Pressure-induced structural transformations in nanomaterials: towards high accuracy large length- and time-scale simulations

Niccolò R. C. Corsini

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O homem que diz "dou" não dá, porque quem dá mesmo não diz
O homem que diz "vou" não vai, porque quando foi já não quis
O homem que diz "sou" não é, porque quem é mesmo é "não sou"
O homem que diz "tô" não tá, porque ninguém tá quando quer
Coitado do homem que cai no canto de Ossanha, traidor
Coitado do homem que vai atrás de mandinga de amor

Vai! Vai! Vai! Vai! Não vou!
Vai! Vai! Vai! Vai! Não vou!
Vai! Vai! Vai! Vai! Não vou!

Que eu não sou ninguém de ir em conversa de esquecer
A tristeza de um amor que passou
Não, eu só vou se for pra ver uma estrela aparecer
Na manhã de um novo amor
Amigo senhor, saravá, Xangô me mandou lhe dizer

Se é canto de Ossanha, não vá, que muito vai se arrepender
Pergunte ao seu Orizá, o amor só é bom se doer
Pergunte ao seu Orizá o amor só é bom se doer

Vai! Vai! Vai! Vai! Amar!
Vai! Vai! Vai! Sofrer!
Vai! Vai! Vai! Vai! Chorar!
Vai! Vai! Vai! Dizer ...¹

¹"Canto de Ossanha", Os afro-sambas, Baden Powell-Vinicius di Moraes.
To my beloved family
Abstract

The study of pressure-induced structural transformations in nanomaterials is both of fundamental and technological importance. Accurate simulations of these transformations are challenging because large length- and time-scales have to be simulated to make contact with experiments whilst retaining the atomic detail for a faithful description. In this thesis, both classical and quantum mechanical techniques are used to model pressure-induced structural transformations in realistic Si, Ge and CdS nanocrystals and comparison made to experiment where possible.

We implement an electronic enthalpy method [1] within the linear-scaling density-functional theory ONETEP code and, after introducing an approach for calibrating the volume definition, investigate the size-dependent pressure-induced amorphisation and polyamorphic transformations in hydrogenated Si and Ge nanocrystals. For the latter, we elucidate the surface-induced amorphisation and the new high-density amorphous metallic Ge phase observed experimentally. We combine this method with the projector-augmented wave and time-dependent density-functional theory methods to study the size and ligand dependence of deformation and optoelectronic properties of CdS nanocrystals with pressure.

We develop a novel classical parametrisation for the simulation of bare and ligated CdS nanocrystals immersed in a pressure-transmitting medium and investigate their transformation under pressure using classical molecular dynamics and the metadynamics method for accelerating rare events. The resulting polymorphic transformation and pressure-induced amorphisation are analysed in detail.
Declaration of originality

The work presented in this thesis was carried out between October 2011 and February 2015 at Imperial College London under the supervision of Prof. Peter D. Haynes, Prof. Carla Molteni and Dr. Nicholas D. M. Hine. I hereby declare that the work in this thesis is my own and any other work has been appropriately referenced and acknowledged.
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2“Bella”, Pablo Neruda.
## Contents

Glossary .......................... 17

Introduction .......................... 18

1 Pressure-induced structural transformations .......................... 21
   1.1 Thermodynamics and kinetics of pressure-induced structural transformations .... 21
   1.2 High pressure experiments ........................................... 23
   1.3 Semiconductors under pressure ........................................ 24
      1.3.1 Polymorphic transformations ..................................... 24
      1.3.2 Amorphisation and polyamorphic transformations ...................... 26
   1.4 Constant pressure simulations of finite systems .......................... 28
      1.4.1 Explicit methods .................................................. 29
      1.4.2 Implicit methods .................................................. 30
      1.4.3 Volume definitions ................................................ 31
      1.4.4 Challenges: simulating large length- and time-scales ..................... 33

2 Classical dynamics ......................... 35
   2.1 Fundamentals of classical molecular dynamics .......................... 36
      2.1.1 Interatomic potentials .......................................... 37
      2.1.2 Thermodynamic ensembles ...................................... 38
      2.1.3 Metastability and rare events .................................... 40
   2.2 Metadynamics ....................................................... 44
      2.2.1 Metadynamics ..................................................... 44
      2.2.2 Choosing collective variables ................................... 46

3 Linear-scaling density-functional theory ......................... 49
   3.1 Density-functional theory ........................................... 50
      3.1.1 The Born-Oppenheimer approximation ................................ 50
      3.1.2 The variational principle and Hellmann-Feynman theorem ............... 52
      3.1.3 Density-functional theory ....................................... 54
      3.1.4 The Kohn-Sham equations ....................................... 55
      3.1.5 Exchange and correlation ........................................ 57
      3.1.6 Pseudopotentials ............................................... 58
      3.1.7 Periodic systems and Bloch’s theorem ................................ 60
3.2 The ONETEP method ........................................ 63
   3.2.1 Density matrix formulation of the Kohn-Sham equations .......... 63
   3.2.2 Locality and Wannier functions .................................... 66
   3.2.3 The ONETEP method ........................................ 67
   3.2.4 Forces and geometry optimisation .................................. 70
3.3 The projector augmented wave method in ONETEP .................... 71
3.4 Theoretical spectroscopy ......................................... 74
   3.4.1 Conduction states ........................................ 76
   3.4.2 The linear-response formalism .................................... 78
   3.4.3 Linear-scaling linear-response time-dependent DFT ............... 80

4 The electronic enthalpy method .................................... 83
   4.1 Methodology ................................................ 83
   4.2 Calibration ................................................ 86
   4.3 Pressure-induced transformations in hydrogenated silicon nanocrystals .... 91
      4.3.1 Experimental and theoretical background ....................... 91
      4.3.2 Structural transformations ..................................... 92
      4.3.3 Electronic properties with pressure ........................... 97
   4.4 Concluding remarks ........................................... 98

5 Amorphisation of hydrogenated germanium nanocrystals .............. 99
   5.1 Experimental and theoretical background .......................... 99
   5.2 Comparison to silicon .......................................... 100
      5.2.1 Structural transformations .................................... 100
      5.2.2 Electronic properties with pressure ........................... 103
      5.2.3 Nanocrystal bulk moduli ..................................... 107
   5.3 Comparison to experiment ....................................... 112
      5.3.1 Experimental background ..................................... 112
      5.3.2 Comparison of simulated and experimental structural and spectroscopic properties .................. 113
      5.3.3 Pressure and size dependence of energy gaps ................. 116
   5.4 Concluding remarks ........................................... 118

6 Deformation and optical properties of cadmium sulphide nanocrystals under pressure: ligand and size dependence ............ 119
   6.1 Experimental and theoretical background .......................... 119
   6.2 Methodology ................................................ 122
      6.2.1 PAW potentials generation and testing ......................... 122
      6.2.2 Geometry optimisations and conduction calculations .......... 124
   6.3 Size and ligand dependence of structural properties under pressure .... 125
   6.4 Size and ligand dependence of electronic structure under pressure .... 129
   6.5 TDDFT optical absorption spectra ................................ 139
### Conclusions and future work

#### Bibliography

#### Appendix A

#### Appendix B
List of Tables

5.1 Comparison of nearest neighbour distances and corresponding internal pressure and bulk moduli................................................................. 107

6.1 Comparison between structural parameters (in Å and GPa) obtained for the WZ, ZB and RS structures with the generated PAW potentials and previous simulations and experiments .................................................. 123

6.2 Thermodynamic transformation pressures estimated by the common tangent method between the bulk WZ, ZB and RS phases in ABINIT ............................................. 124

6.3 Energy levels of band edge orbitals of CdS–H and CdS–phenyl at 0 and 5 GPa . . . 136

6.4 Energy levels of band edge orbitals of the small CdS–H and small CdS–phenyl at 0 and 5 GPa .............................................................................. 136

7.1 Parameters defining the Rabani potential for CdS and CdSe ........................................ 148

7.2 Comparison of Hirsheld partial charges for CdS–H and CdS–phenyl for different chemical environments and their differences at 0 and 5 GPa................................. 222

7.3 Parametrised partial charges and LJ coefficients .................................................. 223

7.4 Parametrised bond stiffness .............................................................................. 224

7.5 Parametrised angle stiffness .............................................................................. 224

7.6 Parametrised dihedral stiffness ........................................................................ 225
List of Figures

1.2.1 Schematic of the diamond anvil cell experimental set-up. 23
1.3.1 Transmission electron micrograph of a fourfold-coordinated CdSe nanocrystal before and after pressurisation. 25
1.3.2 Thermodynamic model of pressure-induced amorphisation. 26
1.3.3 Schematic phase diagram of Si. 28
1.4.1 Schematic of possible volume definitions. 32
2.2.1 Model metadynamics simulation. 45
2.2.2 Z-shaped potential and hysteresis. 47
3.1.1 Schematic of the pseudopotential approximation. 59
3.2.1 Representation of a psinc function in two dimensions. 67
3.2.2 Plot of Kohn-Sham orbital and NGWFs on a peptide. 69
3.3.1 Schematic of the PAW transformation. 72
3.4.1 Comparison of the DOS obtained for C_{60} with CASTEP and ONETEP. 77
4.1.1 Normalised hydrogenic 1s electronic density \( \rho(r) \) and \( \Phi_V(r) \) for different values of \( \alpha \) and \( \sigma \). 84
4.1.2 Electronic volume \( V_e \) as a function of the density cutoff \( \alpha \) for Si_{71}H_{60} relaxed at 0 GPa. 86
4.2.1 Distribution of nearest neighbour Si–Si distances from the centre of the Si_{71}H_{60} nanocrystal. 87
4.2.2 Schematic showing the equivalence between bulk-like core at 0 GPa and a compressed piece of bulk of same shape at \( P_{int} \). 88
4.2.3 Calibration plots of \( P_{eff} \) vs \( P_{in} \) for different volume definitions and parametrisation schemes. 90
4.3.1 Structures of Si_{71}H_{60} at 0, 25, 30 and 50 GPa and on releasing pressure at 20, 10 and 5 GPa. 93
4.3.2 Structural transformations of Si_{71}H_{60} under pressure. 94
4.3.3 Si_{35}H_{36} at 0 and 50 GPa; Si_{71}H_{60} at 0 and 50 GPa, and Si_{181}H_{110} at 0 and 25 GPa. 95
4.3.4 Ring statistics of Si_{71}H_{60} under pressure. 95
4.3.5 3-, 4-, 5-, 6- and 7- membered rings in Si_{71}H_{60} upon pressure release to 5 GPa. 96
4.3.6 Distribution of Si–Si distances in Si_{71}H_{60} under a pressure cycle. 97
4.3.7 HOMO–LUMO gaps of Si_{35}H_{36}, Si_{71}H_{60} and Si_{181}H_{110} under pressure. 98
4.3.8 Structures of Si_{35}H_{36}, Si_{71}H_{60} and Si_{181}H_{110}. 99
5.2.1 Structural transformations of Ge_{71}H_{60} under pressure. 101
5.2.2 Comparison of structural transformations of Ge$\text{$_7$$_1$}$H$_{60}$ and Si$_{71}$H$_{60}$ under pressure.

5.2.3 Ring statistics of Ge$_{71}$H$_{60}$ under pressure.

5.2.4 Structures of amorphised hydrogenated Ge nanocrystals: Ge$_{35}$H$_{36}$ at 50 GPa, Ge$_{71}$H$_{60}$ at 50 GPa and Ge$_{181}$H$_{110}$ at 25 GPa.

5.2.5 Comparison of HOMO–LUMO gaps and HOMO and LUMO energies for Ge$_{71}$H$_{60}$, Ge$_{181}$H$_{110}$, Si$_{71}$H$_{60}$ and Si$_{181}$H$_{110}$ with pressure.

5.2.6 Total DOS of Ge$_{35}$H$_{36}$ at 50 GPa, Ge$_{71}$H$_{60}$ at 50 GPa and Ge$_{181}$H$_{110}$ at 25 GPa.

5.2.7 Electronic density maps for Ge$_{71}$H$_{60}$ at 24, 25 and 50 GPa across (110), (111) and (001) planes.

5.2.8 HOMO and LUMO orbital density isosurfaces of Ge$_{71}$H$_{60}$ at 0, 50 and 5 GPa on decompression.

5.2.9 DOS of Ge$_{71}$H$_{60}$ decomposed in shells around the centre of the nanocrystal at 25 and 50 GPa.

5.3.1 Comparison of the pressure-dependence of the experimental Raman peak position and FWHM with simulations.

5.3.2 Comparison of experimental PL peak position and simulated HOMO–LUMO gaps of Ge$_{71}$H$_{60}$ and Ge$_{181}$H$_{110}$ with pressure.

5.3.3 Comparison of Ge–Ge distance with pressure obtained from EXAFS experiment and simulations.

5.3.4 Comparison of simulated HOMO–LUMO gaps and experimental results for the bandgap of Si and Ge nanocrystals.

6.1.1 Structures of simulated CdS nanocrystals.

6.2.1 Comparison of WZ and ZB structures.

6.2.2 Comparison of DOS for bulk ZB simulated with all-electron ELK and the generated PAW potential with ABINIT.

6.2.3 Comparison of DOS for CdS–phenyl at 5 GPa for different numbers of optimized conduction states.

6.3.1 Distribution of nearest neighbour Cd–S distances for CdS–phenyl at 0, 5 and 10 GPa.

6.3.2 Comparison of the relaxed CdS cores of CdS–H and CdS–phenyl.

6.3.3 Comparison of nearest neighbour Cd–S distances for CdS–H, CdS–phenyl, small CdS–H and small CdS–phenyl at 0 and 5 GPa.

6.4.1 Pressure dependence of HOMO-LUMO gaps for the simulated nanocrystals and comparison with experiment.

6.4.2 Comparison of DOS at 0, 5, 10 and 15 GPa for CdS–H and CdS–phenyl.

6.4.3 Comparison of band edge orbitals of CdS–H at 0 GPa and 5 GPa.

6.4.4 Comparison of band edge orbitals of small CdS–H at 0 GPa and 5 GPa.

6.4.5 Comparison of band edge orbitals of CdS–phenyl at 0 GPa and 5 GPa.

6.4.6 Comparison of band edge orbitals of small CdS–phenyl at 0 GPa and 5 GPa.

6.4.7 DOS projected onto S, Cd and ligand atoms for CdS–H and CdS–phenyl at 0 and 5 GPa.
6.4.8 DOS projected onto S, Cd and ligand atoms for small CdS–H and small CdS–phenyl at 0 and 5 GPa. .......................................................... 138
6.4.9 Dependence of HOMO and LUMO energy levels with pressure for the various nanocrystals ............................................................... 140
6.5.1 Comparison of the TDDFT absorption spectra of small CdS–H at 0 GPa for different number of optimised transitions .................................................. 140
6.5.2 Comparison of the optical absorption spectra with pressure obtained with TDDFT for CdS–H, CdS–phenyl, small CdS–H and small CdS–phenyl. 141

7.1.1 Experimental fraction of RS with pressure at 300 K of Cd$_{32}$S$_{14}$(SC$_6$H$_5$)$_{36}$·4(N(CH$_3$)$_3$) depending on PTM. .................................................. 145
7.1.2 Schematic of the WZ→RS transformation mechanism. .......................... 146
7.1.3 Schematic of the ZB→RS transformation mechanism along Catti’s path. 147
7.2.1 Fragments used in the parametrisation. ................................................. 149
7.2.2 Comparison of the atoms in the CdS core of CdS–phenyl relaxed in ONETEP and LAMMPS using the parametrised forcefield. .......................... 151
7.2.3 Periodic simulation cell showing the simulated Cd$_{216}$S$_{216}$ nanocrystal immersed in THF. ................................................................. 153
7.3.1 Effect of PTM-nanocrystal interaction parameters on the compression and structure of Cd$_{216}$S$_{216}$ at 2 GPa. ................................................. 154
7.3.2 Temperature fluctuations of Cd$_{216}$S$_{216}$ at ambient conditions and $P_{int}$ during stepwise pressure increase. ................................................. 156
7.3.3 Snapshots of Cd$_{216}$S$_{216}$ undergoing HS→RS transformation during MD at 6 GPa ................................................................. 156
7.3.4 Structural changes in Cd$_{216}$S$_{216}$ during compression simulated with MD at 300 K ................................................................. 157
7.3.5 Snapshots of Cd$_{216}$S$_{216}$ undergoing RS→HS transformation during MD at 1 bar upon pressure release from 6 GPa .............................................. 158
7.3.6 Temperature and volume fluctuations of CdS–phenyl at 300 K and 1 bar ........ 159
7.3.7 Structural changes in CdS–phenyl during compression simulated with MD during stepwise pressure increase between 1 bar and 8 GPa at 300 K 160
7.3.8 Snapshots of CdS–phenyl from 3 different angles at 1 bar, 2, 4 and 6 GPa .... 161
7.4.1 Evolution of the enthalpy of Cd$_{216}$S$_{216}$ at 300 K during metadynamics simulation at 2 GPa and 4 GPa ......................................................... 162
7.4.2 Evolution for Cd$_{216}$S$_{216}$ of CV and average coordination during metadynamics of the HS→RS transformation at 2 and 4 GPa .................. 163
7.4.3 Snapshots of Cd$_{216}$S$_{216}$ undergoing a HS→RS transformation via a “sliding-plane” mechanism during metadynamics run at 2 GPa and 300 K. 164
7.4.4 Structural changes in Cd$_{216}$S$_{216}$ during HS→RS transformation simulated with metadynamics at 2 GPa and 300 K. .............................. 165
7.4.5 Evolution of the enthalpy and volume of CdS–phenyl at 300 K during metadynamics simulation at 2 GPa and 6 GPa. ................................. 166
7.4.6 Changes in coordination of CdS–phenyl during metadynamics runs at 300 K at 2 and 6 GPa.

7.4.7 Representative snapshots of the CdS core of CdS–phenyl during a metadynamics simulation at 2 GPa and 300 K.

7.4.8 Structural changes in CdS–phenyl during a metadynamics simulation at 2 GPa and 300 K comparing for representative snapshots.

7.4.9 Representative snapshots of the CdS core during a metadynamics simulation at 6 GPa and 300 K.

7.4.10 Structural changes in CdS–phenyl during metadynamics at 6 GPa and 300 K comparing with the structure at 1 bar for representative snapshots.
Glossary

AE: all-electron
ALDA: adiabatic local density approximation
CV: collective variable
DAC: diamond anvil cell
DFPT: density-functional perturbation theory
DFT: density-functional theory
DMF: dimethylformamide
DOS: density of states
ESP: electrostatic potential
EXAFS: extended X-ray absorption fine structure
FES: free energy surface
FFT: fast Fourier transform
GGA: generalised gradient approximation
HDA: high-density amorphous
HOMO: highest occupied molecular orbital
HS: honeycomb stacked
KS: Kohn-Sham
lda: local density approximation
LDA: low-density amorphous
LDOS: local density of states
LJ: Lennard-Jones
LR: localisation region
LR-TDDFT: linear-response time-dependent density-functional theory
LUMO: lowest unoccupied molecular orbital
MD: molecular dynamics
MEG: multi-exciton generation
MSRD: mean squared relative displacement
NC: nanocrystal
NCPP: norm-conserving pseudopotential
NLCC: non-linear core correction
NGWF: non-orthogonal generalised Wannier function
OA: optical absorption
PAW: projector-augmented wave
PBC: periodic boundary condition
PIA: pressure-induced amorphisation
PL: photoluminescence
PS: pseudo
PTM: pressure-transmitting medium
PWPP: plane-wave pseudopotential
RESP: restrained electrostatic potential
RMS: root mean squared
RS: rocksalt
TDDFT: time-dependent density-functional theory
TEM: transmission electron microscope
THF: tetrahydrofuran
TISE: time-independent Schrodinger equation
TPS: transition path sampling
VDOS: vibrational density of states
vdW: van der Waals
VHDA: very-high-density amorphous
WZ: wurtzite
XC: exchange correlation
XRD: X-ray diffraction
ZB: zincblende
Introduction

Simulating pressure-induced structural transformations in nanomaterials

Human civilisation and technology are inextricably linked to the discovery and elaboration of materials. From the stone age to the silicon age, it is our improved ability to source and turn these materials into the building blocks of technology, whether bricks or transistors, that has defined their respective socio-economic eras. There is little doubt that our capacity as a species to tackle the challenges of the future, from effective medicine to clean energy, will strongly depend on our ability to discover new materials and refine existing ones as the substrate for technological development. Key to this is our understanding of the nature of materials, how they derive their physical properties and how these can be controlled in practice.

Experimental progress in controlling the structure of matter with ever finer detail and accuracy has reached the point that individual atoms can routinely be observed and manipulated with techniques such as atomic force and transmission electron microscopy. Theoretical and computational advances, especially after the birth of quantum mechanics, have allowed us to model ever more complex and large structures with high accuracy. This convergence of theory and experiment at the scale of atoms and molecules, the nanoscale \( \sim 1-100 \, \text{nm} \), holds the promise not only of an improved understanding of existing materials but also of designing novel materials with properties tailored for specific technological uses. Nanomaterials, defined as materials that are structured at the nanoscale, can be seen as being intermediate between atoms or molecules and extended material. They exhibit a plethora of distinct properties and phenomena such as: discretisation of electronic density of states due to quantum confinement effects, composite effects due to the combination of components with distinct properties, size-, surface- and shape-dependent effects.

In particular nanocrystals, that are easy to synthesise and inherit many of the chemophysical properties of bulk crystals while allowing for their fine control, have attracted much scientific and technological attention over the last decades [2]. In part due to their relatively large ratio of surface to volume atoms, nanocrystals display a host of properties that differ from those of their bulk counterparts [3]. New dimensions are added to phase diagrams when the sizes, surface reconstructions and terminations of the nanocrystals are taken into account [4]. Much effort has been directed at harnessing this size- and surface-dependence especially for semiconductor nanocrystals displaying quantum confinement and diverse applications ranging from biomarkers to quantum transistors have been proposed [5–7].

Understanding how nanocrystal properties depend on environmental conditions such as temperature, solvent and pressure is not only of fundamental interest but also has important technological
consequences. In this thesis we are particularly concerned with the role of pressure on the chemo-
physical properties of nanocrystals, that can depend sensitively on their structures [8]. For example,
the elastic structural deformation of nanocrystals under pressure can result in large changes in opto-
electronic properties which can in turn be harnessed for applications such as nanoscale stress sensors
and tunable photovoltaics [9, 10]. Also, at sufficiently high pressures, nanomaterials can undergo
polymorphic or polyamorphic transformations with thermodynamic and kinetic properties that can
differ significantly from their bulk counterparts. The additional surface effects also open the door to
transformation pathways that are not available to the bulk material, potentially allowing a system
to become trapped in metastable states with novel properties [11–13]. Moreover, sufficiently small
nanocrystals can also be synthesised with few or no defects and are thus ideal models to study the ki-
netics of solid-solid phase transitions [14, 15]. Recently, progress has been made in directly observing
structural transformations in nanocrystals [16–18] and bulk single crystals [19]. Direct monitoring
of transformation pathways in nanosystems is, however, still challenging with the resolution of ex-
isting experimental probes and understanding could thus greatly benefit from the insights computer
simulations provide. However, the large length- and time-scales associated with the accurate sim-
ulation of pressure-induced structural transformations still presents theoretical and computational
challenges.

The overarching goal of this thesis is to accurately simulate pressure-induced structural transfor-
mations of realistic semiconductor nanocrystals and compare with experiment wherever possible.
We use a combination of novel and existing approaches to overcome the computational bottleneck
associated with the large time- and length-scales involved.

Outline of dissertation

In Chapter 1 we outline some principles behind pressure-induced structural transformations and
present existing experimental and theoretical results for bulk and nanocrystalline semiconductors.
We review existing techniques for simulating finite systems under pressure and outline computational
challenges that can arise.

In Chapter 2 we describe the formalism behind classical molecular dynamics and analyse the
challenges associated with simulating rare events such as first order pressure-induced structural
transformations. We present the metadynamics method as an approach to overcome this problem
and discuss its practical use.

Chapter 3 introduces density-functional theory and widely used approximations. We then describe
the linear-scaling formalism for density-functional theory, the projector-augmented wave method and
linear-response time-dependent density-functional theory.

In Chapter 4, the electronic enthalpy method and a new approach for calibrating the volume
definition are presented. We apply it to the investigation of the amorphisation and polyamorphic
transformation of hydrogenated Si nanocrystals under pressure.

Chapter 5 compares the amorphisation and polyamorphic transformation of hydrogenated Ge
nanocrystals under pressure using the same method and equivalent nanocrystals to Chapter 4. We
analyse the electronic properties of the nanocrystals, in particular the origin of metallisation, and
introduce a new approach to estimate their bulk moduli. Contact is made with experimental results for the structural and spectroscopic properties of small hydrogenated Ge nanocrystals under pressure and shown to be in good agreement.

Chapter 6 studies the deformation and optical properties of CdS nanocrystals under pressure and investigates the influence of size and ligands. Optical absorption spectra are simulated using time-dependent density-functional theory and implications for the rational design of optoelectronic applications discussed.

In Chapter 7 we investigate the classical dynamics of CdS nanocrystals under pressure using both molecular dynamics and metadynamics. We develop a novel classical parametrisation for ligated and bare CdS nanocrystals immersed in a pressure-transmitting medium and analyse respectively their pressure-induced polymorphic transformation and amorphisation at various pressures. Finally we conclude, present an overview of the results obtained and expand on possible future avenues of exploration.

Publications

The work presented in this thesis has been published in part as follows:


1 Pressure-induced structural transformations

“This is our last dance. This is our last dance. This is ourselves. Under pressure. Under pressure. Pressure.”

In the introduction, we briefly discussed the scientific and technological importance of nanomaterials and understanding their properties and structural transformations under pressure. We also highlighted the role of computer simulations in helping to interpret experiments and design novel materials. In this chapter, we expand on these ideas. First we introduce some theoretical background of relevance to pressure-induced structural transformations. We then present experimental techniques and results for semiconductors under pressure. Finally, we describe approaches for simulating nanomaterials under pressure and the associated computational challenges.

1.1 Thermodynamics and kinetics of pressure-induced structural transformations

The classical theory of thermodynamics, which deals with extensive macroscopic objects in equilibrium [20], defines the pressure \( P \) as

\[
P = -\left( \frac{\partial U}{\partial V} \right)_{S, \{N_i\} = \text{const}},
\]

(1.1.1)

where \( U \) is the internal energy of the system, \( V \) its volume, \( S \) the entropy and \( N_i \) the amount of each chemical component \( i \). The elastic deformation of a bulk material under hydrostatic compression is given by its bulk modulus:

\[
B = -\frac{\partial P}{\partial V} = \frac{V}{\partial^2 U}{\partial V^2}.
\]

(1.1.2)

At constant temperature and pressure, the system is in equilibrium (i.e. globally stable phase) when the Gibbs free energy \( G \), given by:

\[
G = U + PV - TS,
\]

(1.1.3)

is at the global minimum. Local minima in the Gibbs free energy surface correspond to metastable states of the system which should return to the globally stable phase after sufficient time. First order solid-solid transformations involve atomistic rearrangements with energetic barriers that can

\(^4\)Queen and David Bowie, “Under pressure”.
be large compared to the thermal energy and result in long-lived metastability. Diamond is a famous example of a metastable structure which should revert to graphite, the stable polymorph at ambient conditions, but the transformation is not observed.\(^2\) The Gibbs free energy surface can change with environmental conditions and the relative height of local minima altered which can in turn lead to phase transitions. A pressure-induced phase transition can occur between two phases when the difference in Gibbs free energy, at given pressure \(P_T\), between the two phases is zero. The pressure \(P_T\) is known as the thermodynamic transition pressure and the system can in principle transform back and forth between the two phases. The kinetics of the transformation are determined by the temperature and energetic barrier to transformation. Under practical experimental conditions, the observed upstroke (low to high pressure) transition pressure is often larger than \(P_T\), and conversely the downstroke (high to low pressure) lower. Such hysteretic behaviour, with large separation between upstroke and downstroke pressures, is often observed in reconstructive first order transitions and is the signature of a large energetic barrier to transformation.

High pressure experiments on nanocrystals are typically performed using a diamond anvil cell (DAC) set-up. The sample is immersed in a pressure transmitting medium (PTM) to ensure a hydrostatic compression of the nanocrystals. Microscopically, the compression happens because of collisions between PTM molecules and nanocrystal surfaces. Due to the small number of constituent atoms, nanocrystals exhibit large fluctuations and non-equilibrium properties. The microscopic details become important and coarse-grained macroscopic concepts such as pressure can fail to capture the chemistry of the PTM-nanocrystal interaction. The concept of thermodynamic phase becomes ill-defined at the nanoscale and thermodynamic concepts need to be revisited for non-extensive systems [21]. \(G\) does, however, provide the driving force for transformation at the nanoscale and one can make successful predictions once surface and solvent energetics are accounted for. Eq. (1.1.3) can be extended to include surface and interface contributions and at constant \(P\) and \(T\), the system will tend to minimise the Gibbs free energy. These contributions include surface stress that depends on faceting, termination and solvent-nanocrystal interaction, as well as polarisation energy due to the solvent and cavitation energy due to the energetic cost of forming a solvent cavity containing the nanocrystal [22, 23]. Surface and solvent can both have a significant effect on the transformation’s energetics, by changing the relative Gibbs free energy of structures, as well as the kinetics, by altering energetic barriers to transformation, compared to the bulk.

Due to challenges in evaluating the entropy \(S\) and the PTM-nanocrystal interaction accurately, the general approach is to assess structural stability of nanocrystals at high pressures by focussing on the enthalpy \(\mathcal{H}\)

\[
\mathcal{H} = U + PV.
\]

This is expected to be a reasonable approximation for nanocrystals under conditions of high-pressures and ambient temperatures investigated in this work, as the relative changes in Gibbs free energy due to changes in volume, especially for reconstructive first order solid-solid transformations, are expected to dominate. Entropic and solvent-induced effects may prove important in some systems and the validity of the approximation is ultimately to be tested against experiment.

\(^2\)Hence jewellers’ somewhat overconfident claim that “diamonds are forever.”
First order structural transformations proceed when a nucleus of atoms of the new phase larger than a critical size is formed. The nucleation is an activated process requiring energetically unfavourable local bonding rearrangements. The presence of defects and interfaces can lower the barrier to nucleation and these are thus preferred nucleation sites. The nucleated phase then grows and spreads through the rest of the material. Bulk crystals, even of the highest purity, have defects and microstructures and the new phase will tend to nucleate at defects or grain boundaries in single or multiple nucleation events. As a result, multiple crystalline or amorphous domains form by processes such as fracture or twinning. Nanocrystals smaller than the typical size of bulk domains can be synthesised and obtained with few or no defects due to the proximity of surfaces they can anneal to. Single nucleation events, expected to occur at the surface, lead to the formation of a single crystalline domain of the new phase and are accompanied by changes in shape reflecting the underlying transformation mechanism. Nanocrystals can therefore provide a much simplified picture of the kinetics of solid-solid transformations and can afford direct insight in the transformation mechanisms.

1.2 High pressure experiments

Experimental investigations at pressures in excess of 600 GPa have been made possible by apparatuses such as the DAC (Figure 1.2.1) [25]. The sample to be compressed is placed between a gasket and the culets (flat faces) of two diamonds. Hydrostatic compression can be achieved by immersing the sample, for example the nanocrystals, in a suitable PTM contained within a chamber placed inside the DAC. The PTM is generally chosen to have high freezing pressures at ambient temperature so as to prevent solidification and anisotropic stresses on the sample. Examples of commonly used PTM are helium, argon, xenon, silicone oil and mixtures of ethanol-methanol. The pressure inside

Figure 1.2.1: Schematic of the diamond anvil cell experimental set-up. Figure reproduced from Ref. [24].
the chamber can be monitored from the shift in fluorescence line of a laser-excited reference material such as ruby.

Diamond is transparent over a wide range of the microwave, optical and X-ray spectra. The compressed sample can therefore be probed in situ by a host of spectroscopic techniques such as X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), nuclear magnetic resonance, optical absorption, Raman scattering and electrical conductivity measurements [26–29]. The temperature inside the chamber can be controlled by attaching electrodes or heating with pulsed laser radiation and temperatures ranging between mK and thousands of K can be reached [30].

The relentless improvements in spectroscopic techniques in the last decades, with increased spectral and spatial resolutions as well as better coherences and shorter measurement times, allow us to uncover the atomic structure and dynamics of materials with an exquisite level of detail [31–35]. The resolution attained with the latest generation of experiments makes it possible to measure the structural transformation of nanocrystals in real-time using ultrafast optical [17] and XRD measurements [18]. While much progress has been made, important information is still beyond experimental reach even when multiple techniques are combined. For example, the detailed atomic structure of small nanocrystals and their surfaces are difficult to resolve, and it is hard to assign the electronic origin of spectral peaks unambiguously.

1.3 Semiconductors under pressure

1.3.1 Polymorphic transformations

Pressure-induced structural transformations in crystalline semiconductors often involve large structural rearrangements involving the formation or rupture of bonds. Such transformations are termed as reconstructive and are first-order in nature as they involve discontinuous changes in specific volume (often as large as 15-20%) and absorption or release of a fixed amount of latent heat. These transformations often display large hysteresis due to the large Gibbs free energy barriers between phases. In general, the pressure-induced transformations are reversible so that the low pressure structure is recovered upon pressure release. In some cases, however, the high-pressure phase can be kinetically trapped and this metastable phase recovered at lower pressures.

Semiconductor materials made of group IVA elements (e.g. C, Si and Ge) and the diatomic compounds made of group IIIA-VA (e.g. GaAs) and group IIIB-VIA (e.g. CdSe and CdS) have many structural properties in common both at ambient conditions and under pressure. Being tetravalent, these materials form tetrahedral bonding geometries at ambient conditions. Under pressure, the bonding geometry becomes more compact with larger coordination numbers. Most of these semiconductor materials undergo pressure-induced phase transitions between a fourfold-coordinated crystalline structure such as diamond cubic (Fd3m), the binary equivalent zincblende (ZB, F-43m, sphalerite) or wurtzite (WZ, P63mc) and a sixfold-coordinated one such as β-Sn (I41/amd) or rocksalt (RS, Fm-3m, NaCl-type).

Upon further compression, Si is observed to go through the fourfold coordinated Imma phase, eightfold-coordinated simple hexagonal (sh, P6/mmm), sixfold-coordinated Cmca, twelvefold-coordinated
hexagonal closed packed (hcp, \(P6_3/mmc\)) and face-centred cubic (fcc, \(Fm3m\)) phases. Upon pressure release, the \(sh\) and \(\beta\)-Sn phases are observed but the diamond phase is not recovered at ambient pressure. Instead, a host of crystalline and amorphous metastable structures are observed, the most common of which are the BC8 (\(Ia\bar{3}\)) and R8 (\(R\bar{3}\)) phases that correspond to fourfold-coordinated distorted tetrahedral structures.

Similarly for Ge, the fourfold coordinated \(Imma\) [36], eightfold-coordinated \(sh\) [37], sixfold coordinated \(Cmca\) and twelvefold coordinated hcp phases are observed upon compression. Ge also displays a number of metastable phases upon pressure release from \(\beta\)-Sn: the distorted simple tetragonal ST12 (\(P4_32_12(D_4^8)\)) and R8 phases are obtained on slow pressure release and the BC8 phase on rapid release [38].

For CdS and CdSe, \(Pmmn\) and \(Cmcm\) phases have been observed upon compression of the RS phase [39, 40]. On decompressing the RS phase, CdSe transforms to a fourfold coordinated structure consisting of lamellar regions with WZ and ZB stacking [41].

In semiconductor nanocrystals, the importance of surface and interface energetics can strongly affect the thermodynamics and kinetics of transformation compared to their bulk counterparts. The surfaces and interfaces in small nanocrystals can stabilise structures above the bulk transition pressures. Alivisatos and Tolbert found an enhancement of transition pressure between WZ and RS in CdSe nanocrystals [3, 42]. Also, increased metastability upon decompression is found. Changing the solvent or ligand can alter the stability and kinetics, as observed in small CdS nanocrystals by Chen et al. [11], and these can in principle be used to gain better control and stabilise metastable structures. For example, CdS nanocrystals of 2 nm diameter have been recovered in the high-pressure RS structure at ambient conditions [43]. This increased stability enables the study of structures under pressure and temperature conditions not available to the bulk. As mentioned previously, small nanocrystals can be synthesised with few or no defects much simplifying the kinetics compared to the bulk. Homogeneous nucleation of the RS structure has been observed in CdSe WZ nanocrystals, and the increasing energetic barrier with size has been interpreted as the transformation occurring due to a collective bond rearrangement (similar to martensitic transformations) [11]. The mechanism
Figure 1.3.2: Thermodynamic model of pressure-induced amorphisation. The Gibbs free energy landscapes of the initial material (sample 1) and the same material at critical conditions (sample 2) are shown. The difference between sample 1 and 2 can be induced for example by a change in size or ligands. Instead of undergoing polymorphic transformation between phase A and phase B, sample 2 amorphises and reaches a large amorphous basin C.

of transformation can also show dependence on size and compression rate (e.g. Figure 1.3.1). The accompanying shape-change provides information about the underlying transformation mechanism [15].

Pressure, size and surface morphology can be used as important synthetic tools and open the door for recovering high-pressure metastable structures at ambient conditions

1.3.2 Amorphisation and polyamorphic transformations

Semiconductor materials can also be found in the amorphous solid state. While technologically important and showing unique chemophysical properties, amorphous semiconductors have received less attention than their crystalline counterparts and are comparatively poorly understood. Unlike crystals that are ordered and can be defined by a periodically repeating unit cell, amorphous materials lack long-range atomic order. Because of this disorder, amorphous structures are metastable compared to symmetric crystalline structures and one cannot strictly talk about amorphous thermodynamic phases. Amorphous solids can be produced experimentally in a variety of ways: cooling a liquid or vapour below its freezing point faster than the timescale for structural relaxation and crystallisation, irradiation, chemical reaction such as polymerisation and pressurisation of a crystal below its melting point [44]. In the present thesis we are particularly interested in the latter phenomenon referred to as pressure-induced amorphisation (PIA) or “cold melting”.

PIA was originally proposed by Mishima et al. for solid materials such as ice, that contract on melting and whose melting temperature falls with pressure [45]. When compressed at a sufficiently low temperature, Mishima predicted that such solids could become kinetically trapped and the transformation to other crystalline phase suppressed. Various models have been proposed to describe the PIA phenomenon including thermodynamic, mechanical and percolation ones but it remains poorly understood [46]. Figure 1.3.2 shows a thermodynamic model of PIA: the Gibbs free energy
landscape of the material under pressure is modified, for example by a change in size or ligands, so that it amorphises instead of undergoing polymorphic transformation. While devoid of long-range order, amorphous material exhibit short-range and medium-range order similar to that found in the corresponding crystal phase. When changing the pressure or temperature, amorphous materials undergo structural changes that can be classified as follows: reversible elastic transformation with no change in the topology of the amorphous network, irreversible structural relaxation depending on the kinetics of equilibration, plastic transformations associated with changes in short-range order such as changes of coordination in first and second shells, plastic transformation due to changes in medium-range order. Amorphous materials can transform between different types of amorphous structures and polymorphic transformations present many analogies with the polymorphic transitions of bulk crystals that are still the subject of active experimental and theoretical investigation [47]. These polymorphic transformations can occur via first-order-like transformation, with sharp changes in structure and properties, or via smoother transformations with a series of intermediate metastable states.

Polyamorphism was first observed in ice which forms a tetrahedral network of water molecules bonded together by van der Waals (vdW) and hydrogen bonds. Under pressure, ice has been observed to transform between fourfold-coordinated low-density amorphous (LDA), approximately fivefold-coordinated high-density amorphous (HDA) and sixfold-coordinated very high density amorphous (VHDA) structures. HDA and VHDA structures differ from the LDA structure because of respectively one and two water molecules occupying interstitial positions. Experimental findings suggest that the LDA→HDA transformation is first-order like and accompanied by sharp changes in density. Instead, the HDA→VHDA transformation is smoother and smeared over a larger pressure range. VHDA gradually transforms back to HDA upon decompression and LDA is recovered upon further pressure release [47]. Following the work of Mishima et al. and Aptekar [48], the polyamorphic transformations between LDA-HDA-VHDA are often interpreted as low-temperature versions of the corresponding liquid-liquid transformations between LDL-HDL-VHDL phases.

Solid Si and Ge share many characteristics with ice such as the fact that they contract upon melting and the melting temperature falls with pressure. They also form open tetrahedral networks due to covalent bonding. This led Mishima to predict polyamorphic transformations in Si and Ge analogous to those in ice. Experimental evidence based on conductivity measurements of multiple amorphous phases in Si has been obtained by Shimomura et al. XRD, Raman spectroscopic and electrical conductivity measurements have provided further evidence of transformation between tetrahedral LDA and 5-6 fold coordinated HDA structures in porous and bulk amorphous Si [49–52]. Experiments are challenging due to the fast recrystallisation kinetics and simulations can provide valuable insight. Ab initio MD simulations indicate that in Si, the polyamorphic transformations between LDA-HDA-VHDA resemble those in ice but also map onto the polymorphic transitions of bulk Si diamond→β-Sn→sh with similarities in coordination and short-range order (Figure 1.3.3) [53–55]. Much less is understood about polyamorphism in Ge and no direct observation of the LDA→HDA transformation has been reported, although simulations [56] have predicted transformations between LDA-HDA-VHDA structures similar to Si albeit at different pressures.

Amorphous structures and PIA in nanocrystals are still very much emerging topics. Depending on
size, hydrogenated Si nanocrystals have been recovered in amorphous structures upon decompression [57]. Size-dependent PIA has also been observed in TiO\textsubscript{2} [58–61], Y\textsubscript{2}O\textsubscript{3} [62] and PbTe [63, 64] nanocrystals below a critical size that are found to amorphise instead of undergoing polymorphic transition. The greater tendency of nanocrystals to undergo PIA is thought to be due to the important surface and interface energetics suppressing the polymorphic transformation as well as surface defects or ligand-induced disorder [65]. Recent experiments have found PIA in TiO\textsubscript{2} to depend on surface functionalisation [66], suggesting ligands and solvents can impede recrystallisation and induce amorphisation. The size, surface and interfaces of nanocrystals can therefore be tuned to induce amorphisation, including in materials that are hard to amorphise in the bulk, but also to stabilise and recover amorphous structures at ambient conditions.

This has important technological consequences as amorphous nanoparticles have unique chemo-physical properties [67] such as specific photoluminescence [68], enhanced catalytic properties [69] and bioactivity [70]. Understanding PIA at the nanoscale and the stability of nanoamorphous structures is of high importance for nanomaterial design and much insight can be gleaned from atomistic simulations.

1.4 Constant pressure simulations of finite systems

Constant pressure simulations of bulk systems have been performed successfully ever since the introduction of the Andersen [71] and Parrinello-Rahman [72–75] methods in the early 1980s. These methods rely on defining an extended Lagrangian for the system

\[ \mathcal{L} = T - V - P V_{cell}, \]  

(1.4.1)
where \( T \) is the kinetic energy, \( V \) the potential energy, \( P \) the pressure and \( V_{\text{cell}} \) the volume of the periodic simulation cell. In the Andersen method, the shape of the cell is kept constant unlike the Parrinello-Rahman approach where the cell edges and angles are treated as dynamic variables and its shape is allowed to change in the course of a simulation. Instead, constant pressure simulations of finite systems have only been performed in the last two decades [13,76–99]. This is partly due to the conceptual difficulties associated with the volume definition in finite systems, unlike periodic ones which are unambiguously defined by their primitive unit cell. Two families of approaches have been adopted to simulate finite systems under pressure [100]: methods using an explicit description of the PTM and its interaction with the finite system, and implicit approaches for which an extended Lagrangian is used following a volume definition of the finite system. We will now review these in more detail.

### 1.4.1 Explicit methods

In explicit approaches, the finite system (e.g. a nanocrystal) is immersed in a PTM that acts as a pressure-reservoir by virtue of the collisions between solvent molecules and nanocrystal imparting momentum. This mimics the situation in high pressure experiments (Section 1.2) where nanocrystals are dissolved in a PTM and pressurised in a DAC. This approach was first proposed by Martoňák, Molteni and Parrinello who used an auxiliary PTM described by a repulsive short-ranged classical potential while describing the nanocrystal by density-functional theory (DFT) [76], tight-binding [79] or classical potentials [83,84]. The Lagrangian is extended to include the interactions between PTM molecules with the nanocrystal and with one another:

\[
\mathcal{L} = T_{\text{NC}} - V_{\text{NC}} + T_{\text{PTM}} - V_{\text{PTM-PTM}} - V_{\text{PTM-NC}}
\] (1.4.2)

The whole system of PTM and nanocrystal is placed in a simulation cell of fixed volume and shape, and periodic boundary conditions (PBC) are employed. The cell must be sufficiently large to prevent interactions between periodic images of the nanocrystal. In order for the PTM to apply a realistic hydrostatic pressure, a sufficiently large number of molecules must be included and the PTM must flow sufficiently rapidly to accommodate structural changes in the nanocrystal. \( V_{\text{PTM-PTM}} \) can be tuned to prevent the liquid from freezing at high pressures. Similarly, \( V_{\text{PTM-NC}} \) must be chosen carefully to describe a realistic interaction between PTM molecules and nanocrystal. Martoňák, Molteni and Parrinello originally chose a purely repulsive soft-sphere potential to describe both \( V_{\text{PTM-NC}} \) and \( V_{\text{PTM-PTM}} \) taking the form [101]

\[
V_{\text{soft}} = \epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{R_{\alpha\beta}} \right)^{12},
\] (1.4.3)

where \( R_{\alpha\beta} \) is the distance between two particles \( \alpha \) and \( \beta \), \( \epsilon_{\alpha\beta} \) defines the strength and \( \sigma_{\alpha\beta} \) the range of the interaction. The repulsive nature of \( V_{\text{soft}} \) prevents the PTM from freezing up to high pressures. The PTM obeys a well-defined equation of state

\[
P = \frac{N_{\text{PTM}} k_B T}{V_{\text{PTM}}} f(z)
\] (1.4.4)
with $N_{\text{PTM}}$ the number of PTM particles, $k_B$ is the Boltzmann constant and $V_{\text{PTM}}$ the volume occupied by the PTM. $z$ is the reduced density

$$z = \frac{N_{\text{PTM}} \sigma_{\text{PTM}}^3}{\sqrt{2} V_{\text{PTM}}} \left( \frac{\epsilon_{\text{PTM}}}{k_B T} \right)^{1/4},$$

(1.4.5)

and the function $f(z)$ is obtained from simulations [102]. Once the value of $\epsilon_{\text{PTM}}$ and $\frac{N_{\text{PTM}}}{V_{\text{PTM}}}$ is set, for a given $T$ the choice of $\sigma_{\text{PTM}}$ fully determines $P$. $\sigma_{\text{PTM}}$ can thus be chosen to tune the applied pressure in simulations. The parameter $\sigma_{\text{PTM}-\text{NC}}$ was arbitrarily chosen to be sufficiently large to prevent penetration of PTM particles inside the nanocrystal up to high pressures and sufficiently small to make the $P V$ contribution dominant compared to the interface tension energy.

A conceptually similar ideal gas barostat approach was developed by Grünwald and Dellago [91]. The applied pressure is controlled by adjusting the number of gas particles in a shell around the nanocrystal. Closer to the approach presented in Chapter 7, isothermal-isobaric simulations of a whole system including PTM and nanocrystal were performed using the Lennard-Jones (LJ) potential to describe the interaction between PTM and nanocrystal [81, 85].

Most studies conducted so far have neglected the ligands that generally coat nanocrystals in experiments. Ligands play a crucial role both in the interaction of nanocrystals with their environment such as for example facilitating the dissolution in the PTM; it also has a strong effect on the structural behaviour of nanocrystal especially at the surfaces. It is therefore crucial to provide an adequate description of the ligands and their interaction both with the PTM and the rest of the nanocrystal.

### 1.4.2 Implicit methods

In a similar fashion to the Parrinello-Rahman approach, it is possible to use an extended Lagrangian for finite systems once a volume definition for the nanocrystal $V_{\text{NC}}$ is available:

$$\mathcal{L} = T - V - PV_{\text{NC}}.$$

(1.4.6)

The system associated with the Lagrangian defined in Eq. (1.4.6) evolves according to the equation of motion

$$\mathbf{F}_\alpha = m_\alpha \frac{d^2 \mathbf{R}_\alpha}{dt^2} = -\nabla_\alpha V - P \nabla_\alpha V_{\text{NC}},$$

(1.4.7)

where $\mathbf{R}_\alpha$ is the position and $m_\alpha$ the mass of each atom $\alpha$. The total force $\mathbf{F}_\alpha$ acting on each atom contains the conventional contribution from the interatomic potential and a contribution arising from the $P V$ term. If the system is stably bound, but not necessarily in thermal equilibrium, the virial theorem applies and

$$\left\langle \sum_{\alpha=1}^N m_\alpha \dot{\mathbf{R}}_\alpha^2 \right\rangle = -\left\langle \sum_{\alpha=1}^N \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha \right\rangle,$$

(1.4.8)
where $\langle \rangle$ denotes a temporal average. Substituting Eq. (1.4.7) into Eq. (1.4.8) yields

$$
\left\langle \sum_{\alpha=1}^{N} m_\alpha \mathbf{R}_\alpha^2 - \sum_{\alpha=1}^{N} \mathbf{R}_\alpha \cdot \nabla_\alpha V - \sum_{\alpha=1}^{N} \mathbf{R}_\alpha \cdot P \nabla_\alpha V_{NC} \right\rangle = 0.
$$

(1.4.9)

Using Euler’s theorem

$$
\sum_{\alpha=1}^{N} \mathbf{R}_\alpha \cdot \nabla_\alpha V_{NC} = 3V_{NC},
$$

(1.4.10)

we obtain

$$
P = \left\langle \frac{1}{3} \langle V_{NC} \rangle \left( \sum_{\alpha=1}^{N} m_\alpha \mathbf{R}_\alpha^2 - \sum_{\alpha=1}^{N} \mathbf{R}_\alpha \cdot \nabla_\alpha V \right) \right\rangle = \langle P_{\text{virial}} \rangle.
$$

(1.4.11)

On average, $P_{\text{virial}}$ balances the external pressure $P$ and the system defined by Eq. (1.4.6) evolves under isobaric-isothermal conditions when coupled to a suitable heat bath. $P_{\text{virial}}$ can be used to estimate the internal pressure in a nanocrystal, even when an explicit PTM is used, but will differ from the external pressure due to PTM-nanocrystal interactions. A conceptually different implicit approach was proposed by Kohanoff et al. [95]. After defining its surface, the nanocrystal interacts with a virtual bath modelled by stochastic forces applied on the surface atoms instead of the collisions with PTM particles of explicit approaches.

These different approaches have been compared elsewhere [100] and were shown to qualitatively reproduce results obtained with explicit solvents. The $PV$ approach relies on a volume definition for the finite system and we now outline a few examples of definitions.

### 1.4.3 Volume definitions

A variety of volume definitions have been suggested based on atomic or electronic coordinates and we refer the interested reader to the review by Baltazar et al. [100] for a more in depth comparison. We outline a couple of illustrative examples (Figure 1.4.1):

1. Sun and Gong proposed a definition of $V$ based on a sum of individual atomic volumes [103].
2. A method devised by Landau calculates the volume based on the average interatomic distance $R_{\text{av}}$ as $V \sim R_{\text{av}}^3$ [104].
3. Calvo and Doye introduced a volume definition based on the smallest convex polyhedron to inscribe all atoms [98, 99]. An extension to non-convex shapes is possible [97].
4. Corti et al. introduced a definition based on a shell atom [105–107].
5. Cococcioni et al. proposed a method whereby the volume is defined in terms of the electronic density by defining a charge isosurface of a certain cutoff value [1]. We shall discuss it in more detail in Chapter 4.
7. A volume definition by Sun and Gong approximates the finite object by simple geometrical shapes to evaluate the volume from the inertia tensor eigenvalues [112].

31
The latter was used as a post-processing volume evaluation in Chapter 7 so we shall now dwell on a few examples. The original definition by Sun and Gong estimated the volume of quasi-spherical Al clusters by inserting radii of gyration of the cluster into the equation for the volume of a sphere

\[ V = \frac{4}{3} \pi R^3 \] or an ellipsoid

\[ V = \frac{4}{3} \pi R_1 R_2 R_3. \]

For an ellipsoid, the principal semi-axes \( R_i \) are related to the radii of gyration about centroidal axes \( G_i \) as

\[ R_i = \sqrt{C G_i} = \sqrt{\frac{C I_i}{N}}. \] (1.4.12)

\( N \) is the number of atoms and \( C \) is a constant taking the value of \( \frac{3}{2} \) for a shell and \( \frac{5}{2} \) for a bulky ellipsoidal cluster. \( I_i \) are the principle moments about the centroidal axes obtained by diagonalising the \( 3 \times 3 \) massless (mass is unimportant in defining volume) inertia tensor \( I \) defined as:

\[ I_{jk} = \sum_{\alpha=1}^{N} R_{\alpha}^2 \delta_{ij} - R_{i,\alpha} R_{j,\alpha}. \] (1.4.13)

The volume of the ellipsoid can then be conveniently calculated from

\[ V = \frac{4}{3} \pi R_1 R_2 R_3 = \frac{4}{3} \pi \left( \frac{C}{N} \right)^{3/2} (I_1 I_2 I_3)^{1/2}. \] (1.4.14)
The product $I_1 I_2 I_3$ is the determinant of the inertia tensor which can be calculated without diagonalisation. More generally, for ellipsoidal (non-spherical) clusters we can write

$$V_{\text{ellip}} = \frac{4}{3} \pi \left( \frac{C}{N} \right)^{3/2} \sqrt{(-I_1 + I_2 + I_3) (I_1 - I_2 + I_3) (I_1 + I_2 - I_3)}. \quad (1.4.15)$$

This expression is only formally true for ellipsoidal clusters and will be approximate for shapes that deviate from it, Eq. (1.4.15) has the advantage of simplicity and can easily be evaluated as a postprocessing step [112] or used in dynamical simulations such as constant pressure MD from the atomic positions [100]. The same idea can also be extended to other geometrical shapes [114]. It can be shown that a cylinder of length $L$ and elliptical basis with semi-axes $a$ and $b$, has a volume

$$V_{\text{cyl}} = \pi abL = \pi \sqrt{\frac{24}{N^3}} (-I_1 + I_2 + I_3) (I_1 - I_2 + I_3) (I_1 + I_2 - I_3). \quad (1.4.16)$$

Similarly, for a cuboid of sides $a$, $b$ and $c$ we have

$$V_{\text{cub}} = abc = \sqrt{\frac{216}{N^3}} (-I_1 + I_2 + I_3) (I_1 - I_2 + I_3) (I_1 + I_2 - I_3). \quad (1.4.17)$$

1.4.4 Challenges: simulating large length- and time-scales

The nanocrystals of interest in this work are of an intermediate size: larger than molecules but too small to be treated satisfactorily with macroscopic concepts such as strain and stress fields in continuum models. An atomistic treatment is crucial to capture the details of the structural changes, including the shape and surface effects. The complex bonding rearrangements associated with structural transformations of materials such as semiconductors mean that \textit{ab initio} methods such as DFT are essential to capture the details of the structure and dynamics with accuracy. However, the large length- and time-scales associated with the structural transformations of experimentally relevant systems pose a significant computational challenge. The $O(N^3)$ scaling of the computational effort in traditional methods such as the plane-wave pseudopotential (PWPP) formulation of DFT limits the number of atoms that can be simulated to a few hundred and thereby seriously constrains the attainable sizes of nanocrystals. As outlined in Chapter 3, this can be addressed by working with a linear-scaling DFT code such as ONETEP [115], for which the favourable balance of cost and accuracy allows the investigation of nanocrystals with many thousands of atoms [116, 117]. Even then, the challenge persists of explicitly modelling the pressure transmission between solvent molecules and nanocrystals as in the PTM approach described in Section 1.4. The many degrees of freedom comprising realistic solvents and the many solvent-nanocrystal collisions that need to be averaged over to sample the appropriate thermodynamic ensemble exclude a full \textit{ab initio} treatment. One approach to tackle this challenge is to retain an explicit description of the solvent by embedding an \textit{ab initio} simulation of the nanocrystals within a cheaper classical description of the solvent [76–80, 87, 118]. However, sampling rare events such as structural transformations happening over long time-scales, whilst retaining a sufficiently short time step to describe the PTM-nanocrystal collisions, generally requires unfeasibly large numbers of molecular dynamics (MD) steps to be per-
formed. Transformations can be obtained within shorter simulation times by over-pressurising the systems but comparability with experiment is hindered in the process. Approaches exist to surmount this issue by accelerating the free energy landscape exploration (as discussed in Section 2.2) and have been applied to the pressure-induced structural transformations of nanocrystals [93, 119] and bulk crystals [120–123]. In practice these remain expensive and classical potentials must be used (Section 2.1). In Chapter 7 we perform classical metadynamics simulation of CdS nanocrystals under pressure immersed in an explicit PTM.

Alternatively, constant pressure simulations of finite systems can be performed, in both MD and quasistatic geometry optimisation, by directly optimising the enthalpy once a suitable definition for the finite volume has been made. This can be done in a variety of ways as discussed in Subsection 1.4.3 in terms of atomic or electronic coordinates leading to an implicit description of the PTM. In Chapter 4, we use an electronic enthalpy functional with volume definition based on electronic density isosurface [1]. We perform quasistatic geometry optimisations at zero temperature, removing the need for equilibration with barostats and thermostats thereby giving a comparatively inexpensive way of sampling the enthalpy landscape. We use the approach to simulate pressure-induced structural transformations in hydrogenated Si nanocrystals. In Chapter 5 and 6, we apply this same approach to hydrogenated Ge and CdS nanocrystals capped with phenyl or hydrogen ligands.
2 Classical dynamics

“The first principles of the universe are atoms and empty space; everything else is merely thought to exist.” ¹

“We may regard the present state of the universe as the effect of its past and the cause of its future. An intellect which at a certain moment would know all forces that set nature in motion, and all positions of all items of which nature is composed, if this intellect were also vast enough to submit these data to analysis, it would embrace in a single formula the movements of the greatest bodies of the universe and those of the tiniest atom; for such an intellect nothing would be uncertain and the future just like the past would be present before its eye.” ²

In Chapter 1, we discussed the importance of atomistic simulations for modelling nanomaterials under pressure and described different simulation strategies. The idea that matter, with its myriad of forms and behaviours, is the product of indivisible building blocks³ is an ancient one generally attributed to Indian [126] and Greek [124] philosophers. Laplace famously suggested that if a sufficiently vast intellect knew the positions and momenta of every atom in the Universe, it could determine their past and future values from Newton’s laws and thus know its fate. Such an intellect, as dreamt up by Laplace, became commercially available in the form of computers and their ever expanding power has enabled scientists to perform computer experiments on virtual “universes” with ever increasing sizes and durations. Ever since the first classical atomistic simulations performed in the 1950s, with Metropolis Monte Carlo [127] and MD [128] shortly thereafter, there has been an explosion in their use in a variety of disciplines. In fact, many systems of interest to scientists are composed of a large number of particles and finding analytic solutions describing their behaviour is generally precluded. Numerical approaches such as classical MD then become essential tools. In this chapter, we review fundamental concepts of classical MD such as interatomic potentials, thermodynamic ensembles and the challenge of simulating rare events such as structural transformations. We then describe the metadynamics method which can help accelerate such rare events and reconstruct the free energy surface.

¹ Democritus [124]
² P. S. Laplace [125]
³ The misnomer atom deriving from atomon the Greek for “indivisible”.

35
2.1 Fundamentals of classical molecular dynamics

In Newtonian mechanics, a system composed of \( N \) atoms is fully specified by the knowledge of the individual atomic positions \( \mathbf{R}_\alpha \) and momenta \( \mathbf{P}_\alpha \) at time \( t \) defining the microstate of the system \( \mathbb{M}(t) = \{ \mathbf{R}_1(t), ..., \mathbf{R}_N(t); \mathbf{P}_1(t), ..., \mathbf{P}_N(t) \} \). Its temporal evolution through phase space can be determined numerically by using Newton’s second law:

\[
\mathbf{F}_\alpha(t) = m_\alpha \mathbf{\ddot{R}}_\alpha(t),
\]  

(2.1.1)

where \( m_\alpha \) is the mass of atom \( \alpha \) and \( \mathbf{F}_\alpha \) the total force experienced due to its interaction with all other atoms. The temporal evolution of the system has to be discretised to be handled on computers and \( \mathbb{M}(t) \) is updated every timestep \( \Delta t \). The timestep has to be chosen carefully to guarantee the numerical stability of the algorithm. An appropriate choice is generally dictated by the fastest dynamics in the system under investigation, but is generally of the order of femtoseconds to capture hydrogen atom vibrations. In practice, a trade-off has to be struck in choosing a large timestep allowing the simulation of long trajectories, but sufficiently small to preserve numerical stability. Various algorithms exist to integrate the equations of motions but it is essential that they be stable, conserve total energy over long durations, and are time-reversible. A widely used algorithm which satisfies these criteria is the velocity-Verlet [129]. By Taylor expansion we have:

\[
\mathbf{R}_\alpha(t+\Delta t) = \mathbf{R}_\alpha(t) + \mathbf{\dot{R}}_\alpha(t) \Delta t + \frac{1}{2} \mathbf{\ddot{R}}_\alpha(t) (\Delta t)^2
\]  

(2.1.2)

\[
\mathbf{\dot{R}}_\alpha(t+\Delta t) = \mathbf{\dot{R}}_\alpha(t) + \frac{\mathbf{F}_\alpha(t) + \mathbf{F}_\alpha(t + \Delta t)}{2m_\alpha} \Delta t.
\]

(2.1.3)

The velocity Verlet MD algorithm works in the following steps:

1. Initialise \( \mathbf{R}_\alpha(t) \) and \( \mathbf{P}_\alpha(t) \);
2. Calculate the forces acting on each atom for a given configuration;
3. Update the positions:

\[
\mathbf{R}_\alpha(t+\Delta t) = \mathbf{R}_\alpha(t) + \mathbf{\dot{R}}_\alpha(t) \Delta t + \frac{1}{2} \mathbf{\ddot{R}}_\alpha(t) (\Delta t)^2;
\]  

(2.1.4)

4. Calculate \( \mathbf{F}_\alpha(t + \Delta t) \) with the updated coordinates \( \mathbf{R}_\alpha(t+\Delta t) \);
5. Update the velocities:

\[
\mathbf{\dot{R}}_\alpha(t+\Delta t) = \mathbf{\dot{R}}_\alpha(t) + \frac{\mathbf{F}_\alpha(t) + \mathbf{F}_\alpha(t + \Delta t)}{2m_\alpha} \Delta t;
\]

(2.1.5)

6. Repeat starting from step 2.
2.1.1 Interatomic potentials

A vital consideration in classical atomistic simulations is the question of how to model and approximate the interatomic potentials [130]. As we shall discuss in Chapter 3, starting from the many-body quantum mechanical Hamiltonian is generally too challenging. Approximations can be made to simplify the problem whilst retaining sufficient accuracy and the essential physics of the interaction. The interatomic potential can be constructed in a variety of ways but a simple approach consists in splitting the interatomic potential as:

\[
V(\{R_\alpha\}) = \sum_{\alpha \neq \beta} V^{(2)}(R_\alpha, R_\beta) + \sum_{\alpha \neq \beta \neq \gamma} V^{(3)}(R_\alpha, R_\beta, R_\gamma) + ..., \tag{2.1.6}
\]

where the two-body, three-body and higher order contributions are fitted either to experimental or theoretical (especially \textit{ab initio}) data. A crucial virtue of any fitted potential is its transferability: the ability to accurately reproduce properties and structures it was not fitted for. Another important consideration regards the computational expense incurred when evaluating forces as it dictates the time and length-scales that can be simulated. In practice, accuracy and computational economy are competing requirements and a compromise has to be found. It is thus essential to test the range of applicability and limitations of empirical potentials before employing them.

PBCs are commonly used to simulate periodic systems with reduced computational cost [131]. Even then, each of \(N\) atoms in the simulation cell interacts not only with the other \(N - 1\) atoms but also with an infinite number of periodic images. A cutoff radius \(R_c\) is generally introduced so that each atom only interacts with an average \(n_{av}\) neighbouring atoms within \(R_c\) and the force evaluation workload scales linearly (or \(O(n_{av}N)\) ) as opposed to quadratically. The terms in Eq. (2.1.6) account for the chemophysical interactions of the system and include bonded contributions for bond-stretching, angle-bending and dihedral torsion but also non-bonded ones such as vdW and Coulomb interactions. The widely used LJ potential [132] contains a repulsive part scaling as \(R_{\alpha\beta}^{-12}\), approximating the Pauli exclusion at short ranges, and an attractive long-range part scaling as \(R_{\alpha\beta}^{-6}\) which describes spontaneous dipole-induced dipole interactions (also known as London dispersion). It takes the form:

\[
V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{R_{\alpha\beta}} \right)^{12} - \left( \frac{\sigma}{R_{\alpha\beta}} \right)^{6} \right], \tag{2.1.7}
\]

where \(R_{\alpha\beta}\) is the separation between atoms \(\alpha\) and \(\beta\), \(\sigma\) defines the position of its minimum (at \(R_{\alpha\beta} = 2^{1/6}\sigma\)) and \(\epsilon\) its depth. These parameters are determined by mixing rules when different atomic species, labelled \(a\) and \(b\), are interacting. In this work, we use the Lorentz-Berthelot rule defined as:

\[
\sigma_{ab} = \sigma_{ba} = \frac{\sigma_{aa} + \sigma_{bb}}{2}, \tag{2.1.8}
\]

\[
\epsilon_{ab} = \epsilon_{ba} = \sqrt{\epsilon_{aa}\epsilon_{bb}}. \tag{2.1.9}
\]

Electrostatic interactions are accounted for by partitioning the total charge density into partial charges associated with individual atoms. The interaction between two atoms with partial charges
\(q_\alpha\) and \(q_\beta\) is described \(^4\) by the pairwise Coulomb potential:

\[
V_{\text{Coulomb}} = \frac{q_\alpha q_\beta}{R_{\alpha\beta}}.
\] (2.1.10)

The partial charges are not well-defined quantum mechanical observables and there is no unique way of determining them. Various schemes have been proposed for the partitioning \([133–136]\) and a commonly used one consists in deriving the partial charges from a least-square fit to the electrostatic potential \([137]\). This is the basis of the restrained electrostatic potential fitting (RESP) \([134,138,139]\) we employ in this work. It consists in assigning charges that reproduce the electrostatic potential obtained by *ab initio* simulations on a cavity around the molecule defined by its atomic vdw radii. Long-range forces, such as Coulomb or vdw forces, can be calculated efficiently in real and reciprocal space using methods such as Ewald summations \([140]\). Truncations can lead to artifacts and tail corrections can be used \([141]\).

There exists a wealth of interatomic potentials describing the bonded interactions, all tailored to specific materials and applications. Potentials such as the Tersoff \([142]\), Stillinger-Weber \([143]\) and other machine-learning ones are widely used for covalently bonded materials. A widely used potential for organic molecules is the generalized AMBER forcefield \([144, 145]\), which includes bonded terms and takes the general form:

\[
V_{\text{Amber}}(\{R_\alpha\}) = \sum_{\text{bonds}} k_b (l - l_0)^2 + \sum_{\text{angles}} k_a (\theta - \theta_0)^2
\]

\[
+ \sum_{\text{dihedrals}} k_d [1 + d \cos(n \phi)] + \sum_{\alpha \neq \beta} \left[ \frac{q_\alpha q_\beta}{R_{\alpha\beta}} + 4 \epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{R_{\alpha\beta}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{R_{\alpha\beta}} \right)^6 \right],
\] (2.1.11)

where \(l_0\) and \(\theta_0\) are equilibrium bond lengths and angles; \(k_b\), \(k_a\) and \(k_d\) are force constants; \(n\) is the multiplicity and \(d\) a phase factor of the dihedral (taking the value +1 or −1). All the parameters can be fitted to *ab initio* or experimental data.

Materials such as CdS and CdSe with partly ionic bonding can be modelled with a simple pair potential such as the Rabani potential \([146]\) defined as:

\[
V_{\text{Rabani}} = \frac{q_\alpha q_\beta}{R_{\alpha\beta}} + 4 \epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{R_{\alpha\beta}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{R_{\alpha\beta}} \right)^6.
\] (2.1.13)

Containing Coulombic and LJ components, it has been shown to reproduce experimental lattice and elastic constants as well as phonon dispersion curves of bulk CdS and CdSe WZ, ZB and RS phases.

### 2.1.2 Thermodynamic ensembles

The equilibrium properties of macroscopic systems are well-described by thermodynamics and statistical mechanics provides the link between the atomistic and macroscopic properties. Statistical mechanics introduces probability distributions, called thermodynamic ensembles, for microscopic configurations to yield macroscopic properties under equilibrium conditions. An important example

\(^4\)Using Hartree atomic units throughout: \(4\pi\varepsilon_0 = \hbar = m_e = e = 1\).
is the microcanonical ensemble which corresponds to an isolated system in a state of equilibrium and constant particle number \( N \), volume \( V \) and internal energy \( U \) (also referred to as \( NVE \)). Newton’s equations are time-reversible and according to Noether’s theorem energy-conserving. Thus the MD simulation of an isolated system can in principle approximate the microcanonical ensemble. There can, however, be a large discrepancy between the time- and length-scale of atomic processes and macroscopic measurements conducted in the laboratory. The finite spatial and temporal resolution of probes imply that experimental observations are the result of a statistical averaging over the many atomic configurations adopted in the duration and sample of the measurement. For a given observable \( \mathcal{O} \), whose instantaneous value at time \( t \) is a function of the microstate \( \mathcal{O}(M(t)) \), contact can be made with the experimental value \( \mathcal{O}_{\text{exp}} \) by averaging out the microscopic properties over a sufficiently long MD simulation with \( N_{\text{steps}} \) timesteps and duration \( \tau = N_{\text{steps}} \Delta t \):

\[
\mathcal{O}_{\text{exp}} = \langle \mathcal{O}(t) \rangle \approx \frac{1}{N_{\text{steps}}} \sum_{n=0}^{N_{\text{steps}}} \mathcal{O}(M(t_n)).
\]

The principle of equal a priori probabilities states that in the microcanonical ensemble, every accessible microstate of the system will be equiprobably explored over sufficiently long periods of time. This implies that ensemble averages and temporal averages are equivalent over sufficiently long simulations.

Most experiments, however, are carried out under different conditions such as for example constant temperature \( T \) and pressure \( P \) and corresponding statistical ensembles can be derived starting from the principle of equal a priori probabilities. A key result of equilibrium statistical mechanics is that the probability \( p(M(t)) \) of a microstate of a system in equilibrium with a heat, pressure or particle reservoirs is respectively weighted by \( e^{-U/k_B T} \), \( e^{-PV/k_B T} \) and \( e^{-\mu N/k_B T} \) where \( \mu \) is the chemical potential. In the canonical (or \( NVT \)) ensemble, summing over all possible microstates and normalising gives us the probability distribution:

\[
p(M) = \frac{1}{Z} e^{-U/k_B T},
\]

with the partition function given by

\[
Z(N, V, T) = \int_{M} e^{-U/k_B T} dM.
\]

The characteristic thermodynamic potential, that is minimised at equilibrium, is the Helmoltz free energy given by:

\[
F = U - TS = -k_B T \ln Z.
\]

Following Guggenheim [147], the partition function for the isobaric-isothermal (or \( NPT \)) ensemble can be constructed as

\[
\Delta(N, P, T) = \int_{V} Z(N, V, T) e^{-PV/k_B T} dV/V_0,
\]

where \( V_0 \) defines the volume scale and in the thermodynamic limit

\[
V_0 = \frac{k_B T}{P}.
\]

39
The characteristic thermodynamic potential is the Gibbs free energy given by

\[ G = U + PV - TS = -k_B T \ln \Delta. \]  

(2.1.20)

There are subtleties associated with the choice of \( V_0 \) away from the thermodynamic limit and the reader is referred to Corti et al. for discussions [106, 107].

It is useful to introduce thermostats and barostats in MD simulations in an attempt to reproduce these ensembles. A broad gamut of thermostats exist that are designed to mimic the effect of an external heat reservoir and perform isothermal simulations. Widely used examples include velocity rescaling [131], Andersen [71], Berendsen [148], Nosé [149] and Bussi [150] thermostats. The Langevin thermostat modifies Newton’s equation to include a stochastic term:

\[ \dot{P}_\alpha(t) = F_\alpha(t) - \varsigma_\alpha P_\alpha(t) + f_\alpha(t). \]  

(2.1.21)

\( \varsigma_\alpha \) is a damping coefficient and \( f_\alpha(t) \) a stochastic force related via the fluctuation-dissipation theorem [151] as

\[ \langle f_\alpha(t) f_\alpha(0) \rangle = 2\varsigma_\alpha m_\alpha k_B T \delta t. \]  

(2.1.22)

Various approaches exist for \( NPT \) simulations such as the Parrinello-Rahman [72, 73], Nosé-Hoover [152, 153] or Bussi [154] methods. In the present work we used a Langevin thermostat in conjunction with a Berendsen barostat obeying the equation of motion:

\[ \frac{dP}{dt} = \bar{P} - P, \]  

(2.1.23)

with \( P \) the instantaneous pressure, \( \bar{P} \) the target pressure of the external barostat and \( \tau_P \) the relaxation time constant. The algorithm works by scaling the coordinates and simulation cell vectors by a factor \( \eta^{\frac{1}{3}} \):

\[ \eta = 1 - \frac{\Delta t}{B_T \tau_P} (\bar{P} - P), \]  

(2.1.24)

where \( B_T \) is the isothermal bulk modulus.

2.1.3 Metastability and rare events

Running sufficiently long MD simulations that satisfy the requirement of Eq. (2.1.14) can be impractical especially when the system displays metastability. Metastability occurs in systems characterised by regions of phase space with relatively large probabilities separated by regions of low probability. This translates in the system spending large amounts of time in a high probability region with only occasional hops into other such regions. In other words, such a crossing is a rare event and would take a very long time to be observed. Many natural phenomena of interest are rare events, including chemical reactions and the pressure-induced structural transformations we are interested in. It is useful to make a dimensional reduction [155] of the many \( x \equiv \{x_j\} \) coordinates describing the system, such as atomic positions but also electronic and auxiliary coordinates, in terms of a lower-dimensional set of collective variables (CVs) \( \{S_i(x)\} \) with \( i \in [1, d] \). If a good coarse-grained
description of the system is possible, the evolution of the system can be effectively monitored by looking at a small number \( d \) of CV values \( s_i(t) = S_i(x(t)) \). We distinguish the CV as a function of the coordinates and as a value by using respectively \( S(x) \) and \( s \). The equilibrium probability distribution is given by the histogram

\[
p(s) = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \delta(S(x(t')) - s),
\]

sampled over an infinitely long trajectory. It can be approximated in simulations by a discretised version

\[
p(s) \sim \frac{1}{N_{\text{steps}} \Delta s} \sum_{n=0}^{N_{\text{steps}}} \chi_s(S(x(t'))),
\]

where we introduce the top hat function defined as \( \chi_s(S(x)) = 1 \) if \( S(x) \in [s, s + \Delta s] \) and zero when \( S(x) \not\in [s, s + \Delta s] \). For a system in thermal equilibrium at temperature \( T \) and pressure \( P \), the Gibbs free energy can be obtained as

\[
G(s) = -\frac{1}{\beta} \ln(p(s)),
\]

where \( \beta = \frac{1}{k_B T} \). When the system displays metastability, the system will get trapped in local minima of \( G(s) \) (corresponding to local maxima in \( p(s) \)) and much computer time will be spent redundantly sampling the corresponding well before the systems escapes from it. A variety of methods have been developed over the years to efficiently sample the free energy surface (FES) and accelerate rare events without renouncing the atomistic description (i.e. coarse-graining). These approaches can be classified following Laio and Gervasio [156] as methods based on: bias potentials, transition path searches, saddle point searches and simultaneous free energy sampling. Many of these techniques rely on the dimensional reduction we described above to focus the computational effort along predetermined CVs: either to accelerate a transition over a saddle point, or to reconstruct the free energy along a path. We are particularly interested in methods, such as umbrella sampling [157] or steered MD [158], where an external potential bias is applied to enhance the sampling as a function of predetermined CVs in low probability regions of \( G(s) \). The Gibbs free energy can from Eq. (2.1.15)-(2.1.20) be decomposed into contributions due to kinetic energy, volume and potential energy:

\[
-\beta G = \ln \Delta_T + \ln \Delta_P V + \ln \Delta_V.
\]

Adding a bias potential as a function of the CVs \( V_B(S(x)) \), the biased Gibbs free energy at value \( s' \) is given by

\[
-\beta G'(s') = \ln \Delta_T + \ln \Delta_P V + \ln \sum_x e^{-\beta V_B(S(x))} e^{-\beta V(x)} \delta(s' - S(x))
\]

\[
= \ln \Delta_T + \ln \Delta_P V + \ln e^{-\beta V_B(s')} \sum_x e^{-\beta V(x)} \delta(s' - S(x)).
\]

It is assumed that the bias is sufficiently gentle, and compensated by virial corrections to keep the internal pressure constant despite biases, and the system equilibrated with thermostat and barostat
at all times. When this is the case, the $\Delta T$ and $\Delta PV$ contributions remain constant despite the bias and have a negligible effect on the evolution of the system. This is the justification behind using the configurational free energy only, henceforth referred to as free energy, in many free energy sampling methods. It is generally assumed that the dynamics of the system is well-described by the configurational part of the canonical probability distribution

$$ p(x) = \frac{e^{-\beta V(x)}}{Z},$$  

(2.1.31)

with the partition function given by

$$ Z = \int dx e^{-\beta V(x)}.$$  

(2.1.32)

The probability distribution in terms of a CV is given by:

$$ p(s) = \frac{1}{Z} \int dx \exp (-\beta V(x)) \delta(s - S(x)),$$  

(2.1.33)

and the free energy $F(s)$ is given by

$$ -\beta F(s) = \ln(p(s)) = \ln \left( \frac{1}{Z} \int dx \exp (-\beta V(x)) \delta(s - S(x)) \right).$$  

(2.1.34)

It is instructive to consider the umbrella sampling method which introduces a single collective variable $S_1(x)$ to bias the dynamics with a potential $V_B(S_1(x))$. The biased probability distribution resulting from the inclusion of the bias potential is

$$ p_B(s) = \frac{1}{Z_B} \int dx e^{-\beta (V_B(S_1(x)) + V(x))} \delta(s - S_1(x))$$

$$ = \frac{Z}{Z_B} e^{-\beta V_B(s)} \frac{1}{Z} \int dx e^{-\beta V(x)} \delta(s - S_1(x))$$

(2.1.35)

$$ = \frac{Z}{Z_B} e^{-\beta (V_B(s) + F(s))},$$  

(2.1.36)

where $Z_B$ is the biased canonical partition function. The biased free energy is given by

$$ -\beta F_B(s) = \ln(p_B(s)) = F(s) + V_B(s) + c_B,$$  

(2.1.37)

and shows that the effect of the bias on the free energy is additive. The constant

$$ c_B = \frac{1}{\beta} \ln \frac{Z}{Z_B}$$  

(2.1.38)

has no effect on free energy differences and barrier heights. The unbiased free energy and probability
distribution can always be recovered from Eq. 2.1.37 as
\[ F(s) = -V_B(s) - \frac{1}{\beta} \ln(p_B(s)) + c_B = F_B(s) - V_B(s) + c_B, \] (2.1.39)
and Eq. (2.1.35) as
\[ p(s) = p_B(s)e^{\beta(V_B(s) - c_B)}. \] (2.1.40)

This shows that one can obtain unbiased equilibrium properties from biased simulations by weighting every conformation appropriately. If we knew the shape of \( F(s) \) ahead of time, we could apply a bias \(-V(s)\) to make \( F_B(s) \) flat and barrierless so that all configurations would be sampled during an MD run without getting trapped in metastable configurations. Unfortunately, \( F(s) \) is generally not known ahead of time and adaptative techniques can be used to construct the bias potential [159,160]. If however we have an idea of where free energy barriers are located, without a detailed knowledge of \( F(s) \), we can still drive the system over them by applying a moving restraint on the CV. When including a moving restraint \( V_{\lambda}^{\text{steer}} \) along a predefined trajectory parametrised by \( \lambda(t) \), for example a harmonic potential with stiffness \( k(t) \), the potential is modified as:
\[ V_{\lambda}(x,t) = V(x) + V_{\lambda}^{\text{steer}}(x,t) = V(x) + \frac{k(t)}{2} (s(x) - s_{\lambda}(t))^2. \] (2.1.41)

From Eq. (2.1.40) we have:
\[ p_B = p(s)e^{-\beta\left(\frac{k(t)}{2}(s(x) - s_{\lambda}(t))^2 - c_B\right)}, \] (2.1.42)
and for sufficiently large \( k \) only configurations with values around \( s_{\lambda} \) will be sampled. This is the idea behind steered MD: an MD run can be biased by modifying the potential to include a time dependent external component \( V_{\lambda}^{\text{steer}} \) to sample specific regions of phase space.

It has been shown by Jarzynski [161] that equilibrium free energy differences \( \Delta F \) between two system configurations can be evaluated by averaging over the work \( W \) performed by driving the system fast and out of equilibrium between these two configurations:
\[ \Delta F = -\frac{1}{\beta} \ln e^{-\beta W}, \] (2.1.43)
where
\[ W = \int_0^{t_s} dt \frac{\partial H_{\lambda}(t)}{\partial t}. \] (2.1.44)
The overbar denotes the average over an ensemble of trajectories. In practice however, there will be a large error associated with the evaluation of the work and one has to average over a very large number of trajectories. In 2002, Laio and Parrinello introduced the metadynamics method [162] to address some of the issues of existing free-energy sampling techniques whilst retaining many of their best features. We will now describe the metadynamics method in more detail.
2.2 Metadynamics

2.2.1 Metadynamics

Metadynamics is a versatile and accurate adaptative umbrella sampling method that has ever since its conception been successfully applied to a variety of applications, in fields as disparate as chemistry, condensed matter and biology. Like other approaches, metadynamics relies on a set of predefined CVs that are biased during an MD run. A major difference, however, is that the bias is constructed cumulatively by a history-dependent potential built from the sum of Gaussians deposited along the trajectory in CV space. This approach, metaphorically described as “filling the free energy surface with computational sand” [162], allows one on the one hand to accelerate rare events, and on the other to recursively reconstruct the FES. Different flavours of metadynamics exist and we refer the reader to reviews for a comprehensive perspective [156, 163]. We are interested in so-called “continuous direct” metadynamics where the bias is applied continuously on the microscopic coordinates of the system during an MD simulation. Small repulsive Gaussians, the metaphorical computational sand heaps, are added at time-intervals \( \tau_G \) along the trajectory \( S(x(t)) \) in CV space thereby preventing the system from re-exploring configurations. This history-dependent bias potential \( V_G \) has the form:

\[
V_G(S(x), t) = \omega \sum_{t'=\tau_G,2\tau_G,...}^{t<\tau} \exp \left( - \sum_{i=1}^{d} \frac{(S_i(x) - s_i(t'))^2}{2\delta s_i^2} \right). \tag{2.2.1}
\]

The deposited Gaussians are defined by their height \( \omega \), width \( \delta s_i \) and frequency of deposition \( \frac{1}{\tau_G} \). These parameters have to be chosen carefully for an accurate and effective sampling of the FES [164]. Heuristically, depositing large Gaussians will result in rapidly filling the free energy landscape but will also be afflicted by large errors on the reconstructed FES. On the other hand, using small Gaussians will lead to a better reconstruction at the expense of longer simulation (assuming the same deposition frequency). Careful consideration must also go into the choice of \( \frac{1}{\tau_G} \) as a large value can drive the system too far off-equilibrium or lead to unphysical behaviours such as destroying or jamming the system. Let us illustrate this with a simplified one-dimensional model \( F(s) \) containing three local minima A, B and C. As seen from Figure 2.2.1, the system starts off in a metastable state corresponding to B. The added Gaussians progressively fill the well and allow it to escape into lower minima A after 135 deposition strides by overcoming the saddle point lowest in energy. Once the basins A and B are filled, the system drops into the global minimum of \( F(s) \) associated with basin C at stride 810. After stride 1650, all three basins are filled and the system exhibits diffusive behaviour in \( s \). In contrast, such an exploration of configuration space would take prohibitively long in normal MD, when the barrier heights are larger than thermal fluctuations, and much computer time would be spent sampling the same basin. This example demonstrates the threefold utility of metadynamics in:

- Accelerating rare-events by driving the system away from its starting equilibrium configuration.
- Exploring reaction pathways with no \textit{a priori} knowledge of the landscape as the system will escape through the lowest saddle point in \( F(s) \).
Figure 2.2.1: Model metadynamics simulation where the time $t$ is measured in units of deposition strides $\tau_G$: (a) shows the time evolution of CV $s$ during the run and (b) shows the filling of $F(s)$ over time with the thin line showing $V_G(t)$. Figures reproduced from Ref. [163].

- Once the free energy landscape is filled after time $t = t_{\text{conv}}$ and the system diffuses in CV space, the FES can be reconstructed as

$$F(s) = -V_G(s, t > t_{\text{conv}}) + C,$$

(2.2.2)

where $C$ is an irrelevant constant as we are interested in free energy differences.

Eq. (2.2.2) constitutes a remarkable result as it states that $F(s)$, an equilibrium property, can be obtained by non-equilibrium dynamics. Originally postulated on the basis of intuition, it has been shown both empirically [164–166] and theoretically [167] that a metadynamics run provides an unbiased estimator of the free energy with error

$$\varepsilon \propto \sqrt{\frac{\omega}{D^3} f_d},$$

(2.2.3)

where $D$ is the system dependent diffusion coefficient in CV-space and $f_d(\frac{\delta s}{S})$ is a complicated decreasing function of $\delta s/S$ and depends on the dimension of the CVs [156]. Some important difficulties associated with the metadynamics method:

- Convergence can be problematic for two reasons. On the one hand, the time required to fill a multidimensional well scales exponentially (assuming constant deposition rate) with the dimensionality of CV-space as $(\frac{1}{\delta^d})^d$. On the other hand, the resolution of the reconstructed $F(s)$ is limited by $\delta s$. There is thus a trade-off to be made between increasing the size of the Gaussian to speed up the calculation and reducing it for an accurate reconstruction of $F(s)$ and one is generally confined to 2 or 3 CVs. Also it is not trivial with “discrete continuous” metadynamics to decide when to stop a run as it does not converge asymptotically to a
well-defined bias. This can result in the reconstructed FES having oscillations or overfillings compared to $F(s)$ [166–168].

- Identifying a handful of CVs for describing complex processes is challenging. The set of CVs should distinguish between initial and final states and describe all intermediates, but should also include all slow modes of the system. If an important CV is omitted, transition into orthogonal “hidden” degrees of freedom can lead to hysteresis and overfilling of certain regions of CV-space invalidating Eq. (2.2.2).

Well-tempered metadynamics has been introduced to deal with the first issue and recently proven to work as expected [166, 168, 169]. Besides, it is not a problem when one is interested, as in the present work, in accelerating rare events rather than reconstructing $F(s)$. Instead, overcoming the second problem generally requires physical insight into the process under investigation and one must often proceed by trial and error.

### 2.2.2 Choosing collective variables

An adequate choice of CVs is crucial for metadynamics to work. The set of CVs must satisfy the following requirements:

1. Discriminate between initial, final and all relevant intermediate states of the process under investigation.

2. Be limited in number to 2-3 CVs for convergence purposes.

3. Include all slow modes of the system in their description.

Many systems of interest in physics, chemistry and biology display complex atomistic dynamics resulting from an inherently high-dimensional FES and satisfying all three requirements simultaneously appears difficult. There is, however, a growing body of evidence [170, 171] suggesting that in many cases the low energy portion of the FES, which is most relevant to the chemistry, can be represented in low dimensions. This suggests that it is in principle possible to find CVs that allow the projection of the high-dimensional FES onto a low dimensional one without losing key features such as free energy basins and low lying saddle points. This dimensional reduction inherently consists in discarding information about the high-dimensional atomistic process and doing this incorrectly can distort the dynamics or blur out key features of the FES [172]. It is therefore crucial to use physical intuition about the problem in choosing CVs that distinguish initial and final states as well as important transition states. One can for example run unbiased simulations and monitor candidate CVs during sufficiently long trajectories to determine whether they are good descriptors of the transformation. Running a simulation that samples phase space sufficiently can, however, take unfeasibly long for complex systems. Finding CVs \textit{a priori} solely based on intuition can be daunting and machine-learning approaches such as sketch-map have been introduced to automate this process [172–174].

To illustrate the importance of the third requirement, we consider a Z-shaped potential (Figure 2.2.2) with two metastable states A and B. Starting from basin B and biasing $s_1$, the basin fills
Figure 2.2.2: (a) model Z-shaped potential as function of CVs $s_1$ and $s_2$. (b) the evolution of the $V_G(t)$ when biasing only $s_1$ shows hysteresis in the reconstruction of the free energy. Figures taken from Ref. [163].

up but remains stuck due to a free energy barrier along the orthogonal $s_2$ direction. This results in an overfilling of basin B and consequent overestimation of the saddle point. The overall effect is that the $F(s)$ does not fill up evenly invalidating Eq. (2.2.2). It is crucial when testing CVs, to look out for hysteric behaviour in the free energy reconstruction as it can be symptomatic of hidden orthogonal modes [156, 163, 175]. Replica exchange methods such as parallel tempering [176] have proven useful for sampling transverse coordinates. Multiple copies of the same system are independently simulated at various temperatures and configurations are swapped at regular intervals to prevent the system being trapped in local minima.

Many CVs, based on local or global quantities, have been proposed and used successfully in various applications. We refer the reader to reviews for a more comprehensive list [156, 163]. We outline a few examples of relevance to the rest of the thesis:

- Geometrical CVs: these can include structural information such as bond distances, angles, dihedrals and so forth. They are particularly useful for chemical and biological systems with processes involving structural rearrangements such as chemical reactions or protein folding. Information about the shape of structures is encoded in parameters such as gyration radii and inertia tensor and have been successfully used [114].

- Coordination numbers: the coordination number $N_{\text{coord}}$ can be calculated as:

$$N_{\text{coord}} = \sum_{\alpha \neq \beta} f_{\text{step}}(R_{\alpha\beta}) = \sum_{\alpha \neq \beta} \frac{1 - (R_{\alpha\beta}/R_0)^n}{1 - (R_{\alpha\beta}/R_0)^m},$$

(2.2.4)

where the indices $\alpha$ and $\beta$ run over two sets of atoms and $f_{\text{step}}$ is a smeared step function (so that it can be differentiated) approximately one for $R < R_0$ and zero otherwise. Its asymptotic behaviour and smoothness can be controlled with $n$ and $m$ as for large $R$ we have $f_{\text{step}}(R) \sim 1/R^{m-n}$. Many structural or chemical transformation are accompanied by changes
in coordination numbers and it is therefore a useful and widely used CV.

• Steinhardt parameters: coordination numbers are generally not sufficient to capture the local bonding symmetry. As an example, the LDA or diamond crystalline structures of silicon have the same fourfold coordination. The Steinhardt, or bond order, parameters use an expansion in terms of spherical harmonics to measure the order in the first coordination shell around an atom $\alpha$ [177]. We define the complex vector

$$q_{lm}(\alpha) = \frac{\sum_\beta f_{\text{step}}(R_{\alpha\beta})Y_{lm}(R_{\alpha\beta})}{\sum_\beta f_{\text{step}}(R_{\alpha\beta})},$$

(2.2.5)

where $R_{\alpha\beta}$ is the vector connecting two atoms $\alpha$ and $\beta$, $f_{\text{step}}(R_{\alpha\beta})$ is a switching function analogous to Eq. (2.2.4) and $Y_{lm}$ the $l^{th}$ order spherical harmonic. The Steinhardt parameter is calculated as

$$Q_l(\alpha) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} q_{lm}^*(\alpha)q_{lm}(\alpha).$$

(2.2.6)

Eq. (2.2.6) gives a rotationally invariant value of the local symmetry of an atomic configuration. $Q_3$, $Q_4$ and $Q_6$ are obtained using the 3$^{rd}$, 4$^{th}$ and 6$^{th}$ order spherical harmonics respectively. Together they can distinguish between ordered first shell symmetries such as fcc, bcc and hcp and more disordered structures such as amorphous or liquid. It has been shown [178] that averaging over a group of atoms can help discriminate features due to order in the second coordination shell which is desirable in numerous cases.
3 Linear-scaling density-functional theory

“Nature isn’t classical, dammit, and if you want to make a simulation of nature, you’d better make it quantum mechanical, and by golly it’s a wonderful problem, because it doesn’t look so easy.”

In Chapter 2, we described classical atomistic simulations. A quantum mechanical treatment is, however, needed for an accurate atomistic description of materials. The birth of quantum mechanics at the turn of the 20th century [180–182] has revolutionised our understanding of Nature [183–185] and ushered in paradigmatic shifts [186] in a range of scientific disciplines: including physics, chemistry and materials science but also seemingly remote ones such as biology and geology. Indeed, some of the most basic properties of matter, such as the fact that we do not fall through the floor or the structure of the periodic table, can only be explained by invoking quantum mechanics. While ontological questions remain [187–190], the stunning accuracy [191] and success of the theory in a variety of applications leave little question that one needs to solve the equations of quantum mechanics to understand and predict the behaviour of real materials. Unfortunately, these cannot be solved analytically except for a handful of simple cases and finding a numerical solution to the equations becomes necessary. Even so, the numerical complexity increases exponentially with the size of the system under investigation making computers an indispensable tool for understanding the structure of matter. First-principles, or ab initio, quantum mechanical simulations are particularly appealing as the only prior knowledge required is that of the atomic numbers of the species of interest. A crucial development occurred in the mid-sixties with the introduction of density-functional theory (DFT) [192, 193], greatly reducing the computational cost by working with the electronic density in the three spatial dimensions as opposed to the $3N_e$ dimensional Hilbert space of the full wavefunction, where $N_e$ is the number of electrons and we ignore the spin degree of freedom. The plane-wave pseudopotential (PWPP) approach, with an approximate treatment of exchange and correlation of the interacting electrons, has proven a particularly powerful and versatile tool both for understanding existing materials and predicting new ones that are still beyond the reach of experimental probes. However, the computational cost of traditional PWPP calculations has been found to asymptotically scale as the cube power of the number of atoms $N$, i.e. as $O(N^3)$, limiting the routinely attainable system size with current computer technology to a few hundred atoms. Over the last three decades [194,195], an ongoing research effort has been directed towards developing DFT algorithms for which the computational effort scales linearly with the number of atoms, i.e. as $O(N)$, to make the best possible use of computational resources. Only so can we hope to routinely simulate the larger system.

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R. P. Feynman [179]
sizes, such as nanostructures and proteins, that are of scientific and technological interest.

In this chapter, we describe the formalism of DFT and derive the Kohn-Sham equations. We present the Born-Oppenheimer approximations for decoupling the degrees of freedom of nuclei and electron. We also introduce the pseudopotential and local density approximation for treating exchange and correlation, and Bloch’s theorem to treat periodic systems. We then describe the formalism behind linear-scaling DFT calculations both of energies and forces. We subsequently expand on the projector augmented wave method (PAW) and linear-response time-dependent DFT (LR-TDDFT) within the linear-scaling DFT framework.

3.1 Density-functional theory

3.1.1 The Born-Oppenheimer approximation

Modern quantum mechanics \cite{196–201} postulates that the behaviour of a non-relativistic quantum system described by its wavefunction $|\tilde{\Psi}\rangle$ is dictated by the time-dependent Schrödinger equation \cite{202}:

$$\hat{H}|\tilde{\Psi}\rangle = i\frac{\partial}{\partial t}|\tilde{\Psi}\rangle,$$

where we employ the Dirac bra-ket notation \cite{203} and Hartree atomic units throughout. $\hat{H}$ is the Hamiltonian or energy operator that for the many-body systems of interacting nuclei and electrons respectively located at $R_\alpha$ and $r_i$ takes the form

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_\alpha \frac{1}{2m_\alpha} \nabla_\alpha^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{|r_i - R_\alpha|} + \frac{1}{2}\sum_{i,j\neq i} \frac{1}{|r_i - r_j|} + \frac{1}{2}\sum_\alpha \sum_\beta \neq \alpha \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}. \quad (3.1.2)$$

Latin and Greek indices are respectively used for the electrons and nuclei, and $Z_\alpha$ are the atomic numbers and $m_\alpha$ the atomic masses. For simplicity we neglect spin, the possibility of external fields and finite volume effect of the nuclei. Relativistic effects can become important for heavy atoms but these can be treated in the construction of the pseudopotentials in a post hoc manner.

Except for the smallest of systems, Eq. (3.1.2) becomes analytically and numerically intractable due to the large number of variables. Approximations are thus necessary. Since $\hat{H}$ is time-independent, we proceed by separation of variables and write solutions as

$$|\tilde{\Psi}((r_i), (R_\alpha), t)\rangle = \Phi((r_i), (R_\alpha))\Theta(t), \quad (3.1.3)$$

which upon substitution in Eq. (3.1.1) gives the equations:

$$\hat{H}\Phi((r_i), (R_\alpha)) = \Xi\Phi((r_i), (R_\alpha)) \quad (3.1.4)$$

$$i\frac{\partial}{\partial t}\Theta(t) = \Xi\Theta(t). \quad (3.1.5)$$
Ξ are the vibronic energy eigenvalues, $|\Phi\rangle$ is the time-independent part and $|\Theta\rangle$ the time-dependent part of the many-body wavefunctions. Integrating Eq. (3.1.5) gives the time-dependent form of the eigenfunctions of $\hat{H}$:

$$\tilde{\Psi}(\{r_i\}, \{R_\alpha\}, t) = \Phi(\{r_i\}, \{R_\alpha\})\exp(-i\Xi t). \quad (3.1.6)$$

The vibronic eigenfunctions describe the combined system of nuclei and electrons. To simplify matters further, electronic and ionic degrees of freedom can be decoupled as

$$\Phi(\{r_i\}, \{R_\alpha\}) = \Psi(\{r_i\}; \{R_\alpha\}) \Upsilon(\{R_\alpha\}), \quad (3.1.7)$$

where the electronic wavefunction now depends parametrically on the nuclear coordinates. This is known as the adiabatic Born-Oppenheimer approximation [204] and is physically motivated by the observation that the momenta of electrons and nuclei are of the same order of magnitude considering they have similar electric charges. As the nuclear masses are a few orders of magnitude larger than the electronic masses, the nuclear speeds will be expected to be proportionally smaller to the electronic ones. It is thus reasonable to treat the electrons as relaxing instantaneously to the ground-state configuration $\Psi(\{r_i\}; \{R_\alpha\})$ with electronic energy eigenvalue $E$ given by

$$\hat{H}_e \Psi(\{r_i\}; \{R_\alpha\}) = E_e(\{R_\alpha\}) \Psi(\{r_i\}; \{R_\alpha\}), \quad (3.1.8)$$

where $\hat{H}_e$ corresponds to the time-independent electronic Hamiltonian set up by the static ionic potential

$$\hat{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{|r_i - R_\alpha|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|r_i - r_j|}. \quad (3.1.9)$$

Inserting Eq. (3.1.7) in Eq. (3.1.2) we obtain

$$\hat{H} \Phi(\{r_i\}, \{R_\alpha\}) = \Psi(\{r_i\}; \{R_\alpha\}) \left[ -\sum_\beta \frac{1}{2m_\beta} \nabla_\beta^2 + E_e(\{R_\alpha\}) + \frac{1}{2} \sum_\beta \sum_{\gamma \neq \beta} \frac{Z_\gamma Z_\beta}{|R_\gamma - R_\beta|} \right] \Upsilon(\{R_\alpha\})$$

$$- \sum_\beta \frac{1}{2m_\beta} \left[ \Upsilon(\{R_\alpha\}) \nabla_\beta^2 \Psi(\{r_i\}; \{R_\alpha\}) + 2 \nabla_\beta \Upsilon(\{R_\alpha\}) \cdot \nabla_\beta \Psi(\{r_i\}; \{R_\alpha\}) \right] \quad (3.1.10)$$

where the second line in Eq. (3.1.10) is known as the vibronic or non-adiabatic coupling term and is neglected in the adiabatic limit. In the Born-Oppenheimer approximation Eq. (3.1.4) is satisfied when

$$\left[ -\sum_\beta \frac{1}{2m_\beta} \nabla_\beta^2 + E_e(\{R_\alpha\}) + \sum_\beta \sum_{\gamma \neq \beta} \frac{Z_\gamma Z_\beta}{|R_\gamma - R_\beta|} \right] \Upsilon(\{R_\alpha\}) = \Xi \Upsilon(\{R_\alpha\}) \quad (3.1.11)$$

and the nuclear dynamics are obtained by solving Eq. (3.1.11) where the electronic configuration energy acts as an effective potential to the nuclei. Due to the large mass and consequently classical nature of the nuclei, it is often (with the notable exception of light species such as H atoms) appropriate to solve a classical version of Eq. (3.1.11) using classical molecular dynamics [205, 206].
The non-adiabatic coupling terms give rise to electron-phonon interactions which are important in a variety of phenomena such as superconductivity, photochemistry, zero point motion effects and one has to go beyond Born-Oppenheimer to treat those adequately.

3.1.2 The variational principle and Hellmann-Feynman theorem

The total energy functional, for fixed nuclei, $E[\Psi]$ is defined by the expectation value of the Hamiltonian ($|\Psi\rangle$ is not necessarily normalised)

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3r V_{\text{ext}}(r)n(r) + E_{\text{II}}, \quad (3.1.12)$$

where we have defined the kinetic energy operator for the electrons

$$\hat{T} = -\frac{1}{2} \sum_i \nabla_i^2,$$

the electron-electron interaction operator

$$\hat{V}_{\text{int}} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (3.1.14)$$

the static potential of the nuclei acting on the electrons

$$\hat{V}_{\text{ext}} = -\sum_i \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_\alpha|}, \quad (3.1.15)$$

and $E_{\text{II}}$ is the classical nuclei-nuclei interaction. The variational principle states that finding the stationary values of $E[\Psi]$ with respect to arbitrary variations in $|\Psi\rangle$ so that $\delta E[\Psi] = 0$ is equivalent to solving the Schrödinger equation. The proof relies on noticing that the variation of any functional $\Lambda[\Psi] = A[\Psi]/B[\Psi]$ gives

$$\delta \Lambda = \frac{A + \delta A}{B + \delta B} \frac{A}{B} = \frac{A + \delta A}{B} \left(1 - \frac{\delta B}{B}\right) - \frac{A}{B} = \frac{\delta A}{B} \frac{A \delta B}{B^2} = \frac{\delta A - \Lambda \delta B}{B}, \quad (3.1.16)$$

where we have Taylor expanded $(1 + \delta B/B)^{-1}$ to first order and neglected second order contributions. $\Lambda$ is stationary for $\delta A - \Lambda \delta B = 0$ and Eq. (3.1.12) can thus be recast as a Lagrangian extremisation problem

$$\delta [\langle \Psi | \hat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle] = 0, \quad (3.1.17)$$

where $E$ is an undetermined Lagrangian multiplier associated with the normalisation constraint. This is equivalent to the well known Rayleigh-Ritz problem where the quotient

$$\Omega = \frac{\langle \Psi | \hat{H} - E | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (3.1.18)$$
is stationary at eigensolutions. Neglecting second and higher order terms, the requirement that this
hold for arbitrary variations \( \langle \delta \Psi \rangle \) implies

\[
\hat{H} \Psi = E \Psi
\]  

(3.1.19)

which is the time-independent Schrödinger equation. We are interested in finding the ground-state
wavefunction \( \Psi_0 \) with ground-state energy \( E_0 \). According to the variational principle, it can be
obtained by minimising the total energy through parameters defining a trial wavefunction, under the
fermionic constraint of antisymmetry under exchange of electron coordinates. It can also be shown
that the error in estimating \( E_0 \) is proportional to the square of the error in the eigenstate. This
implies that even when the wavefunction is a poor guess, the estimated energy is comparatively good.
Similarly, excited states correspond to saddle points of the energy with respect to such variations
and are discussed in Section 3.4.

Forces \( F_\lambda \) conjugate to any continuous physical parameter \( \lambda \) in the Hamiltonian can also be
obtained variationally by virtue of the Hellmann-Feynman theorem [207, 208]. Using the derivative
product rule we can write

\[
F_\lambda = -\frac{dE(\lambda)}{d\lambda} = -\langle \Psi_0 | \frac{d\hat{H}}{d\lambda} | \Psi_0 \rangle - \langle \Psi_0 | \hat{H} \frac{d\Psi_0}{d\lambda} | \Psi_0 \rangle - \langle \frac{d\Psi_0}{d\lambda} | \hat{H} | \Psi_0 \rangle.
\]  

(3.1.20)

Assuming we have obtained the normalised ground-state wavefunction \( |\Psi_0\rangle \) via the variational proce-
dure described above, we have \( \hat{H} |\Psi_0\rangle = E_0 |\Psi_0\rangle \) and \( \langle \Psi_0 | \hat{H} = \langle \Psi_0 | E_0 \) (as the Hamiltonian is Her-
mitian). The normalisation condition yields \( \langle \Psi_0 | \Psi_0 \rangle = 1 \) and \( \frac{d}{d\lambda} \langle \Psi_0 | \Psi_0 \rangle = \langle \frac{d\Psi_0}{d\lambda} | \Psi_0 \rangle + \langle \Psi_0 | \frac{d\Psi_0}{d\lambda} \rangle = 0 \), and it follows that

\[
-\frac{dE}{d\lambda} = -\langle \Psi_0 | \frac{d\hat{H}}{d\lambda} | \Psi_0 \rangle - \langle \frac{d\Psi_0}{d\lambda} | E_0 | \Psi_0 \rangle - \langle \Psi_0 | E_0 \frac{d\Psi_0}{d\lambda} \rangle
\]

\[
= -\langle \Psi_0 | \frac{d\hat{H}}{d\lambda} | \Psi_0 \rangle - E_0 \left( \langle \frac{d\Psi_0}{d\lambda} | \Psi_0 \rangle + \langle \Psi_0 | \frac{d\Psi_0}{d\lambda} \rangle \right)
\]

(3.1.21)

Following the Born-Oppenheimer approximation, the Hamiltonian in Eq. (3.1.21) depends paramet-
rically on the ionic positions \( R_\alpha \) and only the terms of the Hamiltonian with an explicit dependence
on \( R_\alpha \) contribute to the conjugate force

\[
F_I = -\frac{dE}{dR_\alpha} = - \int d^3r \frac{\partial V_{\text{ext}}(r)}{\partial R_\alpha} n(r) - \frac{\partial E_{\text{II}}}{\partial R_\alpha}.
\]  

(3.1.22)

Hence the force on a nucleus only depends on the position of the other ions and the ground-state
electronic density \( n(r) \). In practical calculations, correction terms have to be introduced when
using non-local potentials (as in pseudopotentials), the basis set is atom position-dependent or the
wavefunction is not in the exact ground-state. We discuss such Pulay terms [209] in more detail in
Subsection 3.2.4.
3.1.3 Density-functional theory

Except for the simplest electronic systems, the computation of the equations of the previous two sections using the \(N_e\)-electron wavefunction with \(3N_e\) spatial variables (ignoring spin) is impractical. Inspired by the work of Thomas [210] and Fermi [211], in their foundational work of 1964 Hohenberg and Kohn [192] proved that all ground-state properties of the interacting many-body electronic system can in principle be obtained by a universal functional of the electronic density and using a variational principle. This bypasses the need to find \(|\Psi\rangle\) and greatly simplifies the problem. We define

\[
\hat{H} = \hat{F} + \hat{V}_{\text{ext}}
\]

where \(\hat{V}_{\text{ext}}\) is the static external potential induced by the nuclei, following the Born-Oppenheimer approximation, and \(\hat{F}\) is a universal electronic operator defined as

\[
\hat{F} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} .
\]  

(3.1.23)

The ground-state \(|\Psi_0\rangle\) giving rise to ground-state charge density \(n_0(r)\) is entirely specified by the number of electrons \(N_e\) and \(\hat{V}_{\text{ext}}\). \(^2\) DFT is based on two theorems we will now prove:

THEOREM 1: For any interacting system of \(N_e\)-electrons, there is a one-to-one mapping between the ground-state density \(n_0(r)\) and the potential \(\hat{V}_{\text{ext}}\) acting upon it.

This can be proven by \textit{reductio ad absurdum} assuming first that another \(\hat{V}_{\text{ext}}'\) with ground-state wavefunction \(|\Psi_0'\rangle\), Hamiltonian \(\hat{H}' = \hat{F} + \hat{V}_{\text{ext}}'\) and ground-state energy \(E_0'\) producing the same ground-state density \(n_0(r)\). As \(|\Psi_0\rangle\) is not the ground-state of \(\hat{H}\), from the variational principle we have the following inequality:

\[
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi_0' | \hat{H} | \Psi_0' \rangle
= \langle \Psi_0' | \hat{H}' | \Psi_0' \rangle + \langle \Psi_0' | (\hat{H} - \hat{H}') | \Psi_0' \rangle
= E_0' + \int d^3 r n_0(r) [V_{\text{ext}}(r) - V_{\text{ext}}'(r)].
\]

(3.1.24)

Similarly, we have

\[
E_0' < \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle
= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | (\hat{H}' - \hat{H}) | \Psi_0 \rangle
= E_0 - \int d^3 r n_0(r) [V_{\text{ext}}(r) - V_{\text{ext}}'(r)],
\]

(3.1.25)

and adding these equations up we arrive at the contradictory result

\[
E_0 + E_0' < E_0' + E_0.
\]

(3.1.26)

From this it follows that \(V_{\text{ext}}\) is uniquely determined, to within a constant, by \(n_0(r)\). The number of electrons \(N_e = \int d^3 r n_0(r)\) and \(V_{\text{ext}}\) fully determine the Hamiltonian and many-body wavefunction

\(^2\)Where potentials that differ by a constant are considered equivalent.
of all ground and excited states. It therefore follows as a corollary that all the properties of the system are completely determined by the ground-state density $n_0(r)$.

**THEOREM 2**: A valid energy functional $E[n]$ can be constructed for any $\hat{V}_{\text{ext}}$. For any $V$-representable trial density $n(r)$, $E[n] \geq E_0$ where the global minimum of the functional is the ground-state energy $E_0 = E[n_0]$ obtained for the ground-state density $n_0(r)$.

From the first Hohenberg-Kohn theorem, a given trial charge density $n(r)$ uniquely defines, within a constant, its own $\hat{V}_{\text{ext}}$ and ground-state $|\Psi'_0\rangle$. If we use $|\Psi'_0\rangle$ as a trial wave-function for the Hamiltonian with external potential $\hat{V}_{\text{ext}}$, we have by virtue of the variational principle:

$$
\langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle = \langle \Psi'_0 | \hat{F} | \Psi'_0 \rangle + \langle \Psi'_0 | \hat{\mathcal{V}}_{\text{ext}} | \Psi'_0 \rangle = F[n] + \int d^3 r n(r) V_{\text{ext}}(r) = E[n] \geq E_0.
$$

(3.1.27)

The equality holds, for non-degenerate ground-states, when $|\Psi'_0\rangle$ is the ground-state corresponding to $\hat{V}_{\text{ext}}$. As a corollary, knowing the functional $E[n]$ is sufficient to determine the ground-state density and energy exactly by recasting the problem as a variational minimisation of $E[n]$ with respect to $V$-representable densities\(^3\). The constrained search formulation of Levy [212, 213] relaxes the need for non-degeneracy and $V$-representability and the only condition becomes that of having an $N_e$-electron wavefunction yielding a density $n(r)$ ($N_e$-representability). This is a much weaker requirement that is equivalent to the density being properly differentiable [214].

### 3.1.4 The Kohn-Sham equations

The remarkable power and simplicity of the Hohenberg-Kohn theorems derives from the existence of a universal energy functional and use of electronic density as central variable. Solving the Schrödinger equation becomes equivalent to variationally optimising the electronic density, so that in principle DFT calculations can be made linear-scaling in size. However, the universal functional $F[n]$ is not known and further approximations are needed. In 1965, Kohn and Sham proposed to map the original many-body problem onto an auxiliary independent-particle problem. The mapping is based on the mean-field definition that the ground-state density of the interacting system is equal to that of an auxiliary, non-interacting one with a Hamiltonian where the usual kinetic energy operator and a local effective potential are used. In the Kohn-Sham approach the universal functional of the interacting system is rewritten as

$$
F_{\text{KS}}[n] = T_s[n] + \frac{1}{2} \int \int d^3 r d^3 r' n(r)n(r') \frac{1}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n],
$$

(3.1.28)

where $T_s[n]$ is defined as the kinetic energy of the non-interacting system. All many-body effects are accounted for by an exchange-correlation functional $E_{\text{xc}}[n]$. Variational minimisation of $E[n]$ with

---

\(^3\)Such that $n(r)$ is non-negative, normalised to $N$ and there exists an external potential $V$ with a corresponding ground state
constraint on the number \( N_e \) of electrons gives

\[
\delta \left[ F[n] + \int d^3r V_{\text{ext}}(r)n(r) - \mu \left( \int d^3r n(r) - N_e \right) \right] = 0, \quad (3.1.29)
\]

and yields the Euler-Lagrange equation:

\[
\frac{\delta F[n]}{\delta n(r)} + V_{\text{ext}}(r) = \mu. \quad (3.1.30)
\]

Since the non-interacting system is required to minimise its energy at the same density as the interacting one, an equivalent expression is expected for the Kohn-Sham system and substituting Eq. (3.1.28) into Eq. (3.1.30) we get:

\[
\frac{\delta T_s[n]}{\delta n(r)} + V_{\text{KS}}(r) = \mu, \quad (3.1.31)
\]

with

\[
V_{\text{KS}}(r) = \int d^3r' \frac{n(r')}{|r - r'|} + \frac{\delta E_{\text{xc}}[n]}{\delta n(r)} + V_{\text{ext}}(r). \quad (3.1.32)
\]

This has the form of a non-interacting system moving in an effective external potential \( V_{\text{KS}}(r) \). Moreover, the Kohn-Sham potential is uniquely defined according to the first Hohenberg-Kohn theorem. The kinetic energy of the non-interacting system can be expressed by a sum of single-particle orbital \( \psi_i(r) \) contributions, with the computational advantage that they can easily be calculated in reciprocal space, as:

\[
T_s[n] = -\sum_{i=1}^{N_e/2} \int d^3r \psi_i^*(r) \nabla^2 \psi_i(r). \quad (3.1.33)
\]

Eq (3.1.29) can be solved using a set of \( N_e/2 \) single-particle Schrödinger-like Kohn-Sham equations

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{KS}}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r). \quad (3.1.34)
\]

\( \psi_i \) are known as the Kohn-Sham orbitals with energies \( \varepsilon_i \) which reproduce the electronic density

\[
n(r) = 2 \sum_{i=1}^{N_e/2} |\psi_i(r)|^2. \quad (3.1.35)
\]

and the factor of two accounts for spin degeneracy. The Kohn-Sham problem has to be solved iteratively, due to the non-linearity in the potential, until self-consistent density and Kohn-Sham potential are obtained. The ground-state energy of the interacting system can be obtained, correcting for double-counting, as

\[
E[n] = 2 \sum_i \varepsilon_i - \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r - r'|} - \int d^3r V_{\text{xc}}(r)n(r) + E_{\text{xc}}[n]. \quad (3.1.36)
\]

The sum over Kohn-Sham eigenvalues is frequently called the bandstructure energy \( E_{\text{BS}} \) and the
remaining terms double-counting energy \( E_{d.c.} \). The Kohn-Sham formalism is in principle an exact theory of the ground-state which greatly simplifies the problem. Unfortunately, the exact form of the \( E_{xc}[n] \) functional is not known and approximate forms have to be used.

### 3.1.5 Exchange and correlation

The exchange correlation functional \( E_{xc}[n] \) is the repository of all the complex many-body interactions and is composed of the difference between interacting and non-interacting kinetic energies as well as non-classical electron-electron electrostatic energies. Surprisingly, it can be well approximated as a local or semi-local functional of the density. Kohn and Sham originally suggested to use a local density approximation, used throughout this work, for which it is assumed that the contribution to \( E_{xc}[n] \) from each infinitesimal region of space \( d^3r \) with density \( n(r) \) has the value it would have for a homogeneous electron gas (or jellium) of same density:

\[
E_{\text{lda}}^{\text{xc}}[n] = \int d^3r \epsilon_{\text{xc}}^{\text{lda}}(n(r))n(r)
\]

where \( \epsilon_{\text{xc}}(n) \) is the exchange-correlation energy per particle for jellium of density \( n \) and \( V_{\text{xc}}(r) \) becomes

\[
V_{\text{lda}}^{\text{xc}}(r) = \frac{\delta E_{\text{lda}}^{\text{xc}}[n]}{\delta n(r)} = \epsilon_{\text{xc}}^{\text{lda}}(n(r)) + n(r) \frac{d \epsilon_{\text{xc}}^{\text{lda}}(n)}{dn} \bigg|_{n=n(r)}.
\]

Commonly used parametrisations for the local density approximation functional include Vosko-Wilk-Nusair’s VWN [215], Perdew-Zunger’s CAPZ [216] and Perdew-Wang’s PW92 [217]. These functionals fit an analytical high-density expression due to Gell-Mann and Brueckner [218] and quantum Monte Carlo computation of Ceperley and Alder [219] in the low density limit. The local density approximation becomes formally exact in the limit of slowly varying densities which is not the case in many systems. The approximation can be refined by including gradient corrections to the exchange-correlation energy to account for the spatial variation of the density. This forms the basis for semi-local functionals referred to as generalised gradient approximations (GGA) [220] which can lead to improvements compared to the local density approximation especially in molecular systems. Examples of GGA functionals include Becke’s B86 [221] or B88 [222] exchange functionals combined with Lee-Yang-Parr’s LYP [223] correlation functional, Perdew-Wang’s PW91 [224], Perdew-Burke-Ernzerhof’s PBE [225] and revised PBEs [226–228]. The local density approximation is however found to work well in systems with inhomogeneous densities [229]. The exchange-correlation energy can be recast, via the adiabatic connection [230–233], as the classical electrostatic interaction between the inhomogeneous electronic density \( n(r) \) and an exchange-correlation hole \( n_{\text{xc}}(r, r') \):

\[
E_{\text{xc}}[n] = \frac{1}{2} \int \int d^3rd^3r' \frac{n(r)n_{\text{xc}}(r, r')}{|r - r'|}.
\]

The exchange-correlation hole can be understood as a combined effect of Pauli’s exclusion principle [234], where electrons with the same spin mutually exclude each other from the same region of space, and many-body repulsion between electrons of opposite spin which creates a charge depletion hole around every electron. It can be shown that the true \( E_{\text{xc}}[n] \) depends only on the spherical average
of \( n_{xc}(r, r') \), and that the sum rule
\[
\int d^3r' n_{xc}(r, r') = -1
\]
must be satisfied. It has been postulated that the reasonable accuracy of the local density approximation even for inhomogeneous systems is attributable to it satisfying the sum rule, but also because for many systems the total energy depends only on the spherical average of \( n_{xc}^{\text{uln}}(r, r') \) which is similar to \( n_{xc}(r, r') \) [229]. The local density approximation still suffers from evident flaws, such as self-interaction errors, which lead to systematic underestimation of bond-lengths, local moments, HOMO-LUMO gaps and overestimation of cohesive energies. Recently, much work has gone into developing improved functionals such as hybrid functionals that mix in some exact Hartree-Fock exchange such as the widely used B3LYP [235, 236], range-separated functionals [237–239] and meta-GGAs that include higher order derivatives of the electronic density [240–242]. New constraints have recently been derived that are obeyed by the local density approximation but not by GGAs or hybrids [243]. Ultimately, the choice of functional is dictated by a trade-off between accuracy and computational cost associated with the system one is studying. The local density approximation appears to be a good choice [244] in that respect for semiconductor nanocrystals, and has thus been used throughout this thesis.

### 3.1.6 Pseudopotentials

Since the nuclear Coulomb potential is screened by tightly-bound core orbitals, it is observed that valence eigenstates tend to be less strongly bound to the ions and are thus more sensitive to their chemical environment. By contrast, the core orbitals remain in many cases largely unchanged when atoms are brought together to form crystals and molecules. It therefore makes sense to describe the chemistry of a problem by removing the core electrons and focusing on the computation of energetic changes in the valence electrons which then represent a larger fraction of the total binding energy and become easier to calculate. This is the basis of the widely used pseudopotential approximation [245], in which we replace the strong Coulomb potential with a much weaker pseudopotential describing the combined effect of ions screened by core electrons. Atomic orbitals are orthogonal to one another as they are eigenstates of an atomic Hamiltonian, and maintaining this orthogonality between valence and spatially localised core electrons requires the former to oscillate rapidly in the region of the core. Attaining such spatial resolution generally translates into having a large number of basis functions, or Fourier components. The pseudopotential approximation replaces the valence orbitals with pseudo-orbitals that are much smoother as they do not oscillate in the core region (Figure 3.1.1) [246, 247]. Following the operator approach of Heine [248], we consider an atomic Hamiltonian \( \hat{H} \) with core eigenstates \( \{|\vartheta_n\rangle\} \) and energy eigenvalues \( E_n \). If we assume any valence state \( |\psi\rangle \) can be constructed from a linear combination of core states and a smoother pseudo-orbital \( |\tilde{\psi}\rangle \) as:

\[
|\psi\rangle = |\tilde{\psi}\rangle + \sum_n a_n |\vartheta_n\rangle,
\]

(3.1.41)
by orthogonality we have:

$$\langle \vartheta_n | \tilde{\psi} \rangle = \langle \vartheta_n | \psi \rangle + a_n = 0.$$  (3.1.42)

Hence the expansion coefficients are given by

$$a_n = -\langle \vartheta_n | \tilde{\psi} \rangle,$$  (3.1.43)

and Eq. (3.1.41) can be written as

$$|\psi\rangle = |\tilde{\psi}\rangle - \sum_{n=1}^{\text{core}} \langle \vartheta_n | \tilde{\psi} \rangle |\vartheta_n\rangle.$$  (3.1.44)

Using $\hat{H} |\psi\rangle = E |\psi\rangle$ we obtain:

$$\left[ \hat{H} + \sum_{n=1}^{\text{core}} (E - E_n) |\vartheta_n\rangle \langle \vartheta_n | \right] |\tilde{\psi}\rangle = E |\tilde{\psi}\rangle.$$  (3.1.45)

Thus $|\tilde{\psi}\rangle$ obeys a Schrödinger equation giving the same eigenvalue as $|\psi\rangle$ but with a Hamiltonian modified by a potential term $\hat{V}_{nl}$ given by

$$\hat{V}_{nl}(E) = \sum_{n=1}^{\text{core}} (E - E_n) |\vartheta_n\rangle \langle \vartheta_n |,$$  (3.1.46)

which is repulsive and core-localised. $\{|\vartheta_n\rangle\}$ and the corresponding $E_n$ are generally computed by all-electron calculations of the isolated atom and kept fixed throughout. Changing the chemical environment will naturally change the energy $E$ of the valence state by $\delta E$. If the core and valence states are far apart in energy so that $\delta E \ll E - E_n$, then fixing the value of $E$ in $\hat{V}_{nl}(E)$ to be the
atomic valence eigenvalue is reasonable.

The validity of this approximation determines the transferability of the pseudopotential to different chemical environments. This can be further enforced by constructing pseudopotentials that follow the real potential to first or higher orders in $E$. One family of approaches consist in enforcing norm-conservation \[250–257\]

\[
\int_0^{r_c} d^3r \psi^*(\mathbf{r}) \psi(\mathbf{r}) = \int_0^{r_c} d^3r \tilde{\psi}^*(\mathbf{r}) \tilde{\psi}(\mathbf{r}).
\] (3.1.47)

By imposing Eq. (3.1.47), the real and pseudo-wavefunctions generate the same density outside the core of radius $r_c$ which can be shown \[258\] to be equivalent to the logarithmic derivatives of the wavefunctions and thus their scattering properties being correct to first order. Approaches such as Vanderbilt’s ultrasoft pseudopotentials \[259\] and Blöchl’s projector augmented wave method (PAW) \[260\] relax this condition and we shall discuss this in more detail in Section 3.3.

The norm-conserving pseudopotentials (NCPPs) in the Kleinman-Bylander form \[261\] are used in this work

\[
\hat{V}_{KB} = \hat{V}_{loc} + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \frac{\langle \partial_{l m} \delta \hat{V}_l \rangle \langle \partial_{l m} \delta \hat{V}_l \rangle}{\langle \partial_{l m} \delta \hat{V}_l \rangle \langle \partial_{l m} \delta \hat{V}_l \rangle},
\] (3.1.48)

where $|\psi_{lm}\rangle$ are atomic pseudo-orbitals, $\hat{V}_{loc}$ and $\hat{V}_l$ are the angular momentum independent and dependent parts of the operator and $\delta \hat{V}_l = \hat{V}_l - \hat{V}_{loc}$. $\hat{V}_{KB}$ expressed in this separable and non-local form has the advantage that the cost of calculating the pseudopotential matrix elements scales linearly with the basis set size.

### 3.1.7 Periodic systems and Bloch’s theorem

For a system of non-interacting electrons in the static potential of a perfect crystal with a symmetric and infinite arrangement of nuclei described by Bravais lattice vectors $\{\mathbf{R}\}$, the potential is periodic and

\[
V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}).
\] (3.1.49)

We define \[262\] a translation operator $\hat{T}_{\mathbf{R}}$ for each $\mathbf{R}$, which operating on a function $f(\mathbf{r})$ translates its argument by $\mathbf{R}$:

\[
\hat{T}_{\mathbf{R}} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}).
\] (3.1.50)

Since the potential is periodic, so is the Hamiltonian ($\hat{H}(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})$) and we have

\[
\hat{T}_{\mathbf{R}} (\hat{H}(\mathbf{r}) \psi(\mathbf{r})) = \hat{H}(\mathbf{r} + \mathbf{R}) \psi(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r}) \psi(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r}) \hat{T}_{\mathbf{R}} \psi(\mathbf{r}),
\] (3.1.51)

and hence we obtain the commutation relation $[\hat{H}(\mathbf{r}), \hat{T}_{\mathbf{R}}] = 0$. In addition, the combined effect of two translations is independent of the order in which they are applied:

\[
\hat{T}_{\mathbf{R}} \hat{T}_{\mathbf{R}'} \psi(\mathbf{r}) = \hat{T}_{\mathbf{R}'} \hat{T}_{\mathbf{R}} \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R} + \mathbf{R}').
\] (3.1.52)
Thus the translation operators commute with another \([\hat{T}_\mathbf{R}, \hat{T}'_\mathbf{R}] = 0\). It follows from quantum mechanics and group theory that the eigenstates of the Hamiltonian can be chosen to be simultaneous eigenstates of the translation operators (simultaneously diagonalisable in that basis) and a good quantum number must correspond to each \(\mathbf{R}\):

\[
\hat{H}(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) \quad (3.1.53)
\]

\[
\hat{T}_\mathbf{R}\psi(\mathbf{r}) = c(\mathbf{R})\psi(\mathbf{r}). \quad (3.1.54)
\]

From the periodic boundary conditions we must have

\[
\int_{\text{unit cell}} d^3r |\psi(\mathbf{r} + \mathbf{R})|^2 = \int_{\text{unit cell}} d^3r |\psi(\mathbf{r})|^2 \quad (3.1.55)
\]

and from Eq. (3.2.11) it follows that \(|c(\mathbf{R})|^2 = 1\). Hence

\[
c(\mathbf{R}) = e^{2\pi i\sigma(\mathbf{R})}, \quad (3.1.56)
\]

where \(\sigma(\mathbf{R})\) is a real valued function. Bravais lattice vectors \(\{\mathbf{R}\}\) can be expressed as linear combinations of primitive lattice vectors \(\{\mathbf{a}_i\}\):

\[
\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3. \quad (3.1.57)
\]

\(\hat{T}_\mathbf{R}\) can be decomposed as

\[
\hat{T}_\mathbf{R} = (\hat{T}_{\mathbf{a}_1})^{n_1} (\hat{T}_{\mathbf{a}_2})^{n_2} (\hat{T}_{\mathbf{a}_3})^{n_3}, \quad (3.1.58)
\]

and \(c(\mathbf{R})\) as

\[
c(\mathbf{R}) = c(\mathbf{a}_1)^{n_1} c(\mathbf{a}_2)^{n_2} c(\mathbf{a}_3)^{n_3}. \quad (3.1.59)
\]

From Eq 3.1.56 and Eq 3.1.59 we obtain

\[
2\pi\sigma(\mathbf{R}) = 2\pi n_1\sigma(\mathbf{a}_1) + 2\pi n_2\sigma(\mathbf{a}_2) + 2\pi n_3\sigma(\mathbf{a}_3)
\]

\[
= (\sigma(\mathbf{a}_1)\mathbf{b}_1 + \sigma(\mathbf{a}_2)\mathbf{b}_2 + \sigma(\mathbf{a}_3)\mathbf{b}_3) \cdot (n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3) \quad (3.1.60)
\]

\[
= \mathbf{k} \cdot \mathbf{R},
\]

where \(\{\mathbf{b}_i\}\) are the reciprocal lattice vectors defined as \(\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}\). Thus we end up with Bloch’s theorem [263]:

\[
\hat{T}_\mathbf{R}\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R}) = c(\mathbf{R})\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}}\psi(\mathbf{r}). \quad (3.1.61)
\]

This can be written in an alternative form by consideration of \(u(\mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{r}}\psi(\mathbf{r})\) that has the same periodicity as the lattice as

\[
u(\mathbf{r} + \mathbf{R}) = e^{-i\mathbf{k} \cdot (\mathbf{r} + \mathbf{R})}\psi(\mathbf{r} + \mathbf{R}) = e^{-i\mathbf{k} \cdot \mathbf{r}}\psi(\mathbf{r}) = u(\mathbf{r}) \quad (3.1.62)
\]
We can hence write Bloch’s theorem in the alternative form:

$$\psi(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u(r).$$  \hspace{1cm} (3.1.63)

The band index $n$ and wavevector $\mathbf{k}$ are good quantum numbers, and we can unambiguously label the eigenstates of the Hamiltonian and translation operators as $|\psi_n\rangle$ (known as Bloch states). Using Bloch’s theorem we can show that any Bloch state $|\psi_{nk}'\rangle$ with wavevector $\mathbf{k}' = \mathbf{k} + \mathbf{G}$, where $\mathbf{G}$ is a linear combination of $\{\mathbf{b}_i\}$, can be related to a Bloch state $|\psi_{nk}\rangle$ with wavevector $\mathbf{k}$ in the first Brillouin zone. The first Brillouin zone is defined as the volume in reciprocal space that encapsulates the origin and is bounded by planes normally bisecting lines from the origin to nearby reciprocal lattice points. We can write

$$\psi_{nk}'(r) = e^{i\mathbf{k}' \cdot \mathbf{r}} u_{nk}'(r) = e^{i\mathbf{k} \cdot \mathbf{r}} (e^{i\mathbf{G} \cdot \mathbf{r}} u_{nk}(r)) = e^{i\mathbf{k} \cdot \mathbf{r}} u'(r) = \psi_{nk}(r),$$  \hspace{1cm} (3.1.64)

where $u'(r)$ has the periodicity of the Bravais lattice and the whole expression is a valid Bloch state. We have transformed the problem of finding an infinity of Bloch states in all of k-space to finding a finite number of occupied states at each k-point in the first Brillouin zone. There is an infinite number of such points for an infinite periodic system. The number of k-points can, however, be made finite by choosing a finite periodic system and imposing Born-von Karman periodic boundary conditions for the Bloch states. Furthermore, because the wavefunctions and other properties such as eigenvalues vary smoothly over the Brillouin zone [264], it is sufficient to sample a finite set of carefully selected and weighted k-points. This is known as Brillouin zone sampling and a variety of methods exist to do this in an optimal way [265–271]. In the limit of large systems (or supercells) of volume $\Omega_{\text{cell}}$, the volume of the Brillouin zone, given by

$$\Omega_{\text{BZ}} = \frac{(2\pi)^3}{\Omega_{\text{cell}}},$$  \hspace{1cm} (3.1.65)

becomes so small that only a small number of k-points need to be considered to accurately sample it. Sampling the central $k = 0$ point ($\Gamma$-point) then becomes sufficient, with the added benefit that $|\psi_{nk}\rangle$ can be chosen to be real. Aperiodic systems, such as nanocrystals and molecules, can be studied by enforcing periodicity artificially and placing the system in a sufficiently large supercell so as to avoid spurious interactions with periodic images.

The cell-periodic function $u_{nk}(r)$ can be Fourier expanded in terms of plane-waves as

$$\psi_{nk}(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{nk}(r) = e^{i\mathbf{k} \cdot \mathbf{r}} \left[ \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \right],$$  \hspace{1cm} (3.1.66)

where $c_{n,\mathbf{k}+\mathbf{G}}$ are Fourier coefficients. Plane-waves are thus a natural choice of basis set to represent the Hilbert space of Kohn-Sham wavefunctions for periodic systems. A plane-wave basis set also has the advantage that the kinetic energy, Hartree potential and local pseudopotential can easily be calculated in reciprocal-space, and Fast Fourier Transforms (FFTs) permit efficient transformation of quantities between real and reciprocal representations. They are orthogonal, free of basis set
superposition errors and independent of nuclear positions so that forces are easily calculated without the need for Pulay corrections. While an infinite basis set is in principle needed to perfectly represent wavefunctions at every $k$-point, a finite number of Fourier components are used in practice, by neglecting contributions beyond a cutoff value defined by

$$E_{\text{cut}} = \frac{1}{2} |k + G|^2.$$  

(3.1.67)

This is equivalent to Fourier filtering the wavefunction, and calculations have to be converged with respect to $E_{\text{cut}}$. This convergence is variational with respect to this single parameter. These advantageous properties have made plane-waves combined with the use of the pseudopotential approximation and iterative techniques [272–275] a widely used approach for calculating the electronic structure of periodic systems [276, 277]. The requirement of orthonormality of the Kohn-Sham eigenstates combined with their delocalised nature result in an asymptotically $O(N^3)$ scaling of the computational effort. This puts a severe constraint on the system sizes that are attainable with PWPP DFT and $O(N)$ DFT approaches have over the last three decades addressed this issue in a variety of ways.

### 3.2 The ONETEP method

The properties of electronic matter are local, a quantum mechanical principle known as “nearsightedness” [278, 279]. The $O(N^3)$ computational bottleneck of PWPP approach is therefore not intrinsic to DFT, and $O(N)$ scaling calculations are in theory feasible. It has been shown that for systems with a bandgap, the one-particle density matrix $\rho(r, r')$, which contains all information about the electronic system, decays exponentially as [280, 281]:

$$\rho(r, r') \propto \exp(-\zeta |r - r'|),$$  

(3.2.1)

where the decay constant $\zeta$ has been shown to be proportional to the band gap [282, 283]. This implies that $\rho(r, r')$ is exponentially localised in real-space, and crucially for linear-scaling methods, the elements of $\rho(r, r')$ corresponding to points in space beyond a system-dependent cutoff distance $r_{\text{cut}}$ can be reasonably ignored:

$$\rho(r, r') = 0 \text{ when } |r - r'| > r_{\text{cut}}.$$  

(3.2.2)

A reformulation of the Kohn-Sham equations in terms of $\rho(r, r')$ and localised orbitals are required to exploit this locality.

#### 3.2.1 Density matrix formulation of the Kohn-Sham equations

Following Subsection 3.1.3, the diagonal part of the density operator contains all the necessary information as $n(r) = 2\rho(r, r)$ and all density functionals can be expressed in terms of $\rho(r, r')$. The density operator is a Hermitian operator and has the property of idempotency

$$\hat{\rho}^2 = \hat{\rho}.$$  

(3.2.3)
This can be shown to be equivalent to compliance with the Pauli exclusion principle by forcing the occupancies to be zero or unity and orthonormality of the Kohn-Sham states. The diagonal elements are always found to be real and lie in the \([0,1]\) interval. Another constraint is that the density matrix must remain normalised

\[
N_e = \int d^3r n(r) = 2 \int d^3r \rho(r,r) = 2 \sum_n f_n = 2 \text{Tr}[\hat{\rho}],
\]

(3.2.4)

We can express the Kohn-Sham non-interacting kinetic energy by

\[
T[n] = 2 \sum_n f_n \int d^3r \psi_n^*(r) \left( -\frac{1}{2} \nabla^2 \right) \psi_n(r) = 2 \int d^3r' \left[ -\frac{1}{2} \nabla^2 r \rho(r,r') \right]_{r=r'} = 2 \text{Tr}[\hat{\rho} \hat{T}],
\]

(3.2.5)

where we define \(\hat{T} = -\frac{1}{2} \nabla^2 r\). All the other terms in the Kohn-Sham functional can be expressed in terms of the density matrix by replacing \(n(r) = 2\rho(r,r)\). We can therefore reexpress the Kohn-Sham equations in terms of the single-particle density operator with constraints of idempotency and particle number conservation, instead of the electronic density and constraints of orthonormality and particle number conservation. Respecting these constraints without explicit use of the eigenstates of the Hamiltonian is, however, a numerically challenging task. It can been achieved in a variety of ways. One can define penalty functionals that penalise deviations from idempotency, such as the McWeeny functional \([284]\) defined as

\[
P[\rho] = \text{Tr}[\left( \rho^2 - \rho \right)^2] = \sum_n (f_n^2 - f_n)^2
\]

(3.2.6)

which vanishes when the density matrix is idempotent.

An alternative approach for enforcing idempotency is the purification transformation, whereby the density matrix is iteratively modified according to

\[
\rho_{k+1} = 3\rho_k^2 - 2\rho_k^3,
\]

(3.2.7)

and the equation is to be read like an algorithm with \(k\) the iteration number. The Li-Nunes-Vanderbilt method \([285,286]\) (LNV) combines both ideas by introducing an auxiliary density matrix \(\sigma\) implicitly defined by:

\[
\rho = 3\sigma^2 - 2\sigma^3.
\]

(3.2.8)

The energy is then minimised with respect to \(\sigma\). This can be modified further to enforce particle number conservation by normalising the auxiliary density matrix

\[
\hat{\rho} = \frac{N_e}{2 \text{Tr}[3\sigma^2 - 2\sigma^3]},
\]

(3.2.9)

ONETEP uses various flavours of these methods as described in Ref. [287].
At this stage we note that the density matrix, expressed in terms of eigenstates as:

\[ \rho(\mathbf{r}, \mathbf{r}') = \sum_n f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \]  

(3.2.10)

and the information stored scales as the square of the system size. Besides, the delocalised nature of the Kohn-Sham orbitals over the entire system makes it difficult to exploit the local nature of \( \rho(\mathbf{r}, \mathbf{r}') \). We express the density matrix in separable form by introducing a set of auxiliary orbitals \( \{|\phi_\alpha\rangle\} \) known as support functions, which are not necessarily orthogonal, so that

\[ \psi_n(\mathbf{r}) = \phi_\alpha(\mathbf{r}) M_n^\alpha, \]  

(3.2.11)

where the linear operator \( \hat{M} \) is unitary when the basis is orthonormal and of same size. We have used the Einstein convention of implicit summation over repeated Greek indices and continue to do so in the rest of the thesis unless specified otherwise. The locality and orthogonality of the basis are competing requirements and it can be shown that using a non-orthogonal basis can increase its locality [288] which is advantageous for linear-scaling methods. For the localised and non-orthogonal basis of orbitals \( \{|\phi_\alpha\rangle\} \), Eq. (3.2.10) can be written in a general separable form

\[ \hat{\rho} = \langle \phi_\alpha | K^{\alpha\beta} \langle \phi_\beta |, \]  

(3.2.12)

where \( K^{\alpha\beta} \) is known as the density kernel. When working with a non-orthogonal basis, care must be taken to respect tensorial consistency [289, 290] and a dual basis \( \{|\phi^\alpha\rangle\} \) is introduced where

\[ |\phi^\alpha\rangle = |\phi_\beta\rangle S^{\beta\alpha}. \]  

(3.2.13)

We have introduced the inverse overlap matrix \( S^{\alpha\beta} \) defined as

\[ S^{\alpha\beta} = \langle \phi^\alpha | \phi^\beta \rangle = (S^{-1})^{\alpha\beta}. \]  

(3.2.14)

In the language of tensors, the overlap is the metric which relates covariant and contravariant quantities. The biorthonormality condition is given by

\[ \langle \phi^\alpha | \phi_\beta \rangle = \langle \phi_\alpha | \phi^\beta \rangle = \delta_\beta^\alpha, \]  

(3.2.15)

and the completeness relation is

\[ |\phi^\alpha\rangle \langle \phi_\alpha | = |\phi_\alpha\rangle \langle \phi^\alpha | = |\phi_\alpha\rangle S^{\alpha\beta} \langle \phi_\beta | = \mathbb{I}, \]  

(3.2.16)

where \( \mathbb{I} \) is the identity operator in the space spanned by \( \{|\phi_\alpha\rangle\} \). For an orthonormal basis, the metric is the identity matrix and there is no distinction between covariant and contravariant quantities.

Within this representation, the particle number constraint can be written as

\[ N_e = 2 \int d^3r \rho(\mathbf{r}, \mathbf{r}) = 2K^{\alpha\beta} S_{\beta\alpha} = 2 \text{Tr}[\mathbf{KS}], \]  

(3.2.17)
and the Kohn-Sham bandstructure energy becomes

\[ E_{BS} = 2 \text{Tr}[\hat{H}] = 2H_{\alpha\beta}R^{\beta\alpha} = 2 \text{Tr}[KH] \] (3.2.18)

with

\[ H_{\alpha\beta} = \langle \phi_\alpha | \hat{H} | \phi_\beta \rangle, \] (3.2.19)

and the \( S \) and \( H \) matrices can be made sparse by virtue of the localisation of the orbitals.

### 3.2.2 Locality and Wannier functions

Wannier functions [291] are a natural set of local orbitals defined in terms of a unitary transformation of Bloch states as

\[ w_{nR}(r) = \left( \frac{\Omega_{\text{cell}}}{(2\pi)^3} \right)^{1/2} \int_{1^{\text{st}} BZ} d^3k e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{nk}(r). \] (3.2.20)

The inverse relation is given by:

\[ \psi_{nk}(r) = \left( \frac{\Omega_{\text{cell}}}{(2\pi)^3} \right)^{1/2} \sum_{R} w_{nR}(r) e^{ikR}. \] (3.2.21)

The Wannier functions are localised in different cells, labeled by the lattice vectors \( R \) and obey the orthonormality relation

\[ \int d^3rw_{nR}^*(r)w_{n'R'}(r) = \delta_{nn'}\delta_{RR'}. \] (3.2.22)

The representation is not unique as there is a gauge invariance which can be exploited [292]. We introduce the density operator \( \hat{\rho} \) defined in terms of Kohn-Sham single-particle non-interacting orbitals

\[ \hat{\rho} = \sum_n f_n |\psi_n\rangle \langle \psi_n|, \] (3.2.23)

where we removed the \( k \)-point index assuming \( \Gamma \)-point sampling and \( f_n \) are fractional occupancy numbers. In position representation, the density operator becomes

\[ \rho(r,r') = \langle r | \hat{\rho} | r' \rangle = \sum_n f_n \psi_n(r)\psi_n^*(r'). \] (3.2.24)

For insulating systems, this can be written in terms of Wannier functions as

\[ \rho(r,r') = \sum_n \sum_R f_n w_{nR}(r)w_{nR}^*(r'). \] (3.2.25)

Wannier functions have been shown to be exponentially localised in systems with a gap [280, 281, 293–295], translating into the exponential decay of \( \rho(r,r') \) in Eq. (3.2.1). Linear-scaling methods rely on the exponential localisation of the Wannier functions or \( \rho(r,r') \), ignoring the information associated with electronic structures that are beyond defined cutoff distances. The first \( \mathcal{O}(N) \) DFT algorithm was proposed in 1991 by Yang [296] in his non-variational “divide and conquer”
approach. Closer to the approach in this work is the variational scheme proposed in 1992 by Galli and Parrinello [297], based on a reformulation of Kohn-Sham states in terms of localised orbitals. A plethora of $\mathcal{O}(N)$ methods have been proposed over the years and can be classified in the following categories: “divide and conquer” [296, 298], orbital minimisation [288, 297, 299–309], density matrix minimisation [285, 286, 310–323], Fermi operator projection [324–331], Fermi operator expansion [194, 332, 333], stochastic [334–338] and other methods [210, 320, 339–363]. We refer the reader to reviews [194, 364, 365] for a comprehensive perspective. The approach used in this work is closest to self-consistent density matrix minimisation methods [312–314, 316, 317, 319, 366].

### 3.2.3 The ONETEP method

In this work we have used the ONETEP code [115, 116, 287, 322, 367–372], a linear-scaling energy and force DFT package that uses a reformulation of the Kohn-Sham equation in terms of the density kernel as outlined in the previous subsections. ONETEP uses non-orthogonal Wannier functions [373] (NGWFs) as support functions defined as:

\[
|\phi_{\alpha,R}\rangle = \left(\frac{\Omega_{\text{cell}}}{(2\pi)^{3/2}}\right)^{1/2} \int_{1^*BZ} d^3k e^{-i\mathbf{k} \cdot \mathbf{R}} \sum_{\mathbf{R}}^{N} |\psi_{\mathbf{k}}\rangle \left[ M_{\mathbf{k}}^{\beta \alpha} |\mathbf{k}\rangle S_{\beta \alpha} \right]
\]  

(3.2.26)

\[
= \left(\frac{\Omega_{\text{cell}}}{(2\pi)^{3/2}}\right)^{1/2} \sum_{i=1}^{N} |\psi_{i}\rangle \left[ M_{i}^{\beta \alpha} S_{\beta \alpha} \right],
\]

where $\tilde{M}$ is defined as in Eq. (3.2.11) and the $\mathbf{k}$-index can be dropped for $\Gamma$-point sampling. These NGWFs are themselves expanded in terms of a variational underlying basis set of psinc functions (Figure 3.2.1) [374]. These psincs, also known as periodic bandwidth limited Dirac and Fourier-
Lagrange functions, are defined as follows:

\[
D_n(r) \equiv D(r - r_n) = \frac{1}{N_1N_2N_3} \sum_{p_1=-J_1}^{J_1} \sum_{p_2=-J_2}^{J_2} \sum_{p_3=-J_3}^{J_3} e^{i(p_1b_1 + p_2b_2 + p_3b_3) \cdot (r - r_n)},
\]

(3.2.27)

where \{b_i\} are the reciprocal lattice vectors and \{r_n\} are grid points of the simulation cell. \(N_i = 2J_i + 1\) grid points, \(J_i\) is an integer and the grid is chosen to be odd to guarantee that the basis is real and orthogonal, are chosen along each direction defined by the primitive lattice vectors \{a_i\} as

\[
r_n = \frac{n_1}{N_1} a_1 + \frac{n_2}{N_2} a_2 + \frac{n_3}{N_3} a_3 = \sum_{i=1}^{3} \frac{n_i}{N_i} a_i; \quad n_i \in \{0, 1, ..., N_i - 1\}.
\]

(3.2.28)

The psinc basis is thus equivalent to a truncated planewave basis and the psinc spacing acts as the variational parameter similar to the \(E_{\text{cut}}\) in PWPP calculations [115]. We notice that psincs approximate Dirac delta functions centred at points \(r_n\) as

\[
D_n(r) \approx \delta(r - r_n) = \frac{\Omega_{\text{cell}}}{(2\pi)^3} \int d^3 G e^{iG \cdot (r - r_n)},
\]

(3.2.29)

and they are related to the cardinal sine functions (sinc) in the limit \(N_i \rightarrow \infty\). Furthermore, psincs can be shown [374] to have a host of useful properties such as being localised to a grid point and null at all other grid points, real-valued, orthogonal and cell periodic such that \(D_n(r) = D_n(r + R)\). Besides, the overlap of a real-valued cell periodic function \(f(r)\) with psinc centred at \(r_n\) conveniently reduces to

\[
\int_V d^3 r D_n(r) f(r) = \frac{1}{N_1N_2N_3} \sum_{G} G_{\text{max}} \tilde{f}(G) e^{iG \cdot r_n} = \frac{\Omega_{\text{cell}}}{N_1N_2N_3} f_D(r_n) = \int_V d^3 r D_n(r) f_D(r),
\]

(3.2.30)

where \(f_D(r)\) denotes the bandwidth limited \((G_{\text{max}})\) version. \(\phi_\alpha(r)\) can be expressed as a sum over grid points as

\[
\phi_\alpha(r) = \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} c_{n,\alpha} D_n(r),
\]

(3.2.31)

where the coefficients \(c_{n,\alpha}\) are zero outside of the NGWF localisation region. Overlap integrals between functions represented on the psinc grid and the matrix elements of local and differential operators can all be evaluated efficiently using sums over grid points and FFTs. The equivalence between psinc and planewave basis sets is useful as it allows direct comparison to PWPP calculations and a similar level of accuracy. This makes the use of a psinc basis set particularly elegant for linear-scaling calculations.

One particularity of ONETEP is that the NGWFs, which are real-valued, atom-centred and spatially-truncated vectors, are optimised in situ during the calculation (Figure 3.2.2). This is done by variationally optimising both the expansion coefficients [314] \(c_{n,\alpha}\) and the density kernel.
Figure 3.2.2: Left, a delocalised Kohn-Sham orbital on a peptide obtained with CASTEP. Right, in situ optimised NGWFs calculated with ONETEP on the same peptide. Taken from Ref. [322].

\( K^{\alpha \beta} \) elements [287] in two nested conjugate-gradient loops to minimise the total-energy functional

\[
E_0 = \min_n E[n] = \min_\rho \sum_{\{K^{\alpha \beta}\},\{c_{n,\alpha}\}} E[\{K^{\alpha \beta}\}, \{c_{n,\alpha}\}] = \min_\{K^{\alpha \beta}\},\{c_{n,\alpha}\} \left[ 2 \text{Tr}[K \mathbf{H}] + E_{\text{d.c.}} \right]. \tag{3.2.32}
\]

under constraints of idempotency

\[
K^{\alpha \gamma} S_{\sigma \delta} K^{\delta \beta} = K^{\alpha \beta}. \tag{3.2.33}
\]

and normalisation

\[
2 \text{Tr}[K \mathbf{S}] = N_e. \tag{3.2.34}
\]

This allows for a minimal basis of support functions, without the basis set superposition errors of fixed localised basis sets [368], while retaining plane-wave accuracy.

The localisation of the orbitals is imposed by defining a cutoff radius \( r_\alpha \) for every NGWF so that they are strictly zero on all grid points outside the localisation radii. This leads to sparsity in \( H_{\alpha \beta} \) and \( S_{\alpha \beta} \) which can be harnessed by using efficient sparse matrix algebra. \( H_{\alpha \beta} \) can be evaluated with a computational effort that scales as \( \mathcal{O}(N) \) given that each element can be evaluated in \( \mathcal{O}(1) \) operations. For any two NGWFs \( \phi_\alpha \) and \( \phi_\beta \) separated by \( r_{\alpha \beta} \), the elements of the density kernel \( K^{\alpha \beta} \) are set to zero if \( r_K < r_{\alpha \beta} \), where \( r_K \) is the kernel cutoff. Only with a kernel cutoff can the kernel be made sparse and the evaluation of Eq. (3.2.32) linear-scaling. Its value is system-dependent and in all calculations reported here we have not used any kernel truncation to guarantee numerical stability. The enforced localisation has the additional benefit that vacuum comes at a negligible computational overhead, unlike PWPP approaches, and this proves especially useful for low dimensional systems, such as the nanocrystals considered in this work, as interaction with periodic images can easily be eliminated [375].

In practice, all calculations have to be converged with respect to psinc spacing, number of NGWFs, cutoff radii and kernel cutoff when it is used. Lastly, ONETEP calculates some terms of the total energy such as the kinetic energy in reciprocal space and this can be done effectively with FFTs. We note that the total number \( N_\phi \) of NGWFs scales with system size and so does the number of non-zero matrix elements of the Hamiltonian. Each of these elements requires FFTs over grid points of the entire simulation cell which scales as \( \mathcal{O}(N \log N) \) so that the computational cost associated with the evaluation of the Hamiltonian scales as \( \mathcal{O}(N^2 \log N) \). The linear-scaling of the computational
effort can be recovered by performing the FFTs in smaller regions of the simulation cell whose size is
determined by the largest cutoff $r_\alpha$ which is independent of system size. This technique is known as
the FFT box approximation [374], and it relies on the fact that $\{\phi_\alpha\}$ are localised in space, so their
Fourier transforms are smooth in k-space. The FFT box introduces artificial periodicity but this
has a small effect on accuracy. The FFT box must be chosen large enough to encapsulate the $\phi_\alpha$ in
question and any overlapping neighbour $\phi_\beta$ so that the Hermiticity of all operators is preserved and
their action is consistent throughout the calculation.

A crucial consideration when evaluating the performance of any linear-scaling method is its pref-
actor. In ONETEP, this strongly depends on the size of the FFT boxes which in turn depend on
the NGWF radii, so these have to be carefully tested for optimal performance.

### 3.2.4 Forces and geometry optimisation

As discussed in Subsection 3.1.2, once the ground-state is converged to self-consistency via the
scheme described in Eq. (3.2.32) we obtain:

$$\frac{\partial E}{\partial K^{\alpha\beta}} = 0 \forall \alpha, \beta$$  \hspace{1cm} (3.2.35)

$$\frac{\delta E}{\delta \phi_\alpha(r)} = 0 \forall \alpha.$$  \hspace{1cm} (3.2.36)

Following Pulay [209, 376], the forces can be obtained by application of the Hellmann-Feynman
theorem as

$$F_I = -\frac{dE}{dR_I} = \frac{\partial E}{\partial K^{\alpha\beta}} - \frac{\partial K^{\alpha\beta}}{\partial R_I} - \int d^3r \frac{\delta E}{\delta \phi_\alpha(r)} \frac{\partial \phi_\alpha(r)}{\partial R_I}.$$  \hspace{1cm} (3.2.37)

For a fixed psinc basis, so that $\frac{dD(r)}{dR_I} = 0$, Eq. (3.2.36) becomes

$$\frac{\partial E}{\partial c_{n,\alpha}} \frac{dc_{n,\alpha}}{dR_I} + \sum_{n}^{n \in LR(\alpha)} \frac{\partial E}{\partial D_n(r)} \frac{dD_n(r)}{dR_I} = \frac{\partial E}{\partial c_{n,\alpha}} \frac{dc_{n,\alpha}}{dR_I} = 0.$$  \hspace{1cm} (3.2.38)

For an infinitesimal ionic displacement $\delta R$, the psinc points inside the spherical atom-centred local-
isation region (LR) do not change, so we have the requirement

$$\frac{\partial E}{\partial c_{n,\alpha}(r)} = 0 \forall n, \alpha.$$  \hspace{1cm} (3.2.39)

At self-consistency, only the terms in Eq. (3.2.37) with an explicit dependence on the nuclear coor-
dinates remain, and the terms with an implicit dependence (known as Pulay terms) vanish, leaving

$$F_I = -\frac{\partial E}{\partial R_I} = F_I^{nl} + F_I^{loc} + F_I^{Ewald} + F_I^{nlcc}.$$  \hspace{1cm} (3.2.40)

Here the forces have been decomposed in contributions respectively due to the non-local and local
contributions of the pseudopotential, the Ewald energy [140] and non-linear core correction (NLCC)
[377, 378]. In practice, while the LNV generally results in Eq. (3.2.35) being satisfied to a high
degree, Eq. (3.2.36) is in general only satisfied approximately. This is because while the underlying basis of psinc functions is fixed, when atoms are moved, the LR move relative to the psinc grid and psincs move in and out of the LR, resulting in the NGWFs having a different representation in terms of the psinc basis depending on the exact ionic position. This effect is known as the “egg-box” effect [379, 380] and introduces an error in the energy and force which can be reduced by increasing the LR or using a finer psinc grid [372]. It is also because of the competition between the requirement of strict localisation within the LR and the kinetic energy operator tending to delocalise the orbitals. This results in a Pulay term due to the NGWFs given by

\[ F_{\text{Pulay}}^I = -\int d^3 r \frac{\delta E}{\delta \phi_\alpha(r)} \frac{\partial \phi_\alpha(r)}{\partial R_I}. \] (3.2.41)

The variational principle predicts that the error in energy is proportional to the square of the error in trial wavefunction, while the error in the forces should be proportional and these Pulay forces can become significant. In a similar fashion to Soler et al. [307], one can show that for a Lagrangian with the constraint of orthonormality of the Kohn-Sham orbitals

\[ \frac{\delta E}{\delta \phi_\alpha(r)} = 4 \left[ \hat{H} \phi_\alpha(r) K^{\beta \alpha} - \phi_\beta(r) \left( KHS^{-1} \right)^{\beta \alpha} \right]. \] (3.2.42)

Instead,

\[ \frac{\partial \phi_\alpha(r)}{\partial R_I} = -\nabla_r \phi_\alpha(r) \text{ for } \alpha \text{ on } I \text{ and zero otherwise} \] (3.2.43)

and as described in the previous chapter, the action of differential operator is performed using the FFT box approximation with \( G_{\text{max}} \) and \( N \) psincs inside the box. Using the expansion of NGWFs in terms of psincs

\[ \phi_\alpha(r) = \frac{1}{N} \sum_G G_{\text{max}} \tilde{\phi}_\alpha(G) e^{iG(r-R_\alpha)}, \] (3.2.44)

we obtain

\[ \frac{\partial \phi_\alpha(r)}{\partial R_I} = \frac{1}{N} \sum_G G_{\text{max}} -iG \tilde{\phi}_\alpha(G) e^{iG(r-R_\alpha)} \delta_{\alpha I} \] (3.2.45)

which can be calculated with linear-scaling computational effort [381]. In the present work, we make extensive use of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [382, 383] for geometry optimisations and have used the non-selfconsistent corrections [381] to the forces throughout unless stated otherwise.

### 3.3 The projector augmented wave method in ONETEP

One considerable source of difficulty for electronic structure methods to describe a wide range of materials with a reasonable computational overhead is that the wavefunctions can display strong spatial variations. In the bonding region the wavefunction will tend to be smooth, whereas close to the nuclei the wavefunctions will oscillate strongly due to the large nuclear Coulomb potential. In the PWPP approach, this can translate in the need for a very large basis set for “hard” pseudopotential
associated with for example: first-row elements, systems with \( d \) or \( f \) valence electrons or transition and alkali metals where for accuracy semicore states have to be described as valence states. The philosophy of the projector augmented-wave (PAW) method of Blöchl [260] is to divide space into atom-centred regions, where the wavefunction is expressed in terms of localised partial-waves, and an inter-atomic region where it is expressed in terms of a smoother (more delocalised) basis such as plane-waves. This allows it to combine the chemical accuracy and transferability of all-electron (AE) methods with the computational economy of the PWPP method. It also gives access to the all-electron wavefunction and electric fields near the nuclei useful when calculating nuclear electric field gradients [384], NMR chemical shift tensors [385] and core-level spectroscopy [386].

In PAW, a linear transformation \( \hat{T} \) relates the AE orbital \( |\psi_n\rangle \) to a soft pseudo (PS) orbital \( |\tilde{\psi}_n\rangle \) by augmenting the PS orbital with atom-centred partial waves:

\[
|\psi_n\rangle = \hat{T}|\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle + \left( |\varphi_\nu\rangle - |\tilde{\varphi}_\nu\rangle \right) \langle \tilde{\varphi}_\mu | \tilde{\tilde{\varphi}}_\nu \rangle.
\]

(3.3.1)

The transformation (Figure 3.3.1) is written in terms of projectors \( |\tilde{\tilde{\varphi}}_\nu\rangle \), AE partial waves \( |\varphi_\nu\rangle \) and PS partial waves \( |\tilde{\varphi}_\nu\rangle \) localised within a sphere of radius \( r_{PAW} \) around each atom. The projectors are defined as dual to the pseudo partial waves so that \( \langle \tilde{\varphi}_\nu | \tilde{\varphi}_\mu \rangle = \delta_\mu^\nu \) and together form a complete set within each sphere giving \( |\tilde{\tilde{\varphi}}_\nu\rangle \). Knowing the linear transformation between AE and PS orbitals, the expectation value \( \langle \hat{A} \rangle \) of an operator \( \hat{A} \) can be obtained either directly from \( \langle \psi_n | \hat{A} | \psi_n \rangle \) after transforming to the AE orbitals or as the expectation value \( \langle \tilde{\psi}_n | \hat{A} | \tilde{\psi}_n \rangle \) of a pseudo-operator \( \hat{A} \) in terms of the pseudo-orbitals where \( \hat{A} = \hat{T}^\dagger \hat{A} \hat{T} \). In order to achieve linear scaling, ONETEP’s PAW implementation [387] avoids any reference to Kohn-Sham orbitals by working with a reformulation of the PAW equations in terms of the pseudo-density matrix. We recast

\[
\hat{\rho} = \sum_n f_n \langle \psi_n | \psi_n \rangle = \hat{\rho} + \left( |\varphi_\nu\rangle \langle \varphi_\mu | - |\tilde{\varphi}_\nu\rangle \langle \tilde{\varphi}_\mu | \right) \langle \tilde{\varphi}_\mu \tilde{\tilde{\varphi}}_\nu \rangle |\tilde{\tilde{\varphi}}_\nu\rangle \langle \tilde{\varphi}_\nu | \hat{\rho} |\tilde{\varphi}_\nu \rangle,
\]

(3.3.2)

where \( \hat{\rho} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{\psi}_n \rangle \) is the pseudo-density operator. As with NCPP, the soft density matrix of systems with a bandgap is well represented by the set of \textit{in situ} optimised NGWFs \( \{ \phi_\alpha(r) \} \) as they are built from psinc functions equivalent to plane-waves. We thus apply the same approach described in Section 3.2 of minimising the total energy by optimising \( \hat{\rho} = |\phi_\alpha \rangle K^{\alpha\beta} |\phi_\beta \rangle \) varying the NGWFs and density kernel with the constraint of idempotency and normalisation. For NCPPs
these constraints were applied respectively by $K^{α\nu}S_{\nu\beta}K^{δβ} = K^{αδ}$ and $2K^{αγ}S_{γα} = N_e$. In PAW, the same forms are retained if the overlap matrix is redefined as

$$S_{αβ} = \langle φ_α | \hat{O} | φ_β \rangle = \langle φ_α | (1 + |\tilde{p}^μ|^2) (⟨φ_ν | φ_μ⟩ - ⟨\tilde{φ}_ν | \tilde{φ}_μ⟩) \rangle | φ_β \rangle. \quad (3.3.3)$$

This redefinition allows much of the machinery of ONETEP for NCPPs such as LNV and penalty routines to be readily reused. Because the functions $|\tilde{p}^μ⟩$, $|φ_ν⟩$ and $|\tilde{φ}_ν⟩$ are strictly localised, all scalar products involving these quantities are sparse matrices and can be efficiently evaluated with sparse matrix algebra. In practice, atom-centred quantities are evaluated on radial grids within spheres of radius $r_{PAW}$ centred on the atoms, while the soft quantities are evaluated on a uniform grid. The AE electronic density $n(r)$ is thus broken down [388, 389] into a PS part $\tilde{n}(r)$ evaluated on the uniform grid, an AE atomic part $n^1(r)$ and a PS atomic part $\hat{n}^1(r)$ evaluated on the radial grid,

$$n_v(r) = 2\rho(r, r) = \tilde{n}(r) + n^1(r) - \hat{n}^1(r), \quad (3.3.4)$$

where

$$\tilde{n}(r) = 2φ_α(r)K^{αβ}φ_β(r), \quad (3.3.5)$$

$$n^1(r) = 2φ_ν(r)\rho^{νμ}φ_μ(r), \quad (3.3.6)$$

$$\hat{n}^1(r) = 2\tilde{φ}_ν(r)\rho^{νμ}\tilde{φ}_μ(r). \quad (3.3.7)$$

The matrix $\rho^{νμ}$ is the projection of the density matrix in the augmentation spheres and is defined as

$$\rho^{νμ} = \langle \tilde{p}^ν | φ_α \rangle K^{αβ} \langle φ_β | \tilde{p}^μ \rangle. \quad (3.3.8)$$

Treating the interactions between the densities of different atoms represented on radial grids is difficult and instead long-ranged interactions must be properly accounted for on the regular grid. This is done by defining a soft pseudo-density for the nucleus and core electrons $\tilde{n}_{Zc}$ used in the Hartree term and $\tilde{n}_c$ used in the exchange correlation term instead of their AE versions $n_{Zc}$ and $n_c$. An arbitrary compensation density $\hat{n}(r)$ is introduced to reproduce the multipole moments of the AE charge density outside the augmentation spheres. Using the decomposition of the density of Eq. (3.3.4), we can write the total energy as

$$E = \hat{E} + E^1 - \hat{E}^1, \quad (3.3.9)$$

where

$$\hat{E} = 2K^{αβ}⟨φ_β | -\frac{1}{2} \nabla^2 | φ_α⟩ + E_{xc}[\tilde{n} + \hat{n}_c] + E_H[\tilde{n} + \hat{n}] + \int d^3rV_H[n_{Zc}](\tilde{n} + \hat{n}) + E_{II} \quad (3.3.10)$$

$$E^1 = 2\rho^{νμ}⟨φ_μ | -\frac{1}{2} \nabla^2 | φ_ν⟩ + E_{xc}[n^1 + n_c] + E_H[n^1] + \int d^3rV_H[n_{Zc}][n^1] \quad (3.3.11)$$

$$\hat{E}^1 = 2\rho^{νμ}⟨\tilde{φ}_μ | -\frac{1}{2} \nabla^2 | \tilde{φ}_ν⟩ + E_{xc}[\hat{n}^1 + \hat{n}_c] + E_H[\hat{n}^1 + \hat{n}] + \int d^3rV_H[\hat{n}_{Zc}](\hat{n}^1 + \hat{n}). \quad (3.3.12)$$
The compensation density is not included in the exchange correlation functional as its shape is unphysical and it can lead to numerical instabilities in the XC potential [390]. Differentiating the total energy with respect to the pseudo-density operator gives the pseudo-Hamiltonian operator $\tilde{H}$

$$\tilde{H} = -\frac{1}{2} \nabla^2 + \tilde{V}_{\text{eff}} + \langle \tilde{p}^\nu \rangle D_{\nu\mu} \langle \tilde{p}^\mu \rangle,$$

(3.3.13)

where $D_{\nu\mu}$ is the nonlocal energy and the effective Kohn-Sham potential $\tilde{V}_{\text{eff}}$ is expressed on the uniform grid as

$$\tilde{V}_{\text{eff}} = \tilde{V}_H[\tilde{n} + \tilde{n}] + \tilde{V}_Z[\tilde{n}_Z] + \tilde{V}_\text{xc}[\tilde{n} + \tilde{n}_c].$$

(3.3.14)

Ionic forces are obtained by application of the Hellmann-Feynman theorem, yielding:

$$F_I = -\frac{dE}{dR_I} = F_I^{\text{loc}} + F_I^{\text{nlcc}} + \hat{F}_I + F_I^{\text{nl}},$$

(3.3.15)

with components given by

$$F_I^{\text{loc}} = -\int d^3r (\tilde{n}(r) + \tilde{n}(r)) \frac{\partial \tilde{V}_H[\tilde{n}_Z](r)}{\partial R_I},$$

(3.3.16)

$$F_I^{\text{nlcc}} = -\int d^3r \tilde{V}_Z[\tilde{n} + \tilde{n}_c] \frac{\partial \tilde{n}_c(r)}{\partial R_I},$$

(3.3.17)

$$\hat{F}_I = -\int d^3r \tilde{V}_H[\tilde{n} + \tilde{n} + \tilde{n}_Zc](r) \frac{\partial \tilde{n}(r)}{\partial R_I},$$

(3.3.18)

$$F_I^{\text{nl}} = -2D_{\nu\mu} \langle \tilde{p}^\mu | \phi_\alpha \rangle K^{\alpha\beta} \langle \phi_\beta | \tilde{p}^\nu \rangle D_{\mu\nu} - 2\langle \frac{\partial \tilde{p}^\nu}{\partial R_I} | \phi_\alpha \rangle K^{\alpha\beta} \langle \phi_\beta | \tilde{p}^\mu \rangle D_{\mu\nu}$$

$$+ 2\langle \frac{\partial \tilde{p}^\nu}{\partial R_I} | \phi_\alpha \rangle H^{\gamma\delta} S^{\gamma\delta} \langle \phi_\beta | \tilde{p}^\mu \rangle O_{\mu\nu},$$

(3.3.19)

where the sums $\nu$ and $\mu$ run over projectors on atom $I$.

### 3.4 Theoretical spectroscopy

Spectroscopy is defined as the study of the interaction between matter and radiation and was arguably born when Newton, who coined the term “spectrum”, performed his prismatic experiments in the second half of the 17th century [391]. Spectroscopy encompasses a broad range of techniques relying on various radiation sources [392]: massive particles such as electrons or neutrons, electromagnetic radiation with frequencies ranging from radio-wave to gamma-ray and even acoustic waves. Spectroscopic techniques can be further classified based on the nature of the interaction between radiation and material: absorption, emission, impedance, coherence, elastic and inelastic scattering. The relentless improvements in spectroscopic techniques in the last decades, including increased spectral [393] and spatial resolutions [394] as well as better coherences and shorter measurement times [31–34], have turned them into an essential tool to probe and understand matter in its most intimate details. Some techniques that have proven particularly useful for the characterisation of
materials include: optical absorption (OA) and photoluminescence (PL) to probe the excitation or relaxation of electrons between valence and unoccupied states [395], infra-red (IR) and Raman spectroscopies to probe vibrational properties, EXAFS and XRD [396, 397], which respectively probe excitation or relaxation of electrons between core and unoccupied states and the elastic or inelastic [398] scattering of x-ray off atoms both providing fine details of the atomic structure of materials. The resolution has reached such a point that it is now possible to measure electronic dynamics directly using attosecond or femtosecond lasers and the structural transformation of nanocrystals in real time using ultrafast XRD [18]. While great progress has been made, much information is still beyond experimental reach even when multiple techniques are combined together. For example, the detailed atomic structure of small nanocrystals and their surfaces are difficult to resolve and the electronic origin of spectral peaks tricky to assign unambiguously. This state of affairs, combined with the continuous improvement in theoretical spectroscopy [399], have established the latter as a valuable tool both for interpreting experimental results and predicting the properties of materials that have yet to be synthesised. It opens up the possibility of designing materials with bespoke properties.

In general terms, spectroscopy is based on the perturbation of the system of interest and the subsequent measurement of the system’s response to the excitation. Calculating the ground-state properties is generally not sufficient to accurately simulate spectra. The excitation can come in various forms, but most relevant to this work are charged electronic excitations due to addition or removal of electrons (quasielectrons and quasiholes respectively [400–402]), neutral electronic excitations forming bound electron hole pairs (quasiparticles known as excitons [403]) and lattice excitations (quasiparticles known as phonons). In this work, we are especially interested in optical absorption arising from the neutral excitation which occurs when the electric field of a photon excites an electron from a valence to an unoccupied state. This is motivated on the one hand, because optical spectroscopy is a widely used non-destructive diagnostic tool providing a wealth of information about materials on a range of relevant timescales. On the other hand, optical properties of materials are crucial for many technological applications such as photovoltaics, sensors and light emitting devices and obtaining an accurate and computationally tractable theoretical description is of utmost importance.

Various approaches exist to calculate optical spectra associated with the neutral electronic excitations of interest in this work including, in order of increasing accuracy: perturbation theory using Fermi’s golden rule, time-dependent density-functional theory (TDDFT) [404], many-body perturbation theory in particular GW [405] combined with the Bethe-Salpeter [406–408] equation and quantum chemistry methods such as coupled-cluster response and configuration interaction. In principle, once the ground-state DFT density is obtained, the Hamiltonian and all excited states should be accessible. However, these excited Kohn-Sham states have no formal relation to the true many-body quasiparticle and excited state properties such as bandgap and spectra should not be calculated with ground-state DFT (even if one had the exact functional) as they neglect local-field effects, electron-hole interaction and renormalisation and broadening due to many-body interactions. However, it is worth noting that in practice the obtained spectra are qualitatively acceptable for many systems especially when one uses the scissor operator [409,410] in which the excited eigenvalues
are rigidly shifted so that the gap corresponds to the experimental value. To overcome these shortcomings of ground-state DFT, techniques based on TDDFT and GW have been widely employed in the condensed matter community.

The GW approximation, due to Hedin [405], is based on the explicit inclusion of a self-energy term in terms of the single-particle Green’s function and a screened Coulomb interaction. It is found to yield excellent values for the quasiparticle energies as well as accurate electron-hole interactions when combined with the Bethe-Salpeter equation [406], albeit at a large computational expense.

TDDFT is a formally exact framework for excited states based on a generalisation of the Kohn-Sham equations in terms of time dependent potential and current density due to Runge and Gross [404]. TDDFT is found to be less accurate than GW [411, 412], especially for solids, although more sophisticated functionals such as range-separated and hybrids have improved the state of affairs, but it is much cheaper computationally and simpler to implement in codes. We refer the reader to the review by Onida et al. [399] for comparison between the two methods. In this work, we have used TDDFT as it is found to work well for molecules and sufficiently small nanocrystals [413–416] and can be reformulated in a linear-scaling way [417] as we shall describe in Subsection 3.4.3.

### 3.4.1 Conduction states

In order to calculate the aforementioned spectroscopic properties, unoccupied states have to be accurately represented. In a ONETEP calculation, the energy and density are calculated by simultaneous optimisation of the density matrix and NGWFs without explicit treatment of the Kohn-Sham eigenstates. These eigenstates can always be recovered in a postprocessing step by diagonalising the Hamiltonian in the NGWF representation. However, because the NGWFs are optimised so as to minimise the total energy that depends only on the occupied states, they result in a basis that does not necessarily represent the unoccupied manifold accurately [115]. For some systems, low lying conduction states can be represented well, especially if they are of similar character to the valence states, however conduction states that are higher in energy will tend to be more delocalised and therefore poorly represented by the localised valence states. In practice, this can translate into inaccurate spectra and HOMO-LUMO gaps. Recently, a method was proposed to alleviate this shortcoming by introducing a second set of NGWFs \( \{ \chi_\beta \} \) optimised in a non self-consistent step based on a projection method [419, 420]. Recalling the Kohn-Sham single-particle density operator \( \hat{\rho} \) is defined as:

\[
\hat{\rho} = \sum_{n}^{\text{occ}} f_n |\psi_n\rangle\langle \psi_n| = |\phi_\alpha\rangle K^{\alpha\beta} |\phi_\beta|,
\]

where at idempotency the occupancies \( f_n \) are 1 for valence states and 0 for conduction states. The density operator acts as a projector onto the valence subspace implying that projection of \( \hat{\rho} \) onto \( \hat{H} \) and solving the eigenvalue equation will produce solely the valence eigenstates. Instead, projection of \( \mathbb{I} - \hat{\rho} \), will produce the conduction eigenstates only. Care must be taken to ensure that the Hermiticity of the projected Hamiltonian is preserved as the localisation constraints imposed during a calculation can lead to \( \hat{H} \) and \( \hat{\rho} \) commuting only approximately. This can be remedied by
projecting twice forming a new projected Hamiltonian from:

$$\hat{H} - \hat{\rho} \hat{H} \hat{\rho}. \quad (3.4.2)$$

This, however, causes the valence states to have energies equal to zero which is compatible with conjugate gradients only so long as the conduction energies are negative in energies. This limitation can be circumvented by shifting the energy spectrum so that all valence states are at higher energies than the desired conduction states. This is ensured by choosing a shift $\sigma$ greater than the highest conduction energy. The projected Hamiltonian is then formed by using

$$\hat{H} - \hat{\rho}(\hat{H} - \sigma) \hat{\rho}. \quad (3.4.3)$$

Defining the conduction overlap matrix $S^{\chi}_{\alpha\beta} = \langle \chi_{\alpha} | \chi_{\beta} \rangle$, the valence-conduction cross overlap matrix $T^{\chi\phi}_{\alpha\beta} = \langle \phi_{\alpha} | \chi_{\beta} \rangle$, the conduction Hamiltonian $H^{\chi}$ and the projected conduction Hamiltonian $H^{\chi}_{\text{proj}}$ given by

$$\left( H^{\chi}_{\text{proj}} \right)_{\alpha\beta} = \langle \chi_{\alpha} | \hat{H} - \hat{\rho}(\hat{H} - \sigma) \hat{\rho} | \chi_{\beta} \rangle = H^{\chi}_{\alpha\beta} - \left( T^{\dagger} K H^{\phi} K T \right)_{\alpha\beta} + \sigma \left( T^{\dagger} K S^{\phi} K T \right)_{\alpha\beta}. \quad (3.4.4)$$

We also introduce the conduction density matrix $\rho^{(c)}$ and kernel $K^{(c)}$ related by

$$\hat{\rho}^{(c)} = \sum_{c} f_{c} \langle \psi_{c} | \psi_{c} \rangle = | \chi_{\alpha} \rangle K^{(c)}_{\alpha\beta} \langle \chi_{\beta} | \quad (3.4.5)$$

where the superscript and subscript $c$ denote conduction Kohn-Sham states and “opt” the number of such optimised states. The conduction bandstructure energy $E^{(c)} = 2 \text{Tr}[K^{(c)} H^{\chi}_{\text{proj}}]$ can be
minimised by simultaneous optimisation of $K^{(c)}$ and $\{\chi_\alpha\}$ with an effort that scales linearly with size, as all involved matrices can be made sparse by virtue of kernel truncation and localisation radii of valence and conduction NGWFs (which can be different). The conduction Kohn-Sham eigenstates can be recovered by diagonalising $H^c$ and are found to be in excellent agreement with PWPP for the low lying states (Figure 3.4.1) [419]. Also, when the Hamiltonian is diagonalised in a joint basis of valence and conduction NGWFs, the eigenvalue spectrum is markedly improved. This dual representation approach allows for the accurate description of both the valence manifold and the low energy portion of the conduction manifold with planewave accuracy. One of the key limitations of using such a localised basis is its inability to represent very delocalised conduction states and unbound states. Its applicability is thus restricted to low energy and bound excitations. The same conjugate gradients algorithm as for valence calculations is used except for corrections to the NGWF gradient. For calculations to converge, an energy gap is required between highest optimised and lowest unoptimised conduction states. In practice, obtaining smoothly converging conduction calculations requires careful selection of the number of conduction NGWFs and localisation radii for each atomic species, as well as of the number of extra conduction states.

3.4.2 The linear-response formalism

To describe spectroscopic experiments, we are interested in the response of the electrons to perturbations which can be static such as a constant electric field or strain, or dynamic especially in the limit of low frequency perturbation such as phonons or low energy radiation. Perturbation theory is a general theoretical framework to deal with static and dynamic perturbations [421]. For static perturbation we start with a system in its ground-state described by Hamiltonian $\hat{H}_0$, with eigenstates $\{|\psi_n^{(0)}\rangle\}$ and eigenvalues $\{\varepsilon_n^{(0)}\}$ satisfying the TISE

$$\hat{H}_0|\psi_n^{(0)}\rangle = \varepsilon_n^{(0)}|\psi_n^{(0)}\rangle. \quad (3.4.6)$$

Assuming a small perturbation to the Hamiltonian $\hat{H}_0 \rightarrow \hat{H}_0 + \lambda \Delta \hat{H}$ where $\lambda$ is a small perturbation parameter, the basic ansatz of perturbation theory is that any quantity $X(\lambda)$ (such as the electronic density, Kohn-Sham eigenfunctions and eigenvalues) can be written as a power series of the perturbation parameter

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \ldots + \lambda^k X^{(k)}, \quad (3.4.7)$$

where the superscript $(k)$ indicates the order of perturbation. It can be shown by substituting expansions of $|\psi_n\rangle$ and $\varepsilon_n$ in Eq. (3.4.6) and equating powers of $\lambda$ that:

$$\varepsilon_n^{(1)} = \langle \psi_n^{(0)} | \Delta \hat{H} | \psi_n^{(0)} \rangle, \quad (3.4.8)$$

$$\varepsilon_n^{(2)} = \sum_{i \neq n} \frac{\langle \psi_i^{(0)} | \Delta \hat{H} | \psi_n^{(0)} \rangle^2}{\varepsilon_n^{(0)} - \varepsilon_i^{(0)}}, \quad (3.4.9)$$
\[
\psi_n^{(1)} = \sum_{i \neq n} \frac{\langle \psi_i^{(0)} | \Delta \hat{H} | \psi_n^{(0)} \rangle}{\varepsilon_n^{(0)} - \varepsilon_i^{(0)}} | \psi_i^{(0)} \rangle,
\]

(3.4.10)

\[
n_n^{(1)}(\mathbf{r}) = \sum_{n=1}^{N} \psi_n^{(0)*}(\mathbf{r}) \psi_n^{(1)}(\mathbf{r}) + \psi_n^{(1)*}(\mathbf{r}) \psi_n^{(0)}(\mathbf{r})
\]

\[
= 2 \sum_{n=1}^{N} \sum_{i \neq n} \psi_n^{(0)*}(\mathbf{r}) \psi_i^{(0)}(\mathbf{r}) \frac{\langle \psi_i^{(0)} | \Delta \hat{H} | \psi_n^{(0)} \rangle}{\varepsilon_n^{(0)} - \varepsilon_i^{(0)}},
\]

(3.4.11)

and

\[
\Delta \langle \hat{O} \rangle = \sum_n^{\text{occ}} \langle \psi_n^{(1)} | \hat{O} | \psi_n^{(1)} \rangle = \sum_{n=1}^{\text{occ}} \sum_{i} \frac{\langle \psi_n^{(0)} | \Delta \hat{H} | \psi_i^{(0)} \rangle \langle \psi_i^{(0)} | \hat{O} | \psi_n^{(0)} \rangle}{\varepsilon_n^{(0)} - \varepsilon_i^{(0)}} + \text{c.c.}
\]

(3.4.12)

In the last two equations, it can be seen that contributions from any pair of occupied and pair of unoccupied states vanish. This leads to the important conclusion that only perturbations that couple valence and conduction manifolds have an impact on density and observables.

We define the static density response function for the KS system, which determines much of its electronic properties, as the variation of the electronic density at a point \( \mathbf{r} \) due to a variation of total potential \( \hat{V}_{\text{eff}}(\mathbf{r}) \) at point \( \mathbf{r} = \mathbf{r}' \)

\[
\mathcal{X}^0(\mathbf{r}, \mathbf{r}') = \left. \frac{\delta n(\mathbf{r})}{\delta \hat{V}_{\text{eff}}(\mathbf{r}')} \right|_{\mathbf{r}' = \mathbf{r}}
\]

\[
= 2 \sum_{v=1}^{\text{occ}} \sum_{c} \frac{\langle \psi_v^{(0)}(\mathbf{r}) \psi_c^{(0)}(\mathbf{r}) \psi_v^{(0)*}(\mathbf{r}') \psi_c^{(0)*}(\mathbf{r}') \rangle}{\varepsilon_v^{(0)} - \varepsilon_c^{(0)}},
\]

(3.4.13)

where we have used Eq. (3.4.11) and the fact that for static perturbations \( \Delta \hat{H} = \Delta \hat{V}_{\text{eff}} \). In a self-consistent field theory like DFT, \( \hat{V}_{\text{eff}} = \hat{V}_{\text{ext}} + \hat{V}_{\text{int}}[n] \) and the electrons are treated as independent particles in the effective Kohn-Sham potential \( \hat{V}_{\text{eff}} \). \( \mathcal{X}^0 \) is related to the density response to an external potential \( \mathcal{X} \) as:

\[
\mathcal{X}(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta \hat{V}_{\text{ext}}(\mathbf{r}')} = \frac{\delta n}{\delta \hat{V}_{\text{eff}}} \frac{\delta \hat{V}_{\text{eff}}}{\delta \hat{V}_{\text{ext}}}
\]

\[
= \mathcal{X}^0 \left[ 1 + \frac{\delta V_{\text{int}}}{\delta n} \frac{\delta n}{\delta \hat{V}_{\text{ext}}} \right] = \mathcal{X}^0 [1 + \kappa \mathcal{X}] = \mathcal{X}^0 \left[ 1 - \kappa \mathcal{X}^0 \right]^{-1},
\]

(3.4.14)

where \( \kappa \) is known as the coupling matrix (Eq. (3.4.19)). This has the form of the ubiquitous Dyson equation and \( \mathcal{X} \) is obtained by calculating \( \mathcal{X}^0 \) from Eq. (3.4.13) and iterative substitution into Eq. (3.4.14). This can be extended to dynamic responses by considering frequency dependent \( \hat{V}_{\text{eff}}(\omega) \)

\[
\mathcal{X}(\omega) = \mathcal{X}^0(\omega) \left[ 1 - \kappa(\omega) \mathcal{X}^0(\omega) \right]^{-1}.
\]

(3.4.15)

Eq. (3.4.15) plays a crucial role in determining material properties such as phonon modes and the dielectric response which determines much of the optical properties. More importantly for this work is the property that the poles of \( \mathcal{X}(\omega) \) correspond to the true excitation energies while the non-
interacting \( X^0(\omega) \) has poles at Kohn-Sham orbital energy difference. From now on we drop the (0) superscript assuming ground-state Kohn-Sham eigenfunctions.

### 3.4.3 Linear-scaling linear-response time-dependent DFT

The two main approaches for TDDFT are the time propagation formalism [399, 422] in which the Kohn-Sham eigenvalues are explicitly propagated in time and the linear-response formalism where it is recast as an eigenvalue problem [416,423–428]. We are concerned with the latter as it is the method of choice for calculating the low energy spectra and excitations that we are interested in for optical absorption, and was recently implemented within ONETEP [417]. The Casida equations [416,424] can be arranged in matrix form

\[
\begin{pmatrix} A & B \\ B^\dagger & A^\dagger \end{pmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix},
\]

with

\[
A_{cv,c'}^{v,v'} = \delta_{vv'} \delta_{cc'} (\varepsilon_c - \varepsilon_v) + \kappa_{cv,c'}^{v,v'}
\]

\[
B_{cv,c'}^{v,v'} = \kappa_{cv,v'}^{c,c'}.
\]

The coupling matrix \( \kappa \) is given by

\[
\kappa_{cv,c'}^{v,v'} = \frac{\delta [V_{\text{H,xc}}]_{cv}}{\delta K_{c',c'}} = 2 \int d^3r \int d^3r' \psi^*_v(r) \psi_v(r) \left\{ \frac{1}{|r-r'|} + f_{xc}(r,r',\omega) \right\} \psi^*_{v'}(r') \psi_{v'}(r'),
\]

where

\[
f_{xc}(r,r') = \frac{\delta^2 E_{xc}[n]}{\delta n(r) \delta n(r')} |_{n_0}
\]

is known as the TDDFT exchange-correlation kernel. In this work we choose \( E_{xc}[n] = E_{xc}^{\text{lda}}[n] \), known as the adiabatic local density approximation (ALDA), so that the frequency dependence of the kernel is neglected (no memory effects). We note that we have ignored the spin index for convenience and are limiting ourselves to singlet states. Assuming the off-diagonal elements \( B_{vc,v'c'}^{v,v'} \) to be small, Eq. (3.4.16) reduces to a Hermitian eigenvalue problem

\[
A\vec{X} = \omega\vec{X}.
\]

This is known as the Tamm-Dancoff approximation [429] which is generally found to give good excitation energies whilst violating oscillator strength sum rules. Recently, a linear-scaling reformulation of linear response TDDFT was implemented within ONETEP avoiding reference to the Kohn-Sham orbitals by using the double representation of \{\( |\phi_\alpha\rangle \)\} and \{\( |\chi_\beta\rangle \)\} described in Subsection 3.4.1.

Following Hütter [426] and using the completeness relation, we can write the first order response
density to a trial vector \( x_{cv} \) (an instance of \( \tilde{X} \) in Eq. (3.4.21)):

\[
\begin{align*}
\langle r \mid n^1 \rangle (r) &= \sum_{c,v} \langle r \mid \psi_c \rangle x_{cv} \langle \psi_v \mid r \rangle + c.c. \\
&= \sum_{v} \sum_{c} \langle r \mid \chi^\alpha \rangle \langle \chi^\alpha \mid \psi_c \rangle x_{cv} \langle \psi_v \mid \phi^\beta \rangle \langle \phi^\beta \mid r \rangle \\
&= \chi^\alpha (r) K^{(1),\alpha\beta} (r),
\end{align*}
\]

where the effective response density kernel in mixed valence-conduction NGWF representation is

\[
K^{(1)}_{\alpha\beta} = \sum_{v} \sum_{c} \langle \chi^\alpha \mid \psi_c \rangle x_{cv} \langle \psi_v \mid \chi^\beta \rangle, 
\]

allowing us to express the response density in separable form. Eq. (3.4.23) involves an infinite sum over unoccupied states. In practice, only a few conduction NGWFs are needed to describe \( n^{(1)} \) accurately for the low-energy portion of the spectrum. A better description of higher-energy portions of the spectrum can be achieved by including more conduction states in the optimisation of \( K^{\alpha\beta}_{\{c\}} \) where we define:

\[
K^{\alpha\beta}_{\{v\}} = \sum_{v} \langle \phi^\beta \mid \psi_v \rangle \langle \psi_v \mid \phi^\alpha \rangle \\
K^{\alpha\beta}_{\{c\}} = \sum_{c} \langle \chi^\alpha \mid \psi_c \rangle \langle \psi_c \mid \chi^\beta \rangle.
\]

The lowest \( N_\omega \) excitation with energies \( \omega_i \), response density kernels \( \{K_i^{(1)}\}_{i=1,...N_\omega} \) and actions \( \{q_i^{\chi\phi}; i=1,...N_\omega\} \) are obtained variationally using conjugate gradients [430] by minimising

\[
\begin{align*}
\Omega = \sum_i \omega_i &= \sum_i \frac{\text{Tr}[K_i^{(1)}] S^{\chi} q_i^{\chi\phi} S^{\phi}}{\text{Tr}[K_i^{(1)}] S^{\chi} K_i^{(1)} S^{\phi}} \\
&= \delta_{ij}
\end{align*}
\]

with respect to \( \{K_i^{(1)}\} \) under the constraint of orthonormality of Kohn-Sham orbitals:

\[
\text{Tr}[K_i^{(1)}] S^{\chi} K_j^{(1)} S^{\phi} = \delta_{ij}
\]

The action \( (q^{\chi\phi})^{\alpha\beta} \) of TDDFT matrix \( A \) on trial vector \( \tilde{X} \) in mixed conduction-valence representation is:

\[
(q^{\chi\phi})^{\alpha\beta} = (K^{[c]} H^{\chi} K^{[1]} - K^{(1)} H^{\phi} K^{[v]})^{\alpha\beta} + (K^{[c]} V^{(1)} K^{[1]} K^{[\alpha\beta]}),
\]

where a self-consistent field potential \( V_{\text{SCF}}^{(1)} (r) \) as reaction to the response density is defined as

\[
V_{\text{SCF}}^{(1)} (r) = 2 \int d^3r' n^{(1)}(r') + 2 \int d^3r' \frac{\delta^2 E_{xc}[n]}{\delta n(r) \delta n(r')} |_{n_0} n^{(1)}(r'),
\]
and

\[
\left( V^{(1)}_{\text{SCF}} \right)_{\alpha\beta}^{\chi\phi} = \langle \chi_\alpha | \hat{V}^{(1)}_{\text{SCF}} | \phi_\beta \rangle. \tag{3.4.30}
\]

The oscillator strength of the \( i \)th excitation is given by

\[
f_{\omega_i} = \frac{2\omega_i}{3} |K^{(1),\alpha\beta}_i \langle \phi_\beta | r | \chi_\alpha \rangle|^2. \tag{3.4.31}
\]

This is similar to Fermi’s golden rule except that it also allows for mixed transitions, corresponding to the off-diagonal terms in the response matrix. All matrices \( H^\phi, H^\chi, K^{(c)}, K^{(v)} \) and \( V^{(1)}_{\text{SCF}} \) are all sparse for sufficiently large systems. However, linear-scaling can only be achieved if \( K^{(1),\alpha\beta}_i \) can be truncated similar to the density kernel in standard valence calculation. The sparsity of \( K^{(v)} \) is due to the nearsightedness when a bandgap is present and similarly for \( K^{(c)} \) when a second energy gap is present in the conduction band. This cannot be justified in general but is found to be true for localised excitations of various systems \([422, 431]\). When truncating \( K^{(1)} \), one loses the ability to calculate long-range charge transfer state, but these are generally poorly represented by ALDA TDDFT \([432]\). Truncation of \( K^{(1)} \) can thus be used as a means of excluding unwanted charge transfer states from the calculation. The orthonormality constraint of Eq. (3.4.27) means that the algorithm scales quadratically with the number of excited states, however, the prefactor associated with it is generally found to be small. Even with a fully dense \( K^{(1)} \), the algorithm shows excellent scaling as demonstrated in Ref. [417].
4 The electronic enthalpy method

“Loses the goat with ease. No remorse.”

In previous chapters, we discussed the importance of atomistic simulations (especially \textit{ab initio}) to accurately describe the properties of nanomaterials under pressure. In this chapter, we present an implementation within ONETEP of an electronic enthalpy method \cite{ref1} for the \textit{ab initio} calculation of finite systems under hydrostatic pressure. Based on a definition of the system volume $V_e$ as that enclosed within an electronic density isosurface, it supports both geometry optimisations and molecular dynamics simulations of complex geometries. We introduce a novel approach to calibrate the parameters defining $V_e$ in the context of geometry optimisations and discuss their significance. We investigate size-dependent pressure-induced structural transformations of hydrogenated silicon nanocrystals and obtain results in good agreement with simulations using explicit solvents, thereby validating our approach.

Si nanocrystals are of intrinsic interest due to their potential to overcome the indirect character of the lowest-energy interband transition of bulk Si and to be useful in optoelectronic devices \cite{ref434, ref435, ref436}. Recently, Si nanocrystals with structures based on high-pressure bulk phases have been proposed as candidates for photovoltaic applications as they display multi-exciton generation (MEG) and high quantum efficiencies \cite{ref437}. They are also found to transform under pressure between a variety of crystalline and amorphous structures that are still the subject of theoretical and experimental investigations in both the porous and colloidal forms.

A detailed analysis of the simulated polyamorphic transformations reveals three types of amorphous structures and their persistence on depressurisation is assessed. We also examine variations in the electronic properties such as the energy gap with pressure. $\text{Si}_{181}\text{H}_{110}$, the largest nanocrystal in the present work, of diameter 2.2 nm, is comparable in size to experimentally-tested organically passivated colloidal nanocrystals \cite{ref438} and demonstrates the capability of our approach. The results described in this chapter have been published in part in Ref. \cite{ref439}.

4.1 Methodology

As discussed in Chapter 1, constant pressure simulations of finite systems can be performed, in both MD and quasistatic geometry optimisation, by directly optimising the enthalpy once a suitable definition for the finite volume has been made. This can be done in a variety of ways in terms of

\footnote{\textquotedblleft The I Ching: or book of changes	extquotedblright \cite{ref433}}
atomic or electronic coordinates leading to an implicit description of the solvent. Some examples of total volume definitions have been discussed in Subsection 1.4.3. These different approaches have been compared elsewhere and were shown to qualitatively reproduce results obtained with explicit solvents [100]. By working with quasistatic geometry optimisations at zero temperature, one removes the need for equilibration with barostats and thermostats thereby giving a comparatively inexpensive way of sampling the enthalpy landscape. Depending on system complexity, this may not give a globally optimised structure nor precise information on transition paths; however, it provides the structure and energetics of the nearest local minimum.

The electronic enthalpy method proposed by Cococcioni et al. [1] introduces an electronic enthalpy functional $H = U + P_{in}V_e$, where $U$ is the total Kohn-Sham internal energy of the system, $P_{in}$ the input pressure and $V_e$ a volume definition based on an electronic density isosurface. The latter allows for the description of complex geometries and the enthalpy is optimised within ONETEP.

The nanocrystals were quasistatically relaxed at different pressures using the quasi-Newton BFGS algorithm for geometry optimisation [382]. Pulay corrections to the Hellmann-Feynman forces, as described in Subsection 3.2.4, are required to achieve accurate ionic forces and optimised structures [372,381]. The parameters which control the accuracy of the geometry optimisation must be carefully chosen for the calculations to be converged and the structures correctly relaxed. Unless specified otherwise we used $E_{cut} = 800$ eV, a universal NGWF radius $r_\phi = 4.2$ Å, respectively nine and
one NGWFs for each Si and H atom, an atomic displacement tolerance of $5.3 \times 10^{-3}$ Å, an energy tolerance per atom of $5.4 \times 10^{-4}$ eV and a maximum force tolerance of $5.1 \times 10^{-2}$ eV/Å.

It has been shown that the elastic properties of bulk Si in the diamond phase calculated with ONETEP and the PWPP code CASTEP [440] give equivalent results [441] when using the same norm-conserving Si pseudopotential [256], local density approximation exchange-correlation functional [216, 219] and plane-wave cutoff $E_{\text{cut}}$. Beyond the fact that it is well-described by DFT, Si was used as a test system due to the plethora of experimental data and computational studies with different pressure methods available for comparison. For the calibration we require a reference DFT bulk modulus at zero pressure $B_0$ and its pressure derivative $B_0' = \frac{\partial B}{\partial P}|_{P=0}$. This was calculated with CASTEP using a 2-atom primitive simulation cell, a grid of $8 \times 8 \times 8$ k-points and $E_{\text{cut}} = 800$ eV. By fitting the universal Vinet equation of state [442,443] we obtained the conventional lattice parameter $a_{\text{eq}} = 5.38$ Å, $B_0 = 96.9$ GPa and $B_0' = 4.1$.

In the electronic enthalpy method, the thermodynamic functional $H = U + P_{\text{in}}V_e$ can be minimised self-consistently within DFT algorithms. $V_e$ is defined as the interior of an electronic density isosurface at a chosen cutoff density $\alpha$. After introducing the Heaviside step function in terms of density values $\theta(\rho)$, $V_e$ is calculated as

$$V_e = \int \theta(n(r) - \alpha) d^3r. \quad (4.1.1)$$

For computational purposes, the step function can be approximated by the complementary error function as

$$\theta(n(r) - \alpha) \simeq \frac{1}{2} \text{erfc}\left(\frac{\alpha - n(r)}{\sigma \sqrt{2}}\right). \quad (4.1.2)$$

The parameter $\sigma$ adjusts the sharpness of the step function and plays an important role for numerical reasons. The resulting potential contribution is

$$\Phi_V(r) = P_{\text{in}} \frac{\delta V_e}{\delta n(r)} = \frac{P_{\text{in}}}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(n(r) - \alpha)^2}{2\sigma^2}\right). \quad (4.1.3)$$

Since the potential does not explicitly depend on the nuclear positions, the compression is implicitly transmitted to the nuclei by virtue of the forces obtained from the Hellmann-Feynman theorem [208]. This can be related to the effect of $\Phi_V$, which for a decaying density profile as in Figure 4.1.1, is a distorted Gaussian in real space and favours the compression of the electronic density for positive pressures. The shape of $\Phi_V$ is determined by the pair of input parameters $\alpha$ and $\sigma$, and approximates the solvent-nanocrystal interaction. $\alpha$ defines the excluded volume of the solvent molecules and $\sigma$ controls the range and intensity of interaction in a manner reminiscent of soft-sphere potentials. While the method describes the solvent implicitly, providing a homogeneous and time-averaged description, the emphasis is laid on the role played by electrons as pressure mediators with an account of the shape of the nanocrystal as the pressure is applied normal to the isosurfaces. This results in a natural description that allows the seamless modelling of the excluded volume of intricate
nanocrystal geometries. It also removes the need for expensive equilibration with barostats and focuses the computational effort on the electronic structure of the nanocrystal.

Figure 4.1.2 shows the isosurface bounding $V_e$ for a range of values of $\alpha$. For larger values of $\alpha$, the isosurface describes voids inside the nanocrystal, revealed by changes in slope in the plot, and results in pressure being induced internally which compensates the applied pressure. In order to describe a realistic solvent, $\alpha$ has to be chosen sufficiently small to apply a homogeneous compression without describing the rugosities of the nanocrystal too closely. When going to very small values of $\alpha$, unphysically large excluded volumes are obtained. Figure 4.1.1(c) also shows that a choice of $\alpha = 2.0 \times 10^{-3}$ Å$^{-3}$, $\sigma = 3.4 \times 10^{-3}$ Å$^{-3}$ leads to a $\Phi_V(r)$ that fails to vanish at large radii. From Eq. (4.1.3) it is evident that far from the nanocrystal where $n \to 0$, the potential $\Phi_V \sim (P_{in}/\sigma) \exp(-\alpha^2/2\sigma^2)$, and therefore a sufficiently small value of $\sigma/\alpha$ must therefore be chosen for the excluded volume to be well-defined. However, a sufficiently large value of $\sigma$ must be chosen for the potential $\Phi_V(r)$ to be accurately integrated on the underlying real-space grid, which has a spacing of $\Delta = 0.13$ Å in the present work. The above considerations give us a range of sensible values for $\alpha$ and $\sigma$, but within this range physical properties still depend on the chosen values. An approach is still needed to better resolve these depending on the system.

### 4.2 Calibration

In principle, if the parameters $\alpha$ and $\sigma$ defining a physical $V_e$ were chosen correctly, an effective external pressure $P_{eff}$ equal to the chosen input pressure $P_{in}$ would be applied to the nanocrystal. $V_e$ could be determined for different solvent-nanocrystal interfaces by comparison with simulations using explicit solvents, e.g. with MD. This would however not be practical in a fully ab initio way as explained in Subsection 1.4.4. An empirical parametrisation would also be difficult considering the
limited resolutions of experimental methods. Alternatively, $\alpha$ and $\sigma$ can be calibrated by comparing $P_{\text{eff}}$ and $P_{\text{in}}$ if a satisfactory definition of $P_{\text{eff}}$ is available. This can be done by exploiting the virial theorem in MD simulations [114], but not in geometry optimisation calculations. For these, a promising approach is to exploit the experimental [438] and computational [444] result that bonds in the bulk-like core of sufficiently large alkane-terminated Si nanocrystals in diamond structure display elastic properties similar to the bulk for a range of sizes. $P_{\text{eff}}$ can then be estimated for a range of systems and pressures from the compression of core bonds after quasistatic geometry optimisation. For the bulk we can use the Vinet equation expressed in terms of compressed and equilibrium (0 GPa) bulk conventional lattice parameters $a$ and $a_{\text{eq}}$:

$$E(a) = E_0 + \frac{B_0 a_{\text{eq}}^3}{(B'_0 - 1)^2} \left( 1 - \frac{1}{2} \frac{3a}{a_{\text{eq}}} \left( B'_0 - 1 \right) - 3B'_0 + 5 \right) \times \exp \left[ -\frac{3}{2} \left( B'_0 - 1 \right) \left( \frac{a}{a_{\text{eq}}} - 1 \right) \right].$$  \hspace{1cm} (4.2.1)$$

The internal pressure is obtained from the volume derivative of the Vinet equation of state as:

$$P_{\text{in}}(a) = 3B_0 \left( \frac{a}{a_{\text{eq}}} \right)^{-2} \left( 1 - \frac{a}{a_{\text{eq}}} \right) \times \exp \left[ -\frac{3}{2} \left( B'_0 - 1 \right) \left( \frac{a}{a_{\text{eq}}} - 1 \right) \right].$$  \hspace{1cm} (4.2.2)$$

A hydrogenated tetrahedral Si$_{71}$H$_{60}$ nanocrystal, with (100) and (111) faces, in the diamond structure was used for the calibration as it displays a sizable core which behaves elastically like the
Figure 4.2.2: Schematic showing the equivalence between bulk-like core at 0 GPa and a compressed piece of bulk of same shape at $P_{\text{int}}$. 

bulk. The average Si–Si bond length at 0 GPa is found to be contracted compared to the bulk; the contraction is reduced and tends towards the bulk value as the size of the nanocrystal is increased. Looking at individual Si–Si bonds (Figure 4.2.1), it is found that the outer shell atoms are significantly distorted, which has been interpreted as due to surface stress [445, 446], while inner shells atoms retain bond symmetry and lengths that substantially agree with bulk values. Similar results have been found for Si$_{29}$H$_{36}$ and Si$_{35}$H$_{36}$ using DFT with norm-conserving pseudopotentials and a local density approximation exchange-correlation functional [444]. Eshelby’s classical linear elasticity solution for inhomogeneities, such as embedded inclusions, yields size-independent elastic fields [447]. This is the result of neglecting surface energies which can be justified when the ratio of surface to volume atoms is small.

At the nanoscale, however, this ratio becomes important and the surface induces size-dependent elastic fields that are long-range [448]. One would expect the surfaces to induce a size-dependent strain-field and to distort the core atoms for the nanocrystal sizes investigated in this work. However, the stiffness of Si nanocrystals and the absence of reconstruction of the hydrogen-passivated surfaces result in distortions from the diamond cubic symmetry that are smaller than the displacement tolerance. This limits the effect of the surfaces for the sizes considered and simplifies the mapping between effective pressure and compression. By virtue of the nearsightedness principle, the core region is chemically equivalent to a compressed piece of bulk (Figure 4.2.2) where an internal pressure $P_{\text{int}}(a_{\text{eq}}^{BL})$ can be evaluated using Eq. (4.2.2) from the equilibrium (0 GPa) value of the conventional
lattice parameter in the bulk-like core \( a_{\text{eq}}^{\text{BL}} \). The bulk modulus of the bulk-like core can then be estimated from

\[
B_{\text{core}} = B_0 + P_{\text{int}} B'_0
\]  

(4.2.3)

For Si\textsubscript{71}H\textsubscript{60}, we find that the internal pressure in the bulk-like core due to the surface at 0 GPa is \( P_{\text{int}} = 1.45 \) GPa and using the CASTEP values of \( B_0 \) and \( B'_0 \) with Eq. (4.2.3) gives \( B_{\text{core}} = 102.8 \) GPa. As we are interested in calibrating the external pressure and want to discount for \( P_{\text{int}} \), we adapt Eq. (4.2.1) in terms of the average compressed and equilibrium (0 GPa) bulk-like conventional lattice parameters \( a_{\text{BL}} \) and \( a_{\text{BL}}^{\text{eq}} \) as

\[
E_{\text{BL}}(a_{\text{BL}}^{\text{eq}}) = E_{\text{BL}}^{\text{eq}} + B_{\text{core}} \left( \frac{a_{\text{BL}}^{\text{eq}}}{a_{\text{eq}}^{\text{BL}}} \right)^{3} \left( 1 - \frac{1}{2} \left( \frac{3 \alpha_{\text{BL}}^{\text{eq}}}{a_{\text{eq}}^{\text{BL}}} \right) (B'_0 - 1) - 3B'_0 + 5 \right) \times \exp \left( -\frac{3}{2} \left( B'_0 - 1 \right) \left( \frac{a_{\text{BL}}^{\text{eq}}}{a_{\text{eq}}^{\text{BL}}} - 1 \right) \right). 
\]  

(4.2.4)

We then define the effective pressure as

\[
P_{\text{eff}}(a_{\text{BL}}^{\text{eq}}) = 3B_{\text{core}} \left( \frac{a_{\text{BL}}^{\text{eq}}}{a_{\text{eq}}^{\text{BL}}} \right)^{-2} \left( 1 - \frac{a_{\text{BL}}^{\text{eq}}}{a_{\text{eq}}^{\text{BL}}} \right) \times \exp \left( -\frac{3}{2} \left( B'_0 - 1 \right) \left( \frac{a_{\text{BL}}^{\text{eq}}}{a_{\text{eq}}^{\text{BL}}} - 1 \right) \right). 
\]  

(4.2.5)

While the bond distributions change with the selection of the core atoms, the positions of peaks of the distribution are found to be insensitive, within the displacement tolerance, to that choice when excluding the outer shell atoms. The Vinet equation holds in the absence of phase transitions and was found to give similar, albeit better fitted, results than the Birch-Murnaghan equation [449]. \( P_{\text{eff}} \) can then be compared to the input pressure \( P_{\text{in}} \) that generated the compression, thus allowing the calibration of \( \alpha \) and \( \sigma \).

Figure 4.2.3 shows the results of our calibration for a range of parameter choices. A procedure where \( B_0 \) and \( B'_0 \) were fitted separately from Eq. (4.2.4) for each \( \alpha \) (diamonds) is seen to produce poor agreement between \( P_{\text{eff}} \) and \( P_{\text{in}} \). By contrast, it was found that using fixed values of \( B_0 \) and \( B'_0 \), either from DFT bulk values from CASTEP (crosses) or experimental values (squares), produced very similar results, and the expected linear relationship was observed (Figure 4.2.3(a)). This suggests that the assumptions entering our calibration approach and the volume definition are valid. Figure 4.2.3(b) shows that for a fixed value of \( \alpha \), the \( P_{\text{eff}} \) curves converge as a function of \( \sigma \) towards the \( 3.4 \times 10^{-4} \) Å\(^{-3} \) line. This highlights the importance of tuning \( \sigma \) for an accurate definition of \( V_c \) as discussed in Section 4.1. Finally, given an appropriate choice of \( \sigma \), Figure 4.2.3(c) shows that there is a dependence of the compression on the chosen \( \alpha \). This can be understood from the volume definition Eq. (4.1.1): changing \( \alpha \) corresponds to using a different model of solvent-nanocrystal interaction, by altering the electronic density up to which solvent molecules approach the nanocrystal. The range of \( \alpha \) values \( 2.0 \times 10^{-3} \) to \( 2.0 \times 10^{-2} \) Å\(^{-3} \) is found to give agreement between \( P_{\text{eff}} \) and \( P_{\text{in}} \) within less than 22%. While the parameters were calibrated on Si\textsubscript{71}H\textsubscript{60} and
model a representative solvent-nanocrystal interface, they are expected to be transferable to silicon nanocrystals of different sizes and shapes, particularly if they have similar surface facets, surface reconstructions or ligands. We illustrate this by comparing the effective pressure $P_{\text{eff}}$ obtained at a representative value $P_{\text{in}} = 10$ GPa, with $\alpha = 2.0 \times 10^{-3}$ Å$^{-3}$ and $\sigma = 3.4 \times 10^{-4}$ Å$^{-3}$, for three different nanocrystals $\text{Si}_{35}\text{H}_{36}$, $\text{Si}_{71}\text{H}_{60}$ and $\text{Si}_{181}\text{H}_{110}$ (where $\text{Si}_{35}\text{H}_{36}$ and $\text{Si}_{181}\text{H}_{110}$ are roughly octahedral in shape with (100) and (111) faces). We obtain $P_{\text{eff}}$=12.6, 12.2 and 12.2 GPa, respectively, indicating that the bulk-like cores of $\text{Si}_{71}\text{H}_{60}$ and $\text{Si}_{181}\text{H}_{110}$ have similar responses under pressure while $\text{Si}_{35}\text{H}_{36}$ displays a small discrepancy, which can be understood as due to the small nanocrystal size and consequent small region of bulk-like core. The transferability is expected to hold beyond hydrogenated silicon because all semiconductor nanocrystal surfaces, with or without organic ligands, will display a fairly similar range of values of valence electronic density inside and a similar exponential decay rate outside the surface. The solvent-nanocrystal interface resulting from a given choice of parameters can be considered appropriate so long as the length-scale of the isosurface variations is smaller than the size of the solvent molecules given by their vdW surface.

The numerical resolution in the estimated pressures strongly depends on the level of convergence of the forces. It was found that the limiting factor is the “egg-box” effect which can cause oscillations of the order $5.1 \times 10^{-3}$ eV/Å when the system is rigidly shifted in the simulation cell. The in situ optimisation and Pulay corrections described in Subsection 3.2.4 play an important role in keeping this effect sufficiently small. The magnitude of the “egg-box” effect increases with the coarseness of the underlying real-space grid, which in our calculations was kept at $\Delta = 0.13$ Å. Shifting $\text{Si}_{71}\text{H}_{60}$ by half a psinc spacing in all directions, a difference in lattice parameter $\Delta a_{BL} \sim 5.3 \times 10^{-4}$ Å corresponding to $\Delta P_{\text{eff}} \sim 0.1$ GPa is obtained. This was considered an adequate numerical resolution for the associated computational effort.

We now turn our attention to structural transformations in the Si nanocrystals $\text{Si}_{35}\text{H}_{36}$ and $\text{Si}_{71}\text{H}_{60}$, which have been studied by other methods [76–80]. We then demonstrate capability for
larger system sizes by studying $\text{Si}_{181}\text{H}_{110}$.

4.3 Pressure-induced transformations in hydrogenated silicon nanocrystals

4.3.1 Experimental and theoretical background

Bulk Si is of great technological importance and has been widely used as a semiconductor in both its crystalline and amorphous forms. Its phase diagram has been extensively studied and, under pressure, bulk Si has been observed to transform between 12 different structures. It transforms from the cubic diamond to the $\beta$-Sn phase at 11.7 GPa, followed by the Imma, sh, Cmca, hcp and fcc phases at respectively 13.2, 15.4, 38, 42 and 79 GPa [450–452]. Upon pressure release the sh and $\beta$-Sn phases are observed, but the diamond phase is not recovered upon full release of the pressure. Instead, a host of crystalline and amorphous metastable structures are observed, the most common of which are the BC8 and R8 phases that correspond to distorted tetrahedral structures. Unlike the bulk, the small size and the stabilising effect of the surfaces of Si nanocrystals allows for metastable structures and transformation mechanisms that are still the subject of investigation.

Size-dependence of structural, optical and electronic properties has been reported for a range of nanocrystal sizes in both colloidal [4, 438] and porous forms [49, 453].

Recent XRD experiments on colloidal plasma-synthesised Si nanocrystals, where the surfaces are initially H terminated and later functionalised with dodecane, investigate nanocrystals of diameters 3.2, 3.8 and 4.5 nm under pressures in the range 0–73 GPa at room temperature [438]. A transformation between diamond and what is interpreted to be the sh structure is reported in the range 17–22 GPa although the small size of the sample results in significant broadening of the spectra and makes it difficult to identify the structure. Another structural transformation occurs in the range 40–44 GPa and matches an hcp structure. The sh structure is recovered upon decompression down to as low as 18.4 GPa followed by a stable amorphous structure upon complete decompression.

XRD and Raman spectroscopy experiments [49] performed on porous silicon with average crystallite diameters $\sim$5 nm (with distributions at $\sim$3 nm and $\sim$7 nm) report a transformation from diamond to a HDA structure at 14 GPa which, upon pressure release, transforms to a low-density a LDA structure. More recent work [453] on porous Si with crystallites of $\sim$4 nm average diameter observes a transformation from diamond to sh structure at 20 GPa with no amorphisation up to 39 GPa. A HDA structure is recovered upon decompression around 15 GPa followed by an LDA structure at 4.5 GPa. Under a further pressurisation cycle, an amorphous to crystalline transformation is observed between LDA and sh at 18 GPa. Such reversible transformations between LDA, HDA and sh structures have also been observed for amorphous bulk Si (a-Si) [51, 52, 454].

Theoretical investigations have attempted to characterise these amorphous structures in bulk Si [51–55, 455] and hydrogenated Si nanocrystals [76–80]. The LDA structure has been described as a disordered tetrahedrally coordinated network, the HDA as a deformed tetrahedral network [53] with the presence of interstitials increasing the coordination to 5–6 and finally a VHDA structure has been postulated [55] with coordinations 8–9 as found also in ice [456]. This classification of the
amorphous structures is adopted in this thesis.

We compare our simulations with previously-reported Car-Parrinello MD simulations on \( \text{Si}_{35}\text{H}_{36} \) and \( \text{Si}_{71}\text{H}_{60} \) at 600 K using a classical explicit soft-sphere solvent (Section 1.4.1) [77] and on \( \text{Si}_{35}\text{H}_{36} \) at 300 K using the electronic enthalpy method [1]. In the former simulations, transformations from diamond to an amorphous structure with average coordination of core Si atoms of 7.3 were reported at about 30 GPa for \( \text{Si}_{71}\text{H}_{60} \) and 35 GPa for \( \text{Si}_{35}\text{H}_{36} \). An amorphous structure with average coordination 4.3 is recovered upon decompression to 5 GPa. In the latter simulations, \( \text{Si}_{35}\text{H}_{36} \) is found to amorphise around 26–28 GPa with average coordination of Si atoms reaching \( \sim6.5 \) and to remain amorphous upon pressure release to 0 GPa with an average coordination of \( \sim4. \)

No sensitivity of the results was reported when changing \( \alpha \). This can be understood as resulting from the small range of values chosen, combined with thermal noise concealing the dependence on parameters seen in the present work. Differences in transformation pressure for the same system between MD simulations using an explicit solvent [77] and the electronic enthalpy method [1] are due to the different way that the pressure is applied [114]. We do not expect direct agreement with MD nor experimental results considering that we have used a quasistatic approach: in the absence of thermal fluctuations, one needs to overpressurise the system to overcome the large activation energies associated with the energetic cost of making and breaking bonds. The absence of thermal noise in our simulations does, however, facilitate the detailed monitoring of the amorphisation and provides complementary information to that obtained with MD.

4.3.2 Structural transformations

Structural properties are generally analysed in terms of bond-length distribution, coordination number and bond-angle distribution. Moreover, we employ ring statistics as a way of tracking the evolution of the covalent Si networks. Every Si atom can be treated as a node and bonds as links connecting the nodes. We define an \( n \)-membered ring as a closed path connecting \( n \) atoms according to Guttman’s definition [457, 458], focusing on the total number of rings \( R_T \) and the proportion of nodes belonging to at least one \( n \)-membered ring \( P_n \). Two atoms \( \alpha \) and \( \beta \) are considered to be bonded when separated by a distance \( R_{\alpha\beta} \) smaller than the first minimum of the radial distribution function of the bulk \( R_{\text{cut}} = 2.82 \) Å. All nanocrystals were initially relaxed with geometry optimisation at 0 GPa, and then pressure was applied in steps of 5 GPa or less, relaxing the geometry at every pressure to find the minimal enthalpy configuration. \( \text{Si}_{35}\text{H}_{36} \) and \( \text{Si}_{71}\text{H}_{60} \) were investigated in a pressure range 0–50 GPa while only 0–25 GPa was considered for \( \text{Si}_{181}\text{H}_{110} \) as the system becomes metallic beyond 25 GPa and occupancy smearing would be needed.

A density cutoff value of \( \alpha = 2.0 \times 10^{-3} \) Å\(^{-3} \) was chosen for the rest of the calculations because it was shown to result in a good calibration (Figure 4.2.3) and enables direct comparison with the simulations of Cococcioni et al. [1]

Figure 4.3.1 shows the structures of \( \text{Si}_{71}\text{H}_{60} \) as it is compressed in the range 0–50 GPa and depressurised to 5 GPa, while Figure 4.3.2 shows a range of descriptors of these transitions. The bond angle distribution in Figure 4.3.2(a) initially shows a single peak at 109.5°, typical of the tetrahedral diamond structure. The peak broadens when the pressure applied increases from 0 GPa to 20 GPa,
which reflects a reduced degree of symmetry in the structure. No change in the coordination number of Si atoms is observed at this stage and a tetrahedral coordination is retained for the innermost Si atoms. When the pressure applied is increased to \( \sim 35 \) GPa, a structural change is observed as the nanocrystal amorphises, as evidenced by the broad bond-angle distribution. The transformation is mediated by the breaking and making of bonds which are accompanied by the appearance of interstitial atoms and an increase in coordination numbers (Figure 4.3.2(b)). To better resolve the transformation, calculations for \( \text{Si}_{71}\text{H}_{60} \) were repeated in steps of 2 GPa in the interval 20–30 GPa. Between 21–30 GPa, the average coordination of Si atoms (Figure 4.3.2(c)) increases from 4 at 0–20 GPa, to 5.1 at 27 GPa which is consistent with a transformation from diamond to HDA. However, even at 30 GPa the nearest neighbour peak remains, suggesting that some local order is retained and the first coordination shell is preserved. As the pressure is increased further, the average coordination reaches 8.3 at 50 GPa which matches that of a VHDA structure. Upon pressure release, the average coordination plummets to 6.7 at 20 GPa and 4.3 at 5 GPa corresponding to a disordered tetrahedral network consistent with a LDA structure. Similarly, for \( \text{Si}_{35}\text{H}_{36} \) one obtains a coordination of 4 at 0 GPa, 5.5 at 30 GPa, 7.3 at 40 GPa, 7.7 at 50 GPa, 4.5 upon decompression to 5 GPa and for \( \text{Si}_{181}\text{H}_{110} \) 4 at 0 GPa and 5.5 at 25 GPa (Figure 4.3.3). Figure 4.3.2(d) shows the electronic volume per atom for \( \text{Si}_{71}\text{H}_{60} \). This reveals discontinuous changes in the intervals 20–21 GPa and again at 27–30 GPa, which suggests that the structural transformations from diamond to HDA and HDA to VHDA are first order.
Figure 4.3.2: Structural transformations of Si$_{71}$H$_{60}$ under pressure (the shaded region corresponds to the depressurisation): (a) distribution of the bonded Si–Si–Si angles at 20, 25 and 35 GPa; (b) distribution of the coordination numbers of Si atoms at 20, 25 and 35 GPa; (c) average coordination number of Si atoms with pressure; (d) electronic volume per atom with pressure.
Figure 4.3.3: $\text{Si}_{35}\text{H}_{36}$ at 0 (a) and 50 GPa (d); $\text{Si}_{71}\text{H}_{60}$ at 0 (b) and 50 GPa (c) and $\text{Si}_{181}\text{H}_{110}$ at 0 (c) and 25 GPa (f).

Figure 4.3.4: Ring statistics of $\text{Si}_{71}\text{H}_{60}$ under pressure: (a) total number of rings $R_T$ with pressure; (b) proportion of nodes belonging to at least one $n$-membered ring $P_n$. 
The ring statistics shown in Figure 4.3.4(a) and Figure 4.3.4(b) indicate the presence of four distinct regions. In the interval 0–20 GPa, only 6-membered rings are present. The population of 6-membered rings decays in favour of 3-, 4- and 5-membered rings in the interval 21–30 GPa. Between 30–50 GPa, the 3-membered ring population grows further at the expense of 4- and 5-membered rings and dominates at 50 GPa. Upon pressure release, the 4-, 5-, 6- and 7-membered ring population recovers while the 3-membered ring population drops sharply as the nanocrystal dilates. 6-membered rings are a signature of the corner-sharing tetrahedra in the diamond cubic structure, while 3-membered rings arise through the formation of the equilateral triangles that cause the peak at 60° in the bond-angle distribution (Figure 4.3.2(a)). The presence of 3-, 4- and 5-membered rings indicates amorphisation and the larger 7-membered ring the formation of voids (Figure 4.3.5). Our results are consistent with the existence of three amorphous structures visited during the pressure-induced structural transformation: HDA corresponding to average coordination numbers \( \sim 5-6 \), VHDA with coordinations \( \sim 8-9 \) and LDA with coordination \( \sim 4 \) obtained upon pressure release.

A reversible amorphisation diamond\( \rightarrow \)HDA\( \rightarrow \)diamond is obtained when performing a pressure cycle between 0 and 30 GPa (Figure 4.3.6). By contrast, when increasing the pressure all the way to 50 GPa, irreversible bonding events accompany the transformation, which proceeds as diamond\( \rightarrow \)VHDA\( \rightarrow \)LDA. The final LDA structure is found to be higher in energy compared to the original diamond structure and thus corresponds to a local minimum in energy. The nanocrystals display hysteresis and comparing the upstroke and downstroke 20 GPa structures, it is clear that they are respectively crystalline and amorphous.

This behaviour demonstrates the possibility of trapping nanocrystals in unconventional bonding geometries when performing a pressure cycle, yielding electronic properties different from the bulk. Using pressure as a way of tuning material properties is a promising approach for designing bespoke materials. In particular, the ability of controlling electronic and optical properties using pressure is of interest for a variety of applications.
Figure 4.3.6: Distribution of Si–Si distances in Si$_{71}$H$_{60}$ under a pressure cycle at pressures 0, 20 and 30 GPa upstroke (top panel) and downstroke starting from 30 GPa (bottom panel).

4.3.3 Electronic properties with pressure

Under compression, we find that the HOMO–LUMO gap changes dramatically and the way this happens is strongly size-dependent. While it is well known that the local density approximation underestimates the size of the gap for Si, it does give qualitative information and significant trends [459]. From Figure 4.3.7 we observe that beyond a certain pressure, the gap drops sharply to a lower value. All clusters are semiconductors at low pressure with increased gaps for the smaller nanocrystals compared to the bulk. This can be understood as due to quantum confinement which is significant for the nanocrystals under investigation. The Si$_{181}$H$_{110}$ nanocrystal’s gap sharply drops to 0.04 eV at $\sim$25 GPa showing that it becomes metallic, whereas the smaller clusters retain a sizeable gap even at higher pressures. In the pressure range 0–20 GPa, the gap of Si$_{35}$H$_{36}$ increases with a slope that reduces as the pressure is ramped up. Meanwhile, for Si$_{71}$H$_{60}$, the gap increases at first and decreases in the range 10–20 GPa. For Si$_{181}$H$_{110}$, the gap decreases linearly in the range 5–20 GPa. This size-dependent behaviour can be interpreted as a competition between quantum confinement and the negative pressure coefficient of diamond Si. The former tends to increase the gap as the nanocrystals are compressed, while the latter tends to decrease it due to the dominance of the indirect transition (corresponding to $X_{\text{conduction}} - \Gamma_{\text{valence}}$ in the bulk). Si$_{181}$H$_{110}$, of diameter 2.2 nm, has a change of gap with pressure of -10.7 meV/GPa which is of the same order as the experimental results for 2.6 nm diameter nanocrystals of -17.2 meV/GPa [438]. As the nanocrystal size is increased, the quantum confinement effect is expected to vanish and a linear decrease of the gap remain with a slope tending to the CASTEP value for bulk diamond Si of -14.2 meV/GPa. The above results highlight the capability of our approach to simulate sizes of experimental relevance with DFT accuracy.
Figure 4.3.7: HOMO–LUMO gaps of Si\textsubscript{35}H\textsubscript{36}, Si\textsubscript{71}H\textsubscript{60} and Si\textsubscript{181}H\textsubscript{110} under pressure and comparison with experiment [438, 460] and DFT calculations on bulk Si in the diamond structure.

4.4 Concluding remarks

We have implemented an electronic enthalpy method in ONETEP to simulate nanocrystals under pressure. A novel approach to calibrate the parameters defining the electronic volume in the context of geometry optimisations was proposed, demonstrating how the pressure felt inside the nanocrystal can be successfully matched to the input pressure in the electronic enthalpy functional. We have applied this method to the structural transformations of hydrogenated Si nanocrystals of different sizes and obtained results in good agreement with simulations using explicit solvents. Our quasistatic investigation has allowed for the detailed study of polyamorphic transformations and provided information that would be difficult to extract with the thermal noise of a MD simulation. Size-dependent structural transformations were obtained between the diamond structure and the amorphous LDA, HDA and VHDA structures. The behaviour of the intermediate structures upon pressure release was investigated and depressurising from HDA and VHDA structures was found to give diamond and LDA structures respectively. These have distinct electronic properties and the changes in HOMO–LUMO gaps with pressure were analysed for different nanocrystal sizes and display qualitative agreement with experiment of similar diameters. The present work highlights the capability of our approach; barring further progress in the synthesis and probing of smaller nanocrystal sizes, techniques such as linear-scaling DFT become essential to simulate sizes of experimental relevance with quantum accuracy.
5 Amorphisation of hydrogenated germanium nanocrystals

"Same same but different."\textsuperscript{1}

In Chapter 4, we studied the structural and electronic properties of hydrogenated Si nanocrystals under pressure using an electronic enthalpy method. In this chapter we use the same methodology to study the polyamorphic transformations of equivalent hydrogenated Ge nanocrystals under pressure and make direct comparison to the results obtained for Si.

While silicon has ushered in the era of semiconductor electronics, it is oft-forgotten that the original developments in transistor technology were based on germanium [461]. In the past decade, Ge has attracted renewed interest due to its high charge-carrier mobilities (the highest hole mobility known in any semiconductor) and compatibility with existing Si based technology which make it a particularly promising material for improved transistor technology.

We investigate the evolution of the electronic structure under compression, and especially the origin of metallisation. Lastly, we compare our results to experimental data obtained on Ge nanocrystals of comparable sizes and elucidate the observed surface-induced amorphisation and new high-density amorphous metallic Ge phase. The results described in this chapter have been published in part in Ref. [462].

5.1 Experimental and theoretical background

In its bulk form Ge, like Si, displays an indirect gap (valence band maximum at $\Gamma_{\text{valence}}$ and conduction band minimum at $L_{\text{conduction}}$ as opposed to $X_{\text{conduction}}$ for Si) and is thus a poor light emitter [463, 464]. Recent studies have, however, demonstrated the possibility of inducing a direct bandgap in thin-films [465, 466] and nanomembranes [467] via strain-engineering and greatly increasing light emission. This has the potential of enabling Si-compatible group-IV photonic devices with applications such as solid-state lasers and LEDs. More specifically to nanocrystals, unlike Si nanocrystals which retains the indirect character of the bulk, Ge nanocrystals have been theoretically predicted to display strong HOMO-LUMO transitions rendering them quasi-direct in nature [468–471]. Experimentally, it has been reported that Ge nanocrystals embedded in a silicon-oxide matrix display blue-luminescence [472] which is highly desirable for optoelectronics. Other

\textsuperscript{1}Anonymous indian trader
recent experiments have observed PL due to quantum confinement in unpassivated \[473, 474\] and passivated colloidal Ge \[475–477\]. The narrow bulk bandgap of 0.67 e\(\text{V}\) and large \(\sim 24\) nm exciton Bohr radius make Ge sensitive to quantum confinement effects and a good candidate for MEG \[478\].

Si and Ge belong to the same column of the periodic table and are chemically similar with a \(s^2p^2\) valence shell, however, some interesting structural differences are observed. Upon compression, bulk Ge in the diamond structure (c-Ge) transforms to the metallic \(\beta\)-Sn phase around 10 GPa \[479\]. Further compression leads to the \(Imma\) \[36\], \(sh\) \[37\], \(Cmca\) and hcp \[480, 481\] phases respectively at 66, 90, 100 and 170 GPa. Ge also displays a number of metastable phases upon pressure release from \(\beta\)-Sn: ST12 and R8 phases are obtained on slow pressure release and the BC8 phase on rapid release \[38\]. While similar to the phases observed in Si, the transition pressures in Ge tend to be higher, with the exception of diamond \(\rightarrow\) \(\beta\)-Sn, despite its smaller bulk modulus which is often attributed to the role of \(d\) electrons \[482\]. As discussed in Section 1.3, Ge is one of only three known materials (with ice and Si) that melts under compression and its melting temperature falls with pressure. This led Mishima et al. \[45\] to predict that Ge, like ice and Si, can exhibit PIA and polyamorphism. Simulations on bulk Ge have suggested polyamorphic transformation between LDA-HDA-VHDA analogous to Si but experimental evidence has not been forthcoming \[46, 47\].

5.2 Comparison to silicon

5.2.1 Structural transformations

Following the approach of Chapter 4, we investigate hydrogenated Ge nanocrystals under pressure. We simulate \(\text{Ge}_{35}\)\(\text{H}_{36}\), \(\text{Ge}_{71}\)\(\text{H}_{60}\) and \(\text{Ge}_{181}\)\(\text{H}_{110}\) using a norm-conserving Ge pseudopotential which retains four valence electrons and a local density approximation exchange-correlation functional (CAPZ). These are equivalent in structure to the Si nanocrystals already simulated so as to allow for comparison. The pseudopotential and functional were tested for diamond structure bulk Ge in CASTEP using a 2-atom primitive simulation cell, a grid of \(8 \times 8 \times 8\) k-points and \(E_{\text{cut}} = 800\) e\(\text{V}\). This yielded \(a_{\text{eq}} = 5.59\) Å, \(B_0 = 77.9\) GPa and \(B'_0 = 4.5\) which compares favourably with the experimental values of \(a_{\text{eq}} = 5.57\) Å, \(B_0 = 77\) GPa and \(B'_0 = 4.6\).

\(\text{Ge}_{71}\)\(\text{H}_{60}\), like \(\text{Si}_{71}\)\(\text{H}_{60}\), displays a bulk-like core (Figure 5.2.1(a)) and the parameters defining the electronic volume were calibrated to give \(\alpha = 3.4 \times 10^{-3}\) Å\(^{-3}\) and \(\sigma = 5.6 \times 10^{-4}\) Å\(^{-3}\). Nine and one NGWFs were used for each Ge and H atom, and the same parameters controlling the accuracy of the geometry optimisation as in Chapter 4 were used unless specified otherwise. For the structural analyses, two Ge atoms are considered to be bonded when separated by a distance smaller than the first minimum of the radial distribution function of the bulk, \(R_{\text{cut}} = 2.94\) Å. All nanocrystals were initially relaxed with geometry optimisation at 0 GPa, and then pressure was applied in steps of 5 GPa or less, relaxing the geometry at every pressure to find the minimal enthalpy configuration. \(\text{Ge}_{71}\)\(\text{H}_{60}\), of diameter \(\sim 1.4\) nm, was investigated in a pressure range 0–50 GPa while only 0–30 GPa was considered for \(\text{Ge}_{181}\)\(\text{H}_{110}\), of diameter \(\sim 2.3\) nm, as the system becomes metallic beyond 35 GPa.

Simulations show that \(\text{Ge}_{71}\)\(\text{H}_{60}\) remains in the diamond cubic structure as it is compressed in
Figure 5.2.1: Structural transformations of Ge_{71}H_{60} under pressure: (a) distribution of nearest neighbour distances of Ge and Si atoms at 0 GPa; (b) distribution of nearest neighbour distances of Ge atoms at 0, 20, 25, 30 and 50 GPa.

The range 0–24 GPa as seen from the changes in structural descriptors (Figures 5.2.1 and 5.2.2). Figure 5.2.1(b) shows that the spread in nearest neighbour bond distance increases above 25 GPa indicating an increase in structural disorder. Figure 5.2.2(a) shows that at 25 GPa, the bond angle distribution is still centred around the tetrahedral value of 109.5° but is significantly broadened with large contributions in the range 75°–150°. The average coordination of Ge atoms (Figure 5.2.2(c)) shows a gradual increase from tetrahedral coordination to 4.5 at 35 GPa. As in Si, Figure 5.2.2(d) shows a discontinuous change in volume accompanying the onset of amorphisation between 24–25 GPa.

As the pressure is increased to 50 GPa, the structure amorphises further with the bond angle distribution becoming broader and a peak developing around 50°–60°, which was also observed in Si and interpreted as due to equilateral 3-membered rings forming. The average coordination reaches 6.5 at 50 GPa as the second coordination shell contracts and interstitial atoms appear. The nearest neighbour distance distribution at 50 GPa is as broad as 0.7 Å as the second nearest neighbour shell is pushed in and the first shell is distorted from its tetrahedral arrangement. The pair correlation function (Figure 5.2.2(e)) clearly shows a broadening of the peaks associated with the first and second coordination shell and the collective collapse of the nanocrystal into an amorphous structure. Together, these structural changes are compatible with an amorphisation from diamond to HDA.

Upon pressure release to 5 GPa, the average coordination decreases to 4.1. The pair correlation shows that the peak associated with the second coordination shell remains contracted compared to the initial 0 GPa structure and remains broad unlike the first peak which recovers upon decompression. The bond angle distribution upon pressure release (Figure 5.2.2(a)) recovers a large peak centred around ~105° but remains quite broad, extending in the range 80°–130°. This indicates that the tetrahedral bonding arrangement is largely recovered, although somewhat distorted, but medium range disorder remains. Si shows this same behaviour (Figure 5.2.2(f)) although the hys-
Figure 5.2.2: Comparison of structural transformations of Ge$_{71}$H$_{60}$ and Si$_{71}$H$_{60}$ under pressure: (a) distribution of the bonded Ge–Ge–Ge angles; (b) average nearest neighbour Ge and Si distance; (c) average coordination number of Ge and Si atoms (including H bonds); (d) electronic volume per atom; (e) pair correlation function of Ge atoms; (f) pair correlation function of Si atoms.
teresis is more pronounced. For comparison, the upstroke and downstroke average nearest neighbour distance at 5 GPa is 2.28 Å and 2.44 Å for Si and 2.35 Å and 2.40 Å for Ge. This is consistent with an LDA structure being recovered upon decompression both in Si and Ge.

Analysing the ring statistics (Figure 5.2.3) shows that in the interval 0–24 GPa only 6-membered rings are present. At 25 GPa, the appearance of 3 and 5-membered rings indicates the collapse of the 6-membered tetrahedral rings. Between 25–50 GPa, the population of 3, 4 and 5 membered rings grows at the expense of the 6-membered ring population. The 3-membered ring population dominates at 50 GPa with $P_3 = 0.96$. Upon pressure release the 4-, 5-, 6- and 7-membered ring populations recover while the 3-membered ring population plummets sharply. We therefore observe 3 distinct regions: diamond cubic, HDA with coordination $\sim 5$–6 and LDA with coordination $\sim 4$ upon pressure release. Unlike Si, no VHDA structure is obtained in the interval 0–50 GPa. This can be understood as due to sp-hybridisation occurring more easily in Si compared to Ge due to the smaller difference in the most probable radii of s and p valence orbitals [483, 484]. It is also the reason why the transformation happens at higher pressures despite the smaller bulk modulus. It has been postulated that in Ge such a VHDA phase could be observed at higher pressures [47].

5.2.2 Electronic properties with pressure

We have investigated the change in electronic structure that accompanies the amorphisation of Ge nanocrystals (Figure 5.2.4) and observe, as in Si, a sudden decrease in the HOMO–LUMO gap (Figure 5.2.5(a)) upon amorphisation. A gap is retained, as seen from the DOS in Figure 5.2.6, in the smaller Ge$_{35}$H$_{36}$ and Ge$_{71}$H$_{60}$ nanocrystals while Ge$_{181}$H$_{110}$ becomes metallic above 30 GPa. For Ge$_{71}$H$_{60}$, the gap decreases to 0.43 eV at 50 GPa and recovers a value of 1.16 eV upon pressure release to 5 GPa unlike Si$_{71}$H$_{60}$, whose gap becomes respectively 0.5 eV and 0.6 eV. Separate investigation of the HOMO and LUMO shows that both are delocalised over the whole nanocrystal and it is
Figure 5.2.4: Structures of amorphised Ge nanocrystals: (a) Ge$_{35}$H$_{36}$ at 50 GPa, (b) Ge$_{71}$H$_{60}$ at 50 GPa and (c) Ge$_{181}$H$_{110}$ at 25 GPa.
Figure 5.2.5: Comparison of (a) HOMO–LUMO gaps and (b) HOMO and LUMO energies for Ge$_{71}$H$_{60}$, Ge$_{181}$H$_{110}$, Si$_{71}$H$_{60}$ and Si$_{181}$H$_{110}$ with pressure.

Figure 5.2.6: Total DOS of Ge$_{35}$H$_{36}$ at 50 GPa, Ge$_{71}$H$_{60}$ at 50 GPa and Ge$_{181}$H$_{110}$ at 25 GPa (Gaussian smearing of width 0.1 eV).
mostly an increase in the energy of the HOMO that drives the closing of the HOMO–LUMO gap (Figure 5.2.5(b)). In Si instead, the decrease in the LUMO and increase in the HOMO contribute more evenly. Electronic density maps have been generated in an attempt to understand the origin of amorphisation. Figure 5.2.7 shows the change in electronic density across (110), (111) and (001) planes at 24, 25 and 50 GPa. At 24 GPa, the electronic density is concentrated along the covalent Ge–Ge bonds and delocalises into the interstitial regions as the nanocrystal begins to amorphise at 25 GPa. At 50 GPa, the electronic density is evenly distributed in the core of the nanocrystal with a value $\sim 0.5–0.7 \, \text{e/Å}^3$. Examining the HOMO and the LUMO of Ge$_{71}$H$_{60}$ at different pressures (Figure 5.2.7), we notice that they are delocalised over the whole nanocrystal and show strong density around strongly distorted tetrahedra with overstretched bonds. Strong HOMO and LUMO densities are also associated with dangling and floating bonds due respectively to $\sim 3$ and 5–6 coordinated
Table 5.1: Comparison of nearest neighbour distances (in Å) averaged over the whole nanocrystal \(d\) or bulk-like core \(d_{\text{core}}\) and corresponding internal pressures (in GPa). Bulk moduli (in GPa) estimated both from Eq. (4.2.3) and Cohen’s law [487] (using \(A_{\text{Si}} = 1869\) and \(A_{\text{Ge}} = 1717\) GPa · Å\(^{3.5}\)) are shown for comparison.

<table>
<thead>
<tr>
<th></th>
<th>(d)</th>
<th>(d_{\text{core}})</th>
<th>(P_{\text{int}})</th>
<th>(P_{\text{core}})</th>
<th>(B)</th>
<th>(B_{\text{core}})</th>
<th>(B_{\text{emp}})</th>
<th>(B_{\text{core}}^{\text{emp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(<em>{35})H(</em>{36})</td>
<td>2.32</td>
<td>2.32</td>
<td>2.0</td>
<td>1.7</td>
<td>105</td>
<td>103.9</td>
<td>99.1</td>
<td>98.8</td>
</tr>
<tr>
<td>Si(<em>{71})H(</em>{60})</td>
<td>2.32</td>
<td>2.32</td>
<td>1.9</td>
<td>1.5</td>
<td>104.5</td>
<td>102.8</td>
<td>99.0</td>
<td>98.5</td>
</tr>
<tr>
<td>Si(<em>{181})H(</em>{110})</td>
<td>2.31</td>
<td>2.32</td>
<td>2.5</td>
<td>1.4</td>
<td>107.2</td>
<td>102.4</td>
<td>99.8</td>
<td>98.4</td>
</tr>
<tr>
<td>Bulk Si</td>
<td>2.33</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>96.8</td>
<td>-</td>
<td>96.8</td>
<td>-</td>
</tr>
<tr>
<td>Ge(<em>{35})H(</em>{36})</td>
<td>2.39</td>
<td>2.40</td>
<td>3.0</td>
<td>2.8</td>
<td>91.5</td>
<td>90.4</td>
<td>81.2</td>
<td>81.0</td>
</tr>
<tr>
<td>Ge(<em>{71})H(</em>{60})</td>
<td>2.40</td>
<td>2.40</td>
<td>2.6</td>
<td>2.1</td>
<td>89.8</td>
<td>87.2</td>
<td>80.8</td>
<td>80.2</td>
</tr>
<tr>
<td>Ge(<em>{181})H(</em>{110})</td>
<td>2.40</td>
<td>2.41</td>
<td>2.1</td>
<td>1.4</td>
<td>87.3</td>
<td>84.3</td>
<td>80.2</td>
<td>79.5</td>
</tr>
<tr>
<td>Bulk Ge</td>
<td>2.42</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

atoms [54, 485, 486]. These cause midgap states to appear as has been previously reported by Morishita in the case of bulk Si [54].

The local density of state (LDOS) functionality was used to decompose the electronic DOS into contributions from the different shells of atoms around the centre of the Ge\(_{71}\)H\(_{60}\) nanocrystal at 25 and 50 GPa (Figure 5.2.9). At 25 GPa the HOMO–LUMO gap is reduced but no midgap states are present. We emphasise that at this stage, while the bond angles have a broad distribution the nearest neighbour bond lengths show a narrow distribution. At 50 GPa the HOMO–LUMO gap is further reduced but now midgap states appear due to the strong departure from tetrahedrality and aforementioned defects. It is found that the outer shells have larger contributions to the DOS (Figures 5.2.9(a) and (b)) mostly due to larger number of atoms in these shells. Normalising the LDOS by the number of atoms in each shell shows that they all contribute in similar proportions, although the core ones have a stronger effect on the shift of the conduction band (Figures 5.2.9(c) and (d)).

5.2.3 Nanocrystal bulk moduli

Following the discussion in Section 4.2, we estimated the bulk moduli of the bulk-like cores for the Si and Ge nanocrystals using Eq. (4.2.3) and compared them to the predictions obtained from Cohen’s empirical law [487] and calculations by Cherian et al. [244] on hydrogenated spherical nanocrystals of similar sizes. Cohen’s empirical law predicts a scaling of bulk modulus for covalent tetrahedral semiconductors:

\[
B_{\text{emp}} = A/d^{3.5},
\]

(5.2.1)

where \(d\) is the average nearest-neighbour bond length and \(A\) is a material dependent constant fitted to reproduce the bulk value of \(B_0\) at the equilibrium nearest-neighbour distance \(d_0\). Using the CASTEP derived values of \(B_0\) and \(d_0\) for the bulk diamond structure we obtain \(A_{\text{Si}} = 1869\) and \(A_{\text{Ge}} = 1717\) GPa · Å\(^{3.5}\). We compute \(B_{\text{emp}}\) both averaging only over the bonds in the bulk-like core and over the whole nanocrystals (neglecting the bonds with H) denoted respectively as \(d_{\text{core}}\) and \(d\). The results are listed in Table 5.1.
Figure 5.2.8: HOMO and LUMO 0.02 Å⁻³/² orbital density isosurfaces of \( \text{Ge}_{71}\text{H}_{60} \) at 0 GPa, 50 GPa and 5 GPa on decompression from 50 GPa.
Figure 5.2.9: DOS of Ge$_{71}$H$_{60}$ decomposed in shells around the centre of the nanocrystal: (a) at 25 GPa; (b) at 50 GPa; (c) normalised per Ge atom in each shell at 25 GPa; (d) normalised per Ge atom in each shell at 50 GPa.
Like Cherian *et al.* [244], we find that Cohen’s law fails to capture the enhancement of the bulk modulus for small nanocrystals and its strong dependence on size. It is unclear why this is the case but it is questionable whether Cohen’s empirical law is applicable to nanocrystals with bond lengths that are significantly contracted compared to the bulk. We also find an enhancement of the bulk modulus at small sizes both for Si and Ge. The enhancement is more pronounced if \( d \) is used instead of \( d_{\text{core}} \). The calculations by Cherian *et al.* [244] use PAW potentials and the local density approximation, Ge 3d states are treated as part of the core and the bulk modulus is estimated from

\[
B = V \frac{\partial^2 E}{\partial V^2}.
\]  

(5.2.2)

The volume is calculated by a convex hull algorithm, and the derivatives of the total energy \( E \) are calculated by expanding and contracting the atomic positions, keeping the surface atoms fixed and relaxing the core atoms. Bulk moduli of 117.0, 105.8 and 102.6 GPa are reported for Si with 71, 163 and 247 atoms (including H) comparable in size with Si\(_{35}\)H\(_{36}\), Si\(_{71}\)H\(_{60}\) and Si\(_{181}\)H\(_{110}\). Similarly 99.2, 87.8 and 83.9 GPa are reported for Ge nanocrystals similar in size to Ge\(_{35}\)H\(_{36}\), Ge\(_{71}\)H\(_{60}\) and Ge\(_{181}\)H\(_{110}\). We point out that these are in good agreement with our values especially for the larger two nanocrystal sizes but are not directly comparable given the different shapes and surface energetics. Our results indicate a monotonic decrease with size both of \( B \) and \( B_{\text{core}} \), except for the value of \( B \) for Si\(_{181}\)H\(_{110}\) due to including highly strained outer shell atoms in the averaging procedure.

An important consideration when comparing our estimates of bulk moduli with those of Cherian *et al.*, is that we are neglecting the direct contribution of surface energy to the bulk modulus even though the effect of surfaces is indirectly accounted for by the \( P_{\text{int}} \) it produces. We rewrite Eq. (5.2.2) as

\[
B = V \frac{\partial^2 E}{\partial V^2} = \frac{\partial^2 (E_{\text{core}} + E_{\text{surface}})}{\partial V^2} = B_{\text{core}} + B_{\text{surface}} = B_0 + P_{\text{int}}^0 B_0' + V \frac{\partial^2 E_{\text{surface}}}{\partial V^2}. \tag{5.2.3}
\]

We define an effective surface stress \( \gamma^{\text{eff}} \) for the nanocrystal, obtained by averaging over all facets as

\[
\gamma^{\text{eff}} = \left\langle \gamma_i + A_i \frac{d\gamma_i}{dA_i} \right\rangle_{\text{facets}}, \tag{5.2.4}
\]

where \( A_i \) denotes the area of facet \( i \) and \( \gamma_i \) its surface energy and the total area of the nanocrystal is \( A = \sum_i A_i \). Modelling for simplicity the nanocrystal as a perfect sphere of radius \( R \) and surface energy \( \gamma \), we can write:

\[
E_{\text{surface}} = 4\pi \gamma^{\text{eff}} R^2 = \frac{3\gamma^{\text{eff}} V^{2/3}}{(3/4\pi)^{1/3}}. \tag{5.2.5}
\]

Inserting into Eq. (5.2.3) we obtain:

\[
B_{\text{surface}} = -V \frac{\partial^2 E_{\text{surface}}}{\partial V^2} = -\frac{2\gamma^{\text{eff}}}{3R} + 16\pi R \frac{d\gamma}{dA} + \frac{256}{3} \pi^2 R^3 \frac{d^2\gamma}{dA^2}. \tag{5.2.6}
\]

Assuming for simplicity that for the small nanocrystals under consideration we are in a regime
where the last two terms can be neglected we have

\[ B_{\text{surface}} \sim -\frac{2\gamma_{\text{eff}}}{3R}. \]  

(5.2.7)

Weissmuller and Cahn [488] have shown that in the general case of an anisotropic solid in vacuo,

\[ 3V\langle P_{\text{int}}\rangle = 2A_\gamma + A_{\gamma} \frac{d\gamma_i}{dA} \langle \gamma_i \rangle_{\text{facets}} + L \langle l_j \rangle_{\text{edges}}. \]  

(5.2.8)

where \( L \) is the total length of the edges \( e_j \) given by \( L = \sum_{e_j} e_j \) and \( l_j \) is the line stress. This only assumes absence of body-forces and non-hydrostatic tractions and is generally valid for solids in mechanical equilibrium. It is a remarkable result as it shows that the average internal pressure only depends on \( A \) and \( L \), regardless of facet and edge arrangement, curvature or orientation. In the limit of an isolated spherical nanocrystal, this reduces to the well-known Laplace-Young relation [489] which predicts

\[ P_{\text{int}} = \frac{2\gamma_{\text{eff}}}{R}. \]  

(5.2.9)

Previous work has demonstrated that Eq. (5.2.9) works well even for non-spherical and faceted hydrogenated Si and Ge nanocrystals in the size regime examined in this work [490, 491]. Experimental values of \( \gamma \) for \{100\} and \{110\} non-passivated surfaces in diamond Ge and Si [492] are of the order of \( 10^{-1} \) eV/Å\(^2\). For the nanocrystal sizes in this work, ignoring the second term in Eq. (5.2.4) for simplicity, we obtain \( B_{\text{surface}} \sim -(1-2) \) GPa. This is an overestimate considering the passivation will significantly reduce \( \gamma_{\text{eff}} \) [493]. We point out that \( \gamma_{\text{eff}} \) can in principle be estimated from \textit{ab initio} simulations on bulk surfaces with the relevant reconstruction and passivations [493]. Instead, from our simulations on Si, Eq. (4.2.5) and Eq. (5.2.9), we obtain \( \gamma_{\text{eff}} \sim 5.0 \times 10^{-2} \) eV/Å\(^2\) which produces from Eq. (5.2.7) \( B_{\text{surface}} \sim -(0.5-1) \) GPa. This is an order of magnitude smaller than the reported enhancement in bulk modulus, is negative in value and cannot account for this enhancement. Cherian et al. interpreted the enhancement in bulk modulus as due to a strong interaction between ligands and surface atoms. Instead, our analysis strongly suggests that the enhancement is mainly due to the overcompression of the bonds in the nanocrystal due to the surface stress and small nanocrystal sizes. Our simple model predicts that the bulk modulus of the nanocrystal follows

\[ B = B_{\text{core}} + B_{\text{surface}} = B_0 + \frac{2\gamma_{\text{eff}}}{R} \left( B_0' \frac{1}{3} \right). \]  

(5.2.10)

It is apparent that in the limit of large nanocrystals, the bulk value is recovered. More sophisticated treatments [490, 494] can in principle account for the exact shape (including edges), line and surface stress, and strained outer shell of atoms [448]. Eq. (5.2.10) predicts that the bulk modulus of nanocrystals can be controlled both by tuning their size and surface energetics, the latter being controlled by surface coverage, ligands, solvents, nanocrystal shape and faceting.
5.3 Comparison to experiment

5.3.1 Experimental background

In this section, we compare the simulations described in Section 5.2 and experimental results obtained by the group of Dr Andrei Sapelkin (Queen Mary University London) on small colloidal hydrogenated Ge nanocrystals of size $\sim 3$ nm diameter under pressure. In these experiments, electronic and structural properties were probed by a combination of Raman, PL and XAS spectroscopies as well as TEM microscopy. We refer the reader to Ref. [495] for more details about the methodology.

Experimentally, the PL and Raman signals are lost around 17.5 and 18 GPa respectively (Figures 5.3.1(a) and 5.3.2). Visual examination of the sample also shows that the sample becomes increasingly opaque above 14.8 GPa. Together, these findings suggest a semiconductor-to-metal transition above 15 GPa, unlike bulk diamond Ge which is known to become metallic around 10 GPa [479].

The Raman spectrum, unlike the bulk, shows a highly non-linear pressure dependence of the peak position with pressure (Figure 5.3.1(a)). This was interpreted as a combined effect: on the one hand an up-shift of the peak as the Ge–Ge distance is reduced under compression and on the other hand a down-shift due to disorder and the low wavenumber side of the peak contributing more [498]. This non-linear pressure dependence combined with an increase in peak width with pressure (Figure 5.3.1(b)), indicating an increase in disorder, are consistent with a scenario of gradual surface-induced amorphisation.

Structural information about short-range order up to pressures of 24 GPa was obtained from EX-AFS measurements. These give information on Ge–Ge average distance, mean squared relative displacements (MSRD) of Ge atoms and average coordination numbers of Ge atoms. In Figure 5.3.3(a),
experimental results are compared with results for bulk diamond (c-Ge) [497] and bulk amorphous 
(a-Ge) [496] structures. In stark contrast to previous work on bulk, no sharp changes in Ge–Ge 
distance is observed in the 0–24 GPa pressure range. The bonds are compressed beyond the sta-
bility value of c-Ge without sudden change, suggesting the metallisation proceeds within a local 
structure close to c-Ge. This is in contrast to the experimental results of Yoshiasa et al. for the bulk 
diamond→β-Sn transformation and the bulk LDA→HDA transformation observed by Coppari et al. 
The MSRD data (Figure 5.3.3(b)) show no major decrease with pressure corroborating the gradual 
amorphisation scenario hypothesised from the Raman spectra measurements. The data also show a 
gradual increase in average coordination number above 18 GPa(Figure 5.3.3(c)). 

Upon pressure release, the visual appearance, PL and Raman signals are recovered although the 
latter shows an increase in broadening indicating an increase in disorder after the pressure cycle. 
The EXAFS signal is largely recovered, albeit with an average Ge–Ge distance increased by 0.01 Å 
and MSRD by $10^{-3}$ Å$^2$ indicating again an increase in disorder.

5.3.2 Comparison of simulated and experimental structural and spectroscopic 
properties

Beside the structural simulations described in Section 5.2, we calculated the vibrational density of 
states (VDOS) with the phonon density functional perturbation theory (DFPT) module [499] in 
CASTEP to make further contact with the experiment. The relaxed structures at various pressures 
were taken from ONETEP calculations and the DFPT calculations done within CASTEP with the 
same pseudopotential, local density approximation exchange correlation functional and energy cutoff. 
For the nanocrystals, the calculations were performed at the Γ-point in a cubic periodic simulation 
cell of side 20 Å producing 1 nm vacuum in all directions. Fixed occupancies and the acoustic sum 
rule correction were applied. For c-Ge, the optical phonon frequency was calculated, using a mesh of 
$8 \times 8 \times 8$ k-points, to be 295 cm$^{-1}$ (experimental value [500] of 300.6±0.5 cm$^{-1}$ at ambient conditions). 
To determine the expected behaviour of the Raman peak with pressure, the peak corresponding 
to the TO-like zone centre mode of the VDOS, associated with tetrahedral stretching of Ge–Ge 
bonds [501], was monitored with pressure between 0 and 50 GPa. The Raman activity tensors 
were not calculated due to the computational cost, hence neglecting the frequency dependent and 
Stokes thermal factors. This, however, only affects the intensity of the peaks and not their relative 
positions, and hence does not invalidate the analysis. The DFPT calculations were performed on 
Ge$_{71}$H$_{60}$ which, while smaller than the experimental system, results in computationally tractable 
calculations for the VDOS. Starting in an ordered configuration also helps better identification of 
signatures of structural disorder in the experimental data. Simulations (Figure 5.3.1(a)) show a 
similar trend to experiment albeit shifted to a higher pressure: we observe a non-linear shift of peak 
position with a discontinuity appearing at 25 GPa followed by a plateau between 25–50 GPa. By 
looking at the structures we notice that this discontinuity correlates with the onset of amorphisation, 
as can be seen from structural descriptors described in detail in Section 5.2.

We compare the pressure dependence of HOMO–LUMO gaps obtained from simulations with 
the PL data (Figure 5.3.2). While it is widely known that local density approximation DFT gives
inaccurate values of the gap for c-Ge, the importance of confinement effects at the small nanocrystal sizes considered are expected to conceal this proportionally small error [459]. The HOMO–LUMO gaps obtained from simulations for Ge\textsubscript{71}H\textsubscript{60} show a sharp drop at 25 GPa but no metallisation (gap closure) is observed. As for Si nanocrystals, this is interpreted as due to the pronounced confinement effects for the nanocrystal sizes investigated. The behaviour of Ge\textsubscript{181}H\textsubscript{110}, which overlaps with the smallest experimental size, shows a drop at 25 GPa and closing of the gap above 30 GPa confirms this. The simulations are thus consistent with the experimental loss of PL signal, albeit at lower pressure, and it is expected that simulating larger nanocrystal sizes will lead to a sharp semiconductor-to-metal transition upon amorphisation at pressures closer to the experimental value.

Figure 5.3.2: Comparison of experimental PL peak position and simulated HOMO–LUMO gaps of Ge\textsubscript{71}H\textsubscript{60} and Ge\textsubscript{181}H\textsubscript{110} with pressure.

inaccurate values of the gap for c-Ge, the importance of confinement effects at the small nanocrystal sizes considered are expected to conceal this proportionally small error [459]. The HOMO–LUMO gaps obtained from simulations for Ge\textsubscript{71}H\textsubscript{60} show a sharp drop at 25 GPa but no metallisation (gap closure) is observed. As for Si nanocrystals, this is interpreted as due to the pronounced confinement effects for the nanocrystal sizes investigated. The behaviour of Ge\textsubscript{181}H\textsubscript{110}, which overlaps with the smallest experimental size, shows a drop at 25 GPa and closing of the gap above 30 GPa confirms this. The simulations are thus consistent with the experimental loss of PL signal, albeit at lower pressure, and it is expected that simulating larger nanocrystal sizes will lead to a sharp semiconductor-to-metal transition upon amorphisation at pressures closer to the experimental value.

Figure 5.3.3(a) compares Ge–Ge nearest neighbour distance from experimental measurements and simulations. A Ge–Ge bond cutoff of $R_{\text{cut}} = 2.45$ Å is employed in the analysis of simulations as the experimental Ge–Ge distances correspond to an average over the first peak of the Fourier transformed EXAFS signal. Also, bonds containing H are not captured experimentally so we do not include them in the simulated average coordination numbers (Figure 5.3.3(c)). The experimental data is in good agreement with simulations considering again the expected overestimation in transformation pressure in the simulations – the onset of transformation is shifted to 25 GPa due to the lack of temperature, solvation and smaller system sizes. Upon pressure release, the average Ge–Ge distance largely recovers both in experiment and simulation although increased by 0.01 Å and 0.02 Å respectively.

Together, the experimental and simulation results provide strong evidence that small hydrogenated Ge nanocrystals amorphise from cubic diamond to HDA accompanied by a semiconductor-to-metal transition. This behaviour is distinct from that of bulk Ge and larger Ge nanocrystals [502], for which a diamond→β-Sn transition is observed. The origin of this difference can be understood as due to the prominent role of surfaces, which alter the Gibbs free energy landscape and lead to
Figure 5.3.3: Comparison of EXAFS experiment and simulations: (a) Ge–Ge distance from EXAFS experiment and simulations with pressure (value on decompression also included for reference) and comparison with experimental c-Ge [497] and a-Ge [496]; (b) experimental Ge–Ge MSRD obtained from the EXAFS Debye-Waller factor with pressure and comparison with experimental c-Ge and a-Ge; (c) average coordination from experiment and simulations (without H bonds).
new transformation pathways and metastable configurations compared to the bulk. In the bulk, the diamond→β-Sn transition proceeds by a bending of bond angles from the tetrahedral value of 109.5° to 150° in the octahedral arrangement. This flattening of the tetrahedra opens voids for the second nearest neighbour shell to contract inwards. This also leads to an increase in the first coordination shell distance and large change in $c/a$ ratio from 1.414 to 0.55 [503]. For a spherical nanocrystal, such a change in $c/a$ ratio would lead to an increase in surface to volume ratio and the collective transformation would be impeded by the associated energetic cost. For larger nanocrystals, this leads to an increase in transformation pressure depending on surface energetics and can result in fragmentation often initiated at defects. For nanocrystals below a certain size, the prominence of the surfaces, possible lack of defects and high energetic cost of fragmentation drive the amorphisation as a way of releasing the local strain and geometric frustration. It is important to note that in the experiment an amorphous surface layer is present and acts as a precursor that lowers the energetic barrier to amorphisation into LDA. The amorphisation then starts around $\sim$5 GPa, as seen by a small and gradual increase in MSRD (Figure 5.3.3(b)), while the diamond-structured core remains stable up to 18 GPa. Instead, in simulations we start off in an ordered configuration and this can also be an additional reason for the higher transformation pressure.

Experimentally, it has proven difficult to conclusively observe LDA-HDA transitions in the bulk (a-Si [49,50] and a-Ge [56,496,504,505]) due to unfavourable transition kinetics [506] and nucleation of crystalline phase. The simulations together with experimental data show that size effects can be used to suppress the transition to β-Sn and instead observe an HDA structure upon compression and LDA structure upon pressure release. We predict on the basis of the simulations in Chapter 4, that similar behaviour can be expected in small Si nanocrystals. Our findings suggest that in small nanocrystals, surface and PIA are more pervasive than in bulk systems and have important implications for the synthesis of amorphous materials (including metallic ones).

### 5.3.3 Pressure and size dependence of energy gaps

We analyse the pressure dependence of the PL signal and HOMO–LUMO gaps further. Unlike bulk Si whose lowest energy gap follows $\Gamma_{\text{valence}} - X_{\text{conduction}}$ across the pressure range [57], c-Ge shows a strong qualitative dependence on pressure [471,507]. At small pressures, the $\Gamma_{\text{valence}} - \Gamma_{\text{conduction}}$ gap is lowest and as pressure is increased, $\Gamma_{\text{valence}} - L_{\text{conduction}}$ becomes lowest followed by $\Gamma_{\text{valence}} - X_{\text{conduction}}$. Depending on the compression, the bulk gap will have the corresponding pressure coefficients of 147, 58 and $-7$ meV/GPa [508]. For small nanocrystals, the confinement effects also affect the pressure-dependence of the gap in addition to the pressure-coefficients associated with bond compression of bulk and we expect this to be more pronounced for Ge compared to Si as it has a smaller effective mass. Weissker et al. found [471] that discounting the effect of the confinement in Si and Ge, unreconstructed nanocrystals displayed a pressure-dependence of the gap that closely followed that of the bulk. This can be rationalised by the orbitals in the unreconstructed nanocrystal, delocalised over the whole core, being derived from the bulk states and therefore displaying similar pressure-dependence. Accounting for surface reconstructions significantly alters the observed behaviour, which remained qualitatively similar to the bulk but was much reduced.
in magnitude. It is worth mentioning that Weissker et al. treated compression as a homogeneous scaling of atomic coordinates and this could affect the validity of the results at higher pressures, as it neglects the pressure dependence of surface reconstructions.

The present simulations show that the HOMO–LUMO gaps have a pressure coefficient of $15.8$, $11.85$ and $-0.4$ meV/GPa for Ge$_{35}$H$_{36}$, Ge$_{71}$H$_{69}$ and Ge$_{181}$H$_{110}$ respectively compared to $-0.03$ meV/GPa from the experimental PL signal. This is a large discrepancy compared to the bulk value of $-7$ meV/GPa expected at large compressions. Si$_{181}$H$_{110}$ instead, gave a value of $-10.7$ meV/GPa in closer agreement to the experimental $-14$ meV/GPa bulk $\Gamma$ valence $-X$ conduction pressure coefficient. We rationalise this by the more pronounced confinement effects in Ge that mean that bulk-like pressure dependence is attained for comparatively larger nanocrystals than Si.

We compare the size dependence of the HOMO–LUMO gap with experimental results from Bochstedt et al. [473, 474] (Figure 5.3.4) for bare Ge nanocrystals. Experiments find that confinement is more pronounced in Ge than Si and find a bandgap crossing for small nanocrystals of size $\sim 2.3$ nm. In our simulations, Ge nanocrystals also show a larger gap than Si but we do not observe the crossing in the examined size range. We do expect a crossing at larger sizes considering the larger bulk HOMO–LUMO gap value of Si compared to Ge. This qualitatively agrees with predictions based on effective mass and tight-binding models but contradicts the results from Reboredo and Zunger [510]. The latter argued on the basis of a $L_{\text{conduction}} - X_{\text{conduction}}$ crossing of the conduction band, the lowest conduction orbital goes from being $X_{\text{conduction}}$ to $L_{\text{conduction}}$ derived depending on nanocrystal size, that such a bandgap crossing should not be observed. As pointed out by Bochstedt, the systems used by Reboredo and Zunger are unrelaxed and passivated with pseudohydrogen and other studies have since confirmed the importance of these factors that we believe are realistically captured in our calculations. The good agreement of simulated energy gaps with experiment is likely to be fortuitous considering that we are using a single-particle treatment and neglect self-energy and electron-hole
interactions.

5.4 Concluding remarks

We have simulated the structural transformations of hydrogenated Ge nanocrystals under pressure and compared them to the equivalent Si nanocrystals of Chapter 4. We observe PIA from diamond to HDA and polyamorphic transformation HDA to LDA upon pressure release. Unlike Si, no VHDA structure is observed in the examined pressure range. We have also analysed the factors driving the metallisation in Ge nanocrystals during amorphisation and find that it is driven by highly-distorted tetrahedra and defects such as dangling bonds. A method was introduced to estimate the bulk moduli of Si and Ge nanocrystals and find that the enhancement with small sizes can, largely, be explained by compression of the bonds in the bulk-like core. We compare our simulations to recent experiments on Ge nanocrystals of similar sizes and find good consistency between the two and help elucidate the surface-induced amorphisation and new high-density amorphous metallic phase that is observed.
6 Deformation and optical properties of cadmium sulphide nanocrystals under pressure: ligand and size dependence

"More is different."

In Chapters 4 and 5, we have focussed on the size-dependence of structural and electronic properties of hydrogenated Si and Ge nanocrystals. In this chapter, we investigate CdS nanocrystals displaying tunable chemophysical properties. CdS and CdSe nanocrystals have received much attention due to their broad absorption spectra in the visible range, narrow emission spectra, high fluorescence quantum yield, colloidal processability and stability under a wide range of operating conditions. A plethora of potential applications have been proposed ranging from biomarkers [6] to nanosensors [9, 512]. For any such application, the ability to control nanocrystal properties is crucial and relies on a detailed understanding of how these properties depend on size, shape, stoichiometry, defects, surface chemistry (including ligands) and environmental conditions such as temperature, pressure and solvent.

We investigate the impact of size and ligand on the structural and optoelectronic properties of CdS nanocrystals under pressure. We then simulate their optical absorption spectra with pressure using TDDFT and deconvolve the various mechanisms affecting them. Lastly, we discuss implications of the simulations for the rational design of optoelectronic devices.

6.1 Experimental and theoretical background

Advances in nanotechnology are intimately linked to progress in the synthesis of well-characterised samples. Colloidally produced nanocrystals generally come with a distribution of sizes and structures which makes it difficult to understand and control their properties. Besides, existing spectroscopic techniques are limited in their ability to characterise individual nanocrystals and their surfaces, and an accurate knowledge of the structure is often unavailable. Over the last decade, much theoretical and experimental effort has focused on the size-dependence of optoelectronic properties of nanocrystals [5, 513, 514]. Nevertheless, a rigorous understanding of the role of surface morphology on the optoelectronic and structural properties of nanocrystals is still lacking.

P. W. Anderson [511]
Much insight could be gained from *ab initio* simulations but nanocrystals with realistic sizes and ligands are composed of a large number of atoms that are computationally challenging to simulate. In experiments, organic ligands with large HOMO-LUMO gaps are often used to passivate nanocrystal surfaces and saturate dangling bonds as the latter can negatively affect optical properties (e.g. non-radiative charge recombination). Thus far, due to lack of information about nanocrystal structure and computational cost, most simulations of CdS and CdSe nanocrystals, with a few exceptions [515–524], have approximated them by extracting small pieces of bulk and terminating dangling bonds with H atoms. It is, however, becoming increasingly clear that a proper description of nanocrystal-ligand interaction is essential to retain comparability with experiment as its impact on the chemophysical properties goes beyond simple passivation [525–527]. Ligands can be used to functionalise nanocrystals and tune their chemophysical properties in a variety of ways: increase their solubility, prevent nanocrystal agglomeration, tune band-edge energy levels (important for charge transfer) [528], prevent corrosion [529] and tune their optical properties [530].

Remarkably, single-sized nanocrystals can be obtained in a few cases [531–537] through crystallisation of nanocrystals into superlattices. Their structure has been well-characterised by single-crystal XRD measurements performed on the superlattice, as well as EXAFS and other spectroscopic measurements both on the superlattice and dissolved nanocrystals. A notable example is the superlattice based on the Cd$_{32}$S$_{14}$(SC$_6$H$_5$)$_{36}$DMF$_4$ nanocrystal synthesised by Herron *et al.* [534]. The system is a tetrahedron with an 82 atom ZB core (∼1.5 nm diameter), surfaces passivated by phenyl rings and corners capped with dimethylformamide (DMF) molecules. An interesting feature is the presence of open clefts running along the tetrahedral edges. The centre of the nanocrystal is composed of 10 atoms (4 Cd and 6 S) with the same arrangement as bulk ZB. The average Cd–S bond length is found to be contracted (2.503 Å) compared to the bulk (2.519 Å). The nanocrystal dissolves intact in tetrahydrofuran (THF) and at 77 K displays a sharp absorption peak at 366 nm (3.39 eV) and a broader and weaker one at 313 nm (3.97 eV). At room temperature, the lowest peak shifts to ∼358 nm (3.47 eV) and this position is found to be independent of solvent polarity suggesting the ground or excited state have a small dipole moment. This led Herron *et al.* to suggest that this peak corresponds to a quantum-confined exciton state.

The dependence of nanocrystal structural and optoelectronic properties on pressure and how they vary with size and ligands is still very much an open question. It is not only of fundamental interest but is also of technological importance for applications such as pressure sensors and other tunable optoelectronic devices. In this chapter, we simulate Cd$_{32}$S$_{14}$(SC$_6$H$_5$)$_{36}$·4(N(CH$_3$)$_3$) (referred to as CdS–phenyl) which is chemically analogous to the structure of Herron *et al.* except for a CHO group substituting a CH$_3$ group at each corner. We also investigate a hydrogen capped version Cd$_{32}$S$_{14}$(SH)$_{36}$·4NH$_3$ with the same core and smaller versions with similar shape and stoichiometry Cd$_{10}$S$_{4}$(SC$_6$H$_5$)$_{12}$·4(N(CH$_3$)$_3$) and Cd$_{10}$S$_{4}$(SH)$_{12}$·4NH$_3$ (respectively referred to as CdS–H, small CdS–phenyl and small CdS–H). We also constructed Cd$_{32}$S$_{28}$(SH)$_{12}$·4NH$_3$, a model RS structure with similar corner and surface terminations as CdS–H. All structures are shown in Figure 6.1.1.
Figure 6.1.1: Simulated CdS nanocrystal structures: (a) Cd_{10}S_4(SH)_{12} \cdot 4NH_3 (small CdS–H); (b) Cd_{10}S_4(SC_6H_5)_{12} \cdot 4(N(CH_3)_3) (small CdS–phenyl); (c) Cd_{32}S_{14}(SH)_{36} \cdot 4NH_3 (CdS–H); (d) Cd_{32}S_{14}(SC_6H_5)_{36} \cdot 4(N(CH_3)_3) (CdS–phenyl); (e) Cd_{32}S_{28}(SH)_{12} \cdot 4NH_3 (RS model)
6.2 Methodology

6.2.1 PAW potentials generation and testing

The CdS nanocrystals were simulated using the implementation of PAW [387] within ONETEP described in Section 3.3. PAW atomic datasets were generated with the Atom-PAW code [539] with the threefold goal of accuracy, efficiency and transferability for the following electronic configurations:

- Cadmium with 12 valence electrons including semi-core \(4d\) states: \([\text{Kr}]4d^{10}5s^{1,5}p^{0,5}\)
- Sulphur with 14 valence electrons (denoted by \(S^{14}\)) including semi-core \(2s\) and \(2p\) states: \([\text{He}]2s^22p^63s^23p^4\)
- Sulphur with 6 valence electrons (denoted by \(S^{6}\)): \([\text{Ne}]3s^23p^4\)
- Nitrogen with 5 valence electrons: \([\text{He}]2s^22p^3\)
- Carbon with 4 valence electrons: \([\text{He}]2s^22p^2\)
- Hydrogen with a single valence electron: \(1s^1\)

The datasets were tested on the bulk WZ, ZB and RS structures (Figure 6.2.1 compares the WZ and ZB structures) within the PAW implementation of ABINIT [388], and compared to simulations by Ping et al. [540] and experimental results by Mujica et al. [541]. The structures were first relaxed to find equilibrium lattice parameters. Total energies were then calculated at various primitive cell volumes by scaling the cell parameters and performing constant volume optimisations. For WZ, the
Table 6.1: Comparison of structural parameters obtained for the WZ, ZB and RS phases in ABINIT using $S^6$ and $S^{14}$ (denoted with subscripts “6” and “14”) with DFT simulations with CASTEP by Ping et al. [540] using ultrasoft pseudopotentials with the same electronic configuration as Cd and $S^6$ (denoted by subscript “sim” ). Experimental results obtained by Mujica et al. [541] are also listed for reference (denoted by subscript “exp” ).

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$c$</th>
<th>$c/a$</th>
<th>$B_0$</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZB$_{14}$</td>
<td>5.76</td>
<td></td>
<td></td>
<td>67.9</td>
<td>4.6</td>
</tr>
<tr>
<td>WZ$_{14}$</td>
<td>4.07</td>
<td>6.65</td>
<td>1.633</td>
<td>67.7</td>
<td>4.7</td>
</tr>
<tr>
<td>RS$_{14}$</td>
<td>5.34</td>
<td></td>
<td></td>
<td>92.3</td>
<td>4.7</td>
</tr>
<tr>
<td>ZB$_{6}$</td>
<td>5.76</td>
<td></td>
<td></td>
<td>69.6</td>
<td>4.6</td>
</tr>
<tr>
<td>WZ$_{6}$</td>
<td>4.07</td>
<td>6.65</td>
<td>1.633</td>
<td>67.8</td>
<td>4.7</td>
</tr>
<tr>
<td>RS$_{6}$</td>
<td>5.34</td>
<td></td>
<td></td>
<td>92.5</td>
<td>4.7</td>
</tr>
<tr>
<td>ZB$_{exp}$</td>
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<td></td>
<td>62.0</td>
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<tr>
<td>WZ$_{exp}$</td>
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<td>1.62</td>
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<tr>
<td>RS$_{exp}$</td>
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<td></td>
<td>86.7</td>
<td>4.4</td>
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<td>ZB$_{sim}$</td>
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<td></td>
<td></td>
<td>66.0</td>
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</tr>
<tr>
<td>WZ$_{sim}$</td>
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<td>6.66</td>
<td>1.625</td>
<td>66.9</td>
<td></td>
</tr>
<tr>
<td>RS$_{sim}$</td>
<td>5.36</td>
<td></td>
<td></td>
<td>90.1</td>
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</tr>
</tbody>
</table>

cell parameters were scaled keeping the $c/a$ ratio constant and using the equilibrium value of $u$ as a starting point. The energy versus volume curves were fitted with the Birch-Murnaghan equation to evaluate $B_0$, $B'_0$, the equilibrium volume per atom $V_0$ and energy per atom $E_0$. The thermodynamic transition pressures were calculated using the common tangent method on the fitted curves.

Convergence tests were performed with respect to the following parameters: number of core and valence states, occupancies, number of partial waves per valence state, reference energies of the partial waves, augmentation radii, pseudisation scheme and shape functions. The potentials for Cd and S were generated by solving a scalar-relativistic Dirac equation [542] as relativistic effects become important for heavy elements. The PW92 local-density approximation exchange-correlation functional [217] was used both in the dataset generation and subsequent ONETEP calculations. It was found that using two partial waves per angular momentum channel, one at the atomic energy level and the additional one corresponding to a conduction state chosen arbitrarily 27.2 eV or more above the atomic level, was found to produce good agreement with all-electron calculations using ELK [543]. In the case of $S^6$, an additional $d$ partial wave was generated at reference energy 0 eV to ease convergence for a variety of crystal symmetries. Similarly, partial waves corresponding to valence and conduction $5p$ states were generated for Cd. The local pseudopotential was constructed to reproduce high angular momentum scattering properties (including the $f$ channel, shown to be important at surfaces by Kiejna et al. [544]) by matching the logarithmic derivatives of the radial wave functions of the pseudo and all-electron atom. For Cd, S and N, the RRKJ scheme [255] was used for pseudising partial waves and found to yield projectors optimally localised in reciprocal space and thus efficient calculations. Instead for C and H, the Vanderbilt scheme [259] was used as found to produce efficient calculations. The projectors were generated and orthogonalised to pseudo-partial waves via a Gram-Schmidt-like procedure. Bessel shapefunctions [389] were found to lead to stable convergence and were used throughout.
Table 6.2: Thermodynamic transformation pressures (in GPa) estimated by the common tangent method between the bulk WZ, ZB and RS phases in ABINIT for different $E_{\text{cut}}$ (in eV).

<table>
<thead>
<tr>
<th>$E_{\text{cut}}$</th>
<th>WZ$\rightarrow$RS with $S_{14}$</th>
<th>ZB$\rightarrow$RS with $S_{14}$</th>
<th>WZ$\rightarrow$RS with $S_{6}$</th>
<th>ZB$\rightarrow$RS with $S_{6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>1.8</td>
<td>1.7</td>
<td>2.1</td>
<td>2.1</td>
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<tr>
<td>650</td>
<td>3.1</td>
<td>3.1</td>
<td>2.2</td>
<td>2.2</td>
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<tr>
<td>975</td>
<td>2.0</td>
<td>2.0</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>1300</td>
<td>2.0</td>
<td>2.0</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The structural parameters obtained with ABINIT using the generated PAW potentials, the PW92 local-density approximation exchange-correlation functional, plane-wave cutoff $E_c = 800$ eV and a grid of $6 \times 6 \times 6$ k-points are listed in Table 6.1 and compared to simulations of Ping et al. [540] and experimental results of Mujica et al. [541]. The simulations of Ping et al. [540] were performed with CASTEP using ultrasoft pseudopotentials for Cd and S with configuration [Kr]$4d^{10}5s^2$ and [Ne]$3s^23p^4$, the CAPZ local density approximation exchange-correlation functional [216, 219], and plane-wave cutoff $E_{\text{cut}} = 290$ eV. Grids of $7 \times 7 \times 7, 4 \times 4 \times 4$ and $6 \times 6 \times 6$ k-points were used respectively for WZ, ZB and RS. Both $S_{14}$ and $S_{6}$ are found to produce almost identical structural properties in good agreement both with the simulations of Ping et al. [540] and experiment. Table 6.2 compares the ZB/WZ$\rightarrow$RS transition pressures, a sensitive convergence test, for different energy cutoffs and S potentials. Using a grid of $6 \times 6 \times 6$ k-points, it is found that the transition pressure is converged within 0.1 GPa for $E_{\text{cut}} = 650$ eV cutoff in the case of $S_{6}$ and $E_{\text{cut}} = 975$ eV for $S_{14}$. Thermodynamic transition pressures for WZ/ZB$\rightarrow$RS of 2.0 GPa using $S_{14}$ and 2.2 GPa using $S_{6}$ are obtained. For comparison, Ping et al. report a transition pressure of 2.18 GPa for WZ$\rightarrow$RS. A sensitivity analysis shows that values of transition pressure depend most strongly on the error in $E_0$. We thus find that using $S_{6}$ produces sufficiently accurate results whilst avoiding the computational overhead associated with the highly-localised semi-core states. This contrasts with Cd, for which retaining the semi-core $4d$ states is found to be important.

As a further test, the DOS for bulk ZB, RS and WZ obtained with all-electron ELK code and ABINIT using the generated Cd and $S_{6}$ PAW potentials were compared. Figure 6.2.2 shows that except for a semi-core state at -9 eV shifted by $\sim 0.5$ eV, a good agreement is found both in the valence and conduction bands. Highly energetic transitions associated with such semi-core states have little importance for the low-energy portion of the optical absorption spectra that are of interest in this work. We thus used the $S_{6}$ potential throughout.

### 6.2.2 Geometry optimisations and conduction calculations

The ONETEP calculations were performed using the same tolerances as in Chapter 4 except for a tighter displacement tolerance for the geometry optimisation of $5.3 \times 10^{-4}$ Å. The PW92 local density approximation exchange-correlation functional was used in all calculations. The parameters defining the electronic volume were set as $\alpha = 2.0 \times 10^{-3}$ Å$^{-3}$ and $\sigma = 3.4 \times 10^{-4}$ Å$^{-3}$. Nine valence NGWFs were used for Cd and S, four for N and C, and one for H, all with a universal NGWF radius $r_\phi = 4.8$ Å. Similarly for the conduction NGWFs, except that five NGWFs were employed.
for each H and a universal conduction radius of $r_\chi = 6.3$ Å was used. Both valence and conduction NGWFs are initialised with a pseudoatomic solver, solving the Kohn-Sham equation for the isolated pseudoatom, which produces an ideal atomic orbital basis [305,307,545–547]. The 4$d$ semicore states were removed from the conduction set when optimising the conduction NGWFs as they are fully occupied.

Tests were conducted to determine the required number of optimised conduction NGWFs for an accurate description of the low-energy part of the conduction manifold that is important for optical properties. Figure 6.2.3(a) shows the large discrepancy obtained between using the joint conduction+valence basis of NGWFs as opposed to valence only. Figure 6.2.3(b) shows that using 30 conduction states gives equivalent results to using 80 across a large range of energies and that the conduction optimisation procedure is satisfactory.

6.3 Size and ligand dependence of structural properties under pressure

We performed geometry relaxations of the various CdS nanocrystals to investigate the size and ligand dependence of their structural properties under pressure. Figure 6.3.1 clearly shows that unlike Si and Ge, CdS nanocrystals display a complex pattern of Cd–S bond contraction and dilation depending on the distance from surface. Even at the centre of the nanocrystal, the bonds are strained well beyond the bulk ZB values and, unlike Si and Ge nanocrystals, we cannot talk about a bulk-like core. CdS–phenyl at 0 GPa has an average Cd–S bond length of 2.501 Å, in excellent agreement with the experimental value of 2.503 Å by Herron et al. for $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}\text{DMF}_4$. It is apparent

Figure 6.2.2: Comparison of DOS for bulk ZB simulated with all-electron ELK and the generated PAW potential with ABINIT.
Figure 6.2.3: Comparison of DOS for CdS–phenyl at 5 GPa: (a) with a valence or joint conduction+valence basis using 80 additional conduction states; (b) in the joint conduction+valence basis using 30 or 80 additional conduction states.

Figure 6.3.1: Comparison of the distribution of nearest neighbour Cd–S distances of CdS–phenyl at 0, 5 and 10 GPa with the bulk ZB values, computed with ABINIT, at 0, 5 and 10 GPa shown for reference.
from Figure 6.3.1 that the pressure dependence of the strain pattern is not merely an isotropic scaling of atomic coordinates as is often assumed. As an example, Weissker et al. [471] relaxed Ge nanocrystals at 0 GPa and approximated the effect of pressure by isotropically scaling the atomic coordinates. This approximation may be acceptable for Si and Ge nanocrystals but not for the CdS nanocrystals examined here. Instead, the electronic enthalpy method used here allows for non-isotropic pressure-dependent structural relaxation. It is also apparent from the simulations that the strain pattern is strongly dependent on the size and ligands. Figure 6.3.2 shows the difference between the relaxed 0 GPa structure of CdS–phenyl and CdS–H. At 0 GPa, the structure of CdS–H and CdS–phenyl show significant differences despite having the same CdS core. The CdS core of CdS–phenyl is less symmetric compared to CdS–H, showing distortions that are most pronounced at the surface. Figure 6.3.3 shows a detailed comparison of Cd–S bond distributions for the various sizes and ligands with pressure. It is apparent from Figure 6.3.3(a), that at 0 GPa both CdS–H and CdS–phenyl show significant distortions compared to bulk ZB (as much as 0.04 Å at the surface). CdS–phenyl is more disordered than CdS–H, as seen by the spread in Cd–S bond lengths for a given shell of ~0.02 Å. It is interesting to note that in CdS–phenyl, this spread extends all the way to the centre of the nanocrystal, although reduced in magnitude. At 5 GPa (Figure 6.3.3(b)), the spread is reduced but is still more pronounced for the CdS–phenyl compared to CdS–H both in magnitude and shell position from centre. This indicates that the nanocrystal contracts differently depending on the ligand and can be attributed to differences in surface energy and ligand-surface interactions.

Looking at Figure 6.3.3(c) and (d), the smaller CdS–H and CdS–phenyl nanocrystals show similar trends in strain with ligands but the small size and prominent surface leads to more pronounced distortions compared to the larger nanocrystals. Again, the phenyl-capped nanocrystal is more distorted than the hydrogen-capped one. At 5 GPa, the distortions are very pronounced, with as much as ~0.1 Å difference in the bond length compared with bulk ZB and a spread in position from

Figure 6.3.2: Comparison of the structure of the CdS core of CdS–phenyl and CdS–H (overlaid in blue) relaxed at 0 GPa: (a) top and (b) side view.
Figure 6.3.3: Comparison of nearest neighbour Cd–S distances for: (a) CdS–H and CdS–phenyl at 0 GPa; (b) CdS–H and CdS–phenyl at 5 GPa; (c) small CdS–H and small CdS–phenyl at 0 GPa; (d) small CdS–H and small CdS–phenyl at 5 GPa.
the centre for a given shell of $\sim 1 \text{ Å}$, as opposed to $\sim 0.01 \text{ Å}$ and $\sim 0.1 \text{ Å}$ for the larger nanocrystals. We also investigated the bond angle distributions, which further corroborate this picture. Distortions, as seen in the spread in bond angle distribution, increase with pressure and decrease with size, and are more pronounced in the phenyl-capped nanocrystals.

The above results demonstrate that the CdS nanocrystals examined in this work are not merely passivated pieces of bulk with elastic responses dictated by their bulk moduli. Instead, large structural rearrangements compared to the bulk are observed with pressure and depend on size, shape (not examined here) and surface chemistry in a complex fashion.

### 6.4 Size and ligand dependence of electronic structure under pressure

The effect of size and ligands on the properties of nanocrystals under pressure is not limited to structure but also has a strong impact on their optoelectronic properties. Figure 6.4.1 shows the behaviour of the HOMO-LUMO gap with pressure for the different nanocrystals, and compares it to experiments on bulk WZ [548] and ABINIT DFT simulations for bulk ZB. Strong quantitative and qualitative differences between pressure coefficients for the various simulated nanocrystals are observed. The energy gap of CdS–H increases linearly between 0 and 5 GPa with a coefficient of 28 meV/GPa, compared to 30 meV/GPa for bulk ZB simulated with DFT. Experimentally, bulk CdS in the WZ structure (the stable structure at ambient conditions) has a pressure coefficient of 44 meV/GPa and is found to transform to RS around 2.5 GPa with the energy gap dropping to 1.6 eV and remaining flat up to 10 GPa. Above 5 GPa, the energy gap of CdS–H is found...
to decrease as the distortions become important and decreases to 2.13 eV at 15 GPa. It is worth mentioning that the quasistatic approach used in this work can artificially trap the structure in metastable configurations, especially when large activation barriers are associated with structural transformation, and the inclusion of thermal effects is expected to lead to structural transformations before 15 GPa. Instead, the CdS–phenyl departs from the bulk-like behaviour at smaller pressures of ~1 GPa due to the more pronounced surface-induced distortions. The smaller CdS–H does not follow the bulk trends but increases slightly between 0–3 GPa and remains flat throughout the 3–15 GPa pressure range. Again we interpret this difference compared to the larger CdS–H as due to more pronounced distortions and prominence of surface energetics. The small CdS–phenyl’s gap decreases throughout the examined pressure range, in qualitative difference with the aforementioned nanocrystals. Lastly, the model RS structure is found to have a flat dependence with pressure between 10–15 GPa. Figure 6.4.2 shows the total DOS with pressure for CdS–H and CdS–phenyl and emphasises the qualitative differences in the behaviour of the nanocrystals’ electronic structure with pressure.

The rich phenomenology of the simulated nanocrystals with pressure is the result of a complex interplay between geometry and electronic structure. We investigate the band edge orbitals with pressure to gain further insight into the chemistry of the problem. Figure 6.4.3 shows the nature of the HOMO and LUMO for CdS–H at 0 and 5 GPa. The HOMO belongs to a set of three degenerate π-orbitals delocalised over the whole nanocrystal with most weight on S atoms. The LUMO, instead,
Figure 6.4.3: Comparison of band edge orbitals of CdS–H (0.01 Å$^{-3/2}$ orbital density isosurface) at 0 GPa and 5 GPa.
Figure 6.4.4: Comparison of band edge orbitals of small CdS–H \((0.01 \text{ Å}^{-3/2})\) orbital density isosurface) at 0 GPa and 5 GPa.
Figure 6.4.5: Comparison of band edge orbitals of CdS–phenyl (0.01 Å$^{-3/2}$ orbital density isosurface) at 0 GPa and 5 GPa.

is a mid-bulk-gap state typical of non-stoichiometric anion-rich ionic nanocrystals [524]. The LUMO is also delocalised over the whole nanocrystal but with relatively more weight on the Cd atoms. The LUMO+1 is part of a set of three degenerate states localised on the corners, and separated from the LUMO by a significant energy gap of \( \sim 0.5 \) eV. The ordering and character of the band edge orbitals remains largely unchanged going from 0 to 5 GPa. Figure 6.4.4 shows that the small CdS–H nanocrystal has similar, albeit less symmetric, orbitals compared to CdS–H but they appear to distort more strongly with pressure which could explain why the trends of the energy gap differ from the bulk-like behaviour of CdS–H.

Figure 6.4.5 shows that for CdS–phenyl, the HOMO is localised more strongly over surface S atoms and phenyl groups, while the LUMO is more evenly distributed over both Cd and S in the core and less delocalised over the phenyl rings. This is in agreement with the experimental observation that phenyl rings act as good hole acceptors [528]. The HOMO and LUMO of CdS–phenyl are found to be similar in character to those of CdS–H. Increasing the pressure from 0 to 5 GPa has the effect of delocalising the HOMO more evenly over the core and the LUMO over the phenyl ligands. We see from Figure 6.4.6, that the band edge orbitals for the small CdS–phenyl are similar in character to those of CdS–phenyl although more strongly hybridised over the phenyl ligands. It is also apparent that the orbitals tend to be more evenly delocalised over the whole nanocrystal compared to CdS–
Figure 6.4.6: Comparison of band edge orbitals of small CdS–phenyl (0.01 Å$^{-3/2}$ orbital density isosurface) at 0 GPa and 5 GPa.
phenyl. We can deconvolve some of the mechanisms affecting the electronic structure by considering four key factors:

1. Quantum confinement: the band edge orbitals tend to be delocalised over the whole nanocrystal and confinement effects become important in the size regime under consideration (in bulk WZ CdS, Wannier-Mott excitons with Bohr radii of ~3 nm form [549]). Confinement has the effect of increasing the energy gap compared to the bulk value as the nanocrystal size is reduced. This is apparent from the energy gap at 0 GPa (Figure 6.4.1): the small CdS–H has a gap of 2.91 eV and the CdS–H of 2.56 eV compared to 1.45 eV for bulk ZB. Interestingly, the energy gap of the small CdS–phenyl of 2.77 eV is reduced compared to the small CdS–H despite having the same core. This can be understood as the band edge orbitals of the small CdS–phenyl nanocrystal delocalising over the phenyl and leading to an increased effective radius. In the CdS–phenyl the energy gap is of 2.58 eV, similar to CdS–H as the orbitals are not fully delocalised over the whole nanocrystal.

2. Hybridisation: the interaction between the phenyl ligands and the nanocrystal surface leads to a coupling between the phenyl HOMO and nanocrystal valence band edge orbitals. This coupling produces hybrid orbitals at the organic-inorganic interface that have a mixed character of both ligand and nanocrystal. The phenyl rings are covalently bonded to surface S atoms and the aromatic rings also act as hole acceptors accentuating the delocalisation of valence edge orbitals onto them. The strength of hybridisation depends strongly on the alignment of the energy levels of phenyl HOMO and nanocrystal valence edge orbitals, as well as spatial overlap and symmetry of the orbitals and can be estimated from perturbation theory [550]. The HOMO of the phenyl has $\pi$-type symmetry while the valence band-edge of the nanocrystal is mostly composed of S 3p orbitals with considerable density at the surface and mixing is both symmetrically and spatially allowed. As the ligand and nanocrystal energy levels align, the mixing becomes more resonant and the potential barrier for hole delocalisation is reduced which in turn reduces quantum confinement and the energy gap. The choice of ligand can thus be used as another way of engineering the energy gap as has been demonstrated experimentally for CdSe [551, 552]. We find that hybridisation shows a complex dependence on size and pressure as seen from Figures 6.4.5 and 6.4.6. Delocalisation of charge onto the ligands also has consequences for optical properties as electron-hole overlap and hence recombination rates are affected.

3. Distortion: distortions have the effect of breaking the discrete translational symmetry of the nanocrystal core. For the nanocrystal size regime investigated in this work, distortions can change the charge carrier localisation, band-edge energy levels and energy gaps significantly [553–557]. The electronic structure can then be “strain-engineered” by adjusting the size, ligands and pressure. Breaking the translational symmetry of the core has the effect of lifting the degeneracy of certain electronic states and can also change their ordering. Unlike CdS–H, it is apparent that the ordering of the band-edge orbitals of CdS–phenyl changes with pressure as seen from the fact that the LUMO+2 and higher orbitals are different in character.
Table 6.3: Energy levels of band edge orbitals (in ev) of CdS–H and CdS–phenyl at 0 and 5 GPa.

<table>
<thead>
<tr>
<th></th>
<th>CdS–H 0 GPa</th>
<th>CdS–H 5 GPa</th>
<th>CdS–phenyl 0 GPa</th>
<th>CdS–phenyl 5 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO-2</td>
<td>-4.5995</td>
<td>-4.6621</td>
<td>-3.6475</td>
<td>-3.1933</td>
</tr>
<tr>
<td>HOMO-1</td>
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<td>-4.6594</td>
<td>-3.6421</td>
<td>-3.1906</td>
</tr>
<tr>
<td>HOMO</td>
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<td>-4.6594</td>
<td>-3.6394</td>
<td>-3.1851</td>
</tr>
<tr>
<td>LUMO</td>
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<td>-1.9475</td>
<td>-1.0608</td>
<td>-0.6637</td>
</tr>
<tr>
<td>LUMO+1</td>
<td>-1.4253</td>
<td>-1.3138</td>
<td>-0.5766</td>
<td>-0.2013</td>
</tr>
<tr>
<td>LUMO+2</td>
<td>-1.4253</td>
<td>-1.3138</td>
<td>-0.5513</td>
<td>-0.1822</td>
</tr>
<tr>
<td>LUMO+3</td>
<td>-1.4226</td>
<td>-1.3138</td>
<td>-0.544</td>
<td>-0.1714</td>
</tr>
</tbody>
</table>

Table 6.4: Energy levels of band edge orbitals (in ev) of the small CdS–H and small CdS–phenyl at 0 and 5 GPa.

<table>
<thead>
<tr>
<th></th>
<th>small CdS–H 0 GPa</th>
<th>small CdS–H 5 GPa</th>
<th>small CdS–phenyl 0 GPa</th>
<th>small CdS–phenyl 5 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO-2</td>
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<td>-4.1344</td>
<td>-4.4418</td>
<td>-3.9766</td>
</tr>
<tr>
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<td>-4.0582</td>
<td>-4.3738</td>
<td>-3.9114</td>
</tr>
<tr>
<td>HOMO</td>
<td>-4.8443</td>
<td>-3.9168</td>
<td>-4.3139</td>
<td>-3.8597</td>
</tr>
<tr>
<td>LUMO</td>
<td>-1.9312</td>
<td>-1.0254</td>
<td>-1.4525</td>
<td>-1.2594</td>
</tr>
<tr>
<td>LUMO+1</td>
<td>-1.292</td>
<td>-0.3454</td>
<td>-1.4117</td>
<td>-1.2022</td>
</tr>
<tr>
<td>LUMO+2</td>
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<td>-0.3400</td>
<td>-1.2512</td>
<td>-0.9792</td>
</tr>
<tr>
<td>LUMO+3</td>
<td>-1.2675</td>
<td>-0.3264</td>
<td>-1.2240</td>
<td>-0.9275</td>
</tr>
</tbody>
</table>

(Figure 6.4.5). Instead, the orbitals close to the band-edges HOMO-HOMO-3 and LUMO-LUMO+1 retain the same character at 0 and 5 GPa. From Table 6.3 we notice that in the CdS–H case, the set of three states HOMO-2–HOMO and LUMO+1–LUMO+3 are nearly-degenerate (splittings of ~3 meV) and remain so at 5 GPa. For CdS–phenyl, these states are comparatively less degenerate with a valence edge splitting of ~8 meV and conduction band edge splitting of ~30 meV. The symmetry breaking is more pronounced in the case of the phenyl capped case due to the strong surface-induced distortions. It is apparent from Table 6.4 that this effect is accentuated for the smaller CdS–H and CdS–phenyl as the surface energetics become more important and the distortions even more pronounced. For the small CdS–H at 5 GPa, the valence edge splitting is ~0.2 eV and conduction band edge splitting ~20 meV. Similarly, the small CdS–phenyl at 5 GPa has a valence edge splitting of ~0.12 eV and conduction band splitting of ~0.27 eV. This trend is in line with the structural disorder analysed in Section 6.3.

4. Electrostatics: significant charge redistribution arises due to change in size, surface and pressure. To better resolve them we decompose the DOS into contributions from Cd, S and ligand atoms depending on their chemical environments. Figure 6.4.7 shows the marked difference in trends of the DOS with pressure for CdS–H and CdS–phenyl. The LDOS for CdS–H confirms that valence band edge orbitals are mostly localised on S atoms, especially core and unligated surface ones. At 5 GPa, the occupied DOS from facet unligated S is reduced while the contribution from corner S increases slightly. Also, the unoccupied DOS increases slightly on the facet ligated S. For CdS–phenyl, as for CdS–H, similarly to CdS–H, the application
Figure 6.4.7: DOS projected onto S, Cd and ligand atoms for: (a) CdS–H at 0 GPa; (b) CdS–H at 5 GPa; (c) CdS–phenyl at 0 GPa; (d) CdS–phenyl at 5 GPa. For visibility the DOS is scaled by a factor of 1/10 for C and 1/2 for H atoms.
Figure 6.4.8: DOS projected onto S, Cd and ligand atoms for: (a) small CdS–H at 0 GPa; (b) small CdS–H at 5 GPa; (c) small CdS–phenyl at 0 GPa; (d) small CdS–phenyl at 5 GPa. For visibility the DOS is scaled by a factor of 1/10 for C and 1/2 for H atoms.
of pressure results in a decrease of occupied DOS coming from unligated facet S. The C and ligated S contribute much DOS at the valence band edge at 0 GPa, while the unligated and core S also contribute but in smaller proportion. The midgap LUMO state instead is mostly localised on the surface Cd with much less weight coming from the ligands. At 5 GPa, the ligated surface S and C still contribute most to the valence edge DOS but the core and corner S contributions increase. For the LUMO, the C and H and ligated S begin to contribute in larger proportion compared to 0 GPa. This indicates that the distortions tend to increase the hybridisation. Analysing the small CdS–H and CdS–phenyl shows similar decrease of occupied DOS on facet unligated S with pressure increase and large contributions from the phenyl C. Unlike their larger counterparts, the shape of the DOS of phenyl and H-capped nanocrystal appears qualitatively different, probably because of strong distortions. The changes in partial charges were obtained by Mulliken analysis and listed in Appendix A. While the values obtained are sensitive to the methodology, qualitative trends are expected to be meaningful. Charge redistribution with pressure is observed both in the core and on the ligands. Polarisation effects are important due to ligand-ligand interactions (thiophenol has an intrinsic dipole of 1.24 D pointing towards the phenyl group) and ligand-nanocrystal interactions and produce an interfacial dipole that tends to compensate the intrinsic dipoles. At 0 GPa, dipoles estimated from the Mulliken partial charges in the range 0.8-1.1 D are obtained depending on chemical environment, while at 5 GPa these increase to 1.2-2.0 D. These dipoles tend to shift the relative energy levels of the orbitals depending on their orientation and the localisation. Because the band edge orbitals tend to be delocalised over the whole nanocrystal, their relative energy separation is not significantly altered by the interfacial dipoles [558, 559]. This can be seen from Figure 6.4.9 in that the HOMO and LUMO levels change almost in step.

6.5 TDDFT optical absorption spectra

TDDFT calculations were performed on the relaxed structures following the method described in Subsection 3.4.3 and with optimised conduction NGWFs with the parameters listed in Subsection 6.2.2. Absorption spectra were first converged with respect to the number of optimised transitions as shown in Figure 6.5.1 for small CdS–H. It was found that 12 transitions were needed for the CdS–H and 30 transitions for CdS–phenyl nanocrystals to capture the two absorption peaks as observed experimentally by Herron et al. for Cd32S14(SC6H5)36DMF4 dissolved in THF. The transitions were decomposed into contributions from different single-particle Kohn-Sham orbitals to determine their character. An intriguing size and ligand dependence of the absorption spectra with pressure is observed.

For CdS–H, the first absorption peak retains its oscillator strength between 0 and 5 GPa and is shifted up in energy with pressure with the same pressure coefficient as the HOMO-LUMO gap. Indeed analysis of CdS–H at 0 GPa shows that this peak is composed of pure transitions from the near-degenerate HOMO-2–HOMO states to the LUMO. This is expected considering that the states are delocalised over the whole nanocrystal which remains highly symmetric. The second peak instead arises from transitions between HOMO-8–HOMO-12→LUMO and are more mixed in
Figure 6.4.9: Dependence of HOMO and LUMO energy levels (0 eV corresponds to the vacuum level) with pressure for the various nanocrystals.

Figure 6.5.1: Comparison of the TDDFT absorption spectra of small CdS–H at 0 GPa for different number of optimised transitions.
Figure 6.5.2: Comparison of the optical absorption spectra (Gaussian smearing 0.05 eV) with pressure obtained with TDDFT for: (a) CdS–H; (b) CdS–phenyl; (c) small CdS–H; (d) small CdS–phenyl.
character. Analysis of CdS–H at 5 GPa produces equivalent contributions. Similarly for the small CdS–H, the first peak also arises from HOMO-2–HOMO $\rightarrow$ LUMO while the second peak also has HOMO-5–HOMO-7 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1–LUMO+2 contributions. For the small CdS–H at 5 GPa, the HOMO-3–HOMO-4 $\rightarrow$ LUMO become important contributors to the first peak, while the second peak has a similarly mixed character. Unlike CdS–H, the oscillator strengths of the first peaks are reduced as pressure is increased. This is due to the distortions breaking the symmetry as opposed to a reduction in electron-hole overlap (the band edge orbitals remain delocalised over the whole nanocrystal).

Interestingly, for the CdS–phenyl at 0 GPa, the first peak is mostly due to HOMO-5–HOMO-7 $\rightarrow$ LUMO. The oscillator strengths of transitions due to HOMO-2–HOMO $\rightarrow$ LUMO are suppressed due to hybridisation reducing electron-hole overlap. The second peak is relatively broad and arises from multiple transition that are mixed in character. At 5 GPa, the first peak is due to HOMO-2–HOMO $\rightarrow$ LUMO which regains oscillator strength as the orbitals delocalise more over the core of the nanocrystal and the electron-hole overlap increases. The oscillator strength of the first peak gradually reduces with increasing pressure again something we interpret as mostly due to disorder.

For the small CdS–phenyl, at 0 GPa, the transition between HOMO-2–HOMO $\rightarrow$ LUMO is again suppressed, and the main peak arises from multiple transitions that are mixed in character and include transition from HOMO $\rightarrow$ LUMO+1–LUMO+5. At 5 GPa, HOMO-1 and HOMO-4 also contribute. The main peak is, as for CdS–phenyl, broadened and suppressed with pressure as a result of the degeneracy lifting due to distortions.

We compare the absorption spectra of CdS–H and CdS–phenyl to the experimental one obtained by Herron et al. for Cd$_{32}$S$_{14}$(SC$_6$H$_5$)$_{36}$DMF$_4$ dissolved in THF at 77 K. As in experiment, two absorption peaks are obtained, although the second peak is comparatively suppressed in CdS–phenyl at 0 GPa. While the absolute peak positions are underestimated by $\sim$0.8 eV compared to experiment, as expected with ALDA, their relative separation of $\sim$0.5 eV is in good agreement with the experimental value of 0.58 eV.

We note that solvent effects have been neglected and their screening properties can change the energy levels of band-edge orbitals (especially hybridised ones) with important effects on the absorption spectra [518]. We do, however, expect this effect to be limited in the case of a mildly-polar solvent such as THF (static dielectric constant of 7.6). Temperature effects and vdW interactions have also been neglected throughout but are expected to lead to relatively small structural differences in the high pressure regime under investigation. Electron-phonon interactions, including zero-point motion effects, can significantly renormalise the energy gaps and affect the optical properties and should be investigated further [560]. Methodological errors associated with TDDFT in the ALDA approximation such as spurious low-energy charge-transfer states [561] and the sensitive dependence on choice of exchange-correlation functionals for orbital energy levels are more problematic as shown in a study by Albert et al. [562]. More sophisticated functionals, for example range-separated functionals with a fraction of exact exchange [563], could improve agreement with experiment but the picture is not expected to change qualitatively for the nanocrystal sizes explored here, for which the quantum confinement energy is larger than the exciton binding energy.

142
6.6 Concluding remarks

The overall picture emerging is that of a strong quantitative and qualitative dependence of optoelectronic properties with pressure, with behaviour depending strongly both on size and ligand. An interplay between disorder and electron-hole localisation strongly suppresses certain transitions. This has important technological consequences for applications relying on efficient PL, for example pressure sensors and LEDs, where strong photoexcited electron-hole overlap is important to ensure high charge carrier recombination rates. Hybridisation and distortions can lead to separation of photoexcited electrons and holes and are thus to be avoided in such applications. Experimentally, nanocrystals based on a core-shell design, with type I level alignment, have been favoured for such applications precisely because the shell produces a potential barrier to the states in the core, effectively confining them and avoiding charge transfer to the surface.

For pressure sensors, it is preferable to have an optical response with pressure that is linear, efficient and not too sensitive to environmental fluctuations or ligand conformation. CdS–H shows such behaviour in the 0–5 GPa pressure range, while the other simulated nanocrystals do not. The midgap LUMO state was found to play a dominant role in the low-energy part of the absorption spectrum of the investigated nanocrystals. The presence of such midgap states is strongly dependent on stoichiometry [524], which could thus be used as an important tool for controlling optoelectronic properties. Midgap states can also arise because of defects, due to interstitials or dangling bonds for example, and will in general suppress the PL by localising charge carriers and reducing electron-hole overlap. By analogy with heterojunctions, it is favourable to use insulating ligands (with large HOMO-LUMO gaps) to prevent charges tunneling to the surface and it has been demonstrated experimentally how PL can be enhanced by using insulating instead of hole accepting ligands [528–530, 551].

In applications such as photovoltaics instead, charge transfer is desired because the aim is to transduce photoelectric energy into electrical current. Using again the analogy with heterojunctions, structures with type II level alignment (for example CdSe/ZnSe [564] or CdSe/CdTe [555] heterostructures) facilitate charge separation and one can tailor the ligand-nanocrystal interface (where the ligand layer acts as the shell) so as to create similar behaviour. Applications are conceivable, such as chemical nanosensors, where the fine dependence of nanocrystal optoelectronic properties on surrounding environment and adsorbed molecules can be harnessed.

In this chapter, we have for the first time combined a range of “state of the art” techniques such PAW, LR-TDDFT and the electronic enthalpy method within a linear-scaling framework to simulate realistic CdS nanocrystals under pressure. The simulations in this chapter have shown the strong dependence of structural and optoelectronic properties on the size and ligands of the simulated nanocrystals. It is essential for accurate simulations to use techniques, such as the electronic enthalpy method, that allow for non-isotropic pressure-dependent structural relaxation. Our results for the average Cd–S bond lengths and optical absorption spectra are in good agreement with experiments by Herron et al.
7 Classical dynamics of pressure-induced structural transformations in cadmium sulphide nanocrystals

“Eppur si muove.”

“Insanity: doing the same thing over and over again and expecting a different result.”

As anticipated in Chapter 1, small nanocrystals are ideal systems to study polymorphic solid-solid transformations as they can be synthesised with few or no defects. In Chapters 4, 5 and 6, we have performed quasistatic geometry optimisations and neglected temperature thus requiring overpressurisation for a structural transformation to be observed under pressure. As explained in Chapter 2, first-order polymorphic transformations are rare events happening over long timescales and even after inclusion of temperature in MD simulations, one generally has to overpressurise the system to the point of mechanical instability in order to observe the transformation. When overpressurising, there is no guarantee that the transformation follows the same mechanism as obtained at the experimental transformation pressure. Free energy exploration techniques such as metadynamics have proven very useful in simulating pressure-induced structural transformation closer to the experimental conditions and making contact with experiment. Simulating the large-length scale associated with nanocrystals of experimental dimensions, not to mention the many PTM molecules, is generally prohibitively expensive in a fully \textit{ab initio} way and one must resort to a classical description. Classical MD simulations of nanocrystals under pressure have been performed successfully but have thus far neglected an all-atom description of ligands and PTM which experiments suggest play an important role. In this chapter we introduce a novel classical parametrisation of a CdS nanocrystal and PTM, and simulate a bare WZ nanorod as well as a tetrahedral ZB nanocrystal with phenyl ligands (called CdS–phenyl in Chapter 6) under pressure. We investigate the pressure-induced structural transformation using both MD and metadynamics.

7.1 Experimental and theoretical background

Following the pioneering experimental work of Alivisatos et al. [11,12,17,42,567–569], the WZ/ZB→RS transformation in CdS and CdSe nanocrystals has become prototypical for the study of polymor-

\footnote{Attributed to G. Galilei [565]} \footnote{A. Einstein [566]}
Figure 7.1.1: Fraction of RS with pressure at 300 K of Cd$_{32}$S$_{14}$(SC$_6$H$_5$)$_{36}$·4(N(CH$_3$)$_3$) depending on PTM. Mixtures of THF with CH$_3$OH (methanol) and THF with CHCl$_3$ (chloroform) in 3:1 proportions were used. The fraction of RS is determined by integrating optical absorption features. Model structures based on a compressive WZ→RS mechanism proposed by Tolbert and Alivisatos are included for reference [568]. Figure reproduced from Ref. [11].
pressure. Wang et al. reported for CdSe nanosheets with soft ligands an enhancement of transition pressure compared to the bulk [577]. Chen et al. [11] measured (Figure 7.1.1) the fraction of small monodisperse $\sim 1.5$ nm diameter Cd$_{32}$S$_{14}$SC$_6$H$_5$$_36 \cdot 4$(N(CH$_3$)$_3$)$_3$ nanocrystals, as synthesised by Herron et al. [534] and studied in Chapter 6, transforming from ZB to another structure (interpreted to be RS) under pressure. The width and position of hysteresis curves with pressure are found to change significantly with PTM. Changing the PTM from 3:1 mixtures of THF with chloroform to THF with ethanol results in an increase in thermodynamic transformation pressure, estimated as the midpoint between upstroke and downstroke transformation pressures, of $\sim 3$ GPa; and the hysteresis width is found to increase from $\sim 1$ GPa to $\sim 3$ GPa, indicating a significant enhancement in the energetic barrier to transformation. These results demonstrate the impact of interface on both thermodynamics and kinetics of transformation under pressure for small CdS nanocrystals. Recently, experiments have demonstrated the ability of observing transformation mechanisms in real-time using ultrafast XRD [17, 18]. The limited spatial and temporal experimental resolution, however, prevents a detailed insight into the mechanism of transformation, especially concerning surfaces and small nanocrystals. Atomistic simulations can thus provide vital information and help interpret experimental results.

Different mechanisms have been proposed for the WZ/ZB$\rightarrow$RS transformation both in bulk and nanocrystals based on experiment and simulations [3, 4, 13, 41, 42, 92–94, 122, 123, 568, 569, 578–581]. Alivisatos and Tolbert proposed that WZ$\rightarrow$RS mechanism proceeds by a flattening of hexagons in the $a$-$b$ plane, formation of $2 \times 3$ rectangles and compression of boats and rings along the $c$-direction [568]. A variety of alternative mechanisms have been proposed based on classical or ab initio simulations. Shimojo et al. [582] and Wilson and Madden [583] observed transformation mechanisms for the bulk consistent with the compressive mechanism proposed by Alivisatos and Tolbert. For the bulk, Shimojo et al. [580] also proposed mechanisms based on sliding motion of adjacent (1100) layers sliding in opposite $\pm[0010]$ directions by $a/2$ (hereafter referred to as “sliding-plane” mechanism). Studies based on transition path sampling (TPS) have since suggested alternative mechanisms for the bulk [581]. In the “sliding-plane” mechanism, a metastable hexagonal five-fold coordinated h-MgO structure (HS) is formed by flattening of puckered (0001) layers in the $c$-direction, and the RS structure obtained by a sliding motion in the $a$-$b$ plane (See Figure 7.1.2).
Figure 7.1.3: Schematic of the ZB→RS transformation mechanism along Catti’s path. (a) shows the ZB, (b) the intermediate d-β-Sn and (c) the RS structures along with their unit cells respectively in red, yellow and blue. Figure adapted from Ref. [586].

TPS and metadynamics simulation have shown that near the thermodynamic transition pressure a “sliding-plane” mechanism is favoured for bulk CdSe [578, 584]. For CdSe nanocrystals, experiment, TPS and metadynamics simulation also find the “sliding-plane” mechanism to be favoured [12, 94, 114, 119]. The exact mechanism can depend on size, shape, defects, surface morphology as well as environmental conditions such as PTM, temperature and compression rate [585]. Simulations of nanocrystals show that spherical nanocrystals transform in a similar manner to the bulk, while in faceted nanocrystals the HS structure can be stabilised due to surface energetics [94]. Recent ultrafast XRD experiments on shocked CdSe nanorods [17] have observed the HS structure forming as an intermediate during the WZ→RS transformation as predicted by simulations.

The bulk ZB→RS transition has been studied in a variety of semiconductors. Shimojo et al. carried out MD simulations on SiC and observed a transformation mechanism involving a tetragonal compression along the <100> direction along with a layer-shearing and shift of the cationic and anionic sublattices in a direction parallel to the compression [582]. Following this work, Catti proposed a mechanism and simulated it with DFT for SiC and ZnS [586, 587]. Figure 7.1.3 shows the proposed mechanism, known as Catti’s mechanism, which proceeds by the cation, initially at the centre of an anionic tetrahedron, shifting along the c-direction and ending up at the centre of the edge of the tetrahedron. No bonds are broken and instead two new ones are formed as the octahedral structure is formed. Interestingly, during tetragonal compression and before layer-shearing the structure goes to a transition-state (as opposed to a metastable one) corresponding to a diatomic analogue of the β-Sn structure (d-β-Sn, Pmm2) [583]. Miao and Lambrecht have shown that Catti’s path is universal to all compound semiconductors undergoing the ZB→RS transformation [588].

CdS and CdSe nanocrystals can be synthesised in the ZB structure experimentally and have been studied under pressure by Chen et al. [11]. Morgan and Madden performed classical MD simulations in the NPT ensemble at 500 K on nanocrystals of dodecahedral shape and made of generic ionic material (corresponding to ZnO) immersed in an explicit LJ liquid [85]. The pressure was ramped
up in steps of 0.15 GPa and a transformation to RS was observed around 9 GPa. The larger nanocrystals transformed via Catti’s mechanism, while amorphisation was observed in the smallest nanocrystals (< 1500 atoms). Bealing et al. [584] performed MD and metadynamics simulations on CdSe nanocrystal of dodecahedral shape Cd$_{510}$Se$_{510}$ and Cd$_{3724}$Se$_{3724}$ [589]. The simulations were based on extended Lagrangian $PV$ method (Subsection 1.4.2) with a volume definition based on the inertia tensor eigenvalues of an ellipsoid. Pressure was incremented in steps of 0.5 GPa equilibrating for 40 ps at each pressure. Both Cd$_{510}$Se$_{510}$ and Cd$_{3724}$Se$_{3724}$ were found to transform to RS. The MD on Cd$_{510}$Se$_{510}$ found a transformation to RS via a collective rearrangement, and the end structure was observed to contain a grain boundary. No amorphisation, as reported by Morgan and Madden, was observed which was attributed to the differences in interatomic potential and pressure method. Similarly for metadynamics simulations performed at 2.5 GPa using the inertia tensor eigenvalues as CVs, a sharp and collective transformation to RS was observed along Catti’s path. Metadynamics simulation of Cd$_{3724}$Se$_{3724}$ at 2.5 GPa also resulted in a transformation to RS, albeit more gradual and with larger fluctuations in shape and volume. Unlike Cd$_{510}$Se$_{510}$, the transformation did not happen in a single cooperative motion. Instead, successive layers were transformed with a gradual increase in coordination, the corners remained disordered and multiple grain boundaries formed.

### Table 7.1: Parameters defining the Rabani potential for CdS and CdSe.

<table>
<thead>
<tr>
<th></th>
<th>$q(e)$</th>
<th>$\sigma(\text{Å})$</th>
<th>$\epsilon(\times10^{-3}\text{eV})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.18</td>
<td>1.98</td>
<td>1.45</td>
</tr>
<tr>
<td>S</td>
<td>-1.18</td>
<td>4.90</td>
<td>1.42</td>
</tr>
<tr>
<td>Se</td>
<td>-1.18</td>
<td>5.24</td>
<td>1.28</td>
</tr>
</tbody>
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7.2 Methodology

7.2.1 Parametrisation of forcefield

The Rabani pair potential (Eq. (2.1.13)) [146] was used to describe the ionic bonding of CdS and CdSe nanocrystals. It combines non-bonded Coulomb and LJ interactions using the parameters for CdS and CdSe listed in Table 7.1. The parametrisation has been shown [590] to reproduce experimental lattice and elastic constants, transition pressures as well as phonon dispersion curves of bulk CdS/CdSe WZ, ZB and RS phases. The transferability of the bulk Rabani potential to nanocrystals is formally questionable given that the fitting procedure does not take surface properties into account. Its use is justified a posteriori by the encouraging results obtained in this work and previous studies performed on CdSe [92–94,114,591,592], CdS/ZnS [13] and PbSe [593] nanocrystals. In order to describe realistic nanocrystals covered in ligands and immersed in a PTM, we combine the Rabani potential for the core of the CdS nanocrystal with a generalized AMBER forcefield [145] (Eq. (2.1.12)) for the ligands and PTM molecules. This model does not account for charge transfer nor polarisation effects which can be significant as suggested by the Hirshfeld analysis of Chapter 6. However, the promising results obtained by Schapotschnikow et al. [592] for ligated CdSe nanocrystals in vacuo encouraged us to use this approximation.
Figure 7.2.1: Fragments used in the parametrisation: (a) N(CH$_3$)$_3$; (b) Thiophenol; (c) THF and (d) CdS core.
For the sake of the parametrisation, the system was divided into CdS core, phenyl ligands (approximated as thiophenol), N(CH$_3$)$_3$ corners and THF molecules (Figure 7.2.1). All partial charges, except for the CdS core parametrised by the Rabani potential, were computed by a least-square fit to the electrostatic potential (ESP) on a Cartesian grid on the vdW surface around the molecule. The ESP partial charges were calculated within DFT using a B3LYP exchange-correlation functional (6-311++G** basis set) using GAUSSIAN09 [594]. RESP charges were obtained from the ESP charges by a two-stage fitting procedure within the RESPGEN and RESP programs in AMBER10 [595]. Lastly, LJ coefficients and bonded interactions (bond, angle and dihedral) were obtained from the AMBER antechamber program [596].

Unlike Schapotschnikow et al., we use non-stoichiometric nanocrystals and charge imbalances have to be rigorously accounted for to guarantee the overall charge neutrality of the nanocrystal. The 32 Cd have a partial charge of 1.18 $e$, the 14 bulk S of -1.18 $e$ and each of the 36 SC$_6$H$_5$ needs to compensate the charge surplus (i.e. $(32-14) \times 1.18/36=0.59$ $e$). The partial charge $q_{S_2}$ on the ligated surface S needs to include the partial charge $q_{S_1}$ of the isolated thiophenol S$_1$, the charge $q_{H_2}$ associated with removing the thiophenol H$_2$ and the compensation charge $q_{comp}$:

$$q_{S_2} = q_{S_1} + q_{H_2} + q_{comp} = -0.2184 + 0.1596 - 0.59 = -0.6488 e$$ (7.2.1)

The ligated surface S interacts with the rest of the Cd and S atoms with the Rabani LJ coefficients and other ligand and PTM atoms via the AMBER LJ coefficients. All other atoms interact via the electrostatic, bonded and non-bonded interactions parametrised for the isolated fragments. The Rabani LJ parameters are not technically vdW coefficients and problems can arise because of the non-bonded interaction of surface Cd and S atoms with ligands and PTM molecules. Specifically, the strong interaction between the corner Cd and the O atom of THF molecules can cause the nanocrystal corners to break. Similarly, phenyl rings and surface Cd can interact too strongly and break the nanocrystal. We thus adjusted the corresponding LJ coefficients manually until structural distortions at ambient conditions compared to the relaxed ab initio structures were of the order expected from thermal fluctuations. A proper ab initio parametrisation of these interactions is warranted but beyond the scope of this work. Adjusting these parameters manually was considered an acceptable approximation considering the nanocrystal mostly interacts with the PTM through the ligands and surface S both parametrized within AMBER. This effect is more problematic in the case of bare CdS nanocrystals such as Cd$_{216}$S$_{216}$ for which the non-bonded interaction of THF molecules and surface Cd and S can have a large effect on transformation pressures and mechanisms. We again tuned these parameters until a reasonable behaviour was obtained. Cd–N bond and Cd–N–C angle terms are introduced for the corner N(CH$_3$)$_3$ to prevent excessive distortion upon collision with THF molecules. All parameters are listed in Appendix B.

The parametrisation of CdS–phenyl was tested by comparing the relaxed geometry obtained in vacuo and 0 K using the classical potentials and BFGS algorithm within LAMMPS (version 30/09/2013) [597] and in ONETEP at 0 GPa using the protocol of Chapter 6. Figure 7.2.2 shows the atomic positions of the CdS core relaxed with ONETEP and the superimposed positions obtained after relaxation with LAMMPS starting from the ONETEP structure. The RMSD difference in po-
Figure 7.2.2: Comparison of the atoms in the CdS core of CdS–phenyl relaxed in ONETEP at 0 GPa and LAMMPS (superimposed in blue) in vacuo using the parametrised forcefield: (a) top and (b) side view.

...position is estimated as $\Delta_{\text{rmsd}} \sim 0.01$ Å with the largest absolute difference in position $\Delta_{\text{max}} \sim 0.03$ Å located at the surface. We note that the ONETEP calculations do not include vdW forces and agreement could be even better.

7.2.2 Molecular dynamics testing

The forcefield parametrisation was also tested by performing MD of nanocrystals in vacuo and immersed in the PTM. All MD simulations were performed using LAMMPS and vibrations of bonds containing H atoms were constrained using the SHAKE algorithm [598]. Long-range Coulomb interactions were treated using the PPPM algorithm [599] (closely related to Ewald summations) with a tolerance for the relative error in forces of $5.1 \times 10^{-3}$ eV/Å. LJ interactions were treated using standard arithmetic mixing rules (Eq. (2.1.8)-(2.1.9)) and a relatively large global 16 Å cutoff was imposed to ensure all parts of the nanocrystal interact with each other. The quality of the Verlet integrator and total energy conservation were found to be satisfactory for timesteps smaller than 3 fs. A timestep of 1 fs was, however, used throughout to capture the fast dynamics associated with structural rearrangements in nanocrystals. MD simulations were also performed in vacuo and found to be well-behaved during trajectories of 50 ns. The PTM was modelled using PBCs and a box of $53 \times 53 \times 53$ Å$^3$ with 1206 THF molecules, initially arranged as a lattice at the experimental density at ambient conditions of 890 kg/m$^3$. Different thermostats were tested as dynamical properties can strongly depend on the choice of time constants and thermostats [600]. We tested Berendsen and Langevin thermostats with various time-constants coupled to a Berendsen barostat with a fixed time-constant of 2 ps. While the Langevin thermostat, unlike the Berendsen thermostat, reproduces the canonical ensemble, dynamical and transport properties can be significantly distorted by the velocity randomization [600]. This effect is, however, mitigated by choosing a large time-constant.
and transport properties in good agreement with experiment can be obtained. Performing MD of the PTM using a Langevin thermostat with time-constant 1 ps at ambient conditions, 300 K and 10^5 Pa (1 bar), the self-diffusivity was calculated from the average mean square displacement (Einstein relation) as 5.51 × 10^{-9} m^2/s compared to the experimental value of 2.6–3.4 × 10^{-9} m^2/s [601]. For comparison, using a Berendsen thermostat with time-constant 0.1-1 ps produced a self-diffusivity of ∼ 1 × 10^{-8} m^2/s. A Langevin thermostat with 1 ps time-constant was therefore used in the rest of this work. The self-diffusivity decreases with pressure and reaches a value of 3.35 × 10^{-12} m^2/s at 10 GPa. Pressures above 10 GPa were not examined as the PTM does not flow sufficiently fast to produce a hydrostatic compression while the nanocrystal changes shape.

The nanocrystals were immersed in the THF liquid (Figure 7.2.3) and both nanocrystal and THF thermalised with the same Langevin thermostat with 1 ps time constant. The pressure was applied by using a Berendsen barostat, with 2 ps time constant and 1 GPa bulk modulus, scaling the cell and coordinates of THF but not nanocrystal atoms. The compression is thus transmitted to the nanocrystal via the THF molecules as opposed to an unnatural coordinate scaling. As a further test, hexagonal nanorods Cd_{216}Se_{216} and Cd_{432}Se_{432} (of same shape as Cd_{216}Se_{216} but double the length along the c-direction) obtained by cleaving bulk WZ crystal along (1010) and (0001) surfaces were simulated under compression. Such nanocrystals have been studied experimentally [569, 602] and simulated in previous work using MD, TPS [92] and metadynamics [584, 585] with extended PV Lagrangian or explicit PTM pressure methods. A transformation from HS to a RS structure via a “sliding-plane” mechanism is observed during MD at 300 K around 6 GPa for Cd_{432}Se_{432} using the Rabani LJ parameters for the PTM-nanocrystal interaction. The same RS structure and mechanism was observed in previous metadynamics simulations using gyration radius or average coordination number as CVs [585]. Instead, for constant pressure MD using a PV-term a transformation via a compressive mechanism was observed around 3.25 GPa. The different transition pressures and mechanisms can be attributed to differences in the pressure method and particularly the PTM-nanocrystal interaction as we shall discuss in the following section.

The PLUMED 2.0 plug-in [603] was used to monitor structural parameters during the dynamics as well as performing the metadynamics. Coordination numbers were calculated by using the switching function

\[ N_{\text{coord}} = \sum_{\alpha \neq \beta} \frac{1}{1 - \left( \frac{R_{\alpha\beta}}{R_0} \right)^6} \]

setting \( R_0 = 3.5 \) Å throughout. Only Cd–S bonds were considered when estimating the coordination numbers of Cd and S atoms. Volumes were estimated from the eigenvalues of the massless inertia tensor as described in Subsection 1.4.3, using the formula for \( V_{\text{cyl}} \) (Eq. (1.4.16)) for the nanorods and \( V_{\text{ellip}} \) (Eq. (1.4.15)) for the CdS–phenyl nanocrystal. We note that these are approximate formulas but allow for simple and reasonable estimates of the nanocrystal volumes.
Figure 7.2.3: Periodic simulation cell showing the simulated $\text{Cd}_{216}\text{S}_{216}$ nanocrystal immersed in THF.
Figure 7.3.1: Effect of PTM-nanocrystal LJ interaction parameters on the compression and structure of Cd216S216 at 2 GPa comparing: (a) internal pressure $P_{\text{virial}}$; (b) Cd–S–Cd bond angle distribution; (c) nearest Cd–S bond distance distribution.
7.3 Molecular dynamics simulations

7.3.1 Cd$_{216}$S$_{216}$

We use hexagonal nanorod Cd$_{216}$S$_{216}$, analogous to the Cd$_{216}$Se$_{216}$ nanocrystals described above, as a benchmark system. As found for CdSe nanorods, the Cd$_{216}$S$_{216}$ nanocrystal obtained by cleaving a bulk WZ crystal relaxes to the fivefold-coordinated HS by a compression along the hexagonal c-axis. The HS structure is characterised by a Cd–S–Cd angle distribution peaked at 90°, 120° and 180°. In the bulk, the HS was found to be a metastable structure while the Rabani potential predicts it to be a stable structure in such nanocrystals [92, 94]. As mentioned previously, the PTM-nanocrystal interaction can strongly affect the pressure response of the nanocrystal and has to be calibrated when an adequate parametrisation is not available. The Laplace-Young equation predicts that small nanocrystals of radius $R$ under external pressure $P$ will feel an internal pressure given by:

$$P_{\text{int}} = P + \frac{2\gamma_{\text{eff}}}{R}.$$  (7.3.1)

The effective surface stress $\gamma_{\text{eff}}$ depends on the non-bonded interactions between the Cd$_{216}$S$_{216}$ surface and THF molecules. The CdS Rabani LJ parameters do not correspond to a physical vdW interaction and the LJ interaction must be tuned to give a reasonable pressure response. Anticipating results for CdS–phenyl described in the next section, we expect for a nanocrystal of the size of Cd$_{216}$S$_{216}$ at 2 GPa, an increase in internal pressure due to the Laplace-Young effect of the order of $\sim$1 GPa. We monitor the internal pressure inside the nanocrystal by using $P_{\text{virial}}$ (Eq. (1.4.11)) with the volume definition $V_{\text{cyl}}$. Figure 7.3.1 compares the internal pressure, Cd–S bond distances and Cd–S–Cd bond angle distribution at 2 GPa and 300 K for different LJ interaction coefficients between PTM-nanocrystal. Using the Rabani LJ coefficients leads to $P_{\text{virial}} \sim$1 GPa (Figure 7.3.1(a)) and results in a significantly distorted nanocrystal as evidenced by the broad bond angle distribution (Figure 7.3.1(b)). Setting instead $\sigma = 4.2$ Å and $\epsilon = 2.7$ meV leads to a sharper bond angle distribution and $P_{\text{virial}} \sim$8 GPa, too large to be accounted for by the Laplace-Young effect. This is an overestimate considering the approximate volume definition which does not accurately account for the excluded volume. Instead, using $\sigma = 2.6$ Å and $\epsilon = 2.7$ meV yields a more sensible internal pressure of $\sim$3.5 GPa and was used in subsequent simulations of Cd$_{216}$S$_{216}$.

The nanocrystal and PTM are first thermalised at 300 K and 1 bar for 1 ns with the aforementioned thermostat, barostat and time constants. Figure 7.3.2(a) shows the temperature fluctuations of the PTM+nanocrystal and nanocrystal alone showing larger fluctuations in the latter as expected due to the smaller number of atoms (fluctuations scale as $1/\sqrt{N}$) . The pressure is increased by a stepwise procedure, linearly increased by 2 GPa over 1 ns and then equilibrating at 2 GPa for another 1 ns and so forth (Figure 7.3.2(b)). The pressure is increased up to 10 GPa, pressure beyond which the PTM becomes non-diffusive and the compression is no longer hydrostatic.

A HS$\rightarrow$RS transformation is observed at 6 GPa (10 GPa using the Rabani coefficients) and follows a "sliding-plane" mechanism as found in previous TPS [94,119] and metadynamics [585] studies. The transformation path, shown in Figure 7.3.3, proceeds by adjacent (1100) layers sliding relative to one another in the $a$-$b$ plane along opposite $\pm[0010]$ directions. The new phase nucleates at the
Figure 7.3.2: (a) Temperature fluctuations of Cd$_{216}$S$_{216}$ at 300 K and 1 bar; (b) internal pressure $P_{\text{virial}}$ of Cd$_{216}$S$_{216}$ at 300 K during stepwise pressure increase.

Figure 7.3.3: Snapshots of Cd$_{216}$S$_{216}$ undergoing HS$\rightarrow$RS transformation during MD at 6 GPa
Figure 7.3.4: Structural changes in Cd$_{216}$S$_{216}$ during compression simulated with MD at 300 K: (a) change in the fraction $N_i/N$ of of atoms with coordination $i$ during HS→RS transformation at 6 GPa; (b) volume estimated by $V_{cyl}$ between 0 and 6 GPa; (c) change in total enthalpy between 0 and 6 GPa; (d) change in gyration radii between 0 and 6 GPa.

surface following collisions between THF molecule and nanocrystal surface and propagates into the rest of the nanocrystal within $\sim$3 ps. We note here that the same end structure was reported by Fugallo et al. in metadynamics runs around 2 GPa using the extended Lagrangian $PV$ method for Cd$_{216}$Se$_{216}$ [585].

The transformation is accompanied by a sharp change in coordination and volume typical of reconstructive first-order transformations. Figure 7.3.4(a) shows that the proportion of threefold-, fourfold- and fivefold-coordinated atoms plummets while the number of 6-fold coordinated atoms increases as the nanocrystal transforms to a RS structure. Figure 7.3.4(b) shows a drop in volume of $\sim$420 Å$^3$, and Figure 7.3.4(c) an enthalpy drop of $\sim$11 eV indicating that the RS structure is more stable than HS at the pressure of 6 GPa. Figure 7.3.4(d) shows the gyration radii around the centroidal axes during transformation: $G_1$ and $G_2$ only change slightly ($\sim$0.1 Å) while $G_3$ changes by as much as $\sim$0.8 Å. This indicates a clear change of shape along the corresponding centroidal
Figure 7.3.5: Snapshots of Cd$_{216}$S$_{216}$ undergoing RS→HS transformation during MD at 1 bar upon pressure release from 6 GPa.

Upon pressure release in steps of 2 GPa, the RS structure is retained up to 1 bar, the pressure at which it reverts back to HS. The HS phase nucleates at the surface and unzips across the whole nanocrystal via a “sliding plane” mechanism while RS defects remain in the corners. The recovered shape is different from the original hexagonal nanocrystal showing the hysteretic nature of the transformation.

7.3.2 CdS–phenyl

We perform an MD simulation on the CdS–phenyl nanocrystal at 300 K and 1 bar. It is apparent from the volume fluctuations of the CdS core (Figure 7.3.6(a)) and temperature of nanocrystal Figure 7.3.6(b) that the system is well equilibrated after 1 ns. Figure 7.3.6(a) shows the fluctuations in the volume estimated from $V_{\text{ellip}}$ for CdS–phenyl and CdS core. The former fluctuates significantly due to the librations of the phenyl rings, which alter the estimated volume during the course of the simulations and also exaggerate the fluctuations in $P_{\text{virial}}$.

We ramp up the pressure by the same stepwise procedure of the previous subsection. Figure 7.3.7(a) compares the internal pressure for both CdS–phenyl. At 2 GPa, the internal pressure fluctuates respectively around 3.1 GPa. The reasonable value obtained is attributed to the fact that the interaction between PTM and ligands is parametrised by AMBER and expected to be realistic. Figure 7.3.7(b) compares the volume of CdS–phenyl and CdS core during compression. A large reduction in the CdS–phenyl volume is observed between 1 bar and 2 GPa and is due to distortions and the phenyl rings being flapped onto the corners. At higher pressures, the volume decreases gradually as predicted by the bulk modulus of the CdS core.
Figure 7.3.6: Fluctuations at 300 K and 1 bar of: (a) volume estimated by $V_{\text{ellip}}$ of CdS–phenyl and CdS core; (b) temperature of CdS–phenyl and CdS–phenyl+PTM

Figure 7.3.7(c) shows a gradual increase in fourfold-, fivefold and sixfold-coordinated atoms and concurrent decrease in twofold- and threefold-coordinated atoms. The enthalpy of CdS–phenyl (Figure 7.3.7(d)) also increases gradually with no discontinuity observed in the simulated pressure range. The gyration radii of both CdS–phenyl (Figure 7.3.7(e)) and CdS core (Figure 7.3.7(f)) change gradually by $\sim 0.7$ Å and $\sim 0.3$ Å during the pressure increase between 1 bar and 2 GPa but change little after that. Visual examination (Figure 7.3.8) shows that the change in shape of the nanocrystal is associated with distortions from the initial shape, especially of the corners that distort away from the tetragonal arrangement, under compression between 1 bar and 2 GPa. Unlike Cd$_{216}$S$_{216}$, no sharp transition is observed in the 1 bar and 8 GPa interval. Pressures higher than 8 GPa were not examined and it is unclear whether a limit of mechanical instability can be reached by further overpressurisation.

7.4 Metadynamics

7.4.1 Choosing CVs and hill deposition parameters

As discussed in Subsection 1.4.4, MD suffers from the time-scale problem when the first order transformations involved are rare events. This implies that unfeasibly long MD trajectories have to be simulated to observe the transformation at the thermodynamic transition pressure. Metadynamics, as discussed in Chapter 2, allows the acceleration of such rare events and simulation of the transformation without overpressurising the system. Hill deposition parameters and CVs have to be chosen carefully according to the criteria outlined in Section 2.2. There is no recipe for choosing CVs and one must generally follow physical intuition and proceed by trial and error. A variety of CVs were first tested with steered MD to ensure that a transformation occurred along a physical path for the chosen CV. Coordination numbers, gyration radii, Steinhardt parameters and various combinations
Figure 7.3.7: Structural changes in CdS–phenyl during compression simulated with MD during stepwise pressure increase between 1 bar and 8 GPa at 300 K: (a) evolution of $P_{\text{int}}$ of CdS–phenyl and CdS core during stepwise pressure increase; (b) volume of CdS–phenyl and CdS core estimated by $V_{\text{ellip}}$; (c) change in fraction $N_i/N$ of atoms with coordination $i$; (d) change in enthalpy of CdS–phenyl and CdS core; (e) change in gyration radii of CdS–phenyl; (f) change in gyration radii of CdS core.
Figure 7.3.8: Snapshots of CdS–phenyl from 3 different angles at 1 bar, 2, 4 and 6 GPa.
Coordination numbers are commonly used as efficient CVs. They are particularly relevant here as we are interested in reconstructive pressure-induced transformations that are accompanied by changes in coordination. It was found that simply using the average coordination as the CV can result in the overcoordination of core atoms. This can, however, be mitigated by only biasing atoms that are less than sixfold-coordinated. Using gyration radii as CVs was found to work well in the case of the nanorod for which the HS $\rightarrow$ RS transformation in MD is accompanied by a clear change of shape (Figure 7.3.4(d)). This is not expected to be the case of CdS–phenyl for which the gyration radii only change minutely and have limited effectiveness in discriminating initial and end structures. Preliminary tests were also performed using the Steinhardt parameters $Q_3$, $Q_4$ and $Q_6$ but found to lead to unphysical transformations and structures.

The hill deposition rate $\frac{1}{\tau_G}$, height $\omega$ and width $\delta s_i$ were carefully chosen to ensure a sufficiently gentle bias. While there is no $a$ priori rule for choosing these parameters, it is found in practice that good convergence is obtained when choosing $\omega$ of the order of the energy fluctuation during the unbiased-MD and $\delta s$ is chosen as a fraction of the change in CV value $S$ during transformation. The deposition rate and hill height must be chosen together so that the power pumped into the system is sufficiently small to prevent pushing it too far off-equilibrium. We performed metadynamics simulations using the number of atoms with coordination less than 5.8 as CV in the remainder of the thesis. The hill deposition parameters were chosen as: $\tau_G = 0.25$ ps, $\delta s = 0.5$, $\omega = 0.01$ eV for Cd$_{216}$S$_{216}$ and $\omega = 2.16$ meV for CdS–phenyl.
As already mentioned, we are interested in simulating the structural transformation at the thermodynamic transformation pressure. We estimate it by monitoring changes in total enthalpy at various pressures. At the thermodynamic transformation pressure, the enthalpy is expected to change as the system overcomes energetic barriers, but the initial and final equilibrium configuration should approximately have the same total enthalpy. Figure 7.4.1 shows the enthalpy during a metadynamics run using the aforementioned CV and hill deposition parameters at 2 and 4 GPa. We see from Figure 7.4.1 that at 2 GPa, the enthalpy increases slightly on transformation around 450 ps. Instead, at 4 GPa the enthalpy decreases upon transformation at 100 ps. This indicates that the thermodynamic transition pressure is between 2–4 GPa. Figure 7.4.2 compares the evolution of the CV and average coordination during the metadynamics run at 2 GPa and 4 GPa. In both cases, the same RS structure is recovered but differences in the transformation are apparent. The transformation at

Figure 7.4.2: Evolution for Cd_{216}S_{216} of the proportion of atoms with coordination inferior to 5.8 (used as CV) at (a) 2 GPa and (b) 4 GPa, and average coordination at (c) 2 GPa and (d) 4 GPa during metadynamics simulations of the HS→RS transformation.

7.4.2 Cd_{216}S_{216}

As already mentioned, we are interested in simulating the structural transformation at the thermodynamic transformation pressure. We estimate it by monitoring changes in total enthalpy at various pressures. At the thermodynamic transformation pressure, the enthalpy is expected to change as the system overcomes energetic barriers, but the initial and final equilibrium configuration should approximately have the same total enthalpy. Figure 7.4.1 shows the enthalpy during a metadynamics run using the aforementioned CV and hill deposition parameters at 2 and 4 GPa. We see from Figure 7.4.1 that at 2 GPa, the enthalpy increases slightly on transformation around 450 ps. Instead, at 4 GPa the enthalpy decreases upon transformation at 100 ps. This indicates that the thermodynamic transition pressure is between 2–4 GPa. Figure 7.4.2 compares the evolution of the CV and average coordination during the metadynamics run at 2 GPa and 4 GPa. In both cases, the same RS structure is recovered but differences in the transformation are apparent. The transformation at
Figure 7.4.3: Snapshots of Cd$_{216}$S$_{216}$ undergoing a HS→RS transformation via a “sliding-plane” mechanism during metadynamics run at 2 GPa and 300 K.

2 GPa happens after 300 ps and proceeds by multiple smaller transformations, while at 4 GPa the transformation happens after only 100 ps due to smaller kinetic barrier to transformation and happens in a single transformation accompanied by sharp changes in average coordination. Figure 7.4.3 shows the transformation mechanism at 2 GPa proceeding by the same “sliding-plane” mechanism as observed in MD and the same end structure is obtained. The RS phase nucleates in the centre of the nanocrystal, as opposed to a corner in the case of MD (Subsection 7.3.1), and propagates to the rest of the nanocrystal within 150 ps.

Examining the structural properties during transformation we see from Figure 7.4.4(a), as for the MD at 6 GPa, the number of threefold, fourfold and fivefold-coordinated atoms decreasing while the number of sixfold-coordinated atoms increases. Similarly, Figure 7.4.4(b) shows the radius of gyration $G_3$ drops by $\sim 0.7$ Å. In Figures 7.4.4(c)-(f), we analyse the bond angle distribution, pair correlation function as well as ring statistics for the representative snapshots at 0, 400, 425, 500 and 750 ps along the transformation path of Figure 7.4.3. Figure 7.4.4(c) shows that the peak at 120° in the Cd–S–Cd bond angle distribution vanishes, while those at 90° and 180° increase upon transformation to RS. Figure 7.4.4(d) shows changes in the Cd–S pair correlation function with the appearance of two peaks at 4.5 Å and 6 Å instead of the second peak at 5 Å. As in Section 4.3, we examine the ring statistics neglecting rings with homoatomic Cd–Cd or S–S bonds. Figures 7.4.4(e) and (f) show the evolution of $P_n$, the proportion of atoms belonging to at least to one $n$-membered ring, and the total number of rings $R_T$ during transformation. At time 0 ps, the Cd$_{216}$S$_{216}$ nanocrystal in the HS structure is characterised by an approximately equal number
Figure 7.4.4: Structural changes in Cd$_{216}$S$_{216}$ during HS$\rightarrow$RS transformation simulated with meta-dynamics at 2 GPa and 300 K (snapshots shown in Figure 7.4.3): (a) fraction $N_i/N$ of atoms with coordination $i$; (b) gyration radii; (c) Cd–S–Cd bond angle distribution; (d) Cd–S pair correlation function; (e) proportion of atoms belonging to at least one $n$-membered ring $P_n$; (f) total number of rings $R_T$. 
of 4-membered and 6-membered rings. During transformation, the population of 4-membered rings increases at the expense of the 6-membered one between 0 and 750 ps: $P_4$ increases from 0.78 to 0.95 and $P_6$ decreases from 0.59 to 0.25. This change is most apparent from the snapshots of the Cd$_{216}$S$_{216}$ nanorod along the c-direction (Figure 7.4.3) showing how the collective “sliding-plane” mechanism leads to 6-membered rings closing and forming 4-membered ones. We also notice the appearance of 8 and 10-membered rings in the intermediate structures with respectively as many as 33 and 24 rings at 425 ps.

### 7.4.3 CdS–phenyl

Metadynamics simulations of CdS–phenyl at 300 K were performed for 4 ns and 6 ns respectively at 2 GPa and 6 GPa. These were preceded and followed by 1 ns long MD simulations at 300 K without bias to equilibrate the structures before and after the metadynamics. As in the previous subsection, we monitor changes in the total enthalpy during the metadynamics runs (Figures 7.4.5(a) and (b)). Due to the lack of a sharp transformation and approximate volume definition, the thermodynamic transformation pressure is harder to estimate compared to Cd$_{216}$S$_{216}$. Figures 7.4.5(c) and (d) show...
a gradual reduction in the volume during the metadynamics runs at 2 and 6 GPa. At 2 GPa, the volume decreases from 2750 to 2300 Å\(^3\) between 0 and 4 ns and stabilises at 2400 Å\(^3\) during the subsequent unbiased MD run. At 6 GPa, the CdS–phenyl starts off in a more compact configuration with a volume of 2350 Å\(^3\), decreases to 2000 Å\(^3\) after 6 ns of metadynamics and stabilises at 2100 Å\(^3\) after 1 ns of unbiased MD. Both simulations at 2 and 6 GPa show significant fluctuations in volume and enthalpy. The enthalpy at 2 GPa remains approximately flat, except for an initial decrease between 0-1 ns, during the course of the metadynamics with small decreases in volume accompanied by small increases in enthalpy (Figure 7.4.5(a)). At 6 GPa instead, a decrease in enthalpy from -215 eV to -223 eV is apparent and small reductions in volume correlate with small decreases in enthalpy (Figure 7.4.5(b)). We therefore estimate the thermodynamic transformation pressure to be in the 2–6 GPa range.

In Figure 7.4.6, we compare the evolution of coordination numbers at 2 and 6 GPa. Figures 7.4.6(a) and (b) shows the changes in the proportion of atoms with coordination less than 5.8 (used as CV) during metadynamics at 2 and 6 GPa and indicate in both cases a gradual decrease with similar fluctuation patterns of wells and plateaus. This is in contrast with the behaviour for Cd\(_{216}\)S\(_{216}\) which shows a sharp transformation and a “fan-shaped” behaviour of the CV before and after transformation (Figure 7.4.2) with fluctuations of the order 0.01 compared to 0.1 for CdS–phenyl. Figure 7.4.6(c) shows the average coordination of Cd and S atoms during metadynamics at 2 GPa increasing from 3.6 at 0 ps to 4.5 at 3900 ps, and stabilises at 3.9 at 5000 ps after the unbiased MD (respectively 4.0, 4.9 and 4.3 when including S–C bonds). At 6 GPa (Figure 7.4.6(d)), the average coordination increases from 4.1 at 0 ps to 4.8 at 5900 ps, and stabilises at 4.3 at 7000 ps after the unbiased MD (4.5, 5.3 and 4.7 when including S–C bonds). Figures 7.4.6(e) and (f) show the fraction of atoms \(N_i/N\) with coordination number \(i\) at 2 and 6 GPa. At 2 GPa and 0 ps, the fraction of fourfold-, fivefold- and sixfold-coordinated atoms, corresponding to atoms in the core, is of 0.5, 0.1 and 0. The fraction of twofold- and threefold-coordinated atoms, corresponding to edge and surface atoms, is 0.05 and 0.35. The proportion of fivefold-coordinated atoms increases significantly (up to 0.35) during the transformation while the proportion of threefold- and fourfold-coordinated atoms decreases (down to 0.15 and 0.3). Sixfold-coordinated atoms gradually appear and reach a fraction of 0.1 around 3800 ps. At 5000 ps, the CdS–phenyl stabilises after the unbiased MD with fractions of twofold-, threefold-, fourfold-, fivefold- and sixfold-coordinated atoms respectively of 0.05, 0.25, 0.45, 0.25 and 0. This corresponds to an increase in the number of fivefold-coordinated atoms and decrease in the number of threefold- and fourfold-coordinated atoms compared to the structure at 0 ps. The final structure has an enthalpy of -282 eV compared to -276 eV at 0 ps and is therefore more stable.

At 6 GPa and 0 ps, the fraction of twofold-, threefold-, fourfold-, fivefold- and sixfold-coordinated atoms is respectively 0.0, 0.2, 0.5, 0.3 and 0.0. This corresponds to a larger fraction of fivefold-coordinated atoms and a smaller fraction of threefold-coordinated atoms compared to 2 GPa, indicating that at 0 ps the structure is comparatively more transformed with respect to the initial (1 bar) structure. The proportion of fivefold-coordinated atoms increases significantly (up to 0.4) during the metadynamics while the proportion of threefold- and fourfold-coordinated atoms decreases (down to 0.1 and 0.2). Sixfold-coordinated atoms gradually appear and reach a fraction of 0.2 around 5800 ps.
At 7000 ps, the CdS–phenyl stabilises with fractions of twofold-, threefold-, fourfold-, fivefold- and sixfold-coordinated atoms respectively of 0.05, 0.15, 0.4, 0.35 and 0.05. The structure obtained at 7000 ps has an enthalpy of -225 eV, significantly lower than the -215 eV at 0 ps.

Figure 7.4.7 compares the structures of the CdS core of CdS–phenyl at representative snapshots during the metadynamics at 2 GPa at 0, 4000 and 5000 ps. The structure at 0 ps is significantly distorted compared to the one at 1 bar, included for reference, but largely retains the tetrahedral shape and bonding topology. Instead, the structures at 4000 and 5000 ps are largely distorted from the tetrahedral shape and defects are apparent both at the surface and in the core of the nanocrystal. Figure 7.4.8 examines the Cd–S–Cd bond angle distribution, Cd–S pair correlation function and ring statistics for the representative snapshots at 2 GPa and at 1 bar. The structures used for calculating the aforementioned structural parameters at 1 bar and 2 GPa before and after the metadynamics are obtained by averaging the atomic positions over 50 ps trajectories. Figure 7.4.8(a) shows that the bond angle distribution at 2 GPa and 0 ps, as at 1 bar, is peaked around 109.5° showing that the structure before the metadynamics is in the tetragonal ZB structure. The peak broadens and is shifted to 83° at 4000 ps and 90° at 5000 ps upon performing the unbiased MD run. Figure 7.4.8(b) shows that the Cd–S pair correlation has a main peak at 2.6 Å, corresponding to the first coordination shell, and peaks at 4.9 and 6.4 Å for the second and third coordination shells. At 2 GPa and 0 ps, the first peak is unaffected, but the second and third ones broaden and the latter is shifted to 6.1 Å. At 4000 ps, the second and third peaks broaden even further and become indistinguishable. At 5000 ps after performing the unbiased MD, the second and third peaks recover somewhat but remain broad and the third peak contracted to 5.8 Å. The ring statistics in Figures 7.4.8(c)-(d) show that at 1 bar, the structure is mostly composed of 6-membered rings with $P_6$ of 0.95 as opposed to 0.16 for 4-membered rings. At 2 GPa and 0 ps, the proportion of 4-membered rings increases to 0.32 while that of 6-membered rings decreases to 0.86. During the course of the metadynamics, the proportion of 6-membered rings plummets further and reaches 0.35 at 5000 ps while the 4-membered ring population increases to 0.8. 8-membered rings form during the course of the metadynamics and 20 such rings are recovered at 5000 ps. Together, these structural changes provide clear evidence for the amorphisation of the CdS–phenyl nanocrystal at 2 GPa. The transformation appears to occur by gradual and local change in bonding: the Cd–S–Cd angle distribution broadening and shifting to 90°, contraction and broadening of second and third Cd–S shells and formation of 4-membered and 8-membered rings. This is in contrast with the HS $\rightarrow$ RS transformation of Cd$_{216}$S$_{216}$ which proceeds by a collective atomic motion.

Performing a similar analysis for the metadynamics at 6 GPa, we notice from Figure 7.4.9 that the structures are more distorted and compact compared to the ones at 2 GPa. The bond angle distribution at 6 GPa (Figure 7.4.10(a)) is already significantly broadened at 0 ps. The main peak is centred at 85° and does not change significantly during the metadynamics and unbiased MD. Similarly, the pair correlation function (Figure 7.4.10(b)) is found to be have a broad second peak around 5 Å at 0 ps and 6 GPa as opposed to well-defined second and third shells. Again, the pair correlation function changes little after the metadynamics and unbiased MD run. Figures 7.4.10(c) and (d) show that there is a significant population of 4-membered rings and a reduced 6-membered one at 0 ps and 6 GPa with $P_4=0.68$ and $P_6=0.5$. After the unbiased MD run, these change further.
Figure 7.4.6: Changes in coordination of CdS–phenyl during metadynamics runs at 300 K: proportion of atoms with coordination less than 5.8 at (a) 2 GPa and (b) 6 GPa; average coordination at (c) 2 GPa and (d) 6 GPa; fraction of atoms with coordination number i at (e) 2 GPa and (f) 6 GPa.
Figure 7.4.7: Representative snapshots of the CdS core of CdS–phenyl during a metadynamics simulation at 2 GPa and 300 K at 0, 4000 and 5000 ps viewed from two different angles (structure at 1 bar included for reference).
Figure 7.4.8: Structural changes in CdS–phenyl during a metadynamics simulation at 2 GPa and 300 K comparing for representative snapshots of Figure 7.4.7: (a) Cd–S–Cd bond angle distribution; (b) Cd–S pair correlation function; (c) proportion of atoms belonging to at least one n-membered ring $P_n$; (d) total number of rings $R_T$. 

171
Figure 7.4.9: Representative snapshots of the CdS core during a metadynamics simulation at 6 GPa and 300 K.
Figure 7.4.10: Structural changes in CdS–phenyl during metadynamics at 6 GPa and 300 K comparing for representative snapshots of Figure 7.4.9: (a) Cd–S–Cd bond angle distribution; (b) Cd–S pair correlation function; (c) $P_n$; (d) $R_T$. 

173
to $P_4=0.82$ and $P_6=0.38$ as obtained at 6 GPa and 6500 ps. Also, 18 8-membered rings are obtained. These structural descriptors indicate that at 6 GPa and 0 ps, the structure is already significantly amorphous and amorphises further in the course of the metadynamics as indicated most clearly by the increase in 4-membered and 8-membered ring population and decrease of the 6-membered one.

In summary, the transformation between ZB$\rightarrow$RS appears frustrated in the CdS–phenyl nanocrystal. Instead of undergoing the bulk transformation along Catti’s mechanism (Figure 7.1.3), CdS–phenyl is found to amorphise both at 2 and 6 GPa and develops RS features such as a Cd–S–Cd angle distribution peaked around 90°, sixfold-coordinated atoms and 4-membered rings. The small size and energetic importance of the surfaces is expected to be a crucial factor inducing the observed PIA. The large change in $c/a$ ratio and associated energetic cost for the ZB$\rightarrow$RS transformation along Catti’s path could frustrate the polymorphic transformation and cause the nanocrystal to amorphise instead. Ligand and solvent-induced disorder are also expected to play an important role, as suggested by experiments on CdSe nanocrystals by Epifani et al. [604] and the ab initio simulations of Chapter 6, by producing an amorphous precursor on the surface reducing the energetic barrier to transformation.

### 7.5 Concluding remarks

At the nanoscale, pressure-induced structural transformations show a sensitive dependence on surface and interface and simulations need to account for these effect to be truly predictive. We have developed a novel classical parametrisation for the realistic simulations of ligated and bare CdS nanocrystals immersed in THF. Under compression, the Cd$_{216}$S$_{216}$ nanorod was found to undergo a HS$\rightarrow$RS transformation in both MD and metadynamics simulations. Instead, CdS–phenyl was observed to undergo PIA and end up in an amorphous structure with RS features. This result calls into question the interpretation of experimental results of Chen et al. who posited an ordered ZB$\rightarrow$RS transformation based on optical absorption densities. The RS absorption spectrum being featureless, it is conceivable that an amorphous structure is obtained in practice. Simulating the optical absorption spectra of such amorphous nanocrystals could help resolve this matter.

Bulk CdS, unlike Si and Ge, is a poor glass former and the observation of amorphisation for small CdS nanocrystals indicates that the PIA phenomenon could be more common at the nanoscale where the role of surface and interface plays an important role. We notice the intriguing parallel with the Si and Ge nanocrystal of Chapter 4 and 5, which are also found to amorphise instead of transforming between diamond and $\beta$-Sn, and CdS in the ZB (diatomic equivalent of diamond) which should transform via the d-$\beta$-Sn intermediate (diatomic equivalent to $\beta$-Sn). The large change in $c/a$ ratio and associated energetic cost could be a crucial factor influencing the frustration of the polymorphic transformation. Ligand and solvent-induced disorder is also expected to facilitate amorphisation by producing an amorphous precursor on the surface reducing the energetic barrier to transformation. The phenomenon of surface-induced PIA is still poorly understood and a more systematic study for different sizes, PTM, temperatures, compression procedures, shapes and ligands is needed to better understand the crossover between polymorphic transformation and amorphisation.
Conclusions and future work

“Acta est fabula, plaudite!”

Conclusions

I began this thesis by describing the importance of atomistic simulations in helping to interpret experiments and design new materials in a wide range of disciplines. I reviewed experiments on pressure-induced structural transformations in semiconductor nanomaterials, and outlined simulation strategies and the computational challenges associated with the large length- and time-scales involved. Quantum mechanical approaches, such as DFT, are essential to capture the chemistry of such pressure-induced transformations with accuracy. Traditional PWPP DFT is severely constrained in the attainable system size by the $O(N^3)$ scaling of the computational effort. I described a linear-scaling DFT framework that can help overcome this length-scale bottleneck and allow the simulation of system sizes of experimental relevance. The long time-scales associated with the transformations of interest generally preclude a fully \textit{ab initio} treatment and we introduced classical molecular dynamics and metadynamics as a way of simulating rare events without sacrificing the atomistic description.

In Chapter 4, I presented the electronic enthalpy method I have implemented within the linear-scaling DFT code ONETEP, and demonstrated how, after calibration of the volume definition, it can be used to simulate nanocrystals under pressure comparable in size to experiments. In Chapters 4 and 5, I have analysed and compared the pressure-induced amorphisation and polyamorphic transformation of hydrogenated Si and Ge nanocrystals of different sizes. In the case of Si, transformations between the diamond and the amorphous LDA, HDA and VHDA structures are observed. Equivalent Ge nanocrystals are found to undergo similar transformations, albeit at higher pressures, between diamond, LDA and HDA structures but VHDA is not observed in the examined pressure range. Electronic and spectroscopic properties were also analysed with pressure, especially the origin of metallisation. I find good agreement with experiment and help elucidate the recovered new high-density amorphous metallic Ge phase. I also introduced a simple approach for estimating the bulk moduli of these nanocrystals and found that enhancements compared to the bulk value can be largely attributed to surface-induced compression of bonds in their bulk-like cores.

In Chapter 6, I used for the first time a combination of electronic enthalpy, PAW and LR-TDDFT methods within ONETEP to study the deformation and optoelectronic properties with pressure of CdS nanocrystals focussing on the influence of size and ligands. I deconvolved various mechanisms

\footnote{Reported last words of emperor Augustus [605]}
at play to explain the size- and ligand-dependence of their optical absorption spectra with pressure and discussed implications for the rational design of optoelectronic devices.

Chapter 7 investigated the classical dynamics of pressure-induced structural transformations, using a novel parametrisation, in bare and ligated CdS nanocrystals immersed in a PTM. The bare CdS nanorod underwent a polymorphic HS→RS transformation both in MD and metadynamics, while the phenyl-capped CdS nanocrystal was found to undergo PIA during metadynamics. I analysed the transformation in detail and proposed that the bulk ZB→RS transformation is frustrated in such small nanocrystals due to the energetic prominence of the surface. The large change in c/a of the underlying bulk polymorphic transformation and solvent- and ligand-induced surface distortions are expected to be key factors facilitating PIA.

Accurate simulation of the length- and time-scales associated with pressure-induced structural transformations in nanomaterials require a combination of state of the art techniques, as demonstrated in this thesis, and further improvements in simulation methods and computer technology will most probably help them become routinely feasible.

**Future work**

Recent work by Andreussi et al. [23] has shown how the electronic enthalpy method can be refined by the implicit inclusion of solvent effects. A related implicit solvent functionality already exists within ONETEP [606,607] and could be adapted for constant pressure simulations of finite systems. There is a large scope for such simulations within both quasistatic and MD ab initio calculations. Reaching the time-scale of ns needed to observe pressure-induced structural transformations in nanocrystals with ab initio metadynamics is, however, expected to remain prohibitively expensive for years to come. A promising avenue of exploration is to combine classical and linear-scaling DFT calculations for example by using ab initio calculations on the whole nanocrystal to fit the classical forcefield or by performing ab initio calculations on snapshots taken from a metadynamics trajectory.

The latter approach is currently being tested on snapshots taken from the metadynamics of the phenyl-capped CdS nanocrystal under pressure. Performing LR-TDDFT calculations of the optical absorption spectra of nanocrystal structures during transformation would allow for comparison with experiments. This could help determine whether the investigated nanocrystals really do undergo PIA or the polymorphic ZB→RS transformation posited by Chen et al.

The phenomenon of surface-induced PIA is still poorly understood and a systematic study for different sizes, PTM, temperatures, compression procedures, shapes and ligands is warranted to better understand the crossover between polymorphic transformation and amorphisation in nanocrystals.
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Appendix A: Hirshfeld partial charges of CdS–H and CdS–phenyl at 0 and 5 GPa

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<th>CdS–H 0GPa</th>
<th>CdS–H 5GPa</th>
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<th>CdS–ph. 5GPa</th>
<th>diff.</th>
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Table 7.2: Comparison of Hirshfeld partial charges for CdS–H and CdS–phenyl (using the same Cd and S atoms) for different chemical environments and their differences at 0 and 5 GPa.
## Appendix B: Forcefield parameters

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<td>H2</td>
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<td>-</td>
<td>-</td>
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<td>H3</td>
<td>0.1310</td>
<td>0.65</td>
<td>1.300</td>
</tr>
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<td>H4</td>
<td>0.1190</td>
<td>0.65</td>
<td>1.300</td>
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<td>H5</td>
<td>0.1017</td>
<td>0.65</td>
<td>1.300</td>
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<tr>
<td>H6</td>
<td>0.0102</td>
<td>0.68</td>
<td>1.325</td>
</tr>
<tr>
<td>H7</td>
<td>0.0017</td>
<td>0.68</td>
<td>1.325</td>
</tr>
<tr>
<td>C1</td>
<td>-0.1278</td>
<td>4.74</td>
<td>1.700</td>
</tr>
<tr>
<td>C2</td>
<td>-0.0311</td>
<td>3.73</td>
<td>1.700</td>
</tr>
<tr>
<td>C3</td>
<td>-0.0558</td>
<td>3.73</td>
<td>1.700</td>
</tr>
<tr>
<td>C4</td>
<td>-0.1746</td>
<td>3.73</td>
<td>1.700</td>
</tr>
<tr>
<td>C5</td>
<td>-0.0512</td>
<td>3.73</td>
<td>1.700</td>
</tr>
<tr>
<td>C6</td>
<td>0.1809</td>
<td>4.74</td>
<td>1.700</td>
</tr>
<tr>
<td>C7</td>
<td>0.0089</td>
<td>4.74</td>
<td>1.700</td>
</tr>
<tr>
<td>N</td>
<td>-0.0642</td>
<td>7.37</td>
<td>1.625</td>
</tr>
<tr>
<td>O</td>
<td>-0.4272</td>
<td>7.37</td>
<td>1.500</td>
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<td>S1 (TP)</td>
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<td>10.84</td>
<td>1.782</td>
</tr>
<tr>
<td>S2 (Ph.)</td>
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<td>10.985</td>
<td>1.782</td>
</tr>
<tr>
<td>S3 (Rabani)</td>
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<td>1.42</td>
<td>4.900</td>
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<tr>
<td>Cd (Rabani)</td>
<td>1.1800</td>
<td>1.45</td>
<td>1.980</td>
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Table 7.3: Parametrised partial charges and LJ coefficients
<table>
<thead>
<tr>
<th>Bonds</th>
<th>$k_b$(eV/Å$^2$)</th>
<th>$l_0$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C (TP)</td>
<td>20.41</td>
<td>1.387</td>
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<tr>
<td>C-H (TP)</td>
<td>14.92</td>
<td>1.087</td>
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<tr>
<td>C-S (TP)</td>
<td>10.89</td>
<td>1.778</td>
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<tr>
<td>C-N (corner)</td>
<td>13.89</td>
<td>1.470</td>
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<tr>
<td>C-H (corner)</td>
<td>0.14981</td>
<td>1.093</td>
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<tr>
<td>Cd-N</td>
<td>9.72</td>
<td>2.328</td>
</tr>
<tr>
<td>O-C (THF)</td>
<td>13.09</td>
<td>1.439</td>
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<tr>
<td>C-C (THF)</td>
<td>13.12</td>
<td>1.534</td>
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<tr>
<td>C-H (THF)</td>
<td>14.68</td>
<td>1.092</td>
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Table 7.4: Parametrised bond stiffness

<table>
<thead>
<tr>
<th>Angles</th>
<th>$k_\alpha$(eV/rad$^2$)</th>
<th>$\theta_0$(degrees)</th>
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</thead>
<tbody>
<tr>
<td>C-C-C (TP)</td>
<td>2.910</td>
<td>119.97</td>
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<tr>
<td>C-C-S (TP)</td>
<td>3.365</td>
<td>121.78</td>
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<tr>
<td>C-C-H (TP)</td>
<td>2.100</td>
<td>120.01</td>
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<tr>
<td>C-N-C (corner)</td>
<td>2.774</td>
<td>110.9</td>
</tr>
<tr>
<td>H-C-H (corner)</td>
<td>1.697</td>
<td>109.55</td>
</tr>
<tr>
<td>N-C-H (corner)</td>
<td>2.141</td>
<td>109.92</td>
</tr>
<tr>
<td>N-Cd-S</td>
<td>0</td>
<td>96.33</td>
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<tr>
<td>Cd-N-C</td>
<td>1.36</td>
<td>107.5</td>
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<tr>
<td>C-C-O (THF)</td>
<td>2.938</td>
<td>108.42</td>
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<tr>
<td>C-O-C (THF)</td>
<td>2.705</td>
<td>112.45</td>
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<tr>
<td>C-C-C (THF)</td>
<td>2.747</td>
<td>110.63</td>
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<td>H-C-H (THF)</td>
<td>16.986</td>
<td>109.55</td>
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<td>C-C-H (THF)</td>
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<td>110.07</td>
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<tr>
<td>O-C-H (THF)</td>
<td>2.203</td>
<td>108.82</td>
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Table 7.5: Parametrised angle stiffness
<table>
<thead>
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<th>Dihedrals</th>
<th>( k_d ) (eV)</th>
<th>d</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-C-C-C (TP)</td>
<td>0.157</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>S-C-C-H (TP)</td>
<td>0.157</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>C-C-C-C (TP)</td>
<td>0.157</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>C-C-C-H (TP)</td>
<td>0.157</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>H-C-C-H (TP)</td>
<td>0.157</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>C-N-C-H (corner)</td>
<td>0.130</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>C-C-O-C (THF)</td>
<td>0.004</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>C-C-C-O (THF)</td>
<td>0.007</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>C-C-C-H (THF)</td>
<td>0.007</td>
<td>1</td>
<td>3</td>
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<tr>
<td>C-O-C-H (THF)</td>
<td>0.017</td>
<td>1</td>
<td>3</td>
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<tr>
<td>O-C-C-H (THF)</td>
<td>0.011</td>
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<td>1</td>
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<tr>
<td>C-C-C-C (THF)</td>
<td>0.008</td>
<td>-1</td>
<td>1</td>
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<tr>
<td>H-C-C-H (THF)</td>
<td>0.007</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 7.6: Parametrised dihedral stiffness
Pour l’enfant, amoureux de cartes et d’estampes,
L’univers est égal à son vaste appétit.
Ah! que le monde est grand à la clarté des lampes!
Aux yeux du souvenir que le monde est petit!

Un matin nous partons, le cerveau plein de flamme,
Le coeur gros de rancune et de désirs amers,
Et nous allons, suivant le rythme de la lame,
Berçant notre infini sur le fini des mers:

Les uns, joyeux de fuir une patrie infâme;
D’autres, l’horreur de leurs berceaux, et quelques-uns,
Astrologues noyés dans les yeux d’une femme,
La Circe tyrannique aux dangereux parfums.

Pour n’être pas changés en bêtes, ils s’enivrent
D’espace et de lumière et de cieux embrasés;
La glace qui les mord, les soleils qui les cuivrent,
Effacent lentement la marque des baisers.

Mais les vrais voyageurs sont ceux-là seuls qui partent
Pour partir; coeurs légers, semblables aux ballons,
De leur fatalité jamais ils ne s’écartent,
Et, sans savoir pourquoi, disent toujours: Allons!

Ceux-là dont les désirs ont la forme des nues,
Et qui rêvent, ainsi qu’un conscrit le canon,
De vastes voluptés, changeantes, inconnues,
Et dont l’esprit humain n’a jamais su le nom!4

...