGE-ININVARIANT ENERGY VARIATIONAL METHOD
FOR SYSTEMS IN MAGNETIC FIELDS

An energy variational method based on gauge invariance for systems in magnetic fields is developed in this chapter. The problems which arise when the Rayleigh-Ritz energy variational principle is applied to a system in a magnetic field are discussed. A method for obtaining an improved trial wave function which resolves these problems is given. The improved trial wave function is one which is adapted to the gauge of the vector potential. The Rayleigh-Ritz variational principle gives the charge conservation condition, which can be solved to obtain the improved trial wave function. The method can be generalized for a system of $N$ identical particles. The method is primarily of value for systems which do not have rotational symmetry about the field axis. For systems which do have rotational symmetry, a real trial wave function is adapted to the vector potential in the symmetric gauge.

Difficulties with the Variational Method for Systems in Magnetic Fields

The Hamiltonian for a particle of mass $m$ and charge $q$ in a time varying electromagnetic field characterized by the vector potential $\vec{A}(\vec{r},t)$ and the scalar potential $\phi(\vec{r},t)$ is

$$H = \frac{p^2}{2m} - q\phi(\vec{r},t) - \frac{1}{2m} \left[ (\vec{A}(\vec{r},t) \cdot \vec{v})^2 - \dot{\phi}(\vec{r},t) + \frac{1}{2} \vec{v} \cdot \nabla \phi(\vec{r},t) \right].$$
\[ H(\vec{A}, \phi) = (1/2m)(\vec{p} - q\vec{A}/c)^2 + V(\vec{r}) + q\phi, \quad (2.1) \]

where \( \vec{p} = -i\hbar \nabla \) is the canonical momentum operator and \( V(\vec{r}) \) is the potential energy in the absence of the field. The Hamiltonian of Eq. (2.1) is a gauge-dependent operator. Physical quantities must be represented by gauge-invariant operators; \(^{35-38}\) therefore, the expectation value of Eq. (2.1) is not the energy. The gauge-invariant energy operator is

\[ \mathcal{E}(\vec{A}) = (1/2m)(\vec{p} - q\vec{A}/c)^2 + V(\vec{r}). \quad (2.2) \]

If the charged particle interacts with a constant external magnetic field \( \vec{B} \) characterized by the time-independent vector potential \( \vec{A}(\vec{r}) \), then the Hamiltonian is

\[ H(\vec{A}) = (1/2m)(\vec{p} - q\vec{A}/c)^2 + V(\vec{r}). \quad (2.3) \]

In this case the Hamiltonian is equal to the energy operator. The vector potential \( \vec{A} \), such that \( \vec{B} = \nabla \times \vec{A} \), is assumed to be fixed in a definite time-independent gauge. \(^{39}\) The time-independent Schrödinger equation is

\[ H(\vec{A}) \psi = \mathcal{E} \psi, \quad (2.4) \]

where \( \psi \) is the wave function and \( \mathcal{E} \) is the energy.

The Schrödinger equation may be too difficult to solve exactly, so approximation methods may be required. The Rayleigh-Ritz energy variational method may be chosen to obtain an approximate ground-state energy and wave
function. If a normalized trial ground-state wave function $\Psi$ is chosen, with an arbitrary number of variational parameters, or with unknown functions, the expectation value $E$ of the energy operator $H(\vec{A})$ is an upper bound to the true ground-state energy $E_0$:

$$E = \langle \Psi' | H(\vec{A}) | \Psi' \rangle \geq E_0.$$  (2.5)

By minimizing Eq. (2.5) with respect to the variational parameters or functions, an energy $E_{\text{min}}$ is obtained which is the best upper bound consistent with the choice of trial wave function $\Psi$.

There are two difficulties which arise when applying the variational method to systems in magnetic fields. The energy operator is written in terms of the vector potential and the energy $E_{\text{min}}$ obtained by minimization depends upon the gauge of the vector potential. Rather than search for the gauge which gives the lowest energy, Epstein's "optimal" gauge, it is more convenient and more satisfying in principle to adapt the trial wave function to the gauge of the vector potential, so that the energy expectation value is gauge-invariant.

Charge should also be conserved. The quantum mechanical current density $\vec{J}$ is

$$\vec{J} = (q/m) \text{Re} \left\{ \Psi^* (\vec{p} - q \vec{A}/c) \Psi \right\},$$  (2.6)

where $\text{Re}$ denotes the real part and the operator
\[ \overline{p} = \overline{P} - q \overline{A}/c \]  

(2.7)

is the kinetic (or mechanical) momentum \( m\overline{v} \) of the particle in the field. For an arbitrary choice of the trial wave function \( \Psi \) and an arbitrary gauge of vector potential \( \overline{A} \), the divergence of the current density does not, in general, vanish:

\[ \nabla \cdot \overline{J} \neq 0. \]  

(2.8)

For a stationary state the charge density \( \rho = q|\Psi|^2 \) is constant in time:

\[ \partial \rho / \partial t = 0. \]  

(2.9)

Thus, the equation of continuity is violated by Eq. (2.8).

Improved Trial Wave Function

The problems of gauge dependence of the energy expectation value and lack of charge conservation are remedied by the use of an improved trial wave function which is adapted to the gauge of the vector potential. The new trial wave function \( \Psi' \) is obtained from the old trial wave function \( \Psi \) by a phase transformation on the wave function

\[ \Psi' = \exp(iq\Lambda/hc)\Psi, \]  

(2.10)

where \( \Lambda = \Lambda(\overline{r}) \) is an arbitrary real variational function. The expectation value of the energy operator \( H(\overline{A}) \) calculated with respect to the new trial wave function \( \Psi' \) is
When $E'$, which is

$$E' = E[\Lambda] = \langle \exp(iq\Lambda/hc)\Psi | H(\bar{\Lambda}) \exp(iq\Lambda/hc)\Psi \rangle,$$  

is minimized with respect to the arbitrary function $\Lambda(\vec{r})$, an energy lower than $E$ in Eq. (2.5) is in general obtained.

The variation of Eq. (2.12) with respect to $\Lambda$ is

$$E[\Lambda + \delta\Lambda] - E[\Lambda] = \delta E[\Lambda] + \delta^2 E[\Lambda] + \ldots,$$  

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, $\delta^2 E[\Lambda] > 0$. The condition for an extremum is obtained in this section, while in Appendix A it is shown that the extremum is indeed a minimum.

When the first variation of Eq. (2.12) is set equal to zero, the extremum condition is

$$\delta E[\Lambda] = -\frac{2q}{hc} \int d^3r \delta \Lambda(\vec{r}) \mathcal{U}_m \left\{ \Psi^*(\vec{r}) H(\bar{\Lambda}) \Psi(\vec{r}) \right\} = 0,$$  

where $\mathcal{U}_m$ denotes the imaginary part. To obtain Eq. (2.14) from Eq. (2.13) the exponential $\exp(iq\delta\Lambda/hc)$ 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. (2.14) to be satisfied is for the integrand to vanish,

$$\text{Im} \left\{ \Psi'^* H(\hat{A}) \Psi' \right\} = 0 .$$  \hspace{1cm} (2.15)$$

If the energy operator $H(\hat{A})$ defined in Eq. (2.3) is used, then Eq. (2.15) becomes

$$\text{Im} \left\{ \Psi'^* (\vec{\pi})^2 \Psi' \right\} = 0 ,$$  \hspace{1cm} (2.16)$$

where $\vec{\pi}$ is the kinetic momentum operator defined in Eq. (2.7). Since the canonical momentum is $\vec{p} = -i \hbar \nabla$, Eq. (2.16) can be rewritten as

$$\text{Im} \left\{ -i \hbar \nabla \cdot (\Psi'^* \vec{\pi} \Psi') + |\vec{\pi} \Psi'|^2 \right\} = 0 .$$  \hspace{1cm} (2.17)$$

The last term in the brackets in Eq. (2.17) is real, so that Eq. (2.17) gives

$$\nabla \cdot \vec{J}' = 0 ,$$  \hspace{1cm} (2.18)$$

where the new current density,

$$\vec{J}' = (q/m) \Re \left\{ \Psi'^* (\vec{p} - q \vec{A}/c) \Psi' \right\} ,$$  \hspace{1cm} (2.19)$$

is calculated with respect to the improved trial wave function $\Psi'$ in Eq. (2.10). Equation (2.18) shows that charge is conserved when the new wave function $\Psi'$ is used. Minimization of the energy with respect to the variational function $\Lambda(\vec{r})$ thus gives a trial wave function that satisfies charge conservation as well.
The phase function $\Lambda(\vec{r})$ in Eq. (2.10) which minimizes the energy can be determined by substituting Eq. (2.10) into Eq. (2.19) and using it in Eq. (2.18). The partial differential equation obtained for $\Lambda$ is

$$\nabla^2 \Lambda + \nabla \Lambda \cdot \frac{\nabla \rho(\vec{r})}{\rho(\vec{r})} = -\left(\frac{mc}{q}\right) \left[ \frac{\nabla \cdot \vec{J}}{\rho(\vec{r})} \right],$$  \hspace{1cm} (2.20)

where $\rho(\vec{r}) = q|\Psi(\vec{r})|^2$ is the charge density and $\vec{J}$ is the current density in Eq. (2.6) calculated with respect to the original trial wave function $\Psi$. When Eq. (2.20) is solved for $\Lambda$ and the solution is used in Eq. (2.10), the improved trial wave function $\Psi'$ satisfies the charge conservation condition in Eq. (2.18). Since $\vec{J}$ in Eq. (2.20) contains the vector potential, the solution obtained for $\Lambda(\vec{r})$ depends upon the choice of gauge for the vector potential. The improved trial wave function is thus the one that is adapted to the gauge of the vector potential. The same minimum energy $E'_{\text{min}}$ is obtained regardless of what gauge is chosen. Use of the improved trial wave function resolves the problems discussed in the previous section and gives the lowest energy possible for a certain form of trial wave function $\Psi$ and its gauge equivalents. As with the standard variational method, the accuracy of the results still depends upon the suitability of the initial choice of trial wave function.
Many-Particle Systems

The method given above can be generalized for a system of $N$ identical particles of charge $q$ and mass $m$. For a system of $N$ charged particles in a uniform magnetic field the current density operator $\mathbf{J}_{\text{op}}(\mathbf{r})$ is

$$\mathbf{J}_{\text{op}}(\mathbf{r}) = \sum_{i=1}^{N} \frac{q}{2m} \left\{ \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{p}_i \right\}, \quad (2.21)$$

where $\mathbf{p}_i$ is the kinetic momentum and $\mathbf{r}_i$ is the displacement vector of the $i$th particle. The trial wave function $\Psi$ is written

$$\Psi = \Psi(1, 2, 3, \ldots N), \quad (2.22)$$

where $(i) = (\mathbf{r}_i, \sigma_i)$, $(i = 1, 2, \ldots N)$, and $\sigma_i$ is the spin projection of the $i$th particle. The current density is

$$\mathbf{J}(\mathbf{r}) = \langle \Psi | \mathbf{J}_{\text{op}}(\mathbf{r}) | \Psi \rangle$$

$$= \int \cdots dN \left\{ \sum_{i=1}^{N} \frac{q}{2m} \left[ \mathbf{p}_i \Psi'(1 \ldots N) \right]^* \delta(\mathbf{r} - \mathbf{r}_i) \Psi'(1 \ldots N) \\
+ \Psi'^*(1 \ldots N) \sum_{i=1}^{N} \frac{q}{2m} \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{p}_i \Psi'(1 \ldots N) \right\}. \quad (2.23)$$

On performing the integrations, Eq. (2.23) can be written as

$$\mathbf{J}(\mathbf{r}) = \frac{q}{m} \text{Re} \left\{ \mathbf{p} \rho(\mathbf{r}, \mathbf{r}') \right\}|_{\mathbf{r} = \mathbf{r}'}, \quad (2.24)$$
where the single-particle reduced density matrix \( \rho(\vec{r}, \vec{r'}) \)

is defined as

\[
\rho(\vec{r}, \vec{r'}) \equiv N \int d2... dN \Psi^* (\vec{r}, 2...N) \Psi (\vec{r'}, 2...N). \tag{2.25}
\]

Equation (2.24) is derived in Appendix B.

The energy operator for a system of \( N \) charged particles is

\[
H(\vec{A}) = \sum_{\lambda=1}^{N} \left[ \frac{\vec{p}_\lambda^2}{2m} + V(\vec{r}_\lambda^2) \right] + \frac{1}{2} \sum_{\lambda \neq j=1}^{N} V(\vec{r}_\lambda, \vec{r}_j), \tag{2.26}
\]

where the last term is the interaction between the particles. An improved trial wave function for the many-particle system is

\[
\Psi'(1...N) = \exp \left\{ i \frac{q}{\hbar c} \sum_{j=1}^{N} A(\vec{r}_j) \right\} \Psi(1...N). \tag{2.27}
\]

The expectation value of the energy operator in Eq. (2.26) is

\[
E' = E(\Lambda) = \langle \Psi' \mid H(\Lambda) \mid \Psi' \rangle
= \int d1... dN \left\{ \Psi'^*(1...N) H(\Lambda) \Psi'(1...N) \right\}. \tag{2.28}
\]

The variation of Eq. (2.28) with respect to \( \Lambda \) can be written in the same form as Eq. (2.13), where each \( \Lambda(\vec{r}_j^2) \) has an arbitrary real variation \( \delta \Lambda(\vec{r}_j^2) \). In Appendix B the first variation of Eq. (2.28) is set equal to zero. This extremum condition is shown to give the current conservation condition.
\[ \nabla \cdot \vec{J}(\vec{r}) = 0, \]  

(2.29)

where the many-particle current density is given in Eq. (2.24). Equation (2.29) is the charge conservation condition for a system of \( N \) identical charged particles in a stationary state in a static magnetic field. It is also shown in Appendix B that the second variation of Eq. (2.28) is positive; therefore, the extremum is a minimum.

Application to Systems With and Without Rotational Symmetry in the Field

If the gauge of vector potential \( \vec{A} \) and the initial choice of trial wave function \( \Psi \) are not adapted to each other, then \( \nabla \cdot \vec{J} \neq 0 \) and the gauge-invariant method described in this chapter gives lower energies. If, however, the wave function \( \Psi \) happens to be one already adapted to the gauge of the potential, then \( \nabla \cdot \vec{J} = 0 \), the solution to Eq. (2.20) is \( \vec{A} = 0 \), and the method gives no improvement in energy.

An example of the latter case is a system which has rotational symmetry about the field direction, i.e., cylindrical symmetry in the field. For such a system the ground-state trial wave function should be cylindrically symmetric about the field axis. The obvious choice of gauge is the symmetric gauge (or cylindrical gauge) \( \vec{A} = \frac{e}{2} \vec{B} \times \vec{r} \), which also has cylindrical symmetry about the field axis. For a cylindrically symmetric real trial wave function and the symmetric gauge, the charge conservation condition is obtained.
such systems the trial wave function is already adapted to the gauge of the vector potential.

For anisotropic systems which do not have rotational symmetry in the field, adaptation of the trial wave function to the gauge of the vector potential is not trivial. In the next chapter the anisotropic harmonic oscillator in a uniform magnetic field is used as a simple example to demonstrate the gauge-invariant variational method and contrast it with the standard gauge-dependent approach.
CHAPTER III

ANISOTROPIC HARMONIC OSCILLATOR IN A UNIFORM MAGNETIC FIELD

The gauge-invariant variational method developed in Chapter II is applied here to an anisotropic harmonic oscillator in a constant magnetic field \( B \) which is taken to be in an arbitrary direction. The energy operator for the oscillator is written with the vector potential \( \mathbf{A} \) in the mixed gauge.\(^5\) The arbitrary gauge parameters in the mixed gauge are an indicator of whether energy expectation values are gauge invariant or gauge dependent. The energy expectation value is then calculated with a real trial wave function in the standard variational approach and with a trial wave function adapted to the gauge in the gauge-invariant approach. When a real trial wave function is used, the energy expectation value is gauge dependent and charge is not conserved. When the improved trial wave function is used, the energy expectation value is gauge invariant and charge is conserved. When the energy expectation values are numerically minimized, the gauge-dependent energy expectation value gives different ground-state energies for different gauges of the vector potential. The ground-state energies for all gauges are higher than the gauge-invariant energy at the same field. Finally, the gauge-invariant method is shown to give an
exact solution for the ground-state energy when the field is along a principal axis of the oscillator.

Energy Operator

The energy operator in Eq. (2.3) involves the potential energy $V(\vec{r})$ and the vector potential $\vec{A}$. The potential energy $V(\vec{r})$ for an anisotropic harmonic oscillator with frequencies $\omega_1$, $\omega_2$, and $\omega_3$ is

$$V(\vec{r}) = \frac{m}{2}(\omega_1^2 x_1^2 + \omega_2^2 x_2^2 + \omega_3^2 x_3^2), \quad (3.1)$$

where $\vec{r} = (x_1, x_2, x_3)$ is the displacement.

The magnetic induction field $\vec{B} = (B_1, B_2, B_3)$ is given in terms of the vector potential by

$$\vec{B} = \nabla \times \vec{A}. \quad (3.2)$$

The vector potential $\vec{A} = (A_1, A_2, A_3)$ which describes this constant $\vec{B}$ is chosen to be in the mixed gauge with components

$$A_{i,j} = \left(1 - \frac{\xi_j}{\xi_k}\right) B_j x_k - x_j \frac{\xi_k}{\xi_j} B_k, \quad (3.3)$$

where $(i,j,k)$ are cyclic permutations of $(1,2,3)$, and the gauge parameters ($\xi_1, \xi_2, \xi_3$) are arbitrary real numbers.

If $\xi_1 = \xi_2 = \xi_3 = \xi$, the symmetric gauge is obtained, while if $\xi_1 = \xi_2 = \xi_3 = 0$ or 1, the two Landau gauges are obtained.

The vector potential of Eq. (3.3) satisfies the Coulomb gauge condition $\nabla \cdot \vec{A} = 0$ and thus gives
\[ \overrightarrow{A} \cdot \overrightarrow{p} = \overrightarrow{p} \cdot \overrightarrow{A}. \] (3.4)

When Eq. (3.4) is used, the energy operator of Eq. (2.3) can be written as

\[ H(\overrightarrow{A}) = \frac{p^2}{2m} - \frac{qA \cdot \overrightarrow{p}}{mc} + \frac{q^2A^2}{2mc^2} + V(\overrightarrow{r}). \] (3.5)

When Eqs. (3.1) and (3.3) are substituted into Eq. (3.5), the energy operator for the oscillator is

\[ H(\overrightarrow{A}) = \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} + \frac{iq\hbar}{mc} \left[ (1-\ell_2)B_2 x_3 - x_2 \ell_3 B_3 \right] \frac{\partial}{\partial x_i} \right. \\
+ x_1^2 \left[ \frac{m\omega^2_i}{2} + \frac{q^2}{2mc^2} \left( B_3^2 (1-\ell_3)^2 + \ell_2^2 B_2^2 \right) \right] \\
- x_1 x_2 \left( \frac{q^2}{mc^2} \right) (1-\ell_1) \ell_2 B_2 B_1 \right\} \\
+ \{ \text{cyclic permutations of } 1, 2, 3 \}. \] (3.6)

Standard Variational Treatment

The problems associated with applying the standard Rayleigh-Ritz variational method to systems in magnetic fields are demonstrated here by applying it to the anisotropic harmonic oscillator in a constant magnetic field. Use of a real Gaussian trial wave function is shown to produce gauge-dependent energies and a violation of charge conservation.
Gauge-Dependent Energy Expectation Value

The ground-state energy of the anisotropic oscillator in a constant magnetic field is calculated now using the real normalized Gaussian trial wave function

\[ \Psi = \left( 8 \alpha_1 \alpha_2 \alpha_3 \pi^{-3} \right)^{1/4} e^{\alpha_1 x_1^2 - \alpha_2 x_2^2 - \alpha_3 x_3^2}, \quad (3.7) \]

where \((\alpha_1, \alpha_2, \alpha_3)\) are positive variational parameters.

The expectation value of the energy operator in Eq. (3.6) calculated using \(\Psi\) in Eq. (3.7) is

\[ E(\alpha_1, \alpha_2, \alpha_3) = \langle \Psi | H(\hat{A}) | \Psi \rangle = \left\{ \frac{\hbar^2 \alpha_1}{2m} + \frac{m \omega_0^2}{8 \alpha_1} \right\} \]

\[ + \frac{q^2 B^2}{8mc^2} \left[ \left( \frac{2}{3} - 1 \right)^2 \alpha_2^{-1} + \left( \frac{2}{3} \alpha_3^{-1} \right) \right] \]

\[ + (cyclic \ permutations \ of \ 1, 2, 3), \quad (3.8) \]

where this result is derived in Appendix C. Since the energy in Eq. (3.8) contains the gauge parameters \((\xi_1, \xi_2, \xi_3)\), it is gauge dependent. Equation (3.8) can be minimized with respect to \((\alpha_1, \alpha_2, \alpha_3)\), but the resulting energy is still gauge dependent.

It is apparently not legitimate to minimize Eq. (3.8) with respect to the gauge parameters \((\xi_1, \xi_2, \xi_3)\), since these are fixed parameters in the energy operator \(H(\hat{A})\) and not in the trial wave function. However, this procedure, which was used by Larsen,\(^5\) is justified in Appendix D by means of gauge transformations.
Violation of Charge Conservation

The current density $\vec{J}$ in Eq. (2.4) for the trial wave function in Eq. (3.7) and the vector potential in Eq. (3.3) is

$$\vec{J} = -(q^2/m) \vec{A} \Psi^2. \quad (3.9)$$

The divergence of Eq. (3.9) is

$$\nabla \cdot \vec{J} = \left(\frac{4q^2}{m}\right) \left( A_1 \alpha_1 x_1 + A_2 \alpha_2 x_2 + A_3 \alpha_3 x_3 \right) \Psi^2, \quad (3.10)$$

which does not in general vanish for arbitrary values of the gauge parameters $(\vec{S}_1, \vec{S}_2, \vec{S}_3)$. Since the wave function for a stationary state is time dependent, $\nabla \cdot \vec{J} \neq 0$ implies that charge is not conserved.

Gauge-Invariant Treatment

In this section the gauge-invariant variational method is applied to the anisotropic harmonic oscillator. The trial wave function $\Psi$ is adapted to the gauge of the vector potential using the Rayleigh–Ritz principle. In this method charge is conserved and the energy expectation value is both gauge invariant and lower than the gauge-dependent energy obtained in the previous section.

Improved Trial Wave Function

The improved trial wave function $\Psi'$ is $\Psi' = \exp(iq \vec{A}/\hbar c)$, where $\Psi$ is the normalized Gaussian of Eq. (3.7). The
differential equation for the phase function $\Lambda$ is Eq. (2.20), obtained from the charge conservation condition $\nabla \cdot \mathbf{j}' = 0$.

For the anisotropic oscillator Eq. (2.20) becomes

$$\nabla^2 \Lambda - 4 \left( \alpha_1 x_1 \frac{\partial \Lambda}{\partial x_1} + \alpha_2 x_2 \frac{\partial \Lambda}{\partial x_2} + \alpha_3 x_3 \frac{\partial \Lambda}{\partial x_3} \right)$$

$$= 4 B_1 x_2 x_3 \left[ \frac{5}{3} \alpha_2 + \alpha_3 \left( \frac{3}{3} - 1 \right) \right]$$

$$+ \left( \text{cyclic permutations of } 1, 2, 3 \right), \quad (3.11)$$

where Eqs. (3.3) and (3.10) have been used. In Appendix E a solution of Eq. (3.11) is shown to be

$$\Lambda(\mathbf{r}) = -B_1 x_2 x_3 \left[ \frac{5}{3} \alpha_2 + \left( \frac{3}{3} - 1 \right) \alpha_3 \right] / (\alpha_2 + \alpha_3)$$

$$+ \left( \text{cyclic permutations of } 1, 2, 3 \right). \quad (3.12)$$

When this function is used in Eq. (2.10), $\Psi'$ satisfies the charge conservation condition in Eq. (2.18).

**Gauge-Invariant Energy Expectation Value**

The energy expectation value of the anisotropic oscillator calculated using the improved trial wave function derived in Appendix E is

$$E'(\alpha_1, \alpha_2, \alpha_3) = \langle \Psi' | H(\mathbf{A}) | \Psi' \rangle = \int \frac{\hbar^2}{2m} \alpha_i + \frac{m \omega_i^2}{8 \alpha_i}$$

$$+ \left( \frac{q^2 B_i^2}{8 mc^2 (\alpha_2 + \alpha_3)} \right) + \left( \text{cyclic permutations of } 1, 2, 3 \right), \quad (3.13)$$
where this result is derived in Appendix F. This energy is independent of the gauge parameters \((\mathbf{f}_1, \mathbf{f}_2, \mathbf{f}_3)\) and is therefore gauge invariant. For fixed values of \((\alpha_1, \alpha_2, \alpha_3)\) the energy \(E'\) in Eq. (3.13) is less than or equal to the energy \(E\) in Eq. (3.8). The difference in energies is

\[
E(\alpha_1, \alpha_2, \alpha_3) - E'(\alpha_1, \alpha_2, \alpha_3) = \frac{q^2 B_i^2 [\alpha_3 (\mathbf{f}_1 - 1) + \alpha_2 \mathbf{f}_1]^2}{8 m c^2 \alpha_2 \alpha_3 (\alpha_2 + \alpha_3)}
\]

\(+ (\text{cyclic permutations of } 1, 2, 3) \geq 0, \tag{3.14}\)

since \((\alpha_1, \alpha_2, \alpha_3)\) in Eq. (3.7) must be positive. Equality in Eq. (3.14) holds if \(\mathbf{f}_1 = \alpha_3 / (\alpha_2 + \alpha_3)\), with similar expressions for \(\mathbf{f}_2\) and \(\mathbf{f}_3\) obtained by cyclic permutation.

This gauge condition is the one for which Eqs. (3.10) and (3.12) vanish, which means that the vector potential is adapted to the real trial wave function of Eq. (3.7). Since the gauge invariance of the procedure is being emphasized here, any arbitrary gauge for the vector potential is permitted and the trial wave function is adapted to it. In this method the same energy \(E'\) is obtained in any gauge, and \(E'\) is always less than or equal to \(E\) by Eq. (3.14).

Energy Minimization

In order to find the minimum ground-state energy obtained from the wave function \(\Psi'\) in Eq. (2.10) it is necessary to minimize \(E'(\alpha_1, \alpha_2, \alpha_3)\) in Eq. (3.13) with respect to \(\alpha_i\) \((i = 1, 2, 3)\). If Eq. (3.13) is differentiated with
respect to $\alpha_1$ and set equal to zero, the first equation of minimization is obtained:

$$
\frac{\partial E'}{\partial \alpha_1} = \frac{\hbar^2}{2m} - \frac{m \omega_i^3}{8 \alpha_1^3} - \frac{q^2}{8mc^2} \left[ \frac{B_i^2}{(\alpha_1 + \alpha_3)^2} + \frac{B_2^2}{(\alpha_1 + \alpha_2)^2} \right] = 0.
$$

(3.15)

The other equations, $\frac{\partial E'}{\partial \alpha_2} = 0$ and $\frac{\partial E'}{\partial \alpha_3} = 0$, are obtained from Eq. (3.15) by cyclic permutation of $(1, 2, 3)$. These three equations are coupled in a complicated manner. Although an analytical solution cannot be obtained in the general case, the energy can be numerically minimized using a computer.

**Dimensionless Units**

Numerical computations are more conveniently made in dimensionless units. Thus, the energy and length are expressed in dimensionless units.\textsuperscript{22,23} First, however, it is necessary to define some constants of the system.

The effective Larmor frequency is defined as

$$
\omega_L = \frac{|q|B}{2mc},
$$

(3.16)

the effective Bohr radius is

$$
\alpha_0 = \frac{\hbar^2}{mc^2},
$$

(3.17)

and the effective Rydberg is
where Gaussian units have been used.\textsuperscript{3,41} The dimensionless constants $J_i (i = 1, 2, 3)$ are defined as

$$J_i = \omega_i / \omega_L.$$  

(3.19)

A dimensionless magnetic field parameter is

$$\gamma = \hbar \omega_L / R,$$  

(3.20)

where $\gamma$ is proportional to the field magnitude $B$ and thus gives a measure of the field strength.\textsuperscript{5} The uniform magnetic field is applied at a polar angle $\theta$ with respect to the $x_3$-axis and at an azimuthal angle $\varphi$ with respect to the $x_1$-axis. The field components may be written

$$B_i = BC_i, \quad (i = 1, 2, 3),$$  

(3.21)

where

$$C_1 = \sin \theta \cos \varphi,$$  

(3.22)

$$C_2 = \sin \theta \sin \varphi,$$  

(3.23)

and

$$C_3 = \cos \theta.$$  

(3.24)

When the variational parameters are expressed in units of $1/\alpha_o^2$ and the constants defined above are used in Eq. (3.13), the dimensionless gauge-invariant energy expectation value is

$$\mathcal{R} = \frac{\hbar^2}{2m \alpha_o^2} = \frac{m q^+}{2 \hbar^2},$$  

(3.18)
\[ E' = \left\{ \alpha_i + \frac{\gamma^2 J_i^2}{16 \alpha_i} + \frac{\gamma^2 C_i^2}{4(\alpha_2 + \alpha_3)} \right\} \]

\[ + (\text{cyclic permutations of } 1, 2, 3), \]  \( (3.25) \)

where energy is in units of the effective Rydberg \( \mathcal{R} \) and length is in units of the effective Bohr radius \( a_o \). The dimensionless form of the gauge-dependent energy expectation value in Eq. (3.8) is

\[ E = \left\{ \alpha_i + \frac{\gamma^2 J_i^2}{16 \alpha_i} + \frac{\gamma^2 C_i^2}{4 \left( \frac{(J_i - 1)^2}{\alpha_2} + \frac{J_i^2}{\alpha_3} \right)} \right\} \]

\[ + (\text{cyclic permutations of } 1, 2, 3). \]  \( (3.26) \)

**Variational Ground-State Energy**

Numerical computations were made for the anisotropic oscillator whose frequencies give \( J_1 = 1.0, J_2 = 10.0, \) and \( J_3 = 2.0. \) The magnetic field was chosen such that \( \gamma = 1.0, \mathcal{R} = \frac{h}{e} \omega_l, \) and \( \phi = 45^\circ. \) The variational ground-state energy was then computed for angle \( \Theta \) varying from 0 to 90 degrees. Energies were computed from the gauge-invariant energy expectation value in Eq. (3.25) and from the gauge-dependent energy expectation value in Eq. (3.26) for the symmetric gauge \( (\tilde{J}_1 = \tilde{J}_2 = \tilde{J}_3 = 1) \) and for the Landau gauges \( (\tilde{J}_1 = \tilde{J}_2 = \tilde{J}_3 = 1 \text{ or } 0). \) Equations (3.25) and (3.26) were numerically minimized with respect to the variational parameters \( (\alpha_1, \alpha_2, \alpha_3) \) using the standard
FORTRAN subroutine FMFP\textsuperscript{42} from the IBM System/360 Scientific Subroutine Package. Subroutine FMFP is described in Appendix G.

The variational ground-state energies of the anisotropic harmonic oscillator are listed in Table I and plotted in Fig. 1 as a function of angle $\theta$. The gauge-dependent ground-state energy is a different function of $\theta$ for each choice of the gauge of the vector potential. The ground-state energy for each gauge is higher than the gauge-invariant energy at the same field angle.

Although the energy cannot be minimized analytically in the general case, an analytical solution can be obtained in the special case where the field lies along a principal axis.

Magnetic Field Along a Principal Axis

The special case of the anisotropic oscillator with the magnetic field along the z-axis is considered in this section. The equations of minimization are solved analytically to obtain the minimum ground-state energy. This ground-state energy and the corresponding ground-state wave function are exact.

**Minimum Ground-State Energy**

If the magnetic field lies only along the z-axis, $\hat{B} = (0,0,B_z)$, the energy expectation value $E'$ of Eq. (3.13) reduces to
\[ E' (\alpha_1, \alpha_2, \alpha_3) = \frac{q^2 B_3^2}{8 m c^2 (\alpha_1 + \alpha_2)} + \left\{ \frac{\hbar^2 \alpha_1}{2 m} + \frac{m \omega_3^2}{8 \alpha_1} \right\} + \text{(cyclic permutations of 1, 2, 3)}. \] (3.27)

If Eq. (3.27) is minimized with respect to \( \alpha_3 \), the result is
\[ \frac{\partial E'}{\partial \alpha_3} = \left( \frac{\hbar^2}{2 m} \right) - \left( \frac{m \omega_3^2}{8 \alpha_3^2} \right) = 0, \] (3.28)
the solution of which is
\[ \alpha_3 = \frac{m \omega_3}{2 \hbar}. \] (3.29)

If Eq. (3.27) is minimized with respect to \( \alpha_1 \), the result is
\[ \frac{\partial E'}{\partial \alpha_1} = \frac{\hbar^2}{2 m} - \frac{m \omega_1^2}{8 \alpha_1^2} - \frac{q^2 B_3^2}{8 m c^2 (\alpha_1 + \alpha_2)^2} = 0. \] (3.30)

The equation for \( \frac{\partial E'}{\partial \alpha_2} = 0 \) is the same as Eq. (3.30) but with 1 and 2 interchanged. If these two equations are solved simultaneously, then
\[ \alpha_1 = \left( \frac{m \omega_1}{2 \hbar} \right) \left[ 1 + 4 \frac{\omega_2^2}{(\omega_1 + \omega_2)^2} \right]^{1/2}, \] (3.31)
and \( \alpha_2 \) is Eq. (3.31) with 1 and 2 interchanged. The Larmor frequency \( \omega_L \) in Eq. (3.31) is defined as
\[ \omega_L = \frac{|q| B_3}{2 mc}. \] (3.32)

If the values for \( (\alpha_1, \alpha_2, \alpha_3) \) in Eqs. (3.29) and (3.31) which minimize the energy are used in \( E' (\alpha_1, \alpha_2, \alpha_3) \) in Eq. (3.27), the minimum energy is
\[ E_{\text{min}}' = \left( \frac{\hbar}{2} \right)(\omega_1' + \omega_2' + \omega_3'), \quad (3.33) \]

where the field-shifted angular frequencies \( \omega_1' \) and \( \omega_2' \) are
\[ \frac{\omega_1'}{\omega_1} = \frac{\omega_2'}{\omega_2} = \left[ 1 + 4 \frac{\omega_e^2}{(\omega_1 + \omega_2)^2} \right]^{1/2}. \quad (3.34) \]

The minimum energy in Eq. (3.33) is of the same form as the exact ground-state energy for a free harmonic oscillator of frequencies \( \omega_1', \omega_2', \) and \( \omega_3'. \)

**Exact Ground-State Energy**

If the initial trial wave function of Eq. (3.7) differs from the exact ground-state wave function only by a phase factor, then the exact ground-state energy would be obtained. The wave function \( \Psi' \) in Eq. (2.10) with \( \Psi \) given by Eq. (3.7), \( \Lambda \) given by Eq. (3.12), and the energy minimizing values of \( \{ \alpha_1, \alpha_2, \alpha_3 \} \) given by Eqs. (3.29) and (3.31), is

\[ \Psi' = \left( \frac{m^3 \omega_1' \omega_2' \omega_3}{\pi^3 \hbar^3} \right)^{1/4} \]
\[ \times \exp \left\{ i \left( 2 m \omega_l / \hbar \right) \left[ \omega_1' \hat{S}_3 + \omega_2' \left( \hat{S}_3 - 1 \right) \right] \left( \omega_1' + \omega_2' \right)^{-1} x_1 x_2 \right\} \]
\[ \times \exp \left\{ - \left( m / 2 \hbar \right) \left[ \omega_1' x_1^2 + \omega_2' x_2^2 + \omega_3 x_3^2 \right] \right\}. \quad (3.35) \]

When \( B_1 = B_2 = 0, \) the vector potential in Eq. (3.3) becomes
\[ \vec{A} = (-\hat{S}_3 B_3 x_2, (1-\hat{S}_3) B_3 x_1, 0), \quad (3.36) \]
so that \( \vec{B} = \nabla \times \vec{A} = (0,0,B_3). \) The energy operator is the operator \( H(\vec{A}) \) in Eq. (3.6) with \( B_1 = B_2 = 0. \) When it acts on Eq. (3.35), an eigenvalue equation is obtained:
Equation (3.37) shows that \( \Psi' \) in Eq. (3.35) is the exact ground-state wave function for use with the vector potential in Eq. (3.36). The energy \( E'_{\text{min}} \) of Eq. (3.33) is the exact ground-state energy and is gauge invariant. The exact ground-state energy in Eq. (3.37) was obtained recently by Bergou and Ehlotsky\(^{43} \) in connection with a more general problem. The gauge-invariant variational procedure does not usually provide an exact solution. An exact solution is obtained in this case because the initial trial wave function chosen happened to be gauge-equivalent to the exact ground-state wave function.

In the next chapter the gauge-invariant variational method is applied to a real anisotropic system: shallow donors in anisotropic semiconductors in a high static magnetic field.
CHAPTER IV

ANISOTROPIC SHALLOW DONORS IN A UNIFORM STRONG MAGNETIC FIELD

The gauge-invariant variational method is applied in this chapter to an electron bound to a donor impurity in an anisotropic semiconductor when a uniform strong magnetic field is present. After a brief description of the system, the Hamiltonian is obtained for an arbitrary gauge and expressed in dimensionless units. The charge conservation equation for the anisotropic electron is derived. The equation is solved for the phase function when a normalized Gaussian trial wave function, valid at high magnetic fields, is used. The resulting improved trial wave function is then used to derive the gauge-invariant energy expectation value.

Donor Impurity in a Uniform Magnetic Field

The system consists of a conduction electron bound to a donor impurity (shallow donor) in a semiconductor with an anisotropic conduction band. The impurity concentration is assumed to be sufficiently low that each impurity site can be treated as an isolated center. Then, within the effective mass approximation, the effective interaction potential between the conduction electron and the central ion of the impurity atom is taken to be Coulombic in nature. The validity of the effective mass approximation depends on
having the interaction potential slowly varying over the dimensions of a unit cell, so the effective Bohr radius of the system must be large compared to the lattice constant.\textsuperscript{45} Variational calculations for impurities in this approximation have been made for the case where there is no external field\textsuperscript{44,46-48} and for the ground and excited states of isotropic shallow donors in high magnetic fields.\textsuperscript{24,25} For maximum generality the formalism is developed here for a completely anisotropic semiconductor where the dielectric anisotropy is given by a diagonal dielectric tensor and the effective mass of the bound electron is also a diagonal tensor.\textsuperscript{49}

A Cartesian coordinate system \((x_1,x_2,x_3)\) which diagonalizes the dielectric and effective mass tensors is chosen.\textsuperscript{50} A uniform strong magnetic field is applied at an angle \(\theta\) to the \(x_3\)-axis and at an azimuthal angle \(\phi\) measured from the \(x_1\)-axis. The field components are thus those given by Eqs. (3.21) - (3.24). The field \(\vec{B}\) is given by the curl of a vector potential \(\vec{A}\). For generality and to demonstrate the gauge invariance of the method, the mixed gauge defined in Eq. (3.3) is used.

**Hamiltonian**

For the shallow donor system, the minimally coupled Hamiltonian in Gaussian units is\textsuperscript{30}
\[ H(\vec{r}) = \sum_{i=1}^{3} \left\{ \frac{1}{2 m_i} \left[ -i \hbar \frac{\partial}{\partial x_i} + \frac{e}{c} A_i(\vec{r}) \right]^2 \right\} - \frac{\epsilon^2}{(K_1 K_2 K_3)^{1/2} \left[ \left( \frac{X_1^2}{K_1} \right) + \left( \frac{X_2^2}{K_2} \right) + \left( \frac{X_3^2}{K_3} \right) \right]^{1/2}}, \]  

(4.1)

where \( \vec{r} = (x_1, x_2, x_3) \) is the displacement vector of the electron from the ionic center, \( A_i \) (i = 1, 2, 3) are the components of the vector potential, and \( -e \) is the electronic charge. The elements of the diagonal electron effective mass tensor are \( m_i \), and \( K_i = \epsilon_i / \epsilon_0 \) are the elements of the diagonal dielectric tensor \( \epsilon \) divided by the permittivity of free space \( \epsilon_0 \). The Coulomb potential energy term in Eq. (4.1) is derived in Appendix H using Poisson's equation. The Schrödinger equation for the system is

\[ H(\vec{r}) \psi(\vec{r}) = \mathcal{E} \psi(\vec{r}), \]  

(4.2)

where \( \psi(\vec{r}) \) is the electron wave function and \( \mathcal{E} \) is the energy.

**Dimensionless Units**

The energy expectation value of this system is too complicated to minimize analytically. Once again, for convenience in numerical computation, a conversion is made to dimensionless units.
The effective Larmor frequency $\omega_L$, the effective Bohr radius $a_o$, and the effective Rydberg $R$ for the anisotropic shallow donor are defined in Gaussian units as \cite{22,23}

$$\omega_L = eB/(2mc), \quad (4.3)$$

$$a_o = (K_k^2/m e^2), \quad (4.4)$$

and

$$R = \frac{\hbar^2}{2ma_o^2} = \frac{me^4}{2\hbar^2K^2}, \quad (4.5)$$

respectively, where

$$m = (m_1 m_2 m_3)^{1/3}, \quad (4.6)$$

and

$$K = (K_1 K_2 K_3)^{1/3}. \quad (4.7)$$

The dimensionless constants $J_i$ are

$$J_i = m/m_i, \quad (i = 1, 2, 3), \quad (4.8)$$

and the field parameter $\chi$ is

$$\chi = c\omega_L/R. \quad (4.9)$$

Finally, the field components may be written as in Eq. (3.21), where $C_i (i = 1, 2, 3)$ are given by Eqs. (3.22) - (3.24).

In Appendix I the constants defined above and the mixed gauge of Eq. (3.3) are used to obtain the dimensionless Hamiltonian
\[ H(\vec{r}) = \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} + 2i \gamma (Y_1 x_2 + Y'_1 x_3) \frac{\partial}{\partial x_i} ight. \\
+ \gamma^2 (Y_{12} x_3^2 + Y'_{12} x_1 x_2) \right\} - \frac{2}{K^{\nu_2} \left[ (x_1^2/K_1) + (x_2^2/K_2) + (x_3^2/K_3) \right]^{\nu_2}}, \] (4.10)

where energy is in units of the effective Rydberg \( R \) and length is in units of the effective Bohr radius \( a_0 \). The dimensionless functions \( Y_1, Y'_1, Y_{12}, \) and \( Y'_{12} \) are defined to be

\[ Y_1 = \mathfrak{f}_1 \mathfrak{f}_3 C_3, \] (4.11)
\[ Y'_1 = \mathfrak{f}_1 (\mathfrak{f}_2 - 1) C_2, \] (4.12)
\[ Y_{12} = \mathfrak{f}_1 (1 - \mathfrak{f}_2)^2 C_2^2 + \mathfrak{f}_2 \mathfrak{f}_3^2 C_1^2, \] (4.13)

and

\[ Y'_{12} = 2 \mathfrak{f}_3 \mathfrak{f}_2 (\mathfrak{f}_1 - 1) C_1 C_2. \] (4.14)

where each of these equations gives two others through cyclic permutation of \( (1, 2, 3) \).

Improved Trial Wave Function

In this section an initial trial wave function \( \Psi(\vec{r}) \) is chosen which is valid at high magnetic fields. The charge conservation equation for the anisotropic electron is derived and then solved for the corresponding phase factor. The
resulting improved trial wave function \( \Psi'(\mathbf{r}) \) is then expressed in dimensionless units.

**High Field Trial Wave Function**

The system is considered in the high field limit where the field is sufficiently strong to make the field parameter \( \mathcal{Y} \geq 1 \). Since this system is hydrogen-like, a choice of trial wave function can be motivated by examining the case of the hydrogen atom in a high magnetic field.\(^3,4,27\) 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\(^3,4,51\) and hydrogenic systems such as electron-hole pairs (excitons)\(^23\) in high magnetic fields. The three-dimensional normalized Gaussian wave function given in Eq. (3.7) is therefore taken as the initial trial wave function \( \Psi(\mathbf{r}) \), where once again \( (\alpha_1, \alpha_2, \alpha_3) \) are positive variational parameters.

**Charge Conservation Equation for the Anisotropic Electron**

The charge conservation equation given in Eq. (2.20) applies to a single isotropic charged particle in a magnetic
field where the current density $\vec{J}$ is given by Eq. (2.6).

The Hamiltonian of Eq. (4.1) and the improved trial wave function

$$\Psi'(\vec{r}) = \exp\{-i e \Lambda / \hbar c\} \Psi(\vec{r})$$

(4.15)

are used in Eqs. (2.12) and (2.13). The minimization of the energy expectation value gives the charge conservation equation

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

(4.16)

where the current density $\vec{J}'$ for the anisotropic electron is

$$\vec{J}' = \text{Re} \left\{ \Psi' \sum_{i=1}^{3} \frac{e}{m_i} \left( p_i + \frac{e}{c} A_i(\vec{r}) \right) \hat{X}_i \Psi' \right\}.$$

(4.17)

This result is derived in Appendix J. Equations (4.16) and (4.17) give the differential equation for the minimizing $\Lambda$

$$\sum_{i=1}^{3} \int \left[ \frac{\partial^2 \Lambda}{\partial x_i^2} + \left( \frac{\partial \rho}{\partial \rho} \right) \frac{\partial \Lambda}{\partial x_i} \right] = \frac{mc}{e} \left[ \frac{\nabla \cdot \vec{J}}{\rho} \right],$$

(4.18)

where $\partial_i = \partial / \partial x_i$, $(i = 1, 2, 3)$, and the charge density

$$\rho(\vec{r}) = -e |\Psi(\vec{r})|^2.$$ 

Equation (4.18) is solved in Appendix J for $\Lambda$ with the trial wave function $\Psi(\vec{r})$ given by Eq. (3.7).

The minimizing phase function

$$\Lambda = -B x_1 x_2 (\alpha_1 \gamma_1 + \alpha_2 \gamma_2') / (\int_1 \alpha_1 + \int_2 \alpha_2)$$

$$+ (\text{cyclic permutations of } 1, 2, 3)$$

(4.19)
is obtained, where the functions \((Y_1, Y_2, Y_3)\) and \((Y'_1, Y'_2, Y'_3)\) are given by cyclic permutation of \((1, 2, 3)\) in Eqs. (4.11) and (4.12). The dimensionless form of the improved trial wave function, also derived in Appendix J, is

\[
\Psi'(\vec{r}) = \exp \left\{ i \left( g_1 x_1 x_2 + g_2 x_2 x_3 + g_3 x_3 x_1 \right) \right\} \Psi(\vec{r}), \tag{4.20}
\]

where lengths are in units of Bohr radii. The dimensionless function \(g_1\) is

\[
g_1 = \frac{y \left( \alpha_1 Y_1 + \alpha_2 Y'_2 \right)}{\left( \Sigma_1 \alpha_1 + \Sigma_2 \alpha_2 \right)}, \tag{4.21}
\]

where \(g_2\) and \(g_3\) are obtained by cyclic permutation of \((1, 2, 3)\) in Eq. (4.21).

**Gauge-Invariant Energy Expectation Value**

The gauge-invariant energy expectation value is derived in Appendix K using the dimensionless Hamiltonian and improved trial wave function given in Eqs. (4.10) and (4.20), respectively. The trial wave function \(\Psi(\vec{r})\) in Eq. (4.20) is the normalized Gaussian of Eq. (3.7). All the integrals in the energy expectation value can be evaluated analytically except for the potential energy integral. The three-dimensional potential energy integral is partially integrated in Appendix L. When spherical polar coordinates are used, it can be reduced to a one-dimensional elliptical integral.
From Eqs. (K18) and (L23) the gauge-invariant energy expectation value is

\[ E' = \left\{ \int \alpha_i \right\} + \frac{\chi^2 C_i}{4 \left( \alpha_2 \gamma_2 + \alpha_3 \gamma_3 \right)} + \left( \text{cyclic permutations of } 1, 2, 3 \right) \]

\[ - \left[ \frac{32 \alpha_3}{\pi \theta_3} \right]^{1/2} \int_0^1 \frac{du}{\left[ u'' u^4 + b'' u^2 + 1 \right]^{1/2}} \],

(4.22)

where

\[ a'' = \frac{\alpha_3 \theta_1 \theta_2}{\alpha_2 \alpha_1 \theta_3^2} - \frac{\alpha_3 \theta_1 \theta_2 (\alpha_2 \theta_2^{-1} + \alpha_1 \theta_1^{-1})}{\alpha_1 \alpha_2 \theta_3} + 1 \],

(4.23)

\[ b'' = \frac{\alpha_3 \theta_1 \theta_2 (\alpha_2 \theta_2^{-1} + \alpha_1 \theta_1^{-1})}{\alpha_1 \alpha_2 \theta_3} - 2 \],

(4.24)

\[ \theta_i = K/K_i \quad (i = 1, 2, 3) \],

(4.25)

and \( \gamma_i (i = 1, 2, 3) \) are given by Eq. (4.8). The energy expectation value \( E' \) is the sum of a positive kinetic energy, a positive diamagnetic energy shift, and a negative Coulomb potential energy. The diamagnetic term is proportional to \( \chi^2 \) and thus is quadratic in the field magnitude \( B \).\(^{52}\)

In the next chapter the theory is applied to another hydrogenic system, electron-hole pairs (excitons) in anisotropic semiconductors in high magnetic fields.
CHAPTER V
ANISOTROPIC EXCITONS IN A UNIFORM STRONG MAGNETIC FIELD

The gauge-invariant variational method is applied in this chapter to 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. The single-particle effective charge conservation equation for anisotropic excitons is derived. The equation is solved for the phase function when the high field trial wave function given by Eq. (3.7) is used. The resulting improved trial wave function is then used to derive the gauge-invariant energy expectation value. For purposes of comparison, a gauge-dependent energy expectation value is also derived.

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.18 Once again, the validity of the effective mass approximation
depends on having the interaction potential slowly varying over the dimensions of a unit cell, so the exciton dimension must be large compared to the lattice constant. The Wannier exciton may be pictured as an electron in a conduction band bound to a hole in a valence band.\textsuperscript{45} The valence bands of the semiconductor are assumed to be nondegenerate in the magnetic field, when spin effects are neglected.\textsuperscript{27} For non-degenerate valence bands a simple two-band model may be used.\textsuperscript{22} 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.\textsuperscript{49}

The energy spectrum of the Wannier exciton in high magnetic fields has been computed for both isotropic\textsuperscript{28,29} and axially anisotropic\textsuperscript{23,30} semiconductors. The perturbative-adiabatic method of Elliott and Loudon,\textsuperscript{29} where the Coulomb attraction is neglected in the plane perpendicular to the field, has been widely used. For axially anisotropic semiconductors, almost all calculations have been for fields parallel to the crystal axis. In this chapter the energy expectation value is obtained for excitons in totally anisotropic semiconductors when the field is at an arbitrary orientation and the Coulomb attraction is not neglected in the plane perpendicular to the field.

A Cartesian coordinate system \((x_1, x_2, x_3)\) which diagonalizes the dielectric and effective mass tensors is chosen.\textsuperscript{50}
A uniform strong magnetic field is applied at an angle $\theta$ to the $x_3$-axis and at an azimuthal angle $\varphi$ measured from the $x_1$-axis. The field components are again given by Eqs. (3.21) - (3.24), and the vector potential $\vec{A}$ whose curl gives the magnetic field $\vec{B}$ is again written in the mixed gauge defined in Eq. (3.3).

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\(^{30}\)

\[
\hat{H}(\vec{r}_e, \vec{r}_h) = \sum_{i=1}^{3} \left\{ \frac{1}{2 m_{e_i}} \left[ -i \hbar \frac{\partial}{\partial x_{e_i}} + \frac{e}{c} A_i(\vec{r}_e) \right]^2 
+ \frac{1}{2 m_{h_i}} \left[ -i \hbar \frac{\partial}{\partial x_{h_i}} - \frac{e}{c} A_i(\vec{r}_h) \right]^2 \right\} 
- \frac{e^2}{(K_1 K_2 K_3)^{1/2} \left[ \frac{(x_{e_1} - x_{h_1})^2}{K_1} + \frac{(x_{e_2} - x_{h_2})^2}{K_2} + \frac{(x_{e_3} - x_{h_3})^2}{K_3} \right]^{1/2}}, \tag{5.1}
\]

where $\vec{r}_e = (x_{e_1}, x_{e_2}, x_{e_3})$ and $\vec{r}_h = (x_{h_1}, x_{h_2}, x_{h_3})$ 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 $m_{e_i}$ and $m_{h_i}$.
respectively, and $\kappa_i = \varepsilon_i / \varepsilon_0$ are the elements of the diagonal dielectric tensor $\varepsilon$ divided by the permittivity of free space $\varepsilon_0$. The Coulomb potential energy term in Eq. (5.1) is the same as that for the shallow donor system in Eq. (4.1). 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. 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

$$H(F_e, r_h) \overline{\Phi}(\vec{r}_e, \vec{r}_h) = \varepsilon \overline{\Phi}(\vec{r}_e, \vec{r}_h).$$

(5.2)

The envelope function $\overline{\Phi}(\vec{r}_e, \vec{r}_h)$ describes the electron and hole motion on a scale large compared to atomic dimensions. In this case the fundamental states are crystal band states in which the electron moves freely in an average potential with the symmetry of the lattice.

**Separation of the Center-of-Mass and Relative Motions**

The motion of the exciton can be expressed in relative coordinates

$$\vec{r} = \vec{r}_e - \vec{r}_h = (X_1, X_2, X_3),$$

(5.3)

and in center-of-mass coordinates
\[ \vec{R} \equiv (X_1, X_2, X_3) , \quad (5.4) \]

where
\[ X_i = \frac{m_{ei} X_{ei} + m_{hi} X_{hi}}{m_{ei} + m_{hi}} , \quad (i = 1, 2, 3) . \quad (5.5) \]

If the chain rule and Eqs. (5.3) and (5.5) are used, the derivative operators in electron and hole coordinates can be expressed in terms of derivatives in relative and center-of-mass coordinates as

\[ \frac{\partial}{\partial X_{ei}} = m_{ei}' \frac{\partial}{\partial X_i} + \frac{\partial}{\partial X_i} , \quad (5.6) \]

and

\[ \frac{\partial}{\partial X_{hi}} = m_{hi}' \frac{\partial}{\partial X_i} - \frac{\partial}{\partial X_i} , \quad (5.7) \]

where
\[ m_{ei}' = m_{ei} / (m_{ei} + m_{hi}) \quad (5.8) \]

and
\[ m_{hi}' = m_{hi} / (m_{ei} + m_{hi}) . \quad (5.9) \]

In Appendix M the vector potentials in electron and hole coordinates are written in relative and center-of-mass coordinates as

\[ A_i(\vec{r}_e) = A_i(\vec{a}_i \cdot \vec{r}) + A_i(\vec{R}) \quad (5.10) \]

and
\[ A_i(\vec{r}_h) = A_i(\vec{a}_2 \cdot \vec{R}) + A_i(\vec{R}), \]  \hspace{1cm} (5.11)

where the form of Eqs. (5.10) and (5.11) is simplified by using the dyads

\[ \vec{a}_1 = \begin{pmatrix} m'_{h1} & 0 \\ 0 & m'_{h2} \\ 0 & m'_{h3} \end{pmatrix} \]  \hspace{1cm} (5.12)

and

\[ \vec{a}_2 = \begin{pmatrix} -m'_{e1} & 0 \\ 0 & -m'_{e2} \\ 0 & -m'_{e3} \end{pmatrix} \]  \hspace{1cm} (5.13)

to express the first term in weighted relative coordinates.

If Eqs. (5.6), (5.7), (5.10), and (5.11) are used in Eq. (5.1), then the relative and center-of-mass 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. An approximate separation may be achieved, however, if the center-of-mass motion is small compared to the relative motion. In this case Eq. (5.2) can be transformed into a one-particle (quasiparticle) Schrödinger equation for the relative motion in terms of reduced effective masses.

**Single-Particle Effective Hamiltonian in Relative Coordinates**

Lamb, in his pioneering work on the hydrogen atom in a magnetic field, noted that terms in the Schrödinger equation containing the vector potential at the center-of-
mass $\tilde{A}(\vec{R})$ could be removed by the use of a wave function of the form

$$\Phi(\vec{r}_e, \vec{r}_h) = \exp \left[-ie\tilde{A}(\vec{R}) \cdot \vec{r} / \hbar c \right] F(\vec{R}, \vec{r}). \quad (5.14)$$

A similar result was obtained by Palmer and Taylor for the hydrogen atom in a magnetic field. Use of such a wave function requires a unitary transformation on the Hamiltonian with the unitary operator

$$U = \exp \left[ i e \tilde{A}(\vec{R}) \cdot \vec{r} / \hbar c \right]. \quad (5.15)$$

Equation (5.15) is a form of the Power-Zienau-Wooley transformation, but in this case it is not a gauge transformation since it cannot be written in the form

$$\exp \left\{ i \left[ -e \tilde{A}(\vec{r}_e) + e \tilde{A}(\vec{r}_h) \right] / \hbar c \right\} .$$

When a unitary transformation is made on Eq. (5.2) using the operator $U$ defined in Eq. (5.15) and the envelope function defined in Eq. (5.14), the result is

$$\left[ U H(\vec{r}_e, \vec{r}_h) U^\dagger \right] F(\vec{R}, \vec{r}) = \mathcal{E} F(\vec{R}, \vec{r}). \quad (5.16)$$

This partially decoupled Schrödinger equation is shown in Appendix M to be

$$\sum_{i=1}^3 \left\{ -\frac{\hbar^2}{2} \left[ \frac{1}{M_i} \frac{\partial^2}{\partial X_i^2} + \frac{1}{\mu_i} \frac{\partial^2}{\partial x_i^2} \right] - \frac{ie\hbar}{c} \left[ \frac{G_{\text{ei}}(\vec{r}) + G_{\text{hi}}(\vec{r})}{M_i} \frac{\partial}{\partial X_i} \right] \right. + \left. \left( \frac{G_{\text{ei}}(\vec{r}) - G_{\text{hi}}(\vec{r})}{m_{\text{ei}}} \frac{\partial}{\partial x_i} \right) + \frac{\epsilon^2}{2c^2} \left[ \frac{G_{\text{ei}}(\vec{r})}{m_{\text{ei}}} + \frac{G_{\text{hi}}(\vec{r})}{m_{\text{hi}}} \right] \right\} F(\vec{R}, \vec{r})$$

$$+ V(\vec{r}) F(\vec{R}, \vec{r}) = \mathcal{E} F(\vec{R}, \vec{r}), \quad (5.17)$$
where

\[ G_{e_i}(\vec{r}) = A_i(\vec{a}_i \cdot \vec{r}) + m'_{e_i} \left[ (\vec{B} \times \vec{r})_i - A_i(\vec{r}) \right], \tag{5.18} \]

\[ G_{h_i}(\vec{r}) = -A_i(\vec{a}_i \cdot \vec{r}) + m'_{h_i} \left[ (\vec{B} \times \vec{r})_i - A_i(\vec{r}) \right], \tag{5.19} \]

and the potential energy is

\[ \sqrt{\vec{r}} = \frac{-\mathbf{e}^2}{(K_1K_2K_3)^{1/2} \left[ (x_1^2/K_1) + (x_2^2/K_2) + (x_3^2/K_3) \right]^{1/2}}. \tag{5.20} \]

The reduced effective masses \( \mu_i \) and total effective masses \( M_i \) are defined to be

\[ \mu_i = m_{e_i} + m_{h_i} \tag{5.21} \]

and

\[ M_i = m_{e_i} + m_{h_i}. \tag{5.22} \]

All terms containing components of \( \vec{A}(\vec{r}) \) have been removed from Eq. (5.17). This partial decoupling of relative and center-of-mass components can be achieved for any values of the gauge parameters \( (\tilde{\xi}_1, \tilde{\xi}_2, \tilde{\xi}_3) \).

If the center-of-mass motion is assumed to be a plane wave, then the decoupling may be completed by using \( 45, 54, 55 \)

\[ F(\vec{R}, \vec{r}) = \exp \left[ i \vec{k} \cdot \vec{R} \right] \psi(\vec{r}), \tag{5.23} \]

where \( \vec{k} \) is the exciton wave vector and \( \psi(\tilde{\xi}) \) is the envelope function \( 22, 23 \) for the relative motion. Use of Eq. (5.23) transforms Eq. (5.17) into
Terms with $k_i^2$ are the kinetic energy associated with the center-of-mass motion and terms with $k_i$ give the coupling between center-of-mass and relative motions in the field. It is commonly assumed that the center-of-mass of the exciton is at rest ($k = 0$) and calculations made in this approximation give satisfactory results when compared to experimental data. Therefore, the energy associated with the center-of-mass motion is small compared to the energy associated with the relative motion. When the center-of-mass terms are neglected, the single-particle effective Schrödinger equation for the relative motion is

$$
\sum_{i=1}^{3} \left\{ \frac{-\hbar^2}{2 \mu_i} \frac{\partial^2}{\partial x_i^2} - \frac{i e \hbar}{c} \left[ \frac{G_{e_i}}{m_{e_i}} - \frac{G_{hi}}{m_{hi}} \right] \frac{\partial}{\partial x_i} + \frac{e^2}{2 c^2} \left[ \frac{G_{e_i}^2}{m_{e_i}} + \frac{G_{hi}^2}{m_{hi}} \right] \right\} \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}). \tag{5.25}
$$

Equation (5.25) is the sum of the kinetic energy of the quasiparticle for relative motion in the absence of the field, a linear Zeeman term which gives coupling between the orbital
angular momentum and the field, a diamagnetic energy term, and a potential energy term arising from the Coulomb inter-
action between the electron and hole.\textsuperscript{52} It is shown later
that the linear Zeeman term does not contribute to the
ground-state energy obtained from the variational procedure
with the trial wave function used, because the ground-state
is an S state for which the orbital angular momentum quantum
number $\lambda$ is zero. There is therefore no level splitting
arising from the interaction of the orbital angular momentum
with the field. There is a splitting arising from the inter-
action of intrinsic angular momentum (spin) with the field.
The spin term is not coordinate dependent, however, and so
does not affect the variational calculations. As shown
later, spin effects may be taken into account by adding or
subtracting a constant from the variational energy.

The quasiparticle Hamiltonian $H(\vec{r})$ can be written in
another form,

\[
H(\vec{r}) = \sum_{i=1}^{3} \left\{ \frac{1}{2\mu_i^2} \left[ -i\hbar \frac{\partial}{\partial X_i} + \frac{e}{c} A_i \left( \vec{b}_i \cdot \vec{r} \right) \right]^2 + \frac{e^2}{2c^2 \mu_i^2} \left[ (\vec{g} \times \vec{r})_i - A_i^2(\vec{r}) \right] \right. \\
+ A_i^2(\vec{d}_i \cdot \vec{r}) + A_i^2(\vec{a}_i \cdot \vec{r}) + 2 A_i(\vec{a}_i \cdot \vec{r}) A_i(\vec{d}_i \cdot \vec{r}) \left. \right\} + V(\vec{r}), \quad (5.26)
\]

which is derived in Appendix N. In Eq. (5.26) a set of
three new dyads

\[
\vec{b}_i = \left( \frac{\mu_i}{m_{ei}} \right) \vec{a}_i + \left( \frac{\mu_i}{m_{hi}} \right) \vec{d}_i , \quad (i = 1, 2, 3), \quad (5.27)
\]
is used. Equation (5.26) is the sum of the effective kinetic energy of the quasiparticle in the field, in terms of the reduced effective masses \( \mu_i \) which characterize the quasiparticle, a diamagnetic term which is proportional to the square of the field strength, and a potential energy term. If the hole mass is set equal to infinity, then Eq. (5.26) becomes the shallow donor Hamiltonian of Eq. (4.1).

**Dimensionless Units**

The effective Larmor frequency \( \omega_L \), the effective Bohr radius \( a_0 \), and the effective Rydberg \( R \) for the anisotropic exciton are defined in Gaussian units as \( ^{22,23} \)

\[
\omega_L = \frac{eB}{2\mu c}, \tag{5.28}
\]

\[
a_0 = \frac{\hbar^2}{\mu e^2}, \tag{5.29}
\]

and

\[
R = \frac{\hbar^2}{2\mu a_0^3} = \frac{\mu e^4}{2\hbar^2 K^2}, \tag{5.30}
\]

respectively, where

\[
\mu = (\mu_1\mu_2\mu_3)^{1/3} \tag{5.31}
\]

and

\[
K = (K_1K_2K_3)^{1/3}. \tag{5.32}
\]

The dimensionless constants \( S_i \) are

\[
S_i = \frac{\mu}{\mu_i}, \quad (i = 1, 2, 3). \tag{5.33}
\]
The field parameter $\gamma$ is given by Eq. (4.9) and the field components are given by Eqs. (3.21) - (3.24).

In Appendix 0 the constants defined above and Eqs. (3.3), (5.18), and (5.19) are used to obtain the dimensionless Hamiltonian

$$
\mathcal{H}(r) = \left\{ - \sum_{i} \frac{\partial^3}{\partial x_i^3} + 2 i \gamma \left( T_1 x_2 + T_1' x_3 \right) \frac{\partial}{\partial x_i} 
+ \gamma^2 \left( T_{12} x_3^2 + T_{12}' x_1 x_2 \right) + (\text{cyclic permutations of } 1, 2, 3) \right\} - \frac{2}{\kappa^{1/2} \left[ (x_1^2/k_1) + (x_2^2/k_2) + (x_3^2/k_3) \right]^{1/2}},
$$

where energy is in units of the effective Rydberg $\mathcal{R}$ 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 to be

$$
T_1 = (\mathcal{F}_1 \mu_1) C_3 \left( \frac{\Theta_{123}}{m_{e1}} - \frac{n_{213}}{m_{h1}} \right),
$$

$$
T_1' = (\mathcal{F}_1 \mu_1) C_2 \left( \frac{n_{132}}{m_{e1}} - \frac{\Theta_{312}}{m_{h1}} \right),
$$

$$
T_{12}' = -2 (\mathcal{F}_2 \mu_2) C_1 C_2 \left( \frac{n_{321} \Theta_{312}}{m_{e3}} + \frac{\Theta_{231} n_{132}}{m_{h3}} \right),
$$

and

$$
T_{12} = \mathcal{F}_2 \mu_2 \left[ C_2^2 \left( \frac{n_{132}^2}{m_{e1}} + \frac{\Theta_{312}^2}{m_{h1}} \right) + C_1^2 \left( \frac{\Theta_{231}^2}{m_{e2}} + \frac{n_{321}^2}{m_{h2}} \right) \right].
$$
where each of these equations gives two others through cyclic permutation of (1,2,3). Equations (5.35) - (5.38) are written in terms of the gauge-dependent dimensionless functions

$$\eta_{lmn} = (1 - \xi_n) m_h^m + \xi_n m_e^l,$$  \hspace{1cm} (5.39)

and

$$\epsilon_{lmn} = (1 - \xi_n) m_e^l + \xi_n m_h^m,$$  \hspace{1cm} (5.40)

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

Improved Trial Wave Function

The charge conservation equation for the anisotropic exciton is derived in this section and then solved for the high field trial wave function of Eq. (3.7). The resulting improved trial wave function is then expressed in dimensionless units.

**High Field Trial Wave Function**

The system is again considered in the high field limit where $\chi \gg 1$. The exciton, like the shallow donor, is a hydrogenic system and the Gaussian function in Eq. (3.7) is once again taken as the initial ground-state trial wave function.

**Charge Conservation Equation for the Anisotropic Exciton**

The Hamiltonian of Eq. (5.26) and the improved trial wave function
\[ \Psi'(\vec{r}) = \exp \left[ i q' \vec{A}/\hbar c \right] \Psi(\vec{r}), \] \\

where \( q' \) is the effective quasiparticle charge, are used in Eqs. (2.12) and (2.13). The first variation of the energy expectation value is set equal to zero, which gives, as shown in Appendix P, the charge conservation equation

\[ \nabla \cdot \vec{J}' = 0. \] 

The current density \( \vec{J}' \) for the anisotropic exciton in Eq. (5.42) is

\[ \vec{J}' = \text{Re} \left\{ \Psi'^* \sum_{i=1}^{3} \frac{q'}{\mu_i} \left[ \rho_i' - \frac{q'}{c} A_i (\vec{B_i} \cdot \vec{r}) \right] \partial_i \Psi' \right\}. \] 

Equations (5.42) and (5.43) give the differential equation for the minimizing \( \Lambda \)

\[ \sum_{i=1}^{3} \sum_{j=1}^{3} \left[ \partial_i^2 \Lambda + \left( \frac{\partial_i \rho}{\rho} \right) \partial_i \Lambda \right] = -\frac{\mu c}{q'} \left[ \frac{\nabla \cdot \vec{J}'}{\rho} \right], \] 

where the charge density \( \rho(\vec{r}) = q' |\Psi(\vec{r})|^2 \). This equation is solved in Appendix P for \( \Lambda \) with the trial wave function \( \Psi(\vec{r}) \) given by Eq. (3.7). The minimizing function

\[ \Lambda = -B x_1 x_2 \frac{\alpha_1 T_i + \alpha_2 T_2}{\left( \alpha_1 x_1 + \alpha_2 x_2 \right)} \]

\[ + \text{cyclic permutations of } 1, 2, 3 \] 

is obtained, 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. (5.35) and (5.36). The dimensionless form of the improved trial wave function, also derived in Appendix P, is

\[ \Psi'(\vec{r}) = e^{i \left( g_1 x_1 x_2 + g_2 x_2 x_3 + g_3 x_3 x_1 \right)} \Psi(\vec{r}), \quad (5.46) \]

where lengths are in units of Bohr radii. The dimensionless functions \((g_1, g_2, g_3)\) are given by cyclic permutation of (1,2,3) in the equation

\[ g_i = \frac{\gamma \left( \alpha_i T_1 + \alpha_2 T_2' \right)}{\left( \gamma \alpha_1 \alpha_2 \right)}. \quad (5.47) \]

Gauge-Invariant Energy Expectation Value

The gauge-invariant energy expectation value is derived in Appendix Q using the dimensionless Hamiltonian of Eq. (5.34) and the improved trial wave function of Eq. (5.46). The trial wave function \(\Psi(\vec{r})\) in Eq. (5.46) is given by Eq. (3.7). All the integrals in the energy expectation value can be evaluated analytically except for the potential energy integral. The potential energy integral is the same as the one for the shallow donor, which is partially integrated in Appendix L. From Eqs. (Q35) and (L23) the gauge-invariant energy expectation value is
\[ E' = \left\{ \int \alpha_1 + \frac{\alpha_2 C_4}{4} \left[ \frac{X_2}{\alpha_3} + \frac{X_3}{\alpha_2} + \frac{X_{23}}{(\alpha_2 + \alpha_3)^2} \right] + (\text{cyclic permutations of } 1, 2, 3) \right\} \]

\[ -\left[ \frac{32 \alpha_3}{\pi \theta_3} \right]^{1/2} \int_0^1 \frac{du}{\left[ a'' u^4 + b'' u^2 + 1 \right]^{1/2}} , \]  

(5.48)

where

\[ a'' = \frac{\alpha_3 \theta_1 \theta_2}{\alpha_2 \alpha_3 \theta_3} - \frac{\alpha_3 \theta_1 \theta_2 (\alpha_2 \theta_2^{-1} + \alpha_1 \theta_1^{-1}) + 1}{\alpha_2 \alpha_3 \theta_3} , \]  

(5.49)

\[ b'' = \frac{\alpha_3 \theta_1 \theta_2 (\alpha_2 \theta_2^{-1} + \alpha_1 \theta_1^{-1})}{\alpha_1 \alpha_2 \theta_3} - 2 , \]  

(5.50)

\[ \theta_i = K K_i \quad (i = 1, 2, 3) , \]  

(5.51)

\[ X_2 = \int_2 \mu_2^2 / m_{e_2} m_{h_2} , \]  

(5.52)

and

\[ X_{23} = \mu_2 \mu_3 \int_{\varphi_2} \left[ \frac{m_{e_2}}{m_{h_3}} - \frac{m_{h_2}}{m_{e_3}} \right]^2 . \]  

(5.53)

The quantities \( X_1, X_3, X_{12}, \) and \( X_{31} \) are obtained from Eqs. (5.52) and (5.53) by cyclic permutation of \( (1, 2, 3) \).

The energy expectation value \( E' \) is the sum of a positive kinetic energy, a positive diamagnetic energy shift, and a negative Coulomb potential energy.

Gauge-Dependent Energy Expectation Value

The energy expectation value of Eq. (5.48) is gauge-invariant because the improved trial wave function \( \Psi'(\vec{r}) \)
has been adjusted to the gauge of the vector potential. For purposes of comparison, the energy expectation value using the real trial wave function $\Psi(\vec{r})$ has been calculated in Appendix R. The potential energy term is the one calculated in Appendix L. The gauge-dependent energy expectation value is

$$E = \left\{ \phi'_1 \alpha_1 + \frac{8^2 C_i^2}{4} \left[ \frac{\chi'_2}{\alpha_3} + \frac{\phi_i^2}{\alpha_3} \frac{\chi'_3}{\alpha_2} + \chi'_3 + (1 - \phi_i)^2 \chi'_{23} \right] \right\}$$

$$+ (\text{cyclic permutations of } l, 2, 3)$$

$$- \left[ \frac{32 \alpha_3}{\pi \theta_3} \right]^{1/2} \int_0^1 \frac{du}{\left[ a^u u^4 + b^u u^2 + 1 \right]^{1/2}} \right\}, \quad (5.54)$$

where

$$\chi'_2 = \frac{\phi'_2 \mu_2}{(m_{e_2} + m_{h_2})}, \quad (5.55)$$

$$\chi'_{32} = \phi'_2 \mu_2 \left[ \frac{m_{h_3}^2}{m_{e_2}} + \frac{m_{e_3}^2}{m_{h_2}} - \frac{1}{(m_{e_2} + m_{h_2})} \right], \quad (5.56)$$

$\chi'_{23}$ is obtained by interchange of indices 3 and 2 in Eq. (5.56), and each of these expressions produces two others by cyclic permutation of (1,2,3). Equation (5.54) is gauge dependent since it contains the gauge parameters ($\phi'_1$, $\phi'_2$, $\phi'_3$).

In the next chapter application of the results of Chapters IV and V to specific semiconductors is considered.
CHAPTER VI
EXCITONS AND SHALLOW DONORS IN AXIALLY ANISOTROPIC CRYSTALS

The energy expectation values derived in Chapters IV and V depend on the dielectric constants and effective masses of the semiconductor. Two semiconductors where these parameters have been measured or calculated from measurements are GaSe\textsuperscript{19,20,52,57} and CdS\textsuperscript{21,22,58,59}. Their shallow donor and exciton ground-state energies can be calculated using the results of Chapters IV and V, respectively. Ground-state energies of GaSe excitons have also been measured experimentally for extremely high magnetic fields\textsuperscript{23} which allows a comparison of the calculations with experiment.

Both GaSe and CdS are axially anisotropic semiconductors. In this chapter the results of Chapters IV and V are specialized to the axially anisotropic case. Material parameters of CdS and GaSe needed to compute the exciton and shallow donor ground-state energies are also calculated using experimentally determined values of the dielectric constants and effective masses.

Axially Anisotropic Crystals

Axially anisotropic crystals have a plane of rotational symmetry perpendicular to the crystal axis (c-axis).\textsuperscript{60} The
dielectric tensor and effective mass tensors can be written in terms of components perpendicular (⊥) or parallel (∥) to the c-axis as

\[ K_1 = K_2 = K_\perp, \]  
\[ m_{hl} = m_{h2} = m_{h\perp}, \]  
\[ m_{el} = m_{e2} = m_{e\perp}, \]  
\[ K_3 = K_\parallel, \]  
\[ m_{h3} = m_{h\parallel}, \]  
\[ m_{e3} = m_{e\parallel}, \]

where the \( x_3 \)-axis is taken to be parallel to the c-axis.

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. The projections of the unit vector in the magnetic field direction onto the axes are then

\[ C_1 = 0, \]  
\[ C_2 = \sin \theta, \]  
\[ C_3 = \cos \theta, \]

where the field is at an angle \( \theta \) to the c-axis. Only the squares of the field components enter the energy expectation.
value, so allowing $\theta$ to vary from 0 to 90 degrees covers all possible energies. The axially anisotropic excitons and shallow donors will not have rotational symmetry in the field unless the field is aligned with the crystal axis. Thus, for arbitrary field angles, the method of Chapter II is needed to adjust the trial wave function to the gauge of the vector potential.

**Axially Anisotropic Excitons**

The reduced effective masses which characterize the exciton are

$$\mu_{1}^{-1} = \mu_{2}^{-1} = \mu_{\perp}^{-1} = \left[ m_{e \perp}^{-1} + m_{h \perp}^{-1} \right], \quad (6.10)$$

and

$$\mu_{3}^{-1} = \mu_{\parallel}^{-1} = \left[ m_{e \parallel}^{-1} + m_{h \parallel}^{-1} \right]. \quad (6.11)$$

The effective Larmor frequency $\omega_{L}$, the effective Bohr radius $a_{o}$, and the effective Rydberg $\mathcal{R}$ for the axially anisotropic exciton are defined to be

$$\omega_{L} = \frac{e B}{2 \mu_{\perp} c}, \quad (6.12)$$

$$a_{o} = \left( k_{\perp} k_{\parallel} \right)^{1/2} \frac{\hbar^2}{\mu_{\perp} e^2}, \quad (6.13)$$

and

$$\mathcal{R} = \frac{\hbar^2}{2 \mu_{\perp} a_{o}^2} = \frac{\mu_{\perp} e^4}{2 \hbar^2 k_{\perp} k_{\parallel}}, \quad (6.14)$$

respectively. The field parameter $\gamma$ is still given by

Eq. (4.9) with $\mathcal{R}$ and $\omega_{L}$ defined above. Equations (6.12) - (6.14) are Eqs. (5.28) - (5.30) with $\mu$ replaced by $\mu_{\perp}$.
and \( K \) replaced by \( (K_{||}, K_{\perp})^{1/2} \). If these substitutions are made in Eqs. (5.33) and (5.51), then the dimensionless constants \( Y_1 \) and \( \theta_1 \) \((i = 1, 2, 3)\) become

\[
Y_1 = Y_2 = 1, \quad (6.15)
\]

\[
Y_3 = \gamma = \mu_\perp / \mu_{||}, \quad (6.16)
\]

\[
\theta_1 = \theta_2 = 1, \quad (6.17)
\]

\[
\theta_3 = \theta = K_{\perp} / K_{||}, \quad (6.18)
\]

where \( \gamma \) and \( \theta \) now give the ratios of the reduced effective masses and dielectric constants, respectively.

**Gauge-Invariant Energy Expectation Value**

When Eqs. (6.1) - (6.11) and (6.15) - (6.18) are used in Eqs. (5.48) - (5.53), the gauge-invariant energy expectation value for anisotropic excitons is

\[
E' = \left[ \alpha_1 + \alpha_2 + \gamma \alpha_3 \right] + \frac{\gamma^2 C_2^2}{4} \left[ \frac{X_3}{\alpha_1} + \frac{X_1}{\alpha_3} \right] + \frac{X_{21}}{\left( \alpha_1 + \gamma \alpha_3 \right)} + \frac{\gamma^2 C_3^2}{4} \left[ \frac{X_1}{\alpha_1} + \frac{X_2}{\alpha_2} + \frac{X_{12}}{\left( \alpha_1 + \alpha_2 \right)} \right]
\]

\[
- \left[ \frac{32 \alpha_3}{\pi \theta} \right]^{1/2} \int_0^1 \frac{du}{\left[ a'' u^4 + b'' u^2 + 1 \right]^{1/2}}, \quad (6.19)
\]

where

\[
a'' = \frac{\alpha_2^2}{\theta^2 \alpha_2 \alpha_1} - \frac{\alpha_3 \left( \alpha_1 + \alpha_2 \right)}{\theta \alpha_2 \alpha_1} + 1, \quad (6.20)
\]
\[ b'' = \frac{\alpha_3 (\alpha_1 + \alpha_3)}{\beta \alpha_1 \alpha_2} - 2 \quad (6.21) \]

\[ x_1 = x_2 = \frac{\mu_1^2}{m_{e\perp} m_{h\perp}} \quad (6.22) \]

\[ x_3 = \frac{\mu_\perp \mu_\parallel}{m_{e\parallel} m_{h\parallel}} \quad (6.23) \]

\[ x_{31} = \mu_\perp \mu_\parallel \left[ \frac{m_{e\perp}}{m_{h\parallel}} - \frac{m_{h\perp}}{m_{e\parallel}} \right] \quad (6.24) \]

and

\[ x_{12} = \frac{(m_{e\perp} - m_{h\perp})^2}{(m_{e\perp} + m_{h\perp})^2} \quad (6.25) \]

Equation (6.19) contains only two diamagnetic terms since the field has no component along the \( x_\perp \)-axis. The terms in Eq. (6.19) are kinetic energy, diamagnetic energy, and potential energy.

**Gauge-Dependent Energy Expectation Value**

The gauge-dependent energy expectation value of Eq. (5.54) is, for the axially anisotropic case,

\[
E = \left[ \alpha_1 + \alpha_2 + \frac{\gamma}{4} \alpha_3 \right] + \frac{\gamma^2 C_2}{4} \left[ \frac{x_2'}{\alpha_1'} + \frac{x_1'}{\alpha_3'} + \frac{\gamma^2 x_1'}{\alpha_i} \right] \\
+ \left[ \frac{(1 - \frac{\gamma^2}{\alpha_2})^2 x_3'}{\alpha_3} \right] + \frac{\gamma^2 C_3}{4} \left[ \frac{x_1'}{\alpha_1'} + \frac{x_1'}{\alpha_2'} + x_1' \left( \frac{\gamma^2}{\alpha_2} + \left(1 - \frac{\gamma^2}{\alpha_3} \right)^2 \right) \right] \\
- \left[ \frac{32 \alpha_3}{\pi \beta} \right]^{\frac{1}{2}} \int_0^1 \frac{du}{a'' u^4 + b'' u^2 + 1} \left[ a'' u^4 + b'' u^2 + 1 \right] \quad (6.26)
\]
where

\[ \chi_3' = \frac{\mu_\perp}{(m_{e\perp} + m_{h\parallel})} = \frac{\mu_\perp}{m_{e\perp} m_{h\parallel}} = \chi_3, \quad (6.27) \]

\[ \chi_0' = \chi_2' = \frac{\mu_\perp}{m_{e\perp} m_{h\perp}} = \chi_0, \quad (6.28) \]

\[ \chi_{12}' = \chi_{21}' = \frac{(m_{e\perp} - m_{h\perp})^2}{(m_{e\perp} + m_{h\perp})^3} = \chi_{12}, \quad (6.29) \]

\[ \chi_{31}' = \mu_\perp \left[ \frac{m_{e\parallel}^2 + m_{e\perp}^2}{m_{e\perp} m_{h\perp}} - \frac{1}{(m_{e\perp} + m_{h\perp})} \right], \quad (6.30) \]

and

\[ \chi_{13}' = \mu_\perp \left[ \frac{m_{h\perp}^2 + m_{e\perp}^2}{m_{e\perp} m_{h\perp}} - \frac{1}{(m_{e\perp} + m_{h\perp})} \right], \quad (6.31) \]

The functions \( a" \) and \( b" \) are given by Eqs. (6.20) and (6.21). The energy \( E \) depends only on two gauge parameters, \( \xi_2 \) and \( \xi_3 \), for a field lying in the \( x_2-x_3 \) plane.

**Axially Anisotropic Shallow Donors**

The effective Larmor frequency \( \omega_L \), the effective Bohr radius \( a_o \), and the effective Rydberg \( R \) for the axially anisotropic shallow donor are

\[ \omega_L = e B / 2 m_{e\perp} c, \quad (6.32) \]

\[ a_o = (K_\perp K_\parallel)^{1/2} \frac{\hbar^2}{m_{e\perp} e^2}, \quad (6.33) \]

and

\[ R = \frac{\hbar^2}{2 m_{e\perp} a_o^2} = \frac{m_{e\perp} e^4}{2 \hbar^2 K_\perp K_\parallel}. \quad (6.34) \]
Equations (6.32) – (6.34) are Eqs. (4.3) – (4.5) with $m$ replaced by $m_{e_{\perp}}$ and $K$ replaced by $(K_{\perp}K_{\parallel})^{1/2}$. The constants $\mathcal{F}_{i}$ in Eq. (4.8) become

$$\mathcal{F}_{1} = \mathcal{F}_{2} = 1$$

and

$$\mathcal{F}_{3} = \mathcal{F} = m_{e_{\perp}} / m_{e_{\parallel}}.$$  

The constants $\mathcal{F}_{i}$ in Eq. (4.25) become those of Eqs. (6.17) and (6.18).

The shallow donor energy expectation value of Eq. (4.22) becomes, for the axially anisotropic case,

$$\mathcal{E}' = \left[ \alpha_{1} + \alpha_{2} + \mathcal{F}_{3} \alpha_{3} \right] + \chi^{2} \left[ \frac{\mathcal{F}_{2} \tilde{c}_{2}^{2}}{(\alpha_{1} + \mathcal{F}_{3} \alpha_{3})} + \frac{\tilde{c}_{3}^{2}}{(\alpha_{1} + \alpha_{2})} \right]$$

$$- \left[ \frac{32 \alpha_{3}}{\pi \mathcal{F}_{3}} \right] \sqrt{\int_{0}^{t} \frac{du}{[a''u'' + b''u'' + 1]^{1/2}}}$$

where $a''$ and $b''$ are given by Eqs. (6.20) and (6.21).

Equation (6.19) for the exciton reduces to Eq. (6.37) in the limit of an infinitely massive hole.

Material Parameters of CdS

In a magnetic field CdS has three nondegenerate valence bands $A$, $B$, and $C$. Parameters for excitons formed from the $A$-valence band, associated with the lowest energy gap, have been determined by Seiler, et al., using two-photon magneto-optical spectroscopy at a temperature of 1.8°K and by Hopfield and Thomas using linear magneto-optical absorption at 1.6°K.
Effective masses and dielectric constants for CdS obtained from the above sources are listed in Table II. Parameters which characterize CdS A-excitons, either obtained from the above sources or calculated from values given in them, are also listed in Table II. Values which are not referenced are calculated from referenced parameters. Parameters which characterize CdS shallow donors, also calculated from the effective masses and dielectric constants of Table II, are listed in Table III. Uncertainties have been included when given in the references and used in calculated values.

Material Parameters of GaSe

Effective masses of direct excitons in GaSe have been determined by Ottaviani, et al.,\(^{19}\) using transport measurements and results of magneto-optical absorption measurements at liquid helium temperatures.\(^{52,63}\) Parallel and perpendicular components of the dielectric tensor for GaSe have been measured by Leung, et al.\(^{20}\)

Effective masses, dielectric constants, and exciton parameters for GaSe, obtained from the above sources or calculated from values given in them, are listed in Table II. Shallow donor parameters for GaSe, calculated using the values of Table II, are listed in Table III. Although no uncertainties are given in Ref. 19, effective mass values of GaSe are uncertain to at least \(\pm 10\) per cent, since the
reduced effective masses used to calculate them have this degree of uncertainty.

The parameters of Tables II and III and the energy expectation values given earlier are used in the next chapter to calculate exciton and shallow donor ground-state energies of CdS and GaSe.
CHAPTER VII

GROUND-STATE ENERGIES OF AXIALLY ANISOTROPIC EXCITONS AND SHALLOW DONORS

In this chapter the gauge-invariant energy expectation values of Eqs. (6.19) and (6.37) and the material parameters given in Tables II and III are used to calculate the variational ground-state energies of GaSe excitons, CdS A-excitons, and GaSe and CdS shallow donors 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.\textsuperscript{23} for GaSe excitons in high fields. The results of the theoretical calculations agree with experiment 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 degrees. As a demonstration of how widely results can vary using the gauge-dependent approach, the gauge-dependent energy expectation value of Eq. (6.26) 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 results. The effects of spin
splitting on the ground-state exciton spectrum are considered. Finally, the ground-state energy of GaSe shallow donors is calculated for fields ranging from $\gamma = 1.0$ to $\gamma = 2.5$ and field angles varying from 0 to 90 degrees. Energies of CdS shallow donors are computed only for a single case, $\gamma = 1.0$, since the small dielectric anisotropy ($\varrho = 0.988$) and nearly isotropic conduction band ($\mathcal{J} = \frac{m_e}{m_H} = 1.029$) make this a virtually isotropic system whose energies have little dependence on field orientation.

Energy Minimization

The gauge-invariant energy expectation values of Eqs. (6.19) and (6.37) were numerically minimized with respect to the variational parameters ($\alpha_1$, $\alpha_2$, $\alpha_3$) using a program written in FORTRAN IVG and run on a NAS/5000 computer. The program utilizes the standard subroutines FMFP$^{42}$ and QG5$^{64}$ from the IBM System/360 Scientific Subroutine Package to minimize the energy and evaluate the integrals, respectively. These subroutines are described in Appendix G.

For a given set of material parameters, energies calculated by the program are accurate to within $\pm 0.00005$ effective Rydbergs. From Table II the effective exciton Rydbergs are 24.5 meV for GaSe and 27.1 meV for CdS. From Table III the effective shallow donor Rydbergs are 29.8 meV for GaSe and 36.0 meV for CdS. These values give a computational error of less than $\pm 0.002$ 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 the high field region.

Comparison with Experimental Data for GaSe Excitons

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

Aldrich, et al. 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 ($\theta = 0^\circ$) up to nearly 200T. Data were taken at sample temperatures of 6.5°C. The fields, produced by explosive flux compression, had rise times (from 0.5 maximum to peak) on the order to 5-10 μsec. A pulse of intense reasonably white light from an argon source was transmitted through the sample and then reflected into a rotating-mirror spectrographic camera, where it was time and wavelength resolved. Thus, the complete visible spectrum over the high field range was recorded in a single shot.
Although the magnetic fields were a function of time in the experiment, the instantaneous field strengths were determined by integrating voltage signals from pickup coils of known area in the high field region. These fields were then correlated with particular parts of the time-resolved spectrum. The data thus correspond to the instantaneous optical energies for these fields. As has been shown by Kennedy and Kobe, the eigenvalues of the energy operator for time-dependent fields depend upon time as a parameter. These instantaneous energies are the same as for static fields of identical magnitude and the theory developed for static fields should be applicable. Indeed, the theoretical calculations which accompanied these data were done for static fields.

The optical exciton energies are the sum of the direct band gap energy $E_g$ and the exciton binding energy for the particular state considered. The band gap energy for GaSe at extremely low temperatures ($1.7^\circ$K) was determined by Mooser and Schlüter to be $E_g = 2,129.5 \pm 0.05$ meV. If this value is subtracted from the optical energies, the experimental ground-state binding energies are obtained. These energies are plotted in Fig. 2. Field values range from 63 to 167T. Because of difficulties in resolution due to diffraction fringes, the energies are only accurate to $\pm 20$ cm$^{-1}$ or roughly $\pm 2.5$ meV. For this reason the experimental data in Fig. 2 are given as error bars 5 meV wide. Theoretical
values obtained from the variational calculations described in the previous 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.

Energy as a Function of Field Strength and Orientation for GaSe and CdS Excitons

The data taken by Aldrich, et al. are for fields parallel to the c-axis (Θ = 0°). Data for the perpendicular orientation have been taken for GaSe and CdS but only for Θ ≤ 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 of CdS A-excitons and GaSe excitons are listed in Tables IV and V, respectively, for fields ranging from γ = 1.0 to γ = 3.0 and for angles from 0 to 90 degrees. These energies are plotted as a function of field angle in Figs. 3 and 4, respectively. The energy shift with angle for CdS and GaSe excitons is plotted in Figs. 5 and 6, respectively. The energy for CdS excitons decreases strongly 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.

Interpretation of Results

In order to interpret the results given in Figs. 3 - 6, the effect of shifting the field from a parallel to a perpendicular orientation must be examined for the negative Coulomb term and the positive kinetic and diamagnetic energy terms in Eq. (6.19).

The diamagnetic energy will change with field orientation as a result of the anisotropy of the reduced effective mass tensor $\mathbf{\mu}$. Physically, the increase (decrease) of the diamagnetic energy corresponds to a decrease (increase) in the components of the reduced effective mass tensor perpendicular to the field. For GaSe $\mathbf{J} = \mu_\perp / \mu_\parallel = 1.17$, which indicates a decrease in the components of $\mathbf{\mu}$ perpendicular to the field for off-axis fields. The positive diamagnetic shift increases which explains the field-dependent rise in energy for GaSe excitons as the polar angle $\Theta$ increases from zero. For CdS $\mathbf{J} = 0.806$, which indicates an increase in the components of $\mathbf{\mu}$ perpendicular to the field for off-axis fields and a decrease in the diamagnetic energy for off-axis fields.
The effect of the angular shift on the Coulomb and kinetic energy terms can be seen by examining the changes in the exciton wave function due to magnetic binding. For magnetic fields parallel to the c-axis only the Coulomb attraction binds the exciton in the c-axis direction. In the plane perpendicular to the c-axis, however, the exciton is more tightly bound due to the magnetic field. In the high field limit the effect of the field is larger than the Coulomb effect, which is the adiabatic approximation of Elliott and Loudon.\textsuperscript{29} Thus the parameters $\alpha_1$ and $\alpha_2$ of the Gaussian wave function will be large compared to the parameter $\alpha_3$, which indicates weaker binding in the c-axis direction. As the field shifts off-axis the field component perpendicular to the c-axis increases. The exciton is more tightly bound in the $x_3$-direction, $\alpha_3$ becomes larger, and $\alpha_2$ becomes smaller.

The kinetic energy term in Eq. (6.19) is the sum of $\alpha_1$, $\alpha_2$, and $J\alpha_3$. Since $J > 1$ for GaSe, the increase in $J\alpha_3$ for off-axis fields more than compensates for the decrease in $\alpha_2$ and the kinetic energy should increase. The opposite is true for CdS where $J < 1$.

The Coulomb term in Eq. (6.19) is multiplied by a constant which is proportional to the square root of $\alpha_3$. For off-axis fields where the exciton is more tightly bound in the c-axis direction, the negative Coulomb term should increase. The Coulomb term is also inversely proportional to
the square root of $K_{\perp}/K_{\parallel}$, which is the parameter $\theta$ in Table II. Since $\theta$ is smaller for CdS, the Coulomb term should increase with angle more rapidly in CdS than in GaSe and the energy decreases more rapidly with angle in CdS.

To summarize, the rise and fall of the GaSe exciton energies as the field moves off axis occurs because of competition between the increasingly positive kinetic and diamagnetic terms and the increasingly negative Coulomb term. For CdS excitons the decrease in the diamagnetic and kinetic terms and the increase in the Coulomb term all tend to reduce the energy. Finally, the energy shift for GaSe as a function of angle is smaller than for CdS because of the competition between positive and negative terms and because the larger dielectric anisotropy makes the Coulomb term increase more slowly.

**Possibility of Experimental Verification**

Experimental verification of these results would be difficult because of the high fields needed, because of the difficulty in getting correct crystal alignment at angles between the parallel and perpendicular cases, and because of the accuracy required (experimental error was $\pm 2.5$ meV in the data of Ref. 23). For GaSe excitons at $\gamma = 3.0$ ($B = 177.9T$), Table V shows 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 200T 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 at fields of 600T and higher, listed in Table VI, show that energy shifts of GaSe excitons could also be resolved at these fields. Since fields of over 1000T have been produced, such measurements are possible. Fowler has recently expressed interest in making measurements of exciton energy shift with angle, provided the energy shifts involved are large enough to be detectable.

Gauge-Dependent Energies of GaSe Excitons for the Landau and Symmetric Gauges

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. (6.26) in the Landau \( (\vec{\alpha}_1 = \vec{\alpha}_2 = \vec{\alpha}_3 = 1) \) and symmetric \( (\vec{\alpha}_1 = \vec{\alpha}_2 = \vec{\alpha}_3 = \frac{1}{2}) \) gauges. Gauge-dependent energies of GaSe excitons as a function of field angle for \( \gamma = 3.0 \) are listed in Table VII and plotted in Fig. 7. The Landau and symmetric gauge values differ strongly, 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 cylindrically symmetric 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 \( J = \mu_\perp / \mu_\parallel = 1.17 \). 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.

**Exciton Ground-State Spin Splitting**

The energies calculated so far, using the minimally coupled Hamiltonian of Eq. (5.1), neglect the effects of exciton 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 one-half 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 anti-parallel and three triplets of total spin \( S = 1 \), where the component of total spin parallel to the field \( S_B = +1, 0, -1 \). \(^{52}\) The variational calculation using Eq. (6.19) 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\textsuperscript{21} and GaSe\textsuperscript{52} 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\textsuperscript{22,23}

$$H_s = \frac{e\hbar}{4\mu_\perp c} (g_z^* S_z B) ,$$

(7.1)

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. Equation (7.1) can also be written

$$H_s = (g_z^* S_z) \mu^*_\text{B}(0) B ,$$

(7.2)

where

$$\mu^*_\text{B}(0) = \frac{e\hbar}{2\mu_\perp c}$$

(7.3)

is the effective Bohr magneton of the exciton for fields at $\Theta = 0^\circ$. The definition of the effective exciton Larmor frequency $\omega_L$ in Eq. (6.12), together with Eq. (7.3) gives the relation

$$\mu^*_\text{B}(0) B = \hbar \omega_L .$$

(7.4)

If Eq. (7.2) is divided by the effective exciton Rydberg in Eq. (6.14), the dimensionless spin Hamiltonian is
\[ H_s = \frac{g_z^* S_z \gamma}{2} = \pm \frac{g_z^* \gamma}{2}. \] (7.5)

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 spin splitting in parallel fields has been determined from measurement to be \( g_z = 2.7 \pm 0.2 \) for GaSe\(^{52} \) and \( g_z = 2.93 \pm 0.03 \) for CdS.\(^{21} \) Care must be used in applying these values since they are calculated from the energy separation \( \Delta E_s \) using the equation

\[ g_z = \frac{\Delta E_s}{\mu_B B}, \] (7.6)

where \( \mu_B \) is the free electron Bohr magneton.\(^{52} \) For the exciton splitting of Eq. (7.5), the factor \( \mu_e/m_0 \), where \( m_0 \) is the free electron mass, must be multiplied by \( g_z \). The result is \( g_z^* = 0.38 \) for GaSe and \( g_z^* = 0.463 \) for CdS. The spin splitting of GaSe and CdS 1s triplets is plotted in Fig. 8 for on-axis fields. In experimental measurements it may be difficult to resolve exactly the triplet splitting. Aldrich, et al.,\(^{23} \) were able to measure only the center of gravity of the ground-state triplets with any precision.\(^{67} \) Since this energy corresponds to the energy of the middle triplet, with spin component \( S_z = 0 \), the data agrees very
well with the variational upper bound to the $S_z = 0$ level calculated neglecting spin effects.

For off-axis fields the effective Bohr magneton no longer has the simple form of Eq. (7.3), since the reduced effective mass of the exciton is not symmetric in the plane perpendicular to the field. In Appendix S the effective Bohr magneton for a field at angle $\theta$ to the c-axis is shown to be

$$\mu_B^*(\theta) = \mu_B^*(0) \left[ \frac{\mu_{\|} \cos^2 \theta + \mu_{\perp} \sin^2 \theta}{\mu_{\|}} \right]^{1/2}. \quad (7.7)$$

For arbitrary orientations the spin contribution is

$$H_S = \pm \frac{g_\theta^*}{2} \delta \left[ \frac{\mu_{\|} \cos^2 \theta + \mu_{\perp} \sin^2 \theta}{\mu_{\|}} \right]^{1/2}, \quad (7.8)$$

where $g_\theta^*$ is the g-factor for fields at angle $\theta$. Since $g_\theta^*$ 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. 3 and 4.

Energy as a Function of Field Strength and Orientation for GaSe and CdS Shallow Donors

The shallow donor material parameters listed in Table III and the gauge-invariant energy expectation value of Eq. (6.37) are used to calculate the ground-state energies of GaSe and
CdS shallow donors. The ground-state energies of GaSe shallow donors are listed in Table VIII for fields ranging from \( y = 1.0 \) to \( y = 2.5 \) and field angles varying from 0 to 90 degrees. These energies are plotted as a function of field angle in Fig. 9. The variation of energy with angle resembles that of CdS excitons. The energy decrease as the field moves off-axis and the decrease is larger for higher field values. The effective mass anisotropy parameter \( (\mathcal{J} = m_{e\perp}/m_{e\|} = 0.57) \) indicates that the components of the effective electron mass tensor perpendicular to the field increase as the field shifts off-axis. Thus, the diamagnetic energy decreases. The Coulomb term increases due to increased binding along the c-axis direction. Both of these effects reduce the energy.

The small dielectric anisotropy \( (\mathcal{Q} = 0.988) \) and nearly isotropic conduction band \( (\mathcal{J} = 1.029) \) of CdS make the CdS shallow donor a virtually isotropic system whose energies have little dependence on field orientation. As an example, energies were computed for \( y = 1.0 \) (\( B = 130T \)). These energies are listed in Table IX. The energy variation with angle is only 0.4 meV even for a field in the megagauss range.
CHAPTER VIII
CONCLUSION

Variational methods are often used to calculate approximate values for the ground-state energies of atoms and molecules in magnetic fields. For systems where the trial wave function $\Psi$ and the choice of gauge of the vector potential $\vec{A}$ give a current density $\vec{J}$ for which $\nabla \cdot \vec{J} \neq 0$, a lower energy may be obtained by using a new trial wave function $\Psi' = \exp(iq \wedge \vec{\mathcal{A}}) \Psi$. When the energy is minimized with respect to the function $\wedge(\vec{\mathcal{A}})$, the charge conservation condition $\nabla \cdot \vec{J}' = 0$ is obtained, where $\vec{J}'$ is the current density calculated from the new trial wave function. This procedure adapts the trial wave function to the choice of vector potential. The energy expectation values obtained by this method are gauge invariant, charge conservation is satisfied, and the energy is the lowest possible which can be obtained for the set of all trial wave functions gauge-equivalent to the initial choice of trial wave function.

The method can be extended to many particle systems. It is applicable to all quantum mechanical systems for which the energy variational principle can be applied, but it is primarily useful for anisotropic systems which do not have rotational symmetry in the magnetic field. For such systems, adaptation of the trial wave function to the gauge of the...
vector potential is not trivial. For complicated trial wave functions an analytical solution to the differential equation for the phase function $\Lambda$ may be difficult. A parameterized $\Lambda$ could be used, but in this case the method is no longer exactly gauge invariant.

The method is applied first to an anisotropic harmonic oscillator in a constant magnetic field. If an arbitrary gauge for the vector potential and a real trial wave function are chosen, a gauge-dependent energy is obtained and charge conservation is violated. When the wave function is improved by using a phase factor depending on the spatial coordinates, charge is conserved and a lower, gauge-invariant energy is obtained. When the magnetic field is chosen to be $\mathbf{B} = (0,0,B_3)$, the minimum ground-state energy is equal to the exact ground-state energy. The trial wave function is also the exact ground-state wave function. An exact solution is obtained in this case because the initial trial wave function chosen happened to be gauge-equivalent to a wave function of the same form as the exact ground-state wave function.

The method is then 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.,\textsuperscript{23} 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. This decrease arises from an increased binding of the exciton along the c-axis direction and an increase of the effective mass in the plane perpendicular to the field. 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. This behavior is produced by competition between the increased binding along the c-axis direction, which tends to lower the energy, and a decrease of the effective mass perpendicular to the field, which tends to raise it. Because of this competition and because the dielectric anisotropy (K\textsubscript{\perp}/K\textsubscript{\parallel}) of GaSe is larger than that of CdS, the change in energy with respect to angle is smaller in GaSe than in CdS. 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.

Finally, the method is applied to GaSe and CdS shallow donors in high magnetic fields. The variation of ground-state energy with field angle for GaSe shallow donors is similar to that of CdS excitons. The energy decreases as
the angle of the field with the crystal axis increases. Ground-state energies of CdS shallow donors are virtually independent of field orientation, since this is almost an isotropic system.

Experimental verification of the exciton and shallow donor calculations would be difficult because of the high magnetic fields needed, difficulties with crystal alignment, and large experimental errors. For CdS excitons and GaSe shallow donors, however, the energy shifts are sufficiently large to be resolved at fields below 200T. Fowler\textsuperscript{67} has expressed interest in making such measurements. 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\textsuperscript{68} and CdSe.\textsuperscript{59,69}

The energy expressions for excitons can be specialized to the case of shallow acceptors in semiconductors with non-degenerate valence bands by setting the effective electron mass equal to infinity.\textsuperscript{45} Semiconductors with degenerate valence bands could only be treated for the case of shallow donors.

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.
APPENDIX A

THE EXTREMUM IS A MINIMUM

The second variation $\delta^2 E[\Lambda]$ of Eq. (2.12) involves terms quadratic in $\delta \Lambda$. In this appendix it is shown that $\delta^2 E[\Lambda] > 0$, so that the extremum condition in Eq. (2.18) indeed describes a minimum.

The second variation of Eq. (2.12) is

$$\delta^2 E[\Lambda] = (\hbar^2 \kappa^2 c^2) \left\{ \langle \delta \Lambda \Psi' | H(\bar{\Lambda}) \delta \Lambda \Psi' \rangle - \Re \langle (\delta \Lambda)^2 \Psi' | H(\bar{\Lambda}) \Psi' \rangle \right\}. \tag{A1}$$

If the energy operator of Eq. (2.3) is substituted into Eq. (A1), the result is

$$\delta^2 E[\Lambda] = (1/2m)(\hbar^2 \kappa^2 c^2) \left\{ \langle \delta \Lambda \Psi' | \pi^2 \delta \Lambda \Psi' \rangle - \Re \langle (\delta \Lambda)^2 \Psi' | \pi^2 \Psi' \rangle \right\}. \tag{A2}$$

Since the kinetic momentum $\pi$ in Eq. (2.7) is Hermitian, Eq. (A2) becomes

$$\delta^2 E[\Lambda] = (1/2m)(\hbar^2 \kappa^2 c^2) \left\{ \langle \pi \delta \Lambda \Psi' | \cdot \pi \delta \Lambda \Psi' \rangle - \Re \langle \pi (\delta \Lambda)^2 \Psi' | \cdot \pi \Psi' \rangle \right\}. \tag{A3}$$

Using Eq. (2.7) and the canonical momentum $\bar{p} = -i \hbar \nabla$, Eq. (A3) can be rewritten as

$$\delta^2 E[\Lambda] = (1/2m)(\hbar^2 \kappa^2 c^2) \left\{ \langle \bar{p} \delta \Lambda \Psi' | \cdot (\bar{p} \delta \Lambda) \Psi' \rangle - \Re \langle \bar{p} (\delta \Lambda)^2 \Psi' | \cdot \bar{p} \Psi' \rangle \right\} > 0. \tag{A4}$$
since the other terms cancel. Equation (A4) shows that the extremum condition in Eq. (2.18) gives a minimum.
APPENDIX B

CURRENT DENSITY AND CHARGE CONSERVATION
EQUATION FOR MANY-PARTICLE SYSTEMS

The current density, energy minimization, and charge conservation equation for a system of \( N \) identical particles in a uniform magnetic field is derived here. After a derivation of the many-particle current density, the energy expectation value calculated using an improved trial wave function is minimized with respect to the phase function. The extremum condition is shown to give the charge conservation condition for the many-particle system. The second variation is shown to be positive; thus, the extremum condition gives a minimum.

Current Density

The current density operator \( \mathbf{J}_{\text{op}}(\mathbf{r}) \) and the trial wave function \( \Psi \) for this system are given in Eqs. (2.21) and (2.22), respectively. The current density of the many-particle system is

\[
\mathbf{J}(\mathbf{r}) = \langle \Psi | \mathbf{J}_{\text{op}}(\mathbf{r}) | \Psi \rangle \\
= \int d\mathbf{r}_{1} \ldots d\mathbf{r}_{N} \left\{ \sum_{i=1}^{N} \frac{q}{2m} \left[ \mathbf{\pi}_{i} \Psi(1 \ldots N) \right]\delta(\mathbf{r}-\mathbf{r}_{i}) \Psi(1 \ldots N) \right. \\
+ \left. \Psi^{*}(1 \ldots N) \sum_{i=1}^{N} \frac{q}{2m} \delta(\mathbf{r}-\mathbf{r}_{i}) \mathbf{\pi}_{i} \Psi(1 \ldots N) \right\} \ .
\]

(Bl)
Since the particles are identical, Eq. (Bl) can be written

\[
\overrightarrow{J}(\vec{r}) = \frac{qN}{2m} \int d\vec{r}_1 \ldots d\vec{r}_N \left\{ \left[ \overline{\overrightarrow{p}}_i \Psi(1 \ldots N) \right]^* \delta(\vec{r} - \vec{r}_i) \Psi(1 \ldots N) \\
+ \Psi^*(1 \ldots N) \delta(\vec{r} - \vec{r}_i) \overline{\overrightarrow{p}}_i \Psi(1 \ldots N) \right\}
\]

\[
= \frac{qN}{2m} \int d\vec{r}_2 \ldots d\vec{r}_N \left\{ \left[ \overline{\overrightarrow{p}}_r \Psi(\vec{r}', 2 \ldots N) \right]^* \Psi(\vec{r}, 2 \ldots N) \\
+ \Psi^*(\vec{r}, 2 \ldots N) \overline{\overrightarrow{p}}_r \Psi(\vec{r}', 2 \ldots N) \right\} \bigg| _{\vec{r} = \vec{r}_r} .
\]  

(B2)

If the single-particle reduced density matrix \( \rho(\vec{r}, \vec{r}') \) given by Eq. (2.25) is used, then the current density can be written in the form

\[
\overrightarrow{J}(\vec{r}) = \frac{q}{2m} \left[ \overline{\overrightarrow{p}}_r^\dagger \rho(\vec{r}, \vec{r}') + \overline{\overrightarrow{p}}_r \rho(\vec{r}, \vec{r}') \right] \bigg| _{\vec{r} = \vec{r}_r}
\]

\[
= \frac{q}{m} \text{Re} \left[ \overline{\overrightarrow{p}}_r \rho(\vec{r}, \vec{r}') \right] \bigg| _{\vec{r} = \vec{r}_r} .
\]  

(B3)

Energy Minimization

The energy operator for a system of \( N \) charged particles is given in Eq. (2.26). An improved trial wave function for the system is given in Eq. (2.27). The energy expectation value obtained using Eqs. (2.26) and (2.27) is given in Eq. (2.28). The variation with respect to \( \Lambda \) of Eq. (2.28) is obtained by letting each \( \Lambda_\vec{r}_j \) have an arbitrary real variation \( \delta \Lambda_\vec{r}_j \). When the definition
\[ \delta \Lambda = \sum_{j=1}^{N} \delta \Lambda \left( \vec{r}_j \right) \]  

is used, the energy variation can be written in the form\(^{70}\)

\[
E[\Lambda + \delta \Lambda] = \left\langle \exp \left( i \frac{\delta \Lambda}{\hbar c} \right) \Psi' \middle| H(\bar{A}) \exp \left( i \frac{\delta \Lambda}{\hbar c} \right) \Psi' \right\rangle
\]

\[ = \left\langle \Psi' \middle| \exp \left( -i \frac{\delta \Lambda}{\hbar c} \right) H(\bar{A}) \exp \left( i \frac{\delta \Lambda}{\hbar c} \right) \Psi' \right\rangle \]

\[ = \left\langle \Psi' \middle| \left\{ H(\bar{A}) + \left( -i \frac{\delta \Lambda}{\hbar c} \right) [\delta \Lambda, H(\bar{A})] \right. \right. \]

\[ + \frac{1}{2!} \left( -i \frac{\delta \Lambda}{\hbar c} \right)^2 \left[ \delta \Lambda, [\delta \Lambda, H(\bar{A})] \right] + \ldots \left. \right\} \Psi' \right\rangle \]

\[ = E[\Lambda] + \delta E[\Lambda] + \delta^2 E[\Lambda] + \ldots . \]  

Equation (B5) is of the same form as Eq. (2.13) for the single particle case. When the second variation is positive, the extremum condition obtained by setting the first variation equal to zero gives the energy minimum.

**Extremum Condition**

The extremum condition is

\[ 0 = \delta E[\Lambda] = -i \frac{\hbar c}{\lambda} \left\langle \Psi' \middle| [\delta \Lambda, H(\bar{A})] \Psi' \right\rangle . \]  

The last two terms of \( H(\bar{A}) \) in Eq. (2.26) commute with \( \delta \Lambda \); therefore, the commutator in Eq. (B6) can be written
The anticommutator of arbitrary vectors \( \vec{c} \) and \( \vec{d} \) is defined as

\[
\{ \vec{c}, \vec{d} \} = \vec{c} \cdot \vec{d} + \vec{d} \cdot \vec{c}.
\]  

If Eq. (B7) is used in Eq. (B6) and use is made of the fact that the particles are identical, Eq. (B6) becomes

\[
O = N \int \ldots dN \, \Psi^* \left[ (\nabla \delta \Lambda(\vec{r}_i)) \cdot \vec{\pi}^i 
+ \vec{\pi}^i \cdot (\nabla \delta \Lambda(\vec{r}_i)) \right] \Psi'.
\]  

When the Hermiticity of \( \vec{\pi}_1 \) is used, Eq. (B9) becomes

\[
O = N \int \ldots dN \, \delta \Lambda(\vec{r}_i) \nabla \cdot 2 \Re \{ \Psi^* \vec{\pi} \Psi' \} 
= 2 \int \ldots dN \, \delta \Lambda(\vec{r}_i) N \int \ldots dN \nabla \cdot \Re \{ \Psi^* \vec{\pi} \Psi' \}.
\]  

The integral vanishes for arbitrary \( \delta \Lambda \) only if
\[ \nabla_i \cdot \Re \left\{ N \int d2 \ldots dN \Psi^* (1 \ldots N) \overline{\pi}_i \Psi (1 \ldots N) \right\} = 0. \quad (B11) \]

Finally, Eqs. (2.25) and (B3) can be used in Eq. (B11) to obtain

\[ \nabla_i \cdot \overline{\mathbf{J}}' (\mathbf{r}_i) = 0, \quad (B12) \]

which is the charge conservation condition for a system of \( N \) identical particles in a stationary state in a static magnetic field.

**Extremum is a Minimum**

From Eq. (B5) the second variation of the energy with respect to \( \Lambda \) is

\[ \delta^2 \mathcal{E}[\Lambda] = \frac{1}{2!} \left( -\frac{i}{\hbar c} \right)^2 \left\langle \Psi' \left[ [\delta \Lambda, [\delta \Lambda, \mathcal{H}(\Lambda)]] \right] \Psi' \right\rangle. \quad (B13) \]

Equation (B7) can be used to evaluate the double commutator in Eq. (B13):

\[ [\delta \Lambda, [\delta \Lambda, \mathcal{H}(\Lambda)]] = \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ \delta \Lambda (\mathbf{r}_j) \right], \]

\[ \frac{i \hbar}{2m} \left\{ \left( \nabla_i \delta \Lambda (\mathbf{r}_j) \right), \cdot \overline{\pi}_k \right\} \]

\[ = \left( \frac{i \hbar}{2m} \right) \sum_{i=1}^{N} \left[ \delta \Lambda (\mathbf{r}_i), 2 \left( \nabla_i \delta \Lambda (\mathbf{r}_i) \right) \cdot \overline{\pi}_i \right] \]
If Eq. (B14) is used in Eq. (B13), then for identical particles Eq. (B13) can be written

\[ \delta^2 E[A] = \frac{q^2 N}{2 c^2 m} \int I_1 \ldots I_N \frac{dN}{dV} \frac{d^3 \Psi'}{d^3 \Psi} \left[ \left( \nabla_i \delta \Lambda \left( \vec{r}_i \right) \right)^2 \right] \Psi' \]

\[ = \frac{q^2 N}{2 c^2 m} \int I_1 \ldots I_N \left[ \left( \nabla_i \delta \Lambda \left( \vec{r}_i \right) \Psi' \right)^* \left( \nabla_i \delta \Lambda \left( \vec{r}_i \right) \Psi' \right) \right] \]

\[ = \frac{q^2 N}{2 c^2 m} \int I_1 \ldots I_N \left[ \left( \nabla_i \delta \Lambda \left( \vec{r}_i \right) \Psi' \right)^* \left( \nabla_i \delta \Lambda \left( \vec{r}_i \right) \Psi' \right) \right] \geq 0. \quad (B15) \]

Since Eq. (B15) is positive definite for \( \nabla_1 \delta \Lambda \left( \vec{r}_1 \right) \neq 0 \), the extremum condition in Eq. (B12) gives a minimum.
APPENDIX C

DERIVATION OF THE GAUGE-DEPENDENT ENERGY EXPECTATION VALUE FOR THE ANISOTROPIC OSCILLATOR

The gauge-dependent energy expectation value for the anisotropic harmonic oscillator is derived in this appendix using the normalized Gaussian trial wave function in Eq. (3.7) and the energy operator of Eq. (3.6). For simplicity Eq. (3.6) is rewritten in the form

\[
H(\vec{A}) = \left\{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} + \frac{i\hbar}{mc} \left( \frac{\partial}{\partial x_i} \left( \frac{\partial^2}{\partial x_j^2} \right) + \frac{\partial^2}{\partial x_j^2} \left( \frac{\partial}{\partial x_i} \right) \right) + x_i^2 T_{23} 
+ x_i x_j T_{12} \right\} + \text{(cyclic permutations of } 1, 2, 3),
\]  

(C1)

where the constants used are

\[
T_1 = - \frac{\hbar^2}{3} B_3 , \\
T_1' = (1 - \frac{\hbar}{\omega}) B_2 , \\
T_{23} = \frac{m \omega_i^2}{2} + \frac{q^2}{2mc^2} \left[ B_3^2 (1 - \frac{\hbar}{\omega_3})^2 + \frac{q^2}{\omega_3^2} B_2^2 \right] , \\
T_{12} = - \left( \frac{q}{mc^2} \right) \left( 1 - \frac{\hbar}{\omega} \right) \frac{\hbar}{\omega_2} B_2 B_1 ,
\]

and cyclic permutations of these with respect to \((1, 2, 3)\).

When \(H(\vec{A})\) operates on \(\Psi\), the equation
\[ H(\vec{A}) \psi = \psi \left\{ \frac{\hbar^2 \alpha_i}{m} + x_i^2 S_i + x_i x_2 S_{12} + (\text{cyclic permutations of } 1,2,3) \right\} \] (C6)

is obtained, where
\[ S_i = -\frac{2\hbar^2 \alpha_i^2}{m} + T_{23}, \] (C7)
\[ S_{12} = T_{12} - \frac{2i \hbar \alpha_i}{mc} (\alpha_i T_1 + \alpha_2 T_2'), \] (C8)

and \( S_2, S_3, S_{23}, \) and \( S_{31} \) are given by cyclic permutation of \((1,2,3)\).

When Eq. (C6) is used, the energy expectation value can be written as
\[
E = \langle \psi | H(\vec{A}) \psi \rangle = \iint d^3x \, |\psi|^2 \left\{ \left( \frac{\hbar^2 \alpha_i}{m} \right) + x_i^2 S_i + x_i x_2 S_{12} + (\text{cyclic permutations of } 1,2,3) \right\}.
\] (C9)

The integrals over the quadratic terms in Eq. (C9) are
\[
\iint d^3x \, |\psi|^2 x_i^2 S_i = S_i/4 \alpha_i, \quad (i = 1, 2, 3),
\] (C10)

where the Gaussian wave function in Eq. (3.7) has been used. The integrals over the cross terms in Eq. (C9) are zero because the integrand is an odd function integrated over symmetric limits. Equation (C9) is now
$$E = \frac{\hbar^2 \alpha_i}{m} + \frac{S_i}{4 \alpha_i} + \left( \text{cyclic permutations of } 1, 2, 3 \right). \quad (C11)$$

When Eqs. (C4) and (C7) are used in Eq. (C11), the gauge-dependent energy expectation value

$$E = \left\{ \frac{\hbar^2 \alpha_i}{m} + \frac{m \omega_i^2}{8 \alpha_i} + \frac{q^2 B_i^2}{8 mc^2} \left[ \frac{\dot{x}_i^2}{4} \alpha_i^2 - \frac{1}{4} \left( 1 - \frac{\dot{x}_i}{x_i} \right)^2 \alpha_i^2 \right] \right\}$$

$$+ \left( \text{cyclic permutations of } 1, 2, 3 \right). \quad (C12)$$

is obtained, which is Eq. (3.8).
APPENDIX D

JUSTIFICATION FOR VARYING THE ENERGY WITH RESPECT TO GAUGE PARAMETERS

A procedure used by Larsen is to vary the energy expectation value with respect to the gauge parameters. For the anisotropic oscillator this procedure is to vary Eq. (3.8) with respect to \( (\hat{S}_1, \hat{S}_2, \hat{S}_3) \). However, since these are parameters in the Hamiltonian and not in the wave function, there seems to be no justification for varying with respect to the gauge parameters. In this appendix the procedure is justified from the standpoint of the Rayleigh-Ritz principle.

The energy in Eq. (3.8) can be written equivalently as

\[
E(\alpha_1, \alpha_2, \alpha_3) = \langle \Psi'' | H(\vec{A}'') | \Psi'' \rangle,
\]

where the gauge-transformed wave function is

\[
\Psi'' = \exp(iq\lambda/\hbar c) \Psi
\]

and the gauge-transformed vector potential is

\[
\vec{A}'' = \vec{A} + \nabla \lambda.
\]

If a \( \lambda \) can be found which makes \( \vec{A}'' \) independent of the gauge parameters \( (\hat{S}_1, \hat{S}_2, \hat{S}_3) \) in Eq. (3.3), the dependence of the Hamiltonian on them will be eliminated and the parameters will appear in the new wave function \( \Psi'' \). Suppose the new vector potential is
\[ \vec{A}'' = (B_2 x_3, B_3 x_1, B_1 x_2), \] (D4)

for which \( \vec{A} = \nabla \times \vec{A}'' \). Then the gauge function \( \lambda \) is

\[ \lambda(\vec{r}) = B_1 \Phi_3 x_2 x_3 + \text{(cyclic permutations of \(1, 2, 3\))}. \] (D5)

The expectation value in Eq. (D1) is therefore taken with respect to the wave function \( \Psi'' \) in Eq. (D2) which depends on \((\Phi_1, \Phi_2, \Phi_3)\) through Eq. (D5). The Hamiltonian \( H(\vec{A}'') \) does not depend on \((\Phi_1, \Phi_2, \Phi_3)\) because of Eq. (D4).

Since Eq. (D1) is equal to Eq. (3.8), the energy \( E(\alpha_1, \alpha_2, \alpha_3) \) can be varied with respect to \((\Phi_1, \Phi_2, \Phi_3)\) to obtain a lower upper bound on the exact energy. When Eq. (3.8) is varied with respect to \( \Phi_1 \), the first minimization equation is obtained:

\[ \frac{\partial E}{\partial \Phi_1} = (q^2/4\pi m c^2)B_1^2 \left[ (\Phi_1 - 1) \alpha_2^{-1} + \Phi_1 \alpha_3^{-1} \right] = 0. \] (D6)

The other minimization equations \( \frac{\partial E}{\partial \Phi_2} = 0 \) and \( \frac{\partial E}{\partial \Phi_3} = 0 \) are obtained by cyclic permutation of \((1, 2, 3)\) in Eq. (D6). If Eq. (D6) is solved for \( \Phi_1 \), the result is

\[ \Phi_1 = \frac{\alpha_3}{\alpha_2 + \alpha_3}. \] (D7)

The other parameters \( \Phi_2 \) and \( \Phi_3 \) are obtained by cyclic permutation of \((1, 2, 3)\) in Eq. (D7).

When Eq. (D7) for \( \Phi_1 \) and similar expressions for \( \Phi_2 \) and \( \Phi_3 \) are substituted into Eq. (3.8), the result for the minimum energy is
\[ \min_{\varphi} E(\alpha_1, \alpha_2, \alpha_3) = E'(\alpha_1, \alpha_2, \alpha_3), \]  

where \( E' \) is given by Eq. (3.13). By minimizing with respect to the gauge parameters \((\varphi_1, \varphi_2, \varphi_3)\), the gauge of the vector potential has been adapted to the real trial wave function \( \Psi \) in Eq. (3.7). This method makes it necessary to use a specific gauge. In the method of Chapter II an arbitrary gauge is used throughout.
APPENDIX E  
SOLUTION OF THE CHARGE CONSERVATION EQUATION  
FOR THE ANISOTROPIC OSCILLATOR

The charge conservation equation for the anisotropic harmonic oscillator is solved in this appendix for the minimizing phase function $A$. This function is used in Eq. (2.10) for the improved trial wave function $\Psi'$.  

The charge conservation equation in Eq. (2.18) gives an equation for $A$:

$$|\Psi|^2 \nabla^2 A + \nabla A \cdot \nabla |\Psi|^2 = -\frac{m \epsilon c}{q^2} (\nabla \cdot \vec{j}). \quad (E1)$$

If the Gaussian trial wave function of Eq. (3.7) is used in Eq. (E1), the result is

$$\nabla |\Psi|^2 = -4 |\Psi|^2 \sum_{i=1}^{N} (\alpha_i x_i) \hat{\chi}_i. \quad (E2)$$

For the same wave function $\nabla \cdot \vec{j}$ is given by Eq. (3.10). If Eqs. (E2) and (3.10) are substituted into Eq. (E1) and Eq. (3.3) is used, the differential equation for $A$ becomes

$$\nabla^2 A - 4 \left[ \alpha_1 x_1 \frac{\partial A}{\partial x_1} + \alpha_2 x_2 \frac{\partial A}{\partial x_2} + \alpha_3 x_3 \frac{\partial A}{\partial x_3} \right]$$

$$= 4 B_i x_i x_3 \left[ \frac{s_i}{D} \alpha_2 + \alpha_3 \left( \frac{s_i}{D} - 1 \right) \right].$$

101
A function $\Lambda$ which solves Eq. (E3) must be continuous over all space and finite and nonsingular at finite distances from the origin. The boundary conditions are that $\Lambda$ is zero at the origin and that at infinity $\Lambda$ should have no more than a quadratic dependence on $x_i (i = 1, 2, 3)$.

An Ansatz for a solution can be motivated by considering solutions of Laplace's equation

$$\nabla^2 \Lambda = 0,$$  \hspace{1cm} (E4)

which are also solutions of the first order differential equation

$$\alpha_i x_i \frac{\partial \Lambda}{\partial x_i} + B_i x_2 x_3 \left[ \alpha_2 + \alpha_3 (\frac{3}{2} - 1) \right]$$

$$+ \text{(cyclic permutations of 1, 2, 3)} = 0.$$  \hspace{1cm} (E5)

The only function $\Lambda$ which is quadratic in the coordinates and satisfies both Eqs. (E4) and (E5) is of the form

$$\Lambda = \lambda_1 x_1 x_2 + \lambda_2 x_2 x_3 + \lambda_3 x_3 x_3,$$  \hspace{1cm} (E6)

where $(\lambda_1, \lambda_2, \lambda_3)$ are constants to be determined. If Eq. (E6) is substituted into Eq. (E3), the result is

$$x_1 x_2 \left\{ B_3 \left[ \alpha_2 \left( \frac{3}{2} - 1 \right) + \alpha_3 \right] + \lambda_1 (\alpha_1 + \alpha_2) \right\}$$

$$+ \text{(cyclic permutations of 1, 2, 3)} = 0.$$  \hspace{1cm} (E7)
The solution of Eq. (E7) is

$$\lambda_1 = -B_3 \left[ \alpha_1 \frac{d}{3} + \alpha_2 \left( \frac{d}{3} - 1 \right) \right]/(\alpha_1 + \alpha_2),$$  \hspace{1cm} (E8)

where $\lambda_2$ and $\lambda_3$ are given by cyclic permutation of $(1, 2, 3)$.

The improved trial wave function of Eq. (2.10) can now be written in the form

$$\Psi' = \exp \left\{ i \left( g_1 x_1 x_2 + g_2 x_2 x_3 + g_3 x_3 x_1 \right) \right\} \Psi,$$ \hspace{1cm} (E9)

where

$$g_1 = -\frac{q B_3}{\hbar c} \left[ \frac{\alpha_1 \frac{d}{3} + \alpha_2 \left( \frac{d}{3} - 1 \right)}{\alpha_1 + \alpha_2} \right],$$ \hspace{1cm} (E10)

and $g_2$ and $g_3$ are given by cyclic permutation of $(1, 2, 3)$. 
APPENDIX F

DERIVATION OF THE GAUGE-ININVARIANT ENERGY EXPECTATION
VALUE FOR THE ANISOTROPIC OSCILLATOR

The gauge-invariant energy expectation value for the anisotropic harmonic oscillator is derived in this appendix using the energy operator of Eq. (3.6) and the improved trial wave function

$$\Psi' = \exp\left[ i \left( g_1 x_1 x_2 + g_2 x_2 x_3 + g_3 x_1 x_3 \right) \right] \Psi, \quad \text{(F1)}$$

where $\Psi$ is the Gaussian of Eq. (3.7) and $(g_1, g_2, g_3)$ are given by cyclic permutation of $(1,2,3)$ in Eq. (E10).

The energy expectation value can be written in the same form as the gauge-dependent energy expectation value in Eq. (C11):

$$E' = \left\langle \Psi' \left| H(\tilde{A}) \right| \Psi' \right\rangle$$

$$= \frac{\hbar^2 \alpha_i}{m} + \frac{S_1}{4\alpha_i} + \left( \text{cyclic permutations of } 1,2,3 \right), \quad \text{(F2)}$$

where $S_1$ in Eq. (F2) is

$$S_1 = -\left( 2\frac{\hbar^2 \alpha_i^2}{m} \right) + T_{23} + \frac{\hbar^2 (g_1 + g_3)}{2m}$$

$$\left( \frac{\hbar q}{mc} \right) \left[ g_1 T_{2} + g_3 T_{3} \right], \quad \text{(F3)}$$

$T'_2$, $T_3$, and $T_{23}$ are given by Eqs. (C2), (C3), and (C4), and $S_2$ and $S_3$ are given by cyclic permutation of $(1,2,3)$ in Eq. (F3).
The first two terms on the right-hand side of Eq. (F2) may be written as

\[
\frac{\hbar^2 \alpha_i}{m} + \frac{S_i}{\sqrt{2} \alpha_i} = \frac{\hbar^2 \alpha_i}{2m} + \frac{m \omega_i^2}{8 \alpha_i} + \frac{R_i}{4 \alpha_i},
\]

where

\[
R_i = \frac{q^2}{2 mc^2} \left[ B_2 \frac{\alpha_i}{B_2} + B_3 (1 - \frac{\alpha_i}{B_3})^2 \right] + \frac{\hbar^2}{2m} \left( g_i^2 + g_3^2 \right) / 2m
\]

\[-(\hbar q / mc) \left[ g_i T_2 + g_3 T_3 \right],
\]

and Eq. (C4) has been used. If terms that depend on the gauge parameter \( \frac{\alpha_i}{B_3} \) are separated from those that depend on \( \frac{\alpha_i}{B_3} \), \( R_1 \) can be written as

\[
R_i = \frac{B_2^2 R_i' (\frac{\alpha_i}{B_3})}{(\alpha_i + \alpha_3)^2} + \frac{B_3^2 R_i'' (\frac{\alpha_i}{B_3})}{(\alpha_i + \alpha_3)^2},
\]

where

\[
R_i' = \left( \frac{q^2}{2 mc^2} \right) \left[ \frac{\alpha_i}{B_3} \left( \alpha_i + \alpha_3 \right)^2 + \left\{ \alpha_3 \frac{\alpha_i}{B_3} + \alpha_i \left( \frac{\alpha_i}{B_3} - 1 \right) \right\}^2 \right. \\
+ 2 \left( \alpha_i + \alpha_3 \right) \left\{ \alpha_3 \frac{\alpha_i}{B_3} + \alpha_i \left( \frac{\alpha_i}{B_3} - 1 \right) \right\} \left( \frac{\alpha_i}{B_3} \right),
\]

\[
R_i'' = \left( \frac{q^2}{2 mc^2} \right) \left[ (1 - \frac{\alpha_i}{B_3})^2 \left( \alpha_i + \alpha_2 \right)^2 + \left\{ \alpha_i \frac{\alpha_i}{B_3} + \alpha_2 \left( \frac{\alpha_i}{B_3} - 1 \right) \right\}^2 \right. \\
+ 2 \left( \alpha_i + \alpha_2 \right) \left\{ \alpha_i \frac{\alpha_i}{B_3} + \alpha_2 \left( \frac{\alpha_i}{B_3} - 1 \right) \right\} \left( \frac{\alpha_i}{B_3} \right)
\]

and Eqs. (C2), (C3), and (E10) have been used.

If Eqs. (F7) and (F8) are simplified, the results are
\[ R'_t = \frac{q^2 \alpha_t^2}{2 mc^2}, \]  

and

\[ R''_t = \frac{q^2 \alpha_t^2}{2 mc^2}. \]

When Eqs. (F6), (F9), and (F10) are substituted into Eq. (F4), the first two terms of Eq. (F2) are

\[ \frac{\hbar^2 \alpha_t}{m} + \frac{S_t}{4 \alpha_t} = \frac{\hbar^2 \alpha_t}{2m} + \frac{m \omega_t^2}{8 \alpha_t} + \frac{q^2 \alpha_t^2}{8 mc^2} \left[ \frac{B_3^2}{(\alpha_1 + \alpha_2)^2} \right. \\
\left. + \frac{B_3^2}{(\alpha_1 + \alpha_3)^2} \right], \]

The other terms are given by cyclic permutation of \((1,2,3)\). All gauge-dependent terms have canceled out. When Eq. (F11) and its cyclic permutations are used in Eq. (F2), the gauge-invariant energy expectation value

\[ E' = \frac{\hbar^2 \alpha_t}{2m} + \frac{m \omega_t^2}{8 \alpha_t} + \frac{q^2 B_3^2}{8 mc^2(\alpha_2 + \alpha_3)} \]

\[ + \text{(cyclic permutations of } 1,2,3) \]  

is obtained which is Eq. (3.13).
APPENDIX G

COMPUTER PROGRAM

The computer program used to minimize the exciton energy expectation values of Eqs. (6.19) and (6.26) and the shallow donor energy expectation value of Eq. (6.37) was written in FORTRAN IV G and run on a NAS/5000 computer. The program utilizes the standard subroutines FMFP and QG5 from the IBM System/360 Scientific Subroutine Package.

The energies are minimized using subroutine FMFP, which computes the unconstrained minimum of a function of several variables using the function and its gradients with respect to each variable. The subroutine uses the method of steepest descent developed by Fletcher and Powell. In this method the gradients with respect to the variables, which give the slope of the energy surface, are used to determine the direction of steepest descent. This direction is then followed using successive iterations until a point on the energy surface is found where all gradients are zero.

Subroutine QG5 is used to evaluate the one-dimensional elliptical integrals in the energy expectation value and its gradients. The subroutine uses a five-point Gaussian quadrature method. In N-point Gaussian quadrature a one-dimensional integral is approximated by the sum of a series of N Legendre polynomials. The approximation to the area
under the curve (value of the integral) becomes more exact as the sum is extended to more terms. For the simple elliptical integrals dealt with in this paper, a five-point quadrature gives accuracy to five places past the decimal point.
APPENDIX H

POTENTIAL ENERGY OF A HYDROGENIC SYSTEM IN A TOTALLY ANISOTROPIC SEMICONDUCTOR

In this appendix the Coulomb potential energy $V$ of an exciton or of a shallow donor in a totally anisotropic semiconductor is derived. The Coulomb potential energy of an anisotropic exciton or shallow donor is

$$ V = -e \phi_h (\vec{r}_e), \quad (H1) $$

where $\phi_h (\vec{r})$ is the scalar potential for the hole or positive donor ion. The scalar potential is obtained from Poisson's equation.

Gauss's law in the presence of polarizable matter is

$$ \nabla \cdot (\hat{\varepsilon} \cdot \vec{E}) = \rho, \quad (H2) $$

where $\vec{E}$ is the electric field, $\rho$ is the free charge density, and $\hat{\varepsilon}$ is the dielectric tensor which characterizes the matter. For static fields

$$ \vec{E} = -\nabla \phi = \sum_{i=1}^{3} -\partial_i \phi \hat{x}_i, \quad (H3) $$

where $\phi$ is the scalar potential and $\partial_i = \partial / \partial x_i (i = 1, 2, 3)$. When Eq. (H3) is substituted into Eq. (H2), Poisson's equation is obtained:

$$ \sum_{i=1}^{3} \sum_{j=1}^{3} (-\varepsilon_{ij} \partial_i \partial_j \phi) = \rho. \quad (H4) $$
The charge density for a hole or positive donor ion is 
\[ \rho = e \delta (r - r_h). \]
When principal axes are chosen which diagonalize the dielectric tensor, Poisson's equation for the hole is
\[ \left[ -\varepsilon_1 \frac{\partial^2}{\partial x_1^2} - \varepsilon_2 \frac{\partial^2}{\partial x_2^2} - \varepsilon_3 \frac{\partial^2}{\partial x_3^2} \right] \phi_h (\hat{r}) = e \delta (\hat{r} - r_h). \quad (H5) \]
This can be more easily solved in the coordinates
\[ x_i' = \sqrt{\Theta_i} x_i, \quad (i = 1, 2, 3), \quad (H6) \]
where
\[ \Theta_i = \left[ \varepsilon_1 \varepsilon_2 \varepsilon_3 \right]^{1/3} / \varepsilon_i, \quad (i = 1, 2, 3), \quad (H7) \]
and
\[ \varepsilon_i' = K_i \varepsilon_0, \quad (i = 1, 2, 3). \quad (H8) \]
In these coordinates, Eq. (H5) becomes
\[ - \left[ \frac{\partial^2}{\partial x_1'^2} + \frac{\partial^2}{\partial x_2'^2} + \frac{\partial^2}{\partial x_3'^2} \right] \phi_h (\hat{r}') = \frac{e (\Theta_1 \Theta_2 \Theta_3)^{1/2}}{(\varepsilon_1 \varepsilon_2 \varepsilon_3)^{1/3}} \delta (x_1' - x_1'h) \delta (x_2' - x_2'h) \delta (x_3' - x_3'h). \quad (H9) \]
Equation (H9) has the Green function solution \( \delta (\hat{r}) = \delta (\hat{r} - r_h). \quad (H10) \)
\[ \phi_h (\hat{r}') = \frac{e}{4 \pi \varepsilon_0 (K_1 K_2 K_3)^{1/3} \left[ (x_1' - x_1'h)^2 + (x_2' - x_2'h)^2 + (x_3' - x_3'h)^2 \right]^{1/2}}, \quad (H10) \]
where Eq. (H10) satisfies the boundary conditions that the scalar potential and its normal derivative are continuous.
at the surface of the semiconductor.\textsuperscript{75}

If Eq. (H10) is changed from M.K.S. to Gaussian units and written in terms of the unprimed coordinate system, the scalar potential for the hole can be written

\[
\phi_h(r) = \frac{e}{(K_1 K_2 K_3)^{1/2} \left[ \frac{1}{K_1} (x_1 - x_{h1})^2 + \frac{1}{K_2} (x_2 - x_{h2})^2 + \frac{1}{K_3} (x_3 - x_{h3})^2 \right]^{1/2}}.
\] (H11)

When Eq. (H11) is inserted into Eq. (H1), the Coulomb potential energy in Gaussian units is

\[
V = \frac{-e^2}{(K_1 K_2 K_3)^{1/2} \left[ \frac{1}{K_1} (x_e - x_{h1})^2 + \frac{1}{K_2} (x_e - x_{h2})^2 + \frac{1}{K_3} (x_e - x_{h3})^2 \right]^{1/2}}.
\] (H12)

This result applies to both excitons and shallow donors in totally anisotropic semiconductors.
The dimensionless Hamiltonian for the anisotropic shallow donor is derived here. When the mixed gauge of Eq. (3.3) is used in Eq. (4.1), the shallow donor Hamiltonian is

\[ H(r) = \left\{ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} - i\frac{e^2}{m_c} \left[ (1 - \frac{\xi_3}{\xi_2}) B_2 x_3 - \frac{\xi_3}{\xi_2} B_3 x_2 \right] \right\} + \left( \text{cyclic permutations of } 1, 2, 3 \right) \]

\[ \frac{\epsilon^2}{K^{3/2}} \left[ \left( \frac{X_1}{K_1} \right)^2 + \left( \frac{X_2}{K_2} \right)^2 + \left( \frac{X_3}{K_3} \right)^2 \right]^{1/2} \]

where \( K \) is defined in Eq. (4.7). When lengths are expressed in units of the effective Bohr radius \( a_0 \) given in Eq. (4.4) and Eqs. (3.21), (4.3), (4.5), and (4.8) are used, Eq. (II) may be written

\[ H(r) = \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_i^2} + 2i\hbar \omega_L \left( Y_{i2} x_2 + Y_{i3} x_3 \right) \frac{\partial}{\partial x_i} \right\} + \left( \text{cyclic permutations of } 1, 2, 3 \right) \]

\[ \frac{\hbar^2 \omega_L}{\hbar} \left( Y_{12} x_3 + Y_{21} x_2 \right) \]
where the dimensionless functions

\[ Y_1 = J_1 J_3 C_3, \]

\[ Y'_1 = J_1 (J_2 - 1) C_2, \]

\[ Y_{12} = J_1 (1 - J_2) C_2^2 + J_2 J_3 C_1^2, \]

\[ Y'_{12} = 2 J_3 J_2 (J_1 - 1) C_1 C_2, \]

and cyclic permutations of these in (1,2,3) have been used.

If Eq. (I2) is divided by the Rydberg and the field parameter \( \gamma \) given by Eq. (4.9) is used, then the dimensionless Hamiltonian in Eq. (4.10) is obtained.
The charge conservation equation for an electron bound to a donor impurity in an anisotropic semiconductor is derived in this appendix and solved for the phase function. The resulting improved trial wave function is expressed in dimensionless units. If the Hamiltonian of Eq. (4.1) and the improved trial wave function

\[ \Psi'(\vec{r}) = \exp \left( -ieA/\hbar \right) \Psi(\vec{r}) \]  

are used in the energy expectation value, then the first variation of the energy expectation value with respect to \( \Lambda \) gives

\[ \text{Im} \left\{ \Psi'^* H(\vec{r}) \Psi' \right\} = 0. \]  

When Eq. (4.1) is used in Eq. (J2), the minimization condition may be written

\[ \text{Im} \left\{ \Psi'^* \left[ \vec{\pi} \cdot \left( \frac{\vec{\pi}'}{m} \right) \cdot \vec{\pi} \right] \Psi' \right\} = 0, \]  

where the kinetic momentum of the electron is

\[ \vec{\pi} = \vec{p} + e\vec{A}(\vec{r})/c, \]
and the reciprocal effective mass tensor is
\[
\mathbf{\tilde{m}} = \begin{pmatrix} \frac{i}{m_1} & 0 & 0 \\ 0 & \frac{i}{m_2} \\ 0 & 0 & \frac{i}{m_3} \end{pmatrix}.
\]  
(J5)

Equation (J3) can be rewritten as
\[
\ell_m \left\{ -i \hbar \nabla \cdot \left[ \Psi' \mathbf{\tilde{m}} (\mathbf{\tilde{m}}) \cdot \mathbf{\tilde{m}} \Psi' \right] + (\mathbf{\tilde{m}} \Psi')^* \cdot \left( \frac{i}{m} \right) \cdot (\mathbf{\tilde{m}} \Psi') \right\} = 0.
\]  
(J6)

The last term in the brackets in Eq. (J6) is real, so that Eq. (J6) gives
\[
\nabla \cdot \mathbf{\tilde{J}}' = 0,
\]  
(J7)

where the current density \( \mathbf{\tilde{J}}' \) for the anisotropic electron is
\[
\mathbf{\tilde{J}}' = \Re \left\{ \Psi'^* \sum_{i=1}^{3} \frac{-e}{m_i} \left( \rho_i + \frac{e}{c} A_i (\mathbf{\hat{r}}) \right) \mathbf{\hat{r}}_i \Psi' \right\}.
\]  
(J8)

When Eq. (J1) is inserted into Eq. (J8), the result is
\[
\mathbf{\tilde{J}}' = \mathbf{\tilde{J}} + \frac{e^2}{mc} \left| \Psi' \right|^2 \sum_{i=1}^{3} \mathbf{\hat{r}}_i \frac{\partial A}{\partial \chi_i} \mathbf{\hat{r}}_i,
\]  
(J9)

where Eqs. (4.6) and (4.8) have been used and \( \mathbf{\tilde{J}} \) is given by Eq. (J8) with \( \Psi' \) replaced by \( \Psi \). Equations (J9) and (J7) give the differential equation for the minimizing \( \mathbf{\hat{A}} \).
where $\partial_i = \partial / \partial x_i$ and the charge density $\rho(\vec{r}) = -e|\Psi(\vec{r})|^2$.

This equation is now solved for $\Lambda$ when the trial wave function $\Psi(\vec{r})$ is given by Eq. (3.7).

For real $\Psi(\vec{r})$ the divergence of the current density $\vec{J}(\vec{r})$ is

$$\nabla \cdot \vec{J}(\vec{r}) = \frac{e}{c} \sum_{i=1}^{3} \frac{A_i(\vec{r})}{m_i} \left( \partial_i \rho \right).$$

The gradient of $\rho$ with respect to $x_i$ for $\Psi(\vec{r})$ given by Eq. (3.7) is

$$\partial_i \rho = \rho (\cdot 4 \alpha_i x_i).$$

When Eqs. (J11) and (J12) are used in Eq. (J10), the charge conservation equation reduces to

$$\sum_{i=1}^{3} \left[ 4 \alpha_i x_i J_i (A_i(\vec{r}) - \partial_i \Lambda) + J_i \partial_i^2 \Lambda \right] = 0.$$  

A solution of Eq. (J13) is of the form

$$\Lambda = \lambda_1 x_1 x_2 + \lambda_2 x_2 x_3 + \lambda_3 x_1 x_3,$$

where $(\lambda_1, \lambda_2, \lambda_3)$ are constants to be determined. Equations (3.3), (3.21), (4.11), and (4.12) can be used to express $A_1(\vec{r})$ as
\[
A_1(\vec{r}) = \frac{-B}{\phi_1} \left( Y'_1 x_3 + Y'_1 x_2 \right),
\]

(J15)

where \(A_2\) and \(A_3\) are given by cyclic permutation of \((1,2,3)\) in Eq. (J15). If Eqs. (J14) and (J15) are inserted into Eq. (J13), the result is

\[
\alpha_1 x_3 \left[ -B (Y'_1 x_3 + Y'_1 x_2) - \Gamma (\lambda_1 x_2 + \lambda_3 x_3) \right] + (\text{cyclic permutations of } 1, 2, 3) = 0.
\]

(J16)

When terms are grouped according to the coordinates, Eq. (J16) becomes

\[
-x_1 x_2 \left[ B (\alpha_1 Y_1 + \alpha_2 Y_2') + \lambda_1 (\Gamma_1 \alpha_1 + \Gamma_2 \alpha_2) \right] + (\text{cyclic permutations of } 1, 2, 3) = 0.
\]

(J17)

The solution of Eq. (J17) is

\[
\lambda_1 = \frac{-B (\alpha_1 Y_1 + \alpha_2 Y_2')} {\Gamma_1 \alpha_1 + \Gamma_2 \alpha_2},
\]

(J18)

where \(\lambda_2\) and \(\lambda_3\) are given by cyclic permutation of \((1,2,3)\) in Eq. (J18).

The improved trial wave function of Eq. (J1) can now be written in the form

\[
|\Psi'\rangle = \exp \left\{ i (g_1 x_1 x_2 + g_2 x_2 x_3 + g_3 x_1 x_3) \right\} |\Psi\rangle.
\]

(J19)
where

\[ g_i = \left( \frac{e B}{\hbar c} \right) \left( \frac{\alpha_1 Y_1 + \alpha_2 Y_2'}{\frac{\gamma}{2} \alpha_1 + \frac{\gamma}{2} \alpha_2} \right), \quad (J20) \]

and \( g_2 \) and \( g_3 \) are given by cyclic permutation of \( (1,2,3) \) in Eq. (J20). When lengths are expressed in units of the effective Bohr radius \( a_0 \) given in Eq. (4.4) and Eqs. (4.3), (4.5), and (4.9) are used, \( \Psi' \) is given by Eq. (J19) with

\[ g_i = \gamma \left( \frac{\alpha_1 Y_1 + \alpha_2 Y_2'}{\frac{\gamma}{2} \alpha_1 + \frac{\gamma}{2} \alpha_2} \right), \quad (J21) \]

and \( g_2 \) and \( g_3 \) given by cyclic permutation of \( (1,2,3) \).
APPENDIX K

GAUGE-INvariant ENERGY EXPECTATION VALUE
FOR ANISOTROPIC SHALLOW DONORS

The gauge-invariant energy expectation value for anisotropic shallow donors is derived here using the improved trial wave function derived in Appendix J:

\[ \Psi'(\vec{r}) = \exp \left[ i \left( g_1 x_1 x_2 + g_2 x_2 x_3 + g_3 x_3 x_1 \right) \right] \Psi(\vec{r}). \] (K1)

In Eq. (K1) \((g_1, g_2, g_3)\) are given by cyclic permutation of \((1,2,3)\) in Eq. (J20) and \(\Psi(\vec{r})\) is the normalized Gaussian trial wave function defined in Eq. (3.7). The dimensionless shallow donor Hamiltonian is

\[ H(\vec{r}) = \left\{ \begin{array}{l}
- \frac{\partial^2}{\partial x_1^2} + 2 i \delta \left( Y_1 x_1 + Y_1' x_3 \right) \frac{\partial}{\partial x_1} \\
+ \delta^2 \left( Y_2 x_3^2 + Y_2' x_1 x_2 \right) \\
+ \text{cyclic permutations of } (1,2,3) \right\} + V(\vec{r}), \] (K2)

where the potential energy is

\[ V(\vec{r}) = \frac{-2}{K^{n/2} \left[ \frac{x_1^2}{K_1} + \frac{x_2^2}{K_2} + \frac{x_3^2}{K_3} \right]^{n/2}}. \] (K3)

When \(H(\vec{r})\) operates on \(\Psi'(\vec{r})\), the result is
\[ H(\vec{r}) \Psi'(\vec{r}) = \Psi'(\vec{r}) \left\{ S_1 x_1^2 + S_{12} x_1 x_2 + 2 \mathcal{P}_1 \alpha_1 \right. \]
\[ + \left. \{ \text{cyclic permutations of } 1, 2, 3 \} \right\} + \Psi'(\vec{r}) V(\vec{r}), \tag{K4} \]

where
\[ S_1 = -4 \mathcal{P}_1 \alpha_1^2 + (g_3 g_3^2 + g_2 g_2^2) + \gamma^2 \gamma_{23} - 2 \gamma (g_1 \gamma_2 + g_3 \gamma_3), \tag{K5} \]
\[ S_{12} = 4 i g_1 (\alpha_1 \mathcal{P}_1 + \alpha_2 \mathcal{P}_2) + 2 g_3 g_2 g_3 + \gamma^2 \gamma_{12} \]
\[ - 4 i \gamma (\alpha_2 \gamma_2 + \alpha_1 \gamma_1) - 2 \gamma (g_3 \gamma_3 + g_2 \gamma_3), \tag{K6} \]

and each of these equations gives two others by cyclic permutation of \((1, 2, 3)\).

When Eq. (K4) is used, the energy expectation value is
\[ E' = \langle \Psi' | H | \Psi' \rangle \]
\[ = \iiint d^3 x \left| \Psi'(\vec{r}) \right|^2 \left\{ S_1 x_1^2 + S_{12} x_1 x_2 + 2 \mathcal{P}_1 \alpha_1 \right. \]
\[ + \left. \{ \text{cyclic permutations of } 1, 2, 3 \} \right\} \]
\[ + \iiint d^3 x \left| \Psi'(\vec{r}) \right|^2 V(\vec{r}). \tag{K7} \]

Except for the potential energy term, the integrals in Eq. (K7) are of the same form as those evaluated in Appendix C for the anisotropic harmonic oscillator. Integrals over the cross terms vanish and those over the quadratic terms are
\[ \iiint d^3 x \left| \Psi'(\vec{r}) \right|^2 x_i^2 = \left( 1/4 \alpha_i^2 \right), \quad (i = 1, 2, 3). \tag{K8} \]

Equation (K7) now becomes
The potential energy term is partially integrated in Appendix L.

The first two terms on the right-hand side of Eq. (K9) may be written as

\[ 2 \alpha_1 J_1 + \left( S_1 / 4 \alpha_1 \right) = \alpha_1 J_1 + \left( R_1 / 4 \alpha_1 \right), \]  

(K10)

where

\[ R_1 = J_3 \gamma^2 \left( \frac{Y_2 \alpha_3 + Y_3 \alpha_2}{\alpha_1 J_1 + \alpha_3 J_3} \right)^2 + J_3 \gamma^2 \left( \frac{Y_1 \alpha_1 + Y_3 \alpha_2}{\alpha_1 J_1 + \alpha_3 J_3} \right)^2 + \gamma^2 \gamma^2 Y_{23} \]

\[ -2 \gamma^2 \left[ \frac{Y_2 \gamma \alpha_1 + Y_2 \gamma \alpha_2}{\alpha_1 J_1 + \alpha_2 J_2} \right] \]

(K11)

and Eq. (4.21) and its cyclic permutations in (1,2,3) have been used for \((g_1,g_2,g_3)\). When terms that depend on the gauge parameter \(\bar{g}_2\) are separated from terms that depend on \(\bar{g}_3\), \(R_1\) can be written

\[ R_1 = \gamma^2 C_2 \frac{R_1' \left( \bar{g}_2 \right)}{\left( \alpha_1 J_1 + \alpha_3 J_3 \right)^2} + \gamma^2 C_3 \frac{R_1'' \left( \bar{g}_3 \right)}{\left( \alpha_1 J_1 + \alpha_2 J_2 \right)^2}. \]  

(K12)

The functions \(R_1' \left( \bar{g}_2 \right)\) and \(R_1'' \left( \bar{g}_3 \right)\) can now be evaluated separately.
If cyclic permutations of Eqs. (4.11) - (4.14) are used in Eq. (K11), then \( R'_1 (\phi_2) \) is

\[
R'_1 = J_3 (\alpha_1 J_1 + \alpha_3 J_3)^2 \phi_2^2 + \frac{\alpha_1^2 \phi_3^2 (1 - \phi_2)^2 - \alpha_3^2 \phi_3^2 \phi_2^2}{2 J_1} \alpha_2 J_3 \phi_2^2
\]

\[
- 2 J_1 \alpha_1 \alpha_2 J_3 \phi_2^2 + 2 J_1 \alpha_2 J_3 \phi_2 (1 - \phi_2). \tag{K13}
\]

When terms in powers of \( \phi_2 \) are collected, Eq. (K13) reduces to

\[
R'_1 = J_3 \phi_2^2 \alpha_1^2. \tag{K14}
\]

The function \( R''_1 (\phi_3) \) is

\[
R''_1 = J_2 (1 - \phi_3)^2 (\alpha_1 J_1 + \alpha_2 J_2)^2 + J_2 \alpha_1^2 \phi_3^2 \phi_2^2 - \frac{\alpha_2^2 \phi_3^2 (1 - \phi_3)^2}{2 J_1} \alpha_1 J_3 \phi_2^2
\]

\[
+ 2 J_1 \alpha_1 \alpha_2 J_3 \phi_2 (1 - \phi_3) - 2 J_1 \alpha_1 \alpha_2 \phi_2 (1 - \phi_3)^2. \tag{K15}
\]

When terms in powers of \( \phi_3 \) are collected, Eq. (K15) reduces to

\[
R''_1 = J_2 \phi_3^2 \alpha_1. \tag{K16}
\]

When Eqs. (K12), (K14), and (K16) are substituted into Eq. (K10), the first two terms on the right-hand side of Eq. (K9) are

\[
2 \alpha_1 J_1 + (S_1 / 4 \alpha_1) = \alpha_1 J_1 + \frac{\gamma^2 C_2}{4} \left[ \frac{\alpha_1 J_1 \phi_3^2}{(\alpha_1 J_1 + \alpha_2 J_2)^3} \right]
\]

\[
+ \frac{\gamma^2 C_2}{4} \left[ \frac{\alpha_1 \phi_3^2}{(\alpha_1 J_1 + \alpha_2 \phi_2)^2} \right]. \tag{K17}
\]
The other terms are given by cyclic permutation of \((1,2,3)\) in Eq. (K17). All gauge-dependent terms, containing \(\xi_i\ (i = 1,2,3)\), have canceled. When Eq. (K17) and its cyclic permutations are used in Eq. (K9), the gauge-invariant energy expectation value

\[
E' = \left\{ \xi_i \alpha_i + \frac{\delta^2 C^2 \xi_i \xi_j}{4(\alpha_1 \xi_2 + \alpha_2 \xi_3)} + \text{cyclic permutations of } 1,2,3 \right\} + \int d^3x \left| \Psi(\vec{r}) \right|^2 V(\vec{r})
\]  

(K18)

is obtained. The terms in brackets in Eq. (K18) are the same as appear in the brackets in Eq. (4.23). The potential energy term is evaluated in Appendix L.
APPENDIX L

POTENTIAL ENERGY INTEGRAL

In this appendix the potential energy term of the energy expectation value for anisotropic excitons and anisotropic shallow donors is evaluated. The potential energy term is a three-dimensional integral which may be written in Cartesian coordinates as

\[
\int d^3x \left| \Psi(\vec{r}) \right|^2 V(\vec{r}) = -2 \frac{8 \alpha_1 \alpha_2 \alpha_3}{\pi^3} \mathcal{I},
\]

where

\[
\mathcal{I} = \int d^3x \exp\left[ -2 \alpha_1 x_1^2 - 2 \alpha_2 x_2^2 - 2 \alpha_3 x_3^2 \right]
K^{\frac{1}{2}} \left[ (x_1^2/K_1) + (x_2^2/K_2) + (x_3^2/K_3) \right]^{\frac{1}{2}},
\]

When a transformation into spherical coordinates \((r', \Theta, \Phi)\) is made using

\[
x_1 = \beta_1^{\frac{1}{2}} r' \sin \Theta \cos \Phi,
\]

\[
x_2 = \beta_2^{\frac{1}{2}} r' \sin \Theta \sin \Phi,
\]

\[
x_3 = \beta_3^{\frac{1}{2}} r' \cos \Theta,
\]

\[
r'^2 = \beta_1 x_1^2 + \beta_2 x_2^2 + \beta_3 x_3^2,
\]

and
\( \theta_i = K/K_i, \quad (i = 1, 2, 3), \) \hspace{2cm} (L7)

then the integral in Eq. (L2) becomes

\[
I = (\theta_1 \theta_2 \theta_3)^{-\frac{1}{2}} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \ d\theta \int_0^\infty r' \ dr' \exp(-2 r'^2 R), \] \hspace{2cm} (L8)

where

\[
R = \alpha_1 \theta_1^{-1} \sin^2 \theta \cos^2 \phi + \alpha_2 \theta_2^{-1} \sin^2 \theta \sin^2 \phi + \alpha_3 \theta_3^{-1} \cos^2 \theta. \] \hspace{2cm} (L9)

The integral over the radial coordinate is

\[
\int_0^\infty r' \ dr' \exp(-2 r'^2 R) = 1/4R. \] \hspace{2cm} (L10)

If \( R \) is rewritten as

\[
R = b^2 \sin^2 \phi + a^2 \cos^2 \phi, \] \hspace{2cm} (L11)

where

\[
b^2 = \alpha_2 \theta_2^{-1} \sin^2 \theta + \alpha_3 \theta_3^{-1} \cos^2 \theta \] \hspace{2cm} (L12)

and

\[
a^2 = \alpha_1 \theta_1^{-1} \sin^2 \theta + \alpha_3 \theta_3^{-1} \cos^2 \theta, \] \hspace{2cm} (L13)

then the integral \( I \) can be written

\[
I = (\theta_1 \theta_2 \theta_3)^{-\frac{1}{2}} \int_0^{2\pi} \sin \theta \ d\theta \int_0^\pi \frac{d\phi}{b^2 \sin^2 \phi + a^2 \cos^2 \phi}. \] \hspace{2cm} (L14)

The integral over the azimuthal coordinate is
\[ \int_0^{2\pi} d\Theta \left[ b^2 \sin^2 \Theta + a^2 \cos^2 \Theta \right]^{-1} = \frac{2\pi}{ab}, \quad (L15) \]

and thus the integral I becomes

\[ I = \pi \left( \frac{\Theta_1 \Theta_2 \Theta_3}{2} \right)^{-\frac{1}{2}} \int_0^{\pi} \frac{\sin \Theta}{ab} d\Theta, \quad (L16) \]

where

\[(ab)^{-1} = \left[ \alpha_1 \alpha_2 \Theta_1^{-1} \Theta_2^{-1} \sin^2 \theta + \alpha_3 \Theta_3^{-2} \cos^4 \theta \right. \]
\[+ \left. \alpha_3 \Theta_3^{-2} \left( \alpha_1 \Theta_1^{-1} + \alpha_2 \Theta_2^{-1} \right) \cos^2 \theta \sin^2 \theta \right]^{-\frac{1}{2}}. \quad (L17) \]

When the coordinate transformation

\[ u = \cos \theta \quad (L18) \]

and

\[ du = -\sin \theta \, d\theta \quad (L19) \]

is made, Eq. (L16) becomes

\[ I = \pi \left( \frac{\Theta_1 \Theta_2 \Theta_3}{2} \right)^{-\frac{1}{2}} \left( \frac{\Theta_1 \Theta_2}{\alpha_1 \alpha_2} \right)^{\frac{1}{2}} \int_{-1}^{1} \frac{du}{\left[ a'' u^4 + b'' u^2 + 1 \right]^\frac{1}{2}}, \quad (L20) \]

where

\[ a'' = \frac{\alpha_3^2 \Theta_1 \Theta_2}{\Theta_3^2 \alpha_2 \alpha_1} - \frac{\alpha_3 \Theta_3^{-2} \left( \alpha_1 \Theta_1^{-1} + \alpha_2 \Theta_2^{-1} \right)}{\alpha_1 \alpha_2 \Theta_1^{-1} \Theta_2^{-1}} + 1, \quad (L21) \]

and

\[ b'' = \frac{\alpha_3 \Theta_3^{-2} \left( \alpha_1 \Theta_1^{-1} + \alpha_2 \Theta_2^{-1} \right)}{\Theta_1^{-1} \Theta_2^{-1} \alpha_2 \alpha_1} - 2. \quad (L22) \]
When Eq. (L20) is inserted into Eq. (L1), the potential energy integral is

$$
S S S d^3x \ |\Psi|^2 V(r) = -\left[ \frac{32 \alpha_3}{\pi \beta_3} \right]^{1/2} \int' \frac{du}{\left[ a'' u^4 + b'' u^2 + 1 \right]^{1/2}}.
$$

This result is valid for both excitons and shallow donors in anisotropic semiconductors.
APPENDIX M

PARTIAL DECOUPLING OF THE CENTER-OF-MASS AND RELATIVE MOTIONS OF THE EXCITON

In this appendix the center-of-mass and relative motions in the two-particle Schrödinger equation for the exciton are partially decoupled using the wave function

$\Phi = \exp\left(-i e u \mu/c\right) F(R, \vec{r}), \quad (M1)$

where

$u = \vec{A}(R) \cdot \vec{r}. \quad (M2)$

In the mixed gauge of Eq. (3.3), the components of $\vec{A}(R)$ are

$A_i^j(R) = (1 - \delta^i_j) B_j X_k - \delta^j_k B_k X_j, \quad (M3)$

where $X_i$ is defined in Eq. (5.5) and $(i,j,k)$ are cyclic permutations of $(1,2,3)$.

If the Hamiltonian of Eq. (5.1) is expanded, it can be written as

$H = \sum_{i=1}^3 \left\{ \frac{1}{2 m_{e_i}} \left[ -\hbar^2 \frac{\partial^2}{\partial x_{e_i}^2} - \frac{2 i e A_i(\vec{r}_e)}{c} \frac{\partial}{\partial x_{e_i}} \right] \right. \right.

\left. + \frac{e^2}{c^2} A_i^2(\vec{r}_e) \right\} + \frac{1}{2 m_{h_i}} \left[ -\hbar^2 \frac{\partial^2}{\partial x_{h_i}^2} + \frac{2 i e A_i(\vec{r}_h)}{c} \frac{\partial}{\partial x_{h_i}} \right. \right.

\left. \left. + \frac{e^2}{c^2} A_i^2(\vec{r}_h) \right\} + V(\vec{r}), \quad (M4) \right.$
where the potential energy term is

\[ V(\mathbf{r}) = -\frac{e^2}{(K_x K_y K_z)^{1/2}} \left( \frac{x^2}{K_x} + \frac{x^2}{K_y} + \frac{x^2}{K_z} \right)^{1/2} \]  

(M5)

The derivatives of \( \Phi \) with respect to the electron coordinates are

\[
\frac{\partial \Phi}{\partial x_{ei}} = \exp\left(\frac{-ieu}{\hbar c}\right) \left\{ \frac{\partial F}{\partial x_{ei}} \frac{-ieF}{\hbar c} \frac{\partial u}{\partial x_{ei}} \right\},
\]

(M6)

and

\[
\frac{\partial^2 \Phi}{\partial x_{ei}^2} = \exp\left(\frac{-ieu}{\hbar c}\right) \left\{ \frac{\partial^2 F}{\partial x_{ei}^2} \frac{-2ie}{\hbar c} \frac{\partial F}{\partial x_{ei}} \frac{\partial u}{\partial x_{ei}} \right. \\
\left. - \frac{e^2}{\hbar^2 c^2} F \left( \frac{\partial u}{\partial x_{ei}} \right)^2 - \frac{ieF}{\hbar c} \frac{\partial^2 u}{\partial x_{ei}^2} \right\},
\]

(M7)

with equivalent expressions for the hole coordinates. Note that the last term in Eq. (M7) vanishes since \( u \) is only linear in \( x_{ei} \).

When Eq. (M4) operates on Eq. (M1) and Eqs. (M6), (M7), and (5.2) are used, the result is

\[
\sum_{i=1}^{3} \left\{ -\frac{\hbar^2}{2} \left[ \frac{1}{m_{ei}} \frac{\partial^2 F}{\partial x_{ei}^2} + \frac{1}{m_{hi}} \frac{\partial^2 F}{\partial x_{hi}^2} \right] + \frac{i e \hbar}{c} \left[ \frac{1}{m_{ei}} \left( A_{\lambda}(\mathbf{r}_{ei}) - \frac{\partial u}{\partial x_{ei}} \right) \frac{\partial F}{\partial x_{ei}} + \frac{1}{m_{hi}} \left( -A_{\lambda}(\mathbf{r}_{hi}) - \frac{\partial u}{\partial x_{hi}} \right) \frac{\partial F}{\partial x_{hi}} \right] \right. \\
\left. - \frac{e^2}{\hbar^2 c^2} F \left( \frac{\partial u}{\partial x_{ei}} \right)^2 \right\}
\]
After dividing by \( \exp(-iu/\hbar c) \). If the definitions
\[
G_{ei} = A_i(\vec{r}_e) - \partial u / \partial x_{ei} \tag{M9}
\]
and
\[
G_{hi} = -A_i(\vec{r}_h) - \partial u / \partial x_{hi} \tag{M10}
\]
are used, Eq. (M8) becomes
\[
\sum_{i=1}^{3} \left\{ \frac{-\hbar^2}{2} \left[ \frac{1}{m_{ei}} \frac{\partial^2}{\partial x_{ei}^2} + \frac{1}{m_{hi}} \frac{\partial^2}{\partial x_{hi}^2} \right] - \frac{i e \hbar}{c} \left[ \gamma_{ei} \frac{\partial}{\partial x_{ei}} \right] + \frac{e^2}{2c^2} \left[ \frac{G_{ei}^2}{m_{ei}} + \frac{G_{hi}^2}{m_{hi}} \right] \right\} F(\vec{R}, \vec{r}) + V(\vec{r}) F(\vec{R}, \vec{r}) = \varepsilon F(\vec{R}, \vec{r}). \tag{M11}
\]

If the chain rule and Eqs. (5.3) and (5.5) are used, the derivative operators in electron and hole coordinates can be expressed in terms of derivatives in relative and center-of-mass coordinates as
\[
\frac{\partial}{\partial x_{ei}} = m_{ei}' \frac{\partial}{\partial x_i} \tag{M12}
\]
and
\[
\frac{\partial}{\partial x_{hi}} = m_{hi}' \frac{\partial}{\partial x_i} - \frac{\partial}{\partial x_i}. \tag{M13}
\]
where

$$m'_{ei} = m_{ei} / (m_{ei} + m_{hi})$$  \hspace{1cm} (M14)$$

and

$$m'_{hi} = m_{hi} / (m_{ei} + m_{hi}) .$$  \hspace{1cm} (M15)

The components of $\mathbf{r}_e$ and $\mathbf{r}_h$ can also be written in terms of the components of $\mathbf{r}$ and $\mathbf{R}$ as

$$x_{e,i} = m'_{hi} x_i + X_{i,i}$$  \hspace{1cm} (M16)$$

and

$$x_{h,i} = -m'_{ei} x_i + X_{i,i} .$$  \hspace{1cm} (M17)

These definitions can be used to show that $C_{ei}$ and $C_{hi}$ in Eqs. (M9) and (M10) are solely functions of the relative coordinates.

In the mixed gauge the components of the vector potential $\mathbf{A}(\mathbf{r}_e)$ are

$$A_i(\mathbf{r}_e) = \left(1 - \frac{1}{\mathbf{r}}\right) B_j x_{e,k} - \frac{1}{\mathbf{r}} B_k x_{e,j} ,$$  \hspace{1cm} (M18)$$

where $(i,j,k)$ are cyclic permutations of $(1,2,3)$. If Eqs. (M16) and (M17) are used, Eq. (M18) becomes

$$A_i(\mathbf{r}_e) = \left[ (1 - \frac{1}{\mathbf{r}}) B_j m'_{hi} x_k - \frac{1}{\mathbf{r}} B_k m'_{ei} x_j \right]$$

$$+ \left[ (1 - \frac{1}{\mathbf{r}}) B_j X_k - \frac{1}{\mathbf{r}} B_k X_j \right] .$$  \hspace{1cm} (M19)$$

Equation (M21) can be written as
\[ A_i(\vec{r}_e) = A_i(\vec{a}_i \cdot \vec{r}) + A_i(\vec{R}), \]  

(M20)

where the dyad

\[
\vec{a}_i = \begin{pmatrix}
  m'_{h1} & 0 & 0 \\
  0 & m'_{h2} & 0 \\
  0 & 0 & m'_{h3}
\end{pmatrix}
\]

(M21)

is used to express the first term of Eq. (M19) in weighted relative coordinates. Similarly, \( \vec{A}_i(\vec{r}_h) \) can be written as

\[ A_i(\vec{r}_h) = A_i(\vec{a}_2 \cdot \vec{r}) + A_i(\vec{R}), \]  

(M22)

where

\[
\vec{a}_2 = \begin{pmatrix}
  -m'_{e1} & 0 & 0 \\
  0 & -m'_{e2} & 0 \\
  0 & 0 & -m_{e3}
\end{pmatrix}
\]

(M23)

If Eqs. (M12) and (M13) are substituted into Eqs. (M9) and (M10), the result is

\[ G_{e_i} = A_i(\vec{a}_i \cdot \vec{r}) + A_i(\vec{R}) - \left( \frac{\partial u}{\partial x_i} \right) - m'_{e_i} \left( \frac{\partial u}{\partial x_i} \right) \]  

(M24)

and

\[ G_{h_i} = -A_i(\vec{a}_2 \cdot \vec{r}) + A_i(\vec{R}) + \left( \frac{\partial u}{\partial x_i} \right) + m'_{h_i} \left( \frac{\partial u}{\partial x_i} \right), \]  

(M25)

respectively.

From Eqs. (M2) and (M3) \( u \) may be written as

\[ u = \left[ \left( 1 - \frac{r_2}{B_2} \right) B_2 X_3 - \frac{r_2}{B_3} B_3 X_2 \right] x_i. \]
\[ + \text{(cyclic permutations of } 1, 2, 3) \, . \quad (M26) \]

The derivatives of \( u \) are

\[ \frac{\partial u}{\partial x_{\lambda}} = A_{\lambda}(\vec{\mathbf{R}}) \quad (M27) \]

and

\[ \frac{\partial u}{\partial \mathbf{X}_{\lambda}} = (1 - \delta_{k}) B_{k} x_{j} - \delta_{j} B_{j} x_{k} \]
\[ = \left[ (1 - \delta_{j}) B_{j} x_{k} - \delta_{k} B_{k} x_{j} \right] \]
\[ - \left[ B_{j} x_{k} - B_{k} x_{j} \right] \]
\[ = A_{\lambda}(\vec{\mathbf{r}}) - (\vec{\mathbf{B}} \times \vec{\mathbf{r}})_{\lambda} \quad (M28) \]

Finally, when Eqs. (M27) and (M28) are used in Eqs. (M24) and (M25), all terms in center-of-mass coordinates cancel, which gives

\[ G_{ei}(\vec{\mathbf{r}}) = A_{\lambda}(\vec{\mathbf{a}}_{i} \cdot \vec{\mathbf{r}}) + m'_{ei} \left[ (\vec{\mathbf{B}} \times \vec{\mathbf{r}})_{i} - A_{i}(\vec{\mathbf{r}}) \right] \quad (M29) \]

and

\[ G_{hi}(\vec{\mathbf{r}}) = -A_{\lambda}(\vec{\mathbf{a}}_{i} \cdot \vec{\mathbf{r}}) + m'_{\lambda i} \left[ (\vec{\mathbf{B}} \times \vec{\mathbf{r}})_{i} - A_{i}(\vec{\mathbf{r}}) \right] . \quad (M30) \]

If Eqs. (M12) and (M13) are inserted into Eq. (M11), the partially decoupled Schrödinger equation in relative and center-of-mass coordinates is
\[
\sum_{i=1}^{3} \left\{ -\hbar^2 \left[ \frac{1}{M_i} \frac{\partial^2}{\partial X_i^2} + \frac{1}{\mu_i} \frac{\partial^2}{\partial X_i^2} \right] - \frac{i e \hbar}{c} \left[ \left( \frac{G_{ei} + G_{hi}}{M_i} \right) \frac{\partial}{\partial X_i} \right] 
+ \left( \frac{G_{ei}}{m_{ei}} - \frac{G_{hi}}{m_{hi}} \right) \frac{\partial}{\partial X_i} \right] + \frac{e^2}{4c^2} \left[ \frac{G_{ei}^2}{m_{ei}^2} + \frac{G_{hi}^2}{m_{hi}^2} \right] \right\} F(\vec{R}, \vec{r}) 
+ \nabla(\vec{r}) F(\vec{R}, \vec{r}) = \varepsilon F(\vec{R}, \vec{r}), \tag{M31}
\]

where \( M_i \) is the total effective mass

\[
M_i = m_{ei} + m_{hi}, \ (i = 1, 2, 3), \tag{M32}
\]

and \( \mu_i \) is the reduced effective mass

\[
\mu_i = m_{ei}^{-1} + m_{hi}^{-1}, \ (i = 1, 2, 3), \tag{M33}
\]

in terms of the components of the effective mass tensors.
APPENDIX N

SINGLE-PARTICLE EFFECTIVE HAMILTONIAN
FOR THE EXCITON

The single-particle effective Hamiltonian for the exciton given by Eq. (5.26) is derived in this appendix. From Eq. (5.25) the single-particle effective Hamiltonian is

\[
\hat{H}(\vec{r}) = \sum_{i=1}^{3} \left\{ -\frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial X_i^2} - \frac{ie\hbar}{c} \left[ \frac{G_{e_i}}{m_{e_i}} - \frac{G_{h_i}}{m_{h_i}} \right] \frac{\partial}{\partial X_i} \right. \\
+ \left. \frac{e^2}{2c^2} \left[ \frac{G_{e_i}}{m_{e_i}} + \frac{G_{h_i}}{m_{h_i}} \right] \right\} + V(\vec{r}).
\]  

When Eqs. (5.18) and (5.19) are used, the functions in the brackets above are

\[
\frac{G_{e_i}}{m_{e_i}} - \frac{G_{h_i}}{m_{h_i}} = A_i \left( \hat{a}_1 \cdot \vec{r} \right) + A_i \left( \hat{a}_2 \cdot \vec{r} \right) 
\]

and

\[
\frac{G_{e_i}^2}{m_{e_i}} + \frac{G_{h_i}^2}{m_{h_i}} = A_i^2 \left( \hat{a}_1 \cdot \vec{r} \right) + A_i^2 \left( \hat{a}_2 \cdot \vec{r} \right) \\
+ \left[ A_i (\vec{r}) - (\vec{B} \times \vec{r})_i \right] \left\{ A_i (\vec{r}) \cdot (\vec{B} \times \vec{r})_i - 2 A_i (\hat{a}_1 \cdot \vec{r}) + 2 A_i (\hat{a}_2 \cdot \vec{r}) \right\}. 
\]

The last two terms in Eq. (N3) may be written as
where \((i,j,k)\) are cyclic permutations of \((1,2,3)\). From Eqs. (5.8) and (5.9)

\[
\frac{m_{e_i}}{m_{h_i}} + \frac{m_{h_i}}{m_{e_i}} = \frac{m_{e_i} + m_{h_i}}{M_i} = \frac{1}{M_i},
\]  

which may be used in Eq. (N4) to give

\[
2 \left[ A_i (\vec{a}_i \cdot \vec{r}) - A_i (\vec{a}_i^* \cdot \vec{r}) \right] = -2 A_i (\vec{r}).
\]  

If Eq. (N6) is used in Eq. (N3), the result is

\[
\frac{G_{e_i}^2}{m_{e_i}} + \frac{G_{h_i}^2}{m_{h_i}} = \frac{A_i^2 (\vec{a}_i \cdot \vec{r})}{m_{e_i}} + \frac{A_i^2 (\vec{a}_i^* \cdot \vec{r})}{m_{h_i}} - \frac{A_i (\vec{r})}{M_i} + \frac{(\vec{B} \times \vec{r})_i^2}{M_i}.
\]  

When Eqs. (N7) and (N2) are inserted into Eq. (N1), \(H(\vec{r})\) may be written

\[
H(\vec{r}) = \sum_{i=1}^{3} \left\{ \frac{p_i^2}{2 \mu_i} + \frac{e_p}{c} \left[ \frac{A_i (\vec{a}_i \cdot \vec{r})}{m_{e_i}} + \frac{A_i (\vec{a}_i^* \cdot \vec{r})}{m_{h_i}} \right] + \frac{e^2}{2 c^2} \left[ \frac{A_i^2 (\vec{a}_i \cdot \vec{r})}{m_{e_i}} \right. \\
+ \frac{A_i^2 (\vec{a}_i^* \cdot \vec{r})}{m_{h_i}} - \frac{A_i (\vec{r})}{M_i} + \frac{(\vec{B} \times \vec{r})_i^2}{M_i} \left] \right\} + V(\vec{r}),
\]  

where \(p_i \) are the components of the canonical momentum

\[
p_i = -i \hbar \left( \frac{\partial}{\partial x_i} \right).
\]
The terms in the brackets of the effective Hamiltonian in Eq. (N8) can be written as the sum of an effective kinetic energy term and a diamagnetic energy term. When the second term in the brackets in Eq. (N8) is multiplied and divided by the reduced effective mass, the result is

\[
\frac{e p_i}{\mu_i c} \left[ \frac{A_i (\vec{a}_i \cdot \vec{r}) \mu_i}{m_{e_i}} + \frac{A_i (\vec{a}_2 \cdot \vec{r}) \mu_i}{m_{h_i}} \right] 
\]

\[
= \frac{e p_i}{\mu_i c} \left\{ (1 - \xi_j) B_j x_k \left[ \frac{m'_{h_k} \mu_i}{m_{e_i}} - \frac{m'_{e_k} \mu_i}{m_{h_i}} \right] - \xi_k B_k x_j \left[ \frac{m'_{h_j} \mu_i}{m_{e_i}} - \frac{m'_{e_j} \mu_i}{m_{h_i}} \right] \right\}
\]

\[
= \left( \frac{e p_i}{\mu_i c} \right) A_i (\vec{b}_i \cdot \vec{r}), \quad (N10)
\]

if a set of three new dyads

\[
\vec{b}_i = \frac{\vec{a}_i \mu_i}{m_{e_i}} + \frac{\vec{a}_2 \mu_i}{m_{h_i}}, \quad (N11)
\]

is defined. The first two terms in the brackets in Eq. (N8) are thus the first two terms of an effective kinetic energy

\[
\frac{1}{2 \mu_i} \left[ p_i + \frac{e}{c} A_i (\vec{b}_i \cdot \vec{r}) \right]^2 = \frac{p_i^2}{2 \mu_i} + \frac{p_i e}{\mu_i c} A_i (\vec{b}_i \cdot \vec{r}) 
\]

\[
+ \frac{e^2}{2 \mu_i c^2} A_i^2 (\vec{b}_i \cdot \vec{r}). \quad (N12)
\]
The square may be completed in Eq. (N8) by adding and subtracting the last term in Eq. (N12), which gives

\[ H(\vec{r}) = \sum_{i=1}^{3} \left\{ \frac{1}{2\mu_i} \left[ p_i + \frac{e}{c} A_i(\vec{b}_i \cdot \vec{r}) \right]^2 - \frac{e^2}{2\mu_i c^2} A_i^2(\vec{b}_i \cdot \vec{r}) \right\} - \frac{e^2}{2\mu_i c^2} A_i^2(\vec{b}_i \cdot \vec{r}) + \frac{e^2}{2 c^2} \left[ \frac{A_i^2(\vec{a}_i \cdot \vec{r}) + A_i^2(\vec{a}_2 \cdot \vec{r}) - A_i^2(\vec{r}) + (\vec{b} \times \vec{r})^2_i} \right] + V(\vec{r}). \] (N13)

Equation (N13) can be further simplified by expanding out the second term as

\[ -\frac{e^2}{2\mu_i c^2} A_i^2(\vec{b}_i \cdot \vec{r}) = \frac{-e^2}{2\mu_i c^2} \left[ \left( \frac{\mu_i}{m_{ei}} \right)^2 A_i^2(\vec{a}_i \cdot \vec{r}) \right] \]

\[ + \left( \frac{\mu_i}{m_{hi}} \right)^2 A_i^2(\vec{a}_2 \cdot \vec{r}) + \frac{2\mu_i}{m_{ei} m_{hi}} A_i(\vec{a}_i \cdot \vec{r}) A_i(\vec{a}_2 \cdot \vec{r}) \]. \] (N14)

When Eq. (5.21) is used, \( \mu_i \) may be written as

\[ \mu_i = m_{ei} m_{hi} / M_i, \] (N15)

and Eq. (N14) becomes

\[ -\frac{e^2}{2\mu_i c^2} A_i^2(\vec{b}_i \cdot \vec{r}) = -\frac{e^2}{2 c^2} \left[ \frac{m_{hi}}{m_{ei}} A_i^2(\vec{a}_i \cdot \vec{r}) \right] \]

\[ + \frac{m_{ei}}{m_{hi}} A_i^2(\vec{a}_2 \cdot \vec{r}) + \frac{2}{M_i} A_i(\vec{a}_i \cdot \vec{r}) A_i(\vec{a}_2 \cdot \vec{r}) \]. \] (N16)

Finally, if Eq. (N16) is used in Eq. (N13), then the single-particle effective Hamiltonian in Eq. (5.26) is obtained.
APPENDIX O

DERIVATION OF THE DIMENSIONLESS HAMILTONIAN FOR THE ANISOTROPIC EXCITON

The dimensionless Hamiltonian for the anisotropic exciton is derived here. From Eq. (5.25) the single-particle effective Hamiltonian is

$$H(\vec{r}) = \sum_{i=x,y,z} \left\{ \frac{-\hbar^2}{2\mu_i} \frac{\partial^2}{\partial x_i^2} - \frac{i e \hbar}{c} \left[ \frac{G_{ei}}{m_{ei}} - \frac{G_{hi}}{m_{hi}} \right] \frac{\partial}{\partial x_i} \right\} + \frac{e^2}{2\epsilon^2} \left[ \frac{G_{ei}}{m_{ei}} + \frac{G_{hi}}{m_{hi}} \right] + V(\vec{r}). \quad (01)$$

From Eq. (5.18) $G_{ei}$ can be written

$$G_{ei} = A_i (\vec{q} \cdot \vec{r}) + m_{ei}' \left[ (\vec{B} \times \vec{r})_i - A_i (\vec{r}) \right] = \left[ (1-\xi_j) B_j x_k m_{hk} - \xi_k B_k x_j m_{hj} \right] + m_{ei}' \left[ B_j x_k - B_k x_j \right] - \xi_k B_k x_j \right] - m_{ei}' \left[ m_{ej} \right] + (1-\xi_k) m_{ei}'. \quad (02)$$

where $(i,j,k)$ are cyclic permutations of $(1,2,3)$. Similarly, from Eq. (5.19) $G_{hi}$ is

$$G_{hi} = B_j x_k \left[ (1-\xi_j) m_{ek} + \xi_j m_{hi} \right] - B_k x_j \left[ \xi_k m_{ej} + (1-\xi_k) m_{hi} \right]. \quad (03)$$

When the dimensionless functions
\[ \eta_{\ell,m,n} = (1 - \xi_n^\ell) m_{hm} + \xi_n^\ell m_{e\ell} \]  

(04)

and

\[ \theta_{\ell,m,n} = (1 - \xi_n^\ell) m_{e\ell} + \xi_n^m m_{hm} \],

(05)

where \((l,m,n)\) are cyclic permutations of \((1,2,3)\), are used, Eqs. (02) and (03) can be rewritten as

\[ G_{\ell j} = B_j x_k \eta_{i,kj} - B_k x_j \theta_{i,jk} \]  

(06)

and

\[ G_{hi} = B_j x_k \theta_{k,ij} - B_k x_j \eta_{j,ik} \]  

(07)

If Eqs. (06), (07), and (3.21) are used, Eq. (01) can be written as

\[
H(\vec{\nu}) = \left\{ -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial x_i^2} - \frac{ie\hbar B}{c} \left[ C_2 x_3 \left( \frac{\eta_{123}}{m_{e1}} - \frac{\theta_{123}}{m_{h1}} \right) \right. \right. \\
- C_3 x_2 \left( \frac{\theta_{123}^2}{m_{e1}} - \frac{\eta_{213}}{m_{h1}} \right) \left. \frac{\partial}{\partial x_i} \right] + \frac{e^2 B^2}{2c^2} \left[ C_2 x_3 \left( \frac{\eta_{132}^2}{m_{e1}} + \frac{\theta_{132}^2}{m_{h1}} \right) \right. \\
+ C_3 x_2 \left( \frac{\theta_{123}^2}{m_{e1}} + \frac{\eta_{213}^2}{m_{h1}} \right) - 2 C_3 C_2 x_3 x_2 \left( \frac{\eta_{132} \theta_{123} + \theta_{312} \eta_{213}}{m_{e1} m_{h1}} \right) \left. \right. \\
+ \left. \left. \left. \text{(cyclic permutations of 1,2,3)} \right) \right] + V(\vec{\nu}). \right. \]  

(08)

Another set of dimensionless functions is

\[ T_i = (\xi_1 \mu_1) C_3 \left( \frac{\theta_{123}}{m_{e1}} - \frac{\eta_{213}}{m_{h1}} \right), \]  

(09)
\[ T_i' = (- \mathbf{l}_i, \mu_i) C_2 \left( \frac{n_{122}}{m_{e_i}} - \frac{\theta_{312}}{m_{h_i}} \right), \]  
(010)

\[ T_{12}' = -2 \left( \mathbf{l}_2, \mu_2 \right) C_2 \left( \frac{n_{321}}{m_{e_3}} \theta_{312} + \frac{\theta_{231}}{m_{h_3}} n_{132} \right), \]  
(011)

and

\[ T_{12} = \left( \mathbf{l}_2, \mu_2 \right) C_2 \left( \frac{n_{132}^2}{m_{e_1}} + \frac{\theta_{312}^2}{m_{h_1}} \right) + \left( \mathbf{l}_2, \mu_2 \right) C_2 \left( \frac{\theta_{231}^2}{m_{e_2}} + \frac{n_{321}^2}{m_{h_2}} \right), \]  
(012)

where each of these equations gives two others by cyclic permutation of (1, 2, 3). Equation (018) may now be written in terms of these functions as

\[ H(\vec{r}) = \left\{ -\frac{\hbar^2}{2 \mu} \frac{\partial^2}{\partial x_i^2} + i \frac{e \hbar B}{c \mu} \left[ T_i' x_3 + T_j x_2 \right] \frac{\partial}{\partial x_i} \right. \]

\[ + \frac{e^2 B^2}{2 c^2 \mu} \left[ T_{12} x_3^2 + T_{12}' x_3 x_2 \right] + \text{(cyclic permutations of 1, 2, 3)} \right\}^2 + V(\vec{r}). \]  
(013)

When the lengths are expressed in units of the effective Bohr radius given in Eq. (5.29) and Eqs. (5.20), (5.28), (5.30), (5.32), and (5.33) are used, Eq. (013) becomes

\[ H(\vec{r}) = \left\{ -\mathbf{l}_i \frac{\partial}{\partial x_i^2} + 2 i \hbar \omega_L \left( T_i' x_3 + T_j x_2 \right) \frac{\partial}{\partial x_i} \right. \]

\[ + \left( \frac{\hbar^2 \omega_L^2}{\mathcal{R}} \right) \left( T_{12} x_3^2 + T_{12}' x_3 x_2 \right) \]

\[ + \text{(cyclic permutations of 1, 2, 3)} \right\}^2 \]
If Eq. (02) is divided by the Rydberg and the field parameter $\gamma$ given by Eq. (4.9) is used, then the dimensionless Hamiltonian in Eq. (5.34) is obtained.
APPENDIX P

CHARGE CONSERVATION EQUATION FOR THE ANISOTROPIC EXCITON

The charge conservation equation for an exciton in an anisotropic semiconductor is derived in this appendix and solved for the phase factor. The resulting improved trial wave function is expressed in dimensionless units. The Hamiltonian of Eq. (5.26) and the improved trial wave function

$$\Psi' (\vec{r}) = \exp \left( i \frac{q' A}{\hbar c} \right) \Psi (\vec{r}) ,$$

where $q'$ is the effective charge of the quasiparticle, are used in Eqs. (2.12) and (2.13) for the energy expectation value. The energy expectation value is minimized with respect to $\Lambda$, which gives

$$\text{Im} \left\{ \Psi' \ast H (\vec{r}) \Psi' \right\} = 0 .$$

When Eq. (5.26) is used in Eq. (P2), the minimization condition may be written

$$\text{Im} \left\{ \Psi' \ast \left[ \vec{p}_{\text{eff}} \cdot \left( \frac{\vec{i}}{\mu} \right) \cdot \vec{p}_{\text{eff}} \right] \Psi' \right\} = 0 ,$$

where the effective kinetic momentum of the quasiparticle in the magnetic field is
with \( q' = -e \). The reciprocal of the reduced effective mass tensor is

\[
\begin{pmatrix}
\frac{1}{\mu_1} & 0 & 0 \\
0 & \frac{1}{\mu_2} & 0 \\
0 & 0 & \frac{1}{\mu_3}
\end{pmatrix}
\]  \hspace{1cm} (P5)

Equation (P3) can be rewritten as

\[
\text{Im} \left\{ -i \hbar \nabla \cdot \left[ \Psi' \star \left( \frac{1}{\mu} \right) \cdot \vec{\pi}_{\text{eff}} \cdot \Psi' \right] 
+ \left( \vec{\pi}_{\text{eff}} \Psi' \right) \star \left( \frac{1}{\mu} \right) \cdot \left( \vec{\pi}_{\text{eff}} \Psi' \right) \right\} = 0. \]  \hspace{1cm} (P6)

The last term in the brackets in Eq. (P6) is real, so that Eq. (P6) gives

\[
\nabla \cdot \vec{J}' = 0, \]  \hspace{1cm} (P7)

where the current density \( \vec{J}' \) for the anisotropic exciton is

\[
\vec{J}' = \text{Re} \left\{ \Psi' \star \sum_{i=1}^{3} \frac{q'}{\mu_i} \left[ \vec{p}_i - \frac{q'}{c} \vec{A}_i (\vec{b}_i \cdot \vec{r}) \right] \chi_i \Psi' \right\} \]  \hspace{1cm} (P8)

When Eq. (P1) is inserted into Eq. (P8), the result is

\[
\vec{J}' = \vec{J} + \frac{q'^2}{\mu c} |\Psi'|^2 \sum_{i=1}^{3} \chi_i \frac{\partial \Lambda}{\partial x_i} \chi_i, \]  \hspace{1cm} (P9)
where Eqs. (5.31) and (5.33) have been used and \( \mathcal{J} \) is given by Eq. (P9) with \( \Psi' \) replaced by \( \Psi \). Equations (P9) and (P7) give the differential equation for the minimizing \( \Lambda \),

\[
\sum_{i=1}^{3} \mathcal{J}_i \left[ \partial_i^2 \Lambda + \left( \frac{\partial_i \rho}{\rho} \right) \partial_i \Lambda \right] = -\frac{\mu_c}{q'} \left[ \nabla \cdot \mathcal{J} \right],
\]

(P10)

where \( \partial_i = \partial / \partial x_i \) and the charge density \( \rho(\mathbf{r}) = q' |\Psi(\mathbf{r})|^2 \). This equation is solved for \( \Lambda \) when the trial wave function \( \Psi(\mathbf{r}) \) is given by Eq. (3.7).

For real \( \Psi(\mathbf{r}) \) the divergence of the current density \( \mathcal{J}(\mathbf{r}) \) is

\[
\nabla \cdot \mathcal{J}(\mathbf{r}) = -\frac{q'}{c} \sum_{i=1}^{3} \left[ \left( \partial_i \rho \right) \frac{A_i(\hat{b}_i \cdot \mathbf{r})}{\mu_i} \right. \\
+ \rho \partial_i \left( \frac{A_i(\hat{b}_i \cdot \mathbf{r})}{\mu_i} \right) \right].
\]

(P11)

If Eq. (5.27) is used, then a set of functions \( G_i (i = 1, 2, 3) \) can be defined as

\[
G_i = \frac{A_i(\hat{b}_i \cdot \mathbf{r})}{\mu_i}
= \frac{A_i(\hat{a}_i \cdot \mathbf{r})}{m_{e_i}} + \frac{A_i(\hat{a}_i \cdot \mathbf{r})}{m_{h_i}}.
\]

(P12)

The gradient of \( G_i \) with respect to \( x_i \) is

\[
\partial_i G_i = \frac{\partial}{\partial x_i} \left[ (1 - \mathbf{f}_j) B_j x_k \left( \frac{m_{h_k}}{m_{e_i}} - \frac{m_{e_k}}{m_{h_i}} \right) \right]
\]
\[ + \sum_{k} B_k x_j \left( \frac{m_{hij}}{m_{ei}} - \frac{m_{eij}}{m_{hij}} \right) = 0, \quad \text{(P13)} \]

which vanishes since \((i,j,k)\) are cyclic permutations of \((1,2,3)\). Thus, Eq. (P11) becomes

\[ \nabla \cdot \vec{J}(\vec{r}) = -q' \sum_{i=1}^{3} (\partial_i \rho) G_i. \quad \text{(P14)} \]

When Eq. (3.7) is used for \(\Psi(\vec{r})\), the gradient of \(\rho(\vec{r})\) with respect to \(x_i\) is

\[ \partial_i \rho = \rho \left( -4 \alpha_i x_i \right). \quad \text{(P15)} \]

Finally, when Eqs. (P15) and (P14) are used in Eq. (P9), the charge conservation equation reduces to

\[ \sum_{i=1}^{3} \left[ 4 \alpha_i x_i \right] \left( \mu_i G_i - \partial_i \Lambda \right) + \Lambda \partial_i^2 \Lambda = 0. \quad \text{(P16)} \]

A solution of Eq. (P16) is of the form

\[ \Lambda = \lambda_1 x_1 x_2 + \lambda_2 x_2 x_3 + \lambda_3 x_3 x_1, \quad \text{(P17)} \]

where \((\lambda_1, \lambda_2, \lambda_3)\) are constants to be determined.

Equations (P12), (5.39), and (5.40) can be used to express \(G_1\) as

\[ G_1 = B_2 x_3 \left( \frac{n_{322}}{m_{e1}} - \frac{\theta_{312}}{m_{h1}} \right) - B_2 x_3 \left( \frac{\theta_{323}}{m_{e1}} - \frac{n_{213}}{m_{h1}} \right), \quad \text{(P18)} \]

where \(G_2\) and \(G_3\) are given by Eq. (P18) with cyclic permutation.
of \((1, 2, 3)\). Now if Eqs. (5.35) and (5.36) are used, Eq. (P18) can be written

\[
G_i = \frac{-B}{\gamma_i \mu_i} \left( T_i' x_3 + T_i x_2 \right), \tag{P19}
\]

with \(G_2\) and \(G_3\) given by cyclic permutation of \((1, 2, 3)\). If Eqs. (P19) and (P17) are inserted into Eq. (P16), the result is

\[
\alpha_i x_i \left[ -B \left( T_i' x_3 + T_i x_2 \right) - \gamma_i \left( \lambda_1 x_2 + \lambda_3 x_3 \right) \right] + \left( \text{cyclic permutations of } 1, 2, 3 \right) = 0. \tag{P20}
\]

When terms are grouped according to the coordinates, Eq. (P20) becomes

\[
-x_i x_2 \left[ B \left( \alpha_1 T_1 + \alpha_2 T_2' \right) + \lambda_i \left( \gamma_1 \alpha_i + \gamma_2 \alpha_2 \right) \right] + \left( \text{cyclic permutations of } 1, 2, 3 \right) = 0. \tag{P21}
\]

The solution of Eq. (P21) is

\[
\lambda_i = \frac{-B \left( \alpha_1 T_1 + \alpha_2 T_2' \right)}{\left( \gamma_1 \alpha_i + \gamma_2 \alpha_2 \right)}, \tag{P22}
\]

where \(\lambda_2\) and \(\lambda_3\) are given by cyclic permutation of \((1, 2, 3)\) in Eq. (P22).

The improved trial wave function of Eq. (P1) can now be written in the form of Eq. (4.20) where now
\[ g_1 = \left( \frac{eB}{\hbar c} \right) \frac{\left( \alpha, T, + \alpha_2 T_2' \right)}{\left( \gamma, \alpha, + \gamma_2 \alpha_2 \right)}, \]  

and \( g_2 \) and \( g_3 \) are given by cyclic permutation of \((1,2,3)\) in Eq. (P23). When Eqs. (5.28) - (5.30) and (4.9) are used, \( \Psi' \) in dimensionless form is given by Eq. (4.20) with lengths in units of Bohr radii,

\[ g_1 = \gamma \left( \alpha, T, + \alpha_2 T_2' \right), \]  

and \( g_2 \) and \( g_3 \) given by cyclic permutation of \((1,2,3)\).
APPENDIX Q

GAUGE-IN Variant ENERGY EXPECTATION VALUE FOR ANISOTROPIC EXCITONS

The gauge-invariant energy expectation value for anisotropic excitons is derived here using the improved trial wave function derived in Appendix P:

\[ \Psi'(\vec{r}) = \exp \left[ i \left( g_1 x_1 + g_2 x_2 + g_3 x_3 \right) \right] \Psi(\vec{r}). \]  \hspace{1cm} (Q1)

In Eq. (Q1) \((g_1, g_2, g_3)\) are given by cyclic permutation of \((1,2,3)\) in Eq. (5.47) and \(\Psi(\vec{r})\) is the normalized Gaussian trial wave function defined in Eq. (3.7). The dimensionless exciton Hamiltonian is given in Eq. (5.34). When \(H(\vec{r})\) operates on \(\Psi'(\vec{r})\), the result is

\[ H(\vec{r}) \Psi'(\vec{r}) = \Psi'(\vec{r}) \left\{ S_1 x_1^2 + S_{12} x_1 x_2 + 2 S_2 \alpha_1 \right\} \]

\[ + \text{(cyclic permutations of } 1,2,3) \} + \Psi'(\vec{r}) V(\vec{r}), \]  \hspace{1cm} (Q2)

where

\[ S_1 = -4 i \gamma \left[ \alpha_1 x_1^2 + \left( g_3 g_3^2 + \gamma^2 T_2 \right) - 2 \gamma \left( g_2 + g_3 T_3 \right) \right], \]  \hspace{1cm} (Q3)

\[ S_{12} = 4 i g_1 \left( \alpha_1 S_1 + \alpha_2 S_2 \right) + 2 g_3 g_2 + \gamma^2 T_{12} \]

\[ - 4 i \gamma \left( \alpha_2 T_2 + \alpha_1 T_1 \right) - 2 \gamma \left( g_3 T_3 + g_2 T_3 \right), \]  \hspace{1cm} (Q4)

and each of these equations gives two others by cyclic permutation of \((1,2,3)\).
When Eq. (Q2) is used, the energy expectation value is

\[ E' = \langle \Psi' | H | \Psi' \rangle \]
\[ = \iiint d^3x \left| \Psi(\vec{r}) \right|^2 \left\{ S_i x_i^2 + S_{ij} x_i x_j + 2 \xi_i \alpha_i^2 \right\} \]
\[ + \left( \text{cyclic permutations of } 1, 2, 3 \right) \]
\[ + \iiint d^3x \left| \Psi(\vec{r}) \right|^2 V(\vec{r}) . \]  \hspace{1cm} (Q5)

Except for the potential energy term, these are integrals of the same form as those evaluated in Appendix C for the anisotropic harmonic oscillator. Integrals over the cross terms vanish and those over the quadratic terms are

\[ \iiint d^3x \left| \Psi(\vec{r}) \right|^2 \chi_i^2 = \left( \frac{1}{4\alpha_i} \right), \quad (i = 1, 2, 3) . \]  \hspace{1cm} (Q6)

Equation (Q5) now becomes

\[ E' = \left\{ 2 \xi_i \alpha_i + \left( \frac{S_i}{4\alpha_i} \right) + \left( \text{cyclic permutations of } 1, 2, 3 \right) \right\} + \iiint d^3x \left| \Psi(\vec{r}) \right|^2 V(\vec{r}) . \]  \hspace{1cm} (Q7)

The potential energy term is partially integrated in Appendix L. The first two terms on the right-hand side of Eq. (Q7) may be written

\[ 2 \alpha_i \xi_i + \left( \frac{S_i}{4\alpha_i} \right) = \alpha_i \xi_i + \left( R_i / 4 \alpha_i \right) , \]  \hspace{1cm} (Q8)

where
\[ R_i = \mathcal{J}_3 \gamma^2 \left( \frac{T_3 \alpha_3 + T_1' \alpha_i}{\alpha_1 \mathcal{J}_i + \alpha_3 \mathcal{J}_3} \right)^2 + \mathcal{J}_2 \gamma^2 \left( \frac{T_i \alpha_i + T_2' \alpha_2}{\alpha_1 \mathcal{J}_i + \alpha_2 \mathcal{J}_2} \right)^2 + \gamma^2 T_{23} \]

\[ - 2 \gamma^2 \left[ \frac{(T_2' T_i \alpha_i + T_2' \alpha_2)}{(\alpha_1 \mathcal{J}_i + \alpha_2 \mathcal{J}_2)} + \frac{(T_i T_3 \alpha_i + T_3^2 \alpha_3)}{(\alpha_1 \mathcal{J}_i + \alpha_3 \mathcal{J}_3)} \right], \]  

(Eq. 9)

and Eq. (5.47) and its cyclic permutations have been used for \((g_1, g_2, g_3)\). When terms that depend on the gauge parameter \(\mathcal{J}_2\) are separated from terms that depend on \(\mathcal{J}_3\), \(R_1\) can be written

\[ R_i = \frac{\gamma^2 C_2 R'_i(\mathcal{J}_2)}{(\alpha_1 \mathcal{J}_i + \alpha_3 \mathcal{J}_3)^2} + \frac{\gamma^2 C_2 R''_i(\mathcal{J}_3)}{(\alpha_1 \mathcal{J}_i + \alpha_2 \mathcal{J}_2)^2}. \]  

(Eq. 10)

The functions \(R'_i(\mathcal{J}_2)\) and \(R''_i(\mathcal{J}_3)\) can now be evaluated separately.

If cyclic permutation of Eq. (5.38) is used to obtain \(T_{23}\), then \(R'_i(\mathcal{J}_2)\) is

\[ R'_i = (\mathcal{J}_3 \mu_3)(\alpha_3 \mathcal{J}_3 + \alpha_i \mathcal{J}_i) \left( \frac{\mathcal{B}_{312}^2}{m_{e3}} + \frac{\mathcal{B}_{132}^2}{m_{e3}} \right) + \mathcal{J}_3 \left( \frac{T_3 \alpha_3 + T_i \alpha_i}{C_2} \right)^2 \]

\[ - 2 \frac{(\alpha_3 \mathcal{J}_3 + \alpha_i \mathcal{J}_i)}{C_2} \left( T_i T_3 \alpha_i + T_3^2 \alpha_3 \right). \]  

(Eq. 11)

Equation (5.33) gives the relation

\[ \mu = \mathcal{J}_3 \mu_3 = \mathcal{J}_i \mu_i. \]  

(Eq. 12)

When Eqs. (12), (5.35), (5.36), and cyclic permutations of these are used, Eq. (11) can be written
\[ R'_1 = \mu (\alpha_3 \gamma_3 + \alpha_i \gamma_i)^2 z_3 + \gamma_3^2 \alpha_i^2 \mu \mu_3 z_i^2 \]
\[ + 2 \alpha_i \gamma_i \gamma_3 \mu \mu_3 z_i z_2 - \mu \mu_3 (\gamma_3^2 \alpha_i^2 + 2 \gamma_i \gamma_3 \alpha_i \alpha_3) z_2^2, \tag{Q13} \]

where
\[ z_3 = \left( \frac{\eta_{312}}{m_{e3}} + \frac{\eta_{132}}{m_{h3}} \right), \tag{Q14} \]
\[ z_2 = \left( \frac{\eta_{312}}{m_{e3}} - \frac{\eta_{132}}{m_{h3}} \right), \tag{Q15} \]

and
\[ z_1 = \left( \frac{\eta_{132}}{m_{e1}} - \frac{\eta_{312}}{m_{h1}} \right). \tag{Q16} \]

The square in the last term of Eq. (Q13) can be completed. Equation (Q13) then becomes
\[ R'_1 = \mu (\alpha_3 \gamma_3 + \alpha_i \gamma_i)^2 z_3 + \alpha_i^2 \mu \mu_3 (\gamma_3 z_i + \gamma_i z_2)^2 \]
\[ - \mu \mu_3 (\alpha_i \gamma_i + \alpha_3 \gamma_3)^2 z_2^2. \tag{Q17} \]

Finally, when terms in \( \eta_{132}^2, \eta_{312}^2, \) and \( \eta_{132} \eta_{312} \) are collected, Eq. (Q17) becomes
\[ R'_1 = \gamma_3^2 \mu_3^2 \left( \frac{\alpha_3 \gamma_3 + \alpha_i \gamma_i}{m_{e3} m_{h3}} \right)^2 \left( \frac{\eta_{312}}{m_{h1}} - \frac{\eta_{132}}{m_{e3}} \right)^2 \]
\[ + \gamma_3^2 \mu_3^2 \alpha_i^2 \left[ \frac{\eta_{312}}{m_{h1}} - \frac{\eta_{132}}{m_{e3}} \right]^2. \tag{Q18} \]
The gauge-dependent functions
\[ \eta_{132} = (1 - \xi_2) m'_{h3} + \xi_2 m'_{e1}, \]
(Q19)

and
\[ \Phi_{312} = (1 - \xi_2) m'_{e3} + \xi_2 m'_{h1}, \]
(Q20)

are obtained from Eqs. (5.39) and (5.40). If Eqs. (Q19) and (Q20) are used, along with
\[ \xi_1 \left( \frac{m'_{e1}}{m_{h3}} - \frac{m'_{h1}}{m_{e3}} \right) = \xi_3 \left( \frac{m'_{e3}}{m_{h1}} - \frac{m'_{h3}}{m_{e1}} \right), \]
(Q21)

then the expressions
\[ \Phi_{312} + \eta_{132} = 1, \]
(Q22)

and
\[ \Phi_{312} \left( \frac{\xi_3}{m_{h1}} - \frac{\xi_1}{m_{e3}} \right) - \eta_{132} \left( \frac{\xi_3}{m_{e1}} - \frac{\xi_1}{m_{h3}} \right) = \xi_3 \left( \frac{m'_{e3}}{m_{h1}} - \frac{m'_{h3}}{m_{e1}} \right), \]
(Q23)

may be obtained. All gauge-dependent terms containing \( \xi_i \) (i = 1, 2, 3) cancel out. The gauge-invariant result for \( R_1' \) is
\[ R_1' = \chi_3 (\alpha_3 \xi_3 + \alpha_1 \xi_1)^2 + \alpha_1^2 D_{31}, \]
(Q24)

where the constants \( \chi_3 \) and \( D_{31} \) are
\[ \chi_3 = \frac{\xi_3 \mu_3^2}{m_{e3} m_{h3}}, \]
(Q25)
and
\[ D_{31} = \mu_3^2 \beta_3^2 \left( \frac{m_{e3}^2}{m_{h3}} - \frac{m_{h3}^2}{m_{e3}} \right)^2. \]  
(Q26)

The function \( R''_1(\beta_3) \) is
\[ R''_1 = (\mu_2 \mu_3)(\alpha_2 \beta_2 + \alpha_1 \beta_1)^2 \left( \frac{\eta_{23}^2}{m_{e2}} + \frac{\eta_{13}^2}{m_{h2}} \right) + \beta_2 \left( T_2 \alpha_1 + T_2' \alpha_2 \right)^2 \]
\[ + \frac{2(\alpha_2 \beta_2 + \alpha_3 \beta_3)}{C_3^2} \left( T_2' T_1 \alpha_1 + T_2' \alpha_2 \right). \]  
(Q27)

When Eq. (Q27) is analyzed in the same way as for \( R'_1 \), the result is
\[ R''_1 = \chi_2 \left( \alpha_2 \beta_2 + \alpha_1 \beta_1 \right)^2 + \alpha_1^2 \alpha_2^2 D_{21}, \]  
(Q28)

where \( \chi_2 \) and \( D_{21} \) are given by Eqs. (Q25) and (Q26) with 3 replaced by 2.

If Eqs. (Q10), (Q24), and (Q28) are substituted into Eq. (Q8), then the first two terms on the right-hand side of Eq. (Q7) are
\[ \left[ 2 \alpha_1 \beta_1 + \frac{S_1}{4 \alpha_1} \right] = \alpha_1 \beta_1 + \frac{\gamma^2 C_2^2}{4} \left[ \chi_3 \frac{\chi_2}{\alpha_1} + \frac{\alpha_1 D_{31}}{(\alpha_3 \beta_3 + \alpha_1 \beta_1)^2} \right. \]
\[ + \frac{\gamma^2 C_3^2}{4} \left( \frac{\chi_2}{\alpha_2} + \frac{\alpha_1 D_{31}}{(\alpha_2 \beta_2 + \alpha_1 \beta_1)^2} \right). \]  
(Q29)

The other terms are given by cyclic permutation of (1,2,3) in Eq. (Q29). Note that \( D_{13} \neq D_{31} \), which complicates the form of the final expression for the energy expectation value. To simplify the energy, the definitions
\[ D_{13} = \mathcal{Y}_3 \chi_{13} \]  

(Q30)

and

\[ D_{31} = \mathcal{Y}_1 \chi_{31} \]  

(Q31)

can be used, where

\[ \chi_{31} = \mu_1 \mu_3 \mathcal{Y}_3^2 \left[ \frac{m_e^3}{m_{h1}} - \frac{m_{h3}}{m_{e1}} \right]^2, \]  

(Q32)

\[ \chi_{13} = \mu_2 \mu_1 \mathcal{Y}_1^2 \left[ \frac{m_e^1}{m_{h3}} - \frac{m_{h1}}{m_{e3}} \right]^2, \]  

(Q33)

and, from Eq. (Q21),

\[ \chi_{31} = \chi_{13}. \]  

(Q34)

When Eqs. (Q29), (Q30), (Q31), and cyclic permutations of these are used in Eq. (Q7), the gauge-invariant energy expectation value

\[ E' = \left\{ \mathcal{Y}_i \alpha_i + \delta_i \mathcal{C}_i \left[ \frac{\chi_2}{\alpha_3} + \frac{\chi_3}{\alpha_2} + \frac{\chi_{23}}{\alpha_2 \alpha_3 + \alpha_3 \alpha_3 \mathcal{Y}_3} \right] \right\} 

+ \left( \text{cyclic permutations of} \, 1,2,3 \right) 

+ \int_S d^3x \left| \Psi(p) \right|^2 V(p) \]  

(Q35)

is obtained. The terms in brackets in Eq. (Q35) are the same as appear in the brackets in Eq. (5.48). The potential energy integral is evaluated in Appendix L.
APPENDIX R

GAUGE-DEPENDENT ENERGY EXPECTATION VALUE
FOR ANISOTROPIC EXCITONS

The gauge-dependent energy expectation value for anisotropic excitons is derived in this appendix using the dimensionless Hamiltonian of Eq. (5.34) and the unmodified trial wave function of Eq. (3.7). When the procedure of Appendix Q is used, the energy expectation value can be written in the same form as the gauge-invariant energy expectation value in Eq. (Q7):

\[ E = \langle \Psi | H | \Psi \rangle \]

\[ = \left\{ 2 \mathfrak{J}_i \alpha_i + \left( S_i / 4 \alpha_i \right) + \text{(cyclic permutations of } 1, 2, 3) \right\} + \iint d^3x \left| \Psi(\vec{r}) \right|^2 V(\vec{r}), \]  \hspace{1cm} (R1)

where now

\[ S_i = -4 \mathfrak{J}_i \alpha_i^2 + 8^2 \mathfrak{T}_{23}, \]  \hspace{1cm} (R2)

and \( S_2 \) and \( S_3 \) are given by cyclic permutation of \( (1,2,3) \).

The potential energy term is the same as that evaluated in Appendix L. The first two terms on the right-hand side of Eq. (R1) can be written

\[ 2 \alpha_i \mathfrak{J}_i + \left( S_i / 4 \alpha_i \right) = \alpha_i \mathfrak{J}_i + \left( R_i / 4 \alpha_i \right), \]  \hspace{1cm} (R3)
with the function

\[ R_1 = \gamma^2 T_{23} = \gamma^2 \left[ C_2^2 R'_1(\xi_2) + C_3^2 R''_1(\xi_3) \right]. \]  

(R4)

When Eq. (5.38) is used to obtain \( T_{23} \), \( R'_1(\xi_2) \) is

\[ R'_1 = (\xi_2 \mu_2) \left( \frac{\beta_{312}^2}{m_{e3}} + \frac{\eta_{122}^2}{m_{h3}} \right). \]  

(R5)

Now if Eqs. (5.39) and (5.40) are substituted into Eq. (R5), \( R'_1 \) can be written

\[ R'_1 = \chi'_3 + \xi_3 \chi'_{13}, \]  

(R6)

with the constants

\[ \chi'_3 = \frac{\xi_3 \mu_3}{(m_{e3} + m_{h3})}, \]  

(R7)

and

\[ \chi'_{13} = \xi_3 \mu_3 \left[ \frac{m_{n1}^2}{m_{e3}^2} + \frac{m_{e1}^2}{m_{h3}^2} - \frac{1}{(m_{e3} + m_{h3})} \right]. \]  

(R8)

Similarly, \( R''_1(\xi_3) \) is

\[ R''_1 = (\xi_2 \mu_2) \left( \frac{\eta_{213}^2}{m_{e2}} + \frac{\beta_{132}^2}{m_{h2}} \right), \]  

(R9)

which can be written

\[ R''_1 = \chi'_2 + (1 - \xi_3)^2 \chi'_{12}. \]  

(R10)
Equation (R3) now becomes

\[ 2 \alpha_1 \tilde{j}_1 + \left( S_1 / \alpha_1 \right) = \alpha_1 \tilde{j}_1 + \frac{\gamma^2 C_2^2}{4 \alpha_1} \left[ \chi'_3 + \tilde{s}_2^2 \chi'_3, \tilde{r}_2 \chi'_3 \right] \\
+ \frac{\gamma^2 C_3^2}{4 \alpha_1} \left[ \chi'_2 + (1 - \tilde{s}_3)^2 \chi'_{12} \right]. \quad (R11) \]

When Eq. (R11) and its cyclic permutations are used in Eq. (R1), the gauge-dependent energy expectation value

\[ E = \left\{ \alpha_1 \tilde{j}_1 + \frac{\gamma^2 C_2^2}{4} \left[ \frac{\chi'_2}{\alpha_3} + \frac{\tilde{s}_1 \chi'_{32}}{\alpha_3} + \frac{\chi'_3}{\alpha_2} \right] + \frac{(1 - \tilde{s}_3)^2 \chi'_{23}}{\alpha_2} \right\} + \left( \text{cyclic permutations of 1, 2, 3} \right) \]

\[ + \int \int \int d^3 \chi \left| \Psi(\vec{r}) \right|^2 V(\vec{r}) \quad (R12) \]

is obtained. The terms in brackets in Eq. (R12) are the same as appear in the brackets in Eq. (5.54). The potential energy integral is evaluated in Appendix L.
APPENDIX S

EFFECTIVE BOHR MAGNETON OF THE EXCITON
FOR ARBITRARY FIELDS

The effective Bohr magneton of the exciton for fields at an angle $\theta$ to the c-axis is derived here. For a particle with a diagonal effective mass tensor $\mu$ in a field of arbitrary orientation $\mathbf{B}(\theta, \phi)$, the effective Larmor frequency is\(^{76}\)

$$\omega^*_L(\theta, \phi) = \frac{e}{2c} \left[ \frac{\mathbf{B} \cdot \mu \cdot \mathbf{B}}{\mu_1 \mu_2 \mu_3} \right]^{1/2}$$

$$= \frac{eB}{2c} \left[ \frac{\mu, \alpha^2 + \mu_2 \beta^2 + \mu_3 \gamma^2}{\mu_1 \mu_2 \mu_3} \right]^{1/2}, \quad (S1)$$

where $(\alpha, \beta, \gamma)$ are the constants which project the field vector onto the principal axes. For the axially anisotropic system of Chapter VI, this expression becomes

$$\omega^*_L(\theta) = \frac{eB}{2 \mu_1 c} \left[ \frac{\mu_{11} \cos^2 \theta + \mu_{12} \sin^2 \theta}{\mu_{11}} \right]^{1/2}. \quad (S2)$$

When

$$\hbar \omega^*_L(\theta) = \mu^*_B(\theta) B$$

is used, in analogy to Eq. (7.4), the effective Bohr magneton of the exciton for fields at an angle $\theta$ to the c-axis is Eq. (7.7).
### TABLE I

GROUND-STATE ENERGIES\(^a\) OF AN ANISOTROPIC HARMONIC OSCILLATOR\(^b\)

<table>
<thead>
<tr>
<th>(\theta)</th>
<th>Gauge Invariant</th>
<th>Symmetric Gauge(^c)</th>
<th>Landau-1 Gauge(^d)</th>
<th>Landau-0 Gauge(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>6.590</td>
<td>6.732</td>
<td>6.599</td>
<td>7.118</td>
</tr>
<tr>
<td>15°</td>
<td>6.598</td>
<td>6.734</td>
<td>6.642</td>
<td>7.108</td>
</tr>
<tr>
<td>30°</td>
<td>6.619</td>
<td>6.737</td>
<td>6.748</td>
<td>7.073</td>
</tr>
<tr>
<td>45°</td>
<td>6.647</td>
<td>6.741</td>
<td>6.875</td>
<td>7.009</td>
</tr>
<tr>
<td>60°</td>
<td>6.673</td>
<td>6.743</td>
<td>6.988</td>
<td>6.917</td>
</tr>
<tr>
<td>75°</td>
<td>6.692</td>
<td>6.743</td>
<td>7.064</td>
<td>6.821</td>
</tr>
<tr>
<td>90°</td>
<td>6.699</td>
<td>6.743</td>
<td>7.091</td>
<td>6.775</td>
</tr>
</tbody>
</table>

\(^a\)Energies are calculated for \(\Omega = 45^\circ\), \(\gamma = 1.0\), and \(\Omega = \hbar \omega_L\). All values are in Rydbergs.

\(^b\)The oscillator has frequencies \(\omega_1 = \omega_L\), \(\omega_2 = 10 \omega_L\), and \(\omega_3 = 2 \omega_L\).

\(^c\) \(\xi_i = \frac{1}{2}\), \((i = 1, 2, 3)\), in Eq. (3.26).

\(^d\) \(\xi_i = 1\) in Eq. (3.26).

\(^e\) \(\xi_i = 0\) in Eq. (3.26).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>GaSe Value</th>
<th>CdS Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e^\perp / m_o$</td>
<td>$0.17^c$</td>
<td>$0.210 \pm 0.003^e$</td>
<td></td>
</tr>
<tr>
<td>$m_h^\perp / m_o$</td>
<td>$0.8^c$</td>
<td>$0.64 \pm 0.02^e$</td>
<td></td>
</tr>
<tr>
<td>$m_e^\parallel / m_o$</td>
<td>$0.3^c$</td>
<td>$0.204 \pm 0.01^f$</td>
<td></td>
</tr>
<tr>
<td>$m_h^\parallel / m_o$</td>
<td>$0.2^c$</td>
<td>$5.0^f$</td>
<td></td>
</tr>
<tr>
<td>$(K_\perp K_\parallel)^{1/2}$</td>
<td>$8.8^d$</td>
<td>$8.9 \pm 0.2^e$</td>
<td></td>
</tr>
<tr>
<td>$\Theta$</td>
<td>$K_\perp / K_\parallel$</td>
<td>$1.34^d$</td>
<td>$0.988 \pm 0.075^g$</td>
</tr>
<tr>
<td>$\mu^\perp / m_o$</td>
<td>$[m_o (m_e^\perp + m_h^\perp)]^{-1}$</td>
<td>$0.14$</td>
<td>$0.158 \pm 0.002^e$</td>
</tr>
<tr>
<td>$\mu^\parallel / m_o$</td>
<td>$[m_o (m_e^\parallel + m_h^\parallel)]^{-1}$</td>
<td>$0.12$</td>
<td>$0.196 \pm 0.01$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$\mu^\perp / \mu^\parallel$</td>
<td>$1.17$</td>
<td>$0.806 \pm 0.05$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$\frac{\mu^\perp e^4}{2K_\perp K_\parallel \hbar^2}$</td>
<td>$24.5 \text{ meV}$</td>
<td>$27.1 \pm 1.5 \text{ meV}$</td>
</tr>
<tr>
<td>$\alpha_o$</td>
<td>$\frac{(K_\perp K_\parallel)^{1/2} \hbar^2}{\mu^\perp e^2}$</td>
<td>$33.3 \AA$</td>
<td>$29.9 \pm 1.0 \AA$</td>
</tr>
<tr>
<td>$B(\delta = 1.0)$</td>
<td>$\frac{\mu^\perp e^3}{K_\perp K_\parallel \hbar^3}$</td>
<td>$59.3 \text{ T}$</td>
<td>$74.0 \pm 5.0 \text{ T}$</td>
</tr>
</tbody>
</table>
TABLE II—Continued

\( a \) The symbol \( m_0 \) is the free electron mass.

\( b \) Values for CdS are for the \( A \) valence band.

\( c \) From Ref. 19.

\( d \) From Ref. 20.

\( e \) From Ref. 22.

\( f \) From Ref. 21.

\( g \) From \( \mu_1 \), \( \mu_2 \), and \( \frac{\mu_1 K_1}{\mu_2 K_2} = 0.797 \pm 0.013 \) in Ref. 22.

\[ (k_{jl}K) = 0.797 + 0.013 \]
### TABLE III

**MATERIAL PARAMETERS OF CADMIUM SULFIDE AND GALLIUM SELENIDE SHALLOW DONORS**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>GaSe Value</th>
<th>CdS Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f )</td>
<td>( m_{e\perp}/m_{e\parallel} )</td>
<td>0.57</td>
<td>1.029 ± 0.06</td>
</tr>
<tr>
<td>( \mathcal{R} )</td>
<td>( \frac{m_{e\perp}e^4}{2\hbar^2K_{\perp}K_{\parallel}} )</td>
<td>29.8 meV</td>
<td>36.0 ± 2.2 meV</td>
</tr>
<tr>
<td>( a_0 )</td>
<td>( \frac{(K_{\perp}K_{\parallel})^{1/2}\hbar^2}{m_{e\perp}e^2} )</td>
<td>27.5 Å</td>
<td>22.5 ± 0.8 Å</td>
</tr>
<tr>
<td>( B(\gamma = 1.0) )</td>
<td>( \frac{m_{e\perp}ce^3}{K_{\perp}K_{\parallel}\hbar^3} )</td>
<td>87.4 T</td>
<td>130.0 ± 10.0 T</td>
</tr>
</tbody>
</table>

*Calculated from effective masses and dielectric constants listed in Table II.*

---

163
<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\gamma = 1.0$</th>
<th>$\gamma = 1.5$</th>
<th>$\gamma = 2.0$</th>
<th>$\gamma = 2.5$</th>
<th>$\gamma = 3.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>-16.51</td>
<td>-8.97</td>
<td>-0.42</td>
<td>8.81</td>
<td>18.52</td>
</tr>
<tr>
<td>15°</td>
<td>-16.76</td>
<td>-9.39</td>
<td>-0.98</td>
<td>8.11</td>
<td>17.71</td>
</tr>
<tr>
<td>30°</td>
<td>-17.49</td>
<td>-10.62</td>
<td>-2.71</td>
<td>5.91</td>
<td>15.05</td>
</tr>
<tr>
<td>45°</td>
<td>-18.58</td>
<td>-12.56</td>
<td>-5.54</td>
<td>2.18</td>
<td>10.42</td>
</tr>
<tr>
<td>60°</td>
<td>-19.82</td>
<td>-14.88</td>
<td>-9.03</td>
<td>-2.56</td>
<td>4.38</td>
</tr>
<tr>
<td>75°</td>
<td>-20.85</td>
<td>-16.91</td>
<td>-12.24</td>
<td>-7.06</td>
<td>-1.49</td>
</tr>
</tbody>
</table>

$^a$All energies are in units of meV. Field strengths in Tesla are $\gamma \times (74.0 \text{T})$. 

164
### TABLE V

THEORETICAL GROUND-STATE ENERGIES OF GALLIUM SELENIDE EXCITONS

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\gamma = 1.0$</th>
<th>$\gamma = 1.5$</th>
<th>$\gamma = 2.0$</th>
<th>$\gamma = 2.5$</th>
<th>$\gamma = 3.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^\circ$</td>
<td>-8.79</td>
<td>-1.09</td>
<td>7.44</td>
<td>16.51</td>
<td>25.97</td>
</tr>
<tr>
<td>$15^\circ$</td>
<td>-8.78</td>
<td>-1.03</td>
<td>7.58</td>
<td>16.76</td>
<td>26.35</td>
</tr>
<tr>
<td>$30^\circ$</td>
<td>-8.79</td>
<td>-0.97</td>
<td>7.76</td>
<td>17.11</td>
<td>26.90</td>
</tr>
<tr>
<td>$45^\circ$</td>
<td>-8.90</td>
<td>-1.11</td>
<td>7.61</td>
<td>16.96</td>
<td>26.78</td>
</tr>
<tr>
<td>$60^\circ$</td>
<td>-9.11</td>
<td>-1.51</td>
<td>7.01</td>
<td>16.14</td>
<td>25.71</td>
</tr>
<tr>
<td>$75^\circ$</td>
<td>-9.33</td>
<td>-1.98</td>
<td>6.23</td>
<td>15.00</td>
<td>24.19</td>
</tr>
<tr>
<td>$90^\circ$</td>
<td>-9.43</td>
<td>-2.20</td>
<td>5.85</td>
<td>14.44</td>
<td>23.41</td>
</tr>
</tbody>
</table>

\(^a\text{All energies are in units of meV. Field strengths in Tesla are } \gamma \times (59.3T).\)
TABLE VI
ULTRA-HIGH FIELD GROUND-STATE ENERGIES
OF GALLIUM SELENIDE EXCITONS

<table>
<thead>
<tr>
<th>θ</th>
<th>ξ = 10.0</th>
<th>ξ = 15.0</th>
<th>ξ = 20.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>174.13</td>
<td>286.74</td>
<td>401.60</td>
</tr>
<tr>
<td>15°</td>
<td>178.01</td>
<td>294.27</td>
<td>413.39</td>
</tr>
<tr>
<td>30°</td>
<td>183.38</td>
<td>304.16</td>
<td>428.21</td>
</tr>
<tr>
<td>45°</td>
<td>184.30</td>
<td>306.18</td>
<td>431.47</td>
</tr>
<tr>
<td>60°</td>
<td>179.28</td>
<td>298.06</td>
<td>420.13</td>
</tr>
<tr>
<td>75°</td>
<td>170.42</td>
<td>282.97</td>
<td>398.41</td>
</tr>
<tr>
<td>90°</td>
<td>164.93</td>
<td>272.94</td>
<td>383.28</td>
</tr>
</tbody>
</table>

AnAll energies are in units of meV. Field strengths in Tesla are ξ x (59.3T).
**TABLE VII**

GAUGE-DEPENDENT GROUND-STATE ENERGIES OF GALLIUM SELENIDE EXCITONS$^a$

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>Symmetric Gauge</th>
<th>Landau Gauge</th>
<th>Gauge Invariant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>25.97</td>
<td>34.79</td>
<td>25.97</td>
</tr>
<tr>
<td>15°</td>
<td>26.36</td>
<td>35.10</td>
<td>26.35</td>
</tr>
<tr>
<td>30°</td>
<td>26.95</td>
<td>35.31</td>
<td>26.90</td>
</tr>
<tr>
<td>45°</td>
<td>26.91</td>
<td>34.23</td>
<td>26.78</td>
</tr>
<tr>
<td>60°</td>
<td>25.89</td>
<td>31.35</td>
<td>25.71</td>
</tr>
<tr>
<td>75°</td>
<td>24.30</td>
<td>27.29</td>
<td>24.19</td>
</tr>
<tr>
<td>90°</td>
<td>23.42</td>
<td>24.86</td>
<td>23.41</td>
</tr>
</tbody>
</table>

$^a$All energies are calculated for $\gamma = 3.0$ (B = 177.9T) and are in units of meV.
TABLE VIII
THEORETICAL GROUND-STATE ENERGIES OF GALLIUM SELENIDE SHALLOW DONORS\textsuperscript{a}

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\gamma = 1.0$</th>
<th>$\gamma = 1.5$</th>
<th>$\gamma = 2.0$</th>
<th>$\gamma = 2.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>-18.66</td>
<td>-10.45</td>
<td>-1.12</td>
<td>8.95</td>
</tr>
<tr>
<td>15°</td>
<td>-18.84</td>
<td>-10.74</td>
<td>-1.52</td>
<td>8.45</td>
</tr>
<tr>
<td>30°</td>
<td>-19.35</td>
<td>-11.61</td>
<td>-2.74</td>
<td>6.89</td>
</tr>
<tr>
<td>45°</td>
<td>-20.11</td>
<td>-12.95</td>
<td>-4.68</td>
<td>4.34</td>
</tr>
<tr>
<td>60°</td>
<td>-20.96</td>
<td>-14.51</td>
<td>-7.01</td>
<td>1.20</td>
</tr>
<tr>
<td>75°</td>
<td>-21.65</td>
<td>-15.84</td>
<td>-9.06</td>
<td>-1.63</td>
</tr>
<tr>
<td>90°</td>
<td>-21.92</td>
<td>-16.37</td>
<td>-9.92</td>
<td>-2.84</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All energies are in units of meV. Field strengths in Tesla are $\gamma \times (87.42T)$. 
TABLE IX
THEORETICAL GROUND-STATE ENERGIES OF
CADMIUM SULFIDE SHALLOW DONORS

<table>
<thead>
<tr>
<th>θ</th>
<th>Ψ = 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>-18.63</td>
</tr>
<tr>
<td>15°</td>
<td>-18.54</td>
</tr>
<tr>
<td>30°</td>
<td>-18.36</td>
</tr>
<tr>
<td>45°</td>
<td>-18.23</td>
</tr>
<tr>
<td>60°</td>
<td>-18.23</td>
</tr>
<tr>
<td>75°</td>
<td>-18.32</td>
</tr>
<tr>
<td>90°</td>
<td>-18.36</td>
</tr>
</tbody>
</table>

\(^a\)All energies are in units of meV. Field strengths in Tesla are \( \Psi \times (130.0 T)\).
Fig. 1--Theoretical ground-state energies of the anisotropic harmonic oscillator as a function of field angle $\theta$. For this system $\gamma_1 = 1.0$, $\gamma_2 = 10.0$, $\gamma_3 = 2.0$, $\gamma = 1.0$, $\Omega = \hbar \omega_L$, and $Q = 45^\circ$. 
Fig. 2—Ground-state energies of GaSe excitons for fields parallel to the c-axis ($\theta = 0^\circ$). Error bars are experimental data from Ref. 23. Dots are theoretical values calculated using Eq. (6.19).
Fig. 3—Theoretical ground-state energies of CdS A-excitons as a function of field angle.
Fig. 4—Theoretical ground-state energies of GaSe excitons as a function of field angle.
Fig. 5—Variation of ground-state energy with field angle for CdS \( \Lambda \)-excitons.
Fig. 6--Variation of ground-state energy with field angle for GaSe excitons.
Fig. 7—Gauge-dependent ground-state energies of GaSe excitons as a function of field angle for Landau and symmetric gauges ($\delta = 3.0$).
Fig. 8--Spin splitting of the 1s triplet energies of GaSe and CdS excitons for fields parallel to the c-axis.
Fig. 9—Theoretical ground-state energies of GaSe shallow donors as a function of field angle.
REFERENCES AND NOTES


39. It is assumed that only time-independent gauge transformations are used, so that the vector potential remains time independent, and the Hamiltonian remains the energy operator.


60. Reference 50, p. 12.


64. Reference 42, p. 300.


67. C. M. Fowler, private communication.


75. Reference 73, p. 162.