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Synthesis and Spectroscopic Characterization of Manganese Doped Zinc Sulfide Quantum Dot Nanocrystals

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF MANGANESE DOPED ZINC SULFIDE QUANTUM DOT NANOCRYSTALS

by

Pedro A. Gonzalez Beerman

A Dissertation
Submitted to the
Faculty of the Graduate College
in partial fulfillment of the
requirement for the
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Western Michigan University
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Zinc sulphide quantum dots were synthesized in aqueous media using sodium polyphosphate as the stabilizer. The nanoparticles were 2.5±0.5 nm and 5.0±0.5 nm diameter depending on the synthetic procedure employed and the amount of Mn doped varied from 0.003 to 0.32% (w/w). The nanoparticles were characterized by UV-Vis absorption, luminescence, EPR, near edge x-ray absorption fine structure (NEXAFS), and x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD), and transmission electron microscopy (TEM). These quantum dots show a strong emission at 590 nm due to the $^4T_1\rightarrow^6A_1$ transition characteristic of Mn occupying Zn positions in the lattice in a slightly distorted $T_d$ site. The intensity of the emission at 590 nm increases asymptotically with the concentration of Mn(II) while the lifetime of this emission decreases. The EPR data reveal that Mn$^{2+}$ exists in at least three different types of environments: a slightly distorted $T_d$ site, a highly distorted site near the surface of the nanoparticle and surface sites where Mn$^{2+}$ is adsorbed. The sites responsible for the luminescence of ZnS:Mn are the $T_d$ sites inside the nanoparticle. The 590 nm emission is enhanced when the nanoparticles photo-react with cysteine. This change in intensity could be employed for the design of nanosensors.
I would like to begin by thanking my research advisor Dr. Subra Muralidharan for his guidance, support, dedication and patience through this research.

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I especially extend my grateful thanks to Dr. Raymond Sung for his many helpful suggestions and advice on EPR experiments and discussion on theoretical aspects of EPR. I also thank Dr. Bruce McGarvey from University of Windsor for his cooperation and advice in this research.

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Pedro A. Gonzalez Beerman
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Quantum dots are semiconductor materials with dimensions of the order of a few nanometers. Because of their size, they are also called nanoparticles or semiconductor nanocrystals. One of the most interesting characteristics of this type of materials is the quantum confinement of electrons in a small space. Quantum confinement confers special properties to these semiconductor nanoparticles which are very different from the bulk materials. By controlling the size and shape of quantum dots, it is possible to tune their optical and electronic properties making them suitable for numerous applications in electronics, sensing devices, and catalysis.

During the last few decades a great deal of research has been performed on different types of semiconductor nanoparticles. Among the most studied are the III-V semiconductors (GaN, GaP, InP, etc) and II-VI semiconductors (CdSe, CdS, ZnS, ZnSe). In general, the electron orbitals in these semiconductors overlap forming bands. Electrons fill the lowest energy band, called the valence band, leaving the high energy band, the conduction band, mostly unoccupied. The energy difference between the lowest state of the conduction band and the highest state of the valence band is the band gap, $E_g$.

When electrons in the valence band are excited with enough energy to reach the conduction band, they leave a positive charge (holes), in the valence band. Holes act as
distinctive particles with an effective mass $m_n$. The system arising from the interaction of the excited electron and the corresponding hole is called “exciton”. The behavior of the exciton depends on the magnitude of the quantum confinement.

Quantum confinement becomes important when the dimension of the potential well created in the boundaries of the nanoparticles is nearly the size of the period of the wave of the confined particle. In such conditions, the energy of the system is quantized in discrete levels[1]. The energies of the allowed states increases when the dimension of the system is reduced[2]. The dependence of the values of the energy with respect to the system dimensions is given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mR^2}$$

where $n$ is a quantum number which represent the levels of energy, $R$ is the radius of the nanoparticle, the mass of the electron, and $\hbar$ the Plank constant.

In semiconductor materials the quantum confinement produces an increase in the band gap energy. This increase in the band gap leads to an increase in the probability of radiative recombination of electron and holes. This effect is manifested as an enhancement of the quantum efficiency of the luminescence of these nanomaterials[3].

In the case of small particles, the effective mass of holes is much larger than the electron effective mass. In such systems, the reduced mass $\mu$ of the exciton can be replaced by $m_e^*$. The electron wave function is confined and the hole interacts through the Coulomb potential.
The effective mass approximation model derived by Brus and Kayanuma [4, 5] which includes Coulomb correlation energy terms, enables the derivation of an expression that models energies and provides a reasonable guide to particle size as a function of $E_g$.

\[
\Delta E = \frac{\hbar^2 \pi^2}{2m^* R^2}
\]  

(3)

where $E(R)$ is the Rydberg energy for the bulk semiconductor, $\varepsilon_r$ is the dielectric constant of the semiconductor:

\[
E(R) = E_s + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.786 e^2}{\varepsilon_r R} + 0.284 E_R
\]

(4)

where $E_R$ is the Rydberg energy for the bulk semiconductor, $\varepsilon_r$ is the dielectric constant of the semiconductor:

\[
E_R = \left( \frac{13.606 m_o}{\varepsilon_r^2 \left( 1/m_e + 1/m_h \right)} \right) eV
\]

(5)

1.786 $e^2/\varepsilon_r$R is the Coulomb term and 0.248 $E_R$ gives the spatial correlation energy. This method is known to overestimate the energy value $E(R)$, particularly for particles smaller than 2 nm[1]. Suyver et al.[6], based on the Brus’s approximation have proposed an empirical equation that relates the band gap energy to the particles radius for ZnS nanoparticles

\[
r(E_g) = \frac{0.32 - 2.9 \sqrt{E_g - 3.49}}{2(3.50 - E_g)}
\]

(6)

The central hypothesis of this research is that high quality quantum dot nanocrystals can be synthesized under mild conditions in the aqueous phase and doped with appropriate
metal ions to systematically change their luminescence and other spectroscopic properties.

One of the most interesting aspects of ZnS:Mn nanoparticles is the elucidation of factors that influence the shortening of their luminescence lifetime which is important for their applications as phosphor and sensor materials. While several researchers have investigated this, it is not well understood. The motivation for this research, as stated in the central hypothesis, is to perform a systematic study in order to gain a fundamental understanding of the factors influence the luminescence of ZnS:Mn nanoparticles.

The research has been performed along the objective listed below:

1. Synthesize doped manganese ZnS nanoparticles with sizes \( \leq 5 \) nm in aqueous media. Optimize the synthetic procedure to control the particle size, size distribution and optical, and physicochemical properties of the nanoparticles.
2. Prepare different types of core-shell nanoparticles in order to study the effect of the distribution of Mn\(^{2+}\) ions on the luminescence intensity and lifetime and EPR spectra.
3. Determine the morphology and particle size of the ZnS:Mn nanoparticles using transmission electron microscopy (TEM) and x-ray diffraction spectroscopy.
4. Characterize the physicochemical properties of the ZnS:Mn nanoparticles by different spectroscopic techniques such as luminescence, UV-Vis, electron paramagnetic resonance (EPR), X-ray diffraction (XRD), X-Ray photoelectron
(XPS) and near edge X-Ray absorption fine structure (NEXAFS) spectroscopy, and secondary ion mass spectrometry (SIMS).

5. Investigate the influence of Mn$^{2+}$ concentration on the optical properties of Mn doped ZnS nanoparticles.

6. Develop a model to explain the dependence of luminescence lifetime and intensity of ZnS:Mn$^{2+}$ nanoparticles on the concentration of Mn$^{2+}$.

7. Perform a detailed study of the paramagnetic properties of Mn$^{2+}$ in the ZnS:Mn nanoparticles using EPR spectroscopy in order to understand the nature of the Mn doping and Mn distribution inside the particle.

8. Characterize the binding of cysteine to ZnS:Mn quantum dots without and with UV irradiation by monitoring the kinetics of this process following the change in the luminescence signal.

A fundamental understanding of the ZnS:Mn nanoparticle system is critical for the development of nanosensors in our research group for both biotechnology and environmental applications.
CHAPTER II

EXPERIMENTAL PROCEDURES

2.1 Reagents

Sodium polyphosphate +80 mesh, Aldrich 50813-16-6
Manganese (II) acetate tetrahydrate 99+% , Aldrich CAS 6156-78-1
Zinc acetate dehydrate, 98+% Aldrich 5970-45-6
Zinc Sulfate heptahydrate 99%, Sigma-Aldrich CAS 7446-20-0
Sodium sulfide nonahydrate 99.99+% , Aldrich CAS 1313-84-4
L-Cysteine hydrochloride hydrate 99%, Aldrich C12, 180-0

All reagents were used as received. Water was purified by a Milli Q water purification system (resistance 18.2 kΩ).

2.2 Apparatus

2.2.1 UV-Visible Spectrometer

UV-Vis absorption were recorded with a HP 8453 UV-visible Spectrometer (Agilent Technologies). Data collection and analysis were performed by Agilent UV-visible ChemStation Software.
2.2.2 Luminescence Spectrometer

Emission and excitation spectra were recorded with a LSB-50b Perkin Elmer Luminescence Spectrometer equipped with a Xenon Flash lamp and a R928 Red-Sensitive Photomultiplier. The following conditions were employed in most studies. In those experiments where the conditions are different, the appropriate conditions will be indicated.

Luminescence Mode: Phosphorescence
Delay Times: 0 ms
Gate: 5 ms
Cycle: 16 ms
Flash: 1
Emission Filter: 390 nm Cut-Off
Excitation Slit: 10 nm
Emission Slit: 10 nm
Excitation Wavelength for the emission spectra: 290 nm
Emission Wavelength for the excitation spectra: 590 nm

2.2.3 Transmission Electron Microscope

The morphology and size of the nanoparticles were determined using a JEOL JEM-1230 Transmission Electron Microscope (TEM) operated at an accelerating voltage of 80 kV
and a JEOL JEM-2010F Field Emission Electron Microscope (FTEM) operated at 200 kV using a High Angle Annular Dark Field imaging technique. Sample were dispersed in a Cu grid from aqueous solutions and allowed to dry.

2.2.4 X-Ray Diffractometer

X-Ray powder diffraction analysis was performed at room temperature on the following instruments:

a. Bruker AXS DS Discover X-Ray Diffractometer at the University of Windsor, using a Cu K\(_{\alpha 1}\) radiation with \(\lambda=0.15405\) nm operated at 40 kV and 40 mA. Samples were placed in a zero background glass substrate.

b. XDS 2000 Scintac diffractometer at Northwestern University, using a Cu K\(_{\alpha 1}\) radiation with \(\lambda=0.15405\) nm. Samples were placed in a zero background glass substrate.

2.2.5 X-Ray Photoelectron Spectrometer

X-Ray Photoelectron Spectroscopy (XPS) analyses were performed at the Keck Interdisciplinary Surface Science Center, Northwestern University, using an Omicron ESCA probe equipped with an EA125 energy analyzer. A low energy electron flood gun was used for charge neutralization.
Samples were prepared by evenly spreading a thin layer of the powders on carbon tabs (Spectro Grade Carbon Cat# 77826-12), which were then placed in the entry-load chamber and pumped for 12 h prior analysis.

2.2.6 Time of Flight-Secondary Ion Mass Spectrometer

Time of Flight-Secondary Ion Mass spectrometry (TOF-SIMS) were performed at the Keck Interdisciplinary Surface Science Center, Northwestern University, using a Physical Electronics PHI TRIFF II equipped with a pulsed Ga$^+$ liquid ion gun operated at 15 kV. The ion source was operated with a current of 600 pA. A pulsed low energy electron flood gun was used for charge neutralization. The secondary ions were accelerated to ±3 kV by applying bias on the sample. SIM spectra were acquired using a raster area of 100x100 mm and the total ion dose was about $2 \times 10^{12}$ ions/cm$^2$ in order to ensure static conditions.

2.2.7 Electron Paramagnetic Resonance Spectrometer

Electron Paramagnetic Resonance (EPR) spectra were recorded at room temperature on a X-Band Bruker ESP 300E spectrometer at Windsor University, equipped with an electromagnet capable of providing a magnetic field range from 50 G to 15 kG, a microwave counter and a gaussmeter. Typical measurement conditions were: microwave power 20 mW, microwave frequency 9.7 GHz, modulation frequency 100 kHz, modulation amplitude 0.962 G, and 4 k of data points covering a sweep width range from
450 to 5500 G. The powder samples used in the experimental measurements were sealed under vacuum in quartz tubes.

2.2.8 Near Edge X-Ray Absorption Fine Structure (NEXAFS) Spectroscopy

NEXFAS spectra were performed on the PEEM2 installed at the bending magnet beamline 7.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley Laboratory. The beamline was specifically designed for X-Ray Magnetic Circular Dichroism (XMCD) microscopy. The spherical grating monochromator is entrance slitless and delivers monochromatic radiation in the energy range of 175-1300 eV. PEEM2 works with a low line density of the grating (200 lines/mm) with a typical view of 30 µm and an energy dispersion of 1 eV/mm at 285 eV and 10 eV at 800 eV. The photon flux was $3 \times 10^{12}$ photons/s in a 30 µm spot when the storage ring was operated at 1.9 GeV with a ring current of 400 mA in a design bandpass of 1 eV at 1000 eV.[7-9]

2.3 Synthesis of manganese doped zinc sulfide nanoparticles

2.3.1 Synthesis of Manganese doped Zinc Sulfide Nanoparticles (Method I)

Nanoparticles were prepared in aqueous media using sodium polyphosphate, Na(PO$_3$)$_n$ as stabilizer. Sodium polyphosphate, 10.2 g was dissolved in water and the total volume was adjusted to 70 mL. A 10.0 mL volume of 1.0 M zinc acetate was added to this under vigorous stirring. The solution was kept stirred for 90 min and after this time it was
filtered through a 0.22 µm Millipore filter using vacuum suction. A desired amount of 0.1 M manganese acetate was added to this solution (each mL of 0.1 M manganese acetate corresponds to 1 mol % of manganese). Following the addition of 0.1 M manganese acetate, 10.0 mL of 1.0 M sodium sulfide was added at 0.7 mL/min using a peristaltic pump. The colloidal suspension was transferred to 50 mL Nalgene tubes and the solid was separated by centrifugation at 3000 rpm. The supernatant obtained after the first centrifugation (which contains an excess of sodium polyphosphate) was discarded. The remaining solid was washed three times with water and separated by centrifugation after each washing. The colloidal suspension obtained from the third washing was kept for further luminescence experiments.

The nanoparticles were dried under vacuum for 24 h with a liquid nitrogen trap to obtain a dry powder. The dried solid was ground using an agate mortar and stored in glass vials for further studies.

2.3.2 Synthesis of Manganese doped Zinc Sulfide Nanoparticles (Method II)

In a similar procedure, manganese doped zinc sulfide nanoparticles were prepared in aqueous media using sodium polyphosphate, Na(PO₃)ₙ as stabilizer. In this method zinc sulfate and manganese sulfate salts were used instead of acetate salts. The other reagents and steps were the same as in Method I.
2.3.3 Synthesis of Core(\text{ZnS:Mn}) / Shell(\text{ZnS}) Nanoparticles (Method III)

Sodium polyphosphate, 10.2 g was dissolved in water and the total volume was adjusted to 70 mL. To this, 10.0 mL of 1.0 M zinc acetate was added under vigorous stirring. The solution was kept stirred for 90 min and after this time it was filtered through a 0.22 \mu m Millipore filter using vacuum suction. After filtration, the total volume was adjusted to 100 mL with water. A 25 mL volume of this solution was taken out for later use. A desired amount of 0.1 M manganese acetate was added to this solution (each mL of 0.1 M manganese acetate corresponds to 1 mol\% of manganese). Immediately, 7.5 mL of 1.0 M sodium sulfide was added at 0.7 mL/min using a peristaltic pump. The colloidal suspension was transferred to 50 mL Nalgene tubes and the solid separated by centrifugation at 3000 rpm. The supernatant obtained after the first centrifugation was discarded. The remaining solid was washed twice with 10 mL of an aqueous solution containing 0.15 g of polyphosphate/mL and separated by centrifugation after each washing. The 25 mL of Zn/Polyphosphate solution taken out previously was mixed with the wet solid and stirred. An additional volume of 2.5 mL of sodium sulfide was added at 0.7 mL/min using a peristaltic pump. The remaining steps were the same as described in Method I.

2.3.4 Synthesis of Core(\text{ZnS}) / Shell(\text{ZnS:Mn}) nanoparticles (Method IV)

Sodium polyphosphate, 10.2 g was dissolved in water and the total volume was adjusted to 70 mL. A 10.0 mL volume of 1.0 M zinc acetate was added to this under vigorous
stirring. The solution was kept stirred for 90 min and this time it was filtered through a 0.22 µm Millipore filter using vacuum suction. After filtration, the total volume was adjusted to 100 mL with water. A 25 mL portion of this solution was taken out for utilization later. A 7.5 mL volume of 1.0 M sodium sulfide was immediately added at 0.7 mL/min using a peristaltic pump. The colloidal suspension was transferred to 50 mL Nalgene tubes and the solid separated by centrifugation at 3000 rpm. The supernatant obtained after the first centrifugation was discarded. The remaining solid was washed twice with 10 mL of an aqueous solution containing 0.15 g of polyphosphate/mL and separated by centrifugation after each washing. The 25 mL of Zn/Polyphosphate solution taken out previously was mixed with the wet solid and stirred. A desired amount of 0.1 M manganese acetate was added to this solution (each mL of 0.1M manganese acetate corresponds to 1 mol % of manganese). An additional volume of 2.5 mL of sodium sulfide was added at 0.7 mL/min using a peristaltic pump. The remaining separation steps are the same as described in Method I.

2.3.5 Synthesis of cysteine capped ZnS:Mn$^{2+}$ Nanoparticles (Method V)

The synthesis of cysteine capped ZnS:Mn$^{2+}$ nanoparticles was performed following the initial steps of Method I described in section 2.3.1. After the solid was washed twice with water, 10 mL of 1.0 M cysteine (pH 7 adjusted with NaOH) was added to the slurry and stirred for 30 min. The emulsion was separated by centrifugation and washed twice with water.
The synthesized cysteine capped ZnS:Mn$^{2+}$ nanoparticles were dried under vacuum with a liquid nitrogen trap to obtain a dry sample. The dried solid was ground using an agate mortar and stored in glass vials for further studies.

2.4 elemental analysis

The amount of Mn$^{2+}$ doped into the ZnS was determined using a Varian Liberty 110 ICP (Chemisar Laboratories Inc., Ontario, Canada or Desert Analytical, Tucson, Arizona). About 50-100 mg of sample was accurately weighed and digested for 1h in 5 mL of concentrated nitric acid. The digested sample solution was then cooled and diluted to a final volume of 25 mL using ultra-high-purity Millipore R.O. water prior to analysis using ICP-AES. Calibration was performed using a NIST traceable standard for manganese.
CHAPTER III

SYNTHESIS AND OPTICAL PROPERTIES OF ZnS:Mn NANOPARTICLES

3.1 Synthesis of Manganese doped Zinc Sulfide Nanoparticles

During the past few years, a great deal of attention has been devoted to the preparation and characterization of semiconductors materials in the nanometer size scale which are a new kind of condensed matter in reduced dimensions that could provide materials with novel characteristics. These materials are interesting from a physical and chemical point of view, mainly because their properties are very different from those of bulk materials. The band gap of nanoparticles is highly dependent on the particle size which makes it possible to tune the emission and excitation properties by varying their radii. Furthermore, their high surface area provides unique platforms for binding different kinds of ligand which could be used for sensing and other applications[10, 11].

Doped semiconductor nanoparticles are Manganese (II) doped ZnS nanoparticles, usually denoted as ZnS:Mn, are one of the most studied doped nanoparticle systems[12]. Even though the synthesis of ZnS:Mn is a simple process, making them in high quality is a challenging task. Since Bhargava, et al. [13] synthesized for the first time ZnS:Mn nanoparticles using the surfactant methacrylic acid as stabilizer, many other authors have reported the synthesis of ZnS:Mn nanoparticles by a variety of procedures[14]. Some of these procedures are: microemulsion synthesis with hydrothermal treatment [15], room
temperature synthesis of colloidal solutions using acetate as precursor salts and polyphosphate as stabilizer [16-18], nanocrystal/Pyrex glass composites of ZnS:Mn by melting methods [19], co-precipitation of ZnS:Mn in methanol and subsequent reaction with PAA (poly-methylmethacrylate) to form a composite film which was deposited on glass surface by spin-coating [20], reverse micelle synthesis utilizing MAA (methacrylic acid) [21] followed by UV light treatment to promote passivation of the nanoparticle surface [22], ZnS:Mn nanoparticles embedded in photonic crystals formed by packing submicron polymer spheres [23], preparation of ZnS:Mn nanoclusters incorporated in zeolites-Y by solid state diffusion at high temperature [24], thin films of ZnS:Mn fabricated using sputter deposition [25], spray pyrolysis of aerosol of ZnS:Mn [26], and core/shell ZnS:Mn nanoparticles coated with a shell of ZnS using reverse micelle methods [27, 28].

Modification of nanoparticle surfaces by inorganic or organic materials has been studied by several groups [29]. It is assumed that these polymers block the nonradiative pathways at the surface of the nanoparticle by reducing dangling bonds and defect states at the surfaces. Furthermore, some polymers could participate in the energy transfer from absorbing groups to near-surface Mn$^{2+}$ ions of ZnS:Mn so that those groups and ZnS can be excited simultaneously. This energy transfer process contributes to the enhancement of the photoluminescence of ZnS:Mn nanoparticles [21].

Besides the passivating action of polymer on the surface of nanoparticles, they could undergo polymerization upon irradiation with UV light or thermal treatment which
results in better passivation on the surface of the nanoparticle [17, 29]. Also some authors have proposed that photooxidation of the ZnS nanocrystal surface in the presence of oxygen and water led to the formation of ZnSO₄ and Zn(OH)₂, which could contribute as passivating barriers on ZnS nanoparticles surface [28].

Sodium polyphosphate is one of the most used stabilizing compounds in nanoparticle synthesis. This compound has the molecular formula

\[ \text{Na}^+\text{O}(\text{PO}_3)_n \]

where \( n \approx 6 \) [30].

Two series of manganese doped zinc sulfide nanoparticles with different concentrations of manganese were prepared according to the Methods I and II described in Chapter II. Batch I samples were obtained by using the acetate salts, while Batch II samples were obtained with sulfate salts. The manganese content in the powder samples was determined by Chemisar Laboratories Inc according to the procedure described in section 2.4. The results obtained are given in Table 3.1
<table>
<thead>
<tr>
<th>Batch I</th>
<th>Mn$^{2+}$ (% w/w)</th>
<th>I$_{120}$</th>
<th>I$_{580}$</th>
<th>I$_{800}$</th>
<th>Batch II</th>
<th>Mn$^{2+}$ (% w/w)</th>
<th>I$_{120}$</th>
<th>I$_{580}$</th>
<th>I$_{800}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.014</td>
<td>14954</td>
<td>17518</td>
<td>1.17</td>
<td>a</td>
<td>0.022</td>
<td>19301</td>
<td>30404</td>
<td>1.57</td>
</tr>
<tr>
<td>b</td>
<td>0.026</td>
<td>17796</td>
<td>19604</td>
<td>1.10</td>
<td>b</td>
<td>0.038</td>
<td>24688</td>
<td>46828</td>
<td>1.90</td>
</tr>
<tr>
<td>c</td>
<td>0.037</td>
<td>27001</td>
<td>26132</td>
<td>0.96</td>
<td>c</td>
<td>0.057</td>
<td>20542</td>
<td>65826</td>
<td>3.20</td>
</tr>
<tr>
<td>d</td>
<td>0.050</td>
<td>37497</td>
<td>30739</td>
<td>0.82</td>
<td>d</td>
<td>0.065</td>
<td>11314</td>
<td>53381</td>
<td>4.72</td>
</tr>
<tr>
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<td>0.052</td>
<td>48537</td>
<td>50426</td>
<td>1.03</td>
<td>e</td>
<td>0.072</td>
<td>13758</td>
<td>76058</td>
<td>3.53</td>
</tr>
<tr>
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<td>52553</td>
<td>44249</td>
<td>0.84</td>
<td>f</td>
<td>0.090</td>
<td>13984</td>
<td>77810</td>
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</tr>
<tr>
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<td>44139</td>
<td>36916</td>
<td>0.84</td>
<td>g</td>
<td>0.159</td>
<td>18153</td>
<td>119477</td>
<td>6.58</td>
</tr>
<tr>
<td>h</td>
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<td>59268</td>
<td>1.08</td>
<td>h</td>
<td>0.173</td>
<td>18232</td>
<td>119470</td>
<td>6.55</td>
</tr>
<tr>
<td>i</td>
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<td>140950</td>
<td>7.23</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 3.1 Analytical concentrations of samples corresponding to Batch I (Acetate synthesis) and Batch II (Sulfate synthesis).

From Table 3.1 we can find that the amount of Mn incorporated in the lattice is a small fraction of the initial Mn added during the synthesis.

The synthetic procedure employed in our study is a modification of the one described by Bol et al, 2001 [17]. We observed the formation of a white solid after the addition of Zn$^{2+}$ ions to the solution of polyphosphate and the amount of the white precipitate was larger when the anion was acetate compared to sulfate. The presence of these suspended particles diminishes the quality of the synthesized nanoparticles and colloidal suspensions. In order to avoid the contamination of the nanoparticles by this precipitate, after mixing of Zn$^{2+}$ ions with polyphosphate solution the mixture was stirred for 90 min and the white solid was removed by filtration. The chemical analysis of this solid gave the following results: %Zn = 24.61, %P = 19.20. In Figure 3.1 is shown a TEM image of a suspension of ZnS:Mn nanoparticles without filtration of the Zn/Polyphosphate mixture. The image was taken using High Angle Annular Dark Field Imaging technique in which the heaviest atomic densities appear in white and holes in black. The Energy Dispersive X-Ray Spectroscopy analysis of the white particles in Figure 3.1 shows that
they contain mostly P and O but no Zn, S nor Mn. This suggests that these particles are the result of polymerization of polyphosphate promoted by acetate or sulfate as the $\text{Zn}^{2+}$ salt counter ion.

Figure 3.1 TEM image of a sample without previous filtration of the Zn/Polyphosphate solution using a high angle annular dark field imaging technique. The X-Ray (EDS) analysis of the white particles of about 0.2 $\mu$m gave a high peak for phosphorous, but no Zn or S content.

3.2 Optical Properties of ZnS:Mn Nanoparticles

3.2.1 Absorption Spectra

The absorption spectra of semiconductor nanoparticles are strongly affected by the quantum confinement of the photogenerated electron-hole pair, which results in the shift
to shorter wavelengths[31]. ZnS is a semiconductor ($E_g=3.6$ eV) which is commercially used for phosphor and thin-film electroluminescence applications, especially if doped with Mn$^{2+}$.

According to Bhattacharyya et al.[32], the absorption coefficient can be written as a function of the incident photon energy $h\nu$ as

$$\alpha = \frac{A}{h\nu}(ln\nu - E_g)^m$$  \hspace{1cm} (3.1)

where $A$ is a constant which is different for different transitions indicated by the various values of $m$ and $E_g$ is the corresponding band gap. The value of $m$ depends on the type of transition, namely, 1/2, 3/2, 5/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect, respectively. Taking the logarithm of equation 3.1 we obtain Eq. 3.2, and its first derivative respect to $h\nu$ is expressed in Eq. 3.3:

$$\ln\alpha = \ln A - \ln h\nu + m \ln (h\nu - E_g)$$  \hspace{1cm} (3.2)

and

$$\frac{d(\ln \alpha)}{d(h\nu)} = -\frac{1}{ln\nu} + \frac{m}{(h\nu - E_g)}$$  \hspace{1cm} (3.3)

Equation 3.3 indicates that a plot of $\ln \alpha$ vs $h\nu$ will diverge at $h\nu=E_g$ from where it is possible to obtain the value of $E_g$. The value of $E_g$ can then be used to calculate $m$ from the slope of the plot of $\ln(\alpha h\nu)$ vs $\ln(h\nu-E_g)$. 
Figure 3.2 shows the absorption spectrum of representative sample, II d which corresponds to a Mn concentration of 0.065 % (w/w). Figure 3.4 indicates the result of calculations based on Eq. 3.3, where the point of divergence is observed at 3.93 eV. This result indicates that the change in energy of the band gap for this particular sample is about 0.33 eV above the value of the band gap of bulk ZnS (3.60 eV). The noisy trend observed in Figure 3.3 at values below 3.5 is due to low signal/background ratio.

Figure 3.2 Absorption spectra of sample I-d with a Mn content of 0.065 % (w/w)
Figure 3.3 Plot $\frac{d(ln \alpha)}{d(h\nu)}$ vs $h\nu$ corresponding to sample IId. The value of $h\nu$ at the point divergence was determined to be 3.93 eV for this particular sample.

Figure 3.4 displays the plot of $ln(\alpha h\nu)$ vs $ln(h\nu - E_g)$ corresponding to sample IId. The slope of the linear part of this plot indicates a value of $m \sim 0.5$ for an allowed direct transition. For all samples listed in Table 3.1, the value of $m$ varied from 0.477 to 0.51 while the $E_g$ remained constant at 3.93 eV. These results indicate that the band gap, $E_g$, does not change when the Mn concentration was increased in this range of Mn doping.
ln(hν - E_g)

Figure 3.4 Plot of ln(αhν) vs ln(hν - E_g) for the sample IId. The slope of the linear region of this plot indicates a m value ~ 0.5 for an allowed direct transition.

3.2.2 Luminescence of ZnS:Mn Nanoparticle Colloids

In the photoluminescence process, electrons from the valence band are excited to the conduction band upon the absorption of photons with energy hν. These excited electrons can be deexcited through non-radiative recombination processes to some surface or defect site. The possible pathway is the energy transfer to Mn^{2+} ions in the \(^4T_1\) level and the subsequent radiative decay to the \(^6A_1\) level [33, 34]. The incorporation of Mn\(^{2+}\) into the ZnS lattice reduces the probability of non-radiative recombination and as a consequence the \(^4T_1 \rightarrow ^6A_1\) becomes a more efficient process. The emission for this transition corresponds to an energy of 2.2 eV (590 nm). In Figure 3.5 the energy diagram for the electronic states of Mn\(^{2+}\) (d\(^5\)) is shown. The first column are the energy states of a free ion, the second column shows the splitting of these states due to the presence of a
cubic crystal field, and in the last column, enclosed by boxes (1) and (2) the splitting due to spin-orbit interaction [35].

![Energy diagram of the electronic states of Mn²⁺](image)

Figure 3.5 Energy diagram of the electronic states of Mn²⁺

Electron-hole recombination results in exciton emission from nanocrystals at an energy that correspond to the band gap. Emission spectra of a collection of nanocrystals usually show broad emission lines. The reason for this homogeneous broadening is variable particle size which results in changes in band gap and each nanoparticle emits at slightly different energies. For small particles, the particle size effect is much more pronounced and the peak width has a stronger dependence on the particle size [6]. In order to eliminate the effect of inhomogeneous broadening and ensemble averaging, it has recently become possible to image and take emission spectra from single quantum dots.
This techniques has been very successful in extracting new microscopic information from these ensemble systems [36].

The emission at 430 nm, has been termed “self-activated”. According to Sooklal, et al.,[31] this emission is due to sulfur vacancies in the lattice; these vacancies produce localized donor sites which are ionized at room temperature and populate the conduction band. Thus, the emission appears to result from band-gap or near band gap recombination. In the case of ZnS nanoparticles, the emission is more likely to be due to shallow traps as recombination centers for photogenerated charge carriers [31].

Semimagnetic semiconductors as ZnS:Mn will exhibit both the exchange interaction effect and the quantum confinement. The exchange interaction of the exciton with the neighbor magnetic ion aligns the spin of the magnetic ions ferromagnetically to the exciton (electron or hole) spin direction. Such state is known as magnetic polaron state [2]. Quantum confinement theoretically permits one to tune the wavelength of the photoluminescence emission by changing the mean size of the nanocrystal [3].

Figure 3.6 displays the excitation spectrum of a representative sample of Batch II nanoparticles. The excitation spectra were taken by fixing the emission wavelength at 590 nm and scanning the excitation from 200 nm to 390 nm. The excitation spectra for all samples listed in Table 3.1 have similar shape varying only in intensity depending on the Mn$^{2+}$ concentration of each sample. The excitation spectrum largely resembles the
absorption spectrum. The excitation spectrum below 240 nm has a large scattered light component and hence is unreliable.

![Figure 3.6 Excitation spectrum of a colloidal solution of ZnS:Mn nanoparticles](image)

The luminescence spectra of the colloidal suspensions of ZnS:Mn excited at 290 nm are displayed in Figures 3.7 and 3.8. Two main luminescence peaks were observed in the emission spectra, the first peak at about 430 nm which is related to ZnS fast surface recombination processes [37] and the second one at 590 nm which corresponds to the forbidden transition $^4T_1 \rightarrow 6A_1$ of manganese centers [38]. The intensity maxima of the peak at 590 nm are also shown in Table 3.1. It is evident from the ratio of intensities of the 590nm/430nm peaks that the energy transfer from the host ZnS to the Mn(II) ions is a very efficient process [39].
As shown in Figure 3.9, there is an initial increase in the emission intensity at 590 nm with increasing Mn$^{2+}$ concentration up to about 0.2%, after which it reaches a steady state value. It is possible that at high Mn$^{2+}$ concentrations the intensity at 590 nm decreases but this is difficult to discern from the emission spectrum for 0.3% Mn$^{2+}$. The synthetic procedure employed at room temperature does not yield Mn$^{2+}$ doping higher than 0.3% for Batch II. The observed emission intensity at 590 nm with increasing Mn$^{2+}$ concentration appears to strongly depend on the number of Mn$^{2+}$ ions in $T_d$ sites (see Chapter VIII), their distribution, and interaction within the host lattice. The emission transition $^4T_1(G) \rightarrow {}^6A_1(S)$ originates from the Mn$^{2+}$ ions at the $T_d$ site which provides the necessary environment for this transition.

Figure 3.7 Emission spectra of Batch I
The dependence of the intensity of the 590 nm peak on Mn(II) concentration, showed in Table 3.1, resembles a Langmuir isotherm which can be expressed as:

$$I = \frac{[Mn]I_\infty}{kI_\infty + [Mn]}$$  \hspace{1cm} (3.4)

where [Mn] is the concentration of Mn(II) incorporated into the nanoparticle expressed as \%Mn (w/w), $I_\infty$ is the maximum value of intensity at high [Mn], and $I$ is the intensity at a given [Mn]. In Figure 3.9, the plot of $I_{590}$ vs \%Mn(w/w) is shown from which the values $k=6.019 \times 10^{-7}$ and $I_\infty=198228$ a.u. have been determined. Equation 3.4 fits very well the experimental intensities especially for manganese concentrations below 0.10 \%(w/w). At very low Mn(II) concentration the luminescence intensity was directly proportional to the concentration of Mn(II) with a proportionality constant $I/k$. The probability of emission
from Mn(II) in T\textsubscript{d} sites can be calculated as $kI/[Mn]$. The probability of emission decreases as the Mn(II) concentration increased due to interaction between Mn centers and this is the reason for the plateauing in the curve $I$ vs $[\text{Mn}]$ shown in Figure 3.9

![Figure 3.9 Dependence of the luminescence intensity at 590 nm on the Mn content of ZnS:Mn nanoparticles](image)

The luminescence intensity changed with increased Mn concentration could be due to quenching arising from Mn – Mn interactions. The detailed discussion in Chapter VII based on experiments will demonstrate that the intensity of the peak at 590 nm is a direct function of the amount of Mn located in T\textsubscript{d} sites inside the nanoparticle. The EPR spectra of these samples indicated the presence of Mn(II) located on the surface of the nanoparticles. As discussed in Chapter VII, these Mn(II) ions do not luminesce, but they interact with Mn ions in the T\textsubscript{d} sites. Therefore, the apparent plateau of the luminescence intensity was due to the photo inactive surface sites and the quenching of the
luminescence of the Mn(II) in the $T_d$ sites by those ions in the surface sites. Figure 3.10 compares the emission spectra of a shell doped sample (SD) and a normal doped sample, I-b with Mn concentrations 0.027 and 0.026 %Mn(w/w) respectively. In the case of the sample SD, Mn(II) ions are located near or on the surface. Even though these samples had similar Mn concentrations, the intensity of the 590 nm peak in sample SD was very weak compared to the normal doped sample. This indicates that Mn(II) ions close to the surface do not luminesce.

Figure 3.10 Comparison between the emission spectra of a sample normal doping sample and a Mn shell doping sample with similar Mn concentrations, I_b = 0.026% Mn and SD=0.027% respectively.
4.1 X-Ray Diffraction Analysis

When crystallites are less than approximately 1 µm in size, an appreciable broadening in the x-ray diffraction lines occurs. In the diffraction domain pattern, the broadening could be due to three different components: strains, defects and crystalline domain size. In the absence of strain, the average size can be estimated from a single diffraction peak using Scherrer’s formula [40, 41].

According to Scherrer’s formula the particle size is given by [41]

\[ L = \frac{0.9\lambda}{\beta \cos(\theta)} \] (4.1)

where \( L \) is the coherence length, \( \lambda \) is the wavelength of the x-ray radiation, \( \beta \) is the peak full width at half maximum (measured in radians) and \( \theta \) the angle in radians. The calculation of \( \beta \) was performed by adjusting the parameters \( I_c, \theta_c \) and \( \sigma \) of the gaussian function Eq. 4.2 to the experimental peak corresponding to (1,1,1) face using a stochastic minimization method.

\[ I = I_c e^{-\left(\theta - \theta_c\right)^2 / 2\sigma^2} \] (4.2)
In equation 4.2 $I_c$ is the maximum peak intensity, $\theta_c$ is the peak position in degrees and the parameter $\sigma$ is related to the full peak width at half of the maximum by the following equation

$$\beta_{rad} = 2.355\sigma_{rad} \quad (4.3)$$

For spherical crystallites, the diameter of the particle is given by $D = \frac{3}{4} L$. The various parameters used in these calculations are indicated in Figure 4.1 and the resulting gaussian curve (dotted line) that best fit this particular experimental peak is also shown. For all spectra, the drift in the baseline was corrected to zero using the software Origin 5.0 before performing any fitting treatment.

![Figure 4.1 Particle size calculation using the Scherrer’s formula](image-url)
The x-ray diffraction patterns of samples SD and Batch II are shown in Figure 4.2. These spectra exhibited three broad peaks corresponding to the (111), (220) and (311) reflecting planes of the cubic ZnS structure. The average crystallite size, calculated from full widths at half maximum ($\beta$) of the diffraction peaks and Scherrer’s formula, was 2.5±0.3 nm.

The particle size calculated from Scherrer’s formula is similar to the size obtained from TEM imaging and optical absorption.

![XRD pattern of batch I powder samples at room temperature, showing the (111), (220) and (311) reflection planes of the cubic ZnS structure. Mn$^{2+}$ concentrations are given in parentheses.](image-url)
4.2  X-Ray Photoelectron Spectroscopy (XPS/ESCA)

The 2p\textsubscript{3/2} x-ray photoelectron spectra of isoelectronic ions are similar, but vary with the magnitude of the binding energies separating multiplet peaks. This energy splitting increases for ions of successively higher atomic numbers. In the case of Mn(2p) the XPS was characterized by the coupling of angular momentum associated with partially filled core and valence shell containing unpaired electrons [42].

Figure 4.3 shows a survey scan of the XPS of the powder samples IIe and IIi with 0.072% and 0.316% Mn\textsuperscript{2+} concentrations, respectively. Spectrum for a sample with 15.9% Mn\textsuperscript{2+} synthesized at 80 °C is also shown for comparison. The small inset clearly shows Mn 2p\textsubscript{3/2} and Mn 2p\textsubscript{1/2} lines at 641eV and 653eV, respectively, which are barely visible in sample IIi of high Mn\textsuperscript{2+} content. The weak signal from Mn is due to its very low sensitivity factor which makes Mn XPS undetectable at low concentrations. This limitation in the Mn detection makes difficult any interpretation of the XPS spectra in the Mn(2p) region.

The O 1s core level spectra taken from two representative samples, IIb and IIi, are given in Figures 4.4 and 4.5. These spectra show maxima at 531.7 eV and 531.8 eV respectively, which are related to non-bridging oxygen that are associated with the single P tetrahedron (P-O\textsuperscript{-}) from polyphosphate [43, 44]. As we can observe in Figures 4.4 and 4.5, the O 1s peaks have slightly distorted gaussian shapes, with small shoulders at 531.5 eV and 533 eV. The presence of these shoulders could be due to other types of O bonds,
for example, bridging oxygens (P-O-P) that link two neighboring phosphate groups (533.4 eV) [44] or P=O bonds (534.5) and the formation of metal-oxygen bond with Zn or Mn (530.5±1 eV)[43, 45].

Figure 4.3 XPS of powder specimens IIe and IIi with the respective Mn$^{2+}$ concentration given in parenthesis. The inset shows Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ lines for the specimen with 15.9% Mn$^{2+}$ concentration and 5 nm particle size.
Figure 4.4 XPS spectra of the O 1s region from sample IIb.

Figure 4.5 XPS spectra of the O 1s region from sample III.
The non-bridging oxygens associated with each phosphate are similar enough to be indistinguishable in the O 1s spectra. This can be explained based on resonance structures of the type \(^\text{O-P=O} \leftrightarrow \text{O=P-O}\).

![Figure 4.6 XPS spectra of the O 1s region from a sample with 15.9% Mn. The presence of a component at 529.1 eV is clearer. This could be associated to Mn-O bonding.](image)

Figure 4.6 displays the O 1s spectrum of a sample with an analytical Mn concentration of 15.9 %(w/w) which was synthesized at 80 °C. In this spectrum, the 529.1 eV component is more prominent than in the spectra of samples IIb and III. This strongly indicates the presence of Mn-O bonds due to the high Mn concentration and the associated O 1s signals are readily observable. The dotted lines, a and b, in Figure 4.6 represent the two components obtained from fitting the experimental spectra using the multi-peaks (gaussian) algorithm from the software Origin-5.0. Even though this algorithm gives the best fit for a given spectrum, the number of peaks which contribute to the signal is unknown and an over fitted spectrum can be misleading.
Figure 4.7 shows the P $2p_{3/2}$ core level spectra from sample IIb exhibiting a peak with a maxima at 133.5 eV. This binding energy value matches the value reported in the literature for P-O bond [43].

The P $2p$ spectrum fits a gaussian peak very well with a maximum at 133.83 eV. For all samples the P $2p$ transition showed the same feature and no changes related to an increase in Mn concentration were observed. This suggests that the binding energies for all P in the sample were very similar and that they do not interact directly with Zn or Mn on the surface.
The XPS spectrum of the S 2p region is shown in Figure 4.8. The peaks corresponding to the levels $2p_{1/2}$ and $2p_{3/2}$ are unresolved. The center of these two peaks is at about 162 eV which correspond to S in ZnS lattice [43]. For all samples the position and shape of the XPS spectra were similar. No dependence of the binding energy on Mn concentration was observed.

![Figure 4.8 XPS spectrum of the S 2p region of sample IIf](image)

Figure 4.8 XPS spectrum of the S 2p region of sample IIf
The spectrum of Zn 2p\textsubscript{3/2} and 2p\textsubscript{1/2} core level are centered at 1021.5 eV and 1044.8 eV respectively as shown in Figure 4.9. No changes in the spectral positions and shape were observed for representative samples of Batch II.

4.3 Near Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS)

In x-ray absorption spectroscopy, a bound electron absorbs an x-ray photon and is excited to an unoccupied electronic energy level of the photoexcited system. Transitions to either bound or free final states which satisfy energy conservation $h\nu = E_f - E_i$, are permitted, subject to dipole selection rule. Transitions to bound states can be considered probes of unoccupied atomic or molecular orbitals and transitions to propagating electrons final state can be considered as probes of the local geometry, which provides information on the crystal structure [46].
The study of the x-ray absorption edge L$_{2,3}$ can provide insights on the oxidation states and symmetry of the 3d transition metals. It is also important to note that the 2p$_{3/2}$ and 2p$_{1/2}$ spectral regions are clearly separated by the core-hole spin orbit interaction. This results in sharp multiplet structures in the spectral lines, which can be used as fingerprints to elucidate the characteristics of the surrounding environment of the 3d ions [47].

![NEXAFS survey scan spectra](image)

Figure 4.10 NEXAFS survey scan spectra of a sample with 15.9 % (w/w) of Mn. This sample was synthesized at 80 °C.

Figure 4.10 shows the survey scan spectra obtained from a sample with 15.9 Mn % (w/w). Three regions of absorption are clearly observed in this spectrum. The first region corresponds to the C L-edge that is due to the graphite tab used as support for the powder samples. At a photon energy of about 540 eV, the absorption region of the L-edge of oxygen appeared which comes from polyphosphate ligands or water molecules on the surface of the nanoparticles. In the region from 645-660 eV we can observe the peaks
corresponding to the absorption of the Mn L-edge. In this particular sample the signal in the Mn L-edge was stronger compared with samples of Batch I and Batch II because of its high Mn content.

The region of absorption for the L-edge transition of zinc appear in the region from 1040 to 1110 eV. Figure 4.11 shows the absorption of the Zn L-edge. Because of the low instrumental sensitivity in this region, the features of this absorption region were not very well resolved in all spectra and not much information could be derived from this particular data. The setup of the instrument only allows scanning from 220 eV to 1200 eV. Due to this limitation, the absorption region for the sulfur L-edge (160-190 eV) cannot be observed using this instrument.

![NEXAFS spectrum of the Zn L-edge](image)

Figure 4.11 NEXAFS spectrum of the Zn L-edge for a sample with 15.9 %Mn (w/w). This sample was synthesized at 80 °C.
The Mn L-edge region was scanned with a higher resolution of 0.1 eV and the spectrum obtained is shown if Figure 4.12. The spectrum is characterized by the large 2p core hole spin-orbit coupling energy which separates them into the 2p\(_{3/2}\) and 2p\(_{1/2}\) regions at low and high photon energies respectively. This spectrum indicates a typical line shape of a Mn\(^{2+}\) ionic state located in tetrahedral symmetry, confirming that the Mn\(^{2+}\) ions are well substituted for Zn\(^{2+}\) ions. The branching ratio between the 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks is strongly influenced by the spin-orbit interaction. Due to the predominance of the 3d channel on the 2p \(\rightarrow\) 3s transitions, the 2p absorption is determined by the transition probability 3d\(^n\) \(\rightarrow\) 2p\(^5\)3d\(^{n+1}\) [47].

![Figure 4.12 Mn\(^{2+}\) NEXAFS spectra for the transition 2p \(\rightarrow\) 3d form a sample with 15.9 %Mn (w/w).](image)

In systems with p-d transitions, the branching ratio \(B_{3/2}\) is given by the relation

\[
B_{3/2} = \frac{A(p_{3/2})}{A(p_{3/2}) + A(p_{1/2})}
\]

4.3
where $A(p_{3/2})$ and $A(p_{1/2})$ are the corresponding background-corrected integrated intensities for the peaks $p_{3/2}$ and $p_{1/2}$ respectively [48]. From the spectrum in Figure 4.12 we obtained the values $p_{3/2} = 166357$ and $p_{1/2} = 64987$ which correspond to a branching ratio of 0.72 which is higher than the statistical value 2/3. One can infer that Mn (d$^5$) has a high-spin Hund’s-rule ground state. The value of 0.72 is close to the theoretical value of 0.75 for the high-spin state, but much more than 0.59 for a low-spin state obtained theoretically for a 3d$^5$ ion. This result is also in agreement with calculations done by van der Laan and Kirkman [47]. In this work they provide calculated spectra for a series of systems with configurations from d$^0$ to d$^8$ in T$\text{d}$ and O$_h$ symmetry. According to these calculations the spectrum shown in Figure 4.12 corresponds to a d$^5$ system with a T$_\text{d}$ symmetry and $10 \text{Dq} \leq 0.5$ eV.

The intensities of the absorption in the Mn L-edge for samples with Mn concentration lower than 0.08 % (w/w) were too weak to perform any quantitative analysis. A comparison of samples II, IIf, IIg, IIIi and the sample with 15.9 % Mn is shown in Figure 4.13. The spectra were normalized in order to compare the shape of the peaks and the scaling factors are indicated in the plot. The positions and intensity ratios for all peaks remained almost constant from low to high Mn concentrations. As will be discussed in Chapter 7, the luminescence and EPR spectra indicated that Mn(II) is present in three distinct environments. However, because Mn(II) is present in a low crystal field environment, the spectral features of the Mn L-edge were very similar between a tetrahedral or octahedral symmetry and cannot be distinguished using this technique.
Additionally, these results indicate the absence of Mn clusters in this kind of system that will be manifested by the distortion of the local $T_d$ symmetry around Mn$^{2+}$ ions.

![NEXAFS spectra](image)

Figure 4.13 NEXAFS spectra of three representative samples of batch-II and a sample with 15.9%. The spectra normalize to the maximum at 645 eV. The scale factor for each spectrum is indicated in the graph.

It is important to mention that there was no indication of the presence of oxidation states higher than +2 for Mn in these spectra. Higher oxidation state will shift the position of the peaks to higher energies [49] and will change the nature of the spin-orbit coupling interaction. As a consequence, the characteristics of the spectra for the $d^5$ system in $T_d$ symmetry will change. Furthermore, these results suggest that there was no noticeable hybridization between Mn 3d and the conduction band. If hybridization occurs, the local spin at the Mn center will be suppressed because of the delocalization of the unoccupied states. In such a case, the pre-edge peaks are not visible [49]. This contradicts the
assumption made by Bhargava et al, [13] that a strong p-d hybridization is responsible for the presence of short lifetime components in the luminescence decay of the 590 nm peak.

In Figure 4.14 the spectra of the oxygen K-edge is shown corresponding to the samples IIb (0.038 %Mn), IIh (0.173 %Mn), and a sample with 15.9 %Mn. The bands in the ∼538-556 eV range is due to 1s → 2p transitions. From these x-ray absorption spectra, we observe that the ∼538 eV peak is virtually unaffected by the Mn content in the nanoparticle, while the peak at ∼541.5 decreases when the %Mn is increased. This decrease in the intensity of the signal at 541.5 eV does not agree with the trend of the O 1s signal in the XPS spectra. Most of the oxygen in these samples comes from polyphosphate used as capping material. From chemical analysis is was determined that the average content of P in these samples was about 4.0±0.5%(w/w) so that the change in the 541.5 eV signal intensity cannot be attributed to changes in the amount of
polyphosphate on the surface. A possible source of this variation could be the drift of the x-ray beam intensity which decreases with time while the cyclotron is been used.

Due to this intrinsic instrumental limitation, the comparison of the signal between samples is unreliable and only comparison between signal ratios in the same sample are possible. In this work, NEXAFS was employed to study the characteristics of the local environment of the different species and not as a quantitative tool.

4.4 Secondary Ion Mass Spectrometry (SIMS)

The negative ionization ToF-SIMS spectrum of sample III is shown in Figure 4.15. The most abundant species detected were in order of mass O\(^-\) (15.992 a.u.), OH\(^-\) (16.998 a.u.), S\(^-\) (31.966 a.u.), HS\(^-\) (32.976 a.u.), PO\(_2\)^- (62.952 a.u.) and PO\(_3\)^- (78.944 a.u.).

![Figure 4.15 Negative ToF-SIMS spectrum obtained from sample III.](image)
The abundance of the different negative species detected in ToF-SIMS are reported in Table 4.2. Figure 4.16 displays the variation in abundance of the different negative species detected in ToF-SIMS. It is evident from these data that the amount of $O^-$ ions increased with the Mn concentration while the amount of $S^-$ ions decreased. Also we can see that the species $PO_2^-$ and $PO_3^-$ have similar trends, decreasing rapidly from sample IIb to IIe and maintaining this level with no significant variations. Additionally, $OH^-$ and $HS^-$ ions did not show major variations in their abundance when the Mn concentration increased. The correlation between the abundance of $O^-$ ions and the Mn concentration suggested that Mn could be associated with O, probably from polyphosphate, on the surface of the nanoparticle. This also supports the possible existence of Mn-O bonds suggested by XPS analysis.

Figure 4.16 Dependence of the ToF-SIMS signal of the different species on the concentration of manganese.
Table 4.2 Abundance of the negative ToF-SIMS spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn</th>
<th>O</th>
<th>OH⁻</th>
<th>S</th>
<th>HS</th>
<th>PO₂⁻</th>
<th>PO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>llb</td>
<td>0.0375</td>
<td>0.258</td>
<td>0.092</td>
<td>0.198</td>
<td>0.051</td>
<td>0.183</td>
<td>0.218</td>
</tr>
<tr>
<td>lle</td>
<td>0.0715</td>
<td>0.301</td>
<td>0.098</td>
<td>0.291</td>
<td>0.085</td>
<td>0.107</td>
<td>0.118</td>
</tr>
<tr>
<td>llg</td>
<td>0.1585</td>
<td>0.321</td>
<td>0.096</td>
<td>0.241</td>
<td>0.056</td>
<td>0.137</td>
<td>0.150</td>
</tr>
<tr>
<td>lli</td>
<td>0.3155</td>
<td>0.420</td>
<td>0.113</td>
<td>0.195</td>
<td>0.046</td>
<td>0.113</td>
<td>0.113</td>
</tr>
</tbody>
</table>

The positive ToF-SIMS spectrum of the sample lli is shown in Figure 4.17. In the inset is shown the peak corresponding to Mn with an atomic mass of 54.963 a.u. The most intense peak at 22.99 a.u. was due to Na⁺ from polyphosphate.

![Figure 4.17. ToF-SIM spectrum of powder sample lli. The inset shows the presence of the stable Mn²⁺ isotope with mass 54.94 a.u..](image)

Figure 4.18 contains a plot of the ratio of Mn signal to Zn signal vs %Mn. This ratio as expected was essentially linear with the % Mn.
4.5 Transmission Electron Microscopy (TEM)

Examination of the particles using electron microscopy showed particles of size approximately 3.5 to 5 nm diameter depending on the synthetic method used. In general, the formation of large aggregates was observed. These aggregates form during the evaporation of the sample on the carbon grid and they do not exist in the aqueous suspension. The colloidal solutions of ZnS:Mn were stable for months without any indication of precipitation which should occur rapidly if such aggregates exist in suspension.

The focusing of an electron beam on a small particle or groups of particles of many nanoscale systems can result in a rearrangement of atoms or melting [50].
Figure 4.19 displays the TEM image of a sample of ZnS:Mn nanoparticles. The average size of the nanoparticles from this image was estimated to be 1.9 nm.
Figure 4.20 HRTEM image of a sample of ZnS capped with cysteine (a) normal imaging and (b) image using a high angle annular dark field technique. The arrows indicate the same nanoparticle in both pictures. The average particle size in this sample was 3.9 nm.
Figure 3.1 (see Chapter III) shows the TEM image of a sample without filtration of the Zn-Polyphosphate precipitated formed upon the addition of zinc acetate to the polyphosphate solution. To obtain this image a high angle annular dark field imaging technique was used. The X-Ray (EDS) analysis of the white particles of about 0.2 µm gave a high peak for phosphorous, but no Zn or S content. The formation of aggregates in samples synthesized using the acetate route was very pronounced. Samples prepared using the sulfate salts produced less precipitate of Zn-polyphosphate. In particular, the white aggregate indicate by an arrow in Figure 3.1 seems to be formed of polyphosphate because no Zn or S was detected by the EDS analysis.

Figure 6.1 (Chapter VI) shows the transmission electron microscope image of sample 1. Based on a count of 30 particles, the average particle size was determined to be 5 ± 0.5 nm. The particle shape was spherical. Formation of some aggregates was observed mostly due to the method of preparation of the TEM specimen. The formation of aggregates and melting of the nanoparticles under the microscope x-ray beam was technical limitation in obtaining good quality TEM images.
CHAPTER V

NUMERICAL SIMULATION OF THE EPR SPECTRA of Mn$^{2+}$ IN AXIAL SYMMETRY

5.1 Overview

A considerable amount of research has been carried out on the electron paramagnetic resonance spectra of manganese ions, Mn$^{2+}$, in a variety of systems[51-54]. The ground state of Mn$^{2+}$ ions has a half filled d shell, 3d$^5$, which contain 5 unpaired electrons with a total angular momentum L=0 and total electronic spin S=5/2. Manganese has only one natural isotope, $^{55}$Mn, with a total nuclear spin I=5/2. In ZnS:Mn nanocrystals, Zn$^{2+}$ is replaced by Mn$^{2+}$ in tetrahedral sites of the host lattice. The crystal field imposed by the neighbor anions, S$^{2-}$, splits the electronic energy levels in the Mn$^{2+}$ ions. This complicates the EPR spectra, but at the same time, offers extra features that allow more detailed study of such systems.

This section describes the mathematical approaches used to simulate the EPR spectra of Mn$^{2+}$ ions in the ZnS host lattice. A detailed discussion of EPR theory can be found in the monographs by Wertz and Borton[55] or Orton[56].
5.2 The Spin Hamiltonian

The energy levels that constitute the ground state of a magnetic ion in a crystal can be described in terms of the effective nuclear and electronic spins. The energy levels of the ground state levels can be expressed by means of the spin Hamiltonian. The spin Hamiltonian is a quantum mechanical operator that represents the total electronic energy of the ion. In a crystal, the total energy of the ions can be distributed in large number of discrete energy levels, which correspond to the eigenvalues of the spin Hamiltonian. For a given spin eigenfunction, $\phi_n$, the corresponding energy is determined by the Schrödinger equation:

$$ H \phi_n = E_n \phi_n $$

where $n$ is an appropriate quantum number for the spin energy level, $H$ represents the Hamiltonian operator and $E_n$ the energy related to the quantum number $n$.

In a matrix representation, we have to calculate elements of the form

$$ \langle \phi_i | H | \phi_j \rangle $$

which will depend on the type of interactions considered in the Hamiltonian. This Hamiltonian might contain several terms representing the effect of each interaction, namely, crystal field, Zeeman field, nuclear interaction, etc. From the secular determinant of equation 5.2, the eigenvalues of the system can be obtained.

The can represent the spin states for the Mn$^{2+}$ system in a tetrahedral site (axial symmetry) are represented by the following spin Hamiltonian:
\[ H = \beta_s \hat{S} \cdot g \cdot \vec{B} + D \left[ S_z^2 - \frac{1}{3} S(S + 1) \right] + E \left[ S_z^2 - S_y^2 \right] + \hat{S} \cdot A \cdot \hat{I} - \mu_n \beta_n \hat{I} + Q \left[ I_z^2 - \frac{1}{3} I(I + 1) \right] \]

5.3

The first term in the Hamiltonian represents the electron Zeemann interaction; the second and third are the zero field spin-spin interactions, and the fourth term is the electron spin-nuclear spin interaction. The last two terms correspond to the nuclear Zeemann and nuclear quadrupole interactions that are much smaller and are often ignored, but cannot be ignored for this particular system. The quadrupolar term arises from the interaction of the nucleus with the unsymmetrical electronic distribution and it is important in systems with electrons in d orbitals.

The spin operators \( \hat{S} = (S_x, S_y, S_z) \) and \( \hat{I} = (I_x, I_y, I_z) \) have the following properties:

\[
\begin{align*}
S_z^2 |M\rangle &= S(S + 1) |M\rangle \\
S_z |M\rangle &= M |M\rangle \\
S_+ &= \sqrt{S(S + 1) - M(M - 1)} |M - 1\rangle \\
S_- &= \sqrt{S(S + 1) - M(M + 1)} |M + 1\rangle \\
S_x &= \frac{1}{2} (S_+ + S_-) \\
S_y &= \frac{1}{2} (S_+ - S_-)
\end{align*}
\]

5.4

and

\[
\begin{align*}
I_z^2 |M\rangle &= I(I + 1) |M\rangle \\
I_z |M\rangle &= M |M\rangle \\
I_+ &= \sqrt{I(I + 1) - M(M - 1)} |M - 1\rangle \\
I_- &= \sqrt{I(I + 1) - M(M + 1)} |M + 1\rangle \\
I_x &= \frac{1}{2} (I_+ + I_-) \\
I_y &= \frac{1}{2} (I_+ - I_-)
\end{align*}
\]

5.5
In order to clarify equations 5.4 and 5.5, we present here as an example of the calculation of \( S_x \) for the case \( S=5/2 \). For a total spin \( S=5/2 \), \( M \) has the 6 possible values: +5/2, +3/2, +1/2, -1/2, -3/2, -5/2. We can construct \( S_x \) in its matrix form as:

\[
\begin{pmatrix}
\frac{3}{2} & \frac{3}{2} & \frac{5}{2} & 0 & 0 & 0 \\
\frac{5}{2} & 0 & \frac{3}{2} & 0 & 0 & 0 \\
0 & \frac{\sqrt{2}}{2} & 0 & \frac{3}{2} & 0 & 0 \\
0 & 0 & 3/2 & 0 & \frac{\sqrt{2}}{2} & 0 \\
0 & 0 & 0 & \frac{\sqrt{2}}{2} & 0 & \frac{\sqrt{5}}{2} \\
0 & 0 & 0 & 0 & \frac{\sqrt{5}}{2} & 0
\end{pmatrix}
\]

For each element in this matrix we apply the operators \((S_+ + S_-)/2\) with the “bra” corresponding to the columns and the “ket” to the rows. As an example, for column 2 and row 1 we have:

\[
\langle +3/2 | S_x | +5/2 \rangle = \langle +3/2 | \frac{(S_+ + S_-)}{2} | +5/2 \rangle = \frac{\sqrt{5}}{2} + 0 = \frac{\sqrt{5}}{2}
\]

Spin operators of systems with two spin are the tensor product (Kronecker product \( \otimes \)) of the corresponding spin operators. For example:

\( S_x \otimes 1_{2S+1} \) or \( 1_{2S+1} \otimes I_y \) or \( S_z \otimes I_z \)

In matrix representation the electron Zeeman interaction can be expressed as

\[
H_{EZe} = \beta_e \mathbf{\hat{S}} \cdot \mathbf{g} \cdot \mathbf{\bar{B}} = \beta_e (B_x I_x + B_y I_y + B_z I_z) \begin{pmatrix}
g_{xx} & g_{xy} & g_{xz} & S_x \\
g_{yx} & g_{yy} & g_{yz} & S_y \\
g_{zx} & g_{zy} & g_{zz} & S_z
\end{pmatrix}
\]

where \( B_x, B_y, B_z \) are the x,y,z component of the static magnetic field in the molecular frame coordinates. In general, the matrix g is symmetric and can be transformed to its diagonal form:
\[ g = \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix} \]  \hspace{1cm} 5.8

g_{xx}, g_{yy} and g_{zz} are the principal axis values of the g matrix. In this work we assume that these principal directors define the molecular frame coordinates and the Hamiltonian, Eq. 5.3, will be formulated in this molecular frame.

In the molecular frame \( H_{EZ} \) is transformed into

\[ H_{EZ} = \beta_e \left( g_{xx} B_x S_x \otimes 1_{2I+1} + g_{yy} B_y S_y \otimes 1_{2I+1} + g_{zz} B_z S_z \otimes 1_{2I+1} \right) \]  \hspace{1cm} 5.9

where \( \otimes \) is the Kronecker tensor product and \( 1_{2I+1} \) is an identity matrix of dimensions \((2I+1) \times (2I+1)\).

The eigenframe of the zero-field interaction term is assumed to coincide with the molecular frame. In this case, it can be expressed directly as:

\[ H_{ZF} = \hat{S}^T \cdot \vec{D} \cdot \hat{S} = \vec{D} \left[ S_{zz}^2 - \frac{1}{3} S(S+1) \right] + E \left[ S_{zz}^2 - S_y^2 \right] \]  \hspace{1cm} 5.10

where \( \vec{D} \) is a matrix of the form:

\[ \vec{D} = \begin{pmatrix} -1/3D + E & 0 & 0 \\ 0 & -1/3D - E & 0 \\ 0 & 0 & 2/3D \end{pmatrix} \]  \hspace{1cm} 5.11

the ratio \( \eta = E/D \) is a measure of the orthorhombic distortion, which can vary from \( \eta = 0 \) for full axial symmetry to a maximum orthorhombic distortion value of \( \eta = 1/3 \) [53].
In equation 5.10, $S_x$, $S_y$ and $S_z$ are defined as the Kronecker tensor product of $S_x \otimes I_{2s+1}$, $S_y \otimes I_{2s+1}$ and $S_z \otimes I_{2s+1}$ respectively and the squares are calculated as the dot product of such matrices. For example $S_z^2 = (S_z \otimes I_{2s+1}) \cdot (S_z \otimes I_{2s+1})$.

The hyperfine term stands for the interaction between the nuclear and magnetic spin momentum. This term can be formulated as:

$$H_{HF} = \hat{S}^T \cdot A \cdot \hat{I} = (S_x, S_y, S_z) \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}$$  \hspace{1cm} 5.12

Assuming that the principal axis of the A tensor coincides with the molecular frame; it will be reduced to its diagonal form:

$$A = \begin{pmatrix} A_{xx} & 0 & 0 \\ 0 & A_{yy} & 0 \\ 0 & 0 & A_{zz} \end{pmatrix}$$  \hspace{1cm} 5.13

Then

$$H_{HF} = A_{xx} S_x \otimes I_x + A_{yy} S_y \otimes I_y + A_{zz} S_z \otimes I_z$$  \hspace{1cm} 5.14

The interaction between the nuclear magnetic moment and the Zeeman field is called the nuclear-Zeeman interaction and is described by:

$$H_{NZ} = \mu_B \beta_N \hat{I} \cdot \vec{B} = \beta_N \left( \mu_x B_x 1_{2s+1} \otimes I_x + \mu_y B_y 1_{2s+1} \otimes I_y + \mu_z B_z 1_{2s+1} \otimes I_z \right)$$  \hspace{1cm} 5.15

where $1_{2S+1}$ is an identity matrix of dimensions $(2S+1) \times (2S+1)$. 
The nuclear quadrupole term, represents the interaction of the nucleus with the unsymmetrical electronic distribution and can affect the EPR spectra even though its contribution to the Hamiltonian is smaller than the hyperfine term. If the axis of the quadrupole term corresponds to the z axis, the quadrupolar interaction can be expressed as:

\[ H_{NQ} = Q \left[ I_z^2 - \frac{1}{3}I(I+1) \right] \]  

where Q is a constant value and \( I_z \) should be expressed as \( 1_{2S+1} \otimes I_z \)

5.3 Definition of the Molecular Coordinates

The expression of the spin Hamiltonian depends on the coordinate system used to define the direction of the external magnetic field and the different operators and tensors involved.

Figure 5.1 Coordinate system of the molecular frame used to define the spin Hamiltonian.
The principal axis of the g matrix of the paramagnetic center is defined to coincide with the principal axis of the molecular coordinates. Under such definition, the orientation of the external magnetic field, B, is determined by the angles θ and ϕ as it is indicated in Figure 5.1. The x,y,z components of the static magnetic field are defined by:

\[
\begin{align*}
B_x &= B \sin(\theta) \cos(\phi) \\
B_y &= B \sin(\theta) \sin(\phi) \\
B_z &= B \cos(\theta)
\end{align*}
\]  

5.4 Calculation of the Energy States (eigenvalues) and Wavefunctions (eigenfunctions)

In order to perform the calculations of the energy states, we have separated the Hamiltonian described in Eq. 5.3 in two parts. One, \( H_1 \), which is dependent on the external magnetic field and the second one, \( H_2 \), which is only dependent on the internal interactions [57] as indicated in Eq. 5.18

\[
H(B) = H_1(B) + H_2
\]  

where \( H_1(B) = H_{EZ} + H_{NZ} \) and \( H_2 = H_{ZF} + H_{HF} + H_{NQ} \). \( H(B) \) is a matrix of dimensions \( N = (2S+1)(2I+1) \) which comprises all possible interactions between electrons, nucleus and the Zeeman field.

Equation 5.1 can be transformed to the equivalent representation:

\[
(H(B) - E_n \cdot I) \varphi_n = 0
\]  

where \( I \) is the identity matrix with the same dimensions as \( H(B) \). Equation 5.19 can be expressed as the secular determinant

\[
\det[H(B) - E_n \cdot I] = 0
\]
The decomposition of H(B) to its related eigenvalues and eigenvectors is always possible as long as the matrix H(B) is square. When each eigenvalue is paired to its corresponding eigenvector (eigenfunction) the system is nondegenerate. In the case that two or more eigenvectors are related to a given eigenvalue, the system is said to be degenerate and an additional constraint of orthogonalization is needed.

The solution of equation 5.20 is not computationally trivial. Numerous methods have been used to solve this kind of secular determinant. The selection of the method depends on the size of the matrix H(B) and the nature of such matrix (real or complex). One of the most popular is the Jacobi matrix diagonalization which is very robust for small and big matrices and

This method consists of a sequence of orthogonal similarity transformations of the form:

\[ H' = P_q^r \cdot H \cdot P_{pq} \]  

where \( P_{pq} \) is a Jacobi’s rotation matrix. Each rotation eliminates one off-diagonal element. The sequence of rotations is performed until all off-diagonal elements are zero or lower than a given threshold value. The Jacobi rotation matrix \( P_{pq} \) contains ones (1’s) along the diagonal except for the two elements \( \cos \phi \) in rows and columns \( p \) and \( q \). In addition, all off-diagonal elements are zero except for the elements \( \sin \phi \) and \( -\sin \phi \). The rotation angle \( \phi \) for an initial matrix A is chosen such that

\[ \cot(2\phi) = \frac{a_{pq} - a_{pp}}{2a_{pq}} \]
The resultant diagonal elements of the transformed matrix $H'$, contains the eigenvalues of the eigensystem. The dot product of the $n$ rotation matrix contains the corresponding eigenvectors

\[
\vec{V} = P_1 \cdot P_2 \cdots \cdot P_{n-1} \cdot P_n
\]

5.24

where $\vec{V}$ is a matrix of dimensions $N \times N$ in which each row $i$ corresponds to an eigenfunction $|\varphi_i \rangle$.

The flow diagram presented in Figure 5.2 indicates the sequence of steps involved in the calculation of the eigenvalues and eigenvectors. In continuum wave (cw) EPR experiment, the magnetic field, $B$, is swept in the region of interest. For each value of $B$, a set of eigenvalues and eigenvectors are calculated. The inset in Figure 5.2 shows a plot of the different eigenvalues for a $S=5/2$ system in a crystal field with full orthorhombic distortion ($D=400.0$ and $E=133.33$ gauss). It is interesting to note how the energy diagram changes when the Zeeman field is increased. At low Zeeman field, the crystal field dominates and defines the axis of quantization. When the Zeeman field is increased, it defines the axis of quantization of the system. A transition between two states, $|\varphi_i \rangle \rightarrow |\varphi_j \rangle$, occurs when the difference in energy $\Delta E = E_j - E_i$ is equal to the energy of the spectrometer radiofrequency, $h\nu$; in other words, when the resonance
function, \((\Delta E - h\nu)\), becomes zero[57]. The arrows in the energy diagram in Figure 5.2 indicate possible transitions between two states.

\[
\text{Set up Hamiltonian Parameters} \quad \rightarrow \quad \text{Calculate } H_2 \quad \rightarrow \quad \text{Set Magnetic Field } B \quad \rightarrow \quad \text{Calculate } H(B) \quad \rightarrow \quad \text{Calculate } H(B) = H_1(B) + H_2 \quad \rightarrow \quad \text{Diagonalization} \quad \rightarrow \quad \text{Eigenvalues Eigenvectors}
\]

Figure 5.2 Flow diagram for the calculation of eigenvalues and eigenvectors from a spin Hamiltonian.

5.5 Transition Probability

As we mentioned in the last section, a transition between two states happens when the difference in energy between these two states matches the quantum energy of the radiofrequency radiation.

The magnetic field of the radiofrequency radiation is given by \(B_1 \sin(\omega t)\), where \(B_1\) is the amplitude of the radiation. In general, for a cw EPR experiment, the radiofrequency magnetic field is perpendicular to the Zeeman Field. In this case the signal intensity is proportional to
\[ W_i = \frac{\pi^2}{\hbar^2} g(\nu) \langle \phi_i | H \phi_j \rangle^2 \]  
5.25

where \( \phi_i \) and \( \phi_j \) are the eigenfunctions at a given value of the external magnetic field and \( g(\nu) \) is the line function shape, which is usually taken as Lorentzian[56].

\[ g(B) = \frac{1.0}{1.0 + \sigma^2 \left( \hbar \nu - \Delta E_{ij}(B) \right)^2} \]  
5.26

where \( 1/\sigma^2 \) is the peak width and \( \Delta E_{ij}(B) \) is the energy gap between states \( i,j \) with \( E_j > E_i \) at a given field \( B \).

5.6 Resonance Fields

The literature contains numerous methods to compute the resonance fields for EPR spectral simulation. Most of them are based on interpolation methods in which the diagonalization is performed at two field values \( B_a \) and \( B_b \), and the algorithm search for possible matching at some point between \( B_a \) and \( B_b \) using linear or cubic interpolation[57]. Recently, Stoll et al.[57] proposed a method in which the resonance field is fitted by cubic polynomial (splines) interpolations. The accuracy in the determination of the resonance field depends on the size of the segment used to compute the splines. This method could also fail in the presence of degenerate states or intercrossing between levels. The implementation of an algorithm to find points of degeneracy or intercrossing makes the calculation slower and more difficult. Most of the methods described in the literature need to determine first the resonance fields and then apply a Lorentzian or Gaussian function centered at these points to simulate the spectral peaks.
We have proposed here a simple algorithm that can easily compute the resonance fields and transition probabilities. In our algorithm, we sweep the magnetic field through the region of interest and perform the diagonalization of the Hamiltonian. At each value of magnetic field $B$, we construct a transition matrix, $H'$. In an axial symmetry system $H'$ is given by:

$$H' = S_x \cos(\theta) - S_y \sin(\theta) - I_x \cos(\theta) + I_y \sin(\theta)$$  \hspace{1cm} 5.27

The probability matrix, $M$ is calculated from Eq. 5.25. In matrix representation the portion between bars in Eq. 5.25 can be expressed as

$$M = \langle \varphi_i | H' | \varphi_j \rangle = (\varphi_{i1} \cdots \varphi_{iN}) \begin{pmatrix} H'_{11} & \cdots & H'_{1N} \\ \vdots & \ddots & \vdots \\ H'_{N1} & \cdots & H'_{NN} \end{pmatrix} \begin{pmatrix} \varphi_{j1} \\ \vdots \\ \varphi_{jN} \end{pmatrix}  \hspace{1cm} 5.28$$

The matrix resulting from Eq. 5.28, in the case of axial symmetry is real. In lower symmetry systems, where the operator $S_y$ is involved, Eq. 5.28 gives a complex matrix. In this case, a complex conjugate square should be applied in Eq. 5.25.

The contribution of each transition $i \rightarrow j$ to the total signal is proportional to $W_{ij}$. In this work we calculate the total signal as the summation of all $(N^2/2)-N$ possible transitions.

$$I = I_o \sum_{i=1}^{N} \sum_{j>i} W_{ij}  \hspace{1cm} 5.29$$

where $I_o$ is an scaling factor and the summation is considered for all $j>i$.

As we can see from Eq. 5.26, $g(B) = 1$ when $\Delta \epsilon_{ij} = h\nu$ and rapidly approaches zero when $|\Delta \epsilon_{ij} - h\nu| > 1/\sigma^2$. Because of this property of $g(B)$, the signal is noticeable only in those
field values in which \( g(B) = 1 \) but its actual intensity is a function of the probability of transition, \( M \), given by Eq. 5.28.

We have implemented this algorithm employing Mathematica® and Visual Basic® programs. Complete lists of the programs are given in Appendix A and B respectively.

The Mathematica® output for the energy diagram for a \( S=5/2 \) system in an orthorhombic crystal field with \( D=400.0 \) Gauss and \( E=133.3 \) gauss is displayed in Figure 5.3.

![Figure 5.3 Calculated energy diagram for a system \( S=5/2 \) in orthorhombic symmetry with \( D=400 \) Gauss and \( E=133.3 \) Gauss using Mathematica.](image)

In Figure 5.4 is shown an energy diagram for a system \( S=5/2 \) in orthorhombic symmetry with \( D=40.0 \) and \( E=13.3 \) Gauss. When we compare the plots in Figure 5.3 and Figure 5.4 the effect of the crystal field on the energy levels becomes evident. These changes on the energy levels directly affect the shape of the EPR spectra[58].
Figures 5.5 and 5.6 show the calculated absorption and first derivative EPR spectra of the orthorhombic system $S=5/2$ and $I=5/2$ with $D=40.0$ Gauss and $E=13.3$ Gauss using Mathematica. It is remarkable how these simulated spectra match the experimental ones in both the peak positions and in the peak intensity ratios. It is more important to point out the appearance of five doublets corresponding to forbidden transitions which also appear in the experimental EPR spectra. The application of this algorithm in the simulation of the experimental EPR spectra will be presented in the next chapter.
Figure 5.5 Calculated absorption EPR spectra for a system S=5/2, I=5/2 in orthorhombic symmetry with D=40.0 Gauss and E=13.3 Gauss using Mathematica.

Figure 5.6 Calculated first derivative EPR spectra for a system S=5/2, I=5/2 in orthorhombic symmetry with D=40.0 Gauss and E=13.3 Gauss using Mathematica.
5.7 Powder EPR Spectral Simulation

The spectrum in a polycrystalline material is a superposition of single-crystal spectra, where the single crystal axes are oriented at all possible directions $\theta, \phi$ with respect to the external magnetic field $\mathbf{H}$. The interpretation of electron paramagnetic resonance (EPR) spectra of randomly oriented paramagnetic ions is a difficult problem because the random orientation of the crystallites smears out the spectral features which depend on the angular positions[59, 60].

In the case of axial symmetry it is only necessary to consider the angle $\theta$, since there is not angular dependence on the $\phi$ value. The number of crystallites oriented between $\theta$ and $\theta + d\theta$ is proportional to $\sin(\theta)d\theta$[53] (see Figure 5.1). The powder spectrum can be calculated from the convolution of the single crystal spectrum for orientations $\theta = 0$ to $\theta = \pi$. Each spectra is weighted by a factor $\sin(\theta)$ in order to take into account the number of axes oriented in the solid angle $\theta + d\theta$. The calculation of the absorption powder spectrum can be expressed as:

$$f_{\text{powder}} = k \int_{0}^{\pi} f(H, \theta) \sin(\theta) d\theta$$ \hspace{1cm} 5.30

where $f_{\text{powder}}$ is the calculated powder absorption spectra, $k$ is a proportionality constant and $f(H, \theta)$ is the single crystal spectrum at a given angle $\theta$[61].
CHAPTER VI

ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPIC STUDY OF ZnS:Mn QUANTUM DOT NANOPARTICLES

6.1 Overview

The electron paramagnetic resonance of Mn$^{2+}$ has been the subject of extensive experimental and theoretical research to discern the characteristics of the energy levels occupied by electrons in solids [52]. The manifestation of the EPR spectra in a given solid depends on the population of unpaired electrons in the different energy levels which in most cases is a function of temperature. The lifetime of the paramagnetic state and the character of the interactions between ions and the crystal field determines the spectral linewidth [52].

The EPR spectra of manganese as an impurity in several solids have been studied by several authors [54, 62]. Due to its high diffusivity, Mn$^{2+}$ ions can easily replace metal ions in III-V and IV-VI semiconductors where it exists preferentially in its 2+ charge state with a 3d$^5$ electron configuration[63]. Most of the studies on the EPR spectra of Mn$^{2+}$ as impurity in IV-VI semiconductors suggest that manganese is located in a tetrahedral crystal field, indicating that Mn$^{2+}$ ion substitutes for Zn$^{2+}$ in the lattice.
6.2 The Electron Resonance Spectra of Mn$^{2+}$ Doped Zinc Sulfide Nanoparticles

In a first attempt to address the study of the local electronic environment of Mn$^{2+}$ in ZnS:Mn nanoparticles, we prepared a series of three ZnS:Mn powder samples following Method I (See experimental section). Different initial concentrations of Mn$^{2+}$ salt were used during the synthesis. The analytical Mn concentrations obtained from this series of sample were sample 1: 0.003%, sample 2: 0.008% and sample 3: 15.9%.

![Transmission Electron Microscope image of sample 1. Based on a count of 30 particles, the average particle size was determined to be 5 ± 0.5. The particle shape was spherical. Formation of some aggregates was observed mostly due to the method of preparation of the TEM specimen.](image)

The morphology and size of the nanoparticles were determined using a JEOL JEM-1230 Transmission Electron Microscope at Western Michigan University, operated at an accelerating voltage of 80kV. The average size of the quantum dots was determined to be
5 ± 0.5nm, based on a total count of 30 particles from the TEM micrograph shown in Figure 6.1. The slight aggregation is due to the melting of some of the nanoparticles over a prolonged exposure of the sample to the electron beam.

The powder EPR spectra shown in Figures 6.2 and 6.3 were obtained from samples 1 and 2 with 0.003 and 0.008% Mn$^{2+}$ incorporated in ZnS. The spectra correspond to the transition from the $M_S = -\frac{1}{2}$ to $M_S = \frac{1}{2}$ spin states of Mn$^{2+}$ in a nearly cubic site. The powder pattern of transitions $M_S \neq \frac{1}{2}$ are spread out over a wide range of the magnetic field due to the linear term in their resonance field and will not be experimentally observed. Since this linear term is absent in the $M_S = \frac{1}{2}$, their powder pattern are much sharper and will be the main features of the EPR spectrum [59]. To understand the spectrum we must refer to the spin Hamiltonian described in Chapter V, Eq. 5.3, for the spin system of Mn$^{2+}$ with $S = 5/2$, $I = 5/2$.

\[ H = \beta_s \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + D(\hat{S}_z^2 - \frac{1}{3} S(S + 1)) + E[\hat{S}_x^2 - \hat{S}_y^2] + \hat{S} \cdot \mathbf{A} - \mu_B \beta_n \hat{S} \cdot \hat{I} \cdot \mathbf{B} + Q[\hat{I}_z^2 - \frac{1}{3} I(I + 1)] + P(\hat{I}_x^2 - \hat{I}_y^2) \]

In Eq. 5.3, for the sake of simplicity, as a first approximation we have omitted the anisotropic term, $P(\hat{I}_x^2 - \hat{I}_y^2)$, of the quadrupole interaction. The six main lines of the low Mn$^{2+}$ doped samples shown in Figures 6.2(a) and 6.3(b) are all that we could expect, if $D$ and $E$ were very small compared to $gH/\beta_e$ due to a slightly distorted cubic site symmetry. The anisotropy in line width and shape of the six lines, however, tell us that the site symmetry is lower than cubic. Such asymmetry in the $M_S = -\frac{1}{2}$ to $M_S = \frac{1}{2}$
spectrum can arise from anisotropy in any combination of anisotropy in the $g$, $\mathbf{A}$, zero field matrices and/or nuclear spin interactions. Attempts to duplicate this portion of the spectrum showed that we have to assume anisotropy in all three matrices. A simulated spectrum obtained using the Bruker Simfonia program is shown in Figure 6.2(c) and the parameters used to obtain this simulation are listed in Table 6.1 and compared with those reported in the literature[33, 51, 64-67]. We found that any simulation that did not assume the magnitude of the parameter $E$ to be close to the maximum value of $|D|/3$, produced additional lines from the $M_S = \pm 1/2$ to $M_S = \pm 3/2$ or $M_S = \pm 3/2$ to $M_S = \pm 5/2$ transitions that would be visible due to the narrow line widths needed to fit the observed lines. Also $D$ cannot be much larger in magnitude than the value used to simulate the spectrum in Figure 6.2(b).

![EPR spectra](image)

Figure 6.2 EPR spectra of (a) sample 1: 0.003% and (b) sample 2: 0.008%. (c) Simulation using the program Bruker Simfonia
The Simfonia program cannot simulate the ten peaks, between the main six lines, because they represent forbidden transitions that are not included in the program. The six main lines are $M_S = -\frac{1}{2}$ to $M_S = \frac{1}{2}$ transitions for the six values of $M_I$ with $M_I$ going from $5/2$ to $-5/2$ as magnetic field increases, if $A$ is positive. The weaker lines, in between, are from double spin transitions where both $M_S$ and $M_I$ change simultaneously.

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>Structure</th>
<th>g value</th>
<th>Units of $10^{-4}$ cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS (samples 1 and 2)</td>
<td>Cubic$^e$</td>
<td>$g_{xx} = 2.0064$ $g_{yy} = 2.0064$ $g_{zz} = 2.0066$</td>
<td>$A_{xx} = 63.9$ $A_{yy} = 64.0$ $A_{zz} = 64.4$</td>
<td>This work</td>
</tr>
<tr>
<td>ZnS (sample 3)</td>
<td>Cubic$^e$</td>
<td>2.0025</td>
<td>64</td>
<td>This work</td>
</tr>
<tr>
<td>Zinc blende</td>
<td>Cubic</td>
<td>2.0021</td>
<td>63.7</td>
<td>[66]</td>
</tr>
<tr>
<td>ZnS (Wurtzite)</td>
<td>Hexagonal</td>
<td>2.0016</td>
<td>65 106</td>
<td>[67]</td>
</tr>
<tr>
<td>ZnS</td>
<td></td>
<td>2.0025</td>
<td>64</td>
<td>[51]</td>
</tr>
<tr>
<td>ZnS NC1</td>
<td></td>
<td>2.003</td>
<td>64.5</td>
<td>[65]</td>
</tr>
<tr>
<td>ZnS NC2</td>
<td></td>
<td>2.001</td>
<td>89 500 - 1000</td>
<td>[65]</td>
</tr>
<tr>
<td>ZnS (A, B)</td>
<td></td>
<td>2.001</td>
<td>63.9</td>
<td>[33]</td>
</tr>
<tr>
<td>ZnS (C, D)</td>
<td></td>
<td>2.001</td>
<td>90.0</td>
<td>[33]</td>
</tr>
<tr>
<td>ZnS (E)</td>
<td></td>
<td>2.0025</td>
<td>90.0</td>
<td>[33]</td>
</tr>
<tr>
<td>ZnS, signal I</td>
<td>Cubic</td>
<td>2.0024</td>
<td>64.5</td>
<td>[64]</td>
</tr>
<tr>
<td>ZnS, signal II</td>
<td>Cubic</td>
<td>2.0013</td>
<td>84</td>
<td>[64]</td>
</tr>
</tbody>
</table>

Table 6.1. Spin Hamiltonian parameters obtained from the simulation of samples 1, 2 and 3. We report here for comparison parameters published in the literature for similar systems. The last column indicates the source of such data.

The hyperfine forbidden transitions arise as a result of the mixing of the nuclear spin states by combined effect of the nuclear quadrupole interaction, nuclear Zeeman
interaction and the fine structure terms[68]. The importance of the study of those forbidden transitions lies in the fact that their intensities and line positions are important parameters that can be used to determine the spin-spin interactions and specifically the quadrupole interactions[69]. If there were no nuclear Zeemann or nuclear quadrupole interaction both of these transitions would occur half way between the two main lines but a second order nuclear spin-electron spin interaction term and the first order nuclear Zeemann and Quadrupole terms act to separate the two transitions. Using first and second order perturbation theory, the following equation has been derived[70] for the separation of the pair of lines observed between each pair of main lines[71].

\[ \delta = S(S+1) \frac{A^2}{H_0} + 2 \left( \frac{g_N B_N}{g_e B_e} \right) H_0 - Q(3\cos^2 \Theta - 1)(2M_I - 1) \]  

\[ 6.1 \]

\( A \) and \( Q \) are in units of gauss, \( H_0 \) is the center magnetic field, and \( \Theta \) is the angle between the z-axis and the magnetic field. The above equation was obtained with the assumption that the electronic \( g \) matrix and the \( A \) matrix were isotropic. By definition, the five values of \( M_I \) in the above equation are \( 5/2, 3/2, 1/2, -1/2, \) and \( -3/2 \).

The angular dependence of the quadrupolar term in Eq. 6.1 results in these forbidden transitions having an anisotropic powder spectrum, which is easily seen in both Figures 6.2(a) and 6.2(b). We should, however, get a good estimate of \( \Delta \) by measuring the separation of the derivative peaks. In Figure 6.2(b) the values of \( \Delta \) are 12.7, 13.2, 13.9, 14.5, and 15.3 gauss going from low to high field, giving an average of 13.9 gauss. According to Eq. 6.1 the quadrupole term drops out when we take the average resulting in:
\[ \Delta_{\text{ave}} = S(S+1) \frac{A^2}{H_0} + 2 \left( \frac{g_N \beta_N}{g_e \beta_e} \right) H_0 \]

This equation gives a value of 14.4 gauss for \( \Delta_{\text{ave}} \). This confirms our assignment of these peaks as electron-nuclear spin double spin transitions. Including further anisotropy in the quadrupolar interaction will only introduce another unknown parameter to the equations. It is important to remark that these forbidden transitions would not be visible if the site symmetry at the Mn\(^{2+}\) ion were purely cubic. Their presence strongly indicates the existence of a small distortion from cubic symmetry at these Mn sites.

![Figure 6.3 EPR spectrum of (a) sample 3 (15.9% Mn) and (b) simulated spectrum using Simfonia software package.](image)

Figure 6.3(a) shows the powder spectrum obtained from the sample 3 with 15.9% Mn\(^{2+}\) content. The simulated spectrum as shown in Figure 6.3(b) assumes an isotropic g and A
matrices with magnitudes given in Table 6.1. At this high manganese concentration, the high interaction between Mn centers increases the dipolar interaction effect and the distortion in the Mn sites, which produces a broad peak because of the overlapping of numerous spectra with different peakwidth and intensities.

A full Hamiltonian simulation of samples 1 and 2 was performed using the algorithm described in Chapter V. Isotropic $g$ and $A$ matrix were used in this simulations with a $g$ value of 2.0066 and $A$ value of 68.0 Gauss. Figure 6.4 compares the experimental EPR spectra from sample 1 and the full Hamiltonian simulation performed with this algorithm.

Figure 6.4 Comparison between the experimental EPR spectra from sample 1 and a full Hamiltonian simulation.
Because this algorithm performs an exact diagonalization of the Hamiltonian matrix to calculate the eigenvalues and eigenvectors, it is capable of simulating the five pairs of spin forbidden transitions\[63\]

\[
|M_s, M_I\rangle \rightarrow |M_s + 1, M_I - 1\rangle \quad \text{and,}
\]

\[
|M_s, M_I - 1\rangle \rightarrow |M_s + 1, M_I\rangle .
\]

These forbidden transitions do not appear unless an anisotropic $\mu_N$ matrix in the nuclear-Zeeman term is adopted with the diagonal elements $\mu_x \neq \mu_z$ (See equation 5.15). The values $\mu_x$=2.0, $\mu_y$ =2.0 and $\mu_z$= 6.0 were used to simulate the experimental spectrum of sample 1. The zero field parameters D and E in this simulation were the same as that described in Table 6.1. The inclusion of the nuclear-quadrupole interaction term in the calculations yields new peaks with intensity and positions dependent on the value of Q and the angle $\theta$ with respect to the z axis (See equation 5.16). The simulated spectrum shown on Figure 6.4 was calculated neglecting the nuclear-quadrupole term setting the value of Q=0 and P=0.

6.3 Effect of Mn$^{2+}$ Concentration on the EPR Spectra of ZnS:Mn Nanoparticles.

In order to study the effect of the manganese concentration and synthetic method on the EPR spectra of ZnS:Mn nanoparticles, we studied two sets of samples with manganese concentrations ranging from 0.02 to 0.31 \%. The analytical concentrations of these groups of samples are listed in Chapter III, Table 3.1. The
corresponding EPR spectra from Batch I and Batch II are shown in Figures 6.5 and 6.6 respectively.

Figure 6.5 EPR spectra from samples synthesized using Zn and Mn acetate salts (Batch I). The sample SD was prepared using the synthetic Method IV described in the experimental section, Chapter II.
Figure 6.6 EPR spectra from samples synthesized using Zn and Mn sulfate salts (Batch II).

The spectrum of samples prepared using Method IV (see. Chapter II) is included at the top of Figure 6.5. This sample correspond to nanoparticles with a core of ZnS and a shell of ZnS:Mn.

A gradual change in the features of the EPR spectra of Batch I and Batch II is evident in Figures 6.5 and 6.6. At low Mn concentration, the spectra resemble the one
corresponding to sample 1 (0.003 %Mn) in Figure 6.2. A comparison of the EPR spectra of sample 1 (0.003 %Mn) and sample II a (0.022 %Mn) is displayed in Figure 6.7.

![EPR spectra comparison](image)

**Figure 6.7 Comparison of the EPR spectra of samples 1 and II a**

In Figure 6.7, the six allowed lines were observed and the five pairs of forbidden lines occur at the same position, but their peak widths increase upon increasing the Mn concentration. The gradual change in the EPR spectra observed in Figures 6.6 and 6.7 indicate that when the Mn concentration increases, the contribution from other Mn sites with higher distortion becomes more important and the spectral contribution from $T_d$ sites becomes negligible[54].

One of these Mn sites is a highly distorted site, also characterized by a spectrum with six-line pattern but with a much broader line-width of about 48 gauss, and the average $A$
value of 87 gauss covering a total spectral width of about 435 gauss. They are observed in the samples of high Mn$^{2+}$ concentration and in the SD sample with 0.027% Mn$^{2+}$ content. Later on we will discuss experimental evidence that support the hypothesis that the highly distorted Mn sites is located on the nanoparticle surface where Mn is possibly associated with oxygen atoms from water or polyphosphate. The change in the hyperfine pattern and the associated growth of the signal intensity at increasing Mn$^{2+}$ concentration is due to the larger hyperfine interaction and the large zero field interaction accompanied by a very large nuclear quadrupole interaction. A representative simulation of one of the high concentration samples, Ih with 0.191% Mn$^{2+}$, is shown by the dotted line in Figure 6.8, and the parameters are summarized in Table 6.2.

<table>
<thead>
<tr>
<th>Materials</th>
<th>g value</th>
<th>Units of Gauss$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$</td>
</tr>
<tr>
<td>sample Ib</td>
<td>$g_x = g_y = 2.0075$</td>
<td>$A_x = A_y = 68.3$</td>
</tr>
<tr>
<td></td>
<td>$g_z = 2.004$</td>
<td>$A_z = 69.8$</td>
</tr>
<tr>
<td>sample Ih</td>
<td>$g_x = g_z = 2.006$</td>
<td>$A_x = A_y = 85$</td>
</tr>
<tr>
<td></td>
<td>$g_z = 2.003$</td>
<td>$A_z = 89.9$</td>
</tr>
<tr>
<td>SD sample</td>
<td>$g_x = g_y = 2.006$</td>
<td>$A_x = A_y = 85$</td>
</tr>
<tr>
<td></td>
<td>$g_z = 2.003$</td>
<td>$A_z = 89.9$</td>
</tr>
</tbody>
</table>

Table 6.2 Spin Hamiltonian parameters employed in simulation of EPR spectra in Figure 6.8.
The relatively smaller $D$ value observed in the SD sample of low Mn$^{2+}$ concentration compared with sample Ih, indicates a large structural difference in the local environment of Mn in the sample. The samples obtained from the two synthetic methods exhibit difference in their EPR spectra with nanoparticles prepared with sulfate salts having larger fraction of Mn$^{2+}$ near the surface sites even at low Mn$^{3+}$ concentration compared to the nanoparticles prepared with the acetate salt.
One of our main goals in this research was to elucidate the manganese distribution in ZnS:Mn nanoparticles and how this distribution and the interactions between manganese centers can affect the luminescence behavior of such nanoparticles. Our approach consisted in synthesizing nanoparticles with different radial distributions of Mn and studying their luminescence and EPR characteristics.

We prepared three types of core/shell samples (see Chapter 2) and those are: sample 4: core:ZnS:Mn/shell:ZnS (Method III), sample 5: ZnS:Mn normal doping (Method II), and sample 6: ZnS nanoparticles with Mn adsorbed on the surface. The initial concentration of Mn was 30% mol for each sample. The EPR spectra of samples 4,5 and 6 are shown in Figure 6.9. The analytical concentrations of Mn, P and Zn obtained from these samples are listed in Table 6.3

![EPR spectra of sample 4,5 and 6.](image)
Table 6.3 Analytical concentrations of Mn, Zn and P obtained from samples 4, 5, 6. The analysis was carried out by Desert Analytical Labs. at Tucson, Arizona.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn (w/w)</th>
<th>%Zn (w/w)</th>
<th>%P (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 4</td>
<td>0.05</td>
<td>48.89</td>
<td>5.67</td>
</tr>
<tr>
<td>Sample 5</td>
<td>0.30</td>
<td>43.47</td>
<td>8.43</td>
</tr>
<tr>
<td>Sample 6</td>
<td>0.19</td>
<td>45.25</td>
<td>8.11</td>
</tr>
</tbody>
</table>

A striking difference between the spectra of sample 4 and samples 5 and 6 is evident in Figure 6.9 despite employing the same concentration of Mn$^{2+}$ in the synthesis. This difference is paralleled by the Mn content of the nanoparticle as listed in Table 6.3. The features corresponding to the adsorbed Mn$^{2+}$ site is essentially absent in the EPR spectrum of sample 4 while for samples 5 and 6 they constitute the main contribution to their spectra. It is clear that most of the manganese ions are located on the surface of these nanoparticles and only a small fraction resides in the lattice. It is also important to mention that we can control the location of Mn ions in the nanoparticles by controlling the synthetic procedure.

The EPR spectra of samples 1 and 6 represent Mn$^{2+}$ in predominantly tetrahedral sites and surface sites respectively. This is indicated by a gradual distortion and broadening of the EPR peaks as the Mn concentration is increased. At low Mn concentration, the spectra are similar to the spectra of samples 1 and 2 (0.003 and 0.01 %Mn respectively), and as the Mn concentration increases, a component with a larger hyperfine splitting and peak width emerges. At high Mn concentration, the spectrum is very close in shape to that corresponding to sample 6 (Mn adsorbed on the surface). This suggests that as more Mn is added to the nanoparticle it preferentially occupies surface sites over T$_d$ sites[72]. In
order to illustrate this we have superimposed the spectrum of sample 6 on the spectra of representative samples of Batch II (Figure 6.6). We assume that the spectrum of sample 6 is mainly due to adsorbed sites on the surface of the nanoparticles and is scaled by a factor $k$ which was calculated by minimization of the square of the error in the regions indicated by the dotted arrows in Figure 6.10-12.

The value of the scaling factor $k$ increases with the Mn$^{2+}$ concentration. It is observed in these plots that the spectral features due to adsorbed Mn$^{2+}$ in this sample matches well with the spectral features of the various samples of Batch II indicating that the adsorbed component increased as the Mn$^{2+}$ concentration is increased.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analytical %Mn(w/w)</th>
<th>EPR Int. Site Intensity x 10$^{-7}$</th>
<th>Scaling Factor k</th>
<th>Total EPR Intensity x 10$^{-8}$</th>
<th>Internal/Total Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.0220</td>
<td>2.40</td>
<td>1387.1</td>
<td>3.09</td>
<td>0.0779</td>
</tr>
<tr>
<td>b</td>
<td>0.0375</td>
<td>3.93</td>
<td>2605.1</td>
<td>5.77</td>
<td>0.0681</td>
</tr>
<tr>
<td>c</td>
<td>0.0560</td>
<td>5.61</td>
<td>3727.2</td>
<td>8.96</td>
<td>0.0626</td>
</tr>
<tr>
<td>d</td>
<td>0.0650</td>
<td>6.58</td>
<td>4219.1</td>
<td>10.26</td>
<td>0.0642</td>
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<tr>
<td>e</td>
<td>0.0715</td>
<td>3.42</td>
<td>3792.5</td>
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<td>f</td>
<td>0.0895</td>
<td>6.34</td>
<td>5241.4</td>
<td>12.39</td>
<td>0.0512</td>
</tr>
<tr>
<td>g</td>
<td>0.1585</td>
<td>8.12</td>
<td>9308.1</td>
<td>22.38</td>
<td>0.0363</td>
</tr>
<tr>
<td>h</td>
<td>0.1725</td>
<td>9.78</td>
<td>12895.0</td>
<td>31.20</td>
<td>0.0313</td>
</tr>
<tr>
<td>i</td>
<td>0.3155</td>
<td>14.60</td>
<td>17951.2</td>
<td>44.04</td>
<td>0.0332</td>
</tr>
</tbody>
</table>

Table 6.4 Summary of the results obtained from the superposition of samples 6 with the spectra of Batch II.

In Table 6.4 the results of these calculations were listed for all samples from Batch II. These results strongly support the presence of adsorbed Mn on the surface of ZnS:Mn
nanoparticles and that its contribution to the EPR spectra increases when the Mn doping concentration is increased.

Figure 6.10 Comparison of the EPR spectra of samples IIb and IIg with the spectrum corresponding to sample 7.

Figure 6.10 Comparison of the EPR spectrum from sample IIb with the spectrum from sample 6 (adsorbed Mn). In this plot the sample 6 spectrum was normalized and scale by a factor of 1387.1 in order to minimize the error between both spectra in the region indicated by horizontal arrows.
Figure 6.11 Comparison of the EPR spectrum from sample II\textsubscript{f} with the spectrum from sample 6 (adsorbed Mn). In this plot the sample 6 spectrum was normalized and scaled by a factor of 5141.4 in order to minimize the error between both spectra in the region indicated by horizontal arrows.

Figure 6.12 Comparison of the EPR spectrum from sample II\textsubscript{g} with the spectrum from sample 6 (adsorbed Mn). In this plot the sample 6 spectrum was normalized and scaled by a factor of 9305.4 in order to minimize the error between both spectra in the region indicated by horizontal arrows.
As observed in Figures 6.10-12, due to the increasing contribution from the adsorbed Mn sites and the broadening of the allowed and forbidden peaks from the internal T\textsubscript{d} sites, an enhancement in intensity of some signals was observed at positions corresponding to the left side of each forbidden transition. According to our full Hamiltonian simulations, these features arise when the values of P and Q in the quadrupole term are different from zero. But, because of the complexity of these spectra, it was not possible the determination of such parameters. This suggests the existence of other Mn sites in these nanoparticles with higher distortion in the symmetry of the quadrupolar tensor. Possibly these Mn are located near surface where there is higher freedom of relaxation of the stress due to the insertion of a larger Mn ion inside the ZnS lattice[73].

Figure 6.13 shows the plot of the scaling factor vs the %Mn (w/w) for all samples from Batch-II. A linear behavior of the scaling factor with respect to the Mn concentration was observed. This signifies that at this range of Mn concentrations, the amount of adsorbed Mn varies increases linearly with the %Mn in the samples. We estimated the contribution from the internal sites as the difference of the spectra from Batch-II and sample 6 (adsorbed Mn) which has been scaled by the factor k. In Figure 6.14, the plot corresponding to this contribution of internal sites vs Mn concentration is shown. Despite the intrinsic error of this calculation, these results reveal a non-linear increase in the contribution of internal Mn sites. According to this plot it was apparent that at high Mn concentration the contribution of internal sites tends toward a limiting value which could be rationalized as a limit on the competition rate between manganese and zinc ions for lattice sites during the synthesis.
In this section, experimental evidences for the existence of at least three type of Mn sites in ZnS:Mn nanoparticles have been presented. At low Mn concentration the predominant
component comes from a slightly distorted tetrahedral site [64] which exhibits a sextet of sharp peaks ascribed to the allowed transitions with $\Delta M_S = 1$ and five pairs of forbidden transition distributed between the six allowed peaks. The presence of Mn$^{2+}$ ions adsorbed on the surface of the nanoparticles has been established, and the contribution to the EPR signal from absorbed Mn ions is the main feature in the spectra at high Mn concentration. It was also shown that dipolar interactions between Mn ions are the major factor responsible for the broadening of the EPR peaks in these spectra[74]. Later on in Chapter VII and we will use these EPR results to rationalize the relation between the Mn distribution and the luminescence characteristic of these nanoparticles.
CHAPTER VII

EFFECT OF THE SURFACE ADSORBED Mn$^{2+}$ IONS ON THE LUMINESCENCE LIFETIME OF ZINC SULFIDE NANOPARTICLES

7.1 Overview

Nanoparticles are a class of materials with unique properties that have attracted a great deal of interest in recent years. Mn(II) doped ZnS nanoparticles are a very attractive system because these nanoparticles have novel magnetic and optical properties for the design of sensors [75].

In ZnS:Mn nanoparticles, manganese acts as a luminescence color center, emitting light at about 590 nm in addition to a peak at 430 nm which has been attributed to defect-related emission of ZnS[76]. The 590 nm emission has been attributed to the $^{4}T_{1} \rightarrow ^{6}A_{1}$ spin forbidden transition of Mn$^{2+}$ ions. Some authors have claimed that the lifetime of the excited state responsible for the 590 nm luminescence is shorter in nanocrystalline systems than in the bulk material [77]. Barghava et al. [38] proposed that in ZnS:Mn nanoparticles, quantum confinement causes a strong hybridization between the s-p states of the host and d states of the Mn$^{2+}$ ions. This hybridization could increase the forbidden transition $^{4}T_{1} \rightarrow ^{6}A_{1}$ and also result in a decrease in the lifetime of the emissive state.
This chapter of the study focuses on the study of the effect of manganese distribution in the ZnS:Mn nanocrystals on the luminescence signal at 590 nm. We have performed a systematic study of a series of ZnS:Mn nanoparticles with a wide range of Mn$^{2+}$ concentrations. EPR spectroscopy was employed to determine the local environment of the Mn$^{2+}$ ions and their distribution in the nanoparticle. At least three different types of environments for Mn$^{2+}$ ions have been identified. The first is an internal T$_d$ site with low distortion; the second is a highly distorted site near the surface and the third site on the surface where ions are adsorbed. These studies indicate an excellent agreement between the distribution of Mn$^{2+}$ ions and the intensity and lifetime of the emission at 590 nm.

7.2 Correlation between the Luminescence Signal at 590 nm and the EPR Intensity.

The comparison of the results obtained from samples of Batch II for the luminescence signal at 590 nm (Table 3.1) and the EPR intensity (Table 6.4) indicated that a correlation exists between these two sets of values summarized in Table 7.1.

Figure 7.1 shows a plot of the EPR signal intensity from the internal sites vs the luminescence intensity at 590 nm. This plot shows a direct correlation between both signals, which indicates that, the EPR signal from internal sites and the luminescence intensity at 590 nm have a common source. The origin of both signals can be attributed to Mn$^{2+}$ ions located in internal slightly distorted T$_d$ inside the nanocrystal. Our hypothesis is also supported by the fact that samples with Mn near the surface (sample SD) or adsorbed on the surface (sample 6) do not exhibit any luminescence at 590 nm. It seems
that a necessary condition for luminescence activity in these nanocrystals is the location of Mn\(^{2+}\) ions in T\(_d\) inside the nanoparticle.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analytical %Mn (w/w)</th>
<th>Intensity (590 nm)</th>
<th>EPR Int. Site Intensity x 10(^{-7})</th>
<th>Lum. 590/EPR T(_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.022</td>
<td>30404</td>
<td>2.40</td>
<td>0.0013</td>
</tr>
<tr>
<td>b</td>
<td>0.0375</td>
<td>46828</td>
<td>3.93</td>
<td>0.0012</td>
</tr>
<tr>
<td>c</td>
<td>0.0560</td>
<td>65826</td>
<td>5.61</td>
<td>0.0012</td>
</tr>
<tr>
<td>d</td>
<td>0.065</td>
<td>53381</td>
<td>6.58</td>
<td>0.0008</td>
</tr>
<tr>
<td>e</td>
<td>0.0715</td>
<td>76058</td>
<td>3.42</td>
<td>0.0022</td>
</tr>
<tr>
<td>f</td>
<td>0.0895</td>
<td>77810</td>
<td>6.34</td>
<td>0.0012</td>
</tr>
<tr>
<td>g</td>
<td>0.1585</td>
<td>119477</td>
<td>8.12</td>
<td>0.0015</td>
</tr>
<tr>
<td>h</td>
<td>0.1725</td>
<td>119470</td>
<td>9.78</td>
<td>0.0012</td>
</tr>
<tr>
<td>i</td>
<td>0.3155</td>
<td>140950</td>
<td>14.60</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

Table 7.1 Summary of the luminescence and EPR intensities for Batch II samples.

![Figure 7.1](image-url)  
Figure 7.1 Comparison of the EPR signal from internal sites with the luminescence intensity at 590 nm for samples of Batch II. The correlation coefficient r\(^2\)=0.782.
7.3 Study of the Luminescence Decay for the 590 nm Peak in ZnS:Mn Nanoparticles

Since the original report of Bhargava and coworkers [38] on Mn(II) doped ZnS nanoparticles, a great deal of research has been performed in order to understand the decrease in the luminescence lifetime and the luminescence quenching when the particle size decreases from bulk material to the nanoscale. According to Bhargava, quantum confinement promotes the re-hybridization between s-p conduction band levels of the ZnS host and the 3d energy states of the Mn(II) dopant which increases the rate of energy transfer between the donor and acceptor with the consequent decrease in lifetime. Alternative models have been proposed based on the interaction between Mn(II) luminescence active sites inside the host lattice [78]. Most of these models assume that Mn(II) ions are distributed randomly in the host crystal and that they strongly interact with each other favoring the relaxation of the selection rule for the forbidden transition $^{4}T_{1} \rightarrow ^{6}A_{1}$. Among the possible sources of relaxation of the selection rule are the crystal field effect, spin-orbit coupling, exchange coupling of manganese pairs and phonon coupling.

The luminescence intensity decay as a function of time for three representative samples c, f and i from Batch II are given in Figure 7.2, which correspond to low, medium and high manganese concentrations respectively.
Figure 7.2 Luminescence intensity decay for samples IIc, IIf and III. Dots are the experimental data and the lines the model represented by equation 7.1

As shown in Figure 7.2, the lifetime decreases as the Mn concentration increases. We have observed that the intensity dependence with time has a multiexponential character, which imply the presence of numerous Mn centers with different lifetimes. These lifetimes can be attributed to interactions between Mn centers which can relax the spin forbidden transition $^4T_1 \rightarrow ^6A_1$ and the interaction is a function of the distance between manganese ions in the nanoparticle. Because Mn ions are randomly distributed in the nanoparticle, we expect a distribution of lifetimes and we can also expect that isolated Mn has longer lifetime than manganese with high interaction. Based on these considerations, a mathematical model may be proposed to explain not only the decay behavior, but also for the quantification of the effect of the distribution of Mn centers on the luminescence decay of the 590 nm peak in ZnS:Mn nanoparticles.
7.4 Lifetime Distribution Model

It has been established that the Mn$^{2+}$ ions located in T$_d$ sites are the centers responsible for the luminescence at 590 nm in ZnS:Mn nanoparticles. Even though these Mn$^{2+}$ ions are active in the luminescence process, they experience different levels of interaction with other Mn$^{2+}$ ions which affect their luminescence lifetime and signal intensities. If it is assumed that the interaction among Mn$^{2+}$ centers is responsible for the shortening of lifetime of the luminescence signal at 590 nm, we can expect that for a given configuration $R^N=[R_1,R_2,..R_{N-1}]$ exists a corresponding decay time $\tau$, where $R_i$ values are the distances between the emitting Mn$^{2+}$ center and its neighbor Mn$^{2+}$ ions and $N$ is the number of Mn(II) ions in that particular nanoparticle. For isolated Mn$^{2+}$ ions, in which the decay time is not affected by interactions among Mn$^{2+}$ centers, we assume the lifetime is long, $\tau_1$. In the case of configurations with interacting Mn$^{2+}$ ions, it is reasonable to assume a distribution of lifetimes, $f(\tau)$, which depends on the frequency of occurrence of each configuration $R^N$. Figure 7.3 illustrates one of these configurations in which the Mn center (A) interacts with two neighbors Mn adsorbed on the surface of the nanoparticles. Interaction between Mn$^{2+}$ emitting centers with adsorbed Mn are more likely to occur because of the high proportion of Mn$^{2+}$ ions adsorbed in comparison with the internal Mn$^{2+}$ ions.
Figure 7.3 Diagram that represent the interaction of a emitting \( \text{Mn}^{2+} \) ion inside the nanoparticle (A) with different \( \text{Mn}^{2+} \) ions adsorbed on the surface (B and C). Dotted arrows indicate interactions.

For this type of system the time dependence of the luminescence intensity can be expressed as follows:

\[
\frac{I_t}{I_0} = X_1 e^{-t/\tau_1} + (1 - X_1) \sum_{\tau = 0}^{\infty} f(\tau) e^{-t/\tau} \tag{7.1}
\]

where \( I_t \) and \( I_0 \) are the luminescence intensity at the times \( t \) and \( t=0 \) respectively, \( X_1 \) is the fraction of Mn(II) ions emitting with a decay time \( \tau_1 \), \( f(\tau) \) is the lifetime distribution function for manganese interactions and the summation is performed over all the possible values of \( \tau \). The distribution function, \( f(\tau) \), can be approximately modeled by the following expression:

\[
f(\tau) = N\tau^2 e^{-\tau/\sigma} \tag{7.2}
\]
where $N$ is a normalizing constant equal to $1/2\sigma^3$ and $\sigma$ is a parameter related to the maximum of the $f(\tau)$ distribution as $\tau_{\text{max}} = 2\sigma$ (see inset in Figure 7.2). The results of these calculations for all the samples studied are given in Table 7.2. The measurements for samples (IIa and IIb) with low Mn(II) concentration, show some scatter due to the lower signal/background ratio. The variation in $\sigma$, $\tau_1$ and $X_1$ as a function of manganese concentration provides insights into the distribution of Mn(II) in the nanoparticle.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Mn</th>
<th>$X_1$</th>
<th>$\sigma$</th>
<th>$\tau_1$</th>
<th>Regression($r^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIa</td>
<td>0.022</td>
<td>0.450</td>
<td>0.156</td>
<td>4.10</td>
<td>0.9987</td>
</tr>
<tr>
<td>IIb</td>
<td>0.038</td>
<td>0.347</td>
<td>0.174</td>
<td>4.05</td>
<td>0.9995</td>
</tr>
<tr>
<td>IIc</td>
<td>0.057</td>
<td>0.285</td>
<td>0.190</td>
<td>4.09</td>
<td>0.9999</td>
</tr>
<tr>
<td>IId</td>
<td>0.065</td>
<td>0.322</td>
<td>0.193</td>
<td>4.34</td>
<td>0.9999</td>
</tr>
<tr>
<td>IIe</td>
<td>0.072</td>
<td>0.259</td>
<td>0.200</td>
<td>4.28</td>
<td>0.9999</td>
</tr>
<tr>
<td>IIf</td>
<td>0.090</td>
<td>0.256</td>
<td>0.196</td>
<td>4.14</td>
<td>0.9999</td>
</tr>
<tr>
<td>IIg</td>
<td>0.159</td>
<td>0.189</td>
<td>0.200</td>
<td>4.66</td>
<td>0.9999</td>
</tr>
<tr>
<td>IIh</td>
<td>0.173</td>
<td>0.189</td>
<td>0.192</td>
<td>4.22</td>
<td>0.9999</td>
</tr>
<tr>
<td>IIi</td>
<td>0.316</td>
<td>0.167</td>
<td>0.179</td>
<td>3.93</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

Table 7.2 Results from the application of equation 7.1 to the samples of Batch II.

As shown in Table 7.2, the fraction $X_1$ of Mn$^{2+}$ ions with long luminescence lifetime, $\tau_1$, decreases when the manganese concentration is increased. This can be explained based on the increased amount of interaction between Mn$^{2+}$ centers. If we assume a random distribution of Mn$^{2+}$ ions inside the nanoparticle, we can expect the fraction of isolated Mn$^{2+}$ to decrease exponentially when the Mn$^{2+}$ concentration is increased. While the fraction of isolated Mn$^{2+}$ ions could be expected to be high at low Mn$^{2+}$ concentrations. The $X_1$ values in Table 7.2 indicate that substantial interactions between Mn$^{2+}$ ions occur even at low concentrations. Such an interaction may be due to luminescent Mn$^{2+}$ ions in the interior of the nanoparticle interacting with nonluminescent Mn$^{2+}$ ions adsorbed on the surface. It is reasonable to assume that the total luminescence signal is proportional to
the total amount of Mn\(^{2+}\) ions located in T\(_d\) sites in the interior of the nanoparticles [6], and \(X_1\) corresponds to the fraction of Mn\(^{2+}\) ions located in isolated T\(_d\) sites. Additionally, \(X_1\) does not include Mn\(^{2+}\) ions that are luminescence inactive that could interact with active Mn\(^{2+}\) ions. We can also observe in Figure 3.9 (Chapter III) that the amount of luminescence inactive Mn\(^{2+}\) ions increases with the total Mn\(^{2+}\) concentrations, which could indicate a concentration quenching [79] or in other words, quenching due to interaction with Mn\(^{2+}\) located in sites for which the energy transfer from the ZnS lattice is not favored. Figure 7.4 shows the fitting of equation 7.1 to the experimental data of three representative samples of Batch II. It is remarkable how well this model fits to the experimental points.

Even though the external Mn\(^{2+}\) sites do not contribute to the luminescence signal, they can interact with the internal sites through dipolar interactions affecting their lifetimes. These interactions are more pronounced for Mn\(^{2+}\) centers close to the surface and decreases radially. Figure 7.4 shows the effect of the 0.01 M Mn(II) addition to a suspension of sample 4 on the luminescence intensity decay and the \(f(\tau)\) distribution function respectively (see inset in Figure 7.4). In Figure 7.4, the squares and triangles represent the experimental data and the lines represent the fitting using our model. The concentration of Mn\(^{2+}\) ions on the surface in sample 4 should be very low and upon the addition of Mn\(^{2+}\) ions, the luminescence signal decreases and the lifetime becomes shorter. In the inset in Figure 7.3 we can observe the shift of the \(f(\tau)\) distribution to shorter time constants. These Mn\(^{2+}\) added will adsorb on the surface and interact with the internal Mn\(^{2+}\) ions with the subsequent shortening in lifetime.
The existence of other surface effects that could decrease or increase the lifetime of the luminescence signal of ZnS:Mn nanoparticles cannot be excluded, but our results indicate that the most dominant effect is the interaction of internal luminescent Mn(II) sites with external adsorbed Mn(II) sites.

It is likely that the shortening of lifetime in Mn\(^{2+}\) doped ZnS nanoparticles is mainly due to the adsorption of Mn\(^{2+}\) and not quantum confinement as has been claimed before [38]. This adsorption is facilitated by the presence of stabilizers like polyphosphate on the surface of the nanoparticles with a high surface/volume ratios compared to bulk materials.
8.1 Overview

Nanocrystal properties lie between those of molecules and bulk materials. As molecules, nanocrystals can interact with light via their electronic transition dipoles, but because of their solid state nature, they exhibit unusual photophysics relative to molecules[80]. It is generally accepted that the luminescence process in semiconductors starts with the initial excitation of an electron into the conduction band by UV radiation. Emission then occurs via a radiationless relaxation of the electron or hole to a recombination center followed by the radiative recombination[81]. Surface states or crystal defect can act as recombination centers in nanoparticles promoting energy loss through the creation of phonons in the crystal lattice and enabling the electron or hole to be localized on such recombination centers.

In small nanoparticles the wave functions of electron and holes are delocalized over approximately 100-200 unit cells with little probability density at the surface. Because of this property of the electron-hole wavefunctions, we can expect that in the absence of internal or surface defects the nanoparticles should exhibit unit quantum yield[80]. But,
in real nanomaterials, defects produce recombination centers and hole/electron traps which play a major role in the photophysical behavior of such system[82].

The effect of UV irradiation on the luminescence properties of ZnS:Mn nanoparticles has been the subject of several recent studies[17, 76, 81, 83]. It has been observed by different authors that upon UV irradiation, ZnS:Mn nanoparticles exhibit an increase in their quantum yield. Different explanations have been proposed to understand this effect. Gallagher, et al.[84] explained that the UV irradiation enhances luminescence intensity by the passivation of the surface states due to the polymerization of the capping materials used to stabilize the nanoparticles. Furthermore, Dunstan, et al.[81] suggest that the photocorrosion of the nanoparticle surface could produce Zn, SO$_4^{2-}$ and S which will act as recombination centers, but also they may reduce the rate of nonradiative decay and quenching of the emission. Bol and Meijerink[76] proposed that the UV enhancement in ZnS:Mn can be explained by two mechanisms: UV passivation as result of the polymerization of the capping molecules and passivation by the photooxidation of the surface of the nanoparticles. The passivation of the surface states can enhance the contribution of the radiative recombination in nanomaterials. In the case of ZnS:Mn, trapping of the charge carriers by Mn$^{2+}$, which is a very fast process, competes with trapping of carriers in surface states[76]. The efficiency of the first process over the second one is reflected in the ratio of the peak intensity in the luminescence spectra of ZnS:Mn nanoparticles. Passivation of surface states will reduce the nonradiative recombination rate with the subsequent enhancement in the quantum yield of the nanoparticles.
In this chapter, experimental results on the effect of the UV irradiation on the luminescence of ZnS:Mn nanoparticles and their reaction with the aminoacid cysteine are presented.

8.2 Kinetic Study of the Effect of UV Irradiation on the Luminescence Intensity of ZnS:Mn Nanoparticle Colloidal Solution

The effect of the UV irradiation on the photoluminescence of ZnS:Mn colloidal solution have been established. For this purpose, the experimental setup indicated in Figure 8.1 was designed. For all these experiments, a total volume of 20 mL of colloidal solution of $2 \times 10^{-4}$ M ZnS:Mn (0.057% Mn w/w) nanoparticles was used. The peristaltic pump recycled the colloidal solution at a rate of 10 mL/min. The time the solution spends between the external vial and the flow cell inside the instrument is about 10 s.

In order to exclusively study the effect of the external irradiation, the measurements were taken every 1 s with integration time of 0.1 s. During the time between each measurement...
the instrument lamp was turned off. Using this setup, the instrument lamp only excited a small volume of sample in a short period of time. The external UV-lamp can be turned on and off as required by the experimental design.

Figure 8.2 shows the results of kinetic experiments in which a colloidal solution of ZnS:Mn nanoparticles \((2.0 \times 10^{-4} \text{ M})\) was irradiated with UV light at 365 nm with periods of irradiation and darkness. While the colloidal solution was being recycled in the system by the peristaltic pump, the external irradiation was turned on/off at the times indicated in the figure. The luminescence intensity increased rapidly upon the irradiation by UV light and reaches a steady state in about 250 seconds. When the external UV irradiation was turned off, the luminescence intensity decreased to almost the same intensity it had before the irradiation in about 1750 seconds. The signal enhancement was about four times between periods of darkness and irradiation.

![Figure 8.2. Effect of UV irradiation on the luminescence intensity of ZnS:Mn colloidal solution. The external UV irradiation was turned on and off at the points indicated in the plot.](image-url)
This sequence of irradiation and darkness can be repeated many times, but a gradual drift in the maximum signal was observed. These results contradict the explanations proposed by other authors in which they claim that polymerization of the stabilizing agent is responsible for the increase on the intensity. If any polymerization of polyphosphate occurs in these samples, one may expect that after UV irradiation the luminescence intensity will remain high after irradiation is stopped, but this is not the case.

In Figure 8.3 is shown a plot of the luminescence signal vs time during a period of irradiation followed by a period of darkness.

![Figure 8.3 Curve fitting of the growth and decay of the luminescence signal during periods of irradiation and darkness respectively.](image)

The luminescence intensity follows a first order growth during the period of external UV irradiation with a time constant $\tau = 44.767$ s, ($\tau_{1/2}=0.693\tau$). During the period of darkness (no external irradiation), the decay is biexponential with time constants of 125.64 s and
499.74 s and coefficients 72.47 and 77.95 respectively. The experimental results indicate that during the UV irradiation surfaces states[85] type “A” are transformed into two different states “B” and “C” (equation 8.1) and that this transformation followed a first order kinetics. The subsequent relaxation of states “B” and “C” (equation 8.2 and 8.3) during the period of darkness produces again “A”. States “B” and “C” are independently transformed to “A” via separate first order decays. According to the values of the coefficients obtained in the biexponential decay fitting, states “A” and “B” are formed almost in equal proportions during the irradiation process.

This process is illustrated in the following set of reactions

\[
\begin{align*}
A & \rightarrow B + C \quad \text{(irradiation)} \quad 8.1 \\
B & \rightarrow A \quad \text{(dark)} \quad 8.2 \\
C & \rightarrow A \quad \text{(dark)} \quad 8.3
\end{align*}
\]

The drift observed in the maximum intensity reached during the UV irradiation could be attributed to the formation of some chemical species or defects on the surface of the nanoparticles that can contribute to the quenching of the luminescence signal. A possible source of such changes is the formation of Mn-O bonds on the surfaces upon the UV irradiation.
8.3 Reaction of Cysteine with ZnS:Mn Nanoparticles

In order to study the reaction between cysteine and ZnS:Mn nanoparticles it was necessary to determine the optimum experimental conditions of this system. An important parameter to be accounted for is the pH of the cysteine solution. The pH levels of 0.1 M cysteine solutions were adjusted with NaOH. The starting pH of the 0.1 M hydrochloride salt of cysteine was 2.5 and the pH of the colloidal solution of ZnS:Mn was 7.0. A 3 mL volume of colloidal solution $2 \times 10^{-4}$ M was mixed with 100 µL of 0.1 M cysteine solution in a fluorimeter cell. Emission spectra, with excitation at 300 nm, were taken at different pH values. In Figure 8.4 is shown the plots of the intensities measured at 430 nm and 580 nm at different pH values. The optimum value of pH for such measurements was around 7.0. At low pH the acidity of the medium tends to dissolve the nanoparticles decreasing the luminescence signal.

At higher pH the form of cysteine with deprotonated carboxilic group absorbs light. This absorption affects the intensity, reducing the amount of light for the excitation of the nanoparticles with a subsequent decrease in the signal intensity. The absorption spectra of cysteine solutions at different pH are shown in Figure 8.5.
Figure 8.4 pH dependence of the luminescence intensity of ZnS:Mn colloidal solution (2x10^{-4} M) upon the addition of 100 µL 0.1 M cysteine.

Figure 8.5 Absorption spectra of Cysteine at different pH.
A working pH of 7.0 was chosen in order to maximize the luminescence intensity. Figure 8.6 shows the change in the luminescence spectra upon cysteine addition to colloidal solutions of ZnS and ZnS:Mn nanoparticles.

![Luminescence spectra](image)

Figure 8.6 Effect of cysteine addition to ZnS $2 \times 10^{-4}$ M and ZnS:Mn $2 \times 10^{-3}$ M colloidal suspensions at pH 7.0.

As is illustrated in Figure 8.6, upon cysteine addition the change in intensity was more pronounced in the ZnS:Mn for both the 430 nm and 590 nm peaks. Unlike the Mn doped nanoparticles, the ZnS nanoparticle solution did not show any substantial change in the luminescence intensity upon the addition of cysteine.
Using the same setup illustrated in Figure 8.1, we carried out different experiments to study the effect of the addition of cysteine at pH 7.0 on the luminescence of colloidal solutions of ZnS:Mn nanoparticles. Figures 8.7 displays the behavior of the luminescence intensity when cysteine at pH 7.0 was added to colloidal solutions of ZnS:Mn. No external UV irradiation was used in this case. The luminescence intensity was followed at 430 nm and 580 nm as indicated in Figure 8.7. The luminescence intensity grew very rapidly upon the addition of cysteine. It is also important to note the proportional growth of both peaks which suggest a dependency between the photophysical processes which are responsible for these transitions.

Electron and holes can become trapped at the surface states to create a localized charge layer at the surface, giving rise to an electrostatic field in the near surface region. If a
donor molecule satisfies the energy and symmetry requirements for combining with the surface states, such interaction enables donation of electron density to the semiconductor[10] These interactions of adsorbate with surface states can affect the rate of the recombination processes and eventually produce an increase in the photoluminescence intensity of the semiconductor. This could explain the effect of cysteine on the luminescence intensity of ZnS:Mn nanoparticles in which the intensities of both peak, at 430 nm and 580 nm, are functions of the rate of formation of recombination centers.

The effect of the addition of cysteine at pH 7.0 was also studied on samples under irradiation. Figure 8.8 shows the enhancement of the luminescence signal at both 430 nm and 590 nm upon the cysteine addition while the solution was irradiated by UV light of 365 nm. In these experiments, the intensity of the luminescence signal did not decrease after the UV irradiation was turned off. The reaction of cysteine seems to inhibit the system to return to its initial state as was observed for samples without cysteine (see Figure 8.2). Reactions in equations 8.2 and 8.3 do not occur in presence of cysteine. This suggests the presence of surface states involved in the luminescence process of Mn$^{2+}$ ions. The photoreaction with cysteine stabilizes those nanoparticle surface states with the subsequent enhancement of the luminescence signal, which in this case is irreversible after the UV irradiation.
Figure 8.8 Effect of cysteine addition on the luminescence intensity of ZnS:Mn colloidal solution under UV irradiation. The signal was simultaneously followed at 430 nm and 590 nm.

In a similar experiment, cysteine was allowed to react with a colloidal solution of ZnS:Mn nanoparticles. In this case the sample was not irradiated while cysteine was added. We observed a small increase of the signal intensity upon the addition of cysteine. Once the sample was irradiated by UV light of 365 nm, a large increment in the luminescence intensity was noticeable. The luminescence intensity did not decrease after the UV irradiation was turned off. This experiment supports the idea that UV irradiation favored the reaction between cysteine and the surfaces states involved in the luminescence of Mn$^{2+}$ ions.
Figure 8.9 Effect of cysteine addition on the luminescence intensity of ZnS:Mn colloidal solution under UV irradiation. The UV irradiation was turned on 300 s after the injection of cysteine at pH 7.0.

Theses results also suggest that UV irradiation promotes the formation of surface states and that the efficiency of the radiative transition of Mn\(^{2+}\) in ZnS:Mn nanoparticles depends on the formation of these states. Further studies are needed to discern the nature of such states and how can they be controlled in order to exploit these properties for future applications.

The changes in luminescence intensity vs the concentrations of cysteine added are shown in Figure 8.10. In Figure 8.10, the difference in intensity between the final steady state intensity and the intensity before the addition of cysteine are plotted. At high cysteine concentrations, the surface of the nanoparticles becomes saturated by the adsorption of
cysteine molecules and further addition does not affect substantially the luminescence intensity.

![Graph showing adsorption curve of cysteine on the surface of ZnS:Mn nanoparticles](image)

Figure 8.10 Adsorption curve of cysteine on the surface of ZnS:Mn nanoparticles

Figure 8.11 shows the fitting of this experimental data to the Langmuir adsorption isotherm function. The curve was obtained plotting $1/\theta$ vs $1/[\text{Cys}]$, where $\theta$ is the change in the luminescence signal upon the addition of cysteine, and $[\text{Cys}]$ is the molar concentration of cysteine.
Figure 8.11 Langmuir Isotherm curve fitting of the experimental data plotted in Figure 8.10.

A value of $k = 1.20 \times 10^{-7}$ M was obtained from this calculation. From the adsorption constant, $k$, we can estimate that about 90% of the adsorption sites on the surface will be covered by cysteine when its concentration in solution is about $3.1 \times 10^{-4}$ M.
The central hypothesis of this research that high quality ZnS nanoparticles doped with varying concentrations of manganese can be synthesized under mild conditions in the aqueous phase has been substantiated. The synthetic approach allows the systematic doping of ZnS lattice sites with varying concentrations of Mn$^{2+}$. The EPR and luminescence studies indicated that three types of Mn sites have been established in this work: 1) a slightly distorted T$_d$ site inside the nanoparticle, 2) sites with a high distorted tetrahedral symmetry, which have been attributed to Mn$^{2+}$ ions near the surface, and 3) sites corresponding to Mn$^{2+}$ ions adsorbed on the surface of the nanoparticle with orthorhombic symmetry which are the main component in spectra of ZnS:Mn nanoparticles with high Mn concentration. Other significant conclusions are:

1. Manganese doped zinc sulfide of high optical and chemical characteristics can be obtained by a strict control of the experimental conditions. Using the procedures described in this work ZnS:Mn nanoparticles with different spatial manganese distributions can be readily obtained.

2. The synthesis of different combinations of core/shell ZnS/ZnS:Mn nanoparticles was achieved by maintaining the same experimental conditions and manipulating the addition sequence of Zn$^{2+}$, Mn$^{2+}$ and S$^{2-}$. Particles with different core/shell structures exhibit very different luminescence properties and electron paramagnetic resonance spectra.
3. Two main synthetic routes were developed for the preparation of ZnS:Mn nanoparticles, using acetate and sulfate salts. The morphology of the particles obtained using both routes was similar, but the acetate route produce nanoparticles with higher percentages of amorphous material due to the co-precipitation of Zn by the polymerization of polyphosphate.

4. The maximum doped manganese concentration achieved using mild synthetic conditions was 0.3 %Mn (w/w). At higher temperatures (80 °C) we were able to produce particles with Mn concentrations up to 15.9 %, but of low crystalline quality.

5. The absorption spectra of all samples under study showed a band gap shift of about 0.4 eV to higher energy values in comparison with the bulk ZnS band gap. This shift in the band gap can be attributed to a quantum confinement effect. No noticeable change in the band gap was observed when the Mn concentration was varied by using different synthetic procedures.

6. The emission spectra of ZnS:Mn nanoparticles exhibited two main features: a short lifetime (3 ns) peak at 430 nm associated with surface defects in ZnS and a long lifetime (∼ ms) peak at 590 nm which has been attributed to the spin forbidden transition $^{4}T_1 \rightarrow ^{6}A_1$. The relative intensity of these two peaks strongly depended on the Mn content in the nanoparticle, the synthetic procedure and the distribution of Mn$^{2+}$ ions in the nanoparticle.

7. The excitation spectra of the ZnS:Mn nanoparticles resembles their absorption spectra with a shoulder at about 300 nm. The features below 240 nm are not very dependable due to other absorbing species in solution or species adsorbed on the nanoparticle.
8. The intensity of the emission peak at 590 nm increases as the Mn concentration increases. The initial slope of the curve is mainly linear, but at high concentration it decreased and the intensity tended towards a constant value. This behavior has been attributed to increased in the interactions between manganese centers.

9. According to the XRD analysis, the average particle size for samples synthesized via the acetate and sulfate routes was 2.5 nm. The XRD spectra showed three main peaks corresponding to the reflection planes of the cubic ZnS structure (zinc blende).

10. The XPS spectra indicated the possibility of Mn being associated with oxygen which is reasonable because of the large number of phosphate groups on the surface of the nanoparticle (about 8%(w/w) as P) and the high affinity of Mn for oxygen.

11. Near edge x-ray absorption fine structure spectroscopy (NEXAFS) indicated that Mn$^{2+}$ ions are located in a low crystal field environment with $10D_q \leq 0.5$ eV. At this low crystal field, the features of the NEXAFS spectrum for Mn in a tetrahedral and octahedral crystal field are very similar. Using this technique it was possible to resolve the structure of the spectra in the Mn L-edge, but not to discern the type of local environment around Mn$^{2+}$ ions.

12. No indication of the existence of higher oxidation states for Mn was observed in the NEXAFS spectra of ZnS:Mn samples.

13. Secondary Ion Mass Spectrometry (SIMS) was able to detect some association between Mn and oxygen in the samples studied which agreed with the result obtained in the XPS spectra.

14. The transmission electron microscope (TEM) was able to determine the particle size of the nanoparticles, but because of problems of formation of aggregates and melting
inherent to this type of material under the microscope x-ray beam, the quality of most images was low.

15. Computer simulation of the full spin Hamiltonian implemented using the Mathematica and Visual Basic software, was able to reproduce all the features of the EPR spectra of Mn in ZnS:Mn nanoparticles, including the six hyperfine lines for the allowed spin transitions and the five pairs of forbidden transitions. The results obtained agree with those found in the literature for similar systems.

16. According to the results obtained from the simulation of the EPR spectra, Mn$^{2+}$ ions are located in slightly distorted tetrahedral sites replacing Zn$^{2+}$ ions in the lattice. An axial symmetry was adopted for these calculations which resulted in the following Hamiltonian parameters: $g_{xx}=g_{yy}=2.0063$, $g_{zz}=2.0066$, $A_{xx}=63.9 \times 10^{-4}$ cm$^{-1}$, $A_{yy}=64.0 \times 10^{-4}$ cm$^{-1}$, $A_{zz}=64.4 \times 10^{-4}$ cm$^{-1}$ and the values of $D=37.4 \times 10^{-4}$ cm$^{-1}$ and $E=12.5 \times 10^{-4}$ cm$^{-1}$.

17. An anisotropic nuclear-Zeeman interaction was assumed in order to achieve the simulation of the five pairs of forbidden transitions. The principal values of the $\mu_N$ tensor were set to $\mu_x = \mu_y = 2.0$ and $\mu_z = 6.0$.

18. The quadrupolar term interaction was neglected in the calculations of spectra of ZnS:Mn nanoparticles with low Mn content. This term is important when the Mn sites were highly distorted, as is the case at high levels of Mn doping.

19. The Mn EPR spectrum gradually changed when the Mn concentration is increased. At low concentrations the Mn EPR spectra exhibited the features corresponding to Mn in $T_d$ sites, but as the Mn concentration is increased, new features appeared. The EPR spectra became a mixture of different components and the EPR signals became
broader. When the Mn concentration reached high values (Eg. 15.9 %Mn), only a very broad peak was observed without any hyperfine feature.

20. The exact simulation of those mixed spectra was very difficult as a consequence of the numerous components with different degrees of distortion which contribute to the EPR signal.

21. The luminescence intensity of the peak at 590 nm was directly correlated with the EPR signal from internal sites. This strongly supports the hypothesis that Mn$^{2+}$ ions located in T$_d$ sites are the only centers responsible for the luminescence in ZnS:Mn nanoparticles. Mn$^{2+}$ ions adsorbed on the surface or near the surface do not contribute significantly to the luminescence signal. Instead, they can interact with luminescent Mn$^{2+}$ ions quenching the signal or reducing the lifetime of the radiative relaxation of the spin forbidden transition $^4T_1 \rightarrow ^6A_1$.

22. The interactions between luminescent Mn$^{2+}$ ions and their neighbors depend on the distance between the interacting centers. Due to the high number of possible conformations between the Mn$^{2+}$ ions in the nanoparticle, the result of such interactions is that the lifetimes exhibit a distribution of values. Other factor that can affect relaxation times for a given Mn in the nanoparticles is the distortion of the site where it is located, higher distortion shorter lifetimes.

23. A multiexponential model for the luminescence intensity decay was proposed in this work. This model not only reproduced the decay curves for all ZnS:Mn samples under study, but also allowed inferences to be drawn about the effect of the distribution of manganese in the nanoparticles and rationalize how this distribution can affect the luminescence of the nanoparticles.
24. Manganese doped zinc sulfide nanoparticles exhibited an enhancement in the luminescence intensity upon irradiation of UV light. UV irradiation induced the formation of active surface states that create new pathways for the relaxation of the spin forbidden transition $^{4}T_{1} \rightarrow ^{6}A_{1}$ in Mn$^{2+}$ ions. This process was reversible and after the UV irradiation was stopped, the system returned to its initial less active states with the subsequent decrease of the signal.

25. The reaction of cysteine with ZnS:Mn enhances the luminescence intensity of the nanoparticles. This reaction is more rapid under UV irradiation and made the enhancement of the luminescence intensity permanent. This could be due to the stabilization of the surfaces states involved in the luminescence process of ZnS:Mn nanoparticles.

Future Directions:

This research while addressing the fundamental structure of Mn$^{2+}$ doped ZnS nanoparticles has also provided new directions to explore the structure of nanoparticles and their applications. Some of these are:

1. Synthesis of doped and undoped nanoparticles in the absence of stabilizers like polyphosphate. It may be possible to accomplish this in nonaqueous media, reverse miscelles, microemulsions, etc.

2. Characterize the luminescence and EPR spectroscopic properties of these nanoparticles without stabilizer and compare to those reported in this work.
3. Introduce a codopant such as Eu$^{3+}$ with a primary dopant such as Mn$^{2+}$ and determine the perturbation on the electronic structure manifested in luminescence and EPR spectra.

4. Examine the EPR spectra of the quantum dots in aqueous solution and compare them to solid spectra reported in this work. Solution EPR could be useful to discern the interactions of quantum dots with ligands such as cysteine.

5. Create techniques for the self assembly of quantum dots on substrates such as quartz, silicon, Au with monolayers of ligands that can bind the nanoparticles. Examine the UV-visible absorption and luminescence spectra of these self assembled quantum dots.

6. Investigate the efficacies of self assembled nanoparticles for sensing target molecules such as cysteine exploit them for the design of sensors.
APPENDIX A

PROGRAM FOR SIMULATION OF AXIAL EPR SPECTRA

MATHEMATICA VERSION
Parameter Initialization;

\[ S = \frac{1}{2}; \]
\[ N = \frac{5}{2}; \]

\[ NTOT = (2 + S + 1) \times (2 + N + 1); \]

Hyperfine Interaction;

\[ A_{xx} = 68.0; \]
\[ A_{yy} = 68.0; \]
\[ A_{zz} = 70.0; \]

\textit{g} TENSOR – Electron Zeeman Interaction;

\[ g_{xx} = 2.0062; \]
\[ g_{yy} = 2.0064; \]
\[ g_{zz} = 2.0070; \]

\[ u_{Nx} = 2; \]
\[ u_{Ny} = 2; \]
\[ u_{Nz} = 6; \]

Zero – Field Interaction;

\[ D_z = 40.0; \]
\[ E_z = 13.33; \]

\[ QP = 0; \]
\[ QQ = 0; \]

Zeeman Field Orientation;

\[ \theta = 45 \times \pi / 180.0; \]
\[ \phi = 0 \times \pi / 180.0; \]

\[ B = 3500; \]
\[ Freq = 9.786 \times 10^9; \]

\[ \beta = 9.27314 \times 10^{-21}; \]
\[ BN = 5.05048 \times 10^{-24}; \]
\[ h\text{Plank} = 6.62554 \times 10^{-27}; \]

\[ hv = Freq \times h\text{Plank} / (2.00232 \times \beta); \]
\[ hv \]
\[ Null \]
ElectronicSpinMatrix = Function[(X),
  Clear[DP];
  Clear[Sx, Sy, Splus, Sminus];
  Sx = Table[(DM[i, j] + DM[i + 1, j]) * 1/2 * √X*(X+1) - (i - X - 1) * (j - X - 1), (i, 1, X + 2), (j, 1, X + 2)];
  Sy = Table[(DM[i, j] - DM[i + 1, j]) * i / 2 * √X*(X+1) - (i - X - 1) * (j - X - 1), (i, 1, X + 2), (j, 1, X + 2)];
  Sz = Table[-DM[i, j] * (i - X - 1), (i, 1, X + 2), (j, 1, X + 2)];
  Splus = Sx + 1*Sy;
  Sminus = Sx - 1*Sy;
]

NuclearSpinMatrix = Function[(X),
  Clear[DP];
  Clear[Ix, Iy, Iplus, Iminus];
  Ix = Table[(DM[i, j] + DM[i + 1, j]) * 1/2 * √X*(X+1) - (i - X - 1) * (j - X - 1), (i, 1, X + 2), (j, 1, X + 2)];
  Iy = Table[(DM[i, j] - DM[i + 1, j]) * i / 2 * √X*(X+1) - (i - X - 1) * (j - X - 1), (i, 1, X + 2), (j, 1, X + 2)];
  Iz = Table[-DM[i, j] * (i - X - 1), (i, 1, X + 2), (j, 1, X + 2)];
  Iplus = Ix + 1*Iy;
  Iminus = Ix - 1*Iy;
]

Null

DM = Function[[i, j],
  If[i, j, 1, 0]];

KProd = Function[{N1, M1},
  Clear[DP];
  m1 = Dimensions[M1];
  n1 = Dimensions[N1];
  r = m1[[1]]; t = n1[[1]]; 
  DP = Array[dp, {r*t, r*t}];
  For[p = 1, p <= r,
    For[q = 1, q <= r,
      m = Range[(p - 1)*t + 1, (p - 1)*t + t];
      n = Range[(q - 1)*t + 1, (q - 1)*t + t];
      DP[[m, n]] = M1[[p, q]]*N1;
      q++;
    ];
  ];

UnitS = IdentityMatrix[2*S + 1];
UnitI = IdentityMatrix[2*N1 + 1];
UnitSI = IdentityMatrix[(2*S + 1)*(2*N1 + 1)];

NuclearSpinMatrix[N1];
ElectronicSpinMatrix[S];
KProd[Sx, lx]; Sxlx = DP;
KProd[Sy, ly]; Syly = DP;
KProd[Sz, lz]; Szlz = DP;
KProd[Sx, UnitI]; SxId = DP;
KProd[Sy, UnitI]; SyId = DP;
KProd[Sz, UnitI]; SzId = DP;
KProd[UnitS, lx]; lxId = DP;
KProd[UnitS, ly]; lyId = DP;
KProd[UnitS, lz]; lzId = DP;
KProd[UnitS, Iplus]; lpId = DP;
KProd[UnitS, Iminus]; lmId = DP;
KProd[Splus, UnitI]; SpId = DP;
KProd[Sminus, UnitI]; SmId = DP;

Sx2 = Sx * Sx;
Sy2 = Sy * Sy;
Sz2 = Sz * Sz;

KProd[Sx2, UnitI]; Sx2Id = DP;
KProd[Sy2, UnitI]; Sy2Id = DP;
KProd[Sz2, UnitI]; Sz2Id = DP;

lx2 = lx * lx;
ly2 = ly * ly;
lz2 = lz * lz;

KProd[lx2, UnitS]; lx2Id = DP;
KProd[ly2, UnitS]; ly2Id = DP;
KProd[lz2, UnitS]; lz2Id = DP;

Bx = B * Sin[ ];
By = B * Sin[ ];
Bz = B * Cos[ ];

Ham1 = (gxx * Bx * SxId + gyy * By * SyId + gzz * Bz * SzId) / (2.00232*) - 2.00 * BN * lxId * Bx - 2.00 * BN * lyId * By - 2.00 * BN * lzId * Bz;

Ham2 = Axx * Sxx + Ayy * Syly + Azz * Szlz + Dz * (Sz2Id - 1/3 * S(S+1) * UnitSI) + Ez * (SxId - Sy2Id);

Ham5 = QP * (lz2Id - 1/3 * NI * (NI+1) * UnitSI) + QQ * (lx2Id - ly2Id);
Func2 = Function[{B, n},
    Bx = B*Sin[ ]*Cos[ ];
    By = B*Sin[ ]*Sin[ ];
    Bz = B*Cos[ ];

    Ham1 = (gxx* Bx*SxId + gyy* By*SyId + gzz* Bz*SzId)/(2.00232*) -
            (uNx*BN*Ixl*Bx + uNy*BN*IyId*By + uNz*BN*Izld*Bz)/(2.00232*);

    Ham = Ham1 + Ham2 + Ham5;

    R = Re[Eigenvalues[Ham]];  
    K = Sort[R];  
    y = (K[[n]]/Dz)
    ];

    HRF = SxId*Cos[ ]*SzId*Sin[ ]*Ixl*Cos[ ] + Izld*Sin[ ];

    Func3 = Function[{B},
    Bx = B*Sin[ ]*Cos[ ];
    By = B*Sin[ ]*Sin[ ];
    Bz = B*Cos[ ];

    Ham1 = (gxx* Bx*SxId + gyy* By*SyId + gzz* Bz*SzId)/(2.00232*) -
            (uNx*BN*Ixl*Bx + uNy*BN*IyId*By + uNz*BN*Izld*Bz)/(2.00232*);

    Ham = Ham1 + Ham2 + Ham5;

    R = Eigenvalues[Ham];  
    V = Eigenvectors[Ham];

    Intensity = Table[Re[(V[[i]]*HRF*V[[j]])]^2 -
                        Im[(V[[i]]*HRF*V[[j]])]^2, {i, NTOT}, {j, NTOT}];
    Signal = 0;
    For[i = 1, i < NTOT - 1, i++,
        For[j = i + 1, j < NTOT, j++,
            Tg = Abs[R[[i]] - R[[j]]];
            dS = N[1.0/(1.0 + 0.2*(hv - Tg)*(hv - Tg))*Intensity[[i, j]]];
            Signal = Signal + dS;
        ]];
i++; y=Signal
];

Func4=Function[{B},
  SumT=0;
  For[ =0, 90, = */180.0;
    SumT=SumT+Func3[B];
    = +5];
  y=SumT*Sin[ ]
];

Plot[(Func3[B+0.5]-Func3[B-0.5])/1.0,{B,3200,3800},PlotRange {-0.1,0.1},Frame True,FrameLabel {Magnetic Field (Gauss),"","",""},RotateLabel False]

-Graphics-
-Graphics-

Plot[Func3[B],{B,3200,3800},PlotRange→{0,0.30},Frame→True,FrameLabel→{"Magnetic Field (Gauss)","Absorbance","",""},RotateLabel→True]
-Graphics-

Plot[Func4[B],{B,3200,3800},PlotRange→{0,5},Frame→True,FrameLabel→{Magnetic Field (Gauss),Absorbance,",",""},RotateLabel→False]
APPENDIX B

PROGRAM FOR SIMULATION OF AXIAL EPR SPECTRA

VISUAL BASIC VERSION
Option Explicit

Dim NTOTAL As Integer
Dim MS, MI As Single
Dim Sx() As Single
Dim Sy() As Single
Dim Sz() As Single
Dim Sp() As Single
Dim Sm() As Single
Dim Ix() As Single
Dim Iy() As Single
Dim Iz() As Single
Dim Ip() As Single
Dim Im() As Single
Dim SxId() As Single
Dim SyId() As Single
Dim SzId() As Single
Dim SpId() As Single
Dim SmId() As Single
Dim IxId() As Single
Dim IyId() As Single
Dim IzId() As Single
Dim IpId() As Single
Dim ImId() As Single
Dim SxIx() As Single
Dim SyIy() As Single
Dim SzIz() As Single
Dim Sx2() As Single
Dim Sy2() As Single
Dim Sz2() As Single
Dim Ix2() As Single
Dim Iy2() As Single
Dim Iz2() As Single

Dim Sx2Id() As Single
Dim Sy2Id() As Single
Dim Sz2Id() As Single
Dim Ix2Id() As Single
Dim Iy2Id() As Single
Dim Iz2Id() As Single

Dim MATTR() As Single
Dim MATTR2() As Single
Dim g As Single
Dim gxx As Single
Dim ID As Integer
Dim PowderX As Integer
Dim gyy, gzz, Axx, Azz, Ayy, gNx, gNy, gNz, Be, BN, hPLank, hv As Single

Dim UnitS(), UnitI(), UnitSI() As Single
Dim Dz, Ez As Single
Dim EValues() As Single
Dim SignalY() As Single
Dim SignalZ() As Single

Dim NITER As Integer
Dim sensitivity As Single
Dim Prob() As Single

Dim EndFlag As Single
Dim Hx, Hy, Hz As Single

Dim Hamx() As Single
Dim Hamx3() As Single

Dim Hamx1() As Single
Dim Hamx2() As Single

Dim fieldX As Single
Dim HamxY(99, 99) As Single

Dim Vectors() As Single
Dim RotU() As Single
Dim RotW() As Single
Dim Res1() As Single
Dim Res2() As Single
Dim V() As Single

Dim max(2000) As Single

Private Sub Command1_Click()
    EndFlag = 1
    QuitTotal = 1
End Sub

Sub display()
    Dim i, j As Integer
    Dim sum2 As Single
For i = 0 To NTOTAL - 1
For j = 0 To NTOTAL - 1
If i = j Then
    ShowVectors.ForeColor = RGB(0, 0, 200)
Else
    ShowVectors.ForeColor = RGB(0, 0, 0)
End If
    ShowVectors.CurrentX = j * 1700 + 500
    ShowVectors.CurrentY = i * 200
    ShowVectors.Print Hamx(i, j)
Next j
Next i

For i = 0 To NTOTAL - 1
    sum2 = 0
For j = 0 To NTOTAL - 1
    If i = j Then
        ShowVectors.ForeColor = RGB(0, 0, 200)
    Else
        ShowVectors.ForeColor = RGB(0, 0, 0)
    End If
            ShowVectors.CurrentX = j * 1700 + 500
            ShowVectors.CurrentY = i * 200 + 5000
            ShowVectors.Print Hamx2(i, j)
    sum2 = sum2 + V(i, j) * V(i, j)
Next j
Next i

End Sub

Private Function dm(ByVal i As Single, ByVal j As Single) As Integer
    If i = j Then
        dm = 1
    Else
        dm = 0
    End If
End Function
Private Sub Identity(ByVal My, ByVal Mx, Matrix)
Dim ns As Single
Dim i, j As Integer

If Mx > 0 And My = 0 Then
    ns = (2 * Mx)
End If

If My > 0 And Mx = 0 Then
    ns = 2 * My
End If

If Mx > 0 And My > 0 Then
    ns = (2 * My + 1) * (2 * Mx + 1) - 1
End If

ReDim Matrix(0 To ns, 0 To ns)

For i = 0 To ns
For j = 0 To ns
    If i = j Then
        Matrix(i, j) = 1
    Else
        Matrix(i, j) = 0
    End If
Next j
Next i

End Sub

Private Sub Kron(ByRef MATA, ByRef MATB, ByRef MATC)
Dim n As Integer
Dim W, M, i, j, col, row, k, U As Integer

n = UBound(MATA)
M = UBound(MATB)

W = (n + 1) * (M + 1) - 1

For i = 0 To M
For j = 0 To M
    col = j * (n + 1)
    row = i * (n + 1)
Next j
Next i
For k = 0 To n
For U = 0 To n
    MATC(row + k, col + U) = MATA(k, U) * MATB(i, j)
Next U
Next k
Next j
Next i

'Kron = MATC

End Sub

Private Sub Mat_Mult(MATA, MATB, Matrix)
Dim n As Integer
Dim i, j, k As Integer

n = UBound(MATA)

For i = 0 To n
For j = 0 To n
    Matrix(i, j) = 0
For k = 0 To n
    Matrix(i, j) = Matrix(i, j) + MATA(k, j) * MATB(i, k)
Next k
Next j
Next i

End Sub

Private Function Intensity(ByVal i As Integer, ByVal j As Integer) As Single
Dim n, P, k As Integer
Dim sum As Single
Dim V1() As Single
ReDim V1(0 To NTOTAL - 1)

For P = 0 To NTOTAL - 1
    V1(P) = 0
For k = 0 To NTOTAL - 1
    V1(P) = V1(P) + Vectors(j, k) * Prob(k, P)
Next k
Next P

sum = 0
For k = 0 To NTOTAL - 1
    sum = sum + V1(k) * Vectors(i, k)
Next k

Intensity = sum * sum

End Function

Private Sub Mat_Sum(MATA, MATB, ByVal c As Single, Matrix)
Dim n As Integer
Dim i, j, k As Integer

n = UBound(MATA)

For i = 0 To n
    For j = 0 To n
        Matrix(i, j) = MATA(i, j) + c * MATB(i, j)
    Next j
    Next i
End Sub

Private Sub Mat_Const(MATA, ByVal c As Single, Matrix)
Dim n As Integer
Dim i, j, k As Integer

n = UBound(MATA)

For i = 0 To n
    For j = 0 To n
        Matrix(i, j) = c * MATA(i, j)
    Next j
    Next i
End Sub

Function F1(MATA) As Single
    F1 = MATA
End Function

Private Sub Command10_Click()
Dim angle, maxv, dev, dev2 As Single
Dim PW, PH As Single
Dim npoints As Integer
Dim i, j, k As Integer
Dim Powder() As Single
Dim theta As Single
Dim S(1000, 20) As Single
Dim ang(20) As Single
Dim Y1, Y2, ang1, ang2, slope As Single
Dim sum, sum1, sum2 As Single
Dim ny, np As Integer
Dim M As Single
Dim dtheta As Single

PowderX = 1
QuitTotal = 0
PW = Picture1.Width
PH = Picture1.Height
npoints = Text16.Text

ReDim Powder(1000)
    np = Text56.Text
    ny = 1
dtheta = Text20.Text
For angle = 0 To 90 Step dtheta
    Text17.Text = angle
    theta = angle * 3.1416 / 180#

    Simulation

    For i = 1 To npoints
        Powder(i) = Powder(i) + SignalY(i) * Sin(theta)
    Next i

    maxv = 0
    For i = 1 To npoints
        dev = Powder(i) - Powder(i - 1)
        If Abs(dev) > maxv Then maxv = Abs(dev)
    Next i

    If maxv > 0 Then
        Picture1.Cls
        dev2 = 0
        For k = 1 To npoints
            dev = Powder(k) - Powder(k - 1)
            Picture1.Line ((k - 1) / npoints * PW, PH / 2 - dev2 / maxv * PH / 2) - (k / npoints * PW - PH / 2 - dev / maxv * PH / 2), RGB(0, 0, 50)
            dev2 = dev
        Next k
    End If
ny = ny + 1
If EndFlag = 1 Then Exit Sub

Next angle

End Sub

Private Sub Command1_Click()
  ID = 0
  Testing
  ID = 1
End Sub

Private Sub Command2_Click()
  If ProcessRunning = 1 Then
    Quit = 1
  Else
    End
  End If
End Sub

Function ElectronicMatrix(ByVal X As Single)
  Dim ns, i, j As Single
  Dim M1, M2 As Single

  ns = 2 * X
  ReDim Sx(0 To ns, 0 To ns), Sy(0 To ns, 0 To ns), Sz(0 To ns, 0 To ns), Sp(0 To ns, 0 To ns), Sm(0 To ns, 0 To ns)
  For i = 0 To ns
    For j = 0 To ns
      M1 = -i + X
      M2 = -j + X
      Sx(i, j) = 1 / 2 * (dm(M1, M2 + 1) + dm(M1 + 1, M2)) * Sqr(X * (X + 1) - M1 * M2)
      Sy(i, j) = 1 / 2 * (dm(M1 + 1, M2) - dm(M1, M2 + 1)) * Sqr(X * (X + 1) - M1 * M2)
      Sz(i, j) = dm(M1, M2) * M1
      Sp(i, j) = Sx(i, j) - Sy(i, j)
      Sm(i, j) = Sx(i, j) + Sy(i, j)
      Next j
    Next i
  End Function
Function NuclearMatrix(ByVal X As Single)
Dim ns, M1, M2 As Single
Dim i, j As Integer
ns = 2 * X
ReDim Ix(0 To ns, 0 To ns), Iy(0 To ns, 0 To ns), Iz(0 To ns, 0 To ns), Ip(0 To ns, 0 To ns), Im(0 To ns, 0 To ns)

For i = 0 To ns
For j = 0 To ns
    M1 = -i + X
    M2 = -j + X
    Ix(i, j) = 1 / 2 * (dm(M1, M2 + 1) + dm(M1 + 1, M2)) * Sqr(X * (X + 1) - M1 * M2)
    Iy(i, j) = 1 / 2 * (dm(M1 + 1, M2) - dm(M1, M2 + 1)) * Sqr(X * (X + 1) - M1 * M2)
    Iz(i, j) = dm(M1, M2) * M1
    Ip(i, j) = Ix(i, j) - Iy(i, j)
    Im(i, j) = Ix(i, j) + Iy(i, j)
Next j
Next i
End Function

Private Function Normalize() As Single
Dim maxw As Single
Dim i, j, k As Integer
maxw = 0
For i = 0 To NTOTAL - 1
For j = 0 To NTOTAL - 1
    Hamx(i, j) = Hamx(i, j)
    If Abs(Hamx(i, j)) > maxw Then maxw = Abs(Hamx(i, j))
Next j
Next i
Normalize = maxw
End Function
Private Sub Simulation()
    Dim PW, PH As Integer

    MS = Text1.Text
    MI = Text2.Text

    PW = Picture1.Width
    PH = Picture1.Height

    NTOTAL = (2 * MS + 1) * (2 * MI + 1)

    ReDim SxId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SyId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SzId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SpId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SmId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim IxId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim IyId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim IzId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim IpId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim ImId(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SxIx(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SxIx(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SyIy(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim SzIz(0 To NTOTAL - 1, 0 To NTOTAL - 1)

    ReDim UnitS(0 To 2 * MS, 0 To 2 * MS)
    ReDim UnitI(0 To 2 * MI, 0 To 2 * MI)
    ReDim UnitSI(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim MATTR(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim MATTR2(0 To NTOTAL - 1, 0 To NTOTAL - 1)

    ReDim Hamx(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim Hamx3(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim Hamx2(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim Hamx1(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim Vectors(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim V(0 To NTOTAL - 1, 0 To NTOTAL - 1)

    ReDim RotU(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim RotW(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim Res1(0 To NTOTAL - 1, 0 To NTOTAL - 1)
    ReDim Res2(0 To NTOTAL - 1, 0 To NTOTAL - 1)
ReDim Sx2(0 To 2 * MS, 0 To 2 * MS)
ReDim Sy2(0 To 2 * MS, 0 To 2 * MS)
ReDim Sz2(0 To 2 * MS, 0 To 2 * MS)

ReDim Ix2(0 To 2 * MI, 0 To 2 * MI)
ReDim Iy2(0 To 2 * MI, 0 To 2 * MI)
ReDim Iz2(0 To 2 * MI, 0 To 2 * MI)

ReDim Sx2Id(0 To NTOTAL - 1, 0 To NTOTAL - 1)
ReDim Sy2Id(0 To NTOTAL - 1, 0 To NTOTAL - 1)
ReDim Sz2Id(0 To NTOTAL - 1, 0 To NTOTAL - 1)

ReDim Ix2Id(0 To NTOTAL - 1, 0 To NTOTAL - 1)
ReDim Iy2Id(0 To NTOTAL - 1, 0 To NTOTAL - 1)
ReDim Iz2Id(0 To NTOTAL - 1, 0 To NTOTAL - 1)

Dim ndim As Integer

Dim valor(3) As Single

Dim tr As Single

Dim VXC As Single

Dim Ham2() As Single

Dim field0, field1, dfield, B, maxv As Single
Dim npoints, i, j, nx As Integer
Dim theta, phi As Single
Dim t1 As Single
Dim sensitivity As Single

Dim Param(20) As Single
Dim Konst(20) As Single
Dim Cond(20) As Single
Dim XX As Single

gxx = Text3.Text
gyy = Text4.Text
gzz = Text5.Text

gNx = Text6.Text
gNy = Text7.Text
gNz = Text8.Text
Axx = Text9.Text
Ayy = Text10.Text
Azz = Text11.Text

Dz = Text12.Text
Ez = Text13.Text

sensitivity = Text19.Text

Param(0) = gxx: Param(1) = gyy: Param(2) = gzz
Param(6) = gNx: Param(7) = gNy: Param(8) = gNz
Param(9) = Dz: Param(10) = Ez

Konst(0) = Be
Konst(1) = BN
Konst(2) = hPLank
Konst(3) = 2.00232

field0 = Val(Text14.Text)
field1 = Val(Text15.Text)
npoints = Val(Text16.Text)
theta = Val(Text17.Text)
phi = 0

hv = (Text21.Text * 1000000000# * hPLank) / (2.00232 * Be)

ElectronicMatrix (MS)
NuclearMatrix (MI)

Identity 0, MI, UnitI
Identity MS, 0, UnitS
Identity MS, MI, UnitSI

Kron Sx, UnitI, SxId
Kron Sy, UnitI, SyId
Kron Sz, UnitI, SzId  
Kron Sm, UnitI, SmlId  
Kron Sp, UnitI, SpId  

Mat_Mult Sx, Sx, Sx2  
Mat_Mult Sy, Sy, Sy2  
Mat_Mult Sz, Sz, Sz2  

Kron Sx2, UnitI, Sx2Id  
Kron Sy2, UnitI, Sy2Id  
Kron Sz2, UnitI, Sz2Id  

Mat_Mult Ix, Ix, Ix2  
Mat_Mult Iy, Iy, Iy2  
Mat_Mult Iz, Iz, Iz2  

Kron UnitS, Ix2, Ix2Id  
Kron UnitS, Iy2, Iy2Id  
Kron UnitS, Iz2, Iz2Id  

Kron UnitS, Ix, IxId  
Kron UnitS, Iy, IyId  
Kron UnitS, Iz, IzId  

'ImlId = Kron(UnitS, Im)  
'IpId = Kron(UnitS, Ip)  

Kron Sx, Ix, SxIx  
Kron Sy, Iy, SyIy  
Kron Sz, Iz, SzIz  

ReDim Prob(0 To NTOTAL - 1, 0 To NTOTAL - 1)  

Mat_Const UnitSI, 1 / 3 * MS * (MS + 1), MATTR  
Mat_Const UnitSI, 1 / 3 * MI * (MI + 1), MATTR2  

H2  

theta = theta * 3.1416 / 180#  
phi = phi * 3.1416 / 180#
dfield = (field1 - field0) / npoints

Cond(0) = theta
Cond(1) = phi
Cond(2) = field0
Cond(3) = field1
Cond(4) = dfield
Cond(5) = hv

ndim = UBound(SxId)

For i = 0 To NTOTAL - 1
    For j = 0 To NTOTAL - 1
        Prob(i, j) = SxId(i, j) * Cos(theta) - SzId(i, j) * Sin(theta)
        If MI > 0 Then
            Prob(i, j) = Prob(i, j) - IxId(i, j) * Cos(theta) + IzId(i, j) * Sin(theta)
        End If
    Next j
Next i

ReDim EValues(0 To npoints + 10, 0 To NTOTAL + 10)
ReDim SignalY(0 To npoints + 10)

Shape1.FillColor = RGB(200, 0, 0)
Command3.Enabled = False

SignalY(0) = 0
EndFlag = 0
H1 B, theta, 0

Open "DATA.txt" For Output As #1
Print #1, NTOTAL
Print #1, field0
Print #1, field1
Print #1, hv
Print #1, Text24.Text
Print #1, npoints
For i = 0 To NTOTAL - 1
    For j = 0 To NTOTAL - 1
        Print #1, Hamx(i, j)
        DoEvents
    Next j
Next i
For i = 0 To NTOTAL - 1
For j = 0 To NTOTAL - 1
    Print #1, Hamx2(i, j)
    DoEvents
Next j
Next i
For i = 0 To NTOTAL - 1
    For j = 0 To NTOTAL - 1
        Print #1, Prob(i, j)
        DoEvents
    Next j
Next i
Close #1

Testing

nx = npoints
Open "signal.txt" For Input As #1
nx = 0
While Not EOF(1)
    Input #1, XX, SignalY(nx)
    nx = nx + 1
Wend
Close #1
nx = npoints
If PowderX = 0 Then
    If Option2.Value = True Then
        Plot_Absortion
    End If
    If Option3.Value = True Then
        Plot_Spectra
    End If
End If
Shape1.FillColor = RGB(0, 200, 0)
Command3.Enabled = True

End Sub
Sub Plot_Eigenvalues(ByVal nx As Single, ByVal field0 As Single, ByVal field1 As Single, ByVal npoints As Single)
Dim k, i As Integer
Dim max2 As Single
Dim PW, PH As Single
Dim maxv As Single
```vbnet
Picture1.Cls
PW = Picture1.Width
PH = Picture1.Height

max2 = 0
For k = 1 To nx
    Picture1.Line ((k - 1) / npoints * PW, PH / 2 - max(k - 1) * 1)-(k / npoints * PW, PH / 2 - max(k) * 1), RGB(0, 200, 0)
    Picture1.Line ((k - 1) / npoints * PW, PH / 2)-(k / npoints * PW, PH / 2), RGB(200, 200, 0)
    DoEvents

    For i = 0 To NTOTAL - 1
        Picture1.PSet (k / npoints * PW, PH / 2 - (EValues(k, i) / maxv) * (PH / 2#)), RGB(0, 0, 50)
    Next i
Next k

End Sub

Sub Sort(ByRef A)
Dim k, i As Integer
Dim X As Integer

    For k = 0 To NTOTAL - 1
        For i = k To NTOTAL - 1
            If A(i) < A(k) Then
                X = A(i)
                A(i) = A(k)
                A(k) = X
            End If
        Next i
    Next k
End Sub

Sub Plot_Absortion()
Dim maxv As Single
Dim PH, PW As Single
Dim signal, sigma, df, Tg As Single
Dim i, j, k As Integer
Dim nx As Integer
Dim field0, field1 As Single
```
nx = Text16.Text
field0 = Text14.Text
field1 = Text15.Text

Form2.Show
Form2.pict1.Cls
maxv = 0
PW = Form2.pict1.Width
PH = Form2.pict1.Height

For k = 1 To nx
    If SignalY(k) > maxv Then maxv = SignalY(k)
Next k

For k = 1 To nx
    signal = k / nx
    Form2.pict1.Line ((k - 1) * PW / nx, PH - 500 - SignalY(k - 1) / maxv * PH * 0.8)-(k * PW / nx, PH - 500 - SignalY(k) / maxv * PH * 0.8), RGB(0, 0, 50)
Next k
signal = signal
End Sub

Sub Plot_Spectra()
    Dim maxv As Single
    Dim PW, PH As Single
    Dim fraction As Single
    Dim sigma As Single
    Dim signal As Single
    Dim i, j, k As Integer
    Dim df, Tg, dev, dev2 As Single

    Dim nx As Integer
    Dim field0, field1 As Single

    maxv = 0
    PW = Picture1.Width
    PH = Picture1.Height
    fraction = Text55.Text

    nx = Text16.Text
    field0 = Text14.Text
    field1 = Text15.Text

    DoEvents
SignalY(nx) = signal

Picture1.Cls

maxv = 0

For k = 1 To nx - 1
    If k > 10 Then
        dev = SignalY(k) - SignalY(k - 1)
        If Abs(dev) > maxv Then maxv = Abs(dev)
    End If
Next k

If maxv <> 0 Then
    dev2 = 0
    For k = 2 To nx - 1
        dev = (SignalY(k) - SignalY(k - 1))
        Picture1.Line ((k - 1) / nx * PW, PH * 0.5 - dev2 / maxv * PH * 0.5) - (k / nx * PW, PH * 0.5 - dev / maxv * PH * 0.5), RGB(0, 0, 50)
        dev2 = dev
    Next k
End If
End Sub

Private Sub H1(ByVal H As Single, ByVal theta As Single, ByVal phi As Single)
    Dim MAT() As Single
    Dim X As Single
    Dim i, j As Integer
    ReDim MAT(0 To NTOTAL - 1, 0 To NTOTAL - 1)

    Hx = Sin(theta) * Cos(phi)
    Hy = Sin(theta) * Sin(phi)
    Hz = Cos(theta)

    For i = 0 To NTOTAL - 1
        For j = 0 To NTOTAL - 1
            DoEvents
            Hamx1(i, j) = (gzz * Be * Hz * SzId(i, j) + gyy * Be * Hy * SyId(i, j) + gxx * Be * SxId(i, j) * Hx) / (2.00232 * Be)
        Next j
    Next i
End Sub
Hamx(i, j) = Hamx1(i, j)

If MI > 0 Then
    X = -(gNx * BN * Hx * IxId(i, j) + gNy * BN * Hy * IyId(i, j) + gNz * BN * Hz * IzId(i, j)) / (2.00232 * Be)
    Hamx(i, j) = Hamx(i, j) + X + Dz * (Sz2Id(i, j) - MATTR(i, j)) + Ez * (Sx2Id(i, j) + Sy2Id(i, j))
End If

Next j
Next i

End Sub
Private Sub H2()
    Dim Q, P As Single
    Dim i, j As Integer
    Q = Text56.Text
    P = Text58.Text
    For i = 0 To NTOTAL - 1
        For j = 0 To NTOTAL - 1
            If MI > 0 Then
                Hamx2(i, j) = Axx * SxIx(i, j) - Ayy * SyIy(i, j) + Azz * SzIz(i, j)
            End If
            Hamx2(i, j) = Hamx2(i, j) + Dz * (Sz2Id(i, j) - MATTR(i, j)) + Ez * (Sx2Id(i, j) + Sy2Id(i, j)) + Q * (Iz2Id(i, j) - MATTR2(i, j)) + P * (Ix2Id(i, j) + Iy2Id(i, j))
            DoEvents
        Next j
    Next i
End Sub
Private Sub Command3_Click()
    Dim time1, time2 As Single
    QuitTotal = 0
    PowderX = 0
    time1 = Timer
    Form1.Cls
    Simulation
    time2 = Timer - time1
Form1.Print "Simulation Time:"; time2; " seg"
End Sub

Public Sub LoadFile()
Dim X(6000) As Single
Dim Y(6000) As Single
Dim np, i As Integer
Dim xmax, xmin As Single
Dim PW, PH As Integer
Dim maxim As Single
Dim trt$

trt$ = Form1.File1.Path

Open trt$ + "\" + Form1.FileName.Text For Input As #1
np = 0
maxim = 0
While Not EOF(1)
    Input #1, X(np), Y(np)
    If Abs(Y(np)) > maxim Then maxim = Abs(Y(np))
    np = np + 1
    DoEvents
Wend
Close #1

xmin = Text14.Text
xmax = Text15.Text

For i = 0 To np - 1
    Y(i) = Y(i) / maxim
Next i

PW = Picture1.Width
PH = Picture1.Height
For i = 1 To np - 1
    Picture1.Line ((X(i - 1) - xmin) / (xmax - xmin) * PW, PH / 2 - Y(i - 1) * PH / 2)-((X(i) - xmin) / (xmax - xmin) * PW, PH / 2 - Y(i) * PH / 2), RGB(0, 0, 200)
Next i

End Sub

Private Sub Command6_Click()
Picture1.Cls
Private Sub Command7_Click()
    Mixed.Show
End Sub

Private Sub Command8_Click()
    Dim npoints As Integer
    Dim i As Integer
    Dim field0, field1 As Integer

    npoints = Text16.Text

    field0 = Text14.Text
    field1 = Text15.Text

    For i = 0 To npoints - 1
        SignalZ(i) = 0
    Next i
End Sub

Private Sub Command9_Click()
    Mixed2.Show
End Sub

Public Sub MixedSpectra()
    Dim npoints, i, k As Single
    Dim field0, field1 As Single
    Dim PW, PH, fraction, dev, dev2 As Single
    Dim maxv As Single
    Dim fr(5) As Single
    Dim sum As Single
    Dim sTg() As Single

    npoints = Text16.Text
    field0 = Text14.Text
    field1 = Text15.Text
PW = Picture1.Width
PH = Picture1.Height

ReDim sTg(0 To 4096)

sum = 0
For i = 1 To 5
    fr(i) = Mixed2.Text1(i - 1).Text
    sum = sum + fr(i)
Next i
If sum = 0 Then
    Exit Sub
End If

For i = 1 To 5
    fr(i) = fr(i) / sum
Next i

For i = 0 To npoints - 1
    sum = 0
    For k = 1 To 5
        sum = sum + SignalZ(i, k) * fr(k)
    Next k
    sTg(i) = sum
Next i

Open "C:\epr-sim\Spectrum1.txt" For Output As #1
For i = 0 To npoints - 2
    dev = sTg(i + 1) - sTg(i)
    Print #1, i; ","; dev
Next i
Close #1

maxv = -9999
For i = 0 To npoints - 2
    dev = sTg(i + 1) - sTg(i)
    If Abs(dev) > maxv Then maxv = Abs(dev)
Next i

If maxv = 0 Then
Exit Sub
End If

Picture1.Cls

dev2 = 0
For k = 0 To npoints - 2
    dev = sTg(k + 1) - sTg(k)
    Picture1.Line ((k) / npoints * PW, PH / 2 - dev2 / maxv * PH * 0.5) - ((k + 1) / npoints * PW, PH / 2 - dev / maxv * PH * 0.5), RGB(0, 0, 50)
    dev2 = dev
Next k

End Sub

Private Sub Dir1_Change()
    File1.Path = Dir1.Path
End Sub

Private Sub Exit_Click()
    If ProcessRunning = 1 Then
        Quit = 1
    Else
        End
    End If
End Sub

Private Sub File1_DblClick()
    FileName.Text = File1.FileName
    LoadFile
End Sub

Private Sub Form_Load()
    Dim npoints As Integer
    Be = 9.27314E-21
    BN = 5.05048E-24
    hPLank = 6.62554E-27
    g = 2.00232

    Combo1.AddItem("1/2")
    Combo1.AddItem("1")
    Combo1.AddItem("3/2")
Combo1.AddItem ("5/2")
Combo1.AddItem ("7/2")

Combo2.AddItem ("1/2")
Combo2.AddItem ("1")
Combo2.AddItem ("3/2")
Combo2.AddItem ("5/2")
Combo2.AddItem ("7/2")

Dir1.Path = App.Path

QuitTotal = 0
Quit = 0
ProcessRunning = 0
HScroll1.Value = 0

npoints = Text16.Text
ReDim SignalZ(0 To npoints + 10, 5)

End Sub

Public Sub setspectra(ByVal ns As Integer)

Dim npoints, i As Integer
Dim field0, field1 As Single
Dim maxv As Single

npoints = Text16.Text

field0 = Text14.Text
field1 = Text15.Text
maxv = 0
For i = 0 To npoints - 1
  If SignalY(i) > maxv Then maxv = SignalY(i)
Next i

If maxv > 0 Then

For i = 0 To npoints - 1
  SignalZ(i, ns) = SignalY(i) / maxv

End If
Private Sub Form_Unload(Cancel As Integer)
If ProcessRunning = 1 Then
    Quit = 1
Else
    End
End If
End Sub

Private Sub HScroll1_Change()
Dim X As Single
X = 1 - HScroll1.Value / 100#
Text25.Text = X
End Sub

Private Sub Option3_Click()
    Plot_Spectra
End Sub

Private Sub Option2_Click()
    Plot_Absortion
End Sub

Private Sub Picture1_MouseMove(Button As Integer, Shift As Integer, X As Single, Y As Single)
Dim PW As Integer
Dim field0, field1 As Single

PW = Picture1.Width
field0 = Text14.Text
field1 = Text15.Text

Text54.Text = X / PW * (field1 - field0) + field0
Line3.X1 = X
Line3.X2 = X
End Sub
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