

Chapter 2

Theory of Electron and Phonon Structure

“Truth... is much too complicated to allow anything but approximations.”

— John von Neumann,

“The Mathematician” in ‘The Works of the Mind’, 1947

2.1 Introduction

The research presented in this body of work will be predominantly theoretical and from first principles. The theory behind first principles Density Functional Theory (DFT) is both deep and broad. In order to preserve the fluidity of this work the extensive background theory is reported here as part of a dedicated theory section.

The majority of work presented, in this thesis, is be underpinned by DFT. A review of the basic operations of DFT is presented in this chapter. In addition the specifics of *ab initio* phonon calculations are also presented here. Such phonon calculations lead naturally on to thermal conductivity calculations described in the

following chapter.

2.2 Density Functional Theory

Density functional theory or DFT is today the premier tool for the calculation of electronic structure, both crystals and molecules. DFT is a first principles theoretical approach also called *ab initio*. The Latin expression *ab initio* means "ab"- "from" and "*initio*"-"beginning". In the world of physics and quantum chemistry this means to apply theory with the fewest number of possible assumptions. In DFT the only input assumptions are fundamental constants, electromagnetism and quantum mechanics.

A basic principle of DFT was outlined in 1927 by Llewellyn Thomas in 1927[1]. He described that electrons within the crystal would respond to an effective potential, V , determined by the ionic positions and the distribution of electrons within the solid. This theory is also used and developed by Fermi in 1928[2] and Dirac in 1930[3] who incorporated exchange into the method. However, a modern theory of DFT begins with Hohenberg and Kohn's work on density functionals in 1964[4]. It is the modern formalism of DFT that will be reviewed here with special reference to the lecture notes of Paolo Giannozzi[5].

Modern DFT has become a widely used tool for many reasons. In its current form it is immensely versatile and can be used to calculate far more than electronic structure. Through the application of DFT one can find material properties such as: atomic structure, bulks modulus, formation and binding energies, magnetic polarisation, dielectric response[6], phonon dispersions[7] and, with perturbation theory both electrical[8] and heat transmission[9]. In fact, as we shall see from the Hohenberg-Kohn theorem, any material property can in principal be determined by a functional of the electron density[4].

When describing DFT we are sometimes faced with the problem that, while the core theories are relatively simple, any practical applications of the theory grow rapidly in complexity. This is because there are many, physical and numerical, theories and proofs, that are entirely necessary for practical computation, but are generally superfluous for a detailed understanding of the theory. DFT can sometime be described as “A few good ideas and a books worth of appendices”.

In the description presented here we will use Hartree atomic units ($\hbar = m_e = e = 4\pi/\epsilon_0 = 1$). The problem will be broken down into the a set of questions each corresponding to a section or subsection of the DFT theory:

- section **2.2.1 Many Body Problem**: “Why do we need DFT?”,
- section **2.2.2 Born-Oppenheimer Approximation**: “Why & How can we solve for just electrons and ignore ionic motion?”,
- section **2.2.3 Hohenberg-Kohn Theorem**: “Is a description based on functionals valid?”,
- section **2.2.4 Kohn-Sham Auxiliary System** “How can we handle interacting electrons?” and subsection **2.2.4.1 Kohn-Sham Eigenvalues** “Given our assumptions, are the results still meaningful?”,
- section **2.2.5 The Secular Equation**: “What equation are we solving?” and subsection **2.2.5.1 Orthogonal Basis Set** “How do we solve it?”

2.2.1 Many Body Problem

In quantum mechanics any system can be described by the Schrödinger equation[10]. For a system of electrons in equilibrium the time independent Schrödinger equation

is appropriate and can be written generically as,

$$\hat{H} |\psi_s\rangle = E_s |\psi_s\rangle, \quad (2.1)$$

where $|\psi_s\rangle$ is eigenstate s and E_s is the corresponding energy eigenvalue. Here $|\psi_s\rangle$ is clearly defined as a coupled system of electrons and nuclei,

$$|\psi_s\rangle = |\psi_s(\mathbf{r}_1, \mathbf{R}_1, \dots, \mathbf{r}_{N_i}, \mathbf{R}_{N_n})\rangle. \quad (2.2)$$

Here \mathbf{r}_i is the i 'th electron's position vector and \mathbf{R}_n is the position vector of ion n . The values N_i and N_n are the total number of electrons and ions respectively.

The Hamiltonian of a quantum solid, a system of interacting nuclei and electrons, can be written as

$$\begin{aligned} \hat{H} &= \hat{T}_n + \hat{T}_e + \hat{U} \\ &= \hat{T}_n + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}, \end{aligned} \quad (2.3)$$

where \hat{T} is a kinetic energy operator for the subscripts n and e denoting ions and electrons respectively. \hat{V}_{ee} is the potential energy operator describing the electron-electron interactions while \hat{V}_{en} and \hat{V}_{nn} are the electron-ion and the ion-ion interactions respectively. Expanding out the Hamiltonian gives us

$$\hat{H} = - \sum_n \frac{1}{2M_n} \nabla_n^2 - \frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{ni} \frac{Z_n}{|\mathbf{R}_n - \mathbf{r}_i|} + \frac{1}{2} \sum_{n \neq n'} \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}_{n'}|}. \quad (2.4)$$

Here, the ion n has Z_n as its atomic number and M_n as its mass. The ∇ operator is constructed from derivatives with respect to either ionic position, ∇_n , or electronic positions, ∇_i . There is no general solution to equation 2.4, neither are there any trivial simplifications that can be made.

In order to make this soluble we can separate the ionic and electronic com-

ponents. One may then, with an appropriate choice of base states, and a means of determining the potential \hat{U} , solve for the eigenstates of a quantum solid.

2.2.2 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is often defined very loosely, stating that as electrons are much less massive than ions, any perturbation in the crystal will be compensated for by the motion of electrons before the ions have a chance to react. This implies that for any given displacement of the ions, due to their motion, the electrons will be in their equilibrium state. One may then say that even if a vibration is excited in the lattice the electrons will always occupy their ground state and therefore may be treated as separable.

Here is given a rigorous demonstration of the adiabatic approximation (Born Oppenheimer Approximation to second order[11]). First we define the exact Hamiltonian for a crystal or of molecule as

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \quad (2.5)$$

We can separate the ionic kinetic energy from the electronic and potential terms to give,

$$\hat{H}\Psi_s = \hat{H}_e\Psi_s + \hat{T}_n\Psi_s = E_s\Psi_s \quad (2.6)$$

Now we may let the full coupled molecular/crystal wavefunction, Ψ_s , have separable coupled $\chi_{si}(\mathbf{R})$ and electronic $\varphi_i(\mathbf{r}; \mathbf{R})$ contributions. This does not assume separability, if the states are always coupled $\varphi_i(\mathbf{r}; \mathbf{R})$ will go to unity when,

$$\Psi_s = \sum_i \varphi_i(\mathbf{r}; \mathbf{R})\chi_{si}(\mathbf{R}). \quad (2.7)$$

Here the electron wavefunction is determined by r which itself has a parametric

dependence on R . Meaning that φ_i has a functional dependence on \mathbf{R} .

Now using the definition in equation 2.7 the Schrödinger equation may be rewritten as,

$$\left(\hat{H}_e + \hat{T}_n\right) \sum_i \varphi_i(\mathbf{r}; \mathbf{R}) \chi_{si}(\mathbf{R}) = E_s \sum_i \varphi_i(\mathbf{r}; \mathbf{R}) \chi_{si}(\mathbf{R}) \quad (2.8)$$

If under the adiabatic approximation the coupled wavefunctions are determined by a potential derived from only the electronic wavefunctions then it is valid (or at least consistent) to neglect the coupling and interpret the coupled wavefunctions as ionic wavefunctions. The ionic contribution can then also be neglected when calculating the electron wavefunctions.

In order to derive an ionic Schrödinger equation we evaluate the integrals of the electronic wavefunctions over r . We define this inner-product using Dirac notation as

$$\begin{aligned} \int_{\mathbf{r}} \varphi_{i''}^*(\mathbf{r}; \mathbf{R}) \left(\hat{H}_e + \hat{T}_n\right) \sum_i \varphi_i(\mathbf{r}; \mathbf{R}) \chi_{si}(\mathbf{R}) \, d\mathbf{r} &= \int_{\mathbf{r}} \varphi_{i''}^*(\mathbf{r}; \mathbf{R}) \sum_{i'} \varphi_{i'}(\mathbf{r}; \mathbf{R}) \chi_{si'}(\mathbf{R}) \, d\mathbf{r}, \\ \sum_i \left\langle i'' \left| \hat{H}_e + \hat{T}_n \right| i \right\rangle |\chi_{si}\rangle &= \sum_{i'} E_s \langle i'' | i' \rangle |\chi_{si'}\rangle, \end{aligned} \quad (2.9)$$

where we allow ourselves to express the electronic wavefunction by only its index.

We can observe that the summation drops out of the right hand side of equation 2.9 leaving $E_s |\chi_{si''}\rangle$. Now we evaluate the first term on the left hand side

giving

$$\begin{aligned}
 \sum_i \left(\langle i'' | \hat{H}_e | i \rangle + \langle i'' | \hat{T}_n | i \rangle \right) | \chi_{si} \rangle &= E_s | \chi_{si''} \rangle \\
 \sum_i \left(E_i \langle i'' | i \rangle + \langle i'' | \hat{T}_n | i \rangle \right) | \chi_{si} \rangle &= E_s | \chi_{si''} \rangle \\
 E_{i''} | \chi_{si''} \rangle + \sum_i \langle i'' | \hat{T}_n | i \rangle | \chi_{si} \rangle &= E_s | \chi_{si''} \rangle,
 \end{aligned} \tag{2.10}$$

where the two terms on the left account for the electronic energy and for the electronic transitions due to ionic motion.

We may now rearrange the equation,

$$(E_{i''} - E_s) | \chi_{si''} \rangle = - \sum_i \langle i'' | \hat{T}_n | i \rangle | \chi_{si} \rangle. \tag{2.11}$$

This demonstrates that the difference between the complete coupled energy of the system and the electronic energy is entirely described by the interaction between the ionic kinetic energy operator and the electronic wavefunctions.

To evaluate the right-hand side of equation 2.11 we use the definition

$$\hat{T}_n = - \sum_{\sigma} \frac{1}{2M_{\sigma}} \nabla_{\sigma}^2. \tag{2.12}$$

We now evaluate the to get

$$\sum_{\sigma} \langle i'' | \hat{T}_n | i \rangle | \chi_{si} \rangle = \hat{T}_n | \chi_{si''} \rangle + \sum_i (B_{i''i} + A_{i''i}) | \chi_{si} \rangle, \tag{2.13}$$

where two expressions are convenient to define, from the product rule, $A_{i''i}$ and $B_{i''i}$ corresponding to terms in ∇ and ∇^2 respectively. These terms are defined,

$$A_{ii'} = \sum_{\sigma} \frac{-1}{M_{\sigma}} \langle i | \nabla_{\sigma} | i' \rangle, \tag{2.14}$$

and

$$B_{ii'} = \sum_{\sigma} \frac{-1}{2M_{\sigma}} \langle i | \nabla_{\sigma}^2 | i' \rangle. \quad (2.15)$$

We now substitute back into equation 2.11 to get

$$\left(E_{i''} + \hat{T}_n - E_s \right) |\chi_{si''}\rangle = \sum_i (B_{i''i} + A_{i''i}) |\chi_{si}\rangle \quad (2.16)$$

The terms in the remaining summation can be separated into $i = i''$ and $i \neq i''$. This separates the interactions into those which leave the electron state unchanged and those which do not. Applying this separation gives,

$$\left(E_{i''} + \hat{T}_n - E_s \right) |\chi_{si''}\rangle = -(B_{i''i''} + A_{i''i''}) |\chi_{si''}\rangle - \sum_{i \neq i''} (B_{i''i} + A_{i''i}) |\chi_{si}\rangle. \quad (2.17)$$

At this point we can impose the adiabatic condition. This is done by imposing the condition that ionic motion cannot excite an electronic state, hence all terms in which the initial and final states are different ($i \neq i''$) go to zero. This expresses the notion that ionic motion is slow compared to electronic relaxation rate and so the electrons effectively remain in the ground state in spite of ionic vibration.

We can also remove A_{ii} since it goes to zero. $\nabla \langle i | i \rangle = \nabla[1] = 0$, but by product rule we can say

$$\begin{aligned} \nabla \langle i | i \rangle &= \langle \nabla i | i \rangle + \langle i | \nabla i \rangle \\ \langle \nabla i | i \rangle &= - \langle i | \nabla i \rangle \\ \langle i | \nabla i \rangle^{\dagger} &= - \langle i | \nabla i \rangle \end{aligned} \quad (2.18)$$

The inner product must return a real value, therefore we know that $\langle i | \nabla i \rangle^{\dagger} = \langle i | \nabla i \rangle$ and hence

$$\begin{aligned} \langle i | \nabla i \rangle &= - \langle i | \nabla i \rangle \\ \langle i | \nabla i \rangle &= \langle i | \nabla i \rangle = 0 \end{aligned} \quad (2.19)$$

Now we rewrite 2.17 and rearrange to obtain

$$\left(\hat{T}_n + E_i + B_{ii}\right) |\chi_{si}\rangle = E_s |\chi_{si}\rangle \quad (2.20)$$

Here the term B_{ii} is the Diagonal Born Oppenheimer Correction. At this point the subscripts must be evaluated. The term B_{ii} and E_i can be combined into an effective electronic potential $U_i = B_{ii} + E_i$. This allows us to define an ionic motion equation for each electronic state i ,

$$\left(\hat{T}_n + U_i\right) |\chi_{si}\rangle = E_s |\chi_{si}\rangle \quad (2.21)$$

In reaching this point we have demonstrated that the electronic wavefunctions are separable from the coupled wavefunction, hence demonstrating that under the adiabatic approximation there is no coupling and we can reformulate equation 2.21 as

$$\left(\hat{T}_n + U_i\right) |\chi_{ji}\rangle = E_{ji} |\chi_{ji}\rangle, \quad (2.22)$$

and

$$\left(\hat{T}_n + \mathcal{V}\right) |\chi_j\rangle = E_j |\chi_j\rangle \quad (2.23)$$

where the index j counts over ionic states, thus proving that electronic and ionic states are separable under the adiabatic approximation. We can define the electronic state i that will evolve adiabatically with ionic motion.

It has been demonstrated that, under the adiabatic approximation, the separable electronic states may be defined,

$$\hat{H}_e |\varphi_i\rangle = \left(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}\right) |\varphi_i\rangle, \quad (2.24)$$

allowing calculations of electronic energies and eigenvalues independently of ionic motion. We note that here the ion-ion interaction is dropped since it only has the

effect of applying a static shift to the energies. This term can therefore be neglected without consequence.

2.2.3 Hohenberg-Kohn Theorem

The Hohenberg-Kohn theorem is actually two theories, both central to the concept of DFT. The first Hohenberg-Kohn theorem establishes that the Hamiltonian may be exactly and uniquely determined by an external potential which in turn is determined by a ground state density of interacting particles. Second, it shows that a functional for energy, with a global minimum corresponding to the ground state density, always exists for an external potential.

These two Theorems are stated clearly and without ambiguity by R.Martin[6].

Theorem 1

For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.

and

Theorem 2

A universal function for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

We now expand on these rules.

Theorem 1:

We will now provide the proof for the first Hohenberg-Kohn theorem by contradiction[4]. To achieve this we evoke the variational principle, which states that, for any Hamiltonian $\hat{H}^{(1)}$ there is a corresponding ground state $|1\rangle$ which gives the global minimum of $\langle 1|\hat{H}^{(1)}|1\rangle$. Now suppose that we have two external potentials ($V_{ext}^{(1)}(\mathbf{r})$ and $V_{ext}^{(2)}(\mathbf{r})$) that both return the same ground state density $n_0(\mathbf{r})$. Having two external potentials leads to two Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, each with a corresponding ground state $|1\rangle$ and $|2\rangle$. Remember it is only the ground state density $n_0(\mathbf{r})$ that is chosen to be the same.

We may now state explicitly,

$$E^{(1)} = \langle 1|\hat{H}^{(1)}|1\rangle < \langle 2|\hat{H}^{(1)}|2\rangle. \quad (2.25)$$

It is important to see that we could make an equivalent expression for $E^{(2)}$ by swapping all the state indices ($1 \rightleftharpoons 2$).

$$E^{(2)} = \langle 2|\hat{H}^{(2)}|2\rangle < \langle 1|\hat{H}^{(2)}|1\rangle. \quad (2.26)$$

This inversion of states can be applied at any stage of the derivation.

We may freely define

$$\hat{H}^{(1)} = \hat{H}^{(1)} + \hat{H}^{(2)} - \hat{H}^{(2)} \quad (2.27)$$

and hence

$$\begin{aligned} \langle 2|\hat{H}^{(1)}|2\rangle &= \langle 2|\hat{H}^{(2)}|2\rangle + \langle 2|\hat{H}^{(1)} - \hat{H}^{(2)}|2\rangle \\ &= E^{(2)} + \int \left(V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r}) \right) n_0(\mathbf{r}) d^3\mathbf{r} \end{aligned} \quad (2.28)$$

The only terms of the two Hamiltonians which do not cancel out are the external potential terms. Further, because the external potential is not an operator, the state

vectors may form an inner product and go to unity.

We may now substitute this expression into equation 2.25 to give

$$E^{(1)} < E^{(2)} + \int \left(V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r}) \right) n_0(\mathbf{r}) d^3\mathbf{r}, \quad (2.29)$$

We may again enact the inversion of states performed for equation 2.26 to give

$$E^{(2)} < E^{(1)} + \int \left(V_{ext}^{(2)}(\mathbf{r}) - V_{ext}^{(1)}(\mathbf{r}) \right) n_0(\mathbf{r}) d^3\mathbf{r}, \quad (2.30)$$

Now if we simply add together equations 2.29 & 2.30 we obtain a contradiction.

$$E^{(2)} + E^{(1)} < E^{(1)} + E^{(2)} \quad (2.31)$$

where, clearly the integral terms cancel out. This contradiction demonstrates that for any given ground state density there is a single unique external potential (excluding a constant value difference) associated with it. This shows that it is the particle density that defines the external potential (to within a static shift).

It follows that since the Hamiltonian may be defined in terms of the external potential and the external potential is defined by the particle density, so can the ground state wavefunction be defined in terms of the ground state particle density.

Theorem 2:

The second Hohenberg-Kohn theorem proof proceeds as follows. First we will express the electron-electron (or particle-particle) interaction and the kinetic energy as functionals and define the Hohenberg-Kohn functional,

$$F_{HK}[n] = T[n] + E_{int}[n], \quad (2.32)$$

where $T[n]$ is the kinetic energy functional and $E_{int}[n]$ is the particle-particle inter-

action functional.

We can now define a functional for the total energy as,

$$E_{HK} = F_{HK} + \int V_{ext}(\mathbf{r})n(\mathbf{r}) d^3\mathbf{r}. \quad (2.33)$$

As before we neglect the ion-ion interaction. The first Hohenberg-Kohn theorem shows that an external potential can be determined, with the exception of a constant shift. Because, the ion-ion interaction is, for any system, only a constant shift to the energies, it can be neglected with no consequence to the applicability of the theory.

We put this formulation to the test by considering a specific state $n^{(1)}(\mathbf{r})$ which corresponds to a distinct ground state, energy and wavefunction. We may now write

$$E^{(1)} = E_{HK}[n^{(1)}] = \langle 1 | \hat{H}^{(1)} | 1 \rangle, \quad (2.34)$$

and if we define the energy of state $|2\rangle$ for the same Hamiltonian

$$E^{(2)} = \langle 2 | \hat{H}^{(1)} | 2 \rangle, \quad (2.35)$$

we can say

$$\begin{aligned} \langle 1 | \hat{H}^{(1)} | 1 \rangle &< \langle 2 | \hat{H}^{(1)} | 2 \rangle \\ E^{(1)} &< E^{(2)} \\ E_{HK}[n^{(1)}] &< E_{HK}[n^{(2)}]. \end{aligned} \quad (2.36)$$

Here we have demonstrated that a functional, defined by a particular ground state density, will return a greater energy when acting on a particle density that is not the ground state. This can be restated as having its global minimum when it acts on the ground state density.

2.2.4 Kohn-Sham Auxiliary System

The transformation of the Hohenberg-Kohn theorem from a curiosity into a useful tool takes place via the Kohn-Sham approach. The objective of the Kohn-Sham auxiliary system is to replace the many body system of interacting electrons with an artificial "auxiliary" system of non-interacting electron-like particles. The auxiliary system is built on the assumption that the ground state density of the electron system is the same as the ground state density of the Kohn-Sham particles.

$$n(\mathbf{r}) = \sum_k |\psi_k(\mathbf{r})|^2, \quad (2.37)$$

where each Kohn-Sham orbital ψ_k acts as a single-electron wavefunction. The Hohenberg-Kohn energy functional has already been shown to give the exact ground state energy (in principle). Therefore the requirement that the ground-state particle density is exactly replicated is enough to ensure that the ground-state energy is also replicated.

If we wanted to include spin in the description, a simple sum over spin states would be incorporated into equation 2.37. The Kohn-Sham orbitals are defined according to the condition that E_{HK} is minimized. We now define the energy functional

$$E_{KS}[n] = T_s[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r}) d^3\mathbf{r} + E_H[n] + E_{xc}[n] \quad (2.38)$$

where $T_s[n]$ is the independent particle kinetic energy, E_H is the Hartree energy and $E_{xc}[n]$ is the exchange correlation functional.

We define the independent particle kinetic energy, $T_s[n]$ as,

$$-\frac{1}{2} \sum_k \int \psi_k^*(\mathbf{r}) \nabla^2 \psi_k(\mathbf{r}) d^3\mathbf{r}, \quad (2.39)$$

and the Hartree energy, $E_H[n]$ as,

$$\frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}' \quad (2.40)$$

While this is sufficient to define the energy we cannot define a Kohn-Sham Hamiltonian without potential defined by the functionals.

$$\hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}[n], \quad (2.41)$$

Here $V_{KS}[n]$, is defined such that Kohn-Sham Hamiltonian should return the same energy as the energy functional and that it must obey the same variational principle, such that the ground state wavefunction gives the lowest energy.

We have demonstrated, already, that the Kohn-Sham energy is at a minimum when evaluated at the ground state density and/or wavefunction. We can impose this condition mathematically by setting the differential of the Kohn-Sham energy functional to zero. It is necessary however to include the normalisation condition by Lagrange multiplier technique.

$$\epsilon[\langle\psi|\psi\rangle - 1] = 0, \quad (2.42)$$

where ϵ is, for now, a Lagrange multiplier but, we will soon see, becomes the energy eigenvalue. For this reason we have conveniently selected to represent it using ϵ . The derivative of the Kohn-Sham energy functional is already defined as zero at the ground state, hence we set the derivative of the left hand side of equation 2.38 equal to our Lagrange multiplier condition,

$$\frac{\delta T_s}{\delta \psi_k^*} + \left[\frac{\delta E_{ext}}{\delta n(\mathbf{r})} + \frac{\delta E_H}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right] \frac{\delta n(\mathbf{r})}{\delta \psi_k^*} = \frac{\delta}{\delta \psi_k^*} \epsilon[\langle\psi|\psi\rangle - 1] \quad (2.43)$$

using their definitions (eq. 2.39 & 2.40) we can evaluate the derivatives of T_s and

$n(\mathbf{r})$ as,

$$\frac{\delta T_s}{\delta \psi_k^*} = -\frac{1}{2} \nabla^2 |\psi_k\rangle, \quad (2.44)$$

$$\frac{\delta n(\mathbf{r})}{\delta \psi_k^*} = |\psi_k\rangle, \quad (2.45)$$

and, lastly, the derivative of Lagrange multiplier condition gives,

$$\frac{\delta}{\delta \psi_k^*} \epsilon [\langle \psi | \psi \rangle - 1] = \epsilon |\psi_k\rangle. \quad (2.46)$$

Now, if we recognise the three derivatives with respect to $n(\mathbf{r})$ (eq. 2.43) as potentials and apply the three evaluations (eq. 2.44, 2.45 and 2.46) we can rewrite equation 2.43 as,

$$-\frac{1}{2} \nabla^2 |\psi_k\rangle + V_{ext}(\mathbf{r}) |\psi_k\rangle + V_H(\mathbf{r}) |\psi_k\rangle + V_{xc}(\mathbf{r}) |\psi_k\rangle = \epsilon |\psi_k\rangle \quad (2.47)$$

$$-\frac{1}{2} \nabla^2 |\psi_k\rangle + V_{KS}(\mathbf{r}) |\psi_k\rangle = \epsilon_k |\psi_k\rangle. \quad (2.48)$$

It can be recognised that equation 2.48 is a Schrödinger equation, with a Hamiltonian defined as

$$\hat{H}_{KS} = -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \quad (2.49)$$

We have now expressed the Hamiltonian of the Kohn-Sham auxiliary system in terms of calculable quantities (given the existence of an exchange-correlation functional). However, it is unclear how helpful this auxiliary system is for describing true electronic features of the solid.

2.2.4.1 Kohn-Sham Eigenvalues

It is easy to think that the Kohn-Sham eigenvalues have no physical meaning and while this is true to some degree, the Kohn-Sham eigenvalues are not intrinsically the energies required to add or subtract electrons from an interacting many body

system. This being the case there are two items of research that demonstrate the usefulness of the Kohn-Sham eigenvalues.

First we look at the work of Janak in 1978[12]. In this work, Janak derives an expression for the rate of change of energy of the system with particle number. This is done within the DFT formalism. It is demonstrated that the $\partial E/\partial n_i = \epsilon_i$, thus clearly showing that eigenvalues properly correspond to addition and subtraction energies for the fictitious Kohn-Sham electron-like particles. This is commonly known as the Slater-Janak theorem[6]. It can further be stated that the exact functional energy derivative ($\partial E/\partial n_i = \epsilon_i$) is discontinuous between electrons. The total energy of electrons $E(N)$ may be viewed as a series of straight-line segments intersecting a curve at integer values of electron number. It is the absence of the potential discontinuity (among other factors) that leads the failure of GGA and LDA methods in predicting the bandgaps of Mott insulators; reintroducing this discontinuity is goal of the Hubbard +U correction[13].

In relation to the Slater-Janak theorem it must be noted that part of the exchange correlation potential, $V_{xc}(\mathbf{r})$, depends on the derivative of $E_{xc}[n]$ with respect to $n(\mathbf{r})$ which can change discontinuously between states. This is the “band-gap discontinuity”[14]. It follows that in principle the band-gap is not accurately predicted, however many effective potentials and extended tools exist for correcting this, including hybrid functionals[15] and GW quasiparticle methods[16].

The Slater-Janak theorem establishes a rigorous connection between N and $N + 1$ particles systems. Next we review the work of Levy, Perdew and Sahni[17]. They demonstrate that at asymptotically long-range, the charge density is governed by the occupied state with the highest eigenvalue. If we allow for the existence of an exact exchange correlation functional then we can say, as Levy *et al.* do, that since the particle density is exact then so should the ground-state ionisation energy be exact.

In summary the work of Levy *et al.*[17] lets us state that (for an exact V_{xc}) the highest occupied molecular orbital has the genuine electronic energy eigenvalue. Further, through the work of Janak[12] we can extend this trust somewhat, to nearby occupied states. Some work has also been done to establish DFT as providing well-defined approximations for excitation energies[18]. However, accurate band-gap prediction requires methods beyond DFT[14, 15, 16].

2.2.5 The Secular Equation

The variational principle can be utilised in the construction of an equation which allows us to reduce the many body Schrödinger equation to linear algebra. We must expand the wavefunctions into a finite basis set. The variational principle can then be used to find the optimal coefficients of the expansion. The procedure is very simple, first we express the expectation value as,

$$\langle \psi | \hat{H} | \psi \rangle = \epsilon \langle \psi | \psi \rangle \quad (2.50)$$

We then describe a function equal to the variation in energy as you move away from optimal wavefunction.

$$\mathcal{S}[\psi] = \langle \psi | \hat{H} | \psi \rangle - \epsilon \langle \psi | \psi \rangle \quad (2.51)$$

This is not yet the secular equation, but rather a variational functional.

At this point, we can, by expanding the wavefunctions as a sum of basis sets, differentiate with respect to basis coefficients. Then to identify the minimum energy condition we expand at the turning point where the derivative is equal to zero.

2.2.5.1 Orthogonal Basis Set

The Schrödinger equation for the Kohn-Sham auxiliary system can be written as

$$\hat{H}_{KS} |\psi_k\rangle = -\frac{1}{2} \nabla^2 |\psi_k\rangle + V_{KS}(\mathbf{r}) |\psi_k\rangle = \epsilon_k \quad (2.52)$$

for each Kohn-Sham equation, which is to say, for each value of k a solution can be obtained providing there is a known electron density (strictly it is an electron-like particle density). From this point onward we drop the k index since we will only be concerned with solving any single Kohn-Sham equation.

A Kohn-Sham wavefunction can be defined in terms of a finite basis set,

$$|\psi\rangle = \sum_i^N c_i b_i, \quad (2.53)$$

where b_i is an orthogonal basis function, c_i is the coefficient and N is the total number of base states.

We can now use the definition from equation 2.53 and substitute it into our variational functional (eq. 2.51). This is written

$$\mathcal{S} = \int \sum_i c_i^* b_i^* \hat{H}_{KS} \sum_j c_j b_j d^3\mathbf{r} - \epsilon \sum_{ij} c_i^* c_j \langle b_i | b_j \rangle \quad (2.54)$$

for brevity of notation we allow ourselves to define

$$H_{ij} = \langle b_i | \hat{H}_{KS} | b_j \rangle. \quad (2.55)$$

Assuming the a Kohn-Sham potential can be calculated through means of an exchange correlation functional and using a plain wave basis set (plain waves are orthonormal) the evaluation of each matrix element H_{ij} is now trivial. Each of element of H_{ij} should, for this point onwards, be considered a known quantity.

We can substitute equation 2.55 back into equation 2.54 to get,

$$\begin{aligned}\mathcal{S} &= \sum_{ij} c_i^* c_j H_{ij} - \epsilon \sum_{ij} c_i^* c_j \langle b_i | b_j \rangle \\ &= \sum_{ij} c_i^* c_j \left(H_{ij} - \epsilon \langle b_i | b_j \rangle \right)\end{aligned}\tag{2.56}$$

It is by the differentiation of the variational functional that the minimum energy condition is revealed.

$$\frac{\partial \mathcal{S}}{\partial c_i^*} = 0\tag{2.57}$$

The turning point of the equation gives

$$0 = \sum_{ij} c_j \left(H_{ij} - \epsilon \delta_{ij} \right)\tag{2.58}$$

However, the equation 2.58 is not generally solvable (beyond trivial the case $\vec{c} = 0$). So it is here that we define the secular equation.

$$\det |H_{ij} - \epsilon \delta_{ij}| = 0\tag{2.59}$$

It is an algebraic equation, that admits N roots, each root returning a different eigenvalue. Reformulating this as a matrix equation we have

$$\mathbf{H}\vec{c} = \epsilon\vec{c}\tag{2.60}$$

This is now a standard eigenvector/eigenvalue problem. However, there is a problem, we are seeking the set of coefficients that define a Kohn-Sham state but we have N solutions. This corresponds to an $N \times N$ matrix \mathbf{H} .

This leaves us with N eigenvectors, each one we denote with λ up to a value of N .

$$\psi_\lambda = \sum_i C_{i\lambda} b_i\tag{2.61}$$

we can then define,

$$\hat{H}\psi_\lambda = \epsilon_\lambda\psi_\lambda \quad (2.62)$$

We can now define a Kohn-Sham eigenstate and eigenvalue as

$$\psi_k = \sum_\lambda \psi_\lambda \quad (2.63)$$

$$\epsilon_k = \sum_\lambda \epsilon_\lambda \quad (2.64)$$

It is these values, ϵ_k , that are the energy eigenvalues obtained from DFT. The total energy of the system is found by summing across all the energy eigenvalues of the Kohn-Sham orbitals.

The equation 2.60 is a very common problem in mathematics and computer science; the process of solving such an equation is called diagonalisation.

2.2.6 DFT Summary

This section has derived and defined the theorems and approximations that coalesce to form the fundamental theory of DFT. Section 2.2.1 explored why many body *ab initio* methods are needed and to express the potential benefit they have. The adiabatic approximation is shown, in section 2.2.2, to be sufficient to decouple the electronic and ionic wavefunctions. This establishes the necessary electron Hamiltonian to derive the first and second Hohenberg-Kohn theorems (sec. 2.2.3) which prove that (1st) a functional approach is, in principle, valid and that (2nd) it obeys the variational principle. Section 2.2.4 explores the Kohn-Sham auxiliary system and derives the Kohn-Sham equations. Then are derived the general quantum mechanical principles of solving for the optimal coefficients of a basis set. Section 2.2.5 introduces the secular equation, in which the variational method is reduced to an algebraic problem, and orthogonal basis sets are explored as a method of solving a

Hamiltonian of known or calculable terms (sec. 2.2.5.1). Thus, do we derive the fundamentals of density functional theory and explore the means by which it is solved.

2.3 Functional Choice

Much of the theory of DFT is built upon the assumption of a exact (or at least suitable) exchange correlation functional $E_{xc}[n]$. The Hohenberg-Kohn theorems demonstrate that there exists a functional that describes the physical properties of a set of interacting particles. The Kohn-Sham theorem shows how one may replace the true system of interacting particles with a non-interacting auxiliary system of the same ground state charge density. These foundational theories do not provide a clear indication as to the form of $E_{xc}[n]$. There are many different functionals used in DFT however the majority can be classified as local density approximation (LDA), generalised gradient approximation (GGA) or hybrid functionals. Each method represents a different balance between computational cost and chemical accuracy.

Each functional gives two important physical properties of the system. The first is the total exchange correlation energy. This value is minimised to give optimal charge density of the system. The second is the exchange correlation potential, $V_{xc}(\mathbf{r})$, expressed in equations 2.43 and 2.47. Here are explored three formulations of density functional theory: LDA, GGA and hybrid functionals.

2.3.1 Local Density Approximation

The local density approximation (or local spin density approximation (LSDA) more generally) considers a solid to be a close to the limit of the homogeneous electron gas. As such it depends on the local charge density at each point in space to determine

the exchange correlation energy ($E_{xc}^{LDA}[n]$). Despite the fact that the energy of each point is unchanged by it's environment this approach yields some reasonable results.

The exchange correlation energy may be stated explicitly as,

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \epsilon_{xc}^{LDA} n(\mathbf{r}) d\mathbf{r}, \quad (2.65)$$

where $\epsilon_{xc}^{LDA} \equiv \epsilon_{xc}^{LDA}(n(\mathbf{r}))$ and is the exchange-correlation energy per particle (in the case of LDA, this is the exchange-correlation energy of a homogeneous electron gas). This gives the corresponding exchange correlation potential,

$$V_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \epsilon_{xc}^{LDA} + n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{LDA}}{\partial n(\mathbf{r})} \quad (2.66)$$

The LDA class of functionals are widely considered the least accurate of the three discussed here. The local approximation depends heavily on the assumption that exchange and correlation are very short range. This assumption has no formal justification[6]. This functional can be expected to be most suitable for systems which resemble the homogeneous electron gas (such as nearly free electron like metals). Two common LDA functionals are the PZ (Perdew-Zunger)[19] and the PW92 (Perdew-Wang 1992)[20].

2.3.2 Generalised Gradient Approximation

The generalised gradient approximation is a clear attempt to improve upon LDA by incorporating pseudo non-local effects. In the generalised gradient approximation both the local density and the local gradient of that density are used to determine the exchange correlation energy. This means that while GGA is still a truly local approximation each point inherently carries information about its surroundings. This allows GGA to outperform LDA in most cases with minimal enhancement to the computational cost.

The exchange correlation energy for the GGA functional can be given as,

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int \epsilon_{xc}^{GGA} n(\mathbf{r}) d\mathbf{r}. \quad (2.67)$$

The crucial difference from the LDA is the definition of $\epsilon_{xc}^{GGA} \equiv \epsilon_{xc}^{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$. This principle can be taken further with higher order derivatives constituting the class of meta-GGA functionals[21]. The GGA exchange-correlation potential can be written as

$$V_{xc}^{GGA}(\mathbf{r}) = \frac{\delta E_{xc}^{GGA}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \epsilon_{xc}^{GGA} + n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{GGA}}{\partial n(\mathbf{r})} + \nabla \left(n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{GGA}}{\partial \nabla n(\mathbf{r})} \right) \quad (2.68)$$

Methods for incorporating the gradient effect into the energy are far more varied than for LDA leading to a great many different functional forms. The most widely used GGA functional is PBE (Perdew, Burke and Ernzerhof)[22]. The PBE functional is used for the majority of calculations presented throughout this body of work. The improvements offered by GGA over LDA come at a relatively small cost due to the fact that the diagonalisation (the most time consuming part of the calculation) is unaffected. GGA is however known to under perform compared to LDA in the prediction of lattice constants and the van der Waals gaps. This is often attributed to the cancellation of errors in LDA.

2.3.3 Hybrids

Hybrid functionals are, as the name suggests, a hybrid between the methods of density functional theory and Hartree-Fock. A critical problem of DFT is an underestimation of the exchange, leading to an underestimation of the bandgap. This problem can be severe in cases where the bandgap is of importance. The hybrid functional represents a method for overcoming this obstacle by incorporating the exact exchange. This allows hybrid functionals to be far more accurate for bandgap

prediction than GGA functionals.

The hybrid mixing can be defined as

$$E_{xc}^{hyb} = \lambda E_x^{HF} + (1 - \lambda) E_x^{DFT} + E_c^{DFT}, \quad (2.69)$$

where E_x^{DFT} and E_c^{DFT} are the exchange and correlation of the DFT functional and E_x^{HF} is the exchange energy calculated through Hartree-Fock. Most methodologies fix the mixing parameter, λ , such that it's value is determined by the choice of hybrid functional.

Hybrid functionals offer improvements over the GGA functionals in predicting bandgaps, lattice constants and phonon frequencies[23]. The enhancements due to hybridisation incur a significant computational cost. This is because of the requirement to calculate the Hartree-Fock exchange and because this in turn effects the diagonalization the cost is much more significant for plainwave calculations. Some of the most common hybrid functionals are PBE0 [24], HSE06 [15] and B3LYP [25, 26]. In this body of work the only hybrid functional utilised is HSE06. This is because HSE is a screened hybrid functional, where long range exchange interaction is truncated, vastly improving performance in large supercells.

2.3.4 Functional Summary

Density functional theory and its predictions are dependent on the quality of the functional used. Ultimately DFT lives or dies on how well it agrees with experiment. While it is easy to recognise that the GGA functional, in principle, represents an improvement over LDA, this will not hold for all crystals. For this reason no functional can be said to be a universal improvement on any other, however, it can be recognised that for the vast majority of cases hybrids represent an improvement over GGA, just as GGA is an improvement over LDA. Further *ab initio* methods

exist, providing improvements over DFT at the cost of ever more computational requirements. Such methods include the quasi-particle GW method [27] and the Quantum Monte Carlo [28].

2.4 Phonons

Phonons are lattice vibrations in the harmonic limit. It is a wave of motion carried by the atoms of a crystal, even its name “phonon” is demonstrative of this property. The word phonon, like the word phonics, indicates that it is a quantised sound wave but it is probably best described as a quasi-particle existing in a specific mode of the lattice with a specific frequency and momentum.

Crucially, phonons are the only modes of vibration permitted within a harmonic crystal and this fact carries many consequences. For instance, consider a frozen crystal in which only a single atom is displaced from equilibrium. When the crystal is released the displaced atom will pull, and be pulled, on, and by, neighbouring atoms. Each of these vibrations is a phonon and will propagate through the crystal. Displacement of a single atom is therefore a linear combination of phonons; more than this, any possible deformation of the lattice must be a linear combination of phonons.

While a phonon is often described as a particle of sound it is more interesting to consider that it can also be described as “a particle of heat”. Heat energy is expressed as the random vibration of atoms in a solid but since the only permitted vibrations are phonons, then heat in harmonic solids is in the form of phonons distributed according to the Bose-Einstein distribution.

2.4.1 The harmonic lattice

In this section we must apply the Adiabatic condition examined in section 2.2.2. This condition is required in order to separate the electronic and ionic wavefunctions. The Hamiltonian for lattice vibration can be extracted from equation 2.23 to give,

$$\hat{H} = T_n + \mathcal{V}. \quad (2.70)$$

In this expression T_n is the ionic kinetic energy operator and \mathcal{V} is the crystal potential energy, which is determined by the electron density. In the absence of ionic motion the system total energy would be determined entirely by the potential \mathcal{V} . This energy would be the ground-state total energy calculated by the solution of the Kohn-Sham equations.

The crystal potential is now expanded with respect to the atomic displacements vector

$$\begin{aligned} \mathcal{V} = \mathcal{V}_0 + \sum_{l\sigma} \sum_{\alpha} \frac{\partial \mathcal{V}}{\partial \vec{u}_{\alpha}(l\sigma)} \vec{u}_{\alpha}(l\sigma) \\ + \frac{1}{2} \sum_{l\sigma l'\sigma'} \sum_{\alpha\beta} \frac{\partial^2 \mathcal{V}}{\partial \vec{u}_{\alpha}(l\sigma) \partial \vec{u}_{\beta}(l'\sigma')} \vec{u}_{\alpha}(l\sigma) \vec{u}_{\beta}(l'\sigma'), \end{aligned} \quad (2.71)$$

here $\vec{u}_{\alpha}(l\sigma)$ is the atomic displacement vector of atom σ in unit cell l with polarisation α . The first term in the expansion is the equilibrium potential, the second term goes to zero, by definition, since equilibrium is a natural turning point. It is the third term, the harmonic potential, that is of most interest here.

We may define the elements of a matrix of second order inter-atomic force constants as

$$\Phi_{\alpha\beta}(l\sigma l'\sigma') = \frac{\partial^2 \mathcal{V}}{\partial \vec{u}_{\alpha}(l\sigma) \partial \vec{u}_{\beta}(l'\sigma')}. \quad (2.72)$$

However, the force constants themselves are not of interest. Lattice dynamics and phonon calculations are predominantly concerned with calculation of phonon fre-

quencies.

To find the phonon dispersion in the harmonic approximation we solve the classical equation of motion,

$$M_\sigma \ddot{u}_\alpha(l\sigma) = - \sum_{l'\sigma'\beta} \Phi_{\alpha\beta}(l\sigma l'\sigma') \vec{u}_\beta(l'\sigma'). \quad (2.73)$$

This equation of motion can be solved by using the phonon displacement vector[29]

$$\vec{u}_\alpha(l\sigma) = \frac{1}{\sqrt{M_\sigma}} \sum_{\mathbf{q}} U_\alpha(\mathbf{q}\sigma) e^{i(\mathbf{q}\cdot\mathbf{r}(l)-\omega t)} \quad (2.74)$$

where $\mathbf{r}(l)$ is the position vector to the unit cell l and t is time. $U_\alpha(\mathbf{q}\sigma)$ is an arbitrary function or operator independent of l .

Substituting equation 2.74 into equation 2.73 and dropping the summation over \mathbf{q} , such that $\mathbf{q} = \mathbf{q}'$, yields

$$\omega^2 U_\alpha(\mathbf{q}\sigma) = \sum_{\sigma'\beta} U_\alpha(\mathbf{q}\sigma) \frac{1}{\sqrt{M_\sigma M_{\sigma'}}} \sum_{l'} \Phi_{\alpha\beta}(l\sigma l'\sigma') e^{i\mathbf{q}\cdot(\mathbf{r}(l')-\mathbf{r}(l))} \quad (2.75)$$

Now it is convenient to apply lattice translational symmetry to reduce the problem. The symmetry of the lattice means that $\Phi_{\alpha\beta}(l\sigma l'\sigma')$ is unchanged upon lattice translation, therefore if we choose to translate by $-l$ then we show

$$\Phi_{\alpha\beta}(l\sigma l'\sigma') = \Phi_{\alpha\beta}(0\sigma(l'-l)\sigma') \quad (2.76)$$

We now let $l' - l$ be represented by l' . Applying this symmetry to equation 2.75, gives

$$\omega^2 U_\alpha(\mathbf{q}\sigma) = \sum_{\sigma'\beta} D_{\alpha\beta}(\sigma\sigma'|\mathbf{q}) U_\beta(\mathbf{q}\sigma') \quad (2.77)$$

where we include the dynamical matrix, $D_{\alpha\beta}(\sigma\sigma'|\mathbf{q})$. We use the vertical bar notation to indicate that the dynamical matrix is set for a fixed value of \mathbf{q} . The

dynamical matrix is defined as

$$D_{\alpha\beta}(\sigma\sigma'|\mathbf{q}) = \frac{1}{\sqrt{M_\sigma M_{\sigma'}}} \sum_{l'} \Phi_{\alpha\beta}(0\sigma l'\sigma') e^{i\mathbf{q}\cdot\mathbf{r}(l')} \quad (2.78)$$

As with the secular equation we can determine non-trivial solutions using the determinant,

$$\det|D_{\alpha\beta}(\sigma\sigma'|\mathbf{q}) - \omega^2 \delta_{\alpha\beta} \delta_{\sigma\sigma'}| = 0. \quad (2.79)$$

If we consolidate the directional index and the atomic index, we can easily represent this as a matrix equation. Since α can only be 1, 2, 3 or x, y, z it is straight forward then to change to an index over σ_α .

$$\vec{U}(\mathbf{q}) = \left(U(\mathbf{q}\sigma_x), U(\mathbf{q}\sigma_y), U(\mathbf{q}\sigma_z), U(\mathbf{q}(\sigma+1)_x), U(\mathbf{q}(\sigma+1)_y), U(\mathbf{q}(\sigma+1)_z) \dots \right) \quad (2.80)$$

Using this vector across atomic directions, equation 2.79 can be represented in matrix form, as

$$\vec{U}(\mathbf{q})\mathbf{D}(\mathbf{q}) = \vec{U}(\mathbf{q})\omega^2 \quad (2.81)$$

It is clear from this that to find the phonon frequencies of a structure, described by a set of force constants, one must diagonalise the dynamical matrix. The eigenvalues of the dynamical matrix are the squared angular frequencies. A negative eigenvalue would indicate an atomic directions vector, $\vec{U}(\mathbf{q})$, that returns a positive force i.e. one that does not push the atoms back to the equilibrium positions and therefore fulfills the conditions of an unstable crystal structure.

The difficulty in calculating a phononic structure lies in determining the inter-atomic force constants, $\Phi_{\alpha\beta}(0\sigma l'\sigma')$.

2.4.2 Phonon *ab initio* Calculation Methods

There are three typical *ab initio* methods for the calculation of phonon modes. They are: the frozen phonon method, the planar force constant method and the linear response method also called density functional perturbation theory (DFPT).

The frozen phonon method involves taking static atomic arrangements at small displacements away from equilibrium. Each small displacement corresponds to a "frozen" vibrational mode. Either by calculating second order changes in energy or more easily calculating the inter-atomic force constants matrix. This can then be used to determine the dynamical matrix. This methodology is adopted, for calculations within this work and is described in detail in section 2.4.3.2.

A simplified approach to the problem is offered by the planar force constant model. If we consider a q-vector, then we may define a series of atomic plains perpendicular to that vector (let there be N plains). A vibrational mode corresponding to the considered q-vector will excite either perpendicular or parallel displacements within those plains. This means that the plains are acting as single rigid bodies, each connected to it's neighbors by inter-planar force constants. A force equation can therefore be written for the n 'th plain,

$$-\vec{F}(n) = k_n \vec{U}_0, \quad (2.82)$$

where \vec{U}_0 is the displacement of the zeroth plain and k_n is the force constant between plain 0 and n . A more detailed description of the planar force constant model is provided by Srivastava 1990[29].

The linear response method is described breffly here following the method of Giannozzi *et al.*[30]. In this approach a distortion, u to the lattice can be seen as a static perturbation acting on the electrons. By consideration of the Hellmann-Feynman theorem (see 2.4.3.1) linear variation of the electron density (due to a

static perturbation) determines the second order variation in energy. The electronic energy may be written,

$$E(\mathbf{u}) = E(0) + \delta E(\mathbf{u}\Delta n) \quad (2.83)$$

where Δn is the static change in the charge density. This change in the total energy will lead to a change in the force constants matrix which is entirely determined by the ionic cores and electron density. The ionic component may be determined trivially however the electronic component requires the careful application of the Hellmann-Feynman theorem and can be given as

$$\Phi_{\alpha\sigma\beta\sigma'}(l - l') = \int \frac{\partial n(\mathbf{r})}{\partial u_{\alpha\sigma}(l)} \frac{\partial \mathcal{V}(\mathbf{r})}{\partial u_{\alpha\sigma'}(l')} + n_0(\mathbf{r}) \frac{\partial^2 \mathcal{V}(\mathbf{r})}{\partial u_{\alpha\sigma}(l) \partial u_{\alpha\sigma'}(l')} d\mathbf{r}. \quad (2.84)$$

Here n_0 is the electron density of the unperturbed system and $\partial n / \partial u$ is the electronic response. This provides a means to calculate the force constants matrix. Within the framework of DFT the electronic potential $\mathcal{V}(\mathbf{r}) = V_{KS}(\mathbf{r})$. The self consistent Kohn-Sham potential can be written

$$V_{KS}(\mathbf{r}) = V_{ps}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(n(\mathbf{r})), \quad (2.85)$$

Where V_{ps} is the ionic potential (derived from the pseudopotentials), the second term is the electronic potential and the third term, $V_{xc}(n(\mathbf{r}))$, is the exchange correlation potential. Using density functional perturbation theory one can define the Kohn-Sham potential response to a perturbation as $V_{KS} \rightarrow V_{KS} + \Delta V_{KS}$. To evaluate different elements of the harmonic force constants matrix two values must be found; they are $\Delta n(\mathbf{r})$ and $\Delta V_{KS}(\mathbf{r})$. The Fourier components of $\Delta n(\mathbf{r})$ can be expressed as

$$\Delta n(\mathbf{q} + \mathbf{G}) = \frac{4}{N_0\Omega} \sum_{\mathbf{k}} \sum_{v,c} \left[\frac{\langle \psi_{v,\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{c,\mathbf{k}+\mathbf{q}} \rangle \langle \psi_{c,\mathbf{k}+\mathbf{q}} | \Delta V_{KS} | \psi_{v,\mathbf{k}} \rangle}{\epsilon_{v,\mathbf{k}} - \epsilon_{c,\mathbf{k}+\mathbf{q}}} \right], \quad (2.86)$$

where Ω is the unit cell volume, N_0 is the number of unit cells, G is a reciprocal lattice

vector and ε is the energy eigenvalue at k-point \mathbf{k} and of either the conduction (c) or valence band (v). The perturbation induced change in the electronic Kohn-Sham potential can be written,

$$\Delta V_{KS}(\mathbf{r}) = \Delta V_{ps}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \Delta n(\mathbf{q}) \left[\frac{dV_{xc}(n(\mathbf{r}))}{dn} \right]_{n=n_0} \quad (2.87)$$

These equations are generated from density functional linear response theory[30]. The equations for $\Delta n(\mathbf{r})$ and $\Delta V_{KS}(\mathbf{r})$ solved iteratively. This provides the input values necessary for the calculation of the elements of the dynamical matrix.

2.4.3 Calculating Inter-atomic Force Constants

When calculating the inter-atomic force constants matrix, it is important to understand the inherent symmetries the matrix contains. This understanding reduces the number of terms that must be explicitly calculated (alternatively, it could be used to as an error check). Hence it is important to understand the self term.

$$\Phi_{\alpha\beta}(0\sigma l'\sigma') = - \sum_{l'\sigma' \neq 0\sigma} \Phi_{\alpha\beta}(0\sigma l'\sigma') \quad (2.88)$$

Here, i the condition that the force on an atom due to a displacement x must be equal to the force on all other atoms displaced $-x$.

Another useful property of the inter-atomic force constants is that they remain unchanged under an exchange of indices

$$\Phi_{\alpha\beta}(0\sigma l'\sigma') = \Phi_{\alpha\beta}(l'\sigma'0\sigma), \quad (2.89)$$

This naturally extends to the dynamical matrix $[\mathbf{D}(q)]^T = \mathbf{D}(q)$, which informs the diagonalisation routine.

2.4.3.1 Hellmann Feynman Forces

In order to calculate the force constants on atoms it is useful to have a method for force calculation from DFT. To do this we examine the Hellmann-Feynman forces[31].

In a quantum system, energy is well defined.

$$\langle E \rangle = \int \varphi^*(\mathbf{r}) \hat{H} \varphi(\mathbf{r}) d^3r \quad (2.90)$$

However, to establish a clear, well defined , quantum version of force we can look at the classical definition. Ehrenfest's theorem defines force in a time dependent system[32] but here we explore precisely a molecular systems of atoms, in the time independent case.

Classically,

$$F_\lambda = -\frac{d\mathcal{V}}{d\lambda} \quad (2.91)$$

where \mathcal{V} is the crystal potential energy, λ is just one of any number of parameters which specify nuclear positions. A force F_λ corresponds with λ such that $F_\lambda d\lambda$ measures the work done in displacing the nuclei by $d\lambda$

As has been stated, energy in a quantum system is well defined. In order to move from the classical frame, we replace the variable for energy with the Hamiltonian.

$$F_\lambda = -\left\langle \varphi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \varphi \right\rangle \quad (2.92)$$

Alternatively, we might take $\langle E \rangle$ as the average energy and describe force as,

$$F_\lambda = -\frac{\partial \langle E \rangle}{\partial \lambda} \quad (2.93)$$

We shall follow the method of Feynman[31] and show that each of these definitions

of force is the same, and so demonstrate that all forces on atoms can be treated as classical interactions via the Coulomb law.

Employing the product rule to expand equation 2.93, returns

$$\frac{\partial \langle E \rangle}{\partial \lambda} = \left\langle \varphi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \varphi \right\rangle + \left\langle \frac{\partial \varphi}{\partial \lambda} \left| \hat{H} \right| \varphi \right\rangle + \left\langle \varphi \left| \hat{H} \right| \frac{\partial \varphi}{\partial \lambda} \right\rangle. \quad (2.94)$$

In accordance with our objectives, we wish to show that the final two terms go to zero. The Hamiltonian is a self adjoint,

$$\left\langle \varphi \left| \hat{H} \right| \frac{\partial \varphi}{\partial \lambda} \right\rangle^\dagger = \left\langle \frac{\partial \varphi^*}{\partial \lambda} \left| \hat{H} \right| \varphi^* \right\rangle \quad (2.95)$$

we may also use the fact that $\hat{H} |\varphi^*\rangle = E |\varphi^*\rangle$ to show

$$\frac{\partial \langle E \rangle}{\partial \lambda} = \left\langle \varphi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \varphi \right\rangle + E \left[\left\langle \frac{\partial \varphi}{\partial \lambda} \left| \varphi \right\rangle + \left\langle \varphi \left| \frac{\partial \varphi}{\partial \lambda} \right\rangle \right] \quad (2.96)$$

Now a simple inverse product rule shows,

$$\begin{aligned} \frac{\partial \langle E \rangle}{\partial \lambda} &= \left\langle \varphi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \varphi \right\rangle + E \frac{\partial}{\partial \lambda} [\langle \varphi | \varphi \rangle] \\ \frac{\partial \langle E \rangle}{\partial \lambda} &= \left\langle \varphi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \varphi \right\rangle \end{aligned} \quad (2.97)$$

We can now define a consistent quantum mechanical force using equation 2.23

$$\frac{\partial \hat{H}}{\partial \lambda} = \frac{\partial \mathcal{V}(\lambda)}{\partial \lambda} = -F_\lambda \quad (2.98)$$

This justifies us in using classical Coulombic charge interaction to find the inter-atomic force constants.

In the context of DFT the Hellmann-Feynman forces represent a viable method for the calculating of atomic forces. The principle that forces can be properly calculated as a classical Coulomb interaction enables us to calculate atomic forces from

the charge density and ionic cores. Because charge density is exact, in principle, so will the atomic forces be exact.

2.4.3.2 Frozen Phonon Method

The frozen phonon method is built upon the application of the Hellmann-Feynman forces. In a crystal structure the force on an atom may be written,

$$F_\alpha(l\sigma) = -\frac{\partial \mathcal{V}}{\partial u_\alpha(l\sigma)}, \quad (2.99)$$

hence,

$$\Phi_{\alpha\beta}(0\sigma l'\sigma') = \frac{\partial^2 \mathcal{V}}{\partial u_\alpha(0\sigma) \partial u_\beta(l'\sigma')} = \frac{\partial F_\beta(l'\sigma')}{\partial u_\alpha(0\sigma)}. \quad (2.100)$$

Here, we are able to determine the forces on atoms by displacements of atoms, only, within the primitive cell. We then apply a finite difference method to solve the derivative.

$$\Phi_{\alpha\beta}(0\sigma l'\sigma') = \frac{F_\beta(l'\sigma'; \Delta u_\alpha(0\sigma)) - F_\beta(l'\sigma'; 0)}{\Delta u_\alpha(0\sigma)} \quad (2.101)$$

where we define $F_\beta(l'\sigma'; \Delta u_\alpha(0\sigma))$ as the force in the β direction, on atom σ' , in unit cell l' , evaluated at the displacement $u_\alpha(0\sigma)$, of atom σ in direction α . For a system with a perfectly relaxed atomic geometry $F_\beta(l'\sigma'; 0)$ would have a zero value.

2.4.4 Phonon Summary

It has been shown that the Hellmann-Feynman forces can be extracted from a DFT calculation. It has further been demonstrated that the frozen phonon method may utilise the Hellmann-Feynman forces to determine the interatomic force constants matrix. An exploration of the harmonic lattice gives the relationship between interatomic force constants and the dynamical matrix. For any given \mathbf{q} vector within the Brillouin zone the dynamical matrix may be diagonalised to obtain the squared

angular frequencies and associated atomic displacements. Hence, from the theories presented here, can a full phononic dispersion relation can be calculated.

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