EVALUATION OF HEAT CAPACITY OF CdSe QUANTUM DOTS USING DFT CALCULATIONS

AMIRUL EDHAM ROSLEE

Master of Science (Advanced Materials)

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science in Advanced Materials.

_____

(Supervisor's Signature)

Full Name : PROFESSOR DR. JOSE RAJAN

Position : PROFESSOR

Date :

_____

(Co-supervisor's Signature)

Full Name : PROFESSOR DR. JAMIL BIN ISMAIL

Position : PROFESSOR

Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

_____

(Student's Signature)

Full Name : AMIRUL EDHAM BIN ROSLEE

ID Number : MSM13002

Date :

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Dear Mama and Abah;

Even though you didn’t know the science,
and you hardly even understand the language,
but the pure, true knowledge that you have,
is knowing and understanding me.

Sincerely,
The man who knew nothing

To all my dearest teachers and lecturers,
especially to supervisor and co-supervisor;

Inspiration is nothing without knowledge,
knowledge triggers an idea,
the idea is meaningless without progress,
progress is slow without motivation,
motivation encourages discovery,
discovery leads to this achievement.

From the inspiration to this achievement,
all this means nothing without you.

Honestly,
The problematic, procrastinated student

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LIST OF SYMBOLS

0D	Zero dimension
1D	One dimension
2D	Two dimensions
3D	Three dimensions
2C	2-fold coordination
3C	3-fold coordination
$C_{V,molar}$	Molar constant-volume heat capacity
$C_{V,rot,molar}$	Rotational molar constant-volume heat capacity
$C_{V,total,molar}$	Total molar constant-volume heat capacity
$C_{V,trans,molar}$	Translational molar constant-volume heat capacity
$C_{V,vib}$	Molecular vibrational constant-volume heat capacity
$C_{V,vib,molar}$	Vibrational molar constant-volume heat capacity
$D(\omega)$	Phonon density of state
$D(\omega)d\omega$	Number of phonon modes in the frequency range ω to $\omega + d\omega$
E	Kinetic energy
$E[\rho(r)]$	Total ground state energy
$E[\rho_0(r)]$	Minimum ground state energy
E_0	Total electronic energy
E_{kin}	Total kinetic energy of electronic distribution system
$E_{kin}[\rho(r)]$	Total kinetic energy functional
$E_{kin,KS}$	Total kinetic energy of (non-interacting) Kohn-Sham electrons
$E_{kin,KS}[\rho(r)]$	Total kinetic energy functional of Kohn-Sham electrons
E_n	Energy of quantum lattice vibrations or phonons for QCSs
E_{ZPE}	Zero-point energy
$E_{ZPE,molar}$	Molar zero-point energy
$F[\rho(r)]$	Universal functional in Hohenberg-Kohn theorem
f	Degrees of freedom or total vibrational modes
G	Thermal Gibbs free energy
H	Thermal enthalpy
$\hat{H}$	Hamiltonian operator
h	Planck's constant

$\hbar$	Reduced Planck's constant
i	Imaginary number
k	Wave vector
k_B	Boltzmann's constant
k_D	Cut-off wave vector, called Debye wave vector
L	Quantum confinement size
m	Mass of particle
m_e	Mass of electron
N	Number of particles or atoms
n	Numbers of vibrational mode
$n(k)$	Number of states in the total volume of k-space
$n(\omega)$	Numbers of phonon mode of frequency ω
N_A	Avogadro's number
N_e	Number of electrons
n_{max}	Maximum number of vibrational modes
$<n>$	Average excitation phonon number, given by Bose-Einstein distribution
$<n_{vib,n}>$	Thermal equilibrium occupancy of phonon with vibrational mode n
P	Pressure
p	Momentum
q	Elementary charge
q_{rot}	Rotational partition function
q_{trans}	Translational partition function
R	Gas constant
r	Spatial coordinates
R^2	Coefficient of determination
R_{sphere}	Radius of the sphere in spherical coordinates
S_{molar}	Molar entropy
$S_{rot,molar}$	Rotational molar entropy
S_{total}	Total entropy
$S_{total,molar}$	Total molar entropy
$S_{trans,molar}$	Translational molar entropy

$S_{vib,molar}$	Vibrational molar entropy
T	Temperature
T_D	Debye temperature
$T_D(T^3)$	Determined Debye temperature of Debye T^3 model
$T_D(T^{3/2})$	Determined Debye temperature of $T^{3/2}$ model
T_E	Einstein temperature
$T_{vib,n}$	Characteristic vibrational temperature
U	Total energy
U_{molar}	Molar thermal energy
$U_{rot,molar}$	Rotational molar thermal energy
U_{total}	Total thermal energy
$U_{total,molar}$	Total molar thermal energy
$U_{trans,molar}$	Translational molar thermal energy
U_{vib}	Molecular vibrational thermal energy
$U_{vib,molar}$	Vibrational molar thermal energy
V	Volume
V_C	Correlation potential energy
V_{ee}	Potential energy of electron-electron self-repulsion
$V_{ext}(r)$	External potential
V_{ne}	Potential energy of attraction between electron density and nuclei
V_P	Potential energy
V_{sphere}	Volume of sphere in spherical coordinates
V_{state}	Volume of *k*-space of a single state
V_{total}	Total volume of *k*-space of all number of states
V_X	Exchange potential energy
V_{XC}	Exchange-correlation potential energy
x	Integration variable as a function of energy state and temperature of the system
ε_i	Kohn-Sham eigenvalue of electronic state *i*
θ	Polar angle of spherical coordinates
v_s	Acoustic wave velocity or speed of sound
$\rho(r)$	Electron density

$\rho_0(r)$	Equilibrium electron density at stationary point of structure geometry
φ	Azimuthal angle of spherical coordinates
ψ	Schrödinger wave function
ψ_i	Wave function of electronic state *i*
ω	Frequency
$\omega(k)$	Dispersion relation
ω_D	Cut-off frequency, called Debye frequency
$\omega_{vib,n}$	Characteristic vibrational frequency of vibrational mode *n*
ζ	Zeta

LIST OF ABBREVIATIONS

B3LYP	Becke's three parameters with Lee-Yang-Parr generalised-gradient approximation corrected correlation hybrid functional
CdS	Cadmium sulfide
CdSe	Cadmium selenide
CdTe	Cadmium telluride
CuBr	Copper(I) bromide
CuCl	Copper(I) chloride
DFT	Density functional theory
GaAs	Gallium arsenide
LanL2DZ	Los Alamos effective core potential plus double-ζ quality basis set
QCS	Quantum confined structure
QD	Quantum dot
QS	Quantum sheet
QW	Quantum wire
RMS	Root mean square
TDDFT	Time-dependent density functional theory
UV-Vis	Ultraviolet-visible
XRD	X-ray diffraction
ZnS	Zinc sulfide

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ABSTRAK

Pengurungan kuantum adalah fenomena yang berlaku apabila pengurangan saiz bahan semikonduktor dapat dikawal di bawah jejari Bohr eksiton, yang berevolusi menjadi struktur-struktur terkurung kuantum (QCSs), yang seakan-akan molekul, menunjukkan peralihan tenaga yang diskret. Struktur ini telah diterokai secara meluas untuk pelbagai aplikasi, kerana sifat-sifat fizikal (iaitu, optik dan elektronik) struktur ini yang tersisih dengan ketara daripada yang terdapat pada bahan-bahan pukal. Kajian ini bertujuan untuk menilai ciri-ciri termofizikal QCSs, yang diperincikan kepada dua objektif penyelidikan; (i) untuk mengira muatan haba titik-titik kuantum kadmium selenida (CdSe QDs) menggunakan teori ketumpatan fungsian (DFT), dan (ii) untuk mengkorelasi kesan pengurangan saiz CdSe QDs dengan muatan haba dan suhu Debye. Pengoptimuman struktur kluster-kluster CdSe QD telah dilakukan menggunakan pengiraan DFT pada fungsian hibrid tiga parameter Becke dengan korelasi betulan penghampiran kecerunan menyeluruh Lee-Yang-Parr (B3LYP), bersama dengan set asas keupayaan teras berkesan Los Alamos beserta kualiti ζ ganda dua (LanL2DZ), oleh pakej program Gaussian 09W. Kluster-kluster CdSe QD teroptimum dianalisis menggunakan pengiraan termokimia pada 32 suhu yang berbeza dari 5 ke 400 K untuk menentukan sifat-sifat termofizikal kluster-kluster CdSe QD sebagai fungsi suhu. Keputusan pengiraan termokimia kluster-kluster CdSe QD teroptimum terdiri daripada (i) tenaga elektronik keseluruhan, (ii) tenaga takat sifar, (iii) entropi molar, (iv) tenaga terma molar, (v) muatan haba isipadu malar molar, (vi) entalpi terma, (vii) tenaga bebas Gibbs terma, dan (viii) bilangan mod getaran. Penilaian muatan haba kluster-kluster CdSe QD menunjukkan bahawa QDs tidak betul-betul mengikut model muatan haba T^3 Debye. Dalam kajian ini, dari ketumpatan keadaan-keadaan fonon telah dibuktikan bahawa hubungan sebaran adalah mengikut variasi punca kuasa dua bagi QDs, yang sebaliknya adalah pemalar (kelajuan bunyi) mengikut model T^3 Debye, dan seterusnya muatan haba QDs dibuktikan mengikut $T^{3/2}$. Muatan haba daripada pengiraan termokimia menepati model $T^{3/2}$ dengan sangat baik (> 99 %).

ABSTRACT

Quantum confinement is a phenomenon that occurs upon successful control of size reduction of a semiconducting material below its exciton Bohr radius, which evolved to become quantum confined structures (QCSs), which are molecular-like, showing discrete energy transitions. These structures have been widely explored for many applications as their physical (*i.e.*, optical and electronic) properties are deviated substantially from those of bulk materials. This study attempted to evaluate thermophysical properties of QCSs, which specified in two research objectives; (i) to calculate the heat capacity of cadmium selenide (CdSe) quantum dots (QDs) using density functional theory (DFT), and (ii) to correlate the effect of size reduction of CdSe QDs with heat capacity and Debye temperature. Structure optimisation of CdSe QD clusters were performed using DFT calculations at the Becke's three parameters with Lee-Yang-Parr generalised-gradient approximation corrected correlation (B3LYP) hybrid functional, together with Los Alamos effective core potential plus double-ζ quality (LanL2DZ) basis sets by Gaussian 09W program package. The optimised CdSe QD clusters were analysed by thermochemical calculations of 32 different temperatures from 5 to 400 K to determine thermophysical properties of CdSe QD clusters as a function of temperature. The results of thermochemical calculations of the optimised CdSe QD clusters comprised of (i) total electronic energies, (ii) zero-point energies, (iii) molar entropies, (iv) molar thermal energies, (v) molar constant-volume heat capacities, (vi) thermal enthalpies, (vii) thermal Gibbs free energies, and (viii) numbers of vibrational mode. Evaluation of heat capacities of CdSe QD clusters showed that the QDs do not exactly follow the Debye T^3 model of heat capacity. In this work, from the phonon density of states it was proven that the dispersion relation follows a square root variation for QDs, which otherwise was a constant (speed of sound) according to the Debye T^3 model, and subsequently the heat capacity of the QDs were shown to follow $T^{3/2}$. The thermochemically-calculated heat capacity fit very well (> 99 %) to the $T^{3/2}$ model.

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