

# **Defects and Distortions in Hybrid Halide Perovskites**

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A thesis submitted for the degree of

*Doctor of Philosophy*

August 2019

# Abstract

Hybrid halide perovskites are being developed for use as an absorber material in solar cells, alongside other optoelectronic applications such as the light-emitting diode or laser. Research interest in this material family has grown quickly over the decade, as photovoltaic efficiencies have increased from 10.9% in 2012 to the current record of 24.2%. In addition, the synthesis procedure is a low-temperature solution-deposition method which, when commercialised, may allow for a reduction in solar module production prices.

Materials theory and simulation has struggled to keep up with this rapid progress as many of the physical processes which determine solar cell performance are related to defects (e.g. carrier capture and recombination) and temperature (e.g. degradation and ion migration), which are challenging to model from first-principles. A typical Density Functional Theory (DFT) calculation for a crystalline material assumes that the material is perfectly periodic, with no point or extended defects. In addition, DFT is used to model ground-state properties; to account for temperature effects (e.g. atomic vibrations) it is necessary to combine DFT with other methods (e.g. lattice dynamics). The aim of this PhD project is to move away from the idealised picture of a perfect material at absolute zero and towards a more realistic picture, where the defects and distortions of hybrid halide perovskites are considered.

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# Statement of Authorship

I declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research. Where work is not my own references are given. In addition, I list below the instances where work has been done in conjunction with others.

## **Chapter 2: Theory and simulation of hybrid halide perovskites**

The central idea of this chapter (to review the theory and simulation of hybrid halide perovskites) was provided by Aron Walsh. The contents of the review were a product of discussions between myself, Aron Walsh and Jarvist Frost. Aron Walsh prepared figures 2.1, 2.2–2.4, and Young-Kwang Jung prepared figure 2.3. The primary research underpinning this chapter was performed by Jarvist M. Frost (molecular dynamic and Monte Carlo investigations), Federico Brivio (crystal and electronic structure), Jonathan M. Skelton (lattice dynamics and vibrational spectroscopy), and myself (band-gap deformations).

## **Chapter 4: Electronic band non-parabolicity**

The central idea of this chapter (to investigate, across a range of photovoltaic materials, the sensitivity of DFT calculated effective mass to fitting parameters) was provided by Aron Walsh and Benjamin Morgan. Jarvist Frost suggested weighting the fit to a Fermi-Dirac distribution.

## **Chapter 5: Electron-phonon and phonon-phonon coupling**

Jarvist Frost suggested using a classical heat diffusion model for hot carrier cooling and calculated the temperature dependant bandgap shifts. Jonathan M. Skelton provided scripts to implement the frozen phonon method. Aron Walsh prepared figure 5.1.

## **Chapter 6: H-centre defects**

The central idea of this chapter (to investigate hole capture at an iodine interstitial in  $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) was provided by Aron Walsh. Aron Walsh prepared figure X.

# Publications

The following publications have arisen from this PhD work. Where copyright is retained by the publisher, text and figures are reprinted with permission, as detailed in Appendix E.

## **Chapter 2: Theory and simulation of hybrid halide perovskites**

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## **Chapter 4: Results I: Electronic band non-parabolicity**

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## **Chapter 5: Results II: Electron-phonon and phonon-phonon coupling**

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## **Chapter 6: Results III: H-centre defects**

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## **Appendix C: effmass: An effective mass package**

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# Acknowledgements

Leaving an enjoyable job and returning to study is not an easy decision, but starting a PhD in the Walsh group was one of the best I have made. A huge thanks must be given to Aron Walsh for creating and maintaining a supportive, friendly and productive working environment. I have gained a *huge amount* from working with Aron and other members of the group. Although I have learnt something from every member I will not list everyone here, but a special thanks must go to Jarvist Frost who led book group and helped clarify my sometimes muddled understanding of solid state physics. Another special thanks to the women I have worked with; we are still too few and far between in the physical sciences, but what we lack in quantity we make up for in quality! Thanks also to Benjamin Morgan, my second supervisor, who guided me through my first research project and has provided extensive feedback on my scientific writing.

During the third year of my PhD I became involved with the Research Software Engineering community at Imperial. I would like to thank Katerina Michalickova for organising the Software Carpentry workshops - it is no easy job co-ordinating a rabble of volunteers from across Imperial, but teaching software carpentry has greatly increased my confidence around programming. Thanks also to fellow members of the Imperial RSE community committee, especially Jeremy Cohen who is mentoring me as part of my Software Sustainability Institute fellowship.

The vast majority of the computational analysis in this thesis depends to some degree on the open-source community. Thousands of person-hours, often I suspect squeezed in at weekends or evenings, has produced well-tested, well-documented, easily accessible code. Without the magical Python ‘import’ statement and the generosity of strangers I would probably still be writing an integration routine for my first year project. Thanks also to the admin and technical staff who keep the supercomputers Archer, Thomas and Piz-Daint running. I rarely think about the infrastructure behind my calculations, and this is exactly why I need to say thanks.

Funding for my PhD came from the EPSRC, via the Centre for Doctoral Training in New and Sustainable Photovoltaics. It seems that running a CDT requires staff to go above and beyond - thanks to Ken Durose, Alison Walker, Rob Trehearne and Asim Mumtaz for doing just this.

The biggest thanks must go to my family and friends. I met Richard (in a *romantic* way) towards the start of my PhD. It is now four years on, and we have bought a house, got married and created a very small human being (currently still residing in my tummy). I wouldn’t have expected that all this was compatible with doing a PhD, but being with Richard has made it seem like the most natural thing in the world. He has been with me, and supported me, throughout. It is through Richard’s parents, Andrew and Elspeth, that I was introduced to John and Karen. By gifting me use of a bedroom twice a week for three years, John and Karen have enabled me to live in Birmingham and work in London. I don’t think it would have been possible for me and Richard to ‘settle down’ otherwise and for this I am very grateful.

I'm lucky to have close, reliable and hilarious friends who are always suggesting things to take my mind of work. Thanks especially to Hetta and Blanche for Lipsync and our other little "projects" and Caz for her loyalty and warmth. Ruby, my sister, is equally hilarious and understands me (and sees through me!) in a way that no-one else can. The final thanks is reserved for my parents John and Alison, whose love and support instilled in me a self-confidence that I think is so important when doing science. All of my achievements are theirs, as none of this would have been possible without their investment into me.

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## Abbreviations

<b>AM</b>	Air Mass
<b>CBM</b>	Conduction Band Minimum
<b>CZTS</b>	Copper zinc tin sulfide
<b>DFT</b>	Density Functional Theory
<b>GGA</b>	Generalised gradient approximation
<b>HF</b>	Hartree-Fock
<b>HSE06</b>	Heyd-Scuseria-Ernzerhof screened hybrid DFT functional
<b>LDA</b>	Local density approximation
<b>PBE</b>	Perdew-Burke-Ernzerhof DFT functional
<b>PBEsol</b>	Perdew-Burke-Ernzerhof DFT functional developed for solids
<b>MAPI</b>	Methylammonium lead iodide
<b>MD</b>	Molecular dynamics
<b>PV</b>	Photovoltaic
<b>SRH</b>	Shockley-Reed-Hall
<b>SoC</b>	Spin-orbit coupling
<b>VBM</b>	Valence Band Maximum

# Symbols

$\nabla$	Vector differential operator
$\epsilon$	Energy of a state
$\epsilon_0$	Static dielectric constant
$\epsilon_{\text{inf}}$	High frequency (optical) dielectric constant
$\eta$	Photovoltaic efficiency
$\mu$	Chemical potential
$\nu$	Phonon frequency
$\pi$	Pi constant $\sim 3.14$
$\rho$	Electron density
$\sigma$	Carrier capture cross section
$\tau$	Carrier lifetime
$\phi$	Kohn-Sham orbital
$\Psi$	Many-body wavefunction
$e$	Exponential constant $\sim 2.72$
$h$	Planck constant $\sim 6.63 \times 10^{-34} \text{ Js}$
$\hbar$	Reduced Planck constant $\frac{h}{2\pi}$
$\mathbf{k}$	Wavevector associated with periodic electronic structure
$k_B$	Boltzmann constant $\sim 1.38 \times 10^{-23} \text{ JK}^{-1}$
$n$	Carrier concentration
$\mathbf{r}$	Position vector
$t$	Time
$v$	Group velocity
$E$	Total energy
$E_0$	Ground state energy

$E_F$	.	Fermi level
<b>FF</b>	.	Fill factor
$I_{sc}$	.	Short circuit current
$N_t$	.	Trap density
$P$	.	Pressure
$S$	.	Entropy
$T$	.	Temperature
$V$	.	Volume
$V_{oc}$	.	Open circuit voltage

*For generations, we have assumed that the efforts of mankind would leave the fundamental equilibrium of the world's systems and atmosphere stable. But it is possible that with all these enormous changes (population, agricultural, use of fossil fuels) concentrated into such a short period of time, we have unwittingly begun a massive experiment with the system of this planet itself.*

— Margaret Thatcher

# 1

## Introduction

### 1.1 Motivation

In this section I justify photovoltaic materials research. First, the challenge we face as a human race – global warming – is introduced, followed by why we should take advantage of the sun as an energy source. The section ends with a discussion about the three generation of solar cell materials, and the inherent limitations of silicon solar cells.

#### 1.1.1 Energy use and global warming

Anthropogenic climate change is one of the greatest challenges we face as a human race and, as we have twelve years to limit climate change catastrophe, we are running against the clock. This viewpoint is not party political or the political hyperbole of the green left, as I have tried to allude to with the opening quote – this is the current scientific understanding as established by the International Panel on Climate Change.<sup>1</sup>

The story begins in the 18th century when the industrial revolution enabled unprecedented population growth, from 0.8 billion in 1750 to 7.5 billion in 2017.<sup>2</sup> Industrial expansion combined with a growing population led to an exponential growth in the amount of coal and oil being burnt; between the years 1769 and 2006 there was an 800-fold increase in the world annual coal production.<sup>3</sup> Atmospheric CO<sub>2</sub> concentrations increased as a result, leading to an increase in global temperatures, rising sea levels, and ocean acidification. The years 2014–2018 were the five hottest years on record<sup>4</sup> and there has been a recent increase in extreme weather (heat waves, drought and floods) across the globe.<sup>5</sup> Studies have shown that the probability of heat waves,<sup>6</sup> wildfires<sup>7</sup> and flooding<sup>8,9</sup> have increased as a result climate change.

The threat of climate change seems not to have had a proportionate response from governments or many individuals. One reason for this is that changes in weather patterns are significant only when looked at over long time periods, and so it is difficult to communicate the risk carried by

climate change. Another is that this is an inherently international problem, and that we do not have the political mechanisms in place to coordinate a global response. Despite the dramatic consequences of inaction, there seems to be little public appetite for changes which require a reduction in energy use. Instead there is a push towards technological solutions which may be able to reduce the negative effects of climate change without impacting upon our perceived quality of life.

### 1.1.2 The sun as an energy source

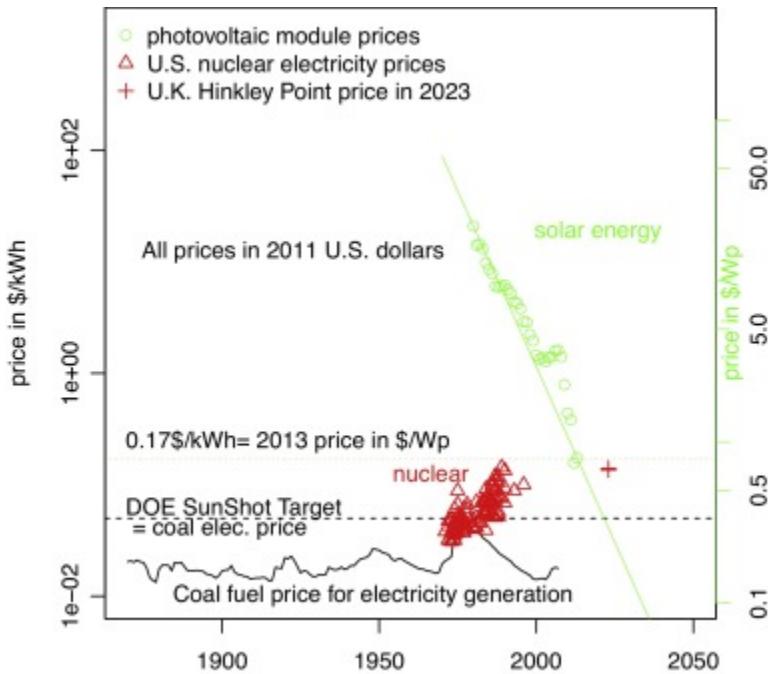
One way to reduce the rate of climate change is to generate energy through processes that do not release net positive amounts of CO<sub>2</sub> into the atmosphere, and harnessing the vast amount of energy that is released from the sun is one way of doing this. This idea has been around for more than sixty years; in 1954 Bell Labs demonstrated that it was possible to convert sunlight into electricity by powering a small toy Ferris wheel and radio transmitter with a silicon solar cell. Reporting this event, The New York Times wrote:

“[the solar cell] may mark the beginning of a new era, leading eventually to the realization of one of mankind’s most cherished dreams—the harnessing of the almost limitless energy of the sun for the uses of civilization.”

A solar flux density of 1361 Wm<sup>-2</sup> reaches the earth’s atmosphere each second, which is almost 10<sup>4</sup> times larger than any other external energy source.<sup>10</sup> A quick back-of-the-envelope calculation shows that if we assume a sunlight to electricity conversion efficiency of 40% (achievable using concentrated solar power) and zero transmission loss, we could meet the world’s electricity demands (22PWh in 2015<sup>11</sup>) by covering an area equivalent to Northumberland county (5000km<sup>2</sup>) with photovoltaic solar panels. However to harness this power we must be able to convert sunlight into electrical energy at a competitive price and at scale. Photovoltaic efficiency is key to price reduction as there are significant costs that scale with area,<sup>12,13</sup> and a higher efficiency module can deliver the same energy for a smaller area.

The first photovoltaic devices could transform sunlight into electrical energy with an efficiency of around 6%. The computing boom of the 1980s encouraged large investment into silicon research and silicon cells with 20% efficiency were reported in 1986.<sup>14</sup> Since 1980 costs have decreased at an average rate of 10% per year<sup>15</sup> (Fig. 1.1) and the global market is growing, from a capacity of 1.9 GW in 2005 to 102 GW in 2016.<sup>16</sup>

In the UK the growth in renewable energy has led to a decreasing dependence on fossil fuels. The UK had its first day without coal in 2017<sup>17</sup> and ran for three days without coal in 2018.<sup>18</sup> There appears to be a growing political will to take advantage of renewable energy; the first UK National Infrastructure Assessment recommends halting the development of nuclear power stations and diverting investment into solar and wind energy generation instead.<sup>19</sup> This switch away from nuclear energy is projected to be at no cost to the consumer.



**Figure 1.1:** Historic and predicted costs of energy generation. The cost of solar energy (green) has been decreasing exponentially (at an average rate of 10% per year) and is now comparable with the cost of energy generated from nuclear power (red). The dashed line corresponds to a solar energy cost target from the US Department of Energy of 0.05 \$/kWh. Reproduced with permission from the work of Farmer et al.<sup>15</sup>

It is widely predicted that solar power will continue to grow – to what extent depends on the source: a recent study from Imperial College London estimates that solar power could supply 23% of global energy demand in 2040.<sup>20</sup> ExxonMobil, a company heavily invested in fossil fuels, predicts that all renewables combined will supply 20% of global power generation in 2040.<sup>21</sup> Note that previous models have consistently underestimated the scale of photovoltaic deployment.<sup>22</sup>

### 1.1.3 Beyond silicon: the need for new photovoltaic materials

Photovoltaic devices are commonly split into three generations. In this section I introduce each generation and discuss what is driving the development of new PV materials in a competitive market that is dominated by silicon.

#### First generation

The first generation devices are based upon mono- and poly-crystalline silicon wafers. They dominate the PV market; in 2016 90% of total PV module production used this technology.<sup>16</sup> They are high efficiency (>20%), reliable (25 year lifetimes) and low cost (<0.5 \$/W). There has been a steady decrease in cost due to i) device engineering improvements (eg: textured surfaces); ii) the economies of scale as silicon industrial processes are driven by a demand for computer chips; and iii) improved industrial practices which allow thinner and thinner wafers to be fabricated with less waste. However there are technological and physical limits to how much

the cost of a crystalline silicon wafer can be reduced. First, the manufacturing process for silicon wafers is energy intensive and requires high temperatures. Second, silicon is an indirect bandgap material and as a result does not absorb sunlight efficiently; wafers have to be a minimum thickness ( $\sim 60\mu\text{m}$ ) to compensate for this. It is difficult to reach this limit without snapping the material during fabrication as silicon is a hard and brittle material.

### Second generation

Second generation devices are fabricated from the direct bandgap materials gallium arsenide (GaAs), cadmium telluride (CdTe), cadmium indium gallium diselenide (CIGS) and amorphous silicon (a-Si). These materials have higher absorption coefficients, so they can be built into lighter thin-film ( $\sim 10\mu\text{m}$ ) architectures. A thin-film is not mechanically stable, it needs a substrate, but this opens up possibility of it being a flexible film.

CdTe was the first thin film to be commercialised and development has been led by the company First Solar, who have installed a total capacity of 17 GW. Lifecycle assessments indicate that the CdTe energy payback time (the time required to generate as much energy as is consumed during production and lifetime operation of the system) is shorter than that of Si.<sup>23</sup> However lower efficiencies are stifling the growth of this technology and there are also concerns about the elemental toxicity and scarcity. CIGS and a-Si each have a smaller market share than CdTe. High efficiency ( $\sim 40\%$ ) GaAs devices have been developed for the high-value, low-volume space market.

### Third generation

Third generation devices are emerging technologies which are not yet in the market. This includes organic and dye-sensitised materials, hybrid halide perovskites, and copper zinc tin sulfide (CZTS). These are abundant materials which can be fabricated through low-cost solution-deposition methods. Only the hybrid-halide perovskites have efficiencies high enough for commercialisation (currently 24.2%).

For the third generation materials commercial success may come from opening up new markets rather than trying to compete directly with well established silicon technologies. For example, organic and hybrid perovskite technologies have tunable bandgaps and are being developed for semi-transparent building integrated photovoltaics. There has also been recent research interest and commercial investment into silicon-perovskite single junction tandem cells.

## 1.2 Key concepts in photovoltaics

This section outlines the physical principles underlying solar cell operation, with a focus on carrier recombination. After introducing the key concepts and vocabulary, the design rules or “wish list” for a successful PV material are outlined.

### 1.2.1 Operating principles

A solar cell converts light into electricity through the following (simplified) process: i) a photon enters the device; ii) the photon is absorbed and creates an electron-hole pair in the absorber layer; iii) the electron and hole disassociate; iv) the electron and hole travel through the absorber layer to their respective contacts; v) the electron and hole are extracted to the external circuit to do electrical work.

#### Device architecture

The device architecture is determined by the properties of the absorber material. For example, in a hybrid halide perovskite material the photogenerated electron and hole are loosely bound to one another and thermal energy is enough to separate them. In this case, a planar *n-i-p* architecture can be used, where *n* is a n-type (electron-doped) material contacted to the cathode, *p* is a p-type (hole-doped) material contacted to the anode and *i* is the intrinsic (undoped) perovskite material (Figure 1.2). In contrast, the photogenerated electron-hole pair in an organic solar cell is strongly bound. In this case, the electron-hole pair disassociate only at an interface and a mesoscopic architecture is used to facilitate this (Figure 1.2). The conventional organic architecture is *p-i-n*, where the anode and p-type material are deposited onto the substrate first. The conventional architectures can be inverted to give *p-i-n* junctions (for inorganic / hybrid absorber layers) or *n-i-p* junctions (for organic absorber layers). In all cases, the n-type and p-type layers provide a built-in electric field that drives photogenerated electrons towards the cathode material and photogenerated holes towards the anode.

Various strategies exist to increase device efficiency via device architecture engineering. For example, the current world record single junction silicon cell ( $\eta = 26.6\%$ ) has an additional wide bandgap material inserted between the absorption layer and contact material to reduce interfacial recombination, and interdigitated back contacts to reduce optical loss.<sup>24</sup> The most efficient solar cells ( $\eta = 46.0\%$ ) combine a multiple pn-junction (tandem) architecture with a lens to concentrate the incoming sunlight.

#### Efficiency and reciprocity

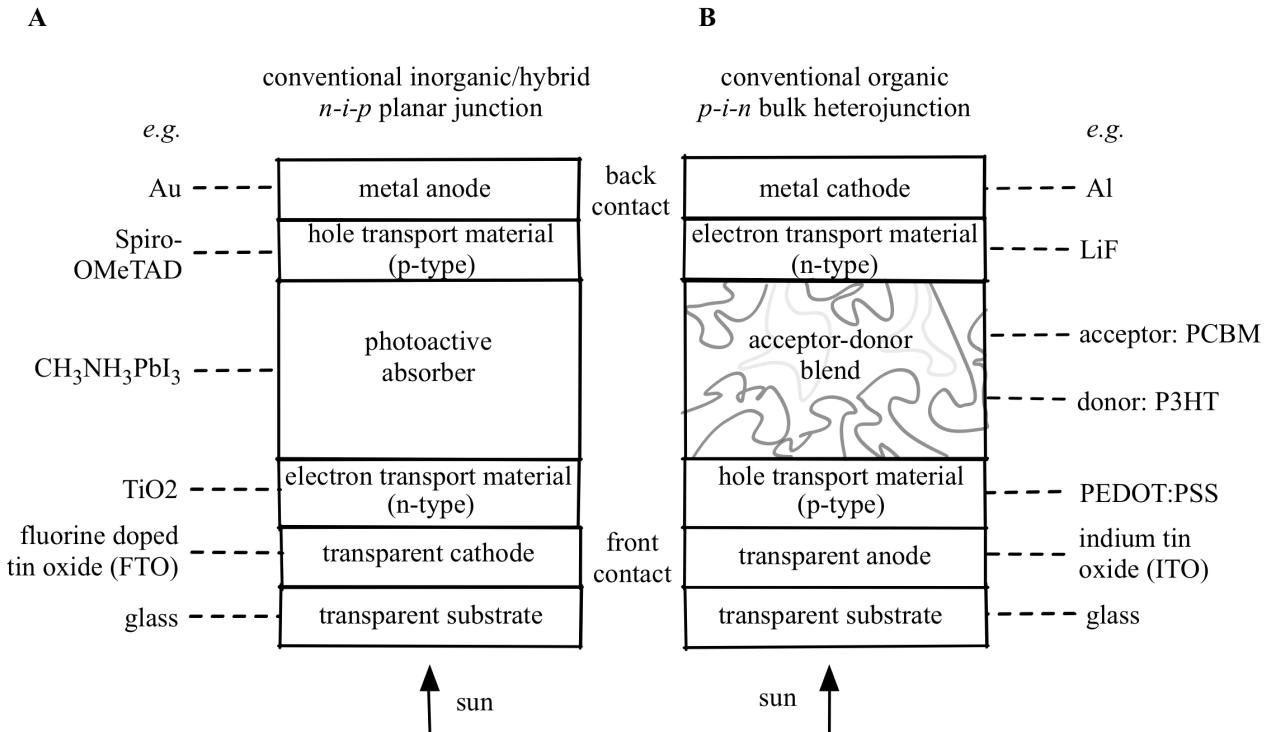
For an external circuit with load  $R$ , a current  $I$  and voltage  $V$  is developed across the cell so that

$$V = IR. \quad (1.1)$$

$I$  and  $V$  are related by a current-voltage curve (Figure 1.3). A solar module operates at the maximum power point  $P_m$ , which is where the product of the voltage and current is maximum:

$$P_m = I_m V_m. \quad (1.2)$$

The open-circuit voltage  $V_{oc}$  is the voltage produced when there is no contact to the external circuit (or, equivalently, the external circuit has an infinite load). The short-circuit current  $I_{SC}$



**Figure 1.2:** (A) Schematic of the typical planar junction solar cell architecture used for an inorganic or hybrid material absorber layer (B) Schematic of the typical bulk heterojunction solar cell architecture used for an organic absorber layer. The mesoscopic architecture provides many interfaces where the electron-hole pair can disassociate. In both cases there is a built-in electric field that drives photogenerated electrons towards the electron transport material and holes towards the hole transport material.

is the current that flows when there is no load on the external circuit. The fill factor FF is defined as:

$$\text{FF} = \frac{I_{\text{m}}V_{\text{m}}}{I_{\text{sc}}V_{\text{oc}}}. \quad (1.3)$$

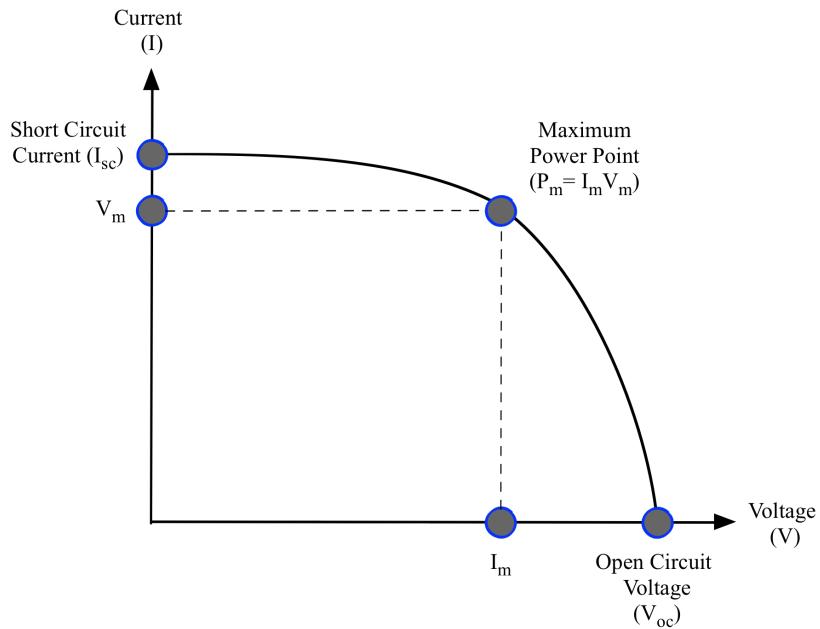
The higher the fill factor, the higher the maximum powerpoint for a given  $V_{\text{oc}}$  and  $I_{\text{sc}}$ .<sup>25</sup> A fill factor of one would correspond to a current-voltage curve which is not *actually* a curve, but a right angle.

The efficiency  $\eta$  of the solar cell under an incident light power of  $P_s$  is given by

$$\eta = \frac{P_{\text{m}}}{P_s} = \frac{I_{\text{m}}V_{\text{m}}}{P_s} = \frac{I_{\text{sc}}V_{\text{oc}}\text{FF}}{P_s}. \quad (1.4)$$

Thus the three key figures of merit for a solar cell are the  $V_{\text{oc}}$ ,  $I_{\text{sc}}$  and FF, and these combine to give the efficiency  $\eta$ . However in all absorber materials there is a trade off between current and voltage; as the bandgap of a material decreases, more photons can be absorbed (higher  $I_{\text{sc}}$ ) but the photogenerated charge carriers have less energy (lower  $V_{\text{oc}}$ ).

At open circuit, all electrons and holes must recombine in the solar cell. In an efficient PV material the recombination is radiative as this is a thermodynamically unavoidable process via



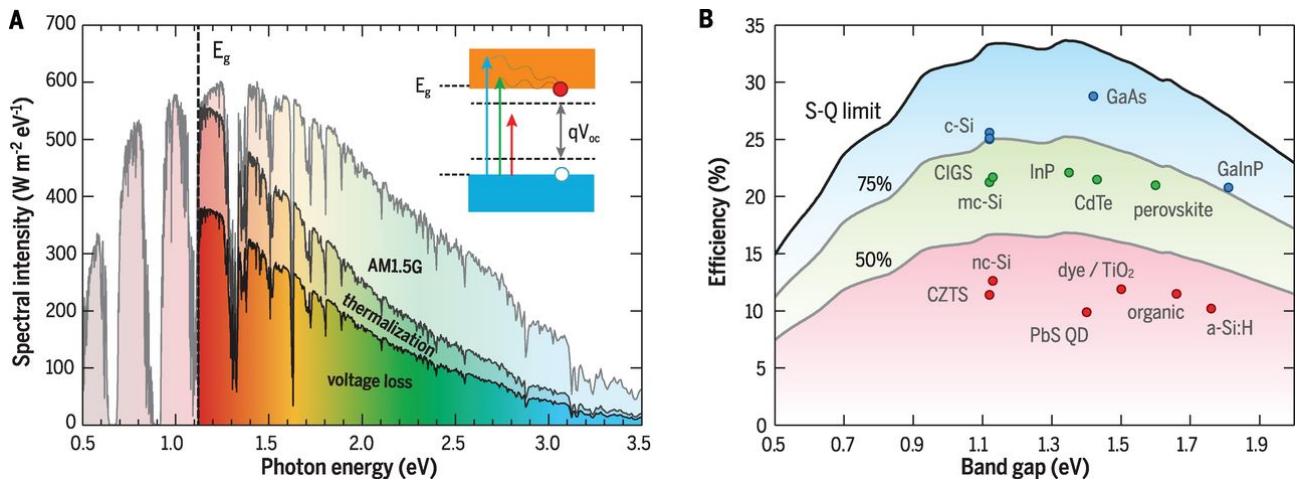
**Figure 1.3:** Schematic of a current-voltage curve for a typical solar cell.

the energy level transitions needed for absorption. Non-radiative recombination, where the energy is dissipated as heat and eventually lost, is avoidable and should be minimised. For a fixed carrier concentration, a higher rate of photon emission corresponds to reduced non-radiative recombination; high radiative efficiency (as measured through e.g. electroluminescence) translates to high open circuit voltage.<sup>26</sup> As a consequence of this reciprocity relation, we can predict the  $V_{oc}$  and  $I_{sc}$  from photoluminescence and photoconductivity studies respectively. This approach has been recently applied to hybrid halide perovskites.<sup>27</sup>

### The Shockley-Queisser limit

The principle of detailed balance states that at equilibrium each microscopic process is balanced by its reverse process: for a photovoltaic device operating at open-circuit this means that the rate of photon absorption equals the rate of photon emission. Shockley and Queisser used the principle of detailed balance to calculate the maximum possible efficiency of a photovoltaic device<sup>28</sup> (an alternative derivation is given in Ref. [25]). The PV efficiency is dependent upon the direct bandgap  $E_g$  of the absorber material and the spectrum of the incident light. Assuming illumination under a standard AM1.5 solar spectrum, the efficiency can be plotted as a function of bandgap. For a single junction solar cell the maximum possible efficiency across is 33%, which corresponds to an ideal bandgap of  $\sim 1.4\text{eV}$  (Figure 1.4).

The model used to calculate the Shockley-Queisser limit is highly idealised. It assumes that all incident light is absorbed, that every absorbed photon creates an electron-hole pair, and that every electron is extracted to the external circuit. In real materials the absorption coefficient is not a step-function, and excited charge carriers can recombine through non-radiative processes



**Figure 1.4:** (A) The AM1.5 spectrum. Photons below the bandgap are not absorbed, whilst energy is lost from above bandgap photons via carrier thermalisation. (B) The Shockley-Queisser efficiency of a single bandgap solar cell under AM1.5 illumination (thick black line). Also included are the top cell efficiencies for various PV materials. Reprinted with permission from the work of Polman et al.<sup>29</sup>

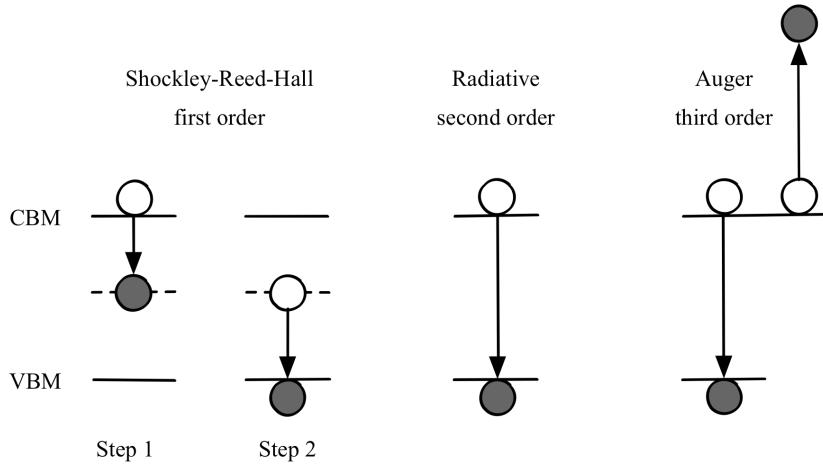
before reaching the circuit. Only three materials have an efficiency above 75% of the Shockley-Queisser limit: crystalline silicon (c-Si), GaAs and GaInP (Figure 1.4). Another metric, the spectroscopic limited maximum efficiency (SLME), accounts for absorption and emission characteristics and reduces the maximum theoretical efficiency.<sup>30</sup> For example, the candidate absorber material CuInS<sub>2</sub> has a Shockley-Queisser maximum efficiency of 33% and SLME of 29%.<sup>31</sup> Non-radiative processes which contribute to the efficiency deficit will be discussed further in Section 1.2.2.

It is possible to exceed the Shockley-Queisser limit by challenging some of the assumptions built into the derivation. For example, the model assumes that once an electron is excited it will thermalise to the band edge, emitting the energy as phonons. This heat energy can no longer do useful work and results in a reduction of the  $V_{OC}$ . However ‘Hot carrier’ cells, which extract electrons before they are able to thermalise, were successfully fabricated in 2014 (although it should be noted that they are currently limited to cryogenic temperatures and an incoming spectrum which is intense and monochromatic).<sup>32</sup>

Another approach is to use tandem solar cells, where several absorber materials are stacked on top of each other. The materials are chosen to have complementary bandgaps, so that more of the solar spectrum can be absorbed with minimal thermalisation losses. GaAs-based four-junction tandem cells have reached an efficiency of 33% and are used for space applications, though their uptake is limited by the costly wafer bonding method required for fabrication. The constraint of lattice matching – that the strain at the interfaces must be minimised for device stability – puts severe limitations on the material combinations which can be used for this approach.

### 1.2.2 Carrier recombination

Electron-hole recombination competes with charge extraction to the external circuit, and as such it is a well examined process. Three pathways for electron-hole recombination are outlined in Figure 1.5. During radiative recombination the electron directly recombines with a hole to produce a photon and, in the case of indirect recombination, phonons. This recombination channel is unavoidable in PV devices as the same channel is used for light absorption. The second pathway, Shockley-Reed-Hall (SRH) recombination, is a two step process mediated via a trap state. In PV devices this pathway should be minimised as the kinetic energy of the electron and hole is transformed to vibrational energy (phonons) and cannot be used for useful work. The third pathway, Auger recombination, is also a non-radiative process. Here the electron directly recombines with a hole, and the resulting energy and momentum is transferred to another conduction band electron.



**Figure 1.5:** A schematic of the three possible electron-hole recombination pathways. In each case, an electron at the conduction band minimum combines with a hole at the valence band maximum. First-, second- and third-order processes correspond to one, two and three particle processes respectively.

Radiative recombination and Auger recombination are unavoidable processes intrinsic to the material, whereas SRH recombination is an avoidable process that can be controlled through defect engineering. The SRH recombination rate is given by

$$U_{\text{SRH}} = \frac{np - n_i^2}{\tau_{n,\text{SRH}}(p + p_t) + \tau_{p,\text{SRH}}(n + n_t)}, \quad (1.5)$$

where  $n$  ( $p$ ) is the density of electrons (holes),  $n_i$  is the intrinsic carrier density and  $n_t$  ( $p_t$ ) is the value of the electron (hole) density when the electron Fermi level is equal to the trap level  $E_t$ :

$$n_t = n_i e^{\frac{(E_t - E_c)}{k_B T}} \quad (1.6)$$

$$n_p = n_i e^{\frac{(E_v - E_t)}{k_B T}}, \quad (1.7)$$

where  $E_c$  and  $E_v$  are the energies of the CBM and VBM respectively. The recombination rate has a maximum when the rates of hole capture and electron capture are comparable. This happens when the trap level is in the middle of the bandgap, and  $n_t = p_t$ .

$\tau_{n,\text{SRH}}$  ( $\tau_{p,\text{SRH}}$ ) is the electron (hole) lifetime. For a trap density  $N_t$ , mean thermal electron (hole) velocity  $v_n$  ( $v_p$ ) and electron (hole) capture cross section  $\sigma_n$  ( $\sigma_p$ ), the lifetimes can be approximated as

$$\tau_{n,\text{SRH}} = \frac{1}{v_n \sigma_n N_t} \quad (1.8)$$

$$\tau_{p,\text{SRH}} = \frac{1}{v_p \sigma_p N_t}. \quad (1.9)$$

The standard approach for calculating the trap density from first principles is give in Chapter 3, and a method for calculating the capture cross section is outlined in the results Chapter ??.

### Experimental measurements of recombination rates

Carrier lifetimes and recombination rates are difficult to measure experimentally as ultra fast optical and electronic sensors are needed to capture transient behaviour, and this must be done in conditions relevant to photovoltaic performance. Time resolved photoluminescence (TRPL) and photoconductivity measurements are used to infer the recombination rates for each recombination pathway. Each pathway scales differently with carrier concentration, as specified by the following rate equation:

$$\frac{dn}{dt} = G - k_1 n - k_2 n^2 - k_3 n^3 \quad (1.10)$$

where  $G$  is the rate of electron-hole generation,  $k_1$  is the rate constant for SRH recombination,  $k_2$  is the rate constant for radiative recombination and  $k_3$  is the rate constant for Auger recombination. SRH recombination via a trap state is a one particle process that scales linearly with the carrier concentration. Radiative recombination is a two particle process that depends on the electron density ( $n_e$ ) and hole density ( $n_h$ ), so scales quadratically with carrier concentration. Auger recombination requires three particles and scales cubically. TRPL uses short laser pulses to excite excess electrons and holes which then decay via recombination or carrier extraction at an interface. Exponential curves are fitted to the TRPL signal at different laser fluences to extract carrier lifetimes. In general, for solar cells operating under 1.5AM illumination, second order SRH recombination is the dominant recombination mechanism.

#### 1.2.3 Design principles for absorber materials

Solid state physics and computational chemistry can connect microscopic material processes to macroscopic observables. The tools of each field have been applied to a range of inorganic and organic materials, and have successfully explained the observed properties of existing materials.

There is also a more recent approach to materials science called “inverse design”. This is where the desired functionality of a new material is stated first, and computational tools are used to predict which materials will exhibit such features.<sup>33</sup> The hope is that this approach will improve upon discovery by trial and error, and accelerate the design of new materials.

High-throughput computational screening is a brute force approach to inverse design. Here, an automated procedure calculates a set of properties across a large number of atomic structures. This approach has been used to identify battery electrolytes,<sup>34</sup> organic photovoltaic materials<sup>35</sup> and materials for carbon capture and storage,<sup>36</sup> amongst others. Materials screening criteria must be defined so that successful materials are identified and selected for further study. Some criteria are easy to identify - for example the thermodynamic stability, which ensures that the material is synthesisable. This criteria can be expanded to include the features found in existing successful materials. For example, hybrid halide perovskites are defect tolerant - they contain a low concentration of defects which are detrimental to opto electronic performance. The electronic parameters which underpin the defect tolerance of hybrid halide perovskites have been identified so that they may be used to screen for new defect-tolerant materials.<sup>37</sup>

With the concept of inverse design in mind, items for a successful PV material “shopping list” are listed below. The final three items (toughness, elemental abundance, elemental non-toxicity) are not necessary for successful devices in the lab, but would promote commercialisation of the technology.

### **Thermodynamic stability**

The material should be thermodynamically stable with regard to competing phases so that it does not degrade over years of operation. The binary compound CdTe was the first thin film PV material to be commercialised and, similar to GaAs, it has no competing phases. Quaternary chalcogenide compounds such as CISSe and CZTS have many more competing phases to consider and the chemical potentials during synthesis must be very finely tuned for stability, which hinders their development.

### **Optimum bandgap**

Ultimately, it is the spectrum of the sun and features of our atmosphere (light scattering and absorption) that dictates the design of solar cells; we must optimise our solar technology to take advantage of the spectrum that is particular to our planet. The Shockley-Queisser limit, discussed in subsection 1.2.1, gives an optimum bandgap of 1.4 eV.<sup>38</sup> Atomic disorder or point defects can reduce the material band gap. Quaternaries with elemental species of a comparable atomic radii are more likely to exhibit atomic disorder – for example in CZTS this leads to a bandgap reduction of 30 meV.<sup>39</sup>

### **Strong light absorption**

The absorption coefficient specifies how much light of a particular wavelength is absorbed by a material. Different semiconductor materials have different absorption coefficients; those with

a higher absorption coefficient will more readily absorb light. Silicon is an indirect bandgap material that requires phonon-assisted absorption. As a result, crystalline silicon absorbs 92% of light in a thickness of 200 µm, whilst CdTe can absorb the same amount in a thickness of 1 µm.<sup>40</sup>

### Low exciton binding energy

After light absorption, a bound electron-hole pair (exciton) is created. The electron and hole must disassociate so that they can travel to their respective contacts. Here, the dielectric response is key, as this determines how readily a material will screen electrostatic perturbations. Organic solar cell materials are limited by low dielectric constants ( $\epsilon_0 \approx 3 - 4$ ) that lead to large exciton binding strengths.<sup>41</sup> In inorganic or hybrid materials the dielectric constants are higher ( $\epsilon_0 = 10.4$  for CdTe,<sup>42</sup> whilst values vary from  $\epsilon_0 = 16.6$  to  $\epsilon_0 = 28.5$  for MAPI<sup>43</sup>).

### High carrier mobility

Some materials may have suitable optical properties but are unable to transport the photo-generated charge efficiently to the contact layers. Carrier mobility quantifies how quickly an electron or hole can move through a material when pulled by an electric charge. Light carrier effective masses (high band dispersions) correspond to higher mobilities. However light effective masses are not sufficient in themselves as there are various scattering channels to consider: lattice scattering, carrier-carrier scattering and defect scattering. The most significant scattering mechanisms in a PV material are lattice scattering and ionized defect scattering. A high dielectric constant is beneficial to carrier mobility as the rate of ionized defect scattering is proportional to  $\frac{1}{\epsilon^2}$ . The composition of the material is also important – for example, vacancies in gallium nitride ( $\text{Ga}(3+)\text{N}(3-)$ ) carry a larger charge and have a larger scattering cross section than vacancies in MAPI ( $\text{CH}_3\text{NH}_3(1+)\text{Pb}(2+)\text{I}(1+)_3$ ).

### Long carrier lifetime

Carrier lifetime has already been discussed in the context of electron-hole recombination in Section 1.2.2. Whereas the concentration of defects is important for carrier mobility, here it is the energy of defect states with respect to the valence and conduction band which is important. This is discussed in Chapter ???. In summary, the key is to minimise non-radiative recombination via deep level defect states (also known as “killer defects”). Carrier diffusion length, another important figure of merit with regard to carrier transport, is proportional to the product of carrier mobility and lifetime.

### Compatibility

For efficient charge extraction, the PV absorber layer must be compatible with suitable contact and/or buffer layers. Firstly, the energy levels of the interfacing materials must align so that there is an electrical potential gradient to extract the charge, without significant loss of  $V_{\text{OC}}$ . For example, band mis-alignments are reported to be the source of poor photovoltaic efficiencies in

the candidate absorber materials BiSI and BiSeI.<sup>44</sup> Secondly, lattice mismatch at the interface should be avoided as this can lead to deep point defects that provide sites for non-radiative recombination and, in the case of more severe strain, an incoherent interface with many defect sites and weak chemical bonding. Computational screening procedures can be used to identify potential electronically and structurally matched contact layers and this has been recently applied to the hybrid halide perovskites.<sup>45</sup>

### Toughness

Silicon is a brittle material; the majority of Si material in a solar cell is used as a mechanical carrier to prevent crack propagation, and glass must be used as a protective layer. The resulting cell is often too heavy to be installed on structures which are made from wood or sheet metal. In addition, the bulk of system costs are higher for heavier cells. Organic photovoltaics, and to some extent perovskites, are tougher and can be made using roll-to-roll print processes onto a flexible substrate.

### Elemental abundance

The power generated from PV installations must exceed 1 TW to make a real impact on global carbon emissions.<sup>46</sup> To meet this demand, PV materials must be made from abundant elements that are in ready supply at reasonable cost. To quantify this criteria, the Herfindahl–Hirschman index (HHI), which is used in economics as a measure of market concentration, can be applied to elements. The HHI indicates that Si is abundant but that production is highly concentrated in a few countries. Elements common to the third generation of materials—Cu, Zn, S, Se, Sn—are less abundant but their production is more highly distributed across the globe.<sup>47</sup>

### Elemental non-toxicity

Finally, toxic elements may hinder the successful commercialisation of future PV technologies. The problem is not insurmountable; cadmium telluride is toxic if ingested but is a commercial solar cell material. Encapsulation and recycling can reduce any risk, but add another level of complexity to the development of new solar technologies.

## 1.3 Summary

To reduce the rate of climate change we must decrease our reliance on fossil fuels, and increasing the proportion of photovoltaic energy is one way to achieve this. This may only be politically feasible if the costs associated with PV energy can continue to exponentially decrease. As the well-established silicon technologies are limited by high capital expenditures, there is an incentive to develop new low-cost, high-efficiency and reliable technologies. Flexible thin-film architectures also allow for expansion into the new market of building integrated photovoltaics. Currently no material has met these requirements,<sup>48</sup> although promising performance from emerging technologies such as the hybrid halide perovskites motivates further research.

## 1.4 Thesis outline

Organic-inorganic halide perovskites, the subject of this thesis, present a number of challenges for first-principles atomistic materials modelling. These ‘plastic crystals’ feature dynamic processes across multiple length-scales and time-scales, which include mixed ionic-electronic transport, highly anharmonic lattice dynamics and strong relativistic (spin-orbit coupling) effects on the electronic band structure. These issues, which affect the operation of solar cells, are outlined in the following chapter. This is followed by a brief introduction to the theory that underlies almost all of the work in this thesis - Density Functional Theory (DFT). To model an imperfect material (one with crystal defects), or temperature effects, a series of post-processing steps must follow the DFT calculation. These are also outlined in Chapter Three.

Chapters Four–Six contain the thesis results. Each results chapter also contains any additional theory where required and calculation steps. Bulk transport and optical properties of the perfect material are calculated using Effective Mass Theory (EMT) in Chapter Three. EMT often assumes a parabolic electronic band dispersion, in this chapter distortions away from parabolicity are considered. Temperature effects are introduced in Chapter Four. At room temperature the inorganic octahedral  $\text{PbI}_3$  units tilt back and forth, and the coupling strength between this tilting and the electronic sub-system is quantified. Point defects are introduced to our model in Chapter Six. Point defects can be benign or harmful to device performance, depending upon the properties of the defect. This chapter reports the properties of the iodine interstitial point defect.

*It's simple mathematics.*

— Mos Def, *Mathematics*

# 2

## Simulation of hybrid halide perovskites

### 2.1 Introduction

In this chapter I address recent progress and current challenges in the theory and simulation of hybrid perovskites. Particular attention is paid to predicting properties that assess the photovoltaic potential of a material. Factors to consider include: light absorption, charge transport, absolute band energies, defect physics and chemical stability.

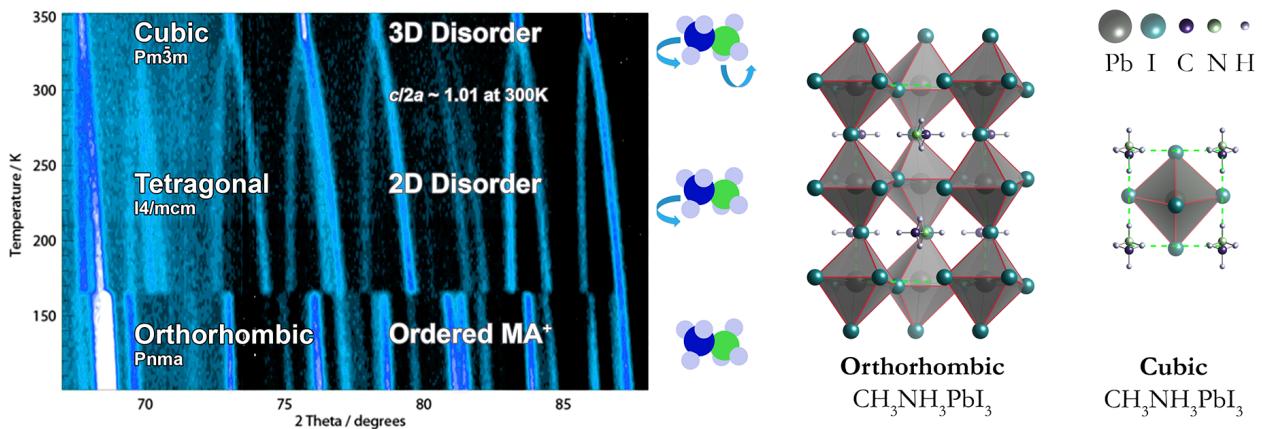
The perovskite mineral,  $\text{CaTiO}_3$ , is the archetype for the structure of many functional materials.<sup>49</sup> Metal halide perovskites have been studied for their semiconducting properties since the 1950s<sup>50</sup>; yet only recently have organic-inorganic perovskites such as  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPI) been applied to solar energy conversion, showing remarkably strong photovoltaic action for a solution processed material.<sup>51</sup> The field has progressed rapidly in the past eight years, with the increase in power conversion efficiency supported by over three thousand research publications.<sup>52–56</sup> Other potential application areas of these materials include thermoelectrics,<sup>57,58</sup> light-emitting diodes,<sup>52,59</sup> and solid-state memory.<sup>60,61</sup>

These materials combine a complex crystal structure, modulated by static and dynamic disorder, with an electronic structure requiring methods beyond density functional theory to treat many-body and relativistic effects. As such, the halide perovskites represent a challenge to predictive materials modelling.

### 2.2 Crystal structures and lattice dynamics

#### 2.2.1 Phase diversity

Hybrid perovskites of the type  $\text{ABX}_3$  form a crystal structure with an organic A site cation contained in an inorganic  $\text{BX}_3$  framework of corner sharing octahedra. Halide substitution on the X site ( $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ), metal substitutions on the B site ( $\text{B} = \text{Pb}^{2+}, \text{Sn}^{2+}$ ), and cation



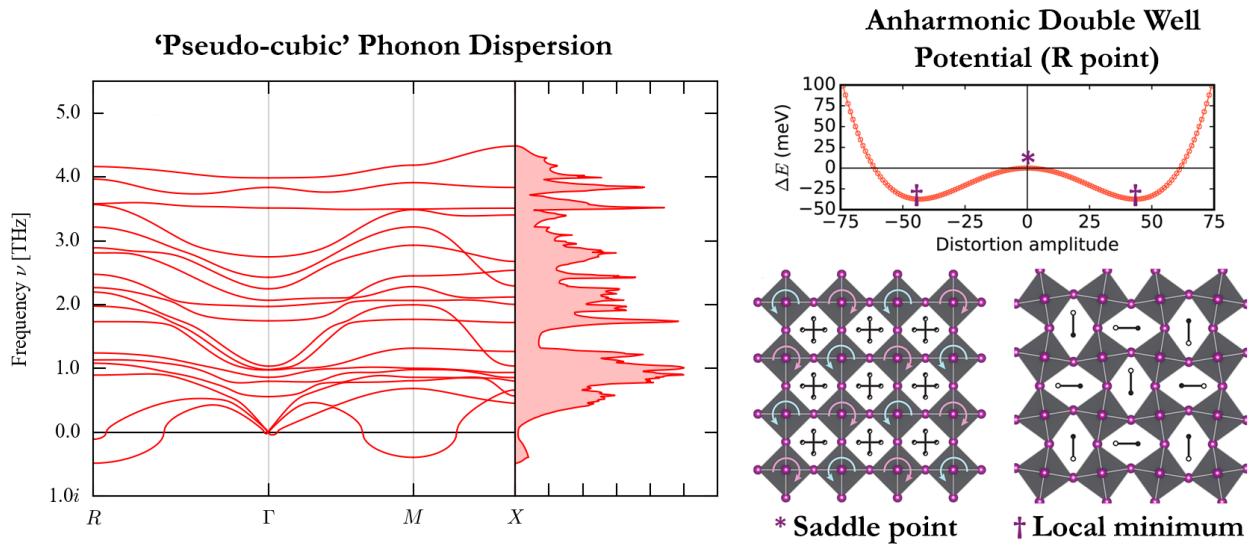
**Figure 2.1:** The high-resolution powder neutron diffraction pattern of the hybrid halide perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is shown in the left panel (adapted with permission from Ref.<sup>62</sup> based on data in Ref.<sup>63</sup>), which illustrates the low and high temperature phase transitions. While an ordered  $\text{CH}_3\text{NH}_3^+$  sub-lattice is expected in the orthorhombic phase, orientation disorder increases with temperature. The crystallographic unit cells of the pseudo-cubic and orthorhombic perovskite phases are shown in the right panel (adapted with permission from Ref.<sup>64</sup>). The associated structure files can be accessed from <https://github.com/WMD-group/hybrid-perovskites>. Figure prepared by Aron Walsh.

substitution on the A site ( $\text{A} = \text{CH}_3\text{NH}_3^+, \text{HC}(\text{NH}_2)_2^+, \text{Cs}^+, \text{Rb}^+$ ) lead to various chemical and physical properties.<sup>65,66</sup> In addition to isoelectronic substitutions (e.g. replacing  $\text{Pb}^{2+}$  by  $\text{Sn}^{2+}$ ), it is possible to perform pairwise substitutions to form double perovskites (e.g. replacing  $2\text{Pb}^{2+}$  by  $\text{Bi}^{3+}$  and  $\text{Ag}^+$ ).<sup>67,68</sup>

In the first report of MAPI by Weber in 1978, the crystal structure was assigned as cubic perovskite (space group  $Pm\bar{3}m$ ).<sup>69,70</sup> The anionic  $\text{PbI}_3^-$  network is charge balanced by the  $\text{CH}_3\text{NH}_3^+$  molecular cation. The symmetry of  $\text{CH}_3\text{NH}_3^+$  ( $C_{3v}$ ) is incompatible with the space group symmetry ( $O_h$ ) unless orientation disorder (static or dynamic) is present. The crystal structure solved from X-ray or neutron diffraction data usually spread the molecules over a number of orientations with partial occupancy of the associated lattice sites. A common feature of perovskites is the existence of phase changes during heating (typically from lower to higher symmetry) as shown in Figure 2.1. In hybrid halides containing methylammonium, these are orthorhombic ( $Pnma$ ), tetragonal ( $I4/mcm$ ) and cubic ( $Pm\bar{3}m$ ) phases.<sup>63</sup> For MAPI the  $Pnma$  to  $I4/mcm$  phase transition is first-order with an associated discontinuity in physical properties, while the  $I4/mcm$  to  $Pm\bar{3}m$  phase transition is second-order with a continuous evolution of the structure and properties.<sup>63,71</sup>

The phase transitions are linked to a change in the tilting pattern of the inorganic octahedral cages, and order-disorder transitions of the molecular sub-lattice.<sup>71–73</sup> X-ray diffraction (XRD) measurements upon cooling (heating) suggest the incursion of tetragonal in orthorhombic phases (and vice versa),<sup>74</sup> which is common for first-order solid-state phase transitions.

Similar phase behaviour tends to be seen for other compositions; however, the transition temperatures vary. In MAPI the orthorhombic to tetragonal transition temperature is 162 K, becoming cubic by around 328 K, while  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  is cubic above 237 K.<sup>75</sup>



**Figure 2.2:** (Left) The harmonic phonon dispersion for  $\text{CH}_3\text{NH}_3\text{PbI}_3$  from a ‘pseudo-cubic’ structure. The imaginary frequencies of acoustic modes at the  $M$  ( $q = \frac{1}{2}, \frac{1}{2}, 0$ ) and  $R$  ( $q = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) Brillouin zone boundary correspond to an instability expressible in a supercell as alternate tilting of the octahedra. (Right) Following the imaginary acoustic mode at the  $R$  Brillouin zone boundary in a  $2 \times 2 \times 2$  supercell expansion shows a double-well potential in the DFT internal energy. The saddle point corresponds to a  $1 \times 1 \times 1$  cubic structure, whilst the two local minima correspond to a distorted structure of lower symmetry. The energy barrier is small enough to allow both minima can be accessed at room temperature, so the system is expected to exhibit dynamic rather than static disorder. Similar behaviour is found at the  $M$  point. Figure adapted by Aron Walsh with permission from Refs.<sup>76</sup> and<sup>77</sup>. The underlying phonon data is available from <https://github.com/WMD-group/Phonons>.

## 2.2.2 Local and average crystal environment

The first electronic structure calculation of hybrid halide perovskites was by Chang, Park and Matsushi in 2004,<sup>78</sup> in the local density approximation (LDA) of density functional theory (DFT). They modelled a static structure where the  $\text{CH}_3\text{NH}_3^+$  molecule was aligned along  $\langle 100 \rangle$  (towards the face of the corner-sharing  $\text{PbI}_3^-$  framework), but found that the barrier for rotation to  $\langle 111 \rangle$  was less than 10 meV. This small barrier for cation rotation gave credence to a prior model that the molecular sub-lattice was dynamically disordered.<sup>75</sup> Similar barriers were later found within the generalised gradient approximation (GGA) of DFT.<sup>79</sup>

*Ab initio* molecular dynamics (MD), neutron scattering<sup>80,81</sup> and time-resolved infra-red<sup>82</sup> data all indicate a 1–10 picosecond reorientation process at room temperature. As a result of anharmonic molecular rotation, and large-scale dynamic distortions along soft vibrational modes, the local structure can deviate considerably from that sampled by diffraction techniques, which do not probe local disorder that preserves long-range order on average.

In spite of the larger cation, FAPI appears to possess a similar timescale of rotation to MAPI<sup>83</sup>. A lighter halide (and therefore smaller cage) results in faster rotation, in spite of the greater steric hindrance.<sup>84</sup> Together, these data suggest that the molecular rotation is a function of the

local inorganic cage tilting, where the relatively insignificant mass of the organic cation follows the pocket distortion.

The spontaneous distortions can also be observed in the vibrational spectra. The calculated harmonic phonon dispersion for MAPI in the cubic phase is presented in Figure 2.2. The acoustic modes soften as they approach the  $M$  ( $q = \frac{1}{2}, \frac{1}{2}, 0$ ) and  $R$  ( $q = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) Brillouin zone boundaries. This zone boundary instability can only be realised in an even supercell expansion, where it corresponds to anti-phase tilting between successive unit cells. This behaviour is characteristic of the perovskite structure, and can be described by the Glazer tilt notation.<sup>85,86</sup>

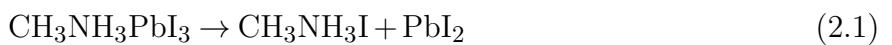
Within the frozen-phonon approximation the potential energy surface can be traced along the soft acoustic  $M$  and  $R$  modes. In both cases this results in a double well with an energy barrier  $\sim k_B T$  at the saddle point;<sup>76</sup> at room temperature the structure is dynamically disordered, with continuous tilting. Indeed, MD simulations show continuous tilting of MAPI and FAPI at room temperature.<sup>83,87,88</sup> As temperature decreases, the structural instability condenses via the  $R$  point (with an energy barrier of 37 meV) into the lower symmetry tetragonal phase. This is followed by condensation of the  $M$  point (with an energy barrier of 19 meV) to the orthorhombic phase.<sup>76</sup>

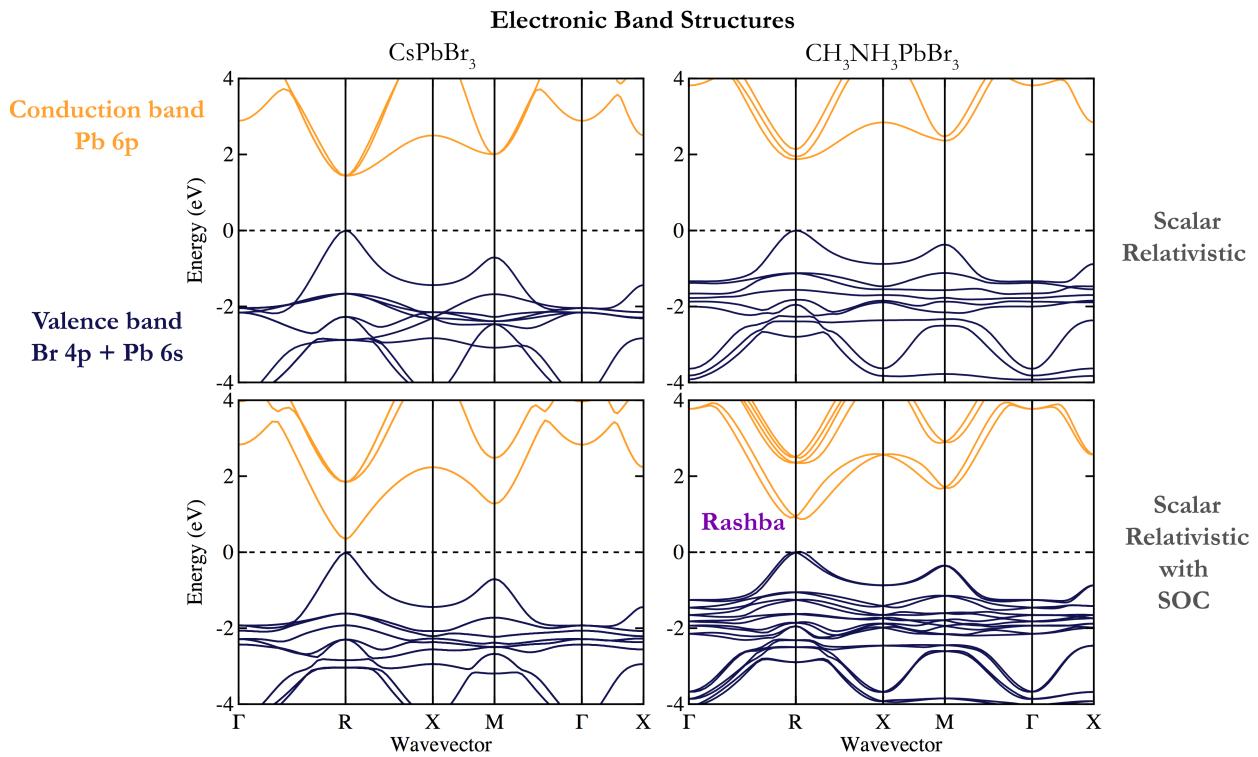
In the static picture – as in the case of an electronic band structure calculated for a single ionic snapshot – the organic cation plays no direct role in optoelectronic properties of the material as the molecular electronic levels lie below that of the inorganic framework. Once motion is considered, the electrostatic and steric interaction between the organic molecule and inorganic framework couples tilting and distortion of the octahedra to the organic cation motion. These tilts and distortions vary the orbital overlap between states, perturbing the band-structure and band-gap.<sup>76,88–90</sup> The electronic structure thus becomes sensitive to temperature, which will be discussed further in Section 2.3.2 and Chapter ??.

### 2.2.3 Thermodynamic and kinetic stability

*Ab initio* thermodynamics has emerged as a powerful tool in materials modelling, with the ability to assess the stability of new materials and place them on equilibrium phase diagrams even before experimental data is available.<sup>91–93</sup> The total energy from DFT calculations approximates the internal energy of the system. By including lattice vibration (phonon) and thermal expansion contributions, the Gibbs free energy and other thermodynamic derivatives can be evaluated.<sup>94</sup> In the context of photovoltaic materials, this has been applied to Cu<sub>2</sub>ZnSnS<sub>4</sub> and used to identify the processing window where a single-phase compound can be grown in equilibrium.<sup>95</sup>

An issue with hybrid perovskites and other metal-organic frameworks is that the calculated heat of formation is close to zero. The decomposition reaction





**Figure 2.3:** The electronic band structures of the inorganic perovskite  $\text{CsPbBr}_3$  and hybrid perovskite  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  in the cubic phase. One effect of the organic cation is to widen the band-gap located at the  $R$  point due to the larger lattice constant. Spin-orbit coupling reduces the band-gap in both materials. The presence of  $\text{CH}_3\text{NH}_3^+$  in the hybrid perovskite results in a non-centrosymmetric crystal, with an associated relativistic Rashba-Dresselhaus splitting of the lower conduction band. While labels of the special points are those of the cubic perovskite structure (space group  $Pm\bar{3}m$ ), the static model of the hybrid perovskite formally has  $P1$  symmetry. Points equivalent for a cubic crystal (e.g.  $M = \frac{1}{2}, \frac{1}{2}, 0$ ;  $M' = 0, \frac{1}{2}, \frac{1}{2}$ ;  $M'' = \frac{1}{2}, 0, \frac{1}{2}$ ) are inequivalent here. Figure prepared by Young-Kwang Jung.

has been predicted to be exothermic. Subsequent calorimetric experiments have supported the prediction that hybrid lead halide perovskites are metastable.<sup>96</sup> It is likely that these materials are only formed due to entropic (configurational, vibrational and rotational) contributions to the free energy.

## 2.2.4 Anharmonic lattice vibrations and thermal conductivity

Kohn-Sham density functional theory is most often carried out in the Born-Oppenheimer approximation where the nuclei are static classical point charges. To consider thermal vibrations, expansion or heat flow the theoretical framework of lattice dynamics can be used.<sup>94</sup>

In the harmonic approximation, the lattice dynamics are fully specified by second-order force-constants of individual atoms, which are then used to build the dynamical matrix. The eigenstates of this matrix are the normal modes of vibration with an associated phonon energy. Thermal expansion coefficients, system anharmonicity (e.g. Grüneisen parameters) and the temperature-dependence of other properties can be calculated in the quasi-harmonic approximation (QHA).

Here the lattice dynamics is harmonic at a given temperature; however, the cell volume is scaled by thermal expansion to give the first-order contribution of finite temperature effects.

The thermal expansion coefficient of MAPI in the cubic phase has been calculated with the QHA. The value is sensitive to the density functional used. For example, a value of  $3.0 \times 10^{-5}/K$  is calculated with the PBE functional with Tkatchenko-Scheffler dispersion corrections,<sup>90</sup> while the PBEsol functional produces a value of  $12.5 \times 10^{-5}/K$ .<sup>64</sup> These compare to finite temperature scattering measures of  $1.91 \times 10^{-5}/K$  by X-ray,<sup>97</sup> and  $13.2 \times 10^{-5}/K$  by neutron diffraction.<sup>63</sup> Even taking the smallest value above, the expansion coefficient is one order of magnitude greater than silicon,<sup>98</sup> highlighting the strong deviation from harmonic behaviour in halide perovskites.

In the harmonic approximation (and similarly the QHA), the dynamic matrix eigenmodes are orthogonal and the resulting phonons are non-interacting. Consequently phonon lifetimes are infinite as the phonons do not scatter; thermal conductivity is infinite. To calculate phonon-phonon scattering, and so its contribution to finite thermal conductivity, anharmonic lattice dynamics need to be considered. A computational route is to use perturbative many-body expansion, e.g. as implemented in PHONO3PY,<sup>99</sup> which includes third-order force constants. For MAPI, 41,544 force evaluations are required for these third-order force constants, compared to 72 for second-order (harmonic) force constants.<sup>76</sup> Consequently, these calculations are vastly more expensive. Using this approach phonon-phonon scattering rates are calculated to be three times larger in MAPI compared to standard covalent semiconductors CdTe and GaAs.<sup>76</sup> Consequently, mean free paths are on the nanometer rather than more typical micrometer scale. Lattice thermal conductivity is extremely low,  $0.05 \text{ Wm}^{-1}\text{K}^{-1}$  at 300 K.<sup>76</sup> This combination of high electrical and low thermal conductivity makes these compounds potential thermoelectric materials.<sup>57,58</sup>

In highly anharmonic systems third-order force constants and perturbation theory may not be sufficient to describe the true dynamics, but going further with lattice dynamics becomes prohibitive. Besides, it is not obvious whether the fundamental tenant of lattice dynamics, of expanding in small displacements around a minimum structure, is correct for these soft and highly anharmonic materials. In contrast, MD treats anharmonic contributions to all orders. As MD stochastically explores the phase space, long integration times are required to sample rare events, and finite size effects mean that only phonon modes commensurate with the supercell are sampled.

## 2.3 Electronic structure

Despite the dynamic disorder just discussed, in many respects halide perovskites display characteristics of traditional inorganic semiconductors, with a well-defined electronic band structure and electron/hole dispersion relations. However, when the electronic structure is correctly modelled, various subtleties emerge.

### 2.3.1 Many-body and relativistic effects

Perhaps surprisingly, local and semi-local exchange-correlation functionals provide a reasonable estimate for the band-gaps of these heavy metal halide materials. This is due to a cancellation of errors. For Pb-based perovskites, the conduction band has mainly Pb 6p character. Due to the large nuclear charge, the electronic kinetic energy requires a relativistic treatment, and spin-orbit coupling (SoC) becomes significant. The first-order effect is a reduction in band-gap by as much as 1 eV<sup>100</sup>, as the degenerate 6p orbitals are split and moved apart. This is shown in Figure 2.3 for the bromide compounds. The typical band-gap underestimation of GGA functionals is offset by the absence of relativistic renormalisation.

SoC is not expected to have a large impact on the structural properties of the Pb-based compounds as the (empty) conduction band is mainly affected, and the force on atoms depends on the electron density (occupied orbitals). Accurate force-constants can be calculated without SoC considerations.<sup>101</sup>

There have been a number of electronic structure calculations considering many-body interactions beyond DFT. Quasi-particle self-consistent *GW* theory shows that the band dispersion (and so density of states, optical character and effective mass) is considerably affected by both the *GW* electron correlation and SoC.<sup>100</sup> Some materials see only a rigid shift of band structure (retaining DFT dispersion relations)<sup>45,102</sup> but this is not the case for hybrid perovskites. The effect of SoC on the band dispersion of MAPI is discussed in Chapter ??.

A consequence of SoC when combined with a local electric field is the Rashba-Dresselhaus effect, a splitting of bands in momentum space.<sup>103</sup> This can be understood as an electromagnetic effect, where the magnetic moment (spin) of the electron interacts with a local electric field, to give rise to a force which displaces it in momentum space. Up and down spins are displaced in opposite directions, and this displacement is a function (in both size and direction) of the local electric field, which will depend on the local dynamic order. For a static structure, this is demonstrated in Figure 2.3 for CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>. Neglecting SoC, the cubic phase has band extrema at the *R* point (a direct band-gap). With SoC the valence and conduction band each split into valleys symmetrical around *R*. The splitting is much more pronounced in the Pb 6p conduction band (compared to the Br 4p valence band), as expected from the  $Z^4$  dependence of spin-orbit coupling. This asymmetry in the band extrema results in direct-gap like absorption and indirect-gap like radiative recombination which is discussed later. For a comparison between SoC and non-SoC bandstructures across a range of materials see Appendix A.

The relativistic spin-splitting can only occur in crystals that lack a centre of inversion symmetry, a prerequisite for generating a local electric field. The cubic representation of CsPbBr<sub>3</sub> has an inversion centre, so while SoC affects the band-gap through the separation of Pb 6p into p<sub>1/2</sub> and p<sub>3/2</sub> combinations, no splitting of the band extrema away from the high symmetry points is observed (see Figure 2.3). This is true only for a static cubic structure and, as discussed earlier, hybrid halides will have continuous local symmetry breaking.

Point defect calculations will be particularly sensitive to the electronic structure method used. Neglection of SoC and self-interaction errors can result in an incorrect position of the valence or conduction band edges, thus introducing spurious errors in defect energy levels and predicted defect concentrations. Du<sup>104</sup> showed how for the case of an iodine vacancy, a deep (0/+) donor level is predicted for GGA without SoC, while a resonant donor level is predicted for GGA-SoC and HSE-SoC treatments of electron-exchange and correlation.

### 2.3.2 Electron-phonon coupling

Going beyond the Born-Oppenheimer approximation, the interaction of the electronic structure with vibrations of the lattice can be considered. Electron-phonon coupling can perturb the electronic band energies (changing the band-gap), and couple electronic excitations (the hole and electron quasi-particles) into vibrational excitations (phonon quasi-particles). In a semiconductor, charge carrier scattering is often dominated by this electron-phonon interaction, and so the strength of these processes set a limiting value on the mobility. Electron-phonon coupling is often calculated in a second-order density functional perturbation theory calculated for a static (rigid ion) structure. In the normal limit, this term is expected to dominate over the first order contribution from the acoustic deformation potential as vibrations are typically small.

In Chapter ?? a method to calculate the electron-phonon interaction of soft modes is outlined, and applied to the acoustic zone boundary tilting modes in hybrid halide perovskites described earlier. A positive band-gap shift of 36 meV ( $R$  point phonon) and 28 meV ( $M$  point phonon) is predicted at T = 300 K. Saidi et al. sampled all non-soft harmonic phonons at the  $\Gamma$  point using a Monte Carlo technique,<sup>90</sup> finding significant differences with the standard perturbation theory results. Electron-phonon interactions can be calculated with MD, but as with phonon-phonon scattering, achieving convergence with respect to electronic ( $k$ -point sampling and basis set) and vibrational ( $q$ -point sampling and supercell size), while maintaining sufficient integration time to capture rare processes, is costly.

Recently a ‘one shot’ method has been developed to calculate band-gap renormalization and phonon-assisted optical absorption, and applied to Si and GaAs.<sup>105</sup> Nuclei positions are carefully chosen as a representative sample from the thermodynamic ensemble, and the electronic structure is needed for this static structure only—a significant increase in computational efficiency. Such techniques may provide a promising method to calculate the electron-phonon coupling of complex materials, but they have not yet been tested for the family of hybrid halide perovskites or other more complicated crystal structures.

### 2.3.3 Charge carrier transport

Charge carrier transport in hybrid halide perovskites is now considered. The minority-carrier diffusion length is the average length a photo-excited (or electronically-injected) carrier travels before recombining. In a photovoltaic device, the diffusion length must be sufficient to reach the contacts. The minority-carrier diffusion length is a product of the diffusivity  $D$  and lifetime  $\tau$  of minority charge carriers,  $L_d = \sqrt{D\tau}$ .

Minority-carrier diffusion lengths in MAPI are reported to be considerably larger than other solution processed semiconductors.<sup>106</sup> Long lifetimes (large  $\tau$ ) can be partly attributed to the ‘defect-tolerance’ of hybrid perovskites (discussed in Section 2.4.3), reducing the rate of ionised-impurity scattering and non-radiative recombination.

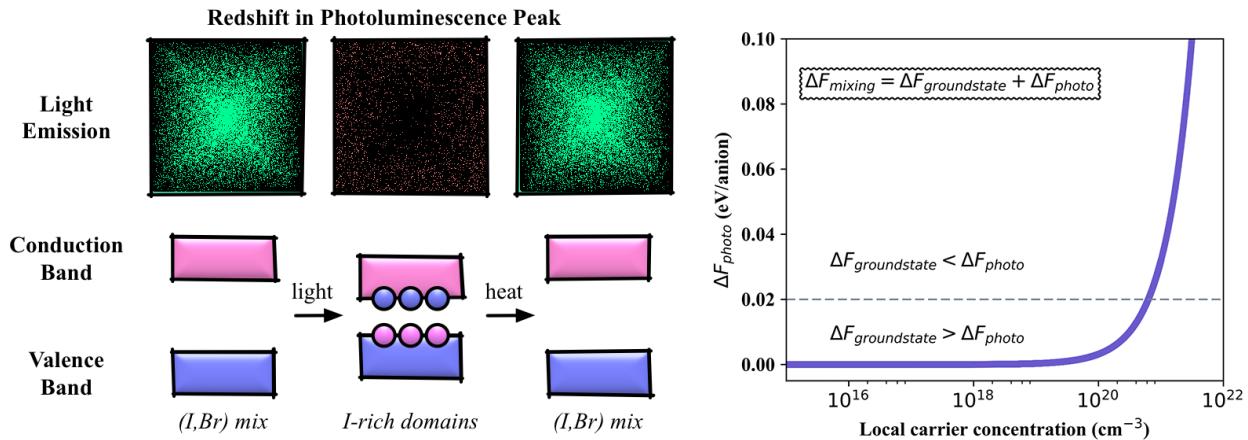
The effective masses of electrons and holes in hybrid halide perovskites are small. Given the effective mass of  $< 0.2m_e$ , the carrier mobility of MAPI ( $< 100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) is modest in comparison to conventional semiconductors such as Si or GaAs ( $> 1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ).<sup>52</sup> Carrier mobility must be limited by strong scattering.

Low temperature mobility in this material reduces as a function of temperature as  $T^{-1.5}$ , which provides circumstantial evidence for being limited by acoustic phonon scattering.<sup>107,108</sup> However, if only the acoustic phonon scattering (which is elastic due to the population of acoustic modes) is considered, the calculated mobility is orders of magnitude larger than experiment. A key realisation is that the soft nature of these semiconductors results in optical phonon modes (see Figure 2.2) below thermal energy.<sup>64,101</sup> Optical phonon scattering is inelastic and dominates once the charge carriers have sufficient energy to generate the phonon modes.<sup>109</sup> Through solving the Boltzmann transport equation parameterised by DFT calculations, scattering from longitudinal optical phonons is identified as the process limiting mobility at room temperature.<sup>110,111</sup>

Mobility will be further limited by scattering from point and extended lattice defects.<sup>112</sup> Fluctuations in electrostatic potential resulting from dynamic disorder provide a macroscopic structure from which carriers will also scatter.<sup>87,113</sup>

## 2.4 Photophysics and solar cells

Hybrid halide perovskites are, in the most part, being researched in the context of solar cell technology. There are areas of the underlying physics which are not yet developed, and which may be limiting progress in the field. Ion migration is poorly understood and has been correlated with the hysteresis effects<sup>116,117</sup> and device degradation. In MAPI, the iodine interstitial defect has been identified as a site for charge trapping<sup>118</sup> (as reported in Chapter ??), but the role of impurities is not understood. Additionally, interfaces have not been optimised for optimal charge carrier extraction. These issues are outlined in the following section.



**Figure 2.4:** Halide perovskites are mixed ionic-electronic conductors. The vacancy-mediated diffusion of halide anions has been associated with both current-voltage hysteresis of solar cells and the rapid interchange between iodide, bromide and chloride materials. One point of controversy remains the reversible ion segregation observed in mixed (Br,I) systems. Alloyed materials have been found to phase separate upon illumination, but recover their initial state when the light source is removed. The phase separation is associated with a striking red-shift in photoluminescence spectra. A statistical mechanical analysis of ground-state DFT calculations suggested a large miscibility gap<sup>114</sup>, while the charge carriers generated upon illumination can provide an additional driving force for phase separation.<sup>115</sup> The results from a simple thermodynamic model are shown in the right panel, where the free energy of mixing contains contributions from the ground-state with an additional component due to the difference in band-gaps between the mixed (I,Br) and phase separated I-rich phases. The latter contribution requires local carrier concentrations approaching  $10^{21} \text{ cm}^{-3}$  to make a substantial contribution to the overall mixing energy. Figure prepared by Aron Walsh.

### 2.4.1 Ion migration

Charged point defects in the bulk allow for mass transport of ions and can result in spatial fluctuations of electrostatic potential. For solid-state diffusion to be appreciable in magnitude, there needs to be a high concentration of defects and a low activation energy for diffusion.

The equilibrium concentration of charged vacancy defects is calculated as being in excess of 0.4% at room temperature in MAPI.<sup>119</sup> Low defect formation energies and free-carrier concentrations found across the halide hybrid perovskites indicate that Schottky defects are prevalent across this family of materials. While each point defect is charged, they are formed in neutral combinations so that a high concentration of lattice vacancies does not require a high concentrations of electrons or holes to provide charge compensation.

The ion migration rate is given by:

$$\Gamma = \nu \exp\left(\frac{-\Delta H^{\text{diff}}}{k_B T}\right) \quad (2.2)$$

where  $\Delta H^{\text{diff}}$  is the activation energy for solid-state diffusion, and  $\nu$  is the attempt frequency. In MAPI the diffusion of methylammonium cations, iodide anions and protons have been considered in the literature. Activation energies calculated from first principles show that the predominant

mechanism for ion migration is the vacancy assisted hopping of iodide ions.<sup>116</sup> This has been confirmed using string simulations<sup>120</sup> which, like the nudged elastic band method, calculate minimum energy paths and from this infer transition rates.

Based on a bulk activation energy of 0.58 eV<sup>116</sup>, a rate of 733 hops per second would be expected at T = 300 K, with an associated diffusion coefficient of  $10^{-12}\text{cm}^{-2}\text{s}^{-1}$ . Effective activation energies as low as 0.1 eV have been reported experimentally,<sup>121,122</sup> which likely correspond to diffusion along extended defects (dislocations, grain boundaries, surfaces)<sup>123,124</sup>. The corresponding diffusion rate of  $10^{-5}\text{cm}^{-2}\text{s}^{-1}$  is very fast, but comparable to surface diffusion of iodine observed in other compounds.<sup>125</sup>

Modelling ion diffusion at device scales is not yet possible with *ab-initio* methods. Parametrised drift-diffusion modelling of ion and electron density indicate that slow moving ions can explain the slow device hysteresis.<sup>117,126</sup> A vacancy diffusion coefficient of the order of  $10^{-12}\text{cm}^2\text{s}^{-1}$  is consistent with both predictions and transient measurements.<sup>116</sup>

It has been suggested that ion migration within mixed-halide compositions is the result of a non-equilibrium process induced by photoexcitation. X-ray diffraction measurements by Hoke et al.<sup>127</sup> show that under illumination the mixed halide perovskite  $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$  segregates into two crystalline phases, one iodide-rich and the other bromide-rich. This segregation leads to reduced photovoltaic performance via charge carrier trapping at the iodide-rich regions. In some reports, after a few minutes in the dark the initial single phase XRD patterns are recovered. This reversible process is unusual and defies the common assumption made that ion and electron transport are decoupled.

A schematic outlining the phase segregation process is shown in Figure 2.4. A phase diagram constructed from first-principles thermodynamics found a miscibility gap for a range of stoichiometries at room temperature.<sup>114</sup> This suggests that a mixed-halide material is metastable and will phase segregate after being excited by light, which follow a decreasing free energy gradient towards halide-rich areas formed prior to light excitation (such as grain boundaries). The accumulation of charge carriers increases lattice strain and drives further halide segregation. Our calculations indicate that the transition between mixing and segregation will occur at a local carrier concentration of  $10^{21}\text{ cm}^{-3}$ , so that charge accumulation in small regions of the material is required for this model.

#### 2.4.2 Electron-hole recombination

The open-circuit voltage ( $V_{oc}$ ) of a solar cell is determined by the rate of charge carrier recombination in the material, as no photogenerated charges are being extracted and so all are recombining. When operating to generate power, the rate of recombination competes with the rate of charge extraction, limiting the fill factor of the solar cell.

Recombination is usually separated into three channels: non-radiative; radiative; and Auger (see Section 1.2.2 for further discussion). While non-radiative recombination is limiting in many inorganic thin-film technologies, hybrid perovskites are not significantly affected. This is surprising given the high density of defects expected for a material processed from solution, leading to hybrid perovskites being described as ‘defect tolerant’.<sup>128</sup>

Radiative (bimolecular) recombination is slower than would be expected for a direct band-gap semiconductor. Recent calculations reveal how relativistic Rashba splitting can suppress radiative recombination at an illumination intensity relevant to an operating solar cell.<sup>129,130</sup> After photoexcitation, electrons thermalise to Rashba pockets in the conduction band minima away from the high symmetry point in reciprocal space. This leads to an indirect charge recombination pathway as the overlap in  $k$ -space between occupied states near upper valence and lower conduction bands diminishes. It has also been suggested that direct recombination is suppressed at very short timescales due to the pockets of minima being spin-protected.<sup>130</sup> Direct gap radiative recombination is reduced by a factor of 350 at solar fluences, as electrons must thermally repopulate back to the direct gap.<sup>129</sup> This is in agreement with the temperature-dependence of the bimolecular rate measured experimentally<sup>74</sup> and calls into question the validity of models where a global radiative recombination rate independent of carrier concentration is used. Auger recombination is only significant at fluences well above solar radiation.

Ferroelectric effects could contribute to electron-hole separation due to electrostatic potential fluctuations in real space. Although the molecular cation plays no direct role in charge generation or separation it could influence charge transport through the formation of polar domains.<sup>113,131</sup> This dynamic polarisation has been explored using a model Hamiltonian parameterized for the inter-molecular dipole interaction in MAPI, explored the results of .<sup>87</sup> This model predicts the formation of antiferroelectric domains that minimise energy via dipole-dipole interaction, and dominate a cage-strain term preferring ferroelectric alignment.<sup>80</sup> The domains would provided electrostatically preferred pathways for electrons and holes to conduct.

### 2.4.3 Defect levels in the band-gap

To understand why defects appear to have a minimal impact upon charge carrier mobility and lifetime,<sup>132</sup> the defect properties of hybrid perovskites can be considered. Under the Shockley-Read-Hall model for semiconductor statistics non-radiative recombination is mediated through deep defect states in the gap.<sup>133</sup> Shallow defect states can act as traps but the carriers are thermally released to the band before recombination can occur. Hybrid perovskites – with high dielectric constant and low effective mass – show a tendency towards benign shallow defects under the hydrogenic model:<sup>134</sup>

$$E_n = -\frac{m^*}{m_0} \frac{1}{2n^2\epsilon_0^2} \quad (2.3)$$

**Table 2.1:** The first shallow donor defect level in MAPI, Si and CdTe calculated from effective mass theory using Equation 2.3. The dielectric constant  $\epsilon_0$  is an important descriptor for photovoltaic materials as several important properties (e.g. rate of impurity scattering) scale with its square.

Material	$\frac{m^*}{m_0}$	$\epsilon_0$	$E_1(\text{meV})$
MAPI	0.15 <sup>131</sup>	25.7 <sup>131</sup>	3
Si	0.45 <sup>137</sup>	11.7 <sup>137</sup>	45
CdTe	0.11 <sup>138</sup>	10.2 <sup>98</sup>	14

where  $\frac{m^*}{m_0}$  is the effective mass ratio,  $\epsilon_0$  is the static dielectric constant and  $n$  is an integer number that labels the energy level. Atomic units are used and so the energy  $E_n$  is given in Hartrees.

In Table 2.1 the first hydrogenic defect levels for MAPI, Si and CdTe are given. The binding energy for MAPI is only 3 meV. For ionic materials, one would expect a large central cell correction that could result in much deeper levels, as seen for the colour centres in alkali halides.<sup>135</sup> However on-site electrostatic potentials in the I-II-VII<sub>3</sub> perovskites are relatively weak due to the small charge of the ions (e.g  $\text{Cs}^+\text{Pb}^{2+}\text{I}_3^-$ ) compared to other perovskite types (e.g.  $\text{Sr}^{2+}\text{Ti}^{4+}\text{O}_3^{2-}$ ),<sup>136</sup> which supports the existence of shallow levels. In addition, arguments based on covalency have also been proposed.<sup>132</sup>

#### 2.4.4 Beyond the bulk: surfaces, grain boundaries and interfaces

As perovskite solar cells approach commercial viability,<sup>54</sup> there are considerations to be made beyond the bulk material. Surfaces, grain boundaries and interfaces will influence device performance and long-term stability, and become increasingly important as the science is scaled up from lab to production line. Halide migration, ion accumulation, charge carrier transport and charge carrier recombination at the defect states are some of the processes to consider when building an accurate interface model. There has been preliminary work, that provides insights, but real systems offer much deeper complexity.

Perovskite films fabricated through solution processing methods are multicrystalline and so the formation of grain boundaries is inevitable. The resulting microstructure provides pathways for ion conduction, electron-hole separation and recombination. Improved device performance with increasing grain size<sup>139</sup> is evidence for shallow traps associated with the grain boundary. Initial calculations suggest that grain boundaries do not introduce deep defects and consequently have negligible effect upon the rate of non-radiative recombination.<sup>140</sup> This is in conflict with spatially resolved photoluminescence<sup>141</sup> and cathodoluminescence<sup>142</sup> measurements which evidence greater non-radiative loss at grain boundaries. Nonadiabatic MD and time-domain density DFT<sup>143</sup> indicate that grain boundaries localize the electron and hole wavefunctions and provide additional phonon modes. This leads to increased electron-phonon coupling which in turn will give a higher rate of non-radiative recombination.

A commonly used hole transport material is spiro-OMeTAD. This material is hygroscopic so stability in humid air is a concern,<sup>144</sup> and screening procedures have been used to identify alternative contacts.<sup>145,146</sup> Band alignment, lattice match and chemical viability via the overlap of atomic positions are used to determine the electronic-lattice-site (ELS) figure of merit.<sup>145</sup> Using this approach Cu<sub>2</sub>O is identified as a possible earth abundant hole extractor, whilst oxide perovskites such as SrTiO<sub>3</sub> and NaNbO<sub>3</sub> are identified as possible electron extractors. As with the majority of screening techniques, the candidate materials meet the necessary but perhaps not sufficient conditions. Further refinements to the screening procedure could consider the change in electronic properties as lattice strain and chemical inhomogeneity at the interface is introduced.

**Table 2.2:** Common issues that arise in the simulation of hybrid perovskites, sourced from members of the Walsh Materials Design Group.

Technique	Symptom	Solution
Geometry optimisation	Partial occupancy in structure files	Test different configurations and check total energy
Geometry optimisation	Missing H in structure files	Include H based on chemical knowledge and electron counting
Geometry optimisation	Slow ionic convergence	Try changing algorithm type and settings
Electronic structure	Bandgap is too large	Include spin-orbit coupling and consider excitonic effects
Electronic structure	Bandgap is too small	Use a more sophisticated exchange-correlation functional
Electronic structure	Bandgap is still too small	Try breaking symmetry, especially for cubic perovskites
Electronic structure	Workfunction is positive	Align to external vacuum level using a non-polar surface
Supercell convergence	Unusual convergence behaviour	Use only even cell expansions (e.g. $2 \times 2 \times 2$ )
Ab initio thermodynamics	No stable chemical potential range	No easy fix (many hybrid materials are metastable)
Berry phase polarisation	Polarisation is too large	Use appropriate reference structure and pathway
Point defects	Negative formation energies	Check for balanced chemical reaction and chemical potential limits
Point defects	Transition levels are deep in band-gap	Check supercell expansion and charged defect corrections
Alloyed systems	Many possible configurations	Use appropriate statistical mechanics
Lattice dynamics	Many imaginary phonon modes	Check supercell size and force convergence
Lattice dynamics	Imaginary modes at zone boundaries	Use mode-following to map out potential energy surface
Molecular dynamics	System melts or decomposes	Check $k$ -points and basis set convergence
Molecular dynamics	Unphysical dynamics	Check equilibration and supercell expansion
Molecular dynamics	No tilting observed	Use an even supercell expansion
Electron-phonon coupling	Values far from experiment	Consider anharmonic terms beyond linear response theory
Drift-diffusion model	Current-voltage behaviour incorrect	Consider role of fluctuating ions and electrostatic potentials

## 2.5 Summary

I have outlined the physical properties which make hybrid perovskites unique semiconductors that are a challenge for theory and simulation. Common issues that can arise in the simulation of hybrid perovskites are summarized in Table 2.2. The volume of work in this area means that all active areas of research cannot be addressed, including perovskite-like structures with lower dimensionality (e.g. Ruddleston-Popper phases)<sup>53,147,148</sup> and double perovskites with pairwise substitutions on the B site,<sup>67,68,149,150</sup> which are both attracting significant interest.

The properties of hybrid halide perovskites which are difficult to model are also those which make them a successful PV material. For example, calculating ground state electronic properties using the approximation of a single static lattice does not capture the effects of strong electronic-ionic coupling. However, it is this coupling screens charge, produces a defect tolerant material, facilitates fast charge separation and suppresses excitonic states. Multi-scale modelling must be used to capture the transport of halide ions via Schottky-like charged vacancy defects. However, it is these defects that provide the low free carrier background concentration necessary for high efficiencies in a p-i-n architecture. Attempts are now being made to distill this understanding into descriptors for the large-scale screening of novel, earth-abundant, non-toxic semiconductors.<sup>44,132</sup>

### Acknowledgements

This work was funded by the EPSRC (grant numbers EP/L01551X/1 and EP/K016288/1), the Royal society, and the ERC (grant no. 277757).

*Two MCs can't occupy the same space at the same time, it's against the laws of physics.*

— Lauryn Hill, *Zealots*

# 3

## Theory and methodology

### 3.1 Introduction

In this chapter I present the theory and methodology that underlies the work in this thesis. The chapter starts with an introduction to Density Functional Theory (DFT); first I introduce the theoretical concepts, then I provide some details about how DFT is implemented in practice. In the second part of the chapter I outline how we can use DFT energies combined with a series of post-processing steps to predict defect formation energies and charge transition levels. The chapter ends with an introduction to the theory of lattice dynamics and how this theory is used to calculate the vibrational properties of a material.

### 3.2 Density Functional Theory

Density Functional Theory is the most commonly used electronic structure method in condensed matter physics and quantum chemistry. DFT can be used to predict the ground state properties of a material including electron density, total energy, equilibrium structure, vibrational frequencies, and properties relating to differences in total energy, such as defect formation energy or surface energy. As DFT is a ground state theory we are not able to calculate properties relating to excited states and, without further calculations such as those outlined in Section 3.4, results do not incorporate the effects of temperature.

The theoretical basis for DFT was established in 1964 through the work of Walter Kohn and Pierre Hohenberg.<sup>151</sup> This was further developed by Walter Kohn and Lu Jeu Sham to produce Kohn-Sham DFT.<sup>152</sup> However it was not until the late 1980's approximations to the exchange-correlation functional were built so that DFT could be used in practice.

There are a growing number of codes that implement DFT. Although some codes aspire to a blackbox approach, with the user protected from the underlying mechanics of DFT, for most

systems of interest an understanding of the underlying approximations and parameters used are required for reliable results.

### 3.2.1 Basic concepts

Firstly, a note on the name. A function accepts one or more numbers as input and produces a number as output. Likewise, a functional accepts one or more *functions* as inputs, and produces a number as output. In DFT the functional is the electron density which is itself a function of space and time.

Throughout this chapter, unless stated otherwise, we use the Born-Oppenheimer approximation: the heavy atomic nuclei are treated as fixed points, and we solve the ground state quantum mechanical problem for the electrons only. This reduces the number of degrees of freedom of the system, a tactic that will be used again later in the chapter.

Although no one single text is followed, concepts for the underlying theory have been taken from References [153], [154] and [155].

#### The Schrödinger equation

A fundamental postulate of quantum mechanics is that for any physical system there is an associated wavefunction that contains all the system information. The Schrödinger equation describes the wavefunction  $\Psi$  of a quantum mechanical system. Once the Schrödinger equation is solved, and a wavefunction is found, all the physical properties for that system follow. To take the simplest possible example, the time-independent non-relativistic Schrödinger equation for a single particle can be written as:

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (3.1)$$

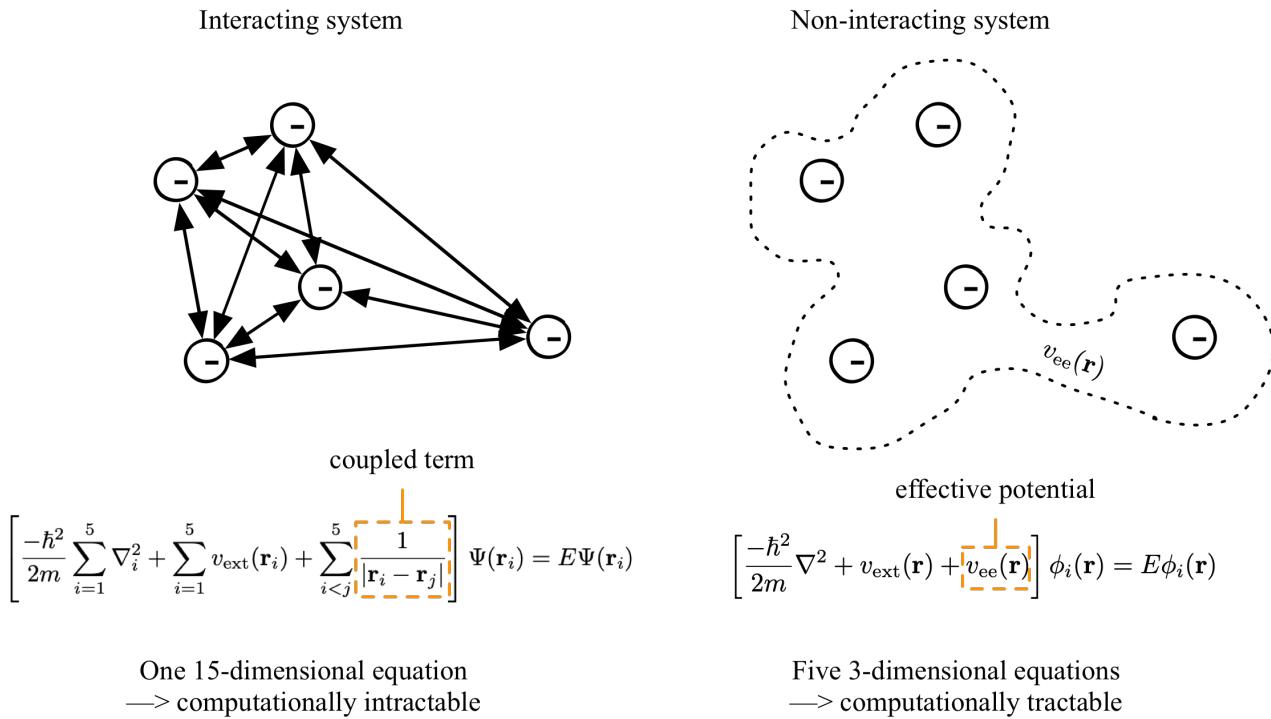
where the first term in the bracket corresponds to the kinetic energy and the second term corresponds to the potential energy. For a single particle in a simple potential, such as the “particle in a box” system or hydrogen atom, the Schrödinger equation can be solved exactly. Unfortunately it is not possible to solve the Schrödinger equation exactly for more complex systems, where there are multiple electrons interacting with each other (N-body or many-body systems). In this case, the Schrödinger equation takes the form:

$$\left[ \frac{-\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) + \sum_{i < j}^N \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r}_i) = E\Psi(\mathbf{r}_i), \quad (3.2)$$

where the third term in the square bracket describes the electrostatic interaction between two particles of charges  $q_i$  and  $q_j$ , and couples the coordinates of the particles together.

Hartree-Fock methods and Kohn-Sham DFT provide a way to obtain an approximate solution to the Schrödinger equation for systems of interest. They do this by mapping the interacting problem

onto a non-interacting problem with an effective potential  $v_{ee}(\mathbf{r})$ . In doing so, the dimensionality of the problem is greatly reduced. Instead of solving one N-dimensional computationally intractable problem, N one-dimensional problems are solved (Figure 3.1). These methods provide a compromise between accuracy and computational efficiency.



**Figure 3.1:** Schematic outlining the equivalence between a system of interacting particles and a system of non-interacting particles in an effective potential. The underlying idea is that an interaction can be replaced by the equivalent potential. This maps the interacting  $3N$ -dimensional problem onto  $N$  3-dimensional problems. A consequence of this mapping is that the effective potential depends on the electron density which is itself dependent on the effective potential – a self-consistent set of equations is formed. For the non-interacting case  $\phi_i$  is used to denote a single particle wavefunction.

## Hartree-Fock methods

Hartree-Fock (HF) methods introduce the concept of fictitious non-interacting one-electron orbitals  $\phi$  as a way of solving the Schrödinger equation. The one-electron orbitals are combined using a Slater determinant to produce the HF many-body wavefunction.<sup>153</sup>

The effective potential, introduced in Figure 3.1, is given by  $v_{ee} = U + E_x$ .  $U$  accounts for the electrostatic interaction between electrons. Hartree-Fock methods model the charge interaction as a coulomb potential for a system of fixed electrons; the electrons feel the average electrostatic field due to the other electrons.  $E_x$  accounts for the spin exchange interaction between electrons. Electrons with the same spin are indistinguishable, and a consequence of this is that the many body wavefunction must be anti-symmetric. This leads to the Pauli Exclusion Principle, whereby two identical electrons (ie, electrons with the same spin and momentum) cannot occupy the

same space at the same time. Hartree Fock methods account for electron exchange  $E_x$ , the repulsion between electrons with parallel spins, exactly.

Hartree-Fock methods do not give an exact solution to the Schrödinger equation as the true many body wavefunction is not formed from a simple Slater determinant. As a result of using a Slater determinant, electron correlation is ignored. This is the correlated motion of electrons with anti-parallel spins as a result of their mutual coulombic repulsion.

### The Hohenberg-Kohn theorems

The 1964 Hohenberg-Kohn paper<sup>151</sup> contains two key results: (i) the ground state electron density uniquely determines the ground state electronic wave function and, following this, all properties of the system; (ii) the true density functional for the electronic energy assumes its minimum for the correct ground-state density.

The potentials (external, coulomb and exchange) in Hartree-Fock methods determine the properties of a system. Hohenberg and Kohn demonstrate that the electron density  $\rho$  can be used instead to uniquely characterise the system; rather than solving the Schrödinger equation for the wavefunction, we can solve it for the electron density. The total energy  $E[\rho]$  can be expressed as

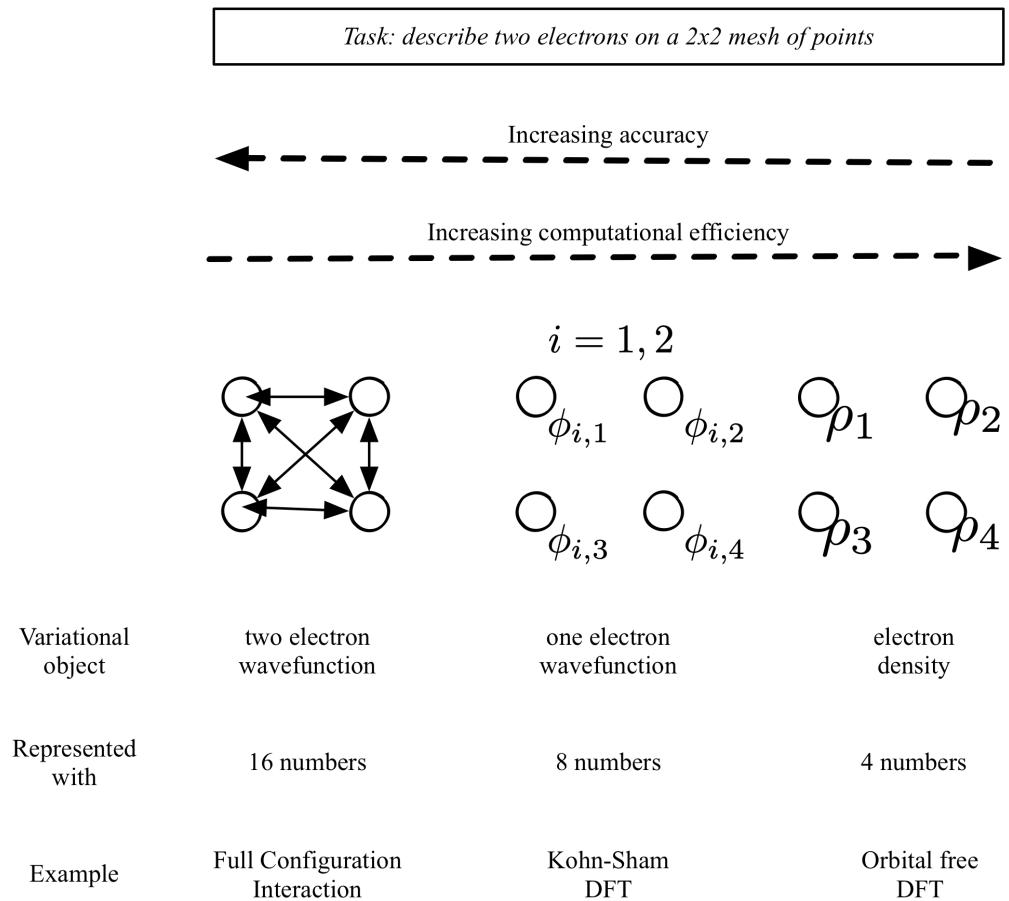
$$E[\rho] = \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + T[\rho] + J[\rho] + E_{\text{xc}}[\rho], \quad (3.3)$$

where  $T[\rho]$ ,  $J[\rho]$  and  $E_{\text{xc}}[\rho]$  describe the kinetic, classical electrostatic and exchange-correlation energies respectively. For a fixed number of electrons the functional  $F[\rho] = T[\rho] + J[\rho] + E_{\text{xc}}[\rho]$  is universal, and the only thing that varies between systems is the external potential (determined by the electron-nuclei interaction).

In reference [151] Hohenberg and Kohn also demonstrate that the ground state energy can be found variationally; the density that minimises the total energy is the true ground state density. This formalism has the advantage that the electron density has a lower dimensionality than the N-electron wavefunction (Figure 3.2). The problem is that although the Hohenberg-Kohn theorem tells us that the terms  $T[\rho]$  and  $E_{\text{xc}}[\rho]$  exist, they are unknown and must be approximated.

### The Kohn-Sham theorem

The Kohn-Sham theorem shows that for any interacting system with ground state density  $\rho(\mathbf{r})$  there exists a non-interacting system with the same ground-state  $\rho(\mathbf{r})$ . To find the ground state energy of the real interacting system, the occupation numbers of *fictitious*, non-interacting one-electron orbitals can be optimised. For a non-interacting system we know how to calculate  $T[\rho]$  and this provides a good approximation to the true kinetic energy, so the Kohn-Sham theorem provide a more practical way to apply DFT. However, the exchange-correlation density functional  $E_{\text{xc}}[\rho]$  is still not known. Only approximations to this functional can be made, leading to approximations for the electronic density, total energy and other system properties.



**Figure 3.2:** To solve the Schrödinger equation we can use a variational object with lower dimensionality and higher computational efficiency, although this will come at the cost of accuracy. This schematic is based on a discussion in Walter Kohn's Nobel Prize lecture.<sup>156</sup>

### 3.2.2 DFT in practice

#### Exchange-correlation functionals

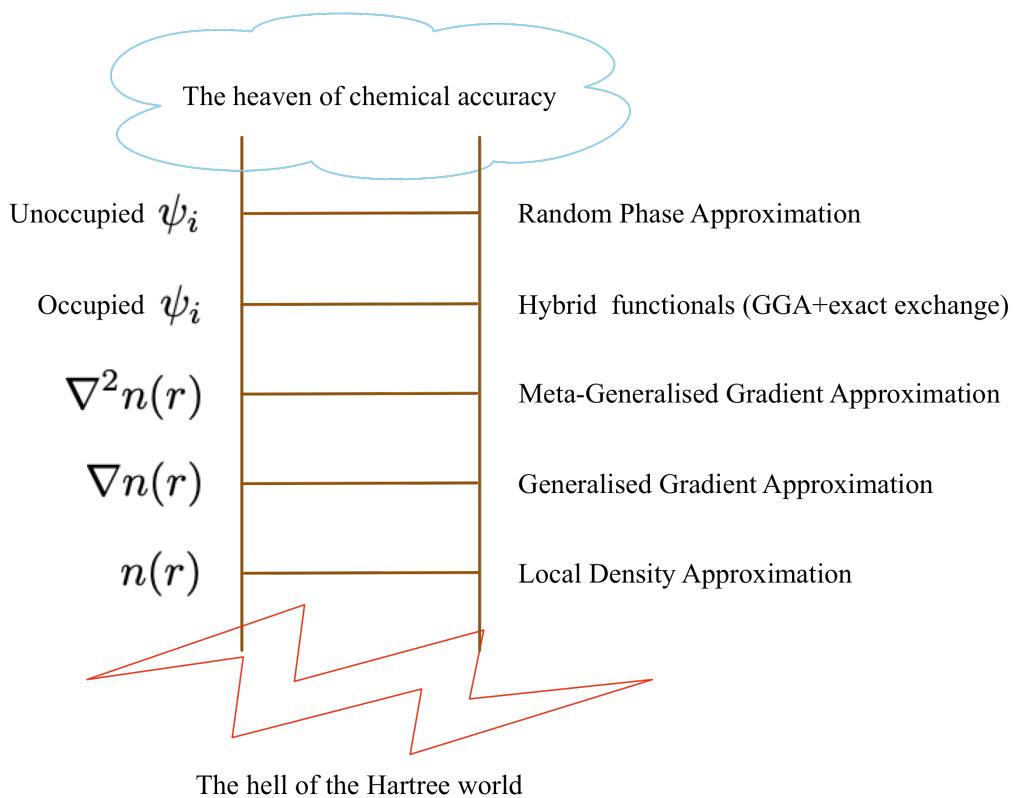
To use Kohn-Sham DFT we must approximate the exchange-correlation functional, and there is a growing list of functionals at varying levels of complexity. John Perdew proposed “Jacob’s Ladder” as a way to categorise these functionals (Figure 3.3). As a general rule, more accurate functionals are constructed by including more parameters and variables.

#### Local Density Approximation

At the lowest rung of the ladder is the local density approximation where only one variable, the electron density for an infinitesimal 3-dimensional volume element, is used to calculate the exchange correlation energy. The exchange energy is calculated exactly

$$E_{\text{LDA,x}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r}, \quad (3.4)$$

and the correlation energy is calculated numerically by fitting to many-body quantum Monte Carlo calculations for an inhomogeneous electron gas. Strictly, the LDA should only be used for



**Figure 3.3:** Jacob’s ladder of exchange correlation functionals. On the right hand side are the various categories of exchange-correlation functionals and on the left hand side are the additional input variables included at each level of theory. As we move up the ladder the chemical accuracy increases, alongside computational expense.

slowly varying densities, however it has performed surprisingly well for predicting the properties of a variety of atoms, solids and molecules. This is due to a cancellation of errors: LDA underestimates the exchange energy and overestimates the correlation energy. However there is a tendency for LDA to overestimate the binding energy and underestimate lattice parameters. This is a particularly pronounced problem in weakly bonded systems.

### Generalised Gradient Approximation

At the next level of theory, two variables are used to determine the exchange-correlation energy: electron density and the density gradient. Due to their dependence on the GGA functionals are semi-local. The parameters of GGA functionals can be derived from physical constraints (non-empirical, as in the widely used PBE functional), or obtained from fitting procedures (empirical, as in the case of the B88 functional). GGAs improve the over-binding of LDA, but tend to underestimate the bandgap of the material.

### Meta-GGA

Meta-GGAs extend the GGA functional to include the non-interacting kinetic energy density as an input variable. This is calculated from the laplacian of the occupied electron orbitals.

### Hybrid functionals

In DFT each electron interacts with itself as the potential derives from the total charge density of the system. This error is particularly pronounced for localised states, after trapping an electron or hole at a defect site for example. Hybrid functionals combine GGA functionals with a proportion of the exact HF exchange energy to correct the self-interaction error. The simplest hybrid functional takes the form

$$E_{\text{hybrid,xc}}[\rho] = \alpha E_{\text{exact,x}} + (1 - \alpha) E_{\text{GGA,xc}}. \quad (3.5)$$

In some studies the proportion of exact exchange is tuned to reproduce the property of interest correctly. For example,  $\alpha = 0.43$  is commonly used to correctly reproduce the bandgap of the hybrid halide perovskite MAPI.

### Random Phase Approximation

Closest to heaven is the Random Phase Approximation (RPA), which uses all of the Kohn-Sham orbitals (occupied and unoccupied) as input variables. The functionals listed so far are inaccurate when there are significant long range effects, as they have no information about the electron density far from an electron. The RPA is able to correctly predict long-range interactions, such as the van der Waals interaction, between non-overlapping electron orbitals.

### Exploiting symmetry

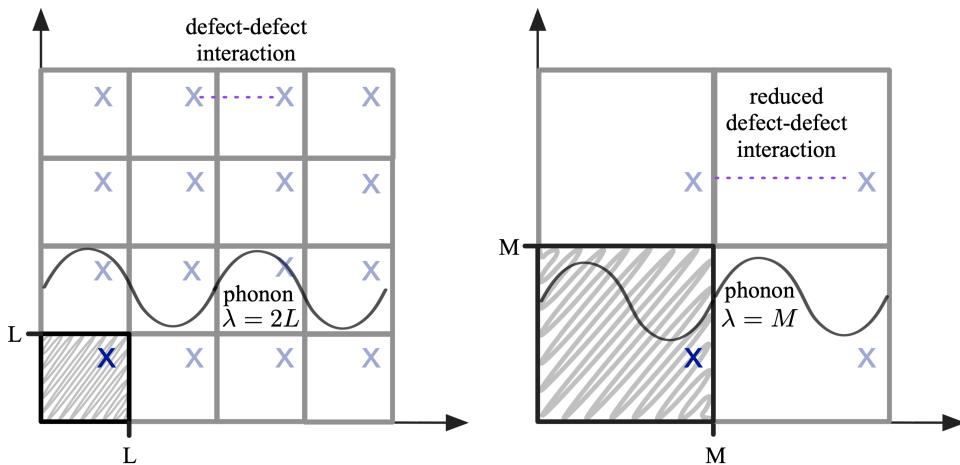
The material studied in this thesis,  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , is a crystalline solid. Although we want to understand the properties of a finite piece of material, we use the standard approach and model the finite crystal as an infinite crystal. This is acceptable if the crystal piece is large enough so that its properties do not depend on size. Born-von Karman (periodic) boundary conditions are used so that the infinite crystal is built from a repeating array of unit cells. There are an infinite number of unit cells of different shapes and sizes that can be used to build an infinite crystal. Any physically significant function of the crystal must have the same periodicity.

In real materials translational symmetry can be broken, for example when there are point defects (as in Results chapter ??). Furthermore, lattice vibrations have a periodicity larger than the unit cell. To model defects or lattice vibrations a supercell is built from multiple unit cells and this is used as the basic repeating unit (Figure 3.4).

When the Schrödinger equation is solved for a hydrogen atom the solution gives wavefunctions corresponding to the 1s, 2s, 2p, etc orbitals found in chemistry. When the Schrödinger equation is solved for a periodic system, wavefunctions are formed by Bloch functions  $\psi_{\mathbf{k}}$ :<sup>157</sup>

$$\psi_{\mathbf{k}} = u_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (3.6)$$

The Bloch function is formed from the product of a basis function  $u_{\mathbf{k}}$  with the same periodicity as the crystal lattice, and a plane wave  $e^{i\mathbf{k}\cdot\mathbf{r}}$ .  $\mathbf{k}$  is the crystal wave vector which forms a space known as reciprocal space; to understand the physical significance of  $\mathbf{k}$  we consider an infinite



**Figure 3.4:** (LHS) An infinite crystal is built from a repeating unit cell of length  $L$ . Point defects (marked with an ‘x’) break translational symmetry in real crystals and care must be taken when modelling these as neighbouring defects can interact with each other in an unphysical way. In addition, vibrational modes can have wavelengths  $> L$  (sine wave). (RHS) A supercell of length  $M = 2L$  can be built to reduce defect-defect interactions and model longer wavelength phonons.

1D chain of hydrogen atoms separated at distance  $L$ . The electron states can be described as a linear combination of hydrogen 1s orbitals  $u_n$  centred at each lattice point:

$$\psi_k = \sum_n u_n e^{iknL} \quad (3.7)$$

$k = 0$  corresponds to the lowest energy bonding state, and  $k = \frac{\pi}{L}$  corresponds to the highest energy anti-bonding state

$$\psi_0 = \sum_n u_n e^0 = u_0 + u_1 + u_2 + u_3 \dots \quad (3.8)$$

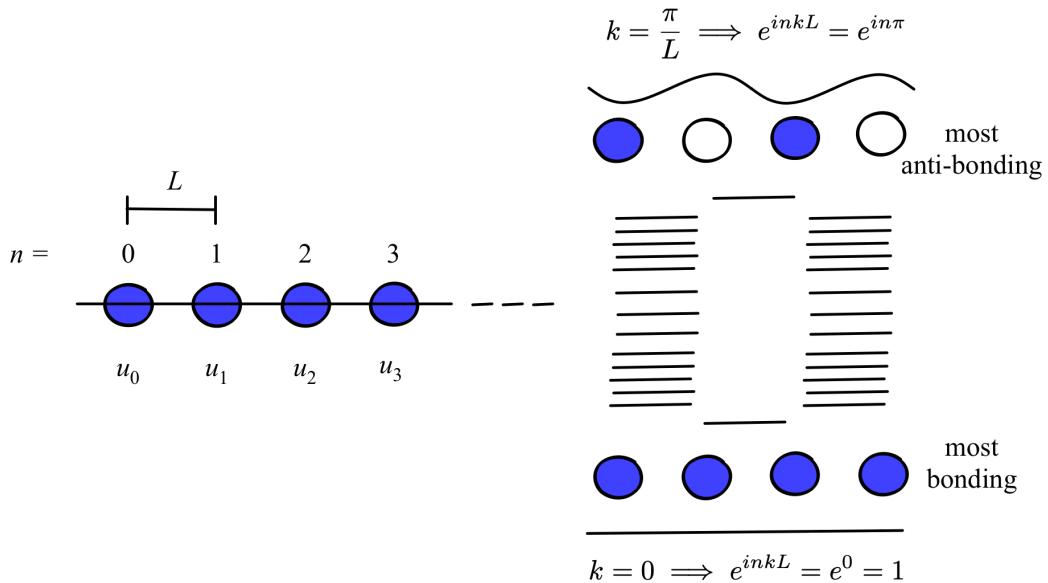
$$\psi_{\frac{\pi}{L}} = \sum_n u_n e^{i\pi n} = u_0 - u_1 + u_2 - u_3 \dots \quad (3.9)$$

Between these two extremes there is a continuum of states forming an electronic band (Figure 3.5).

Returning to the mathematical description of any periodic system, Equation 3.6 substituted into Equation 3.1 gives:

$$\left[ \frac{1}{2m} \left( \frac{\hbar}{i} \nabla + \hbar \mathbf{k} \right)^2 + v_{\text{ext}}(\mathbf{r}) \right] u_{\mathbf{k}} = E(\mathbf{k}) u_{\mathbf{k}}. \quad (3.10)$$

For any  $\mathbf{k}$  we can solve Equation 3.10 with periodic boundary conditions to calculate the electronic bandstructure  $E(\mathbf{k})$ . There are an infinite number of eigenvalues  $E_n(\mathbf{k})$ , where  $n$  is used to label a particular eigenvalue (band). As a result of crystal symmetry,  $E_n(\mathbf{k})$  is periodic and only  $k$ -vectors within a region of space known as the Brillouin Zone ( $|\mathbf{k}| < \frac{\pi}{a}$ ) need to be considered.<sup>158</sup>



**Figure 3.5:** (LHS) A one dimensional infinite lattice where the points are labelled  $n = 0, 1, 2 \dots$ . The point spacing (unit cell length) is  $L$ , and there is a hydrogen 1s orbital (basis function)  $u_n$  centred at each point. The electron states for this system are formed from Bloch functions as given in Equation 3.7. (RHS)  $k = 0$  corresponds to a low energy bonding state and  $k = \frac{\pi}{L}$  corresponds to a high energy anti-bonding states. Between these two extremes there exists a continuum of states.

### Basis Sets

In the example of a 1D linear chain, the lattice periodic part of the Bloch function took the form of a hydrogen 1s orbital. For more complex systems,  $u_k$  can itself be expanded into a plane wave basis set whose wave vectors  $\mathbf{G}$  are reciprocal lattice vectors

$$u_{\mathbf{k}} = \sum_{\mathbf{G}} c_{\mathbf{k}, \mathbf{G}} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}, \quad (3.11)$$

and the complete expanded Kohn-Sham orbital can be expressed as

$$\psi_{\mathbf{k}} = \sum_{\mathbf{G}} c_{\mathbf{k}, \mathbf{G}} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}. \quad (3.12)$$

As a plane wave is inherently periodic this basis set is often used for extended systems. The software used for the DFT calculations in this thesis, VASP<sup>159</sup>, uses a plane wave basis set. For DFT calculations applied to localised systems, such as molecules or nanoparticles, localised basis sets such as gaussian orbitals are more likely to be used.

Sudden changes in electron density are hard to capture using a plane wave basis set; to take an extreme example, the fourier decomposition of a simple top hat in real space requires an infinite summation in reciprocal space. This can be problematic when describing the region around the nucleus where there are strong oscillations in the KS orbitals. However these oscillations are associated with the core electrons which are less important in chemical bonding, and so pseudopotentials - an effective potential without oscillations - can be used. It has been established that for certain systems pseudopotentials are as precise as all-electron calculations.<sup>160</sup>

## Optimising the atomic and electronic structure

In this section the process of optimising the atomic and electronic structure of a system towards the ground-state (minimum energy) configuration is outlined.

As discussed in Section 3.2, the potential  $v_{ee}$  is dependent on the electron density  $\rho$ , which is itself dependent on  $v_{ee}$ . Therefore an iterative approach called the Self Consistent Field method is used to calculate the ground-state electronic structure (Figure 3.6, dashed section). The initial guess for the density  $\rho(\mathbf{r})$  is given by a superposition of the atomic charge densities. This is used to calculate the potential and solve the KS equations, which gives a new  $\rho(\mathbf{r})$ . This process continues until there is convergence within a given energy tolerance. Various optimisation routines are provided in DFT codes for finding the ground state configuration, including the conjugate gradient scheme, Davidson Scheme and RMM-DIIS.

DFT is also used to find the ground state atomic structure. Structures calculated from X-ray Diffraction data are used as a starting guess, so that finding the energetic minimum becomes a local optimisation problem. Atoms in the systems are displaced (either the internal coordinates of the unit cell or the unit cell parameters themselves are adjusted) and the electronic structure for that geometry is solved self-consistently. This process repeats until the forces on each atom are zero to within a given tolerance (Figure 3.6).

## The limits of DFT

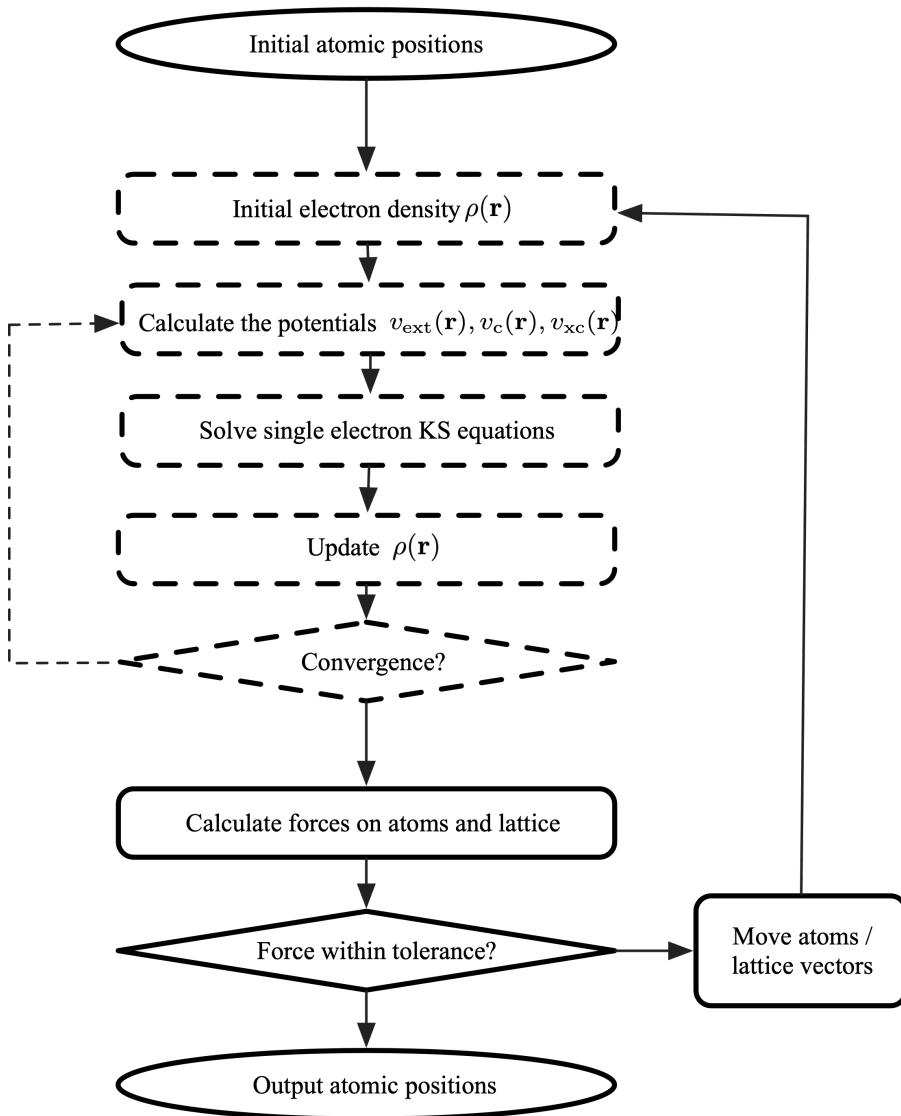
### Theoretical limitations

In Section 3.2 the approximations inherent to DFT calculations were outlined: the Born-Oppenheimer approximation and the unknown exchange-correlation functional. Higher levels of theory, which incorporate the effects of spin and relativity (e.g. spin-orbit coupling) are included in many DFT implementations. However DFT is still restricted to ground-state properties and higher levels of theory (GW or time-dependent DFT) are required to describe excited states. Another inherent limitation is that the KS eigenvalues are artificial; only the ground state electron density and derived properties are correct. However in practice the KS eigenvalues are used to calculate the bandgap. Quantitatively correct bandgaps often require the use of hybrid functionals that are parameterised to give the correct bandgap.

### Numerical limitations

There are also approximations that relate to numerical convergence rather than the underlying theory. We have seen that the KS orbital are expanded in a basis set. In principle an infinite set may be needed to describe the orbitals, but in practice the basis set must be truncated. The kinetic energy operator is given by  $-\frac{\hbar^2 \nabla^2}{2m}$  and when this is applied to the plane wave KS orbitals as given in Equation 3.12, we find that the kinetic energy is proportional to  $|k + G|^2$ ; faster oscillations correspond to higher energy. A cutoff energy  $E_{\text{cut}}$  is defined so that

$$\frac{1}{2}|k + G|^2 < E_{\text{cut}}. \quad (3.13)$$



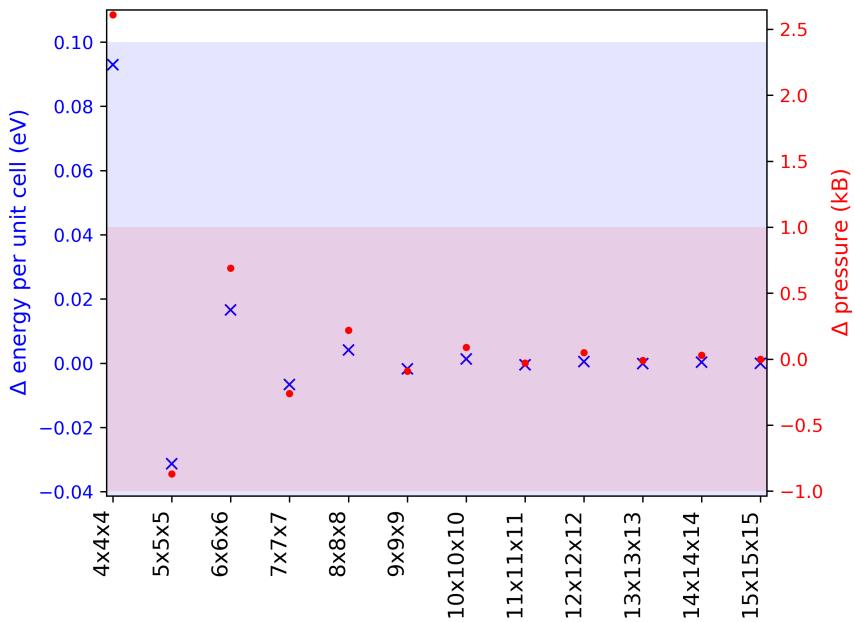
**Figure 3.6:** Nested iterative method for geometry optimisation. The electronic structure relaxation (dashed lines) is nested within the atomic structure relaxation (solid lines).  $v_{\text{ext}}(\mathbf{r})$ ,  $v_c(\mathbf{r})$  and  $v_{\text{xc}}(\mathbf{r})$  correspond to the external, classical and exchange-correlation potentials respectively.

This cutoff energy must be tested to ensure that the property of interest, most often energy, is converged to within a certain tolerance.

To calculate many properties of interest we need to integrate over the Brillouin Zone in reciprocal space. To calculate the total energy of an insulator for example, we use

$$E = \frac{\Omega}{(2\pi)^3} \sum_{\text{occ.}} \int_{\text{BZ}} E(\mathbf{k}) d^3k \quad (3.14)$$

where  $\Omega$  is the volume of the Brillouin zone and the sum is over all occupied bands. In practice we do not know the continuous form for  $E(\mathbf{k})$  and so we numerically evaluate Equation 3.14 as a weighted sum over special points in reciprocal space. These points often form an equally spaced mesh centred on the  $\Gamma$ -point ( $\mathbf{k} = (0, 0, 0)$ ) in reciprocal space. For any given system, the  $k$ -point density scales inversely with cell size; for example, if the unit cell in Figure 3.4 requires



**Figure 3.7:**  $k$ -point convergence of  $\text{CsSnI}_3$ . The  $k$ -point grid size is on the  $x$ -axis. Red dots denote pressure; the region which is within the 1 kbar convergence criteria for this study is shaded red. Blue crosses denote total energy; the region which is within the 0.1 eV convergence criteria is shaded in blue. Only odd grids sample the  $\Gamma$ -point and so there is an oscillation in energy and pressure as points move between odd and even grids.

a  $6 \times 6$   $k$ -point grid, then the larger  $2 \times 2$  supercell requires a  $3 \times 3$   $k$ -point grid. As with plane waves, there is a balance between accuracy (the higher the number of  $k$ -points, the higher the accuracy) and computational expense. An example convergence study is given in Figure 3.7 where a  $5 \times 5 \times 5$   $k$ -point grid is required to converge pressure to within 1 kbar and energy to within 0.1 eV in  $\text{CsSnI}_3$ .

### 3.3 Defects in semiconductors

The second law of thermodynamics states that an isolated system tends towards an equilibrium state with maximum entropy. A consequence of this is that all solids in equilibrium and at finite temperature contain point defects, as the cost in lattice energy is balanced by the increase in configurational entropy. Point defects are associated with a number of microscopic processes that can be either beneficial or detrimental to material performance, including:

- optical: colour centres, up/down conversion
- electrical: conductivity, carrier trapping, ionic hopping
- mechanical: material hardening
- thermal: conductivity, decomposition

Theoretical methods are particularly useful in this area as although it is often possible to estimate the quantity of defects in a material using experimental methods, it is much more challenging to identify the defect species.<sup>161</sup>

In this section I outline the different types of crystal defects and discuss the thermodynamics of (charged) defect formation. The supercell method for calculating defect properties is also outlined. This method is used in Chapter ??.

### 3.3.1 Classification of crystal defects

The first way to classify defects is via their dimensionality. 0-dimensional point defects are localised around isolated sites in the crystal. 1-dimensional dislocations are lines along which the crystal pattern is broken. 2-dimensional grain boundaries or interfaces are surfaces along which distinct crystallites are joined. 3-dimensional defects are changes to the crystal pattern in a finite volume.

0-dimensional point defects are the subject of Chapter ?? . Point defects can be further split into extrinsic or intrinsic defects. Extrinsic point defects (also known as impurities) are a different species from that of the host. These defects may be added intentionally (for example, to increase electrical conductivity) or unintentionally (as a result of the fabrication method). Intrinsic point defects are associated with the host species.

Point defects can also be classified as non-stoichiometric or stoichiometric. Non-stoichiometric defects include interstitials (where an additional atom occupies a site that is unoccupied in the perfect lattice), vacancies (missing atoms) and antisites (where an atom occupies a site that would have been occupied by another species in the perfect lattice). Interstitials can have a ‘split’ structure, in which two atoms are split symmetrically around a single lattice site. Stoichiometric defects include Frenkel pairs and Shottky pairs. Stoichiometric and non-stoichiometric point defects are illustrated in Figure 3.8.

The final classification is into electrically active and electrically benign defects. Whilst electrically benign defects exist only in one charge state, electrically active defects can take more than one charge state; for example, single acceptors exist in a neutral or negatively charged state and single donors exist in a neutral or positively charged states. Amphoteric defects can exist in a negatively charged or positively charged state.

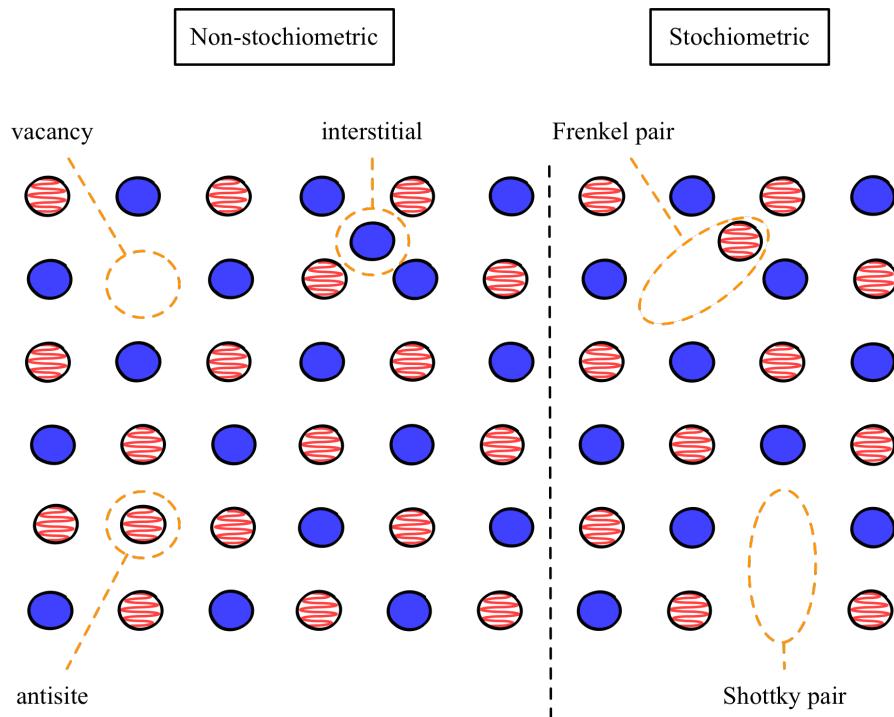
### 3.3.2 Energetics of defect formation

The equilibrium concentration of defects  $n$  at a fixed temperature and pressure is given by the density that minimizes free energy.

$$n = N_{sites} \exp\left(-\frac{\Delta G}{k_B T}\right), \quad (3.15)$$

where  $\Delta G$  is the Gibbs free energy of defect formation. The Gibbs free energy is approximated as the formation energy  $E_f$  of the defect as this dominates over entropic contributions. The formation energy is given by:

$$E_f(q) = E_d(q) - E_b - \sum_i \mu_i n_i + q(\epsilon_{VBM} + E_F) + E_{corr} \quad (3.16)$$



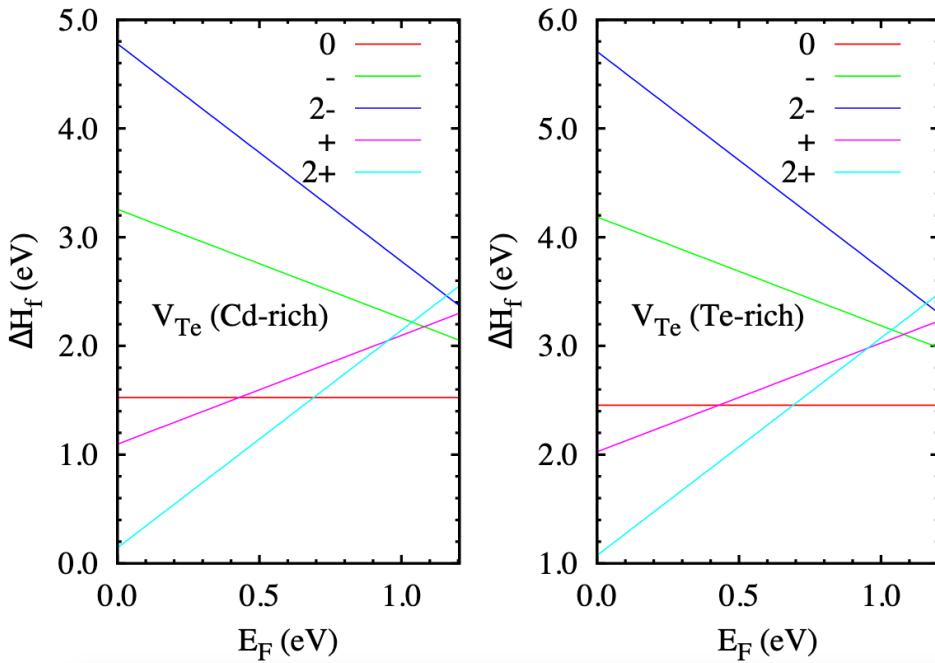
**Figure 3.8:** Non-stoichiometric defects include interstitials (an additional atom), vacancies (a missing atom) and anti-sites. Stoichiometric defects include a Frenkel pair (a vacancy close to an interstitial of the same species), and a Shottky pair (a vacancy on both the anion and cation sub-lattices).

where  $E_d(q)$  is the total energy of the supercell with a defect of charge  $q$  and  $E_b$  is the total energy of the perfect bulk.  $E_{corr}$  is a correction energy that is only needed for charged defects and is discussed Section 3.3.3. The remaining terms describe the energy needed to add or remove atoms or electrons.  $\mu_i$  is the chemical potential of atom  $i$  and  $n_i$  is the number of atoms that are added or removed. The chemical potential can be adjusted to describe different growth conditions; if the growth conditions are rich for species  $i$  then  $\mu_i$  will be low.  $E_F$  is the Fermi level of the electrons, referenced to the valence band maximum  $\epsilon_{VBM}$ .

The total energies can be calculated using DFT. Convergence criteria for calculations must be tight as, due to the exponential dependence of defect concentration on formation energy, small errors in the energy difference can lead to large errors in the defect concentration.

The Fermi level is treated as a parameter, of which the defect formation energy is a linear function with a gradient equal to the defect charge. This allows us to plot a graph of formation energy against Fermi level, as shown in Figure 3.9. Charge transition levels mark the Fermi level at which two charge states have the same defect formation energy. Electrically active defects have at least one charge transition level in the bandgap. The charge transition level is equivalent to thermal ionization energy, the energy needed to add or remove electron(s).

Defect levels deep in the bandgap correspond to localised wavefunctions. Carrier capture processes to these defect states are often associated with a large lattice distortion. Shallow



**Figure 3.9:** Formation energies  $\Delta H_f$  as a function of the Fermi energy for the Te vacancy in CdTe. In a Te-rich environment it is more energetically unfavourable to form a Te-vacancy, as intuition would suggest. The slope of each line corresponds to the defect charge. Charge transition levels correspond to the energies at which the lines intersect. Figure reprinted with permission from Reference [Menendez2016].

defect levels (within thermal energy  $k_B T$  of the valence or conduction band) correspond to delocalised, hydrogenic-like defect wavefunctions.

### 3.3.3 Supercell method

Defect concentrations as low as one part in one million can have an influence on device performance. One way to model point defects in the dilute limit, when defect-defect interactions are negligible, is to build a supercell from multiple unit cells (Figure 3.4). This supercell must be large enough so that there is no interaction between a defect and its periodic images. Although the supercell method captures localised defects well, it cannot capture the behaviour of delocalised (or band resonant) defects due to the enforced periodicity. To remove the constraint of translational symmetry it is possible to use an embedded QM/MM approach whereby a region around the defect is modelled using DFT and embedded in a region that is modelled classically.

#### Supercell corrections

Point defects can be electrically charged, and are able to change charge state through the trapping and de-trapping of electrons and holes. The charge state of a defect can affect a number of defect properties including the preferred lattice position, surrounding lattice distortion, and the rates of diffusion, carrier capture, and carrier recombination. However, due to the long range

nature of the Coulomb interaction, understanding the properties of charged defects is a challenge for DFT with periodic boundary conditions. There are two issues to resolve: Firstly, charged defects can interact with their periodic images; Secondly, a homogeneous ‘jellium’ background charge is introduced to ensure overall charge neutrality and results in an unknown shift to the average electrostatic potential. These are finite-size effects that only a very large, almost infinite, supercell would overcome. However a system this size is computationally intractable, especially considering that higher levels of theory (for example, hybrid functionals) are often required to calculate accurate total energies.

A number of correction schemes have been developed to deal with these issues; a brief historical overview is given below. These schemes are designed to be used as a post-processing step and provide a value for the  $E_{corr}$  term in Eqn.3.16. A more complete description of these issues can be found in References [162, 163]

The Leslie Gillan correction<sup>164</sup> models the defect charge  $q$  as a point charge interacting with its periodic images through an isotropic dielectric medium. This correction takes a simple analytic form that depends on the charge state  $q$ , static dielectric constant  $\epsilon_0$ , separation between defect images  $L$  and the Madelung constant  $\alpha_m$ , which is determined by the lattice geometry:

$$E^{\text{LG}} = \frac{q^2 \alpha_m}{2\epsilon L}. \quad (3.17)$$

The Markov-Payne correction extends the Leslie Gillan correction by including an additional term that accounts for the delocalised part of the defect charge.

$$E^{\text{MP}} = \frac{q^2 \alpha_m}{2\epsilon L} + qQL^{-3}. \quad (3.18)$$

The challenge of the Markoc-Payne approach is in calculating the quadrupole moment  $Q$ . The Lany-Zunger correction<sup>165</sup> combines the Markov-Payne correction, including an approach for calculating  $Q$ , with a potential alignment procedure to correct for the shift in electrostatic potential. The Freyholdt, Neugebauer and van de Walle (FNV) method<sup>166</sup> models the defect charge as a localised gaussian distribution. The difference between the electrostatic potential of the charged defect supercell and the electrostatic potential of the perfect bulk supercell, calculated far from the defect, is aligned with the defect model potential. Kumagai and Oba have extended to FNV method by using atomic site potentials combined with a point charge model for an anisotropic medium.<sup>167</sup>

There is still no standardised approach to defect charge corrections, which can lead to a spread in calculated defect formation energies in the literature, and predicted defect densities which differ by orders of magnitude. Two widely used approaches in the recent literature are the FNV method, and the extension to this provided by Kumagai and Oba. This extension is applied to the iodine interstitial defect in Chapter ??, using an implementation in the package `sxdefectalign`.

## 3.4 Lattice dynamics

This section includes a brief overview of the theory of lattice dynamics, with a particular focus on anharmonic atomic motion. The finite difference method, an intuitive way to calculate the vibrational properties of a crystal, is outlined. This method has been applied to the perfect bulk in Chapter ?? and a defect supercell in Chapter ??.

Heisenberg's uncertainty principle states that it is not possible to know both the position and momentum of a particle exactly. Thus the static lattice model used so far is only an approximation; even at  $T = 0\text{K}$  there is zero point atomic motion. As temperature increases, this vibrational motion increases in amplitude.

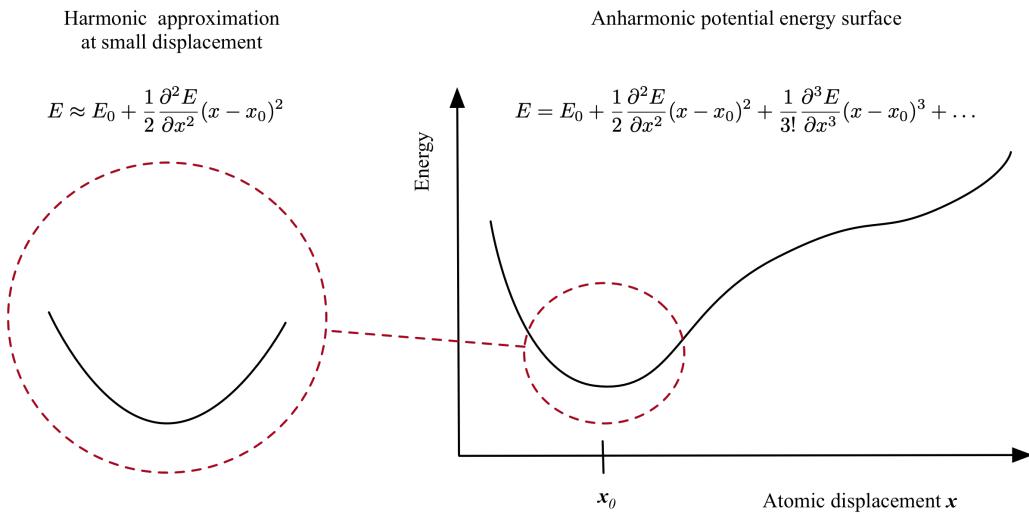
The lattice vibrations of a crystal must be considered to calculate a number of physical properties. Atomic motion has an associated vibrational energy, and this determines crystal stability as a function of temperature via the Gibbs free energy:

$$G = E_0 + E_{\text{vib}} + PV - TS \quad (3.19)$$

where  $E_0$  is the ground state energy, which can be calculated using DFT, and  $E_{\text{vib}}$  is the vibrational contribution to internal energy. Atomic motion also influences the electrical and optical properties of a crystal; this can be seen experimentally in the homogeneous broadening of photoluminescence linewidths with temperature, for example.<sup>168</sup> Other material properties which are only accessible via lattice dynamics include: heat capacity, thermal conductivity, elasticity, thermal expansion coefficients, electron-phonon coupling strengths and static polarization.

For atomic motion at small amplitudes around the potential energy minimum it is common to use the harmonic approximation, where the atom moves as if it is connected by a spring to its neighbouring atoms (Figure 3.11). This is discussed in Section 3.4.1. At larger vibration amplitudes, and to understand processes relating to the creation and annihilation of phonons, we must consider anharmonic motion, and this is considered in Section 3.4.2.

These motions are determined by the force on each atom. For simple systems, for example a one-dimensional diatomic chain, we can calculate atomic position as a function of time analytically. Otherwise methods such as DFT can be used to build a force constant matrix which, after some post-processing steps, gives the eigenvectors (direction) and frequencies of motion. This is discussed in Section 3.4.3. As in the previous sections of this chapter, we use the Born-Oppenheimer approximation and assume that the equilibrium positions in a crystal are the minima of the potential energy surface when the electron and nuclear motion are decoupled.



**Figure 3.10:** The crystal potential energy can be expanded in powers of atomic displacement  $x - x_0$ , where  $x_0$  is the equilibrium position. At small displacements, the anharmonic terms (third order and above) can be ignored, giving the harmonic approximation. For larger displacements, higher order anharmonic terms must be considered. The crystal lattice is relaxed so that all forces on the atoms are zero and there is no first order force term.

### 3.4.1 Harmonic approximation

In this section I connect, using a minimum amount of mathematics, an expression for total lattice energy with the force constant matrix (which can be calculated using DFT calculations). For a more complete derivation I refer the reader to Section 2.2 of Reference [169].

If the atomic displacement from equilibrium is small, the total energy can be Taylor expanded in the form<sup>169</sup>

$$E = \text{kinetic energy} + \text{potential energy} \quad (3.20)$$

$$= \sum_i \frac{1}{2} M \dot{x}_i^2 + \sum_{ij} \frac{1}{2} \mathbf{x}_i \cdot \mathbf{A}_{ij} \cdot \mathbf{x}_j + \text{higher-order terms}, \quad (3.21)$$

where it is assumed that the structure is relaxed and forces are equal to zero so that there is no term linear in  $\mathbf{x}$ . The harmonic approximation ignores the higher order terms in Equation 3.20. For these harmonic systems there exists a basis set so that  $\mathbf{A}_{ij}$  is diagonal and the oscillators are independent of one another:

$$= \sum_j \frac{1}{2} \tilde{M} \dot{Q}_j^2 + \sum_j \frac{1}{2} \tilde{\mathbf{A}}_j Q_j^2, \quad (3.22)$$

where the linear transformation has cast coordinates  $x$  into  $Q$ . The general solution to this system of equations for an  $N$ -atom unit cell in three dimensions is a superposition of  $3N$  normal modes of vibration, each with its own frequency and eigenvector. To calculate the normal modes Newton's second law,  $F = ma$ , is applied. For crystalline solids we take advantage of symmetry and seek normal modes  $\mathbf{e}(\mathbf{k}, t)$  that for a chosen wavevector  $\mathbf{k}$  are a linear combination of a

relative displacement within the unit cell ( $\mathbf{u}_0(i, \mathbf{k})$ ), a phase that depends on the origin  $\mathbf{R}_I$  of cell  $I$  ( $\exp(i\mathbf{k} \cdot \mathbf{R}_I)$ ), and an oscillation in time of well defined frequency  $\omega(\mathbf{k})$  ( $\exp(i\omega(\mathbf{k})t)$ ):

$$\mathbf{e}(\mathbf{k}, t) = \mathbf{u}_0(i, \mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}_I) \exp(i\omega(\mathbf{k})t) \quad (3.23)$$

For displacements of this form, Newton's second law has consistent solutions only if the following secular equation is satisfied:

$$\text{Det} \left| \sum_J A_{\alpha\beta}(iI, jJ) \exp(i\mathbf{k} \cdot \mathbf{R}_J) - M_i \delta_{ij} \omega^2(\mathbf{k}) \right| = 0, \quad (3.24)$$

where the first term in the determinant is the dynamical matrix. The dynamical matrix is built from the force constant matrix  $A_{\alpha\beta}$ :

$$\mathbf{A} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \dots & \frac{\partial^2 E}{\partial x_1 \partial x_n} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \dots & \frac{\partial^2 E}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial x_n \partial x_1} & \frac{\partial^2 E}{\partial x_n \partial x_2} & \dots & \frac{\partial^2 E}{\partial x_n^2} \end{pmatrix} \quad (3.25)$$

The normal mode frequencies  $\omega(\mathbf{k})$  are roots of the secular equation 3.23 and can be found through matrix diagonalisation. Plotting the frequency  $\omega$  against wavevector  $\mathbf{k}$  for a lattice with a periodicity of length  $L$  gives a bandstructure plot with a periodicity of  $\frac{2\pi}{L}$ .

The discussion so far has only used classical mechanics. To introduce quantum effects we recognise that the harmonic lattice vibrations are analogous to a quantum simple harmonic oscillator and so will be restricted to certain energy values  $E_n = \hbar\omega(\mathbf{k})(n + \frac{1}{2})$ . The discrete (quantised) unit of energy  $\hbar\omega(\mathbf{k})$  is a phonon quasiparticle that corresponds to a collective excitation of the crystal lattice.

### 3.4.2 Anharmonicity

Anharmonic atomic motion is described by the higher order terms in Equation 3.20. The third order term accounts for phonon-phonon scattering which, due to the conservation of energy and momentum, is a three particle process (Figure 3.26).<sup>158</sup>

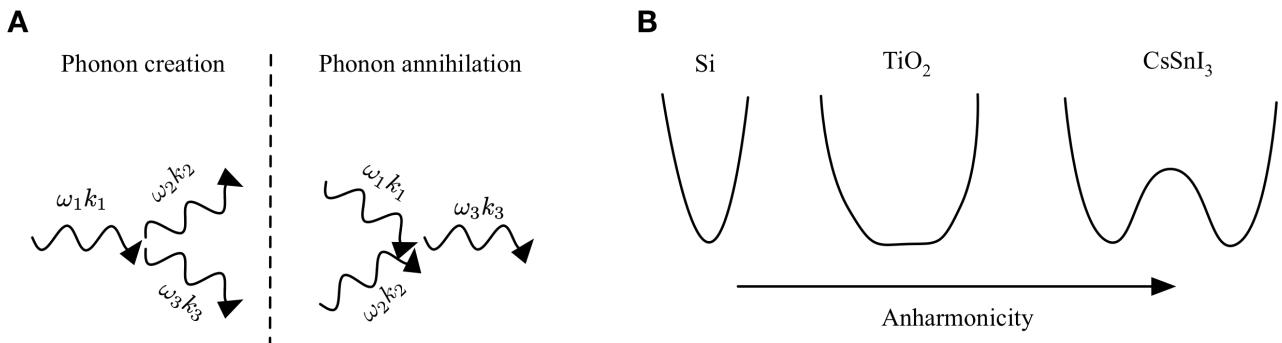
The linear boltzmann transport equation (LBTE) describes a thermodynamic system out of equilibrium. Solving the LBTE under the single mode relaxation time approximation gives an expression for the lattice thermal conductivity  $\kappa$ . The phonon-phonon scattering rate determines the phonon lifetime  $\tau_\lambda$  which is a key quantity in the expression for  $\kappa$ :

$$\kappa = \frac{1}{NV_0} \sum_\lambda C_\lambda v_\lambda \times v_\lambda \tau_\lambda \quad (3.26)$$

where  $N$  is the number of unit cells in the crystal,  $V_0$  is the unit cell volume, and  $C_\lambda$ ,  $v_\lambda$  and  $\tau_\lambda$  are the mode-dependent heat capacity, group velocity and lifetime respectively.  $C_\lambda$  and  $v_\lambda$  can

be calculated using the harmonic approximation. To quantify the strength of the anharmonic phonon interactions that determine  $\tau_\lambda$  it is necessary to calculate a third-order force constant matrix. This is often at high computational cost; in Reference [76] 41,544 DFT calculations were required to calculate the thermal conductivity of a 96-atom unit cell.

Lattice anharmonicity can also be used to describe materials with dynamic disorder. In the halide and oxide perovskites the onset temperature for dynamic disorder is determined by the depth of the double well potential energy surface (Figure 3.26).<sup>170</sup> Chapter ?? calculates the coupling between the anharmonic double well phonon modes and electronic states in MAPI.



**Figure 3.11:** A) Energy and momentum are conserved during the creation or annihilation of phonons, so these are three-phonon processes (or higher); B) Some materials, such as silicon (Si) are well-described by a harmonic potential energy surface at typical solar cell operating temperatures. However other materials with dynamic disorder, such as the organic and inorganic perovskite halides, have highly anharmonic double well potentials.

### 3.4.3 Finite displacement method

There are a number of ways to calculate the second order force constant matrix in Equation 3.25 including: the finite displacement method; density functional perturbation theory; ab-initio molecular dynamics and compressed sensing lattice dynamics. In this work the finite displacement method (also known as the direct or supercell method) is used: a single atom is displaced a small distance from its energetic minimum and there is a self-consistent electronic structure optimisation to calculate the resultant forces. The maximum number of displacements for a system with  $N$  atoms is  $6N$ , although this is reduced through symmetry. To consider phonon wavelengths greater than the unit cell length a supercell is required, and all forces must be well converged (typically to less than  $0.01 \text{ eV } \text{\AA}^{-1}$ ).

## 3.5 Summary

In this chapter I have introduced the key concepts that underly DFT, and the post-processing steps required to calculate the defect and vibrational properties of a crystal. Much of solid state physics is built upon the idea of a translationally invariant crystal, so it should come as little

surprise that additional steps are needed to describe defects that break translational symmetry and work against the fundamental assumptions of the theoretical framework. In contrast, phonons at the gamma point preserve the underlying crystal symmetry, but additional steps are needed to build the force constant matrix from multiple DFT calculations. I have presented the defect and vibrational calculations completely separately. In fact, in Chapter ?? I combine the two approaches, and calculate the vibrational properties of the iodine interstitial defect in MAPI.

*“I don’t know where I’m going from here, but I promise it won’t be boring.”*

— David Bowie

## Closing Remarks

Many opportunities ahead as we pick apart.....(from end of review) include outstanding research questions from late stage review

For my own work: not touched on is toxicity and drive to replace lead. The lead is important for transport properties. The lead is in a 2+ charge state. This means it has the chemical structure 6s<sub>2</sub> 6p<sub>0</sub>. This means that the dispersive s-orbital is active in the valence band. So when charge electrons are excited to the conduction band the holes are in a dispersive valence band and so can provide ambi-polar transport. The iodine provides dispersive conduction band edge (rom real-space structure can see there must be hybridization as there is no Pb overlap). Pb has the edge over Sn based compounds as the s electrons in Pb are deeper down and so harder to remove. In Sn based perovskites the Sn<sub>2</sub> wants to form Sn<sub>4</sub> which kills the transport (dispersion) and leads to breakdown of the material (formation of different phases) – the Sn wants to oxidise. concentrated on prototypical to understand fundamentals

Also ferroelectricity and Evidence for ferroelectric superhighways (predicted in atomistic simulations...): Tetragonal MAPI is ferroelctric from david cahen group. and starrynight.

Future of PV: - being combined with batteries for continuous power, is this the limiting?The other big thing is storage networks. This and BIPV listed as things for large scal PV deployment in Raugil nad Frankl 2009 - BIPV: This is what Dyesol company want to do. They are not going to compete with silicon on the arrays of solar farms. Going to look into market where silicon has not penetrated: where it cannot because of need to be solid single crystal. Aim is functionalisation of buildings with PV. Printing on steel.

It seems that there are technological solutions, but not the political will: what should the role of scientist be?

Modelling - baby in the bathtub. In a complex system with so much interconnected

Analysis software has been made open, testing, documentation - reproducibility in science / reusable

If our motivation is environment, need to think of as whole - battery / timescales

I motivation is for the understanding itself, there is a lot left to understand in hybrid perovskite materials.

Future - ML - <https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.122.225701>

For the wider field:

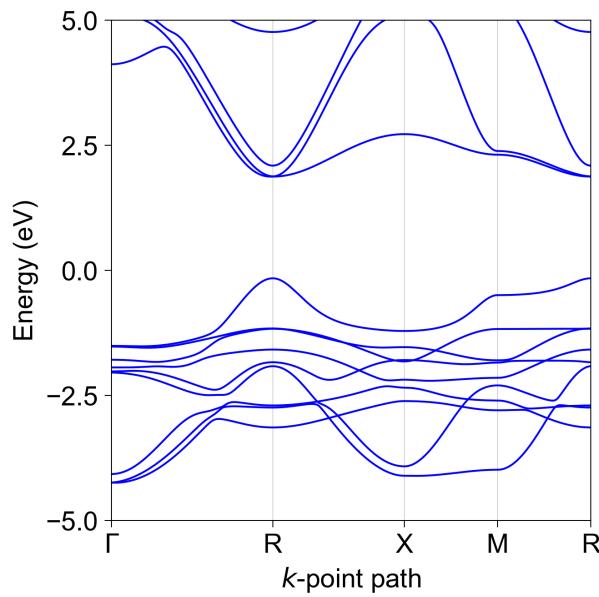
Need to move to offline Reproducibility

# Appendices

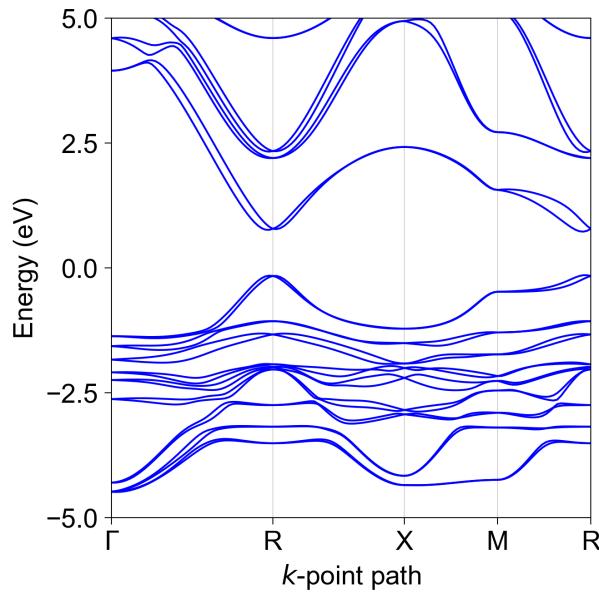
# A

## DFT bandstructures

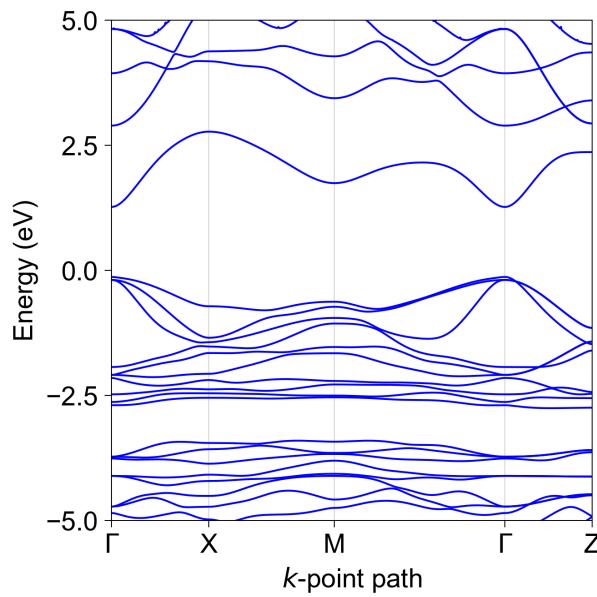
The following pages contain the DFT calculated bandstructures which were analysed to give the effective mass values in Table ???. All DFT calculations use the HSE06 exchange correlation functional, and results are given with and without spin-orbit coupling. The output files for calculations using LDA and PBEsol functionals can be found in an online repository ??.



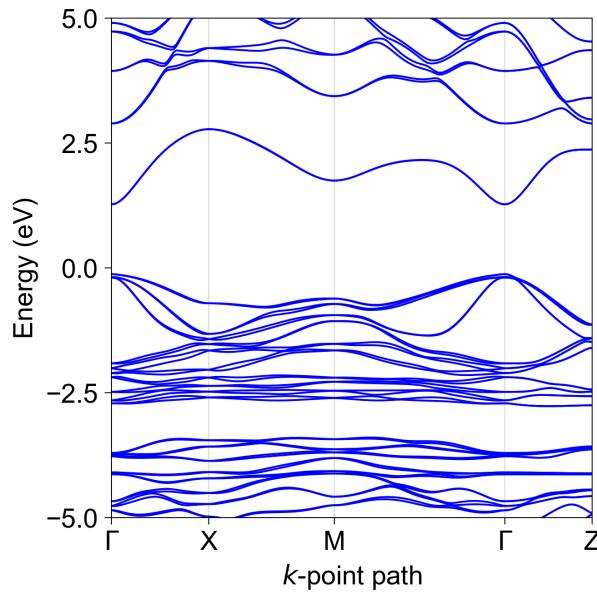
**Figure A.1:** MAPI bandstructure with the HSE06 functional, without spin-orbit coupling.



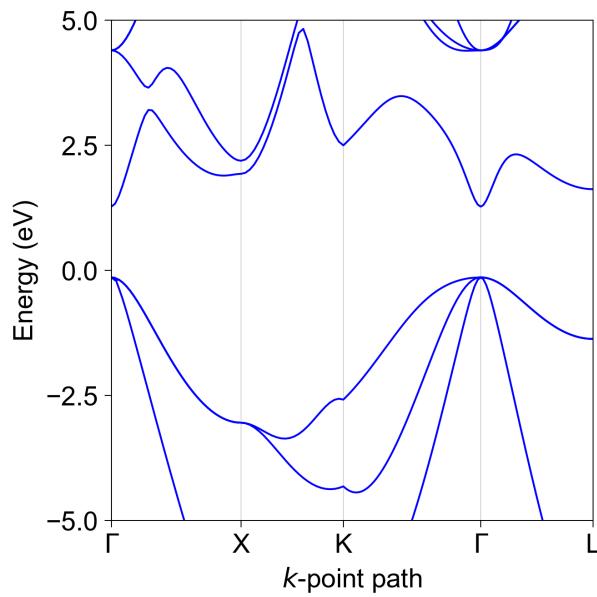
**Figure A.2:** MAPI bandstructure with the HSE06 functional, with spin-orbit coupling.



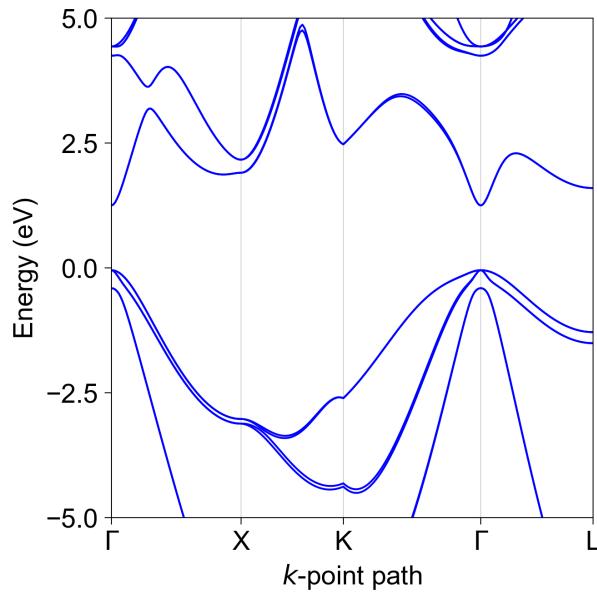
**Figure A.3:** CZTS bandstructure with the HSE06 functional, without spin-orbit coupling.



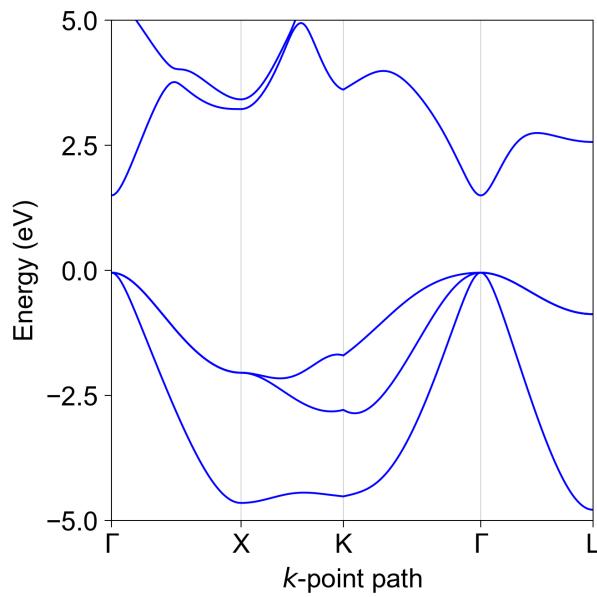
**Figure A.4:** CZTS bandstructure with the HSE06 functional, with spin-orbit coupling.



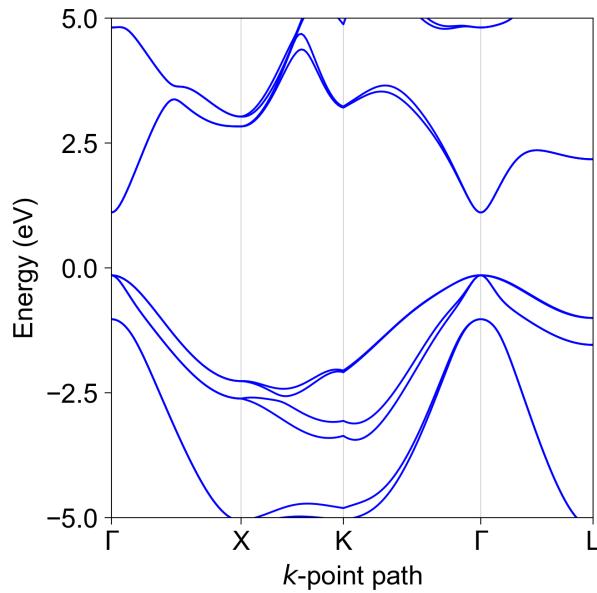
**Figure A.5:** GaAs bandstructure with the HSE06 functional, without spin-orbit coupling.



**Figure A.6:** GaAs bandstructure with the HSE06 functional, with spin-orbit coupling.



**Figure A.7:** CdTe bandstructure with the HSE06 functional, without spin-orbit coupling.



**Figure A.8:** CdTe bandstructure with the HSE06 functional, with spin-orbit coupling.

# B

## Effective mass and $k$ -point spacing

**Table B.1:** The curvature effective mass (Equation ??, in units of electron rest mass) calculated for different  $k$ -point spacings in reciprocal space for an electron in the [100] direction of CZTS. The finite difference fit and unweighted least-squares fit are calculated using three points. The weighted least squares fit is calculated using points up to 0.25 eV in energy. Details of each method are included in the Methods section of Chapter 4 in the main text. Calculations use the PBEsol exchange-correlation functional with spin-orbit coupling.

$k$ -poing spacing ( $\text{\AA}^{-1}$ )	finite diff.	unweighted	weighted
0.005	0.06	0.05	0.07
0.010	0.07	0.06	0.07
0.015	0.08	0.06	0.07
0.020	0.10	0.07	0.07
0.025	0.12	0.08	0.07

# C

## effmass: An effective mass package

### C.1 Summary

Many semiconductor properties depend on the response of electrons to an external perturbation. This perturbation could take the form of an electric field, change in temperature or an applied lattice stress. In a crystal, this response depends on the interaction of the electrons with a periodic potential. The effective mass approximation assumes that the response of an electron in a periodic potential is equivalent to that of a free electron with a renormalised mass (called the “effective mass”). This makes the effective mass a critical parameter in models for the optical and transport properties of a semiconductor.

The effective mass has a number of definitions, depending on the perturbation under consideration. The conventional definition of effective mass is inversely proportional to the second derivative of electron energy with respect to electron momentum<sup>171</sup>. This allows the effective mass to be easily calculated from ab-initio band structures, and there are existing codes which have implemented this (see section “Related packages” below).

We must approximate the band structure with a parabola for the previous definition to be valid<sup>172</sup>. However, this approximation breaks down when there is a high concentration of electrons in the material - when, for example, the material is doped or excited under a laser. Instead, we can then approximate the band structure with the Kane quasi-linear dispersion<sup>173</sup>, and the definition of effective mass is adapted accordingly.

effmass<sup>174</sup> is a Python 3 package for calculating various definitions of effective mass from the electronic bandstructure of a semiconducting material. It contains a core class that calculates the effective mass and other associated properties of selected band structure segments. effmass also contains functions for locating band structure extrema, calculating the Kane quasi-linear dispersion parameters and plotting approximations to the true dispersion. Parsing of electronic structure data is facilitated by the vasppy<sup>175</sup> package.

The effmass package is aimed towards theoretical solid state physicists and chemists who have a basic familiarity with Python. Depending on the functionality and level of approximation you are looking for, it may be that one of the packages listed below will suit your needs better.

## C.2 Related packages

Effective mass calculations are implemented in a number of other packages:

- vasppy<sup>175</sup>: This is installed as a dependency of effmass. Calculates the effective mass using a least-squares quadratic fit for parabolic dispersions.
- sumo<sup>176</sup>: Calculates the effective mass using a least-squares fit for parabolic and non-parabolic dispersions.
- emc<sup>177</sup>: Calculates the effective mass tensor using a finite-difference method for parabolic dispersions.
- pymatgen<sup>178</sup>: This is installed as a dependency of effmass. Calculates an average effective mass tensor for non-parabolic dispersions with multiple bands and extrema. Also calculates the Seebeck effective mass as defined here.

## C.3 Unique features of effmass

To our knowledge, the following features are unique to this package:

- easily compare the values of curvature effective mass calculated using multiple numerical techniques (least-squares and polynomial fitting)
- tailor the polynomial fitting used to approximate the DFT calculated dispersion: by choosing the order of the polynomial and the energy range to fit over.
- visualise the dispersions used to approximate the DFT calculated dispersion
- quantify non-parabolicity through the Kane dispersion parameters: effective mass at band-edge and alpha
- calculate the optical effective mass assuming a Kane dispersion.

## C.4 Acknowledgements

LW would like to thank Aron Walsh, Benjamin Morgan and Jarvist Moore Frost for their guidance during this project. This package was written during a PhD funded by the EPSRC through the Centre for Doctoral Training in New and Sustainable Photovoltaics (grant no. EP/L01551X/1). The input data used for developing and testing this package was generated using the ARCHER UK National Supercomputing Service. We have access to Archer via our membership of the UK's HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202).

# D

## Diffusion equation for a hot sphere

In the case of spherical symmetry

$$\nabla^2 T = \frac{1}{r} \frac{\partial^2 (rT)}{\partial r^2}. \quad (\text{D.1})$$

Substituting this into the fourier equation gives

$$\frac{\partial T}{\partial t} = \frac{D}{r} \frac{d^2 (rT)}{dr^2}, \quad (\text{D.2})$$

and we set the boundary condition as  $T = f(r)$  at  $t = 0$ . Substituting  $u = rT$  into Equation D.2 gives

$$\frac{\partial u}{\partial t} = D \frac{d^2(u)}{dr^2} \quad (\text{D.3})$$

with the boundary conditions  $u = rf(r)$  at  $t = 0$ ,  $u = 0$  at  $r = 0$ . This solution is equivalent to the case of linear flow with one face at zero. To solve, we follow reference [179] and consider a distribution on  $r$  which is equal to but the opposite sign of a distribution on  $-r$ . This initial distribution is convolved with a gaussian kernal to give temperature  $T$  as a function of time  $t$  and position  $r$ :

$$u = rT(r, t) = \frac{\eta}{\sqrt{\pi}} \left[ \int_0^\infty \lambda f(\lambda) e^{-(\lambda-r)^2 \eta^2} \delta\lambda - \int_0^\infty \lambda f(\lambda) e^{-(\lambda+r)^2 \eta^2} \delta\lambda \right], \quad (\text{D.4})$$

where  $\eta = \frac{1}{\sqrt{4Dt}}$  and  $\lambda$  is a variable of integration. Using the following definition for  $\beta$  and  $\beta'$

$$\begin{aligned} \beta &= (\lambda - r)\eta, & \lambda &= \frac{\beta}{\eta} + r \\ \beta' &= (\lambda + r)\eta, & \lambda &= \frac{\beta'}{\eta} - r, \end{aligned} \quad (\text{D.5})$$

we recast Equation D.4 as:

$$T(r, t) = \frac{1}{r\sqrt{\pi}} \left[ \int_{r\eta}^\infty \left( \frac{\beta}{\eta} + r \right) f \left( \frac{\beta}{\eta} + r \right) e^{-\beta^2} \delta\beta - \int_{r\eta}^\infty \left( \frac{\beta'}{\eta} - r \right) f \left( \frac{\beta'}{\eta} - r \right) e^{-\beta'^2} \delta\beta' \right]. \quad (\text{D.6})$$

For a sphere with radius  $R$  at temperature  $T = T_0$ , in a surrounding volume at zero temperature, the expression for  $T(r, t)$  is given by:

$$T(r, t) = \frac{T_0}{r\sqrt{\pi}} \left[ \int_{-r\eta}^{(R-r)\eta} \left( \frac{\beta}{\eta} + r \right) e^{-\beta^2} \delta\beta - \int_{r\eta}^{(R+r)\eta} \left( \frac{\beta}{\eta} - r \right) e^{-\beta^2} \delta\beta \right] \quad (\text{D.7})$$

Using the integral identity

$$\int \beta e^{\beta^2} = \frac{1}{2} e^{\beta^2}, \quad (\text{D.8})$$

and the error function

$$\operatorname{erf}(x) = \int_0^x e^{-\beta^2} \delta\beta, \quad (\text{D.9})$$

we reach the final analytical expression for temperature:

$$T(r, t) = \frac{T_0}{2} \left[ \operatorname{erf}((R-r)\eta) + \operatorname{erf}((R+r)\eta) \right] - \frac{T_0 \sqrt{Dt}}{r\sqrt{\pi}} \left[ e^{-\frac{(R-r)^2}{4Dt}} - e^{-\frac{(R+r)^2}{4Dt}} \right]. \quad (\text{D.10})$$

# E

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**Author:** Lucy D. Whalley, Rachel Crespo-Otero, Aron Walsh  
**Publication:** ACS Energy Letters  
**Publisher:** American Chemical Society  
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