Theory of magneto-optical properties of core-shell spherical quantum dots doped with radial-position-controlled magnetic impurities

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We present a theory for the electronic and magneto-optical properties of spherical quantum dots consisting of an inner core surrounded by an outer shell. This core-shell quantum dot is doped by magnetic Mn impurities all of which are implanted at a preselected radius on a spherical surface within the dot. The spherical symmetry of the dot is broken by the application of an external magnetic field. The electronic states in the presence of a magnetic field are treated in an effective mass model which includes the s-d and p-d exchange interaction with localized Mn d electrons. The strain in the quantum dot due to lattice mismatch between core and shell regions is assumed to be pseudomorphic and the effect of this strain field on the electronic states is also included. The optical properties of the quantum dot are computed using the effective mass electronic states and Fermi’s golden rule.

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I. INTRODUCTION

There has been much interest in III-V and II-VI magnetic semiconductors in which incorporation of magnetic impurities, such as manganese, is used to tailor the electronic, magnetic, and magneto-optical properties.\textsuperscript{1–4} Doping semiconductor quantum dots with magnetic impurities allows magneto-optical properties of quantum dots to be tailored for potential spintronic applications.\textsuperscript{5–9} Radial-position-controlled Mn doping of zinc-blende CdS-ZnS core-shell spherical quantum dots has been achieved using a three-step process, which includes CdS-core growth, Mn-dopant growth in a thin spherical doping layer (inside either core or shell), and ZnS-shell growth.\textsuperscript{10–12} Precise control of magnetic impurity doping in core-shell quantum dots may lead to functional materials with new properties. Recent work shows that Mn-doped CdS-ZnS core-shell quantum dots possess position-dependent electronic and magneto-optical properties.\textsuperscript{13–15} In addition, Mn dopants can be used as a radial pressure gauge for measuring lattice strains due to the lattice mismatch at the core-shell interface.\textsuperscript{16}

II. THEORY

Spherical semiconductor quantum dots have been studied in the effective mass approximation for zinc-blende\textsuperscript{16} and wurtzite quantum dots. Spherical semiconductor core-shell quantum dots have also been studied.\textsuperscript{17–19} To study magnetic impurity doping in core-shell quantum dots, we have developed a theory for the electronic and magneto-optical properties of spherical zinc-blende CdS-ZnS core-shell quantum dots consisting of an inner CdS core surrounded by an outer ZnS shell in a uniform external magnetic field taken to lie along the z axis. This core-shell quantum dot is doped by magnetic Mn\textsuperscript{2+} impurities implanted at a preselected radius, \( R_s \), on an infinitesimally thin spherical surface within the dot. The electronic states in the presence of the magnetic field are treated in an effective mass model which allows for differences in the effective mass parameters in core and shell and s-d and p-d exchange interactions with localized Mn d electrons. Due to the wide band gaps in CdS and ZnS, the conduction and valence band effective mass Hamiltonians are decoupled and treated separately. This is in contrast to our previous work in narrow gap semiconductors where coupling between conduction and valence bands is taken into account.\textsuperscript{16,21} The strain in the quantum dot due to lattice mismatch between core and shell regions is assumed to be pseudomorphic and the effect of this strain field on the electronic states is also included. For simplicity, the Mn impurities are treated in the virtual crystal approximation in which the impurities are smeared out over the surface of an infinitesimally thin spherical Mn doping layer. In addition, the elastic properties of CdS and ZnS are assumed to be isotropic and characterized by a Young’s modulus and Poisson’s ratio. These assumptions gloss over orientation effects in the crystal structure and details of sample specific Mn dopant configurations thus maintaining spherical symmetry. The applied magnetic field breaks the spherical symmetry, but rotational symmetry about the z-axis is still maintained.

A. Quantum Dot Structure

A schematic diagram of the core-shell spherical quantum dot structure is shown in Fig. 1. The quantum dot consists of an inner core of radius \( R_c \) surrounded by a shell with outer radius \( R_s \). In this work the core and shell regions are CdS and ZnS. The dot is doped with radial position controlled magnetic Mn impurities. The Mn impurities are all located in an infinitesimally thin shell at radius \( R_s \) as shown in the figure. The Mn impurity doping shell in Fig. 1 is shown imbedded in the outer shell.
FIG. 1: (color online) Schematic diagram of Mn doped spherical quantum dot structure with an outer shell radius $R$ and an inner core radius $R_c$. The core-shell quantum dot is doped with magnetic Mn impurities in an infinitely thin shell (yellow dashed line) located at radius $R_c$. In general the Mn impurities can be imbedded in either the core or shell regions.

but could equally well be imbedded in the inner core. A static magnetic field is applied which breaks the spherical symmetry and defines the $z$ direction.

B. Effective Mass Hamiltonian

We assume the core and shell are wide gap zinc-blende semiconductors and we ignore the coupling between conduction and valence bands in the effective mass Hamiltonian. This is valid for wide gap materials, but can be extended to narrow gap semiconductors.

Following the convention of Pidgeon and Brown[22], the eight Bloch basis states for conduction and valence electrons can be separated into an upper and lower set which decouple at the zone center i.e. $k_x = 0$. The Bloch basis states for the upper set are

$$|1\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\rangle + |\downarrow\rangle \right)$$

$$|2\rangle = \frac{3}{\sqrt{2}} \left( |\uparrow\rangle + |\downarrow\rangle \right) = \frac{1}{\sqrt{2}} (X + iY) \uparrow$$

$$|3\rangle = \frac{3}{\sqrt{2}} \left( |\uparrow\rangle - |\downarrow\rangle \right) = \frac{1}{\sqrt{2}} (X - iY) \uparrow + Z \downarrow$$

$$|4\rangle = \frac{1}{\sqrt{3}} \left( i|\uparrow\rangle - (X - iY) \uparrow + Z \downarrow \right)$$

which correspond to electron spin-up, heavy-hole spin-up, light-hole spin-up, and split off hole spin-down.

Likewise, the Bloch basis states for the lower set are

$$|5\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\rangle - |\downarrow\rangle \right) = |S \downarrow\rangle$$

$$|6\rangle = \frac{3}{\sqrt{2}} \left( |\uparrow\rangle - |\downarrow\rangle \right) = i\sqrt{2} (X - iY) \downarrow$$

$$|7\rangle = \frac{3}{\sqrt{2}} \left( |\uparrow\rangle + |\downarrow\rangle \right) = i\sqrt{2} (X + iY) \downarrow - 2Z \uparrow$$

$$|8\rangle = \frac{1}{\sqrt{3}} \left( |\uparrow\rangle + |\downarrow\rangle \right) = \frac{1}{\sqrt{3}} (X + iY) \downarrow + Z \uparrow$$

corresponding to electron spin-down, heavy-hole spin-down, light-hole spin-up, and split off hole spin-up.

The total effective mass Hamiltonian for conduction and valence electrons is the sum of four Hamiltonians. These are the Landau Hamiltonian, the Zeeman Hamiltonian, the Strain Hamiltonian due to the lattice mismatch between the core and shell materials, and a Mn Impurity Hamiltonian due to the s-d and p-d exchange interaction with localized Mn d electrons.

1. Landau Hamiltonian

The effective mass Hamiltonian in bulk narrow gap zinc-blende materials is given explicitly in Ref.[11]. To include the interaction with a magnetic field $\mathbf{B} = B \hat{z}$ described by the vector potential $\mathbf{A}$, we replace $p$ in the bulk effective mass Hamiltonian by $\mathbf{p} = \mathbf{p} - e\mathbf{A}/c$ to obtain the Landau Hamiltonian. We use the symmetric gauge $\mathbf{A} = \frac{e}{2} \mathbf{B} \times \mathbf{r}$ so that the Cartesian components of the vector potential are $A = \frac{e}{2} (-y, x, 0)$.

Since we are dealing with wide gap materials, we ignore coupling between conduction and valence bands and arrive at the Landau Hamiltonian

$$H_L = \begin{bmatrix} L_a & L_c \\ L_c^\dagger & L_b \end{bmatrix}$$

with the submatrices $L_a$, $L_b$ and $L_c$ given by

$$L_a = \begin{bmatrix} E_g + A & 0 & 0 \\ 0 & -P - Q & -M \\ 0 & -M & -P + Q \end{bmatrix}$$

$$L_b = \begin{bmatrix} E_g + A & 0 & 0 \\ 0 & -P - Q & -M \sqrt{2} \\ 0 & -M \sqrt{2} & -P + Q \end{bmatrix}$$

$$L_c = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -L \sqrt{2} \sqrt{2} & L \sqrt{2} \sqrt{2} \\ 0 & -i L \sqrt{2} \sqrt{2} & i L \sqrt{2} \sqrt{2} & 0 \end{bmatrix}$$
In Eq. (3), \( E_g \) is the band gap energy, and \( \Delta \) is the spin-orbit splitting. The operators \( A, P, Q, L \) and \( M \) are

\[
A = \frac{1}{2m_0} \left( \pi_x \gamma_4 \pi_x + \pi_y \gamma_4 \pi_y + \pi_z \gamma_4 \pi_z \right), \tag{7a}
\]

\[
P = \frac{1}{2m_0} \left( \pi_x \gamma_1 \pi_x + \pi_y \gamma_1 \pi_y + \pi_z \gamma_1 \pi_z \right), \tag{7b}
\]

\[
Q = \frac{1}{2m_0} \left( \pi_x \gamma_2 \pi_x + \pi_y \gamma_2 \pi_y - 2\pi_z \gamma_2 \pi_z \right), \tag{7c}
\]

\[
L = -\frac{\sqrt{3}}{m_0} \pi_x \gamma_3 \pi_z, \tag{7d}
\]

and

\[
M = \frac{\sqrt{3}}{2m_0} \left[ \pi_x \gamma_3 \pi_x + \pi_y \gamma_3 \pi_y - \pi_z \gamma_3 \pi_z \right]. \tag{7e}
\]

The usual Luttinger parameters\(^\text{22}\) are \( \gamma_1, \gamma_2 \) and \( \gamma_3 \) and we define \( \gamma_4 = m_0/m_0^* \) as the inverse of the electron effective mass. We also define \( \gamma_{1(\pm)} = (\gamma_2 \pm \gamma_3)/2 \) and \( \pi_{1(\pm)} = \pi_x \pm i\pi_y \). The operator ordering in Eq. (7) matters when the material parameters are position dependent and insures that the Hamiltonian matrix remains Hermitian. If we were to adopt the \textit{axial approximation} and set \( \gamma_2 = \gamma_3 = \gamma \), we would have \( \gamma_{(-)} = 0 \) and the second term in Eq. (7d) would vanish.

In the core-shell quantum dot we take \( Q_c = 0.6 \) for the conduction band offset between bulk CdS and ZnS. We take the zero of energy to be the top of the CdS valence band in which case \( H_L \) is given by Eq. (3) without modification. For the ZnS shell the Landau Hamiltonian, \( H_L \) is obtained by subtracting a constant energy from the diagonal operators in Eq. (3) given by

\[
E_0 = \Delta E_g (1 - Q_c), \tag{8}
\]

where \( \Delta E_g = E_g(ZnS) - E_g(CdS) \) is the band gap mismatch between the CdS core and ZnS shell.

\[
2. \text{ Zeeman Hamiltonian}
\]

The Zeeman Hamiltonian is

\[
H_Z = 2 \mu_B B \left[ \begin{array}{cc} Z_a & 0 \\ 0 & -Z_a \end{array} \right] \tag{9}
\]

where \( \mu_B = 5.789 \times 10^{-5} \text{ eV/Tesla} \) is the Bohr magneton and \( B \) is the applied magnetic field in Teslas. The \( 4 \times 4 \) submatrix \( Z_a \) is given by

\[
Z_a = \left[ \begin{array}{cccc} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} \kappa & 0 & 0 \\ 0 & 0 & \frac{1}{2} \kappa & -i\sqrt{\frac{3}{2}}(\kappa + 1) \\ 0 & 0 & i\sqrt{\frac{3}{2}}(\kappa + 1) & \kappa + \frac{1}{2} \end{array} \right]. \tag{10}
\]

For the Luttinger parameter, \( \kappa \), we use the approximation\(^\text{22-25}\)

\[
\kappa = \gamma_3 + \frac{2}{3} \gamma_2 - \frac{1}{3} \gamma_1 - \frac{2}{3}. \tag{11}
\]

By ignoring coupling between conduction and valence bands in the Zeeman Hamiltonian Eq. (9), the effective electron gyromagnetic factor, \( g^* \), describing the spin splitting between the electron spin-up and spin-down Landau levels at the band edge is \( g^* = 2 \). When coupling between conduction and valence bands is taken into account, a correction to \( g^* \) at the band edge can be obtained which is given by\(^\text{16,26}\)

\[
g^* = 2 \left( 1 - \frac{E_p}{2E_g E_g + \Delta} \right) \tag{12}
\]

In the limit of large band gap energies, \( E_g \), this expression reduces to \( g^* = 2 \) as expected. For the wide gap semiconductors CdS and ZnS considered in this study, Eq. (12) gives \( g^* = 1.978 \) and \( g^* = 1.986 \), respectively using material parameters in Table I. Thus we are justified in using the estimate \( g^* = 2 \).

\[
3. \text{ Strain Hamiltonian}
\]

Applying strain to a semiconductor alters the electronic band structure by deforming the unit cell. The effects on the electronic states due to strain induced lattice deformation is described by the Bir-Pikus strain Hamiltonian\(^\text{27}\). The Bir-Pikus Hamiltonian is similar in structure to the Landau Hamiltonian and is given by

\[
H_S = \left[ \begin{array}{cc} S_a & S_c \\ S_c^* & S_b \end{array} \right] \tag{13}
\]

where the submatrices \( S_a, S_b \) and \( S_c \) are

\[
S_a = \left[ \begin{array}{cccc} A_e & 0 & 0 & 0 \\ 0 & -P_e - Q_e & -M_e & i\sqrt{2}M_e \ysi \i & 0 \\ 0 & -M_e^\dagger & -P_e + Q_e & i\sqrt{2}Q_e \ysi \i & 0 \\ 0 & -i\sqrt{2}M_e & -i\sqrt{2}Q_e & -P_e \end{array} \right] \tag{14}
\]

\[
S_b = \left[ \begin{array}{cccc} A_e & 0 & 0 & 0 \\ 0 & -P_e - Q_e & -M_e & i\sqrt{2}M_e \ysi \i & 0 \\ 0 & -M_e^\dagger & -P_e + Q_e & i\sqrt{2}Q_e \ysi \i & 0 \\ 0 & -i\sqrt{2}M_e & -i\sqrt{2}Q_e & -P_e \end{array} \right] \tag{15}
\]

\[
S_c = \left[ \begin{array}{cccc} 0 & 0 & -L_e & -i\sqrt{2}L_e \ysi \i & 0 \\ 0 & 0 & -L_e & i\sqrt{2}L_e \ysi \i & 0 \\ 0 & -i\sqrt{2}L_e & i\sqrt{2}L_e^\dagger & 0 \\ 0 & i\sqrt{2}L_e & -i\sqrt{2}L_e^\dagger & 0 \end{array} \right] \tag{16}
\]
The operators $A_{\varepsilon}$, $P_{\varepsilon}$, $Q_{\varepsilon}$, $L_{\varepsilon}$ and $M_{\varepsilon}$ are related to the strain tensor components $\varepsilon_{ij}$ and the deformation potentials $a_c$, $a_v$, $b$ and $d$ by

$$A_{\varepsilon} = a_c(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \quad (17a)$$

$$P_{\varepsilon} = -a_v(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \quad (17b)$$

$$Q_{\varepsilon} = -\frac{b}{2}(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}), \quad (17c)$$

$$L_{\varepsilon} = id(\varepsilon_{xx} - i\varepsilon_{yz}), \quad (17d)$$

$$M_{\varepsilon} = -\frac{b\sqrt{3}}{4}(\varepsilon_{xx} - \varepsilon_{yy}) + id\varepsilon_{xy}. \quad (17e)$$

In Eq. (17) we make the spherical approximation

$$d = \sqrt{3} b \quad (18)$$

for simplicity.

The strain tensor components $\varepsilon_{ij}$ are related to the displacement field $U(r)$ by

$$\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial U_i}{\partial r_j} + \frac{\partial U_j}{\partial r_i} \right) \quad (19)$$

The lattice constant mismatch between core and shell gives rise to a radial displacement field $U(r) = U(r) \hat{r}$. The calculation of the strain distribution in a spherical core-shell quantum dot is described in the appendix of Ref. 28. In modeling the mechanical properties of the spherical quantum dot, we assume the core and shell are homogenous and isotropic so the stress-strain relation is characterized by Young’s modulus, $E$, and Poisson’s ratio, $\nu$. In the core region ($0 \leq r \leq R_c$) the radial displacement field, $U_c(r)$, is given by

$$U_c(r) = -rP_0 \frac{1 - 2\nu_c}{E_c} \quad (20)$$

where $E_c$ and $\nu_c$ are Young’s modulus and Poisson’s ratio in the core and $P_0$ is the contact pressure at the core-shell interface at $r = R_c$. In the shell region ($R_c \leq r \leq R$) the radial displacement field, $U_s(r)$, in the limit of vanishing external applied pressure is

$$U_s(r) = rP_0 \frac{1 + \nu_s}{E_s} \left[ \frac{1 - 2\nu_s}{1 + \nu_s} + \frac{1}{2} \left( \frac{R}{R_c} \right)^3 \right] - 1 \quad (21)$$

where $E_s$ and $\nu_s$ are Young’s modulus and Poisson’s ratio in the shell. The contact pressure $P_0$ is obtained from the shrink-fit boundary condition

$$U_c(R_c) - U_s(R_c) = 2 \left( \frac{a_{\text{shell}} - a_{\text{core}}}{a_{\text{shell}} + a_{\text{core}}} \right) R_c \quad (22)$$

where $a_{\text{core}}$ and $a_{\text{shell}}$ are the lattice constants in the core and shell regions.

### 4. Manganese Impurity Hamiltonian

The exchange interaction between the Mn$^{++}$ $d$ electrons and the conduction $s$ and valence $p$ electrons is treated in the virtual crystal and molecular field approximation. The resulting Mn exchange Hamiltonian is

$$H_{\text{Mn}} = x N_0 \langle S_z \rangle \begin{bmatrix} D_a & 0 \\ 0 & -D_a \end{bmatrix} \quad (23)$$

where $x$ is the Mn concentration, $N_0$ is the number of cation sites in the sample, and $\langle S_z \rangle$ is the average spin on a Mn site. The $4 \times 4$ submatrix $D_a$ is

$$D_a = \begin{bmatrix} \frac{1}{2}a & 0 & 0 & 0 \\ 0 & \frac{1}{2}b & 0 & 0 \\ 0 & 0 & -\frac{1}{2}b & -i\sqrt{3}b \\ 0 & 0 & i\sqrt{3}b & \frac{1}{2}b \end{bmatrix} \quad (24)$$

where $a$ and $b$ are the exchange integrals.

In the paramagnetic phase, the average spin on a Mn site is given in the limit of noninteracting spins by

$$\langle S_z \rangle = -B S B \left( gS \frac{\mu_B B}{kT} \right) \quad (25)$$

where $g = 2$ and $S = \frac{5}{2}$ for the $3d^5$ electrons of the Mn$^{++}$ ion. The Brillouin function, $B(x)$, is defined as

$$B(x) = \frac{2S + 1}{2S} \coth \left( \frac{2S + 1}{2S} x \right) - \frac{1}{2S} \coth \left( \frac{x}{2S} \right) \quad (26)$$

The antiparallel orientation of $B$ and $\langle S_z \rangle$ is due to the difference in sign of the magnetic moment and the electron spin. Since $B$ is directed along the $z$ axis, the average Mn spin saturates at $\langle S_z \rangle = -\frac{5}{2}$.

The Mn impurities are confined to an infinitely thin Mn doping shell at $r = R_i$ and we assume the Mn ions sit on Cd or Zn sites (Cd$_{1-n}$Mn$_n$S or Zn$_{1-n}$Mn$_n$S). If $N_i$ is the number of Mn impurities in the Mn doping shell, the position dependent Mn concentration, $x$, is given by

$$x(r) = \frac{N_i}{16\pi R_i^3} \delta (r - R_i) \quad (27)$$

where $a_i$ is the lattice constant at $r = R_i$.

The total effective mass Hamiltonian for the radially Mn doped core-shell spherical quantum dot in a magnetic field directed along the $z$ axis is just the sum of the Landau, Zeeman, Strain and $sp$-$d$ exchange contributions, i.e.

$$H = H_L + H_Z + H_S + H_{\text{Mn}}. \quad (28)$$

### C. Electronic States

The single particle electronic state wavefunctions are given by the following expansion

$$|\Psi\rangle = \sum_{\nu} \sum_{nlm} C^{\nu}_{nlm} |nlm\rangle |\nu\rangle \quad (29)$$
where $C_{nlm}^\nu$ are complex expansion coefficients and $|\nu\rangle$ are the eight Bloch basis states $\nu = 1 \ldots 8$ defined in Eqs. 1 and 2.

The summation indices $n$, $l$, and $m$ satisfy $0 \leq n \leq N$, $0 \leq l \leq n$ and $-l \leq m \leq l$. The effective mass envelope basis functions in spherical polar coordinates ($r, \theta, \phi$) are given by the complete orthonormal set

$$|nlm\rangle = R_{nl}(r) \ Y_l^m(\theta, \phi).$$  \hspace{1cm} (30)

The angular envelope basis functions $Y_l^m(\theta, \phi)$ are the usual spherical harmonics as defined in Ref. 30. The radial envelope functions vanish at the surface of the quantum dot and are given by

$$R_{nl}(r) = \sqrt{\frac{2}{R^3}} \ \frac{1}{j_{l+1}(X_n^l)} \ j_l \left( X_n^l \frac{r}{R} \right)$$  \hspace{1cm} (31)

where $j_l(x)$ is the spherical Bessel function and $X_n^l$ is the $n$-th zero of $j_l(x)$.

The energies and expansion coefficients are obtained by solving the effective mass Schrödinger equation

$$\sum_{\nu'} \sum_{n'l'm'} \langle nlm | H_{\nu\nu'} | n'l'm' \rangle \ C_{n'l'm'}^\nu = E \ C_{nlm}^\nu$$  \hspace{1cm} (32)

The 8 × 8 Hamiltonian operators $H_{\nu\nu'}$ are the matrix elements in Eq. 25. In evaluating the matrix elements in the Schrödinger equation 32, we first convert the effective mass Hamiltonian operators in the Landau, Zeeman, Strain and Manganese Impurity Hamiltonians from Cartesian to spherical polar coordinates.

D. Optical Properties

We calculate the magneto-optical absorption coefficient at the photon energy $h\omega$ using the expression

$$\alpha(h\omega) = \frac{\hbar \omega}{(hc)n_r} \ \epsilon_2(h\omega)$$  \hspace{1cm} (33)

where $\epsilon_2(h\omega)$ is the imaginary part of the dielectric function and $n_r$ is the real part of the index of refraction.

In thermal equilibrium, the imaginary part of the dielectric function obtained from Fermi’s golden rule is

$$\epsilon_2(h\omega) = \frac{4\pi^2 e^2}{V_0(h\omega)^2} \sum_{IJ} |\tilde{\varepsilon} \cdot P_{IJ}|^2 f_{IJ} \delta(\Delta E_{IJ} - h\omega).$$  \hspace{1cm} (34)

In the above equation, $V_0$ is the quantum dot volume, $I$ and $J$ label the quantum dot energy levels obtained from solving the effective mass Schrödinger equation, and the transition energies are $\Delta E_{IJ} = E_I - E_J$. In thermal equilibrium $f_{IJ} = f_I - f_J$ where $f_I$, the probability that state $I$ with energy $E_I$ is occupied, is given by the Fermi-Dirac distribution function

$$f_I = \frac{1}{1 + \exp[(E_I - E_f)/kT]}$$  \hspace{1cm} (35)

where $E_f$ is the Fermi level and $kT$ is the thermal energy. The unit electric polarization vector is $\tilde{\varepsilon}$ and $P_{IJ}$ is the momentum matrix element between states $I$ and $J$. Cartesian components of the 8 × 8 momentum operator $P$ in our Bloch state basis are given in Appendix B of Ref. 10.

### Table I: Parameters for Cd$_{1-x}$Mn$_x$S and Zn$_{1-x}$Mn$_x$S

| Parameter                        | Cd$_{1-x}$Mn$_x$S | Zn$_{1-x}$Mn$_x$S |
|----------------------------------|-------------------|-------------------|
| Direct band gap (eV)             | 2.5               | 3.54              |
| Spin orbit splitting (eV)        | 0.08              | 0.07              |
| Electron effective mass $m^*_{e}$ ($m_0$) | 0.15              | 0.28              |
| Luttinger parameters             |                   |                   |
| $\gamma_1$                       | 0.814             | 2.54              |
| $\gamma_2$                       | 0.307             | 0.75              |
| $\gamma_3$                       | 0.307             | 1.08              |
| $\kappa$                         | -0.631            | 3.09              |
| Optical matrix element (eV)      | 19.6              | 20.4              |
| Deformation potentials (eV)      |                   |                   |
| $a_c$                            | -2.08             | -2.78             |
| $a_e$                            | 1.02              | 1.22              |
| $b$                              | -4.7              | -0.7              |
| $d$                              | -8.14             | -1.21             |
| Mn sp-d exchange integrals (eV)  |                   |                   |
| $N_0 \alpha$                     | 0.22              | 0.56              |
| $N_0 \beta$                      | -1.8              | -2.37             |
| Young’s modulus (kbar)           | 461.41            | 702.95            |
| Poisson’s ratio                   | 0.3746            | 0.347             |
| Lattice constant (Å)             | 5.81              | 5.41              |
| Refractive index                  |                   |                   |
| $n_r$                            | 2.28              | 2.27              |

$^a$From Ref. 34
$^b$From Ref. 35
$^c$From Ref. 36
$^d$From Eq. 11
$^e$From Ref. 37
$^f$From Ref. 38
$^g$From Ref. 39
$^h$From Ref. 40
III. RESULTS

The material parameters used in this work are shown in Table I.

A. Undoped CdS-ZnS spherical quantum dot

First we consider magneto-optical properties of an undoped 50 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core in the absence of magnetic impurities.

The band edge of the quantum dot as a function of radius \( r \) is shown in Fig. 2. The 25 Å CdS core has a band gap of 2.5 eV while the 25 Å thick ZnS shell has a 3.54 eV band gap. The band gap mismatch is thus \( \Delta E_g = 1.04 \) eV. In our convention, energies are measured relative to the top of the CdS valence band edge. The conduction band gap offset is taken to be \( Q_c = 0.6 \) which means that 60\% of the band gap mismatch is accommodated in the conduction band and 40\% in the valence band. We can see from Fig. 2 that the CdS core is a spherical well and the ZnS shell is a barrier. The conduction and valence barrier heights are 0.624 eV and 0.416 eV respectively.

The CdS core and ZnS shell are lattice mismatched and this will result in significant modifications to the electronic structure due to the Bir-Pikus strain Hamiltonian \( H_s \) defined in Eq. (13). The spherical symmetry of the core-shell quantum dot and the assumption of homogeneous elastic properties preserves the spherical symmetry of the problem. The strain Hamiltonian is determined by the radial displacement field \( U(r) \). The displacement field \( U(r) \) in the core and shell regions, \( U_c(r) \) and \( U_s(r) \), are defined in Eqs. (20) and (21). The radial displacement field \( U(r) \) is shown in Fig. 3 as a function of \( r \) for a 50 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core. The CdS core has a larger lattice constant \( (a_0 = 5.81 \) Å) than the ZnS shell \( (a_0 = 5.41 \) Å). As a result, the CdS core undergoes compression while the ZnS shell undergoes expansion. There is a discontinuity in the displacement field at the core-shell interface due to the shrink-fit boundary condition in Eq. (22) which is used to determine the contact pressure at the core-shell interface.

In our calculations, the electronic states are given by the expansion in Eq. (24). The basis states are the particle in a spherical box eigenstates \( |n, l, m\rangle \) given in Eq. (29) for a 50 Å spherical box with an infinite barrier. We keep terms in the electronic state expansion up to \( N = 6 \) for a total of 91 \((n, l, m)\) basis states. The ground state conduction band states are pure conduction electron states since conduction and valence band states are decoupled in these wide gap materials. In the absence of a magnetic field, the conduction band ground state is two-fold spin degenerate i.e. pure electron spin-up and spin-down states. For the ground state hole levels, the states are mixed by off diagonal components of the effective mass Hamiltonian. The hole ground state is four-fold degenerate consisting of two predominantly heavy-hole (spin-up and down) states and two predominantly light-hole (spin-up and down) states.

Quantum confinement in a core-shell quantum dot the absence of a magnetic field is illustrated in Fig. 4. We plot the radial probability densities as a function

FIG. 2: (color online) Band edge as a function of radius for a 50 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core. We assume the conduction band offset is \( Q_c = 0.6 \).

FIG. 3: (color online) Radial displacement field \( U(r) \) due to strain as a function of \( r \) in a 50 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core. The strain is due to the lattice mismatch between the CdS core (red) and ZnS shell (blue), whose lattice constants (shown in parentheses) are 5.81 and 5.41 Å respectively. The Young’s modulus, \( E \), and Poisson’s ratio, \( \nu \), in the CdS core and ZnS shell are also indicated. The CdS core with the larger lattice constant undergoes compression while the ZnS shell undergoes expansion.
of \( r \) in a 50 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core for the two-fold degenerate electron ground state (red curve) and the (heavy and light) hole ground states with four-fold degeneracy (blue curve). The holes are more massive than the electrons and are thus more tightly confined in the CdS core region. The reason the heavy and light-holes are degenerate and have the same radial probability densities can be understood from spherical symmetry by noting that the expectation values \( \langle p_x^2 \rangle \), \( \langle p_y^2 \rangle \), and \( \langle p_z^2 \rangle \) are equal in the spherical ground state and hence the expectation value of \( Q \propto p_x^2 + p_y^2 - 2p_z^2 \) in the Landau Hamiltonian must vanish. As a consequence, the heavy and light-hole energy expectation values, proportional to \( \langle P + Q \rangle \) and \( \langle P - Q \rangle \), are also equal.

The computed absorption coefficient as a function of photon energy for linearly polarized light incident on an undoped 50 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core is shown in Fig. 5. We calculate the absorption coefficient using Fermi’s golden rule assuming a linewidth of 2 meV for all transitions. The lower black curve is the computed absorption coefficient neglecting strain effects while the offset red curve is the absorption coefficient obtained with strain effects included. From Fig. 5 we see that the inclusion of strain effects has a pronounced effect on the absorption coefficient, shifting the transition energies about 30 meV to lower energies.

With strain effects included, the lowest transition is at 2.95 eV. This peak is four-fold degenerate with two dipole-allowed transitions between the heavy-hole and conduction states. The remaining two dipole-allowed transitions are from light-hole states to conduction states. For allowed transitions \( \Delta J_z = \pm 1 \), the dipole-allowed heavy-hole transitions \( J = \frac{3}{2}, J_z = \pm \frac{1}{2} \) are \( (\text{hh} \uparrow \rightarrow \text{cb} \downarrow) \) and \( (\text{hh} \downarrow \rightarrow \text{cb} \uparrow) \) and the dipole-allowed light-hole transitions \( (J = \frac{1}{2}, J_z = \pm \frac{1}{2}) \) are \( (\text{lh} \uparrow \rightarrow \text{cb} \downarrow) \) and \( (\text{lh} \downarrow \rightarrow \text{cb} \uparrow) \).

The strong dipole-allowed transition in Fig. 5 at 3.03 eV is a twofold degenerate transition between the lowest split-off hole states \( (J = \frac{1}{2}, J_z = \pm \frac{1}{2}) \) and the lowest conduction states. The two dipole-allowed transitions are \( (\text{sh} \uparrow \rightarrow \text{cb} \downarrow) \), and \( (\text{sh} \downarrow \rightarrow \text{cb} \uparrow) \).

When an external magnetic field, \( B \), is applied, the spin-degenerate energy levels are split. The energy levels for the two lowest conduction states and the four lowest hole states (two heavy and two light) are shown in Fig. 5(a) for magnetic fields up to 100 Tesla. We point out that ultrahigh magnetic fields on the order of hundreds of Tesla can be achieved at a number of pulsed magnetic field facilities.

The spin-up and spin-down states are shown as solid and dashed lines respectively. Note that while there is a break in the energy axis, the energy scales are the same before and after the break. The conduction states are pure spin-up and spin-down states with \( J_z = \pm \frac{1}{2} \). At high fields, we notice a bowing in the energy levels due to the \( A^2 \) terms in the Landau Hamiltonian in Eq. (3). There are two predominantly heavy-hole and two predominantly light-hole states. Because of coupling between states in the \( 6 \times 6 \) valence band effective mass Hamiltonian, the hole states are mixed. For the lowest lying heavy and light-holes the states are better than 99.0% pure, while the excited hole states can exhibit much greater mixing.

At low magnetic fields, the magnetic field induced energy level splitting is proportional to the magnetic field (parallel to \( z \)) and can be described by effective magnetic...
The energy level splitting between spin-up and spin-down states, \( g \) is the effective \( g \)-factor, \( |J_z| \) is the absolute value of the \( z \) component of the spin, \( B \) is the external magnetic field, and \( \mu_B = 5.789 \times 10^{-5} \text{ eV/T} \) is the Bohr magneton. In Fig. 6(a) the effective \( g \) factors are 2.02 for the conduction band states and 0.845 for both the heavy- and light-hole states. The heavy-hole splitting is three times greater than the light-hole splitting since \( J_z = |J_z| \mu_B B \)

\[
\Delta E = 2 |J_z| g \mu_B B \quad (36)
\]

above these arrows are the angular momentum changes between the initial hole state and final electron state. For example, there is an \( h \)-active \( (\sigma_+) \) transition between the heavy-hole spin-down \( J_z = -\frac{3}{2} \) state and the electron spin-down \( J_z = -\frac{1}{2} \) state with a resulting momentum change of \( \Delta J_z = +1 \). Likewise, there’s an \( h \)-active \( (\sigma+) \) transition between the light-hole spin-down \( J_z = -\frac{1}{2} \) state and the electron spin-up \( J_z = \frac{1}{2} \) state also with \( \Delta J_z = +1 \).

We have also considered linear polarization with the electric field polarization vector in the \( xy \) plane (denoted \( x \) polarization) and parallel to magnetic field (denoted \( z \) polarization). In the case of \( z \) polarization, the direction of propagation is perpendicular to the magnetic field and the angular momenta for the initial and final states satisfies \( \Delta J_z = 0 \). In this case, only transitions between light-holes and electrons with the same spin are dipole-allowed. In the case of linear polarization in the \( xy \) plane, the angular momentum selection rule is \( \Delta J_z = \pm 1 \).

The dipole-allowed transition energies for \( h \)-active, \( h \)-active and \( z \) polarized absorption are shown in Fig. 6(b). The line styles are determined by the final state. Transition energies for transitions to the spin-up conduction state are solid lines while transition energies for transitions to the spin-down conduction state are shown as dotted lines. In the case of linear polarization in the \( xy \) plane, the transition energies are the union of the dipole-allowed transition energies for both \( e \) and \( h \)-active polarization \( (\Delta J_z = \pm 1) \) giving rise to four dipole-allowed transitions.

For low magnetic fields, the transition energy, \( E_T(B) \) as a function of the applied magnetic field, \( B \), can be estimated from the transition energy in the absence of a magnetic field, \( E_0 \), and the \( g \) factors and spin quantum numbers, \( J_z \), of the dipole-allowed initial and final states. The transition energies at low fields are given by

\[
E_T(B) = E_0 + (J_z^e g_e - J_z^h g_h) \mu_B B \quad (37)
\]

where \( J_z^e \) and \( J_z^h \) are the angular momenta for the conduction and valence band levels, \( g_e \) and \( g_h \) are the corresponding electron and hole effective \( g \) factors, and \( \mu_B \) is the Bohr magneton.

The absorption spectrum as a function of photon energy and polarization was obtained from Fermi’s golden rule with the delta function in Eq. (33) replaced by a Lorentzian with a full width at half maximum (FWHM) of 2 meV. Waterfall plots of absorption spectra for undoped 50 A CdS-ZnS spherical core-shell quantum dots with a 25 A CdS core are shown in Fig. 7 for magnetic fields up to 100 Tesla.

In Fig. 7(a) the light is assumed to be \( h \)-active circularly polarized. We observe two strong dipole-allowed transitions labeled C1-V4 and C2-V3. In this notation, C1 and C2 are the first two conduction states with spin-down and spin-up respectively. The first four valence states (V1 \( \cdots \) V4) are, respectively, heavy-hole spin-up (V1), light-hole spin-up (V2), light-hole spin-down (V3), and heavy-hole spin-down (V4). The stronger of the two
FIG. 7: (color online) Waterfall plot of absorption spectra for an undoped 50 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core in applied magnetic fields up to 100 Tesla. The photon polarizations are (a) h-active ($\sigma^+$) and (b) e-active ($\sigma^-$) and the FWHM linewidths are all assumed to be 2 meV. Transitions are labeled by conduction and valence state indices relative to the band edge.

Transitions, C1-V4, is a heavy-hole transition while the weaker transition, C2-V3, is a light-hole transition. The transition energy shift for the heavy-hole C1-V4 transition as a function of magnetic field is less than the corresponding transition energy shift for the V2-C3 transition. The reason for this is seen in the fan diagram in Fig. 6(a). The initial and final states in the C1-V4 heavy-hole transition are spin-down states and hence initial and final states are both shifted to lower energies by the magnetic field. The two energy level lines in the fan diagram are nearly parallel leading to a lower transition energy shift in spite of the fact that the heavy-hole levels themselves are shifted more.

In Fig. 7(b) the light is assumed to be e-active circularly polarized and here we also observe two strong dipole-allowed transitions labeled C1-V2 and C2-V1. Again, the stronger transition is a heavy-hole transition while the weaker one is a light-hole transition. Likewise, the heavy-hole transition energy shift is less than the light-hole transition energy shift.

We have also calculated absorption spectra for linearly polarized light as a function of applied magnetic field. We considered linearly polarized light propagating in the direction of the applied magnetic field, $B$, with the electric field polarization vector perpendicular to $B$ in the xy plane referred to as X-polarization. Additionally we also considered linearly polarized light propagating perpendicular to the applied magnetic field $B$ with the electric field polarization vector parallel to $B$ in the z direction referred to as Z-polarization.

Waterfall plots of absorption spectra for undoped 50 Å CdS-ZnS spherical core-shell quantum dots with 25 Å CdS cores are shown in Fig. 8 for magnetic fields up to 100 Tesla and linearly polarized light. Results for X-polarized light are shown in Fig. 8(a). There are four dipole-allowed transitions C1-V2, C2-V1, C1-V4 and C2-V3 in order of increasing energy which satisfy the selection rule $\Delta J_z = \pm 1$. These transitions are, in order of increasing energy, light-hole spin-up, heavy-hole spin-up, heavy-hole spin-down, and light-hole spin-down. Results for Z-polarized light are shown in Fig. 8(b). Here there are only two dipole-allowed transitions C1-V3 and C2-V2
FIG. 9: (color online) Energy levels (a) and Transition energies (b) as functions of an applied magnetic field $B$ for the lowest lying conduction and valence bands in a 25 Å CdS-ZnS spherical core-shell quantum dot with a 25 Å CdS core with a Mn impurity at the center of the CdS core. In (a) the spin-up and down states are solid and dotted lines respectively. dipole-allowed transitions for e-active, h-active, and z-linear polarization are indicated by vertical arrows. The numbers in parentheses are the angular momentum changes between initial and final states. In (b) Transition energies for transitions to the first spin-up conduction state are solid lines while transitions to the first spin-down conduction state are dotted lines.

in order of increasing energy which satisfy the selection rule $\Delta J_z = 0$. These transitions are, respectively, light-hole spin-down and light-hole spin-up.

B. Mn doped CdS-ZnS spherical quantum dot

To illustrate the effect of localized Mn doping on the energy levels and transition energies shown in Fig. 9 we performed a similar calculation but with a single Mn impurity atom at the center of the CdS core. The results are shown in Fig. 9. To facilitate comparison, we plotted everything on the same scales in both figures. Comparing Fig. 9(a) and Fig. 9(b), we notice that the spin splitting for the conduction levels is slightly suppressed while the spin splitting for the heavy-hole and light-hole levels has been greatly enhanced. At low magnetic fields, the effective $g$-factor for the electrons decreases from $g = 2.02$ to $g = 1.85$ while the $g$-factor for heavy and light holes both increase from $g = 0.845$ to $g = 1.67$. This behavior can be traced to the fact that the Mn s-d exchange integral ($N_0 \alpha > 0$) and the p-d exchange integral ($N_0 \beta < 0$) used in our model have different signs. Due to the antiparallel orientation of $B$ and the average spin $\langle S_z \rangle$ in Mn, an exchange integral with a positive sign results in $g$-factor suppression while an exchange integral with negative sign results in $g$-factor enhancement.

Comparing the transition energies in Fig. 9(b) and Fig. 9(b), we find that the magnetic field splitting of all the dipole-allowed transitions is greatly suppressed. This is because the electron and hole $g$-factors, by coincidence, are very nearly equal (1.85 vs 1.67). If the $g$-factors had been exactly equal, the magnetic field induced shifts in the transition energies would be proportional to $\Delta J_z$ between initial and final states which follows as a corollary to Eq. (37).

We calculated magnetic $g$-factors for the lowest lying electron levels and the lowest lying heavy-hole and light-hole levels as a function of doping radius in ensembles of Mn radial position doped 50 Å CdS-ZnS spherical core-shell quantum dots with 25 Å CdS cores. The Mn dopants in the ensemble are treated in the virtual crystal approximation where the Mn impurity Hamiltonian is treated as if all the dopants were smeared out uniformly over an infinitely thin doping shell or radius $R_c$. We find that Mn doping strongly enhances the heavy-hole and light-hole $g$-factors while slightly suppressing $g$-factors for electrons. In general, the Mn impurity interaction with a quantum dot state is large when there’s a large overlap between its effective mass envelope function and the Mn impurity shell.

Our results are shown in Fig. 10 where electron $g$-factors are plotted in red against the left axis and hole $g$-factors are plotted in blue against the right axis. Three sets of curves are shown corresponding to 1, 2, and 4 Mn dopants per quantum dot. As shown in Fig. 10 $g$-factors for heavy and light holes are found to be identical. The Mn doping can dramatically alter the magnetic $g$-factors which are found to be sensitive to the Mn doping radius. For the lowest lying electron and hole levels, the largest change in the $g$-factors is obtained by doping in the center of the CdS core. For a given number of Mn impurities, the $g$-factor changes are strongest at the center of the CdS core and decrease sharply at the core-shell boundary, $R_c$. At the surface of the quantum dot the Mn impurity Hamiltonian vanishes and the $g$-factors return to their undoped quantum dot values. The reason for this is that the effective mass envelope functions vanish at the quantum dot surface and hence can’t overlap with an infinitely thin Mn doping shell at the surface.

For Mn dopants placed at the center of the quantum dot ($R_i = 0$), we find that the electron and hole effective $g$-factors, $g_e$ and $g_h$, as functions of the average number of Mn impurities, $N_{Mn}$, vary linearly as

$$g_e = 2.020 - 0.1568 N_{Mn} \quad (38a)$$
$$g_h = 0.845 + 0.8408 N_{Mn} \quad (38b)$$
From Eq. (38b), we see that if $N_{\text{Mn}} > 12.88$ for Mn doping at the center of the quantum dot, the conduction ground state effective $g$-factor, $g_c$, becomes negative. The hole $g$-factor, $g_h$, on the other hand, is always positive according to Eq. (38b). The electron and hole $g$-factors are equal ($g_c = g_h$) when $N_{\text{Mn}} = 1.18$ at which point the spin splitting vanishes in the low magnetic field limit for e-active and h-active circularly polarized light and linearly polarized light with Z-polarization. For X-polarized light, there is still a two-fold magnetic field splitting when $g_c = g_h$ corresponding to two-fold degenerate transitions with $\Delta J_z = -1$ (low energy) and $\Delta J_z = +1$ (high energy).

IV. SUMMARY AND CONCLUSIONS

We developed an effective mass theory for electronic and magneto-optical properties in CdS-ZnS core-shell spherical quantum dots consisting of an inner CdS core surrounded by a ZnS shell. We performed detailed calculations for 50 Å CdS-ZnS spherical core-shell quantum dots with a 25 Å CdS core. The optical properties of the quantum dot were computed using the effective mass electronic states and Fermi’s golden rule.

The strain in the quantum dot due to lattice mismatch between the CdS core and the ZnS shell was assumed to be pseudomorphic and the effect of this strain on the electronic states was included and found to significantly alter the magneto-optical properties. We maintain the spherical symmetry of the problem by characterizing the elastic properties of the CdS core and ZnS shell by the Young’s modulus and Poisson’s ratio. The CdS core has a larger lattice constant than the ZnS shell. As a result, the CdS core undergoes compression while the ZnS shell undergoes expansion with a discontinuity in the displacement field at the core-shell interface.

This core-shell quantum dot was assumed to be doped by magnetic Mn impurities all implanted in an infinitely thin doping shell of radius $R_i$ within the dot. Our effective mass theory includes the interaction of quantum dot electrons and holes with the Mn dopants through s-d and p-d exchange interactions with the localized Mn d-electrons. In treating the Mn impurities, we used a virtual crystal approximation in which the Mn impurities are smeared out uniformly over the surface of the infinitely thin Mn doping shell. This has the effect of maintaining the spherical symmetry of the problem and leads to a simpler solution. The calculated magneto-optical properties are expected to be characteristic of the average in an ensembles of similar dots.

The spherical symmetry of the dot is broken by the application of an external magnetic field. We calculated magnetic $g$-factors for the lowest lying electron levels and the lowest lying heavy- and light-hole levels as a function of Mn doping radius. We found that Mn doping increases the heavy- and light-hole $g$-factors while reducing $g$-factors for electrons. The Mn impurity interaction with a quantum dot state was found to be large when there’s a large overlap between its effective mass envelope function and the Mn impurity doping shell. For the lowest lying electron and hole levels, the largest change in the $g$-factors is obtained by doping in the center of the CdS core. For Mn dopants placed at the center of the quantum dot ($R_i = 0$), we find that the electron and hole effective $g$-factors vary linearly with the average number of Mn impurities.

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