

Calculating Excited States of Condensed Matter

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Declaration of Originality

I declare that the following thesis is my own original work, written under the guidance of my supervisors Dr. L. Bernasconi and Prof. N. M. Harrison. To the best of my knowledge, all currently published data, figures and statements have been referenced in accordance to the guidelines of Imperial College London. Some results within this thesis have been published in the following articles:

Optical Response of Extended Systems from Time-Dependent Hartree-Fock and Time-Dependent Density-Functional Theory, *J. Phys.: Conf. Ser.*, **367**, 012001, 2012.

Optical Properties of Alkali-Halide Crystals from All-Electron Hybrid TD-DFT Calculations, *J. Chem. Phys.*, **142**, 214705, 2015.

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APS March Meeting 2015, San Antonio, TX. (*Presentation*).

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CECAM conference “Calculating Optical Properties of Nanostructures from First Principles”, Lausanne, CH. (*Presentation & poster*),

and are acknowledged accordingly in this work.

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I dedicate this work to them.

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“All that glitters may not be gold, but at least it contains free electrons.”

- J. D. Bernal

Abstract

The accurate and reliable prediction of the optical properties of extended systems is a powerful tool for the development of nanostructured optical devices, such as photovoltaic materials. One major challenge faced by excited-state electronic structure methods is the treatment of the two-particle electron-hole interaction which is a key component of optical response properties such as optical absorption and charge transport.

In this work we first study the effect of choice of basis set on both ground-state and first-order response properties, extending the molecular studies of Rappoport *et al.* into periodic and crystalline systems. From the conclusions of this basis set study, we employ a series of polarisation-optimised basis sets to calculate the optical gaps of the alkali halide series AX (where A = Li, Na, K, Rb and X = F, Cl, Br). Secondly, we assess the applicability of a range of methods (HF, LDA, PBE and B3LYP) for excited state calculations of extended systems, and examine the dependence of optical properties on the contribution of Hartree-Fock exchange (c_{HF}) to the linear-response TD-B3LYP kernel. We find that TD-B3LYP underestimates both the fundamental gap (E_g) and optical gap (E_o) in comparison to experimental work, and we show that the optical gap can be reproduced at least quantitatively with $c_{HF} \simeq 0.3$.

The last chapter of this work focusses on the calculation of electronic and optical properties of single-walled carbon nanotubes (SWCNTs). We study the effect of geometry relaxation, curvature, basis set and method on one-electron and linear-response properties, comparing our findings to other theoretical and experimental works. Our study shows that B3LYP is able to accurately and reliably calculate the ground-state electronic properties of a large range of nanotubes ($<2\text{-}46$ Å in diameter). Through our geometry optimisations and studies on nanotube diameter, we observe the curvature effect on the qualitative and quantitative properties of the van Hove singularities and Density of States of SWCNTs. We find that TD-B3LYP produces values of E_o that are in good agreement with experimental measurements and GW-BSE calculations, for both metallic and semiconducting nanotubes, however the estimated exciton binding energies for our calculations, E_b (where $E_b = E_g - E_o$) are in poor agreement with previous theoretical calculations. This is likely due to our comparison of two-particle (E_o) values and roughly-estimated values of E_g from single-particle eigenvalues.

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1

Introduction

1.1 Modelling Excited States

Global energy consumption has been increasing over the last 30 years [1]. However, the contribution from renewable energy sources has not grown accordingly and non-renewable energy sources (by definition) are unsuitable for long-term energy production (it is estimated that 35 years of gas reserves remain, for example) [2]. Current methods of extracting energy from most non-renewable sources release carbon dioxide, and contribute directly to climate change [3,4], which has prompted international schemes and policies [2,5] aimed at reducing carbon dioxide emissions. The long-term results of such legislations are unknown, but it has prompted development of 'greener' processes, such as improved methods for carbon capture and storage (*carbon sequestration*) [6].

In addition to reducing carbon dioxide emissions from current energy sources, there is great interest in energy sources which do not produce any waste CO₂ during their operation, *e.g.* renewable energy sources. Solar energy is a popular choice of renewable energy due to the high potential output and lack of carbon emissions [7], however there are hindrances to the spread of existing photovoltaic technology, such as low efficiencies and high costs [8]. Experimental research on optical and photovoltaic systems can be expensive and time-consuming due to material purity and device fabrication, and one approach to this problem is the use of theoretical simulations to directly supplement experimental work. Furthermore, the use of experimental measurements to improve the accuracy of theoretical models can in turn result in more accurate and reliable methods and techniques, leading to reduced costs and the discovery of novel materials.

The independent particle approximation (where each electron can be treated independently of one another) allows for the application of electronic structure methods to large systems (> 1000 atoms), without a significant loss of accuracy. These *one-particle*

calculations can provide accurate electronic, structural and vibrational properties and there are many electronic structure methods available [9]. Density Functional Theory (DFT) is an example of a one-particle method. However, not all properties of a system can be calculated from the nuclear and electronic structures alone - many properties depend on an external influence, such as an electric or magnetic field, and are known as response properties. When used to describe the response of an electronic structure to a perturbation (*i.e.* a time-varying electric field), one-particle methods can provide inexact results; for some specific response properties such as the optical response, a many-body method is required.

There are many variations in the design, structure and components of modern photovoltaic systems, but they all follow the same basic principle - photoabsorption which initiates the motion of electrons through a circuit. Due to the wide variety of approaches to solar energy, the mechanisms of photoabsorption and charge-transport differ for each system, and are often not well understood. A good understanding of the electronic interactions inside a photovoltaic system can lead to optimised and tuned properties. The ability of one-particle methods to 'solve' this problem is limited, as many stages of a photovoltaic cycle involve explicit interactions between electrons and holes (*i.e.* charge-separation and recombination) and have a large effect on the overall device efficiency. Using two-particle methods, the individual processes of a photovoltaic cycle (*i.e.* photoabsorption) can be studied accurately, ultimately leading to the optimisation of experimental devices, resulting in decreased costs and increased efficiencies.

However, unlike one-particle methods which have been tested and developed over 80 years [9], the choice of method for many-body property calculations is limited - in a general sense, the most accurate response calculations are also more computationally expensive. In addition to the time/power constraint, each excited state method has advantages and disadvantages, often similar to those of the parent ground-state calculations (Section 2). As such, the development of response methods is a very active field - the search for a reliable approach to calculating response properties which has suitable accuracy *and* cost is not a trivial task.

1.1.1 Excited State Calculations for Extended Systems

Several high-level quantum chemistry methods are available for excited state calculations of molecules and small clusters of atoms, such as the multiconfigurational methods CASSCF [10] and CASPT2 [11]. However, the number of *configuration state functions* required for accurate calculations is very large, and so their use is restricted to small systems ($\lesssim 10$ electrons).

For excited state calculations in the condensed phase, there are currently two options available - GW-BSE and TD-DFT. An extensive review and comparison of these two methods can be found in the work by Onida *et al.* [12], for example.

GW-BSE

The GW-BSE method [13–15] is a many-body Green’s-function approach to one and two-electron excitations. Although originally devised as a post-HF method to screen the long-range exchange interaction, the GW approximation is now commonly used to compute quasi-particle excitation energies from one-electron DFT orbitals. Many-body perturbation methods rely on calculating the self-energy of the electrons - the contribution to each electron’s energy from interactions between itself and the system (*i.e.* exchange and correlation effects). Hedin’s GW theory [13] proposes that the self-energy can be found through a Taylor expansion of the self-energy into single-particle Green functions, G and the Coulomb interaction, W [14]. The corrections from the GW approximation lead to a shift in the HF or DFT eigenvalues, making GW a popular inclusion for band structure calculations.

The Bethe-Salpeter Equation (BSE) [15] is formally a method used to solve the equations of motion for a two-particle Green’s function, and is used to describe the interactions between electrons and holes. This approach is often implemented after GW calculations to compute the optical properties (*e.g.* excited state energies) of a system. However, the BSE is a computationally expensive approach to a many-body problem due to four-point equations [12] and is at present impractical for large systems.

TD-DFT

This work is focussed primarily on the application of time-dependent density functional theory (TD-DFT) to calculate the optical properties of systems. TD-DFT is a generalisation of ground state DFT, treating systems under the influence of a perturbing external potential, and similarly to DFT, TD-DFT relies on the electron density $\rho(\mathbf{r}, t)$ to create formally exact descriptions of many-body states. However, in practicality, DFT calculations require an approximation to the exchange-correlation energy E_{xc} , which is dependent on the choice of exchange-correlation functional. Analogous to the exchange-correlation functional of DFT, TD-DFT requires a choice of exchange-correlation kernel (f_{xc}) to accurately describe the response to an external perturbation. The relationship between the E_{xc} and f_{xc} can be defined [16] as

$$f_{xc}[\rho](\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta V_{xc}[\rho](\mathbf{r}_1)}{\delta \rho(\mathbf{r}_2)} = \frac{\delta^2 E_{xc}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}, \quad (1.1)$$

where V_{xc} is the exchange-correlation potential (Section 2.3). If the external potential is weak, the response of the electron density to the perturbation can be linearised (Section 2.7.2). This linear-response approach (although the simplest approximation to the response) can produce accurate results for a range of systems, provided sufficiently robust response kernels are employed [17, 18]. The response kernel of a TDDFT calculation is therefore dependent on both the choice of f_{xc} , and any assumption of linear behaviour (*i.e.* a linear-response kernel will be different to a quadratic-response kernel, from the same f_{xc}).

In this work we focus on the ability of the non-empirical exchange-correlation hybrid functional B3LYP to predict response properties and the formation of bound excitons [19–21].

1.2 Optical Absorption

1.2.1 Excitons

Upon the absorption of a photon, an electron situated in an occupied orbital i can be promoted to a virtual (unoccupied) orbital a . This leaves a positive ‘hole’ in the donor orbital (or band), which can interact with the excited electron. This two-body electron-hole pair is known as an exciton.

We can roughly estimate the energy of a photon required for an excitation by finding the difference in energies of i and a . If i is the HOMO and a the LUMO, we call this difference in energy the *energy gap* or *fundamental gap*, E_g . Within crystalline systems, the HOMO and LUMO are the valence band maximum and conduction band minimum, respectively. There is a variety of experimental methods through which the energy gap can be measured. The most direct method for obtaining the experimental value of E_g is the combination of photo-emission spectroscopy (PES) and inverse photo-emission spectroscopy (IPS), which can yield the energies of the HOMO and LUMO, respectively. However, this method is rarely used and so experimental values of the band gap are usually inferred from other measurements. A common method is to conduct UV-Visible spectroscopy and treat the absorbance edge as the energy gap [22]. This is often unclear, as seen in Roessler and Walker’s work on LiF [23] (Section 3), as the exact onset of absorption can be masked by adjacent peaks. Other procedures include the extrapolation of temperature-dependent electronic properties (e.g resistivity), which for

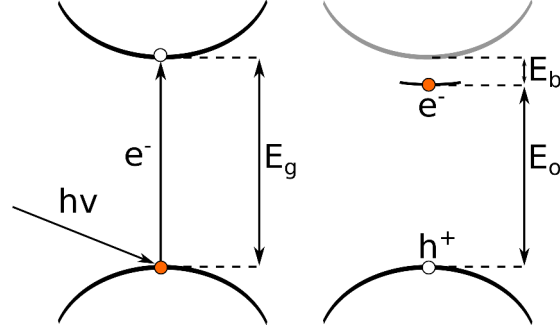


Figure 1.1: Example of optical gap and exciton binding.

a range of simple 3-5 and elemental semiconductors yields results in agreement with spectroscopic methods [24, 25].

The interaction between the excitonic electron and hole can cause a shift in the one-particle orbital energies, resulting in the generation of a new electronic state [12], lower in energy than the unoccupied states. The lowest-energy transition is now between the valence band maximum and the newly-created excitonic state, and as a consequence of this, the lowest-energy excitation is now smaller than (or equal to) E_g . This smaller gap is the optical gap E_o , and the difference between the energy gap and optical gap is the exciton binding energy E_b , such that $E_o = E_g - E_b$. Such excitonic phenomena appear in optical spectra as intense peaks, lower in energy than the absorption onset. The reason for the reduced linewidth in comparison to peaks within the absorption continuum is a low degree of interaction between the exciton and the surrounding environment, as impurities in the system, or acoustic and optical phonons [26] (for example) can result in line-broadening. Although E_g can be calculated with a one-particle method, as it is the difference in energy between two one-particle orbitals, the optical gap cannot, due to the required interaction between both an electron and hole. When the donor and acceptor orbitals are spatially separated (i.e. on different atoms), two different species of exciton arise.

Wannier Excitons

When the interaction between electron and hole is strongly shielded (*i.e.* in a high dielectric constant material) the electron is delocalised over a large radius from the hole, resulting in a small exciton binding energy ($E_b \approx 0.01\text{-}0.1$ eV).

The electron-hole pair of a Wannier exciton can be modelled as a hydrogenic system - an electron orbiting a positive point charge. This means that a series of excitonic peaks

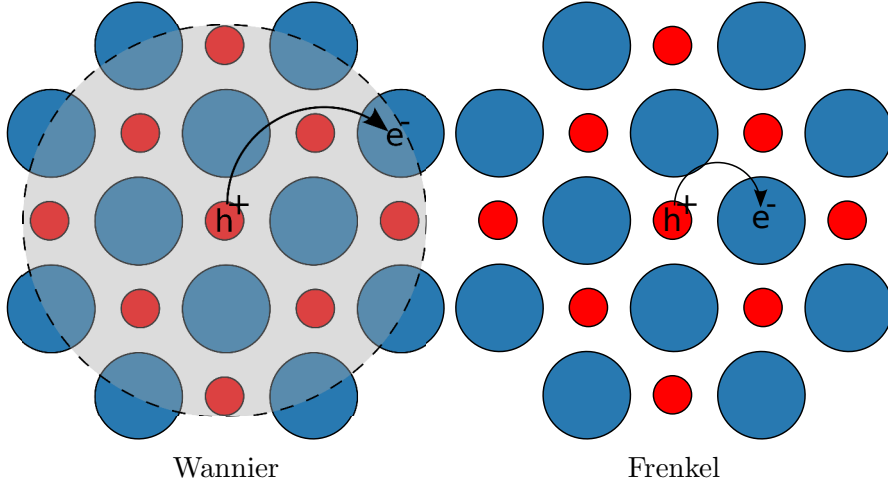


Figure 1.2: Idealised exciton classes.

can be evident in optical spectra, akin to the Rydberg series of hydrogen which can be predicted using the Rydberg formula, Eqn. (1.2), where R_H is the Rydberg constant, and f/i are the principal quantum numbers of the final and initial shells respectively. As the Rydberg equation is strictly only valid for hydrogen-like atoms, such phenomena in crystalline systems are described by the Wannier formula [27], Eqn. (1.3), where ψ_v is the excitonic wavefunction, m_r is the reduced (effective) mass of the conduction and valence band electrons, and $V(\mathbf{r})$ is the dielectric-screened (ϵ) Coulombic interaction between the electron and hole [28]. These peaks denote Wannier excitons of energies between E_o and E_g , caused by the dynamic coupling of the excitation within the crystal [28].

$$E = R_H \left(\frac{1}{f^2} - \frac{1}{i^2} \right) \quad (1.2)$$

$$\begin{aligned} E_b \psi_v(\mathbf{r}) &= \left[-\frac{\nabla^2}{2m_r} + V(\mathbf{r}) \right] \psi_v(\mathbf{r}) \\ m_r^{-1} &= m_c^{-1} - m_v^{-1} \\ V(\mathbf{r}) &= \frac{1}{\epsilon r} \end{aligned} \quad (1.3)$$

Frenkel Excitons

When the interaction between electron and hole is weakly shielded (*i.e.* in a low dielectric constant material) the strong electron-hole interaction causes a low-radius, tightly-bound exciton pair to form, with a large exciton binding energy ($E_b \geq 1$ eV) [29, 30].

One of the largest challenges faced in excited state calculations is the modelling of bound excitons, and it has been shown in previous work [31–33] that in order to describe bound excitonic states correctly, the method needs to account for the non-local response to the perturbation. In addition, excited-state calculations are built upon a framework of single-particle orbitals, and accurate values for the single-particle orbital energies are difficult to obtain from current methods. The aim of this work is to assess the reliability of common time-dependent kernels (see Section 2.7.1), primarily for the case of excited state phenomena, such as excitonic states. To do this, we study the optical properties of a range of systems using the **CRYSTAL** software suite, which is known to describe non-local effects of extended systems efficiently.

We have chosen a range of systems to study due to the variety of system-dependence on the nature of the exciton. For example, the excitons within the bulk crystalline alkali halides are known to share properties of both Frenkel and Wannier models (see Section 3), whilst the pseudo one-dimensionality of carbon nanotubes should lead to a unusually low number of allowed excitations (see Section 4). An ideal excited state method will be both reliable and accurate, and in this work we compare both ground state and excited state properties to experimental measurements and data from other theoretical approaches.

2

Methodology

2.1 Quantum Mechanics

The ground-state properties of an n -electron system can be described by solving the corresponding *time-independent* Schrödinger equation, represented in a simple form as

$$E\Psi = \hat{H}\Psi. \quad (2.1)$$

This means that for a wavefunction Ψ , the total energy E can be found through solutions of the Hamiltonian operator $\hat{H}$ for that wavefunction. Using atomic units ($e^2 = \hbar = m_e = 1$), the time-independent non-relativistic Hamiltonian operator under the Born-Oppenheimer approximation can be written as

$$\begin{aligned} \hat{H} = & \sum_A^N \sum_{B>A}^N \frac{Z_A Z_B}{|\mathbf{R}_{AB}|} \\ & + \sum_i^n \left(-\frac{\nabla_i^2}{2} + \sum_A^N \frac{-Z_A}{|\mathbf{R}_{iA}|} \right) \\ & + \sum_i^n \sum_{j>i}^n \frac{1}{|\mathbf{r}_{ij}|}. \end{aligned} \quad (2.2)$$

The Hamiltonian operator can be split into three parts, based on the number of electronic coordinates required for each interaction, as shown in Eqn. (2.2) where N is the total number of nuclei, n is the total number of electrons, and Z_A and Z_B are the charges of nuclei A and B, respectively. The first term of Eqn. (2.2) is the nuclear interaction energy for the nuclei A and B at a separation of $\mathbf{R}_{AB}$, and is a zero-electron

term. Two separate one-electron interactions are described in the second term - the kinetic energy of electron i , and the potential energy between electron i and nucleus A at a distance of $\mathbf{R}_{iA}$. The final term is the two-electron contribution to the Hamiltonian, and is the potential energy between electron i and j , at the distance $\mathbf{r}_{ij}$.

This is a time-independent operator as the interactions are only dependent on the electronic and nuclear structure. The Born-Oppenheimer (BO) approximation states that electronic motion can be treated independently of nuclear motion, allowing the separation of the wavefunction into an electronic and nuclear part, such that

$$\Psi(n, N) = \Psi_{el}(n, N) \Psi_{at}(N). \quad (2.3)$$

In this work we will use the BO approximation, focussing on the electronic part of the total wavefunction and Hamiltonian, and we suppress the el index.

2.2 The Hartree-Fock Method

The Hartree-Fock (HF) method can be used to approximate the many-body wavefunction of an n -electron system by treating the wavefunction as the antisymmetrised Hartree product of n one-electron spin-orbitals, also known as a Slater determinant (Eqn. (2.4)). Different representations of a Slater determinant are commonly used; in the equation below, the numbers in parentheses are electron indices, the elements with bars are β -spin, and those without are α -spin.

$$\Psi^{(0)} = \frac{1}{\sqrt{n!}} \begin{vmatrix} a(1) & \bar{b}(1) & c(1) & \dots \\ a(2) & \bar{b}(2) & c(2) & \\ a(3) & \bar{b}(3) & c(3) & \\ \dots & & & \dots \end{vmatrix} \quad (2.4)$$

A wavefunction is antisymmetrical when the exchange of two electrons causes the sign of the wavefunction to swap,

$$\Psi(1, 2, 3, \dots, n) = -\Psi(1, 3, 2, \dots, n). \quad (2.5)$$

This is to ensure compliance with Pauli's exclusion principle which states that two electrons cannot occupy the same spin-orbital. The antisymmetric restriction on the wavefunction creates an 'exchange hole' around each electron, where same-spin electrons cannot exist.

Applying the Hamiltonian operator to a single Slater determinant leads to the

Hartree-Fock equation,

$$\hat{F}(1)\phi_i(1) = \epsilon_i\phi_i(1), \quad (2.6)$$

where $\hat{F}$ is the Fock operator, ϕ_i is the i^{th} spin-orbital, and the eigenvalue ϵ_i is the orbital energy of ϕ_i . The Fock operator is the effective form of the Hamiltonian operator for the Hartree-Fock method, and the two-electron contribution to the operator can be separated into the Coulomb integral J_{ij} and Exchange integral K_{ij} , as shown in Eqn. (2.7) where the “bra”-“ket” (also known as Dirac) notation is used to express the functions ϕ_i and ϕ_j [34],

$$\begin{aligned} \hat{F}(1) &= \left(-\frac{\nabla_1^2}{2} + \sum_A^N \frac{-Z_A}{|\mathbf{R}_{1A}|} \right) + \sum_{j=1}^n (2\hat{J}_j(1) - \hat{K}_j(1)) \\ \hat{J}_j(1) &= \langle \phi_j(2) | \frac{1}{r_{12}} | \phi_j(2) \rangle \\ \hat{K}_{ij}(1)\phi_i(1) &= \langle \phi_j(2) | \frac{1}{r_{12}} | \phi_i(2) \rangle \phi_i(1). \end{aligned} \quad (2.7)$$

We solve the Hartree-Fock equations using a self-consistent procedure, as $\hat{F}$ is dependent on the Fock orbitals which are in turn described by $\hat{F}$ [35]. This method is known as the self-consistent field (SCF), and details regarding the SCF within **CRYSTAL** can be found in Section 2.4.2. In Hartree-Fock theory, instead of evaluating the instantaneous electronic interactions, each electron only interacts with the mean field generated by the other $n - 1$ electrons. Because of the mean field approximation, the correlated motions of same-spin electrons are negligible.

2.3 Density Functional Theory

Density functional theory (DFT) is a formally exact method to calculate the energy of a many-electron system. Unlike HF, DFT allows one to compute the total energy of a system from the knowledge of the ground state electron density (ρ_0) alone, removing the requirement of the computationally expensive wavefunction. In this work, we will omit the ground-state index of the density ($\rho = \rho_0$). This means that the total energy is a functional of the electron density ($E[\rho]$), instead of the ground-state many-electron wavefunction, as proven by the Hohenberg-Kohn (HK) theorems [36].

To solve the DFT equations, the Kohn-Sham (KS) approximation [37] is used. The Kohn-Sham approach to DFT requires the introduction of non-interacting orbitals

which are under the influence of an external potential, such that the density of the Kohn-Sham system becomes equal to that of the interacting system.

The Kohn-Sham hamiltonian can be written as

$$\begin{aligned}\hat{H}_{KS} &= -\frac{\nabla^2}{2} + \hat{V}_{KS}(\mathbf{r}), \\ \hat{V}_{KS}(\rho) &= \hat{V}_{ext}(\mathbf{r}) + \hat{V}_H(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r}),\end{aligned}\tag{2.8}$$

where $\hat{V}_{ext}(\mathbf{r})$ is the external potential

$$\hat{V}_{ext}(\mathbf{r}_1) = \sum_A^N \frac{-Z_A}{\mathbf{r}_{1A}},\tag{2.9}$$

$\hat{V}_H(\mathbf{r})$ is the Hartree potential

$$\hat{V}_H(\mathbf{r}_1) = \int \frac{\rho(\mathbf{r}_2)}{\mathbf{r}_{12}} d\mathbf{r}_2,\tag{2.10}$$

and $\hat{V}_{xc}(\mathbf{r})$ is the exchange-correlation potential

$$\hat{V}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}.\tag{2.11}$$

The exchange-correlation energy functional $E_{xc}[\rho]$ originates from the sum of the errors made in the approximations of the Kohn-Sham method - the non-interacting kinetic energy, and the classical treatment of the two-electron interaction [38],

$$E_{xc}[\rho] = (\overline{T}[\rho] - \overline{T}_s[\rho]) + \left(\overline{V}_{ee}[\rho] - \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \right),\tag{2.12}$$

where $\overline{T}[\rho]$ is the kinetic energy of the system, $\overline{T}_s[\rho]$ is the kinetic energy of the reference non-interacting system, and $\overline{V}_{ee}[\rho]$ is the inter-electronic potential of the system.

The exchange-correlation energy is a universal functional of the density, but it is unknown. DFT calculations are often classified by the method used to calculate E_{xc} , as despite being a relatively small term for most systems, the exchange-correlation energy is crucial for accurate KS DFT calculations.

2.3.1 LDA

The Local Density Approximation (LDA) uses the exchange and correlation energies of a homogeneous electron gas to predict a suitable E_{xc} [37]. E_{xc}^{LDA} is only accurate for systems which have a slowly varying n . Whereas the exchange energy E_x^{LDA} of the homogeneous electron gas can be found analytically for all values of n [39, 40] (Eqn. 2.13), the correlation energy E_c^{LDA} cannot, and must be derived numerically [41]. This parameterisation of E_{xc}^{LDA} , where $E_{xc}^{LDA} = E_x^{LDA} + E_c^{LDA}$ has lead to many variations of the LDA method,

$$E_x^{LDA} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int [n(r)]^{4/3} d\mathbf{r}. \quad (2.13)$$

LDA can give reasonably accurate predictions for a number of properties such as geometries of molecules, but it largely underestimates E_g [42]. This is a consequence of an effect called *self-interaction*, where an electron's contribution to the density at r_1 interacts with that electron's other contributions to n throughout the system [38].

2.3.2 GGAs

Whereas E_{xc}^{LDA} depends only on ρ , the generalised-gradient approximation (GGA) generates a value for E_{xc} which depends on both the absolute value and the gradient of ρ . There are many approaches to the GGA methodology, with both semi-empirical (*e.g.* B97-D [43]) and empirical (*e.g.* PWE [44]) parameterised functionals. For solid-state calculations, GGA methods are generally an improvement upon LDA results [42], but there is much variation due to the wide choice of functionals available. The development of GGA methods towards using the local kinetic energy density has resulted in meta-GGA (mGGA) functionals [45]. These approaches show accuracies similar to those of hybrid functionals, with only a slightly greater computational cost [45, 46], in comparison to pure GGA functionals.

2.3.3 Hybrids

Hybrid exchange-correlation functionals rely on a combination of exact (HF) exchange energy with gradient-corrected values for both the exchange and correlation energies. One popular hybrid *xc*-functional is B3LYP, which can be represented as a combination of exchange and correlation energies:

$$E_{xc}^{B3LYP} = (1 - a_0 - a_x)E_x^{LDA} + a_0E_x^{HF} + a_xE_x^{B88} + (1 - a_c)E_c^{VWN} + a_cE_c^{LYP}. \quad (2.14)$$

As we can see in Eq. (2.14) E_x^{B3LYP} is built from contributions of the exchange energy of LDA, HF and the gradient-based Becke88 (B) exchange functional [20], where $a_0 = 0.20$ and $a_x = 0.71$. Similarly, E_c^{B3LYP} is a weighted sum of correlation energies from VWN (one of the available approximations to the correlation energy of LDA) [41] and the correlation functional of Lee, Yang and Parr (LYP) [19], where $a_c = 0.81$.

The admixture of correlation and exchange energies from a variety of methods may seem unusual, but the performance of B3LYP as an xc -functional is above that of most GGAs [47]. One strength of B3LYP is the large variety of classes and properties which can be studied without further (semi-)empirical alterations to the functional. However the performance of B3LYP can be inferior to other functionals in specific problems [48], which can be tailored for such properties. One main objective of this work is to study the applicability of B3LYP towards calculating optical properties and, as B3LYP has been extensively studied for molecular systems, its application towards extended systems. **CRYSTAL** is a well optimised code which is able to run all-electron hybrid DFT calculations for extended systems and is ideal for this task.

2.4 CRYSTAL

CRYSTAL is a software suite specialising in electronic ground state calculations of periodic systems. Through use of the linear combination of atomic orbitals (LCAO) theory and Bloch functions, **CRYSTAL** can efficiently study wide classes of systems, from one dimensional systems such as molecules and polymers, to two-dimensional slabs and surfaces, and three-dimensional crystals. The **CRYSTAL** range of software is written in Fortran and has large development groups in the UK and Turin, Italy. The results in this work come from a development branch of the most recent release - **CRYSTAL14**.

2.4.1 Basis Sets in CRYSTAL

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The **CRYSTAL** software suite utilises LCAO theory to represent wavefunctions. Each ground-state wavefunction is represented in terms of a set of one-particle crystal

orbitals (COs), which are represented by a linear combination of N Bloch functions (BFs) $\phi_\mu(\mathbf{r}, \mathbf{k})$,

$$\psi_i(\mathbf{r}, \mathbf{k}) = \sum_{\mu}^N c_{\mu i}^{\mathbf{k}} \phi_{\mu}(\mathbf{r}, \mathbf{k}). \quad (2.15)$$

Each BF is expressed in terms of local atomic orbital (AO) functions $\varphi_{\mu}(\mathbf{r})$

$$\phi_{\mu}(\mathbf{r}, \mathbf{k}) = \sum_{\mathbf{a}} \varphi_{\mu}(\mathbf{r} - \mathbf{R}_{\mu} - \mathbf{a}) e^{i\mathbf{k} \cdot \mathbf{a}} \quad (2.16)$$

The AOs are the variational basis of the CRYSTAL program and are normalised *contractions* (*i.e.* fixed linear combinations) of normalised real solid harmonic Gaussian-type functions (*primitive* functions) given by

$$\gamma^{lm}(\alpha, \mathbf{r}) = X_l^m(\mathbf{r}) G(\alpha, \mathbf{r}), \quad (2.17)$$

where X_l^m are real solid harmonic functions with integer values l and m , and

$$G(\alpha, \mathbf{r}) = \mathcal{N} e^{-\alpha r^2} \quad (2.18)$$

where $\mathcal{N}$ is a normalisation factor. The AOs are organised in *shells*. AOs ϕ_{μ} belonging to the same shell λ have the same radial part (*i.e.* the same contraction coefficients d_i^{λ}), the same Gaussian exponent α_i^{λ} , and different angular components X_l^m ,

$$\varphi_{\lambda}^{lm} = \mathcal{N}_{\lambda} \sum_i d_i^{\lambda} c_i^{lm} X_l^m G(\alpha_i^{\lambda}, \mathbf{r}). \quad (2.19)$$

The shell normalisation constant $\mathcal{N}_{\lambda}$ is given by

$$\mathcal{N}_{\lambda} = \left[\int d\mathbf{r} \left(\sum_i d_i^{\lambda} c_i^{lm} \gamma^{lm}(\alpha_i^{\lambda}, \mathbf{r}) \right)^2 \right]^{-1/2} \quad (2.20)$$

with

$$c_i^{lm} = \left(\frac{\pi^{3/2} (2l-1)!! (l+|m|)!}{2^{2l+3/2} (2-\delta_{m0}) \alpha_i^{l+3/2} (l-|m|)!} \right)^{-1/2} \quad (2.21)$$

The Gaussian basis set of an atom is completely determined by its number of AO shells and by its contraction coefficients and exponents. In the limit of a *minimal* basis set only shells corresponding to occupied atomic orbitals are included. Additional

shells can be added to improve the representation of the polarisation of the atomic electron density in a molecular or condensed-phase environment. In a crystalline environment however, very small (“diffuse”) exponents may also be necessary to describe accurately extended *e.g.* conduction states. Typically, however, only exponents larger than a given threshold ($\alpha \leq 0.06$ a.u. for most systems) can be included in solid state calculations before the basis set reaches the limit of pseudo linear dependence (giving an ill-conditioned overlap matrix $S_{\mu\nu}^{\mathbf{k}} = \langle \phi_{\mu}(\mathbf{k}) | \phi_{\nu}(\mathbf{k}) \rangle$, typically when eigenvalues of the overlap matrix fall below 10^{-4}) [35]. The problem of linear dependence [50] has been encountered in studies of both molecular [51] and extended systems [52], and is caused by non-orthogonality of orbitals. The simplest approach to removing linear dependence is to remove the diffuse orbitals, however one alternative is to instead set the off-diagonal elements of the square of the overlap matrix to zero. Unfortunately, this method is not yet available within **CRYSTAL**.

2.4.2 SCF in CRYSTAL

The treatment of the Hartree-Fock and Kohn-Sham equations (see Eqn. (2.6) and Section 2.2) using a CO representation of the HF orbitals leads to the Roothaan matrix equations [53] which can be represented in the form

$$\mathbf{FC} = \mathbf{SCE}, \quad (2.22)$$

where $\mathbf{F}$ is a Fock (or KS) matrix, $\mathbf{C}$ is a coefficient matrix, $\mathbf{S}$ is the overlap matrix and $\mathbf{E}$ is a matrix containing the orbital energies [38]. The Fock matrix is defined by the Fock operator ($\hat{f}$) - an approximation to the true Hamiltonian operator of a system (Eqn. 2.23).

$$\hat{f}(i) = \hat{h}(i) + \sum_{j=1}^{n/2} [2\hat{J}_j(i) - \hat{K}_j(i)] \quad (2.23)$$

However, the elements of the Fock matrix are dependent on the coefficients and *vice versa*. This circular dependency is solved by having an initial approximation of $\mathbf{C}$. The SCF procedure is ended when a convergence criterion has been met. Within a ground state SCF the convergence criterion is the change in total energy between cycles, and for the coupled-perturbed SCF the convergence criterion is the change in polarisability between cycles. The thresholds for convergence can be found in Section 3.4.1 and Section 4.6.1. A common SCF procedure would be as follows [35]:

1. Generate a nuclear structure ($\mathbf{R}_A, Z_A, n$).
2. Generate a basis set (ϕ_i).
3. Calculate the one electron (H_{ij}^{core}), two electron ($(ij|ab)$) and overlap (S_{ij}) integrals.
4. Diagonalise the overlap matrix ($\mathbf{S}$).
5. Obtain the transformation matrix ($\mathbf{X}$).
6. Calculate an initial density matrix ($\mathbf{P}$) from estimated coefficients.
7. Calculate the two electron component of $\mathbf{F}$, using $\mathbf{P}$ ($\mathbf{G}$).
8. Create the Fock matrix ($\mathbf{F} = \mathbf{H}_{core} + \mathbf{G}$).
9. Transform $\mathbf{F}$ ($\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$).
10. Diagonalise $\mathbf{F}'$ to obtain $\mathbf{C}'$ and eigenvectors $\mathbf{E}$.
11. 'Back'-transform $\mathbf{C}'$ ($\mathbf{C} = \mathbf{X} \mathbf{C}'$).
12. Calculate a new density matrix ($\mathbf{P}'$).
13. Check convergence criteria.
 - (a) If converged, finish the SCF.
 - (b) If unconverged, return to point 7.

2.5 Density of States

An electronic density of states (DOS) is a measure of the number of electronic states per unit volume per unit energy. Visual analysis of the shape of a density of states plot can provide much information about the system. For example, larger volumes often contain more states, creating a near-continuous DOS as the quantisation of energy levels becomes less distinct. In addition, the general form of the density of states can often give indicators towards the dimensionality or structure of the system, as shown in Figure 2.1.

The contribution to the DOS by each orbital can be calculated by many software packages, including **CRYSTAL** allowing analysis of the composition of conduction and valence bands. The density of states of a system can be calculated through a variety

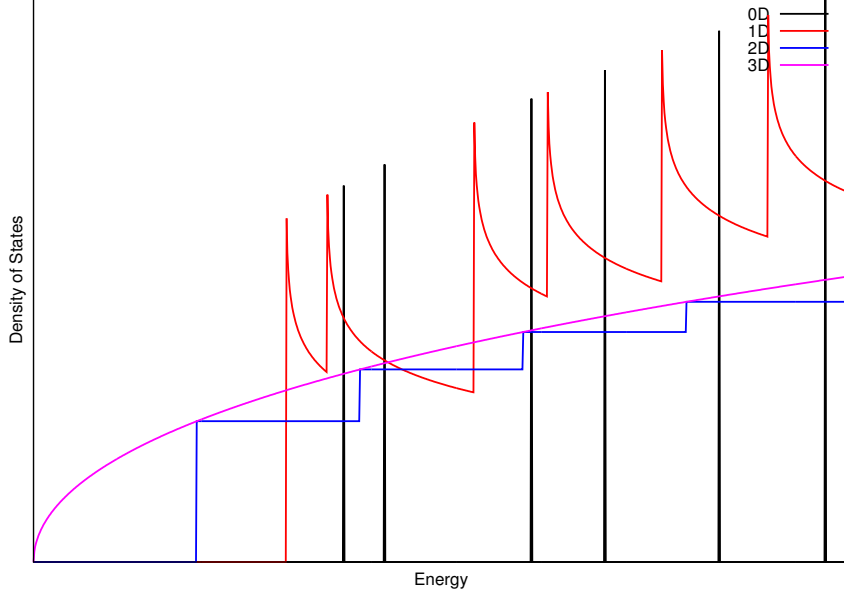


Figure 2.1: An example of the dimension dependence on the electronic DOS

of methods [54,55], and the approach to the density of states calculation in **CRYSTAL** is given in the appendix.

2.6 One-Particle Spectra

There are two common approaches to approximating a optical spectrum using one-particle calculations. The first method is known as a joint density of state (JDOS) calculation. In this approach, the energy of each occupied to unoccupied inter-band transition is calculated, creating a spectrum of same-intensity peaks for the HF/KS band energies differences.

The second process requires coupling the probability elements of an optical matrix with the JDOS of a ground state calculation. This creates the exact *independent-particle* (or *one-particle*) spectrum (IPS). This is often regarded as a pseudo-optical spectrum, due to the introduction of transition intensities, but this approach still lacks excitonic properties and other many-body phenomena.

2.7 TD-DFT

2.7.1 Time-Dependent Schrödinger Equation

The development of DFT into a rigorous and exact many-body method requires the time-dependent Schrödinger equation which, under the Born-Oppenheimer approximation can be written as

$$\hat{H}(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\frac{\delta}{\delta t}\Psi(\mathbf{r}, t). \quad (2.24)$$

Analogous to the ground-state KS equations given in Section (2.3), the time-dependent KS equations are as follows:

$$\begin{aligned} \left[-\frac{1}{2}\nabla_i^2 + \hat{V}_{eff}(\mathbf{r}, t) + \hat{V}_H(\mathbf{r}, t) + \hat{V}_{xc}(\mathbf{r}, t) \right] \Psi_i(\mathbf{r}, t) &= i\frac{\delta}{\delta t}\Psi(\mathbf{r}, t) \\ \hat{V}_{eff}(\mathbf{r}, t) &= v_{ext} \\ \hat{V}_H(\mathbf{r}_1, t) &= \int \frac{\rho(\mathbf{r}_2, t)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \\ \hat{V}_{xc}(\mathbf{r}, t) &= \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r}, t)} \end{aligned} \quad (2.25)$$

Similar to the Hohenberg-Kohn theorems for ground-state DFT [36], theorems exist which prove the viability of TD-DFT as an exact method for calculating excited states. Firstly, the Runge-Gross theorem [56] states that there is a one-to-one mapping between the time-dependent density and time-dependent potential. As such, no two non-degenerate initial states acting under the same potential can produce the same time-dependent density. The second theorem [57] states that there exists for any initial state with an analytic potential (*i.e.* a perturbed system), a second initial state acting under a non-interacting KS potential with the same probability density.

TD-DFT is dependent on the description of the response of electron density to a time-varying field. The time-dependent exchange-correlation kernel f_{xc} reflects how $v_{xc}[\rho](\mathbf{r}, t)$ varies with respect to a change in the time-dependent density $\rho(\mathbf{r}, t)$ [12],

$$f_{xc}(\mathbf{r}, \mathbf{r}', t, t') = \left. \frac{\delta V_{xc}[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r}', t')} \right|_{V_{eff}=0} \quad (2.26)$$

As V_{xc} is unknown, so is f_{xc} and the exact description of the response. Unlike the variety of methods available for the calculation of V_{xc} in ground-state DFT, there are very

few methods in TD-DFT. The most common approach is the adiabatic approximation, which allows the use of ground-state exchange-correlation functionals. However, the use of the ground-state functional limits the accuracy of adiabatic approaches to when the external potential varies slowly with time. The adiabatic LDA (ALDA) method is the most common exchange-correlation kernel, where f_{xc} is approximated by the perturbation-independent functional derivative of the ground-state V_{xc}^{LDA} [12],

$$f_{xc}^{LDA}(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) \frac{V_{xc}^{LDA}(\rho(\mathbf{r}, t))}{\delta\rho(\mathbf{r}_1)}. \quad (2.27)$$

Being derivative of LDA, ALDA suffers from many of the same problems (Section 2.3.1), however ALDA is able to accurately calculate the excitation energies of a range of molecular systems [58]. The adiabatic approach can be extended towards other exchange-correlation functionals, and in this work we use the adiabatic global-hybrid TD-B3LYP exchange-correlation kernel.

2.7.2 Linear Response

A complete solution to the Kohn-Sham equations is not always required within TD-DFT, which is advantageous in practical cases where the KS equations are expensive to solve. The linear response approach to TD-DFT requires only a partial solution of the KS equations, but it is only a reliable method when the external perturbation is low-intensity. Such low-intensity excitations are typical in optical spectroscopy, making linear-response TD-DFT a suitable method for calculating optical and excitonic properties.

The change in density with respect to the time-dependent potential can be treated as a perturbative problem (Eqn. 2.28 [59,60]), where v_{TD} is the applied time-dependent potential and δv_{SCF} is the linear response of the ground state self-consistent field due to the applied potential,

$$\delta v_{eff} = \delta v_{TD} + \delta v_{SCF}. \quad (2.28)$$

The linear response of v_{SCF} is dependent on both the response of the density matrix, and a coupling matrix K ,

$$\begin{aligned} \delta v_{ia}^{SCF}(r, t) &= \sum_{jb} K_{ia,jb}(r, t) \delta P_{jb}(r, t) \\ K_{ia,jb} &= (ia|bj) + (ia|f_{xc}|bj), \end{aligned} \quad (2.29)$$

where we use Mulliken integral notations as defined in Eqn (2.37). Within the linear response approximation, any change in the density matrix $\mathbf{P}$ due to a time-dependent field can be represented as

$$\delta\mathbf{P}_{ia} = \frac{f_i - f_a}{\omega - (\epsilon_i - \epsilon_a)} \delta v_{ia}^{eff}, \quad (2.30)$$

where $f_{i/a}$ and $\epsilon_{i/a}$ are the occupation numbers and energies of the occupied (i) and unoccupied (a) orbitals, respectively.

Within molecular systems, linear response approaches to calculating optical properties with adiabatic methods (ALDA) can yield good comparison to experimental work [58], but the same methods applied to periodic systems produce low-quality spectra, a problem known as the "scale-up" catastrophe [16, 61]. Time-dependent calculations within CRYSTAL follow an approach formally equivalent to a TD-DFT calculation within the adiabatic and linear-response approximations, with improvements made towards computational efficiency and reliability, which avoids the so-called "scale-up" problem [61] (Section 2.8).

2.8 TD-DFT in CRYSTAL

In our approach to excited states in extended systems, a central quantity to be calculated is the mean dynamical polarisability (MDP) per unit cell

$$\begin{aligned} \bar{\alpha}(\omega) &= \frac{1}{3} \text{tr}\{\boldsymbol{\alpha}(\omega)\} \\ &= -\frac{2}{3} \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_i^{N_{\text{occ}}} \sum_d^{N_{\text{vir}}} [U^{\mathbf{k},a}(\omega)]_{di} \Omega_{id}^{\mathbf{k},b} + \Omega_{di}^{\mathbf{k},b} [U^{\mathbf{k},a}(\omega)]_{id} \end{aligned} \quad (2.31)$$

in the limit $\omega \rightarrow 0$. In Equation (2.31) the MDP is treated as a sum over states expression, similar to previous polarisability studies [62–65]. In this expression $N_{\mathbf{k}}$ and $w_{\mathbf{k}}$ are the number and weights of the $\mathbf{k}$ points included in the numerical integrals over the first Brillouin Zone, N_{occ} and N_{vir} are the number of occupied (i) and unoccupied (d) bands, a and b indicate Cartesian components, and $\Omega_{id}^{\mathbf{k},b}$ are the matrix elements of the generalised position operator in the crystalline orbital (CO) basis,

$$\Omega_{id}^{\mathbf{k},b} = i \langle \psi_i(\mathbf{r}, \mathbf{k}) | e^{i\mathbf{k} \cdot \mathbf{r}} \nabla_{k_b} e^{-i\mathbf{k} \cdot \mathbf{r}} | \psi_d(\mathbf{r}, \mathbf{k}) \rangle \quad (2.32)$$

along the Cartesian coordinate b . Within crystalline periodic systems the gener-

alised position operator is translation-invariant, with the form

$$\hat{\mathbf{r}} = ie^{i\mathbf{k}\cdot\mathbf{r}}\nabla_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}, \quad (2.33)$$

where $\nabla_{\mathbf{k}}$ originates from the conversion of the translationally-variant scalar form of the position operator [66, 67].

These matrix elements represent the equivalent of the molecular dipole moment matrix elements in the infinite periodic system, to which they exactly reduce in the limit of an infinitely large unit cell [68–70]. The unitary matrices $[\mathbf{U}^{\mathbf{k},a}(\omega)]_{id}$ describe the mixing of the occupied and unoccupied orbitals at the crystal quasi-momentum $\mathbf{k}$ induced by the coupling of the electronic system to external optical radiation oscillating at frequency ω along the direction a , in the Born-Oppenheimer approximation. These matrices are obtained by solving a set of generalised, energy dependent coupled-perturbed equations [31, 61], in the pure-DFT (LDA or GGA), HF or hybrid-DFT approximations. In the (non-self consistent) limit $\mathbf{U}^{\mathbf{k},a}(\omega) = \mathbf{1}$, $\bar{\alpha}(\omega)$ reduces to the one-particle (Kohn-Sham or Hartree-Fock) MDP $\bar{\alpha}^{IP}(\omega)$. The frequency dependent dielectric tensor is given by

$$\epsilon(\omega) = 1 + \frac{4\pi}{V}\boldsymbol{\alpha}(\omega), \quad (2.34)$$

where V is the unit cell volume.

Once $\bar{\alpha}(\omega)$ has been calculated, many-body excitation energies can be computed from its poles. In particular, the lowest pole, corresponding to the first *optically allowed* transition, gives the optical gap (E_o) of the system. The lowest pole in the uncoupled MDP $\bar{\alpha}^{IP}(\omega)$ corresponds to the lowest optically allowed band gap of the independent-particle system, E'_g .

The positions of the poles can either be computed by examining the dependence of $\bar{\alpha}(\omega)$ on ω within a predefined energy range, or, equivalently [61] by solving the energy-independent anti-Hermitian eigenvalue problem [60, 71],

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega_I \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (2.35)$$

where ω_I are excitation energies, $\mathbf{X}$ and $\mathbf{Y}$ are left and right eigenvectors and the matrix elements of $\mathbf{A}$ and $\mathbf{B}$ are given by

$$\begin{aligned}
A_{ai,bj}^{\mathbf{k}_a\mathbf{k}_i,\mathbf{k}_b\mathbf{k}_j} &= \delta_{ij}\delta_{ab}\delta_{\mathbf{k}_i\mathbf{k}_j}\delta_{\mathbf{k}_a\mathbf{k}_b}(\varepsilon_a^{\mathbf{k}_a} - \varepsilon_i^{\mathbf{k}_i}) + (a\mathbf{k}_a i\mathbf{k}_i | j\mathbf{k}_j b\mathbf{k}_b) - c_{\text{HF}}(a\mathbf{k}_a b\mathbf{k}_b | j\mathbf{k}_j i\mathbf{k}_i) \\
&\quad + (1 - c_{\text{HF}})(a\mathbf{k}_a i\mathbf{k}_i | f_{\text{xc}} | j\mathbf{k}_j b\mathbf{k}_b) \\
B_{ai,bj}^{\mathbf{k}_a\mathbf{k}_i,\mathbf{k}_b\mathbf{k}_j} &= (a\mathbf{k}_a i\mathbf{k}_i | b\mathbf{k}_b j\mathbf{k}_j) - c_{\text{HF}}(a\mathbf{k}_a j\mathbf{k}_j | b\mathbf{k}_b i\mathbf{k}_i) + (1 - c_{\text{HF}})(a\mathbf{k}_a i\mathbf{k}_i | f_{\text{xc}} | b\mathbf{k}_b j\mathbf{k}_j).
\end{aligned} \tag{2.36}$$

In these expressions, $\varepsilon_s^{\mathbf{k}_s}$ are unperturbed one-particle energies, with $s = i, j, \dots$ and $s = a, b, \dots$ for occupied and unoccupied states respectively at the point $\mathbf{k}_s$ in the first Brillouin Zone, and $(p\mathbf{k}_p q\mathbf{k}_q | r\mathbf{k}_r s\mathbf{k}_s)$ are two-electron integrals in Mulliken notation,

$$(p\mathbf{k}_p q\mathbf{k}_q | r\mathbf{k}_r s\mathbf{k}_s) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_p^*(\mathbf{k}_p\mathbf{r}_1)\phi_q(\mathbf{k}_q\mathbf{r}_1) \frac{1}{r_{12}} \phi_r^*(\mathbf{k}_r\mathbf{r}_2)\phi_s(\mathbf{k}_s\mathbf{r}_2), \tag{2.37}$$

where $\phi_r(\mathbf{k}\mathbf{r})$ are one-particle Hartree-Fock/Kohn-Sham orbitals. c_{HF} is the fraction of Hartree-Fock exchange in hybrid TD-DFT calculations and the TD-DFT exchange correlation kernel, which we use here in its adiabatic [72] and local approximations, given by

$$f_{\text{xc}}(\mathbf{r}) = \left. \frac{\delta v^{\text{xc}}(\mathbf{r})}{\delta n(\mathbf{r})} \right|_{n(\mathbf{r})=n^{(0)}(\mathbf{r})}, \tag{2.38}$$

where $v^{\text{xc}}(\mathbf{r})$ is the local exchange-correlation potential and $n(\mathbf{r})$ is the linear density response. The electronic response described by Eqns. (2.36) is therefore non-local only when $c_{\text{HF}} \neq 0$. Although mostly used for molecules, efficient implementations of Eqns. (2.35) have been shown to provide a convenient route to excited state calculations in periodic systems [73–75], including crystalline insulators [76].

2.9 Polarisability in Extended Systems

2.9.1 Energy convergence for ground state

For calculations of ground state energies, suitable basis sets can be developed through the optimisation of the number of shells and the Gaussian exponents, with respect to the total energy at a typical geometry for the system. The convergence of the basis set is measured through the minimisation of the total energy of the system, as per the variational theorem. Typically, basis sets developed for molecular systems (see *e.g.* [77]) offer a suitable starting point for the optimisation procedure within periodic systems

and often high-quality molecular basis sets can be used directly after the removal of diffuse exponents, followed by a reoptimisation of the remaining outermost exponents. For highly ionic or metallic systems however, substantial modifications and additional flexibility in the original molecular basis set may be required. A general and consistent approach to obtaining energy-optimised basis sets of Double- and Triple- ζ Valence plus Polarisation (DZVP and TZVP) quality for crystalline materials has been described in the recent work of Peintinger *et al.* [78]. However, these basis sets are not necessarily suitable for describing the conduction band orbitals and this deficit may result in basis sets which are insufficient for the accurate computing of response functions, explicit correlation corrections and electronic excitations.

2.9.2 Polarisation Convergence for Excited States

Rappoport and Furche (RF) have recently proposed a procedure for optimising basis sets for response calculations on large (< 100 atom) molecular systems [79]. The RF approach is based on optimising basis sets for molecular *response* quantities (*e.g.* molecular polarisabilities), rather than for ground state energies, and seeks to maximise the polarisability using the fewest number of diffuse functions.

The RF method is rigorously justified, based on Hylleraas’ variational principle [80], which states that the functional

$$G[\psi^{(1)}] = \frac{1}{2} \langle \Psi^{(1)} | \mathcal{H}^{(0)} | \Psi^{(1)} \rangle - \langle \Psi^{(1)} | \mathcal{H}^{(1)} | \Psi^{(0)} \rangle \quad (2.39)$$

is minimised by the exact first order perturbed wavefunction $\Psi^{(1)}$. Here, $\mathcal{H}^{(0)}$ is the ground state Hamiltonian, $\mathcal{H}^{(1)}$ is the first-order perturbed Hamiltonian, and $\Psi^{(0)}$ is the ground state wavefunction. Minimisation of the functional in Equation 2.39 for molecular systems can be shown to correspond to a maximisation of the molecular polarisability with respect to the choice of the first-order perturbed wavefunction [79]. Basis sets obtained through the RF approach are less diffuse and smaller than the augmented Dunning or Sadlej basis sets [81–84], with which they have comparable accuracy for molecular polarisabilities.

In this work, we exploit the RF approach to explore the feasibility of a response-property targeted basis set optimisation procedure for crystalline systems. The local atom-centered basis set approach (see Section 2.4.1) implemented in **CRYSTAL** for both ground-state and response [68–70] properties offers an ideal framework for a straightforward generalisation of the RF method to infinite periodic systems.

3

Alkali Halides

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3.1 Structure

The alkali halides are a series of crystalline compounds with the chemical formula AX, where A=Li, Na, K, Rb, Cs and X=F, Cl, Br, I. At room temperature and pressure, the majority of the alkali halides adopt the B1 form (Figure 3.1, left) of the face-centered cubic crystal structure [85]. The caesium halides have the B2 crystal structure (Figure 3.1, right) under standard conditions, apart from CsF which has B1 structure. The reason for differing structures in the alkali halide series is that a large cation/anion radius ratio can cause the B1 structure to be unstable, whilst the B2 structure is less affected by the radius ratio, and still stable [86]. In this work we consider only the alkali halides with B1 structure, studying the alkali halide series AX, where A=Li, Na, K, Rb and X=F, Cl, Br, and focussing on LiF, which has been extensively studied in previous work, both experimentally and theoretically.

3.2 Experimental Review

3.2.1 Roessler

In 1967, Roessler and Walker studied the optical spectrum of bulk LiF using experimental thermoreflectance results [23]. Using freshly-cleaved crystals which were exposed to air for two minutes before being placed under vacuum in the reflectometer, measurements of the reflectance were taken over a nine-day period at 300 K. Through an

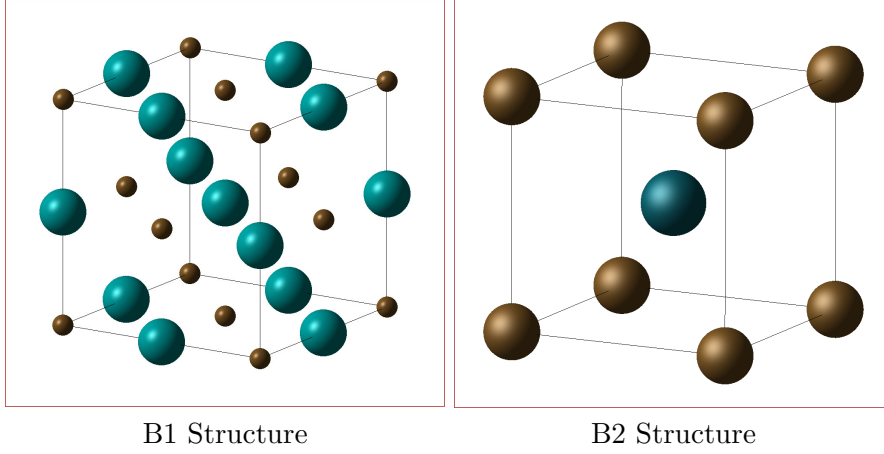


Figure 3.1: Conventional cell structures of the alkali halides.

inversion of their reflectance spectra, they were also able to recover the dielectric properties. The first peak found in the dielectric and reflectance spectra is at 12.62 eV, and is attributed to the optical gap. To uncover any smaller peaks hidden by the broad and asymmetric nature of the exciton peak, they attempted to fit the exciton peak to a Lorentzian lineshape, following the work of Kato *et al.* [87,88]. Knox *et al.* predict that the spin-orbit splitting for the alkali fluorides is of the order of 0.047 eV [30], and the fitting by Roessler *et al.* revealed a new peak at 12.85 eV. The authors reasoned that the new peak was too far away from the excitonic peak to be a spin-orbit split peak of the exciton - a phenomenon commonly seen in other alkali halides [89]. Assuming that the alkali halide excitons can be described by the Wannier model as hydrogenic, then this second peak could be attributed to the second member of a Wannier series (Section 1.2.1). The following Wannier-model E_g would be at 12.93 eV, implying an exciton binding energy, E_b , of 0.31 eV. The authors refer to previous experimental [90] and theoretical work [91,92], and an analysis of their ϵ_2 (imaginary dielectric) data, which indicate that the fundamental gap should be much greater than 12.93 eV. The authors ceded that the second peak is an artifact produced by the fitting of a Lorentzian, and as such the exciton should not be modelled as one. Beyond the exciton peak, the optical spectrum is very broad - through extrapolation of the spectrum, the absorption onset was deduced to be at 13.6 eV. With an optical gap (E_o) of 12.6 eV and a fundamental gap E_g , of 13.6 eV, the E_b of LiF according to Roessler and Walker is 1.0 eV. The authors suggest that this 1.0 eV E_b corresponds to a Bohr radius comparable to that of the nearest-neighbour distance in bulk LiF.

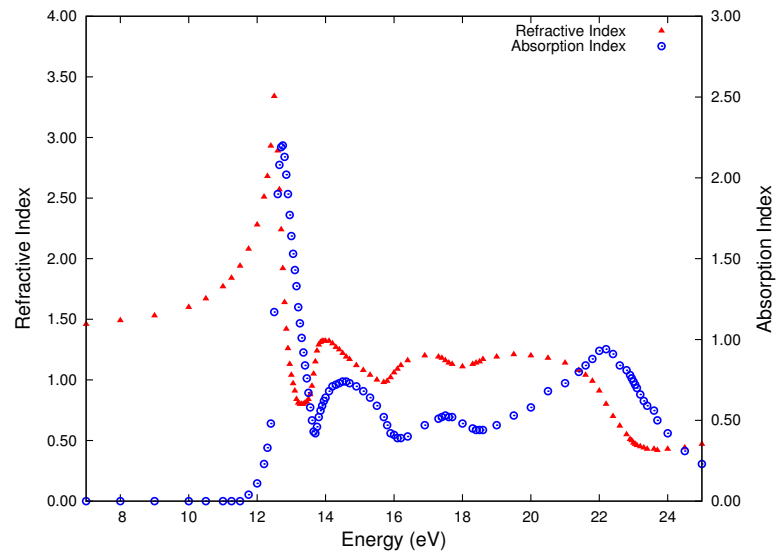


Figure 3.2: Roessler *et al.*'s optical spectrum of LiF.

3.2.2 Piacentini

Eight years after the original publication, M. Piacentini reanalysed the data given by Roessler and Walker and came to a different conclusion [93]. They argued that the inversion utilised by the previous authors is known to be inaccurate around the edge of the absorption onset. In this second analysis of the data, Piacentini claims that in the presence of an exciton, any square-root behaviour is distorted, and thus the square-root model used for the extrapolation of the absorption onset is incorrect. Using Elliot's hydrogenic formula [94], Piacentini obtains a best-fit for the environment around the exciton, when the E_g is 14.53 eV (± 0.02 eV). In the same work, Piacentini calculates the effective radius for the exciton within LiF to be 1.9 Å, using the relationships shown in Equation (3.1), where μ is the effective mass of the electron, m is the electron rest mass, ϵ_∞ is the optical dielectric constant and $\mathbf{r}$ is the effective radius of the exciton. As the nearest-neighbour distance in LiF is 2.014 Å, this finding implies that a single-site excitation view of LiF (where the electron donor and acceptor orbitals are situated on the same atom) is incorrect.

$$E_b = 13.6 \frac{\mu}{m} \left(\frac{1}{\epsilon_\infty} \right)^2 \mathbf{r} = 0.54 \epsilon_\infty \frac{m}{\mu} \quad (3.1)$$

Further work by Piacentini [95], on data from a different thermorefectance experiment, suggests that the E_g of LiF is 14.2 eV (± 0.2 eV). There is, therefore, considerable uncertainty in the measurement of E_g , which comes from the interpretation of the spectra - there is no sharp peak in the imaginary part of the dielectric function, for E_g , like there is for E_o . Piacentini is not the only author to suggest that the E_g in LiF is larger than 13.6 eV - many other groups, such as Miyakawa (14.6 eV) [90], and Milgram and Givens (15.2 eV) [91], also proposed experimental values in that period. Using a method to simulate photoelectron angular distributions, Shirley *et al.* [96] deduce the E_g of LiF, and find it to be 14.4 eV - close to the values of Piacentini and Miyakawa.

Due to the uncertainty in the measurement of E_g , finding a generally accepted value of E_g (and thus E_b) is not a trivial matter. With Piacentini's experimental E_g of 14.2 eV, and the E_o of Roessler and Walker, a new E_b for the LiF exciton is 1.6 eV - much larger than the previous value, and so, still a Frenkel exciton. The effective radius of 1.9 Å supports the idea of a localised electron-hole pair, over a short range, which is again typical of a Frenkel exciton.

	LiF	LiCl	LiBr	NaF	NaCl	NaBr
E_g (eV)	8.94	6.32	4.91	6.16	5.00	4.09
	KF	KCl	KBr	RbF	RbCl	RbBr
E_g (eV)	6.07	5.05	4.31	5.51	4.82	4.20

Table 3.1: PBE planewave energy gaps of the alkali halide series [99].

3.2.3 Abbamonte

More recently, Abbamonte *et al.* attempted to recreate the exciton in LiF using inelastic X-ray scattering (IXS) [97]. Due to a limited change in crystal structure, they conclude that the exciton is tightly bound and immobile, fitting the Frenkel model. Through an inversion of their data, they obtain a time-resolved charge response to the excitation, and their interpretation of the exciton’s dynamics show it to be localised over two unit cells (circa 8 Å). This indicates that the exciton has hybrid properties of both Wannier and Frenkel-type excitons.

Such long-range and tightly-bound excitons are seen often in studies of molecular crystals, where the excited electron is transferred between molecules, in a process known as a charge-transfer excitation [98]. The resulting excitons are localised, but long-range, and with a large E_b . In this work, we will refer to such excitons as CTE (charge-transfer excitons).

3.3 Theoretical Review

3.3.1 Gopikrishnan

Gopikrishnan *et al.* studied the electronic density of states (EDOS) for the alkali halides using VASP (Vienna Ab Initio Software Package) - a planewave-based DFT code [99]. They used projector augmented waves (PAW) to represent the ionic potentials, with the planewave energy cut-off at 500 eV. Using PBE as their exchange-correlation functional, they severely underestimate E_g by 2.5 to 5.5 eV for the alkali halide series.

They found that PBE follows the experimental trend of a decreasing E_g as the atomic number of the halogen increases, and that the valence band maximum and conduction band minimum are dominated by the halogen and alkali ion, respectively.

3.3.2 Rohlfiing

Rohlfiing *et al.* have studied the exciton and optical properties of LiF using GW-BSE [100,101]. Using Gaussian basis sets in combination with non-local *ab initio* pseu-

dopotentials, the authors show the progression of the band structure and joint density of states (Section 2.6) for bulk and (001) surface LiF systems as each level of theory is applied (LDA, GW, BSE). They were able to recreate bound excitons at $h\nu \simeq 12.7$ eV, with an E_b of 1.6 eV, accurately reproducing the experimental optical absorption spectra. However, the electron-hole wavefunction for this lowest-energy excitation shows that the electron is primarily located within the first shell of neighbouring atoms, and partially delocalised over the second shell. This delocalised description of the exciton does not reconcile well with the CTE model [97], which predicts a strongly localised electron and hole.

3.3.3 Pyper

Using an explicitly correlated electronic structure method, Pyper *et al.* calculated the optical properties of alkali halide clusters encapsulated within single-walled carbon nanotubes (SWCNTs) and for bulk crystals [102]. Four possible excitation processes are proposed for the B1-structured bulk alkali halides, depending on the final charge distribution. The dipolar distribution (the excitation of a single electron between a fluorine ion and a lithium ion) is deduced to be the result of the first excitation in the bulk crystal, as this model has the largest total energy from the response to the excitation (E_{tot}^{pol}), maximising the CT excitation energy (Eqn. (3.2)),

$$\Delta E_{CT} = A_H + I_M + \Delta E^{dist} + \Delta E^{disp} + E_{tot}^{pol}. \quad (3.2)$$

This localised dipolar model is in qualitative disagreement with the GW-BSE work by Rohlfing *et al.* [100, 101]. The authors provide calculated values of E_o for a subset of the alkali halide series which does not include LiF. However, for the seven bulk alkali halide crystals studied, the work of Pyper *et al.* is in good agreement (< 0.5 eV difference) with experimental values of E_o .

3.3.4 Novel Kernels

LiF has been previously studied with TD-DFT, using bespoke kernels such as the screened-exact exchange (SXX) kernel by Ullrich *et al.* [103], and the “bootstrap” kernel by Sharma *et al.* [18]. In these semi-empirical calculations, the exciton binding energy within LiF is computed as 1.46 eV for the SXX kernel [103] and 0.32 eV for the “bootstrap” kernel [18]. In addition to the quantitative value of E_b , both the SXX and “bootstrap” kernels reproduce the optical spectrum of LiF with a good agreement to the experimental work of Roessler *et al.* (Section 3.2.1).

However careful application of these methods is required, as the semi-empirical nature can result in values of E_o further away from the experimental data than non-empirical approaches [103].

In this work we are using a global non-empirical hybrid exchange-correlation response kernel to study both qualitative and quantitative properties of the alkali halides.

3.4 This Work

3.4.1 Computational Parameters

Unless otherwise specified, the following calculations on the alkali halide series were carried out with the default parameters of **CRYSTAL09**, using the Restricted Closed-Shell Formalism. The one-dimensional irreducible Brillouin zone is sampled using a Monkhorst-Pack net of shrinking factor 18, resulting in 345 symmetry-inequivalent $\mathbf{k}$ -points, and is sampled using a Gilat net of shrinking factor 18 to generate 345 symmetry-inequivalent $\mathbf{k}$ -points for the calculation of the Fermi energy, E_F . The energy tolerance for convergence of the SCF was set to $10^{-7} E_h$ for the ground-state calculations, and the polarisability tolerance for the convergence of the $\mathbf{k}$ -coupled perturbation calculations was set to $10^{-4} a_0^3$. For all calculations, the first four truncation tolerances were set to 10^{-7} , where the first and second tolerances control the Coulomb summation, and the third and fourth tolerances control the exchange summation. The final truncation tolerance was set to 10^{-14} , and limits the inclusion of long range exchange, controlled by decay of the density matrix. For more information regarding the input and default parameters of **CRYSTAL**, refer to the handbook [104].

3.4.2 Geometry Optimisation

Geometry optimisations of the ground state were carried out in **CRYSTAL** with the m-def2-QZVP (originally from [105], and modified in this work - see Section 3.4.3) basis set series and at the B3LYP level of theory, allowing the relaxation of both cell vectors and atomic positions. The B3LYP-optimised lattice constants for the B1 form of the alkali halide series can be found in Table 3.2. Experimental values for the lattice parameters are also given, to aid in the comparison with experimental measurements and other theoretical approaches. In order to distinguish the effect of theoretical method and basis set on E_g from that of changes in geometry, within this work calculations on the alkali halides were carried out using the experimental lattice parameters given in Table 3.2.

System	Lattice Parameters (Å)	
	Experimental [106]	Calculated
LiF	4.0262	4.027
LiCl	5.1399	5.190
LiBr	5.501	5.598
NaF	4.6329	4.653
NaCl	5.6401	5.713
NaBr	5.9730	6.091
KF	5.344	5.415
KCl	6.2929	6.420
KBr	6.5982	6.777
RbF	5.6516	-
RbCl	6.5898	-
RbBr	6.8908	-

Table 3.2: Experimental and calculated (B3LYP) lattice parameters using the def2-QZVP basis set.

We see that B3LYP is in good agreement with the experimental lattice parameters with a mean absolute error (MAE) of 0.082 Å.

3.4.3 LiF Study

Polarisability

Starting from a pair of basis sets of 61-1G and 7-311G [107] quality optimised for molecular calculations, we built a hierarchy of basis sets for LiF using pruning and the diffuse exponent adjustment techniques described *e.g.* by Peintinger *et al.*. We enforce the conditions that: (1) the total ground state energy is left roughly constant, to guarantee that the representation of the occupied one-particle orbitals retains the quality of the original basis set; (2) the mean dynamical polarisability (MDP, see Section 2.8) per unit cell, or equivalently the trace of the macroscopic dielectric tensor, is maximised as the optimal basis set limit is reached.

In Figure 3.3 we show the dependence of the static ($\omega = 0$) MDP and of the ground state energy on basis set size, measured by the number of AOs per primitive cell of LiF. Consistent with the results of Ref. [79], the MDP per unit cell is found to initially increase with the basis set size to reach a final plateau at its maximum value for $N_{AO} \simeq 50$. For $N_{AO} > 50$ we find that the MDP is converged to ~ 0.05 Bohr³, apart from two basis set pairs, which have inflated values of N_{AO} due to the uncontracted structure of the Li basis set which they share. Original basis sets and the modified

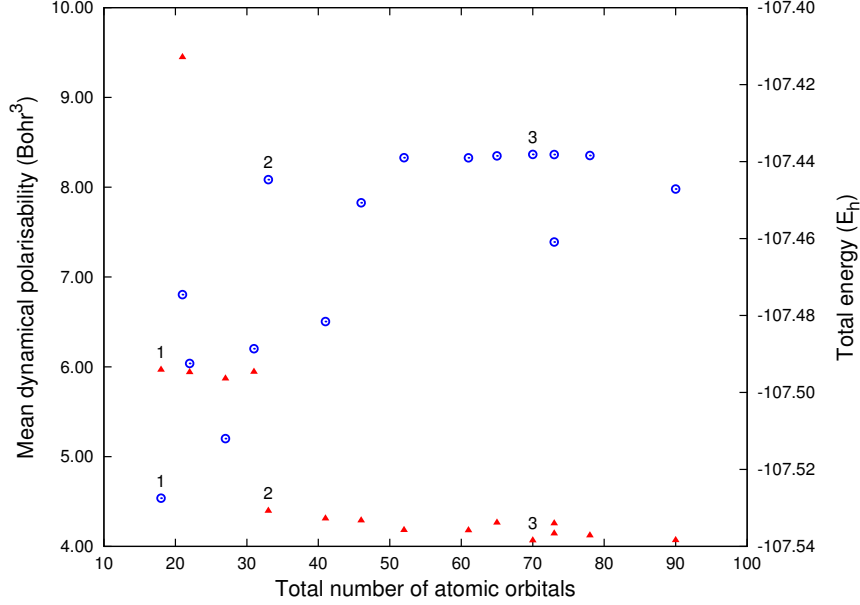


Figure 3.3: MDP and total energy against total number of atomic orbitals within a LiF unit cell. The left axis (blue circle) is the MDP; the right axis (red triangle) is the total energy. 1: Dovesi-Nada, 2: pob-TZVPP, 3: m-def2-QZVP

contraction schemes, coefficients and exponents can be found in the Appendix.

The total energy decreases with N_{AO} , in accordance with the variational principle for the ground state energy, to reach its final minimum value at $N_{AO} \simeq 30$. We notice that the smallest basis sets used as starting points for the optimisation procedure (labelled **1** in Figure 3.3), which have been used in previous work on crystalline LiF [108,109], can be considered partially converged in energy although they are clearly underconverged for polarisability. This study demonstrates that it is possible to perform a calculation of the absolute ground state energy which is converged to $< 5 \times 10^{-3} E_h$ (< 1.3 eV) and a calculation of the MDP which is converged to ~ 0.05 Bohr³, per formula unit. By having a high degree of convergence for these zeroth and first order response properties, we believe we have reached the basis set limit, maximising the effect of diffuse and polarisable orbitals.

The slower convergence rate of the MDP relative to the ground state energy is a direct consequence of the fact that the former quantity depends simultaneously on both occupied *and* unoccupied unperturbed Kohn-Sham/Hartree-Fock orbitals *via* the matrices $\mathbf{U}^{k,a}(\omega)$, *cf.* Eqns. (2.31 and 2.32), whereas the ground-state energy is a functional of the ground state density and/or occupied orbitals only, both in Hartree-

Fock and in density functional theory.

Fundamental Energy Gap

Using both the (partially) energy-optimised basis set pair (Li:61-1G [108], F:7-311G [109]; "Dovesi-Nada") and polarisation-optimised def2-QZVP basis set, the effect of the choice of electronic structure method on E_g can be seen in Table 3.3 for HF, LDA, PBE and B3LYP. These initial basis sets were chosen as they have been previously used in ground-state studies of LiF [109] and LiH [108] within CRYSTAL. Each of the DFT methods underestimate E_g , with both E_g^{LDA} and E_g^{PBE} more than 4 eV beneath the experimental range. Commonly, values of E_g^{B3LYP} are in good agreement with experimental data, for a wide range of wide-gap insulators such as metal oxides [110]. Surprisingly, for the ionic material LiF, E_g^{B3LYP} is at least 2 eV smaller than values deduced from experimental studies. As we would expect, E_g^{HF} is greater than E_g^{expt} , by more than 8 eV.

Basis Set	HF	LDA	PBE	B3LYP	Experiment [23,95]
Dovesi-Nada	21.83	8.93	9.15	11.68	13.6-14.5
def2-QZVP	21.87	8.90	9.15	11.69	

Table 3.3: E_g (eV) for LiF with an energy-optimised (Dovesi-Nada) and polarisation-optimised (def2-QZVP) basis set, at the HF and DFT (LDA, PBE and B3LYP) levels of theory.

It is clear that changes in E_g with respect to the basis set size are essentially negligible. This fact suggests that even a moderately energy-optimised basis set (*e.g.* **1**) can be sufficient for accurate predictions about the size of energy gaps, especially at the hybrid DFT level. However, the choice of a zeroth or first-order property-optimised basis set is still recommended due to the variational principles. This work is consistent with early work on the ability of B3LYP calculations to estimate band gaps of simple semiconductors reliably using Gaussian basis sets [21, 110]. Using the m-def2-QZVP basis set, pseudo linear dependence prevents the convergence of the SCF of the Hartree-Fock method, so the value in Table 3.3 is instead from the pob-TZVP [78] basis set (see Figure 3.3, **2**).

Density of states

We have seen from Table 3.3 that the quantitative nature of the energy gap of LiF is independent of our choice of energy-optimised or polarisation-optimised basis set. In

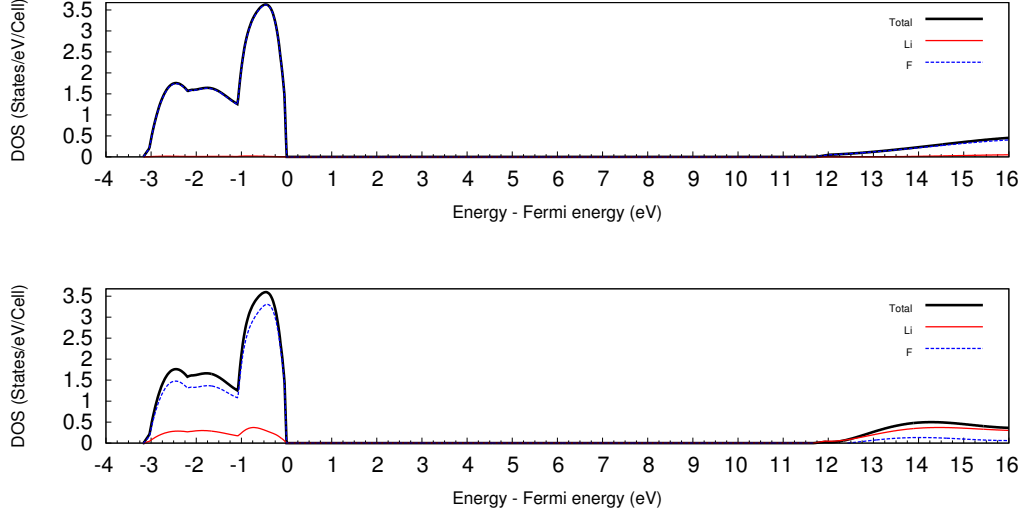


Figure 3.4: LiF EDOS for an energy-optimised (Dovesi-Nada, top) and a polarisation-optimised (m-def2-QZVP, bottom) basis set.

addition, we show in Figure 3.4 a comparison of angular momentum projected EDOSs computed for LiF at the B3LYP level using the energy-optimised Dovesi-Nada basis set pair, labelled **1** in Figure 3.3 (top panel in Figure 3.4) and a polarisation-optimised basis set pair (m-def2-QZVP for both Li and F), **3** in Figure 3.3 (bottom panel in Figure 3.4).

We see that in single-particle theory with the good *ground-state* basis set **1** a qualitatively incorrect description of the excitation is obtained. In the top panel of Figure 3.4 the valence and the conduction bands have exclusively F character, corresponding to an on-site model of the lowest (one-particle) excitation, in which both the Kohn-Sham particle and hole remain well localised on the F sublattice. Whereas with a polarisation-optimised basis set pair **3**, a non-negligible contribution from Li atoms is observed in both bands, as seen in the bottom panel of Figure 3.4. The excitation model has now shifted to a situation akin to an electron transfer from the F to Li sublattice. It is clear that a polarisation-optimised basis set is required in order to obtain a qualitative description of the excitation process that is consistent with the one that would be expected from the standard CTE model *i.e.* the promotion of one electron from an F $2p$ to a vacant $2s$ orbital [97,102], which is consistent with the work of Pyper *et al.*

	TD-HF	TD-LDA	TD-PBE	TD-B3LYP	Experimental
1 E_g (eV)	21.83	8.93	9.15	11.68	13.6-14.5 [23, 95]
E_o (eV)	15.89	8.92	9.15	11.51	12.6 [23]
E_b (eV)	05.94	0.01	0.00	00.19	1.0-1.9
3 E_g (eV)	21.87	8.90	9.15	11.69	13.6-14.5 [23, 95]
E_o (eV)	15.67	8.90	9.15	11.40	12.6 [23]
E_b (eV)	06.20	0.00	0.00	00.29	1.0-1.9

Table 3.4: Optical properties for LiF using energy-optimised (Dovesi-Nada, **1**) and polarisation-optimised (m-def2-QZVP, **3**) basis sets.

Optical Response

The TD-DFT MDP of LiF has been computed using three approximations for the exchange-correlation kernel - LDA, PBE and B3LYP. For comparison, we also performed full time-dependent Hartree-Fock (TD-HF) calculations. In this work, the same exchange-correlation functional is used for both the ground-state and linear response calculations (*e.g.* the B3LYP ground-state energy calculations are followed by TD-B3LYP linear response calculations). The energy dependence on the MDP per unit cell in LiF is summarised in Figures 3.5 and 3.6, and the values of E_g , E_o and E_b are shown in 3.4. The position of the lowest asymptote in the MDP marks the energy of the first many-body (optical) gap at each level of theory.

Figure 3.5 focusses on the first asymptote of the MDP of LiF, studied with the Dovesi-Nada basis set pair. Figure 3.6 is the m-def2-QZVP counterpart to Figure 3.5 (with the exception of HF, which is using the pob-TZVP basis sets). The solid black vertical lines denote the experimental optical gap of LiF (12.6 eV) [23], and for each method there is both a solid line which shows the MDP at each perturbation energy, and a vertical dashed line of the same colour which indicates E_g at the same level of theory.

We see that for the *non-hybrid* TD-DFT methods $E_o \simeq E_g$. This indicates a lack of electron-hole binding, which can be explained by the well-known inability of the ALDA kernel to create bound excitons [12]. For the hybrid-exchange TD-B3LYP, $E_b^{B3LYP} = 0.19 - 0.29$ eV, indicating that the incorporation of exact exchange (even a partial amount) is sufficient for exciton binding. Using TD-HF, E_b^{HF} is found to be ~ 6 eV, which is substantially larger than experimental estimates, consistent with the fact that in Hartree-Fock theory, there is no screening between excited electrons and holes.

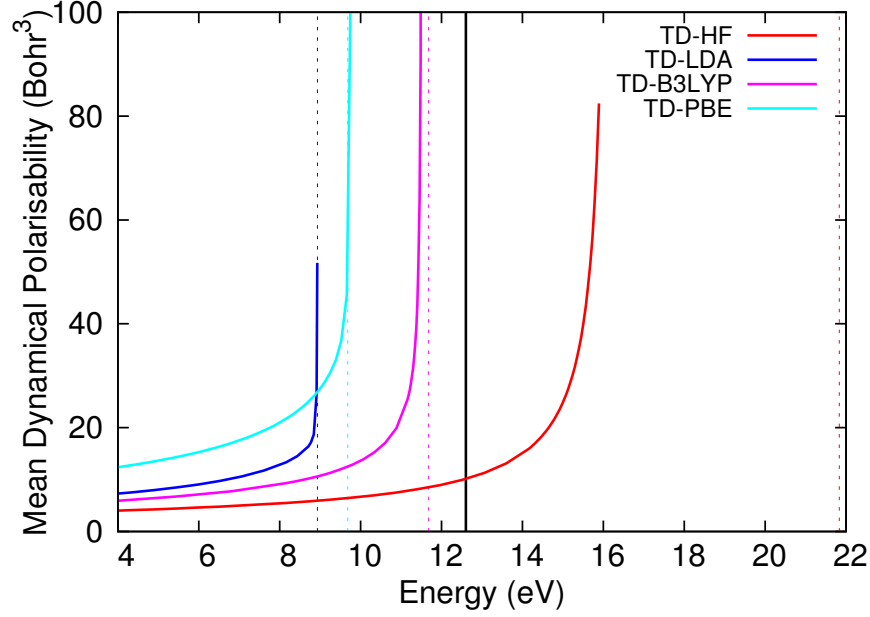


Figure 3.5: Perturbation energy against MDP, using the Dovesi-Nada basis set pair. The dashed lines represent E_g for each method and the solid black line represents the experimental E_o .

Optical Gap Dependence on HF Exchange

As noted in the introduction (Section 1.2), E_o is given by the value of E_g modified by an attractive screened Coulomb energy. The origin of the electron-hole binding in TD-B3LYP and TD-HF can be understood by considering Eqns. (2.35) and (2.36) in the simplified limit of a single $i \rightarrow a$ excitation in a single $\mathbf{k}$ -point calculation (*i.e.* in the Γ point approximation $\mathbf{k} = \mathbf{0}$).

In this case,

$$\begin{aligned} A_{ai,ai} &= (\varepsilon_a - \varepsilon_i) + (ai|ia) - c_{\text{HF}}(aa|ii) + (1 - c_{\text{HF}})(ai|f_{\text{xc}}|ia) \\ B_{ai,ai} &= (ai|ai) - c_{\text{HF}}(ai|ai) + (1 - c_{\text{HF}})(ai|f_{\text{xc}}|ai). \end{aligned} \quad (3.3)$$

If the electron i and the hole a are created by a band gap transition, then $\varepsilon_a - \varepsilon_i = E_g$. If the electron and hole wavefunctions are well localised in disjoint regions of space, as in the case of an ideal CTE model, then Eqns. (3.3) reduce to

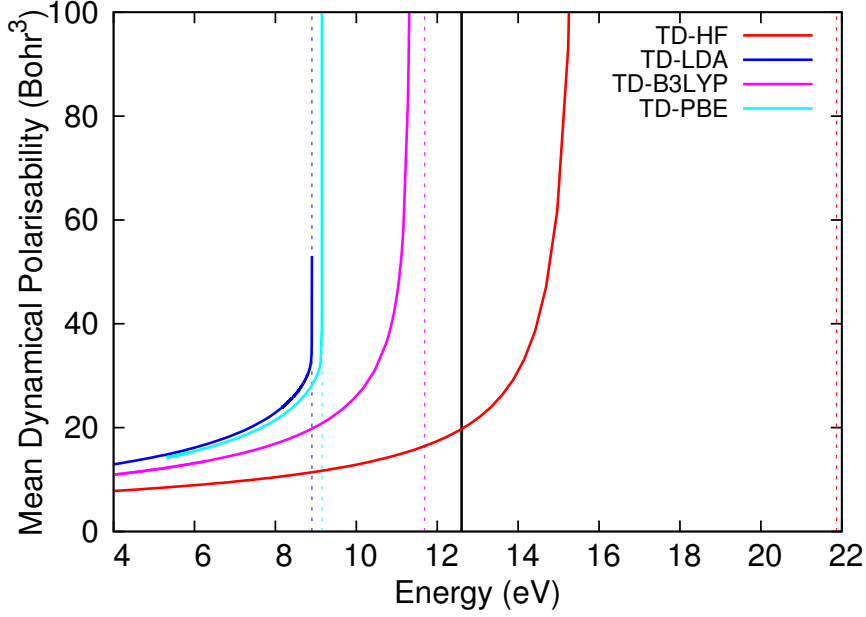


Figure 3.6: Perturbation energy against MDP, using the m-def2-QZVP basis set. The dashed lines represent E_g for each method and the solid black line represents the experimental E_o .

$$\begin{aligned} A_{ai,ai} &\simeq E_g - c_{\text{HF}}(aa|ii) \\ B_{ai,ai} &\simeq 0. \end{aligned} \quad (3.4)$$

The excitation energy $\omega_I = A_{ai,ai}$ is therefore in this case simply given by the difference between the band gap and a screened Coulomb attraction energy between the electron and hole distributions $|\phi_i|^2$ and $|\phi_a|^2$, with a screening parameter c_{HF} ($0 \leq c_{\text{HF}} \leq 1$) independent of the electron hole distance. The latter term is responsible for the exciton binding.

In Figure 3.7 we show the dependence of E_g and E_o on the percentage of Hartree-Fock exchange c_{HF} , when using the Dovesi-Nada basis set pair. The linear dependence of E_g is a consequence of the fact that the B3LYP exchange-correlation energy varies linearly with c_{HF} [19,20],

$$E_{xc}^{\text{B3LYP}} = E_x^{\text{LDA}} + c_{\text{HF}}(E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_x(E_x^{\text{GGA}} - E_x^{\text{LDA}}) + E_c^{\text{LDA}} + a_c(E_c^{\text{GGA}} - E_c^{\text{LDA}}) \quad (3.5)$$

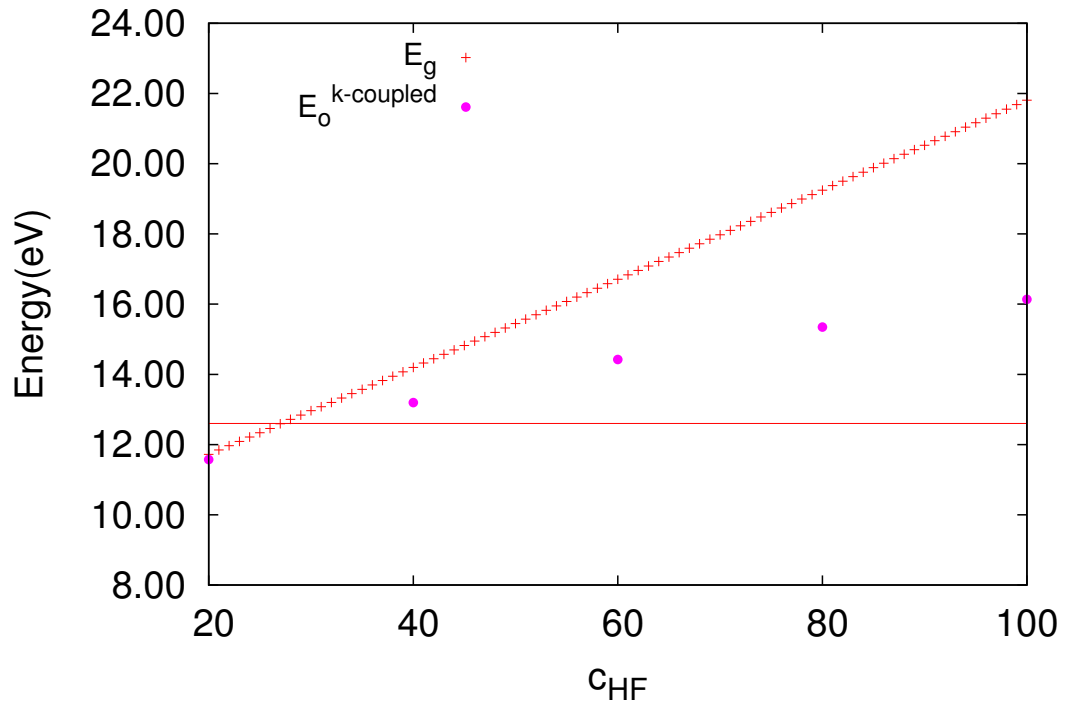


Figure 3.7: The dependence of energy and optical gaps of bulk LiF on the hybrid exchange fraction c_{HF} in B3LYP, using the Dovesi-Nada basis set pair. The horizontal line indicates the experimental optical gap (12.6 eV).

(where $E_{x/c}^{\text{LDA}}$, $E_{x/c}^{\text{GGA}}$ are LDA and GGA exchange/correlation energies, $E_{x/c}^{\text{HF}}$ is the Hartree-Fock exchange energy, $a_x = 0.72$ and $a_c = 0.81$) with a slope given by $\partial E_{xc}^{\text{B3LYP}}/\partial c_{\text{HF}} = E_x^{\text{HF}} - E_x^{\text{LDA}}$.

In hybrid Kohn-Sham theory, increasing c_{HF} results in a progressive attenuation of the spurious self-interaction among occupied orbitals, with a consequent decrease of the energy of all occupied orbitals ϕ_i . E_g as defined above thus increases linearly with c_{HF} , with a slope approximately given by $E_x^{\text{HF}} - E_x^{\text{LDA}}$. The results shown in Figure (3.7) therefore support the underlying assumptions of Eqn. (3.4) of a well localised (Frenkel) and disjoint (charge-transfer) electron-hole pair, consistent with a pure CTE model. Quantitative agreement between the calculated and experimental LiF optical gap can be obtained for a function of the B3LYP form, by setting $c_{\text{HF}} \simeq 0.32$.

The inability of standard local, semi-local and global hybrid ($c_{\text{HF}} < 1$) exchange-correlation functionals to account quantitatively for charge transfer excitations in molecules is well documented in the literature [111]. Our work demonstrates that a similar situation holds for the lowest excitation in crystalline LiF and other alkali halide crystals, as can be seen in Table 3.5. There is however an important difference between a pure charge transfer excitation in an isolated molecule, in which the electron and hole orbitals are well localised in disjoint and finite regions of space, and the CTE model, in which both the electron and the hole have to remain delocalised on a shell of ions because of the constraints imposed by the crystal symmetry. This kind of "residual" delocalisation has also been observed in GW+BSE calculations [100]. The dependence of the localisation properties of the hole orbital on c_{HF} is likely to be more marked than in an isolated molecule, and may result in small variations of the integrals $(aa|ii)$ in Eqn. (3.4) as c_{HF} changes in a global hybrid scheme. Therefore, the dependence of $A_{ai,ai}$, i.e. of the optical gap, on c_{HF} can exhibit a slightly non-linear behaviour. This appears indeed to be the case in LiF according to the optical gap results shown in Figure 3.7. We also note that this non-linearity affects the optical gap, but not the band gap, at least within the levels of accuracy considered in this work. This fact is likely to be a consequence of the coupling of excitations at different $\mathbf{k}$ -points, which amplifies the changes in the localisation properties of individual hole orbitals at different $\mathbf{k}$ -points induced by changes in c_{HF} . This coupling affects the optical gap but it leaves individual one-particle orbitals energies at different $\mathbf{k}$ -points and therefore the Kohn-Sham gap, unchanged.

We find that when $c_{\text{HF}} = 0.32$, we obtain an E_o of 12.57 eV, which is in good agreement with observed experimental values. However, at this contribution of HF exchange the one-particle eigenvalue gap E_g , and the exciton binding energy E_b (which is the

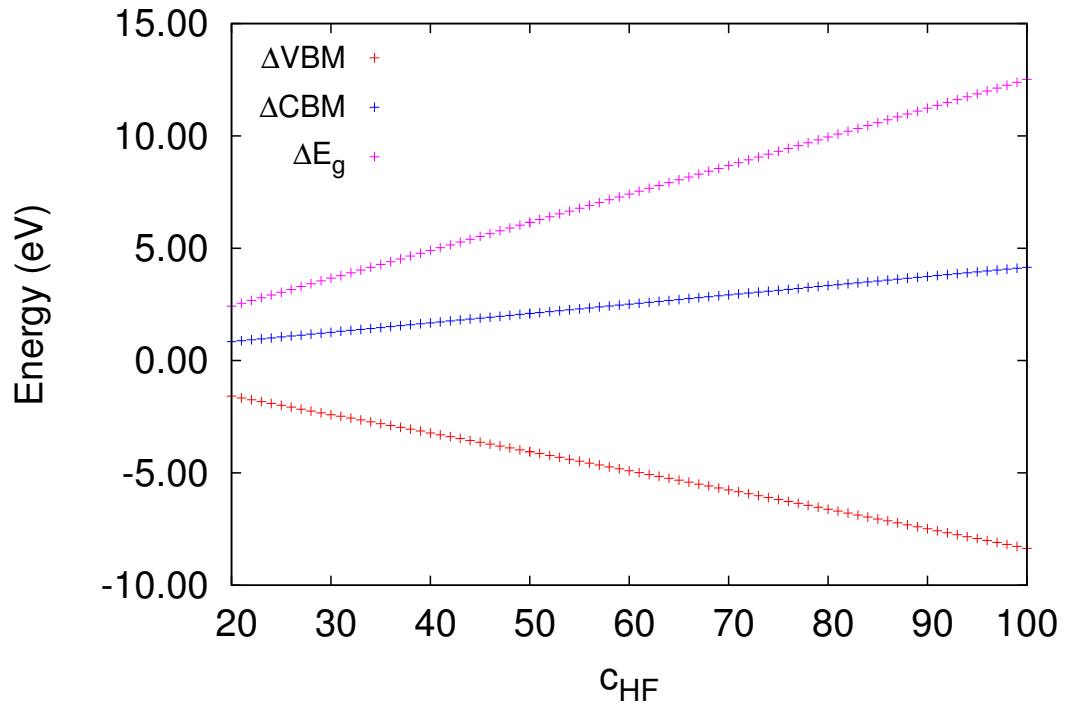


Figure 3.8: The dependence of the CBM and VBM on the HF exchange energy contribution c_{HF} to B3LYP using the Dovesi-Nada basis set pair for bulk LiF.

difference between the one-particle E_g and many-body E_o) are 13.20 eV and 0.63 eV respectively, and still beneath the experimental values. By further increasing c_{HF} to 0.35, E_g now becomes equivalent to the experimental gap, but E_o is overestimated and E_b is underestimated, at 13.57 eV, 12.82 eV and 0.75 eV respectively.

This implies that by changing the contribution of HF exchange to the B3LYP functional, we change the degree of localisation of the exciton. Secondly, as there is no single value of c_{HF} which is able to reproduce both E_g and E_o , B3LYP is unsuitable for describing the CT exciton of LiF. An xc-functional which does not use a constant value of c_{HF} (*e.g.* a range-separated hybrid) may be able to accurately describe both the E_g and E_o in a single calculation, [103, 112, 113].

3.4.4 NaF Study

Equivalent to the study undertaken on the LiF unit cell, a study of the effect of basis set on the static MDP and total energy has been repeated on a NaF unit cell, as can be seen in Figure 3.9. We observe a similar trend of basis set pairs which have reached a minimum in the total energy, but not a maximum in the MDP.

Of particular interest is the basis set pair at 80 AOs per unit cell, which also originates from the Ahlrichs def2-QZVP basis sets [105, 114], as seen in the LiF study. The MDP is at the maxima plateau, and the total energy is the lowest of the 10 studied pairs. However, we find that $E_g^{B3LYP} = 11.90$ eV for this basis set pair, slightly larger than the experimentally obtained value of 11.7 eV [115]. Furthermore, we find that there is a greater dependence of E_g^{B3LYP} on the basis set choice for NaF than for LiF, as shown in Figure 3.10.

We hypothesise that this increased dependence of E_g on basis set quality stems from the polarisability of the alkali cation. A sodium cation is more polarisable than a lithium cation, so an improved description of the diffuse orbitals will lead to a bigger change in character of the sodium species than for the lithium.

3.5 The Alkali Halide Series

3.5.1 Kohn-Sham and Optical Gaps

The dielectric constants of the alkali halides range from ($\epsilon_r \approx 4.8 - 13$) [116]. These are moderately high values, indicating that the alkali halides will generate Wannier excitons. Experimental values for E_g and E_o of members of the alkali halide series are given in Table 3.5. Values of E_g and E_o were deduced from a range of methods, such

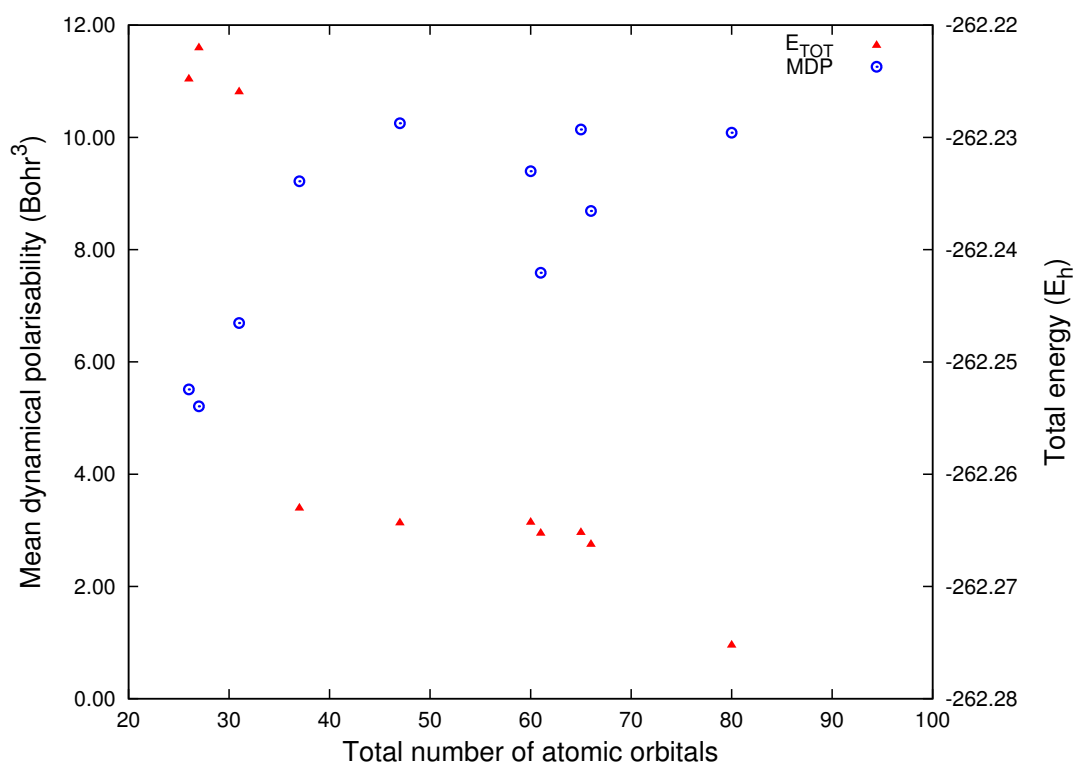


Figure 3.9: MDP and total energy against total number of atomic orbitals within a NaF unit cell. The left axis (blue circle) is the MDP; the right axis (red triangle) is the total energy.

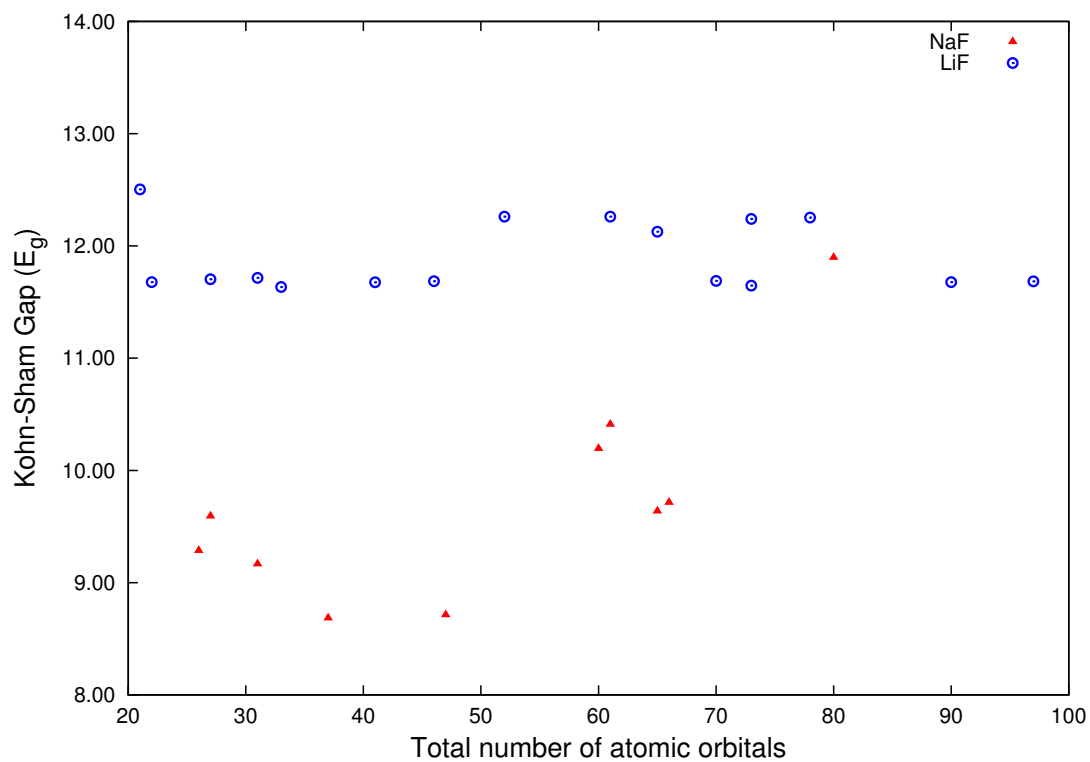


Figure 3.10: E_g^{B3LYP} against the total number of atomic orbitals within LiF and NaF unit cells.

E_g	Fluoride		Chloride		Bromide	
	Expt.	B3LYP	Expt.	B3LYP	Expt.	B3LYP
Li	13.6 ⁱ -14.5 ⁱⁱ	11.686	9.4 ⁱⁱⁱ	8.192	7.6 ⁱⁱⁱ	6.967
Na	11.7 ^{iv}	11.899	8.6 ^v	7.291	7.7 ^v	6.262
K	10.9 ^v	8.426	8.5 ^v	6.845	7.8 ^v	6.215
Rb	10.4 ^v	5.943	8.2 ^v	3.668	7.7 ^v	3.085
E_o	E_o^u E_o^c		E_o^u E_o^c		E_o^u E_o^c	
Li	12.6 ⁱ	11.608 11.40	8.6 ^v	8.089 8.14	7.20 ^{vi}	5.504 6.61
Na	10.7 ⁱ	11.862 9.12	7.96 ^{vi}	7.219 7.08	6.68 ^{vi}	4.836 6.11
K	9.76 ^{vii}	8.380 8.14	7.76 ^{vi}	6.782 6.70	6.77 ^{vi}	4.788 6.04
Rb	9.5 ^{viii}	5.923 4.27	7.51 ^{vi}	3.597 3.55	6.60 ^{vi}	1.902 3.04
E_b	E_b^u E_b^c		E_b^u E_b^c		E_b^u E_b^c	
Li	1.0-1.9	0.078 0.29	0.80	0.103 0.05	0.40	1.463 0.36
Na	1.0	0.037 2.78	0.64	0.072 0.21	1.02	1.426 0.15
K	1.0	0.046 0.29	0.74	0.063 0.15	1.03	1.427 0.18
Rb	0.9	0.021 1.67	0.69	0.071 0.12	1.90	1.183 0.05

i:Ref. [23], *ii*:Ref. [95], *iii*:Ref. [118], *iv*:Ref. [115], *v*:Ref. [89], *vi*:Ref. [119], *vii*:Ref. [117], *viii*:Ref. [120]

Table 3.5: **k**-uncoupled (E^u) and **k**-coupled (E^c) calculated and experimental energy gaps (E_g), optical gaps (E_o) and exciton binding energies (E_b) for the alkali halide crystal series.

as reflectometry of bulk crystals [23, 117], extreme-UV spectroscopy of thin-films on a variety of substrates [118], X-ray absorption of thin-films on Ni substrates [115], and optical and UV absorption spectroscopy of thin-films on LiF substrates [89, 119].

We can clearly see that the E_b of the excitons are far greater than the threshold for Wannier excitons, indicating that the alkali halide series represents a variety of systems in which excitons can exhibit Frenkel, Wannier or intermediate characteristics, with the Wannier and Frenkel models as extreme idealised models. These intermediate characteristics are evidenced in the alkali halides by the strongly coupled electron-hole pair which is delocalised over a large distance, such as the CTE/Frenkel exciton hybrid as described by Abbamonte *et al.* [97].

We list in Table 3.5 E_g^{B3LYP} , E_o^{B3LYP} and E_b^{B3LYP} for the complete alkali halide series obtained at both the **k**-uncoupled (E^u) and **k**-coupled (E^c) levels of TD-B3LYP 2.8, with the polarisation-optimised m-def2-QZVP basis set series. Many software suites are unable to incorporate the coupling of **k**-points into excited state calculations of extended systems, and thus by removing the coupling within CRYSTAL, a better comparison of the data can be made to other uncoupled calculations. It can be clearly seen that the effect of the **k**-coupling on E_o varies widely across the alkali halide series.

The greatest absolute change in E_o is seen in the alkali bromide systems, where the $\mathbf{k}$ -coupled values are > 1 eV greater than the $\mathbf{k}$ -uncoupled data, moving E_o closer to the experimental estimates. In the majority of systems, the inclusion of the $\mathbf{k}$ -coupling leads to greater values of E_b , consistent with a higher degree of localisation of the exciton pair. Similar to the case of LiF, for all systems we observe that TD-B3LYP describes a non-negligible exciton binding energy, regardless of the coupling of $\mathbf{k}$ -points. This indicates that although TD-B3LYP provides a qualitatively correct description of bound excitons with this basis set series, the electron-hole interaction and/or the degree of localisation of their wavefunctions in the exciton pair are not reproduced quantitatively. Similar to LiF and NaF, we expect that a system-dependent and appropriate admixture of Hartree-Fock exchange ($c_{\text{HF}} > 0.2$) will result in larger values of E_b , and a change in the degree of localisation of the excited electrons. Range-separated hybrids and novel screened functionals may prove to be suitable choices for the exchange-correlation approximations of DFT methods, as shown in the preliminary work on LiF using the SXX [103] and bootstrap [18] response kernels.

As highlighted above (Section 3.4.4), the use of the m-def2-QZVP basis set for NaF results in an overestimation of E_g . Adopting the $\mathbf{k}$ -uncoupled method, E_o is still larger than the experimental value for E_g , whilst the $\mathbf{k}$ -coupled method greatly underestimates E_o , and the resulting E_b is ~ 1.8 eV greater than the experimental value. We find that the pob-TZVPP basis set, where the KS gap is > 3 eV smaller than for m-def2-QZVP, generates a bound exciton with $E_o^u = 8.71$ eV and $E_o^c = 8.54$ eV, $E_b^c = 0.17$ eV. Reducing the size of the basis set further, the pob-TZVP basis set has a 10 percent smaller MDP, and creates a bound exciton with $E_o^u = 8.67$ eV and $E_o^c = 8.51$ eV, $E_b^c = 0.17$ eV. It is interesting to note that although the MDP and E_g has changed between these two basis sets, E_b remains unchanged. This confirms that E_g alone should not be used to quantify the suitability of basis sets for excited state calculations.

We also note that a larger mismatch between experimental and theoretical values of E_o and E_g is observed for the heavier element systems, particularly in the Rb series, possibly in consequence to the neglect of relativistic and spin-orbit correction to the KS/HF Hamiltonians [121]. An alternative source for this disparity is the use of basis sets which are underconverged for either the polarisability or total ground state energy. As we can see from Table 3.5, the calculated values of E_o and E_g for the lighter alkali systems are much closer to experimental values, indicating that the halide basis set is not solely responsible for this mismatch in the heavier element systems.

As highlighted earlier in this work, there is a current lack of suitable basis sets

for excited state calculations in extended systems. The vast majority of basis sets are converged with respect to total energy, which is only dependent on the description of occupied orbitals. This study shows that basis sets of extended systems must be chosen carefully for reliable excited state calculations, taking into account first-order response properties, in conjunction with the number of atomic orbitals per formula unit (N_{AO}) for an optimal choice of basis set. On the other hand, high-quality molecular basis sets which are suitably polarisable for excited state calculations are common, which often results in basis sets for extended systems being based upon modified molecular basis sets. One consideration which must be made when importing molecular basis sets for crystalline systems is the introduction of linear dependence. Many basis sets created for molecular ground-state calculations contain diffuse functions with exponents < 0.06 , which may pose no problems in molecular calculations. However, the replication of a unit cell into a bulk material can lead to non-negligible orbital interactions caused by the accumulation of diffuse orbitals, such as linear dependence and incorrect electronic structures. In this work, we followed the pruning plus diffuse exponent adjustment techniques described *e.g.* by Peintinger *et al.* [78]. The pruning method undertaken involves the initial removal of functions containing exponents more diffuse than 0.06, followed by procedural removal of the most diffuse exponents until a stable wavefunction or ground-state density is calculated. Starting from this point, we attempt to make the basis set more diffuse by introducing functions with exponents 0.4 times the size of the currently smallest exponent for that shell, repeating this process until the reintroduction of linear dependence or a clearly incorrect ground state. We believe this method creates basis sets which are reliable for excited state calculations of extended systems.

3.5.2 Comparison to PBE and VASP

To aid in the resolution of this heavy-element disparity, PBE calculations were carried out on the alkali halide series, using polarisation-optimised m-def-QZVP basis sets. This allows for a direct comparison to the PBE calculations of Gopikrishnan *et al.* (Section 3.3.1), where planewaves were used instead of an all-electron basis set. In Table 3.6 we compare our values of E_g^{PBE} to both VASP/PAW results [99] and experimental data.

We see that the VASP/PAW results are further from the experimental values for all systems apart from the rubidium halides, which are also greatly underestimated by this approach. Excluding the rubidium halides, our data for E_g^{PBE} is < 1 eV above the VASP data for all systems apart from NaF, an effect seen for B3LYP and highlighted above (see Section 3.4.4). If the pob-TZVPP basis set is used for the PBE calculation of NaF, our all-electron value of E_g is 6.39 eV, which is in agreement with

	E_g (eV)		
	m-def2-QZVP	Planewave [99]	Experimental
LiF	9.63	8.94	13.6 [23]
LiCl	6.81	6.32	9.4 [118]
LiBr	5.69	4.91	7.6 [118]
NaF	9.61	6.16	11.7 [115]
NaCl	5.88	5.00	8.6 [89]
NaBr	4.97	4.09	7.7 [89]
KF	6.49	6.07	10.9 [89]
KCl	5.45	5.05	8.5 [89]
KBr	4.92	4.31	7.8 [89]
RbF	3.17	5.51	10.4 [89]
RbCl	metal	4.82	8.2 [89]
RbBr	1.92	4.20	7.7 [89]

Table 3.6: Comparison of E_g^{PBE} from this work using the m-def2-QZVP basis set, with the planewave calculations of Gopikrishnan *et al.* [99]

the trend seen for the other alkali halide systems. It is clear that due to this qualitative agreement between all-electron and planewave results, the values of E_g^{B3LYP} for these heavier systems as seen in Table 3.5 are not underestimated solely due to the degree of diffusivity of the all-electron basis set, but is likely due to an effect neglected by both the planewave and all-electron approaches, such as spin-orbit or relativistic effects. The pseudopotential approximation assumes that core electrons are barely affected by molecular and crystalline structures, allowing one to treat an electronic structure as valence electrons affected by fixed ions. However, the choice of pseudopotential used to represent the core electrons can greatly influence the electronic structure of a system, as core electrons are susceptible to relativistic effects.

4

Carbon Nanotubes

4.1 Introduction

Single-walled carbon nanotubes (SWCNTs) are a polymorph of carbon, commonly visualised as sheets of graphene [122, 123] which have been rolled and fused along opposite edges. Their structures have high aspect ratios and remarkable physical properties such as high stiffness, strength and Young’s modulus [124, 125]. In addition, the high surface-area [126, 127], internal volume [128, 129] and porosity [130] has lead to research [131] into the application of carbon nanotubes towards energy storage [132–134] and production [132, 135], composite materials [136], and drug delivery [137, 138].

Graphene is a two-dimensional metallic sheet, due to a remarkable electronic structure with Dirac cones at the point $\mathbf{K}$ in reciprocal space, shown in Figure 4.1 (left). These positions in $\mathbf{k}$ -space are where the conduction band minimum (CBM) and valence band maximum (VBM) touch at a single point (Figure 4.1, right), resulting in massless Dirac fermions (*i.e.* $d\epsilon/d\mathbf{k} = \text{constant}$) which can effortlessly transition between the conduction and valence bands [139].

When creating a SWCNT, the curvature of the graphene sheet results in distortion of its electronic structure, moving the Fermi energy (E_F) out of the Dirac cone, creating a semiconducting system [140]. As a result, the electronic and optical properties of SWCNTs can be changed by altering the diameter of the nanotube or the “roll-up” vectors m and n used to define the tube. Through the creation and functionalisation of defects in nanotubes, the electronic and optical properties can be further tuned [141]. Although we treat SWCNTs as one-dimensional periodic systems of infinite length in this work, the termination of nanotubes further increases the opportunities for controlling the properties of these systems [142, 143].

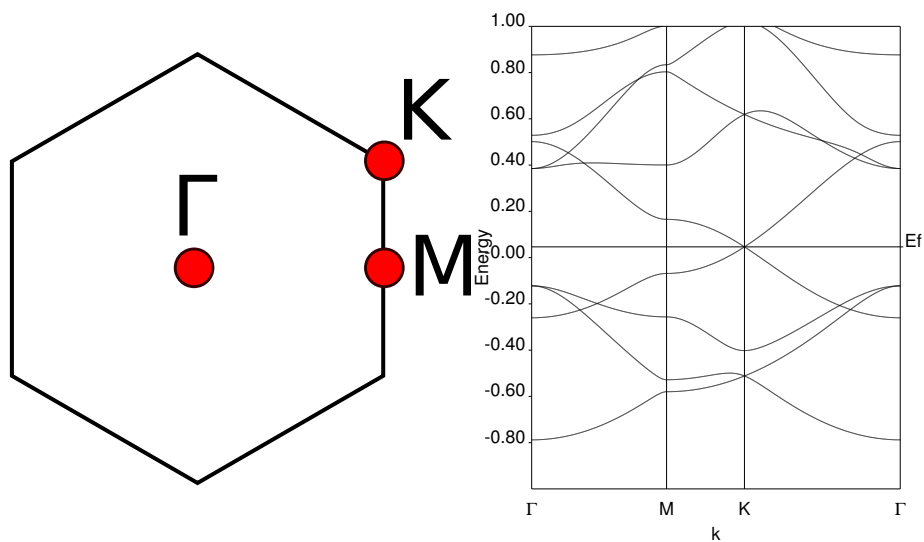


Figure 4.1: First Brillouin zone of graphene, with labelled high-symmetry points (*left*) and the B3LYP band structure of graphene, using the m-def2-QZVP basis set (*right*).

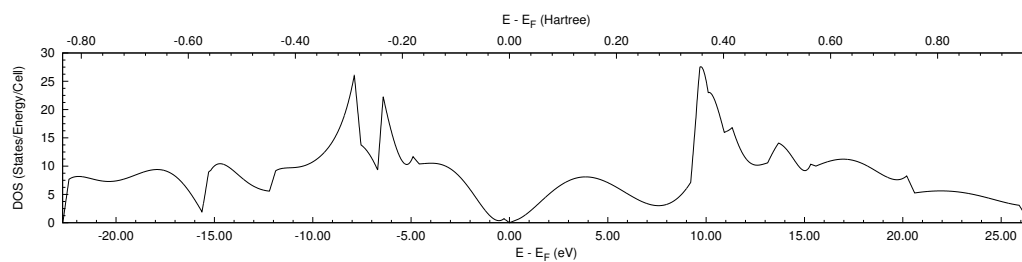


Figure 4.2: Total density of states of graphene, studied with the m-def2-QZVP basis set at the B3LYP level of theory.

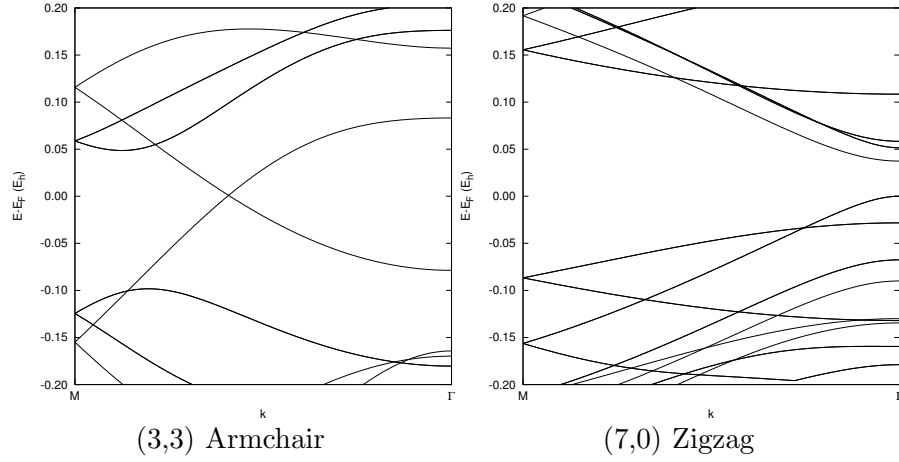


Figure 4.3: Comparison of the band structures of an armchair and semiconducting zigzag nanotube, calculated using B3LYP with the pob-TZVP basis set, using geometry C.

4.2 Classification of Nanotubes

There are three commonly used classifications for the nuclear structures of SWCNTs due to the roll-up vectors used - *armchair* ($m=n$), *zigzag* (m or $n = 0$) and *chiral*. When $(m - n)/3$ is an integer, the nanotube band structure includes the graphene high-symmetry point K , where E_F passes through the Dirac cone, making the nanotube metallic in character (this is further referred to as the *zone-folding* or $(m - n)/3$ rule) [144, 145]. As a result all armchair nanotubes should be metallic ($(m - n)/3 = 0$), whilst zigzag and chiral nanotubes exhibit varying degrees of semiconducting character, unless $(m - n)/3 = \mathbb{Z}$, where $\mathbb{Z}$ represents the mathematical set of all integers. If the electronic structure of graphene is unperturbed by the curvature of the nanotube then the zone-folding classification scheme is reliable [146, 147], as shown experimentally in Scanning Tunnelling Spectroscopy (STS) studies of Wildöer *et al.* [148] and Raman spectroscopy studies of Dresselhaus *et al.* [149] for example. Further STS studies by Ouyang *et al.* [150] have shown that under the influence of curvature effects, the zone-folding scheme is inadequate if left unmodified, which is in agreement with previous theoretical work, such as the pseudopotential LDA and Tight-Binding (TB) studies of Blase *et al.* [151].

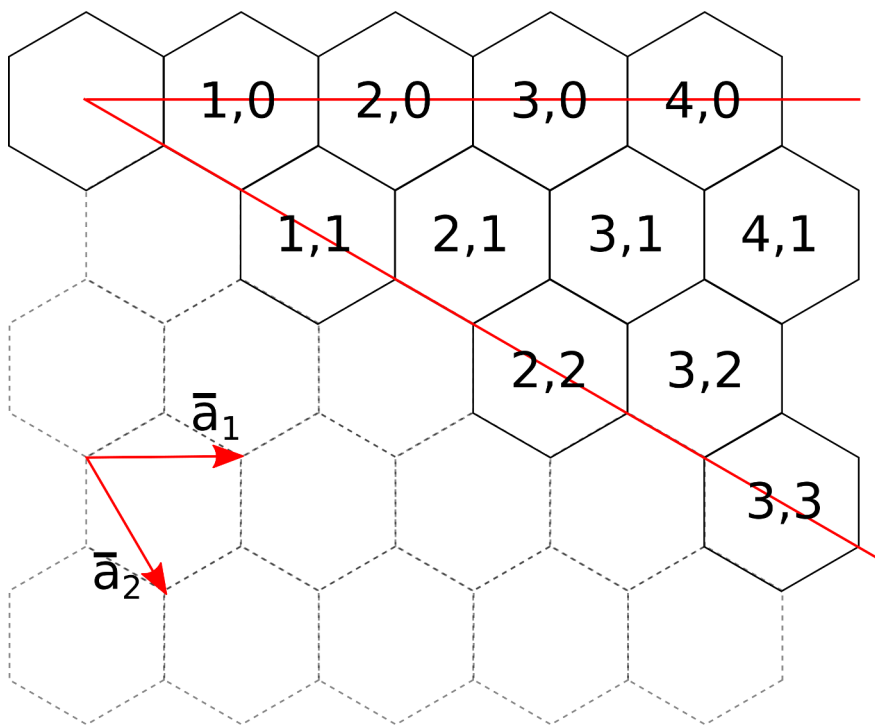


Figure 4.4: Indices and vectors used for nanotube generation.

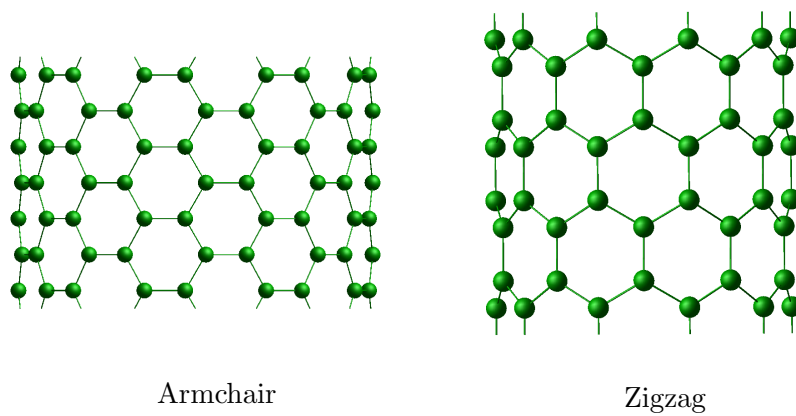


Figure 4.5: A visual comparison of the armchair and zigzag structure types.

4.3 Density of States

The quasi-one-dimensionality of nanotubes introduces phenomena in their density of states, known as van Hove singularities [152] (see Figure 2.1). In a truly one-dimensional system, the van Hove singularities are symmetrical about the Fermi energy (metals) or the center of the band gap $((E_{c1} - E_{v1})/2$, for semiconductors) in both peak energy and density. However the curvature of SWCNTs introduces asymmetry, as seen in the theoretical work by Spataru [153] (Section 4.5) and the experimental work of Wildöer [148] (Section 4.4). By increasing the diameter of a SWCNT, the reduced curvature would result in increased symmetry of the van Hove singularities, around the center of the bandgap, and conversely the two-dimensional nature of the system, removing the singularities.

Optical selection rules show that excitations parallel to the nanotube axis must conserve the magnetic quantum number ($\Delta m = 0$), whilst excitations perpendicular to the nanotube axis involve a singular difference in the magnetic quantum number ($\Delta m = \pm 1$) [154–156]. As a result, optical excitations from polarisation parallel to a nanotube’s axis occur between matching bands with the same magnetic quantum number, and are labelled E_{ii} . Here, i is an index of bands, with $i = 1$ for the conduction and valence bands, which can also be denoted as E_{c1} or E_{v1} respectively. For polarisation perpendicular to the nanotube axis, when the magnetic quantum number changes by one, the resulting excitation is labelled E_{ij} , with the same indexing as for the parallel excitations (*i.e.* where the subscript values indicate the donor and acceptor band indices, respectively). This excitation model only holds true for the absorption of a single photon, and by conducting two-photon absorption, previously symmetry-forbidden (also known as *dark*) excited states can be attained [156].

4.4 Experimental Review

As briefly highlighted in the introduction, studies on SWCNTs fit within many fields of research, leading to a high quantity of modern literature. The works reviewed in the following two sections are a selection of experimental and theoretical studies which focus on the electronic and optical properties of SWCNTs.

Bachilo

Bachilo *et al.* [157] collected spectrofluorimetric measurements for 33 different SWCNT species. In conjunction with Raman studies, they concluded that optical spectroscopy

can be used to characterise the composition of nanotube suspensions, and they supply spectral shifts (E_{11} and E_{22}) and nanotube assignments for the studied systems.

Wildöer

Using scanning-tunneling microscopy (STM) and scanning-tunneling spectroscopy (STS), Wildöer *et al.* [148] studied the diameter and E_g for a range of individual single-walled carbon nanotubes on an Au substrate. They observe that Van Hove peaks in their experimental DOS are not symmetrical around E_F for a semiconducting nanotube, with E_F very close to the valence band. However, the authors provide a calculated DOS for a similar-diameter, semiconducting nanotube which shows symmetry of the singularities around E_F , but they do not supply computational details. The authors suggest the symmetry disparity between experimental and theoretical DOS is indicative of charge-transfer from the Au(111) substrate to the nanotube (*i.e.* the substrate is n-doping the nanotube.)

Maultzsch

Maultzsch *et al.* [156,158] conducted two-photon photoluminescence studies on five different chiral nanotube systems, dispersed in D₂O. As noted in the introduction, the optical selection rules for one-photon excitations in SWCNTs limit the acceptor and donor orbitals to having the same magnetic quantum number for axis-parallel excitations. In addition, the dipole operator for each one-photon excitation is odd-parity, with respect to a plane perpendicular to the nanotube axis. Two-photon excitations are not restricted by the one-photon symmetry rules, and instead can excite into previously *dark* excited states, with even-symmetry of the dipole operator. The authors aimed to compare data from one-particle and two-particle excitations to quantify the Coulombic interaction felt between an electron and hole within each SWCNT (*i.e.* E_b).

Unlike one-photon excitations which can be reliably modelled as a linear response to the external field, two-photon excitations are nonlinear processes, and are commonly generated with bursts of high-intensity laser light (150 fs bursts in this work of Maultzsch *et al.*). Whilst absorption spectroscopy quantifies the absorption of photons of a specific energy, photoluminescence spectroscopy studies the light emitted from the sample after photoabsorption, and is able to quantify time-dependent emissions, allowing further analysis of radiative decay processes (*e.g.* phosphorescence and fluorescence).

By comparing the lowest-energy photon from emission studies (E_{11}^{1u}) to the maxi-

imum absorption intensity from two-photon excitations (E_{11}^{2g}), they find a range of values for E_b^{2g-1u} around 0.24-0.325 eV for the nanotubes studied. They subsequently used GW-BSE calculations in an all-electron Gaussian basis set to compute both one-photon and two-photon excitations.

In the example chiral (6,4) nanotube, they show that the comparison between the two-photon and one-photon absorption ($E_b^{2g-1u} = 0.34$) eV is in good agreement with their experimental data ($E_b^{2g-1u} = 0.325$) eV. By comparison between the one-photon absorption maximum with the electron-hole interaction, and the absorption maximum without the electron-hole interaction (E_g^{GW}), they find E_b to be ~ 0.5 eV.

With an E_b much larger than 0.1 eV, the exciton might usually be classed as Frenkel-like in nature, however the authors show that the exciton wavefunction is delocalised around the axis of the nanotube, and also partially along its length, which is more consistent with a Wannier-type exciton.

Ma

The exciton binding energy of the (8,3) nanotube was studied by Ma *et al.* [159], using transient absorption (TA) spectroscopy. In TA spectroscopy, the time-resolved absorption of light is measured as a function of photon energy, after an initial excitation.

By studying the effect of the probe intensity on the amplitude of the response, and its subsequent decay, the authors were able to characterise a 730 nm excitation as belonging to the “electron-hole continuum” and a 935 nm gap as the exciton-forming state “ E_1 ”. Subtraction of these two values leads to $E_b = 0.41$ eV, a value in good agreement with that deduced from two-photon photoluminescence studies by Maultzsch *et al.* [158].

Miyauchi

Using photoluminescence excitation spectroscopy (PLE) with polarised light, Miyauchi *et al.* were able to study and characterise the nature of a number of excitations occurring within a suspension of SWCNTs [154]. The authors show that the E_{11} and E_{22} excitations arise from photoabsorption parallel to the nanotube axis, and that despite the self-induced depolarisation effect on excitations which are perpendicular to the nanotube axis [160,161], their study finds photoexcitations at energies between that of E_{11} and E_{22} , due to photoabsorption perpendicular to the nanotube axis. This so-called self-induced depolarisation occurs when an external field is applied perpendicular to the nanotube axis, and the induced change in the charge density leads to an electric field

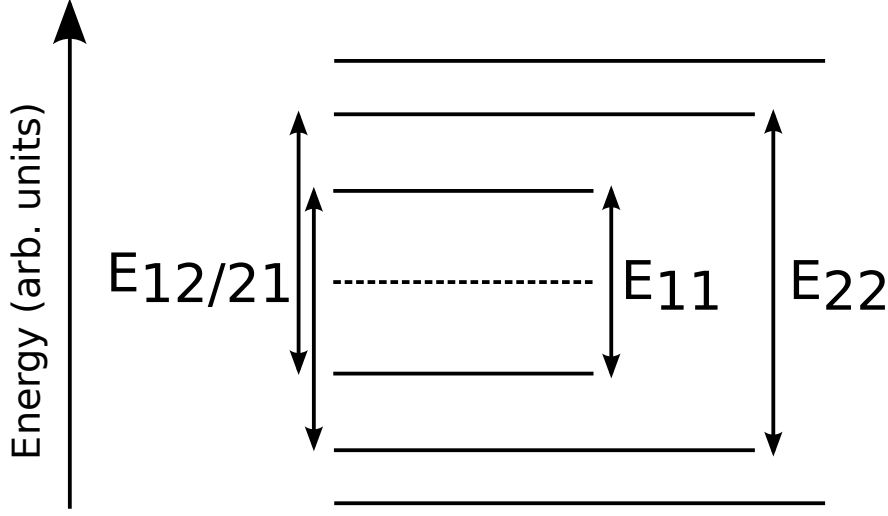


Figure 4.6: Idealised model of the tight-binding energy levels of a carbon nanotube. The horizontal dashed line represents the Fermi energy, E_F .

which opposes the external field [160]. The resultant total electric field is negligible, which leads to a small induced dipole, and a low polarisability.

They provide evidence that there is a large degree of asymmetry in the conduction and valence bands by studying the forbidden E_{12} and E_{21} transitions and comparing to tight-binding (TB) calculations. In the TB models, the conduction and valence bands share a large degree of symmetry which results in similar values for E_{12} and E_{21} ; in the case of purely symmetric bands, $(E_{11} + E_{22})/2 = E_{12} = E_{21}$, as shown in Figure 4.6. The data of Miyauchi and coworkers shows a blue-shift of the values for E_{12} and E_{21} by ~ 0.3 eV above the value of $(E_{11} + E_{22})/2$, leading to the conclusion that the perpendicular excitations (*i.e.* E_{12} , E_{21}) will result in smaller values of E_b .

4.5 Theoretical Review

Spataru

Spataru *et al.* [153] used pseudopotential LDA, followed by GW-BSE calculations to study the optical spectra of the small diameter (3,3), (5,0) and (8,0) nanotubes. The authors point out that due to depolarisation effects in nanotubes [160, 161], a strong optical response is observed only when the applied electric field is parallel to the nanotube axis. Depolarisation in nanotubes occur when self-induced electric fields oppose an external field which is applied perpendicular to the nanotube axis. This effect leads

to optical spectra where the $\Delta m \pm 1$ (e.g. E_{12} , E_{21}) peaks are suppressed and often unseen [160, 162].

They produce a DOS for the metallic (3,3) nanotube which clearly shows asymmetric van Hove singularities, finding that the first optically allowed transition is not between the two singularities closest to E_F , but between the first singularity above E_F , and the second singularity beneath E_F . By comparing their lowest optically allowed GW gap, to the optical gap from the BSE calculation, they find an exciton binding energy of 0.086 eV. The authors also find that the exciton is delocalised over a distance of ~ 50 Å along the nanotube axis, far greater than the distance suggested by the length scale deduced from two-photon photoluminescence studies of Maultzsch and coworkers [158].

They also studied the optical absorption of the (5,0) nanotube which should formally be a semiconductor, using the zone-folding approach, but is affected by strain-induced metallicity. The authors find negligible E_b for this system, which they attribute to the symmetry of the nanotube bands inhibiting any excitonic electron-hole interactions. By comparison to the experimental data of Bachilo *et al.* [157] ($E_{11} = 1.60$ eV, $E_{22} = 1.88$ eV), they find good agreement for the first and second excitation energies calculated with GW-BSE for the (8,0) nanotube ($E_{11} = 1.55$ eV, $E_{22} = 1.80$ eV).

4.6 This Work

4.6.1 Computational Details

As SWCNTs can possess a wide range of electronic properties, ground-state SCF calculations for SWCNTs often require a range of parameters, different to those used for the alkali halide studies (Chapter 3). Unless otherwise noted, for all of the following calculations there is no forced separation of the occupied and unoccupied orbitals, and a small addition of $0.001 E_h$ of thermal energy is introduced, to allow for the convergence of metallic systems. All calculations on SWCNTs were carried out within the CRYSTAL14 software suite, using default parameters unless otherwise specified. The energy tolerance for convergence of the SCF was set to $10^{-7} E_h$ for the ground-state calculations, and the polarisability tolerance for the convergence of the $\mathbf{k}$ -coupled perturbation calculations was set to $10^{-4} a_0^3$. For all calculations, the first four truncation tolerances were set to 10^{-7} , where the first and second tolerances control the Coulomb summation, and the third and fourth tolerances control the exchange summation. For LDA and B3LYP calculations, the final (fifth) truncation tolerance was set to 10^{-14} , whilst HF calculations were undertaken with a tolerance of 10^{-20} (see [104]). This final

tolerance regards the truncation of the Fock summation in direct space, based on the overlap integral of the most diffuse Gaussian function in each shell of basis functions (see Section 2.4.1).

For LDA calculations, the mixing of the previous SCF Fock/KS matrix (see Section 2.2) between the current SCF cycle, and the previous cycle (as shown in Eqn (4.1)) is set to 50 percent.

$$F'_i = (1 - p)F_i + pF'_{i-1} \quad (4.1)$$

The one-dimensional irreducible Brillouin zone is sampled using a Monkhorst-Pack net of shrinking factor 18, resulting in 10 symmetry-inequivalent $\mathbf{k}$ -points, and is sampled using a Gilat net of shrinking factor 36 to generate 19 symmetry-inequivalent $\mathbf{k}$ -points for the calculation of the Fermi energy, E_F . For more information regarding the input and default parameters of CRYSTAL, please refer to the manual [104].

4.6.2 Geometry Optimisation

In graphene, the carbon-carbon bond length has been found experimentally to be 1.42 Å [139,163], the same as that of graphite, found through x-ray diffraction [164]. Full geometry relaxations allowing optimisation of bond lengths and lattice constants were undertaken for a range of SWCNTs created from graphene at the experimental lattice constant. Two different basis sets were used with the B3LYP hybrid functional to create two additional geometries for each nanotube; a nanotube with structure **A** is the unrelaxed geometry (*i.e.* a rolled-up sheet of graphene at the experimental lattice constant), whilst structures **B** and **C** are from optimisations of structure **A** using the pob-TZVP and m-def2-QZVP basis sets, respectively. As nanotubes are strictly two-dimensional with curvature only along one dimension, there are multiple carbon-carbon bond lengths, and in Table 4.1 and Figure 4.7 we show the average bond length for each nanotube.

We see that as the nanotube diameter increases, the average bond length tends toward that of graphene in the cases of all three structure sets. This is reasonable as in the limit of a very large diameter, the curvature of a nanotube tends to zero, and the properties will tend to that of a graphene sheet. However, whilst the pre-optimisation bond-length reaches a maximum at that of graphene, nanotubes with a diameter > 7 Å have an optimised average bond length smaller than that of graphene for **B** geometries (those optimised with the pob-TZVP basis set) - an effect seen in the **C** structures for nanotubes wider than 10 Å (those optimised with the m-def2-QZVP basis

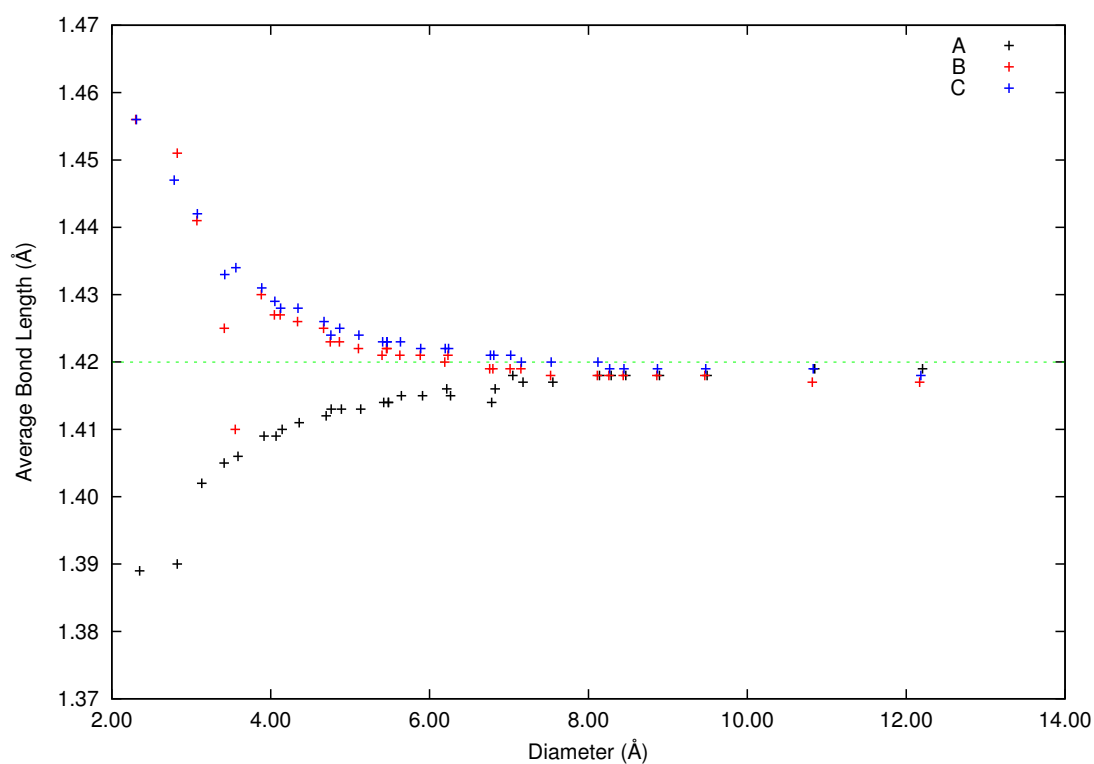


Figure 4.7: Comparison between the average bond length and nanotube diameter, for three different geometry sets - graphene, pob-TZVP optimised and m-def2-QZVP optimised, using B3LYP. The horizontal dashed lined represents the experimental bond length of graphene.

Indices	Graphene (A)		pob-TZVP (B)		def2-QZVP (C)	
	Diam. (Å)	Avg. C-C (Å)	Diam. (Å)	Avg. C-C (Å)	Diam. (Å)	Avg. C-C (Å)
(3,0)	2.350	1.389	2.300	1.456	2.310	1.456
(3,1)	2.824	1.390	2.824	1.451	2.786	1.447
(4,0)	3.132	1.402	3.072	1.441	3.078	1.442
(3,2)	3.414	1.405	3.416	1.425	3.422	1.433
(4,1)	3.588	1.406	3.554	1.410	3.562	1.434
(5,0)	3.916	1.409	3.882	1.430	3.888	1.431
(3,3)	4.068	1.409	4.046	1.427	4.052	1.429
(4,2)	4.144	1.410	4.120	1.427	4.126	1.428
(5,1)	4.360	1.411	4.338	1.426	4.344	1.428
(6,0)	4.698	1.412	4.666	1.425	4.672	1.426
(4,3)	4.762	1.413	4.750	1.423	4.758	1.424
(5,2)	4.890	1.413	4.866	1.423	4.870	1.425
(6,1)	5.134	1.413	5.104	1.422	5.110	1.424
(4,4)	5.424	1.414	5.402	1.421	5.410	1.423
(5,3)	5.482	1.414	5.466	1.422	5.464	1.423
(7,0)	5.482	1.414	5.458	1.422	5.466	1.423
(6,2)	5.646	1.415	5.626	1.421	5.634	1.423
(7,1)	5.912	1.415	5.884	1.421	5.888	1.422
(6,3)	6.216	1.416	6.192	1.420	6.198	1.422
(8,0)	6.264	1.415	6.232	1.421	6.240	1.422
(5,5)	6.782	1.414	6.758	1.419	6.766	1.421
(6,4)	6.826	1.416	6.798	1.419	6.808	1.421
(9,0)	7.048	1.418	7.014	1.419	7.022	1.421
(8,2)	7.176	1.417	7.150	1.419	7.156	1.420
(7,4)	7.552	1.417	7.524	1.418	7.532	1.420
(6,6)	8.138	1.418	8.112	1.418	8.120	1.420
(8,4)	8.286	1.418	8.258	1.418	8.268	1.419
(9,3)	8.470	1.418	8.438	1.418	8.448	1.419
(8,5)	8.894	1.418	8.862	1.418	8.870	1.419
(7,7)	9.494	1.418	9.466	1.418	9.476	1.419
(8,8)	10.850	1.419	10.818	1.417	10.830	1.419
(9,9)	12.206	1.419	12.170	1.417	12.184	1.418

Table 4.1: Average bond lengths and diameters (in Å) for a range of SWCNTs, for three geometries : graphene (**A**), pob-TZVP-B3LYP optimised (**B**) and m-def2-QZVP-B3LYP optimised (**C**).

set). These averaged bond lengths differ from the graphene bond length by ~ 0.001 Å, which is a respectable value for B3LYP-based optimisation [165].

4.6.3 Fundamental Gaps of SWCNTs

In the following section, we study the effect of the choice of method, basis set and structure on the electronic properties of a range of infinite-length SWCNTs, with less than 200 atoms per unit cell. Unlike the alkali halide systems studied in Chapter 3 which have both the conduction band minimum and valence band maximum at the Γ -point, SWCNTs can be direct or indirect bandgap materials, with the CBM or VBM at different locations in reciprocal space. In this work, we will refer to the smallest HF/KS eigenvalue gap as E_g (which may be at any point in reciprocal space), and will refer to the E_g at Γ as E_g^Γ .

Three all-electron basis sets are studied in this work - m-def2-QZVP [105, 114], pob-TZVP [78] and 3-21G [107, 166]. The m-def2-QZVP basis set has been chosen to represent the limit of all-electron basis sets, pob-TZVP has shown promise as a small polarisation-optimised basis, and the 3-21G basis set has been chosen to study if exciton binding can be observed from minimal basis sets.

B3LYP

Using the B3LYP hybrid functional, ground-state calculations were run for a range of nanotubes, and the resulting values of E_g^Γ can be seen in Table 4.3 and Figure 4.3 for the three basis sets studied.

We see that the basis sets are often different, regarding the qualitative character of the electronic structure. This disparity grows further when the B3LYP-optimised geometries **B** and **C** are used - for example, the (7,1) nanotube is correctly described as metallic with the 3-21G basis set with geometry **A**, but the B3LYP-optimised structures lead to semiconducting character - an effect not seen with other basis sets.

Conversely, for a select number of nanotubes ((3,1), (4,0), (5,0)), both optimised basis sets incorrectly characterise the gap in comparison to the band-folding theory, whilst the 3-21G basis set is correct, regardless of the choice of geometry. The diameter-dependence on the character of E_g has also been seen in the work by Spataru *et al.* [153] and is discussed in detail in the study by Lu and Chen [167], and is an effect of the curvature of the nanotube. Planar graphene is an example of the sp^2 hybridisation of carbon, where the 4 valence electrons form a bonding pattern of three σ orbitals in the carbon plane at 120 degrees to each other, and a single π orbital which is perpendicular to the graphene plane, extending above and beneath. Curvature of the nanotube causes rehybridisation of the π orbitals, resulting in the breakdown of the zone-folding rule, as small-diameter nanotubes which are semiconducting in the zone-folding approach

Indices	Energy Gap, E_g^Γ (eV)								
	3-21G			pob-TZVP			m-def2-QZVP		
	A	B	C	A	B	C	A	B	C
(3,0)	0.903	-	-	-	-	-	-	-	-
(3,1)	1.514	-	-	-	-	-	-	-	-
(4,0)	1.950	-	-	-	-	-	-	-	-
(3,2)	2.197	0.955	0.962	1.805	1.655	1.648	1.890	1.685	1.677
(4,1)	-	2.518	2.521	-	-	-	-	-	-
(5,0)	2.578	1.097	1.103	-	-	-	-	-	-
(3,3)	-	-	-	-	-	-	-	-	-
(4,2)	2.443	2.536	2.514	2.172	1.993	1.981	2.114	1.957	1.945
(5,1)	1.462	-	-	1.524	1.022	1.016	1.466	0.982	0.966
(6,0)	-	1.452	1.453	-	-	-	-	-	-
(4,3)	1.762	1.618	1.611	2.360	2.148	2.139	2.328	2.120	2.099
(5,2)	-	2.730	2.711	-	-	-	-	-	-
(6,1)	2.041	1.680	1.666	1.223	1.272	1.261	1.260	1.311	1.305
(4,4)	-	-	-	4.701	4.932	4.938	4.486	4.700	4.674
(5,3)	1.775	1.925	1.918	1.882	1.932	1.924	1.883	1.929	1.929
(7,0)	1.046	-	-	1.365	1.037	1.017	1.284	0.974	0.964
(6,2)	1.192	0.891	0.880	1.847	1.558	1.544	1.782	1.514	1.488
(7,1)	-	2.387	2.410	-	-	-	-	-	-
(6,3)	-	-	-	-	-	-	-	-	-
(8,0)	1.679	1.548	1.524	1.303	1.338	1.327	1.297	1.332	1.329
(5,5)	-	-	-	5.132	-	-	4.864	-	-
(6,4)	1.380	1.476	1.471	1.460	1.506	1.499	1.483	1.509	1.513
(9,0)	-	0.664	0.678	-	-	-	-	-	-
(8,2)	-	-	-	-	-	-	-	-	-
(7,4)	-	-	-	-	-	-	-	-	-
(6,6)	-	-	-	-	-	-	-	-	-
(8,4)	0.925	0.844	0.837	1.253	1.168	1.156	1.223	1.153	1.145
(9,3)	-	-	-	-	-	-	-	-	-
(8,5)	-	-	-	-	-	-	-	-	-
(7,7)	-	-	-	-	-	-	-	-	-
(8,8)	-	-	-	-	-	-	-	-	-
(9,9)	-	-	-	-	-	-	-	-	-

Table 4.2: E_g^Γ for a range of nanotubes calculated using B3LYP, at both graphene **A** and B3LYP-optimised geometries **B**, **C**. A dash represents a metallic system ($E_g = 0$).

(such as the (3,1), (4,0) and (5,0) systems) can be metallic.

Using the graphene geometry, **A**, both the pob-TZVP and m-def2-QZVP basis sets describe the (4,4) and (5,5) nanotubes as semiconductors with $E_g^\Gamma > 4$ eV. By using the relaxed geometries, the (5,5) nanotube becomes metallic, however the (4,4) E_g^Γ

increases, indicating that the strain is more than a band-separating effect but also a band-character effect, agreeing with previous studies [167].

Overall, there is a good fit with the zone-folding rule for the optimised basis sets, regarding the character of the CBM and VBM. We find that with the B3LYP functional, the energy and polarisation-optimised basis sets agree with each other regarding the qualitative nature of the energy gaps, and the quantitative descriptions of E_g^Γ are in good agreement, more so when using the B3LYP-optimised structures. When all three methods are in agreement as to the metallic or semiconducting status of a nanotube, E_g^Γ from the 3-21G basis set is unpredictably above (*e.g.* (4,3)) or beneath (*e.g.* (3,2)) the values agreed upon by the other two basis sets.

We find from this study of E_g^Γ that the effect of basis set on both the quantitative and qualitative properties of the nanotubes is more pronounced for the smaller-diameter nanotubes, and that the B3LYP-optimised structures provide values of E_g^Γ which are in good agreement with each other. Figure 4.8 compares the value of E_g^Γ against the diameter for the semiconducting nanotubes, studied using B3LYP with m-def2-QZVP at the three different geometries. The semiconducting (4,4) and (5,5) nanotubes are clearly seen, as they lie outside the clustered results of the other semiconducting nanotubes.

Use of the 3-21G and pob-TZVP basis sets with the graphene structure **A** leads to indirect bandgaps for the semiconducting armchair and majority of chiral nanotubes, whilst the semiconducting zigzag, (8,4) and (6,2) nanotubes have only direct gaps, at the Γ point. For the 3-21G basis set, differences between E_g^Γ and E_g are of the order of 0.01 eV, whilst the same comparison for the pob-TZVP basis set leads to a difference of ~ 0.2 eV, apart from the (4,4) and (5,5) systems which are incorrectly semiconducting, and the (4,2) nanotube. These two armchair nanotubes have $E_g^\Gamma = \sim 5$ eV, but an indirect gap of ~ 0.7 eV, whilst the (4,2) nanotube is $E_g^\Gamma = \sim 2$ eV, and $E_g = \sim 1$ eV.

At the graphene geometry, the m-def2-QZVP basis set leads to direct gaps for all semiconducting armchair and chiral systems, apart from the (3,2) system - likely due to strain effects, whilst the semiconducting zigzag nanotubes have only direct gaps at the Γ point, as seen with the other two basis sets. As observed for the smaller basis sets, the difference between energy gaps ΔE_g ($\Delta E_g = E_g^\Gamma - E_g$) is of the order 0.1 eV, and similarly, we see that the (4,4), (5,5) and (4,2) nanotubes have the largest differences between E_g^Γ and the lowest-energy direct-gaps, with $\Delta E_g = \sim 3.8$ eV for the armchairs, and $\Delta E_g = \sim 1$ eV for the (4,2) nanotube. Table 4.3 shows ΔE_g and E_g for the semiconducting nanotubes shown in Table 4.3, using the three studied basis sets and geometry set **C**.

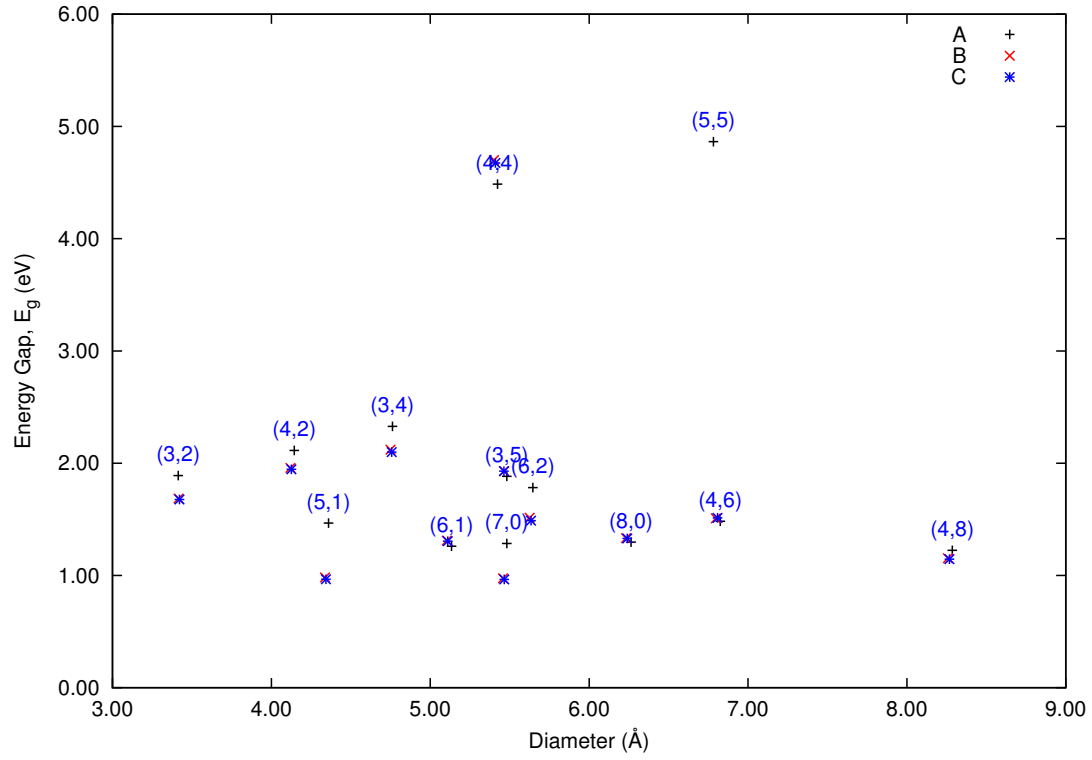


Figure 4.8: Comparison between E_g^Γ and nanotube diameter, for three different geometries - graphene (**A**), pob-TZVP optimised (**B**) and m-def2-QZVP optimised (**C**), using B3LYP and the m-def2-QZVP basis set.

Ind.	3-21G @ C		pob-TZVP @ C		m-def2-QZVP @ C	
	E_g	ΔE_g	E_g	ΔE_g	E_g	ΔE_g
(3,2)	0.962	-	1.335	0.314	1.383	0.294
(4,1)	1.761	0.760	-	-	-	-
(5,0)	1.103	-	-	-	-	-
(4,2)	2.446	0.069	1.004	0.977	1.086	0.859
(5,1)	-	-	0.810	0.205	0.776	0.190
(6,0)	1.453	-	-	-	-	-
(5,2)	0.846	1.865	-	-	-	-
(4,3)	1.609	0.002	1.988	0.205	1.948	0.152
(6,1)	1.633	0.033	1.092	0.168	1.140	0.165
(4,4)	-	-	0.845	4.093	0.848	3.826
(5,3)	1.917	0.001	1.866	0.055	1.883	0.047
(7,0)	-	-	1.107	-	0.964	-
(6,2)	0.879	0.000(1)	1.498	0.046	1.447	0.041
(7,1)	0.863	1.547	-	-	-	-
(8,0)	1.524	-	1.327	-	1.329	-
(9,0)	0.678	-	-	-	-	-
(6,4)	1.471	-	1.459	0.040	1.481	0.032
(8,4)	0.837	-	1.150	0.007	1.140	0.005

Table 4.3: This table shows ΔE_g and E_g for the semiconducting nanotubes studied with B3LYP and B3LYP-optimised geometry **C**, where $\Delta E_g = E_g^\Gamma - E_g$. A dash represents a system where $E_g^\Gamma = E_g$.

Optimisation of the initial graphene-based structures leads to a single change in the qualitative nature of the smallest KS gaps for the m-def2-QZVP basis set - structure **C** for the (4,8) nanotube has become an indirect gap.

By comparing the structure (contraction schemes, Gaussian exponents, and coefficients are given in the Appendix) of the optimised basis sets, we find that the m-def2-QZVP basis set contains exponents which are more diffuse than those in the pob-TZVP basis set, for the p and d shells, and that the pob-TZVP basis set contains no f shells whilst the m-def2-QZVP basis set has one. The difference in diffuse exponents is small, as shown in Table 4.4, and is evidenced by the similar values of E_g from the two basis sets. Due to the diffuse nature of the p and d shells, and the inclusion of an f shell, the m-def2-QZVP basis set can be regarded as the best choice of all-electron basis set in this study, but it may not be at the basis set limit - further study regarding the first-order response properties, similar to that of LiF and NaF (Sections 3.4.3 and 3.4.4 respectively) is required.

shell	Gaussian exponent (a_o^{-2})		
	3-21G	pob-TZVP	m-def2-QZVP
<i>s</i>	0.196	0.164	0.276
<i>p</i>	0.196	0.267	0.189
<i>d</i>	-	0.879	0.649
<i>f</i>	-	-	1.419

Table 4.4: Most diffuse Gaussian exponents for each shell (to 3 d.p.) for the three basis sets studied.

HF

In the previous study of alkali halides (Chapter 3), we observed a large difference between B3LYP and HF values for E_g , E_o and E_b . To study the effect of an increased proportion of HF exchange in the ground state, using Hartree-Fock theory, ground-state calculations were carried out for a range of nanotubes. The resulting values of E_g^Γ can be seen in Table 4.5 and Figure 4.5 for the three basis sets studied, using structures **A**, **B** and **C**.

The qualitative nature of the energy gap is less dependent on the choice of basis set and geometry when using the HF method, in comparison to the B3LYP study. By varying the geometries used for each nanotube, the qualitative nature of E_g^Γ for some systems is corrected (*e.g.* the (4,7) nanotube with the m-def2-QZVP basis set), unchanged (*e.g.* the (4,7) nanotube with the pob-TZVP basis set), or made incorrect (*e.g.* the (3,6) nanotube with the 3-21G basis set).

We see that the curvature-dependence on the metallicity of SWCNTs is far less pronounced for the HF calculations - many small-diameter nanotubes which B3LYP calculates as being metallic (*e.g.* (4,1) and (5,0)) are semiconductors in HF theory, regardless of our choice of basis set or geometry. The metallicity of some small-diameter nanotubes is only seen when using the B3LYP optimised structures (*e.g.* (3,0) and (4,0)). For larger-diameter nanotubes (*e.g.* (7,7), (8,8) and (9,9)), there is a qualitative disagreement between the pob-TZVP and m-def2-QZVP basis, where the pob-TZVP basis set predicts these systems to be semiconductors, whilst the m-def2-QZVP and 3-21G basis sets correctly describe these nanotubes as metallic, regardless of geometry choice. In a quantitative comparison of the semiconducting nanotubes to the results from B3LYP calculations, we find that E_g^Γ from the HF method is always larger, and often twice that of B3LYP. The metallicity of SWCNTs is an unexpected observation, and is likely caused by geometry constrictions, as shown by the semiconducting character of the (7,7), (8,8) and (9,9) systems after geometry relaxation. We find that these

	3-21G			pob-TZVP			m-def2-QZVP		
Ind.	A	B	C	A	B	C	A	B	C
(3,0)	6.480	5.962	5.933	-	-	-	-	-	-
(3,1)	6.873	4.787	4.571	-	5.153	3.154	-	5.132	3.075
(4,0)	5.635	6.244	6.134	3.134	-	-	3.162	-	-
(3,2)	7.414	6.122	6.111	6.482	6.291	6.273	6.567	6.3055	6.290
(4,1)	6.001	8.247	8.248	6.462	7.359	7.345	6.342	7.309	7.309
(5,0)	5.362	3.330	3.343	2.456	2.710	2.701	2.935	2.958	2.954
(3,3)	9.040	-	-	8.662	10.112	10.120	8.450	9.731	9.736
(4,2)	5.195	5.584	5.576	5.578	5.203	5.183	5.457	5.113	5.095
(5,1)	4.065	2.452	2.445	5.329	4.231	4.226	5.154	4.104	4.052
(6,0)	1.219	3.061	3.065	2.312	1.789	1.793	2.322	2.048	2.143
(4,3)	3.987	3.741	3.729	5.400	5.018	5.007	5.458	5.074	5.019
(5,2)	6.126	5.895	5.864	6.935	6.360	6.134	7.027	6.408	6.334
(6,1)	4.174	3.982	3.959	3.860	4.030	4.022	4.160	4.093	4.095
(4,4)	10.822	-	-	10.197	10.566	10.579	9.808	10.094	9.985
(5,3)	3.728	3.969	3.958	4.157	4.241	4.226	4.249	4.281	4.325
(7,0)	2.622	1.776	1.750	4.166	3.512	3.493	3.976	3.376	3.319
(6,2)	2.824	2.302	2.282	4.113	3.595	3.566	4.060	3.618	3.548
(7,1)	4.663	5.069	5.118	4.768	4.861	4.894	4.752	4.849	4.902
(6,3)	-	0.876	0.965	1.714	1.183	-	1.774	1.292	-
(8,0)	3.384	3.550	3.514	2.938	3.543	3.553	3.133	3.557	3.559
(5,5)	-	-	-	10.676	10.639	10.649	10.142	10.205	10.092
(6,4)	2.880	3.038	3.032	3.033	3.177	3.178	3.244	3.239	3.283
(9,0)	0.681	1.356	1.383	0.934	0.669	0.700	1.005	-	0.683
(8,2)	-	7.600	7.617	7.344	-	-	7.290	-	-
(7,4)	-	-	-	-	-	-	2.997	-	-
(6,6)	-	-	-	10.777	10.828	10.834	10.180	10.340	10.355
(8,4)	2.032	1.891	1.878	2.585	2.444	2.430	2.607	2.513	2.500
(9,3)	-	-	-	-	-	-	-	-	-
(8,5)	-	-	-	-	-	-	-	-	-
(7,7)	-	-	-	-	10.864	10.865	-	_*	_*
(8,8)	-	-	-	-	10.972	10.969	-	_*	_*
(9,9)	-	-	-	-	11.118	11.116	-	_*	_*

Table 4.5: E_g^Γ for a range of nanotubes calculated using HF, at both graphene **A** and B3LYP-optimised geometries **B** and **C**. A dash represents a metallic system ($E_g = 0$), and an asterisk denotes systems with changed computational parameters.

larger armchair nanotubes have difficulty converging with the same computational parameters as the rest of the series when using the m-def2-QZVP basis set with optimised geometries. For these three nanotubes, the tolerance of the exchange integrals was set to 10^{-150} (Section 4.6.1) summing integrals over a distance of 66 Å, and the mixing

between the previous and current Fock matrices was set to 50% (Equation (4.1)). The very low tolerance for the summation of exchange integrals was required to obtain a converged ground state energy, as higher tolerances led to ground state SCFs with linear gradients for the total energy, which did not converge.

When using the graphene geometry we find that for all three basis sets studied, the semiconducting zigzag nanotubes are all $E_g = E_g^\Gamma$, whilst all other semiconducting nanotubes have direct non- Γ gaps. By optimising the geometry, both the qualitative and quantitative status of E_g changes, with many direct non- Γ gaps becoming indirect. This effect is dependent on the basis set, and indicates a secondary dependence on the nanotube diameter as the optimised basis sets provide more non- Γ direct gaps than the 3-21G basis set, and the remaining indirect gaps are the two smallest-diameter semiconducting nanotubes. Quantitatively, we see a similar trend in ΔE_g for HF in comparison to B3LYP. For example, the armchair nanotubes have a direct non- Γ gap, which is an order of magnitude beneath E_g^Γ .

LDA

Using the LDA functional for DFT, ground-state calculations were run for a range of nanotubes, and subsequent values of E_g can be seen in Table 4.6 and Figure 4.6 for the three basis sets studied, using optimised structures **C**.

It is clear that the qualitative nature of the gap is strongly dependent on basis and geometry chosen, although for the majority of systems, LDA describes the nanotube as metallic regardless of the choice of basis set, and does not incorrectly describe any systems predicted to be metallic through the zone-folding rule, as semiconductors.

The LDA values of E_g^Γ are in good agreement between the pob-TZVP and m-def2-QZVP basis sets for all but one system, the (7,0) nanotube where m-def2-QZVP describes the nanotube as metallic in structure **A**, whilst the pob-TZVP and 3-21G basis sets create a semiconducting nanotube; this semiconducting character is lost when the structure is optimised.

The 3-21G basis set alone describes many of the small-diameter nanotubes as semiconductors, a likely effect of combining the poor description of the orbitals with the LDA method.

4.6.4 Density of States

Spataru *et al.* [153] created a DOS for the (3,3) nanotube using GW-shifted eigenvalues, showing asymmetry of the van Hove singularities around the Fermi energy. We

	3-21G			pob-TZVP			m-def2-QZVP		
Ind.	A	B	C	A	B	C	A	B	C
(3,0)	-	-	-	-	-	-	-	-	-
(3,1)	0.770	-	-	-	-	-	-	-	-
(4,0)	1.129	-	-	-	-	-	-	-	-
(3,2)	0.949	-	-	0.931	-	-	0.987	-	-
(4,1)	-	1.222	1.227	-	-	-	-	-	-
(5,0)	1.850	-	-	-	-	-	-	-	-
(3,3)	-	-	-	-	-	-	-	-	-
(4,2)	1.759	1.394	1.329	-	-	-	-	-	-
(5,1)	0.879	-	-	-	-	-	-	-	-
(6,0)	-	1.058	1.058	-	-	-	-	-	-
(4,3)	1.221	1.101	1.097	1.611	1.493	1.485	1.596	1.464	1.461
(5,2)	-	-	-	-	-	-	-	-	-
(6,1)	1.516	1.142	1.131	-	-	-	-	-	-
(4,4)	-	-	-	-	-	-	-	-	-
(5,3)	1.293	1.418	1.412	1.302	1.248	1.239	1.275	1.226	1.239
(7,0)	0.687	-	-	0.693	-	-	-	-	-
(6,2)	0.809	-	-	1.342	1.115	1.107	1.282	1.057	1.049
(7,1)	-	-	-	-	-	-	-	-	-
(6,3)	-	-	-	-	-	-	-	-	-
(8,0)	1.258	1.078	1.060	0.733	-	-	0.720	-	-
(5,5)	-	-	-	-	-	-	-	-	-
(6,4)	1.014	1.093	1.089	1.087	1.112	1.107	1.078	1.105	1.100
(9,0)	-	-	-	-	-	-	-	-	-
(8,2)	-	-	-	-	-	-	-	-	-
(7,4)	-	-	-	-	-	-	-	-	-
(6,6)	-	-	-	-	-	-	-	-	-
(8,4)	0.662	-	-	0.940	0.873	0.866	0.907	0.841	0.834
(9,3)	-	-	-	-	-	-	-	-	-
(8,5)	-	-	-	-	-	-	-	-	-
(7,7)	-	-	-	-	-	-	-	-	-
(8,8)	-	-	-	-	-	-	-	-	-
(9,9)	-	-	-	-	-	-	-	-	-

Table 4.6: E_g^Γ for a range of nanotubes calculated using LDA, at both graphene **A** and B3LYP-optimised geometries **B** and **C**. A dash represents a metallic system ($E_g = 0$).

replicated this calculation within CRYSTAL, using B3LYP with the optimised geometry **C**, as shown in Figure 4.9.

In Figure 4.9, we show the DOS of the (3,3) nanotube at geometry **C** using three different basis sets. For each basis set studied, there is zero density around E_F , which

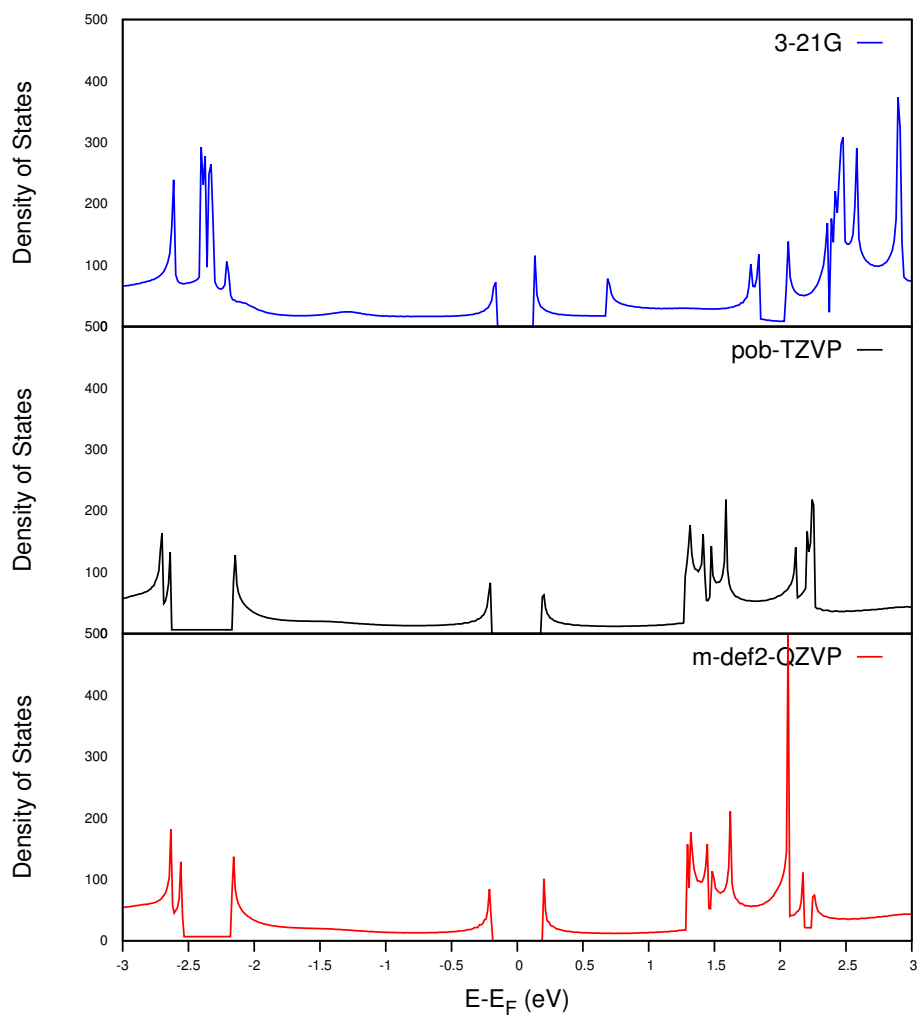


Figure 4.9: DOS for the (3,3) nanotube using geometry **C** and the 3-21G (top), pob-TZVP (middle) and m-def2-QZVP (bottom) basis sets.

implies that the chemical potential of the (3,3) nanotube does not cross through the Dirac cone. In addition, for all three basis sets, we find two van Hove singularities symmetrical about E_F which are unseen in the work by Spataru and coworkers. The m-def2-QZVP band structure around E_F , as shown in Figure 4.10 appears to show the conduction and valence bands touching, however a study of the numerical output from the band structure shows that the conduction and valence bands do not touch, resulting in this small gap and the two singularities seen in the DOS. This character of E_g in zone-folding metallic SWCNTs has been shown experimentally [150], and is supported by previous B3LYP studies [168].

Wildöer *et al.* [148] compared the experimental DOS of a 13 Å, $E_g = 0.65$ eV nanotube, created through analysis of scanning tunnelling spectroscopy (STS) data, to a calculated DOS of a (16,0) nanotube (Section 4.4). Details of the DOS calculation are not supplied, but due to the symmetry of the Van Hove singularities around E_F , it is likely to be created from a tight-binding calculation. From the experimental measurements, we believe the system could be either the (16,0) or the (17,0) nanotube (Table 4.8), and in Figures 4.11 and 4.12, we have calculated the DOS of the (16,0) and (17,0) nanotubes, using the m-def2-QZVP basis set at geometries **A** and **C**.

In Figure 4.11 we show the projected density of states for the (16,0) nanotube, where the horizontal axis is the energy of the state with respect to E_F . The Fermi energy differs for each geometry, and the DOS have been aligned at E_F for ease of comparison. It is clear that the asymmetry of the van Hove singularities around $(E_{c1} + E_{v1})/2$ is still present in the larger-diameter nanotubes, although the DOS is more symmetrical than for the smaller (3,3) nanotube (Figure 4.9). By relaxing the geometry, E_{v2} , E_{c1} and E_{c3} are decreased, causing a red-shift of E_{11} , a blue-shift of E_{22} , and negligible change of E_{21} and E_{12} . For the (17,0) nanotube as shown in Figure 4.12, relaxation of the structure leads to an increase in E_{v2} and E_{c1} , opposite to the effect of relaxation on the (16,0) SWCNT. This means that E_{11} is blue-shifted and E_{22} is red-shifted, whilst the forbidden E_{12} and E_{21} transitions are, again, unchanged.

In comparison to the experimental DOS in the work of Wildöer [148], we find that both the (16,0) and (17,0) nanotubes provide peak positions and intensities that are in agreement with the experimental values. Visual analysis of the relative peak positions in the experimental DOS shows that E_{v3} and $(E_{c1} + E_{c2})/2$ are equidistant around E_F . This relationship is seen clearly in the (16,0) nanotube, and when the relative position of E_{v2} between E_{v1} and E_{v3} is compared to the experimental data, there is a good agreement, which supports the comparison by Wildöer and coworkers, to the (16,0) nanotube.

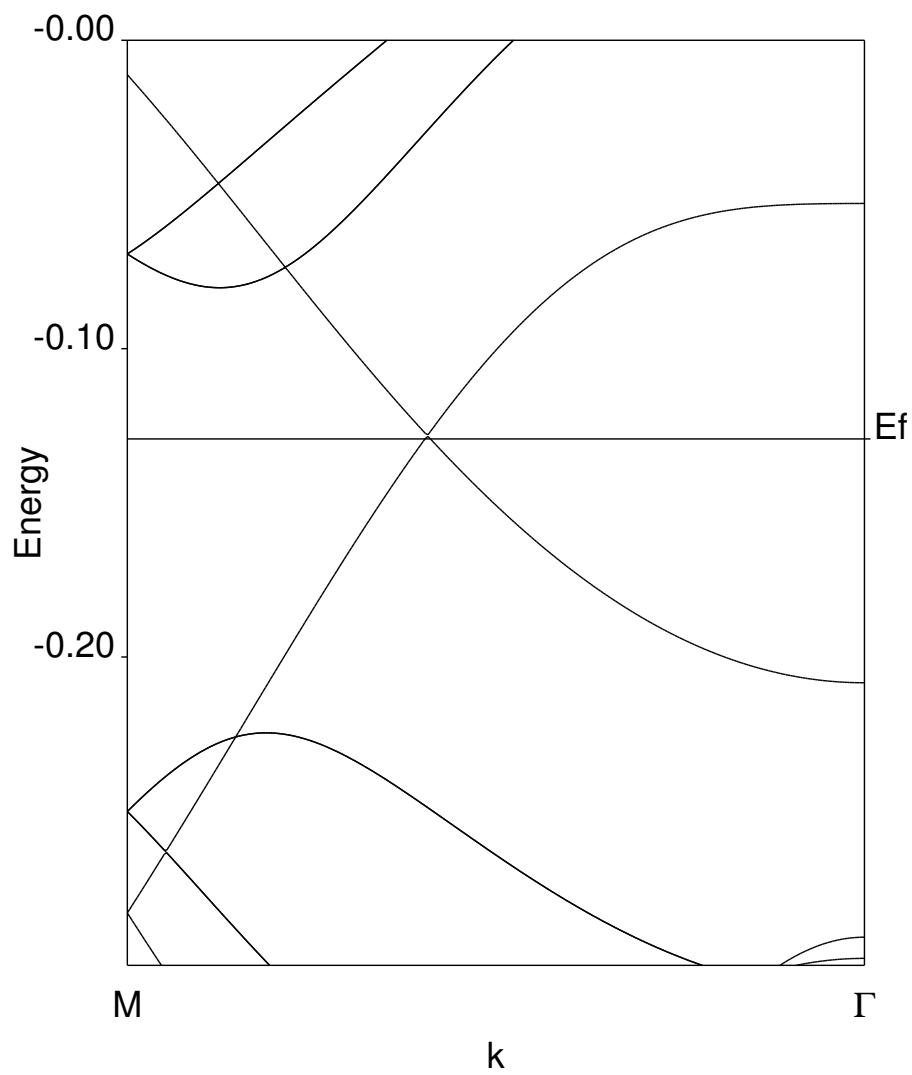


Figure 4.10: Band structure for the (3,3) nanotube using geometry **C** and the m-def2-QZVP basis sets.

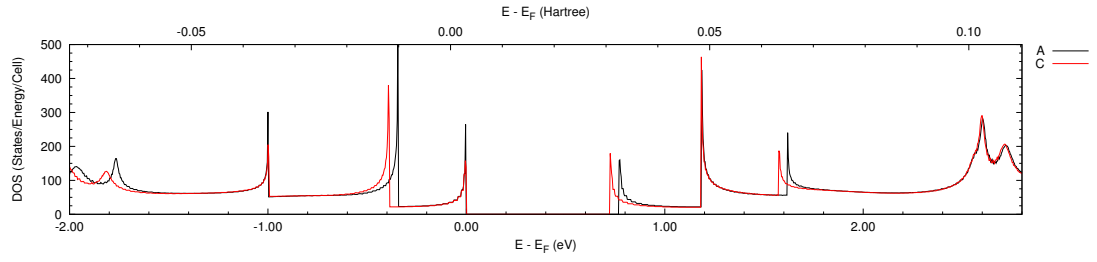


Figure 4.11: Comparison of the density of states for the (16,0) nanotube using geometries **A** and **C** with the m-def2-QZVP basis set.

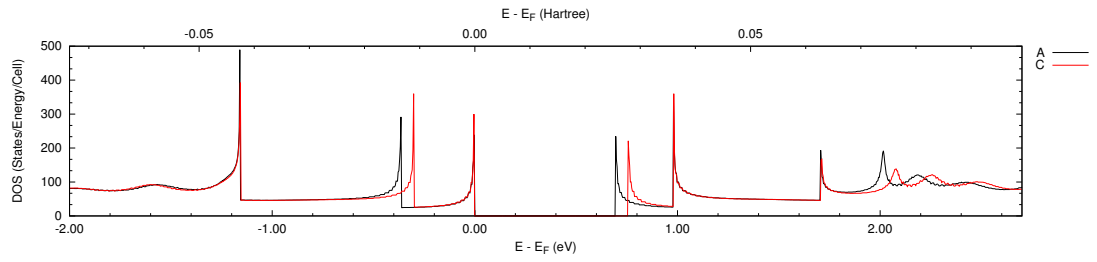


Figure 4.12: Comparison of density of states for the (17,0) nanotube using geometries **A** and **C** with the m-def2-QZVP basis set.

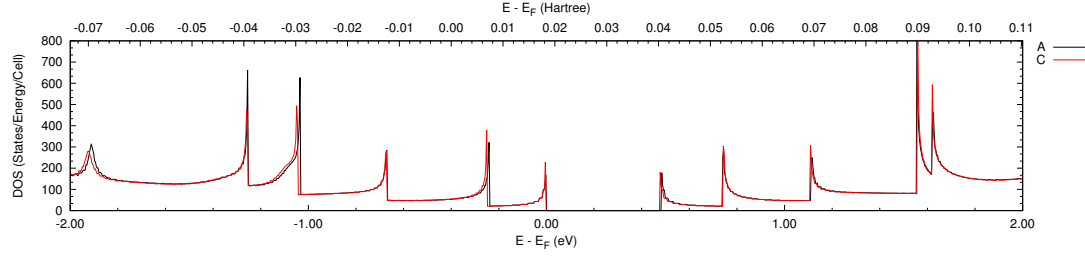


Figure 4.13: Comparison of density of states for the (25,0) nanotube using geometries **A** and **C** with the m-def2-QZVP basis set.

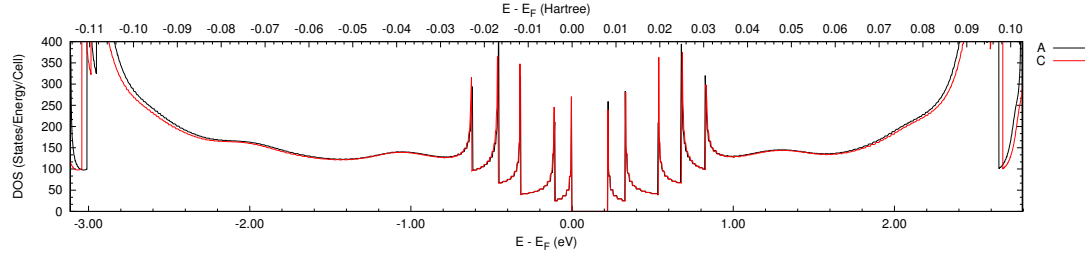


Figure 4.14: Comparison of density of states for the (55,0) nanotube using geometries **A** and **C** with the m-def2-QZVP basis set.

To study the effect of curvature on the asymmetry of the van Hove singularities, we calculated the DOS for the (25,0) and (55,0) SWCNTs, which are shown in Figure 4.13 and Figure 4.14, respectively. The effect of relaxing the geometry for these larger-diameter nanotubes is less pronounced in comparison to the (16,0) and (17,0) nanotubes. As shown in Figure 4.15, the optimisation of larger nanotubes results in a smaller change in the diameter and bond lengths, leading to smaller variations in the electronic structure, as observed here and in (Figure 4.16). The van Hove singularities in the DOS of the (55,0) SWCNT show a great degree of symmetry around $E_{11}/2$ for the grouped singularities within 1.0 eV of E_F , with negligible effect from the geometry relaxation. At higher energies (~ 3 eV) above and beneath E_F , the effect of geometry relaxation is seen for the (55,0) nanotube as the blue-shift of unoccupied bands, and red-shift of occupied bands.

4.6.5 Diameter Effect on Electronic Properties

To explore the diameter dependence on the effect of E_g^Γ for zigzag nanotubes, additional ground state calculations were made for the zigzag series, increasing the diameter of studied nanotubes to ~ 46 Å. Initial calculations on the following series included the same $0.001 E_h$ smearing of the Fermi surface as the smaller-diameter series, and we observe that **CRYSTAL** predicts each $(m,0)$ nanotube wider than the (16,0) to be metallic, when using B3LYP with the m-def2-QZVP basis set and structure **A**. This early and sudden onset of metallicity is unexpected, as the values of E_g^Γ for the (14,0) and (16,0) nanotubes are 0.82 eV and 0.78 eV respectively. Numerical analysis of the eigenvalues however, shows that there is a non-zero gap between the CBM and VBM, despite the metallic character predicted by the zone-folding method, as shown in Table 4.7.

The calculations were repeated using the pob-TZVP and m-def2-QZVP basis sets with B3LYP, at the **A** and **C** geometries, but without the smearing of the Fermi surface, and the data is provided in Tables 4.8 and 4.9.

In a comparison of E_g from the m-def2-QZVP calculations at structure **A**, we see that the $0.001 E_h$ of thermal energy used for the smearing of the Fermi surface has a negligible effect on the quantitative nature of E_g .

4.6.6 Conclusions of Electronic Properties

We have shown that for small-diameter nanotubes the average bond length is greater than that of graphene, and as the nanotube diameter increases, the average carbon-carbon bond length becomes closer to that of graphene. Similar to the study on the alkali halide series, the B3LYP functional is the best method of those tested, with a very good qualitative agreement with the zone-folding method for predicting the character of E_g . When using the LDA functional there is less agreement with the zone-folding predictions of electronic character, with many nanotubes being described as metallic, which are semiconducting in the B3LYP, HF and zone-folding approaches. HF calculations of carbon nanotube ground states create semiconducting electronic structures for the majority of systems studied, with the semiconducting character reducing for the higher-diameter nanotubes, depending on the basis set chosen. The choice of basis set has an effect on the qualitative nature of the gap, with results from the 3-21G basis set often in agreement with the zone-folding predictions in the LDA and HF calculations, but not for B3LYP. Within all three methods studied we find good agreement between the optimised basis sets, regarding both the qualitative and quantitative nature of E_g^Γ ,

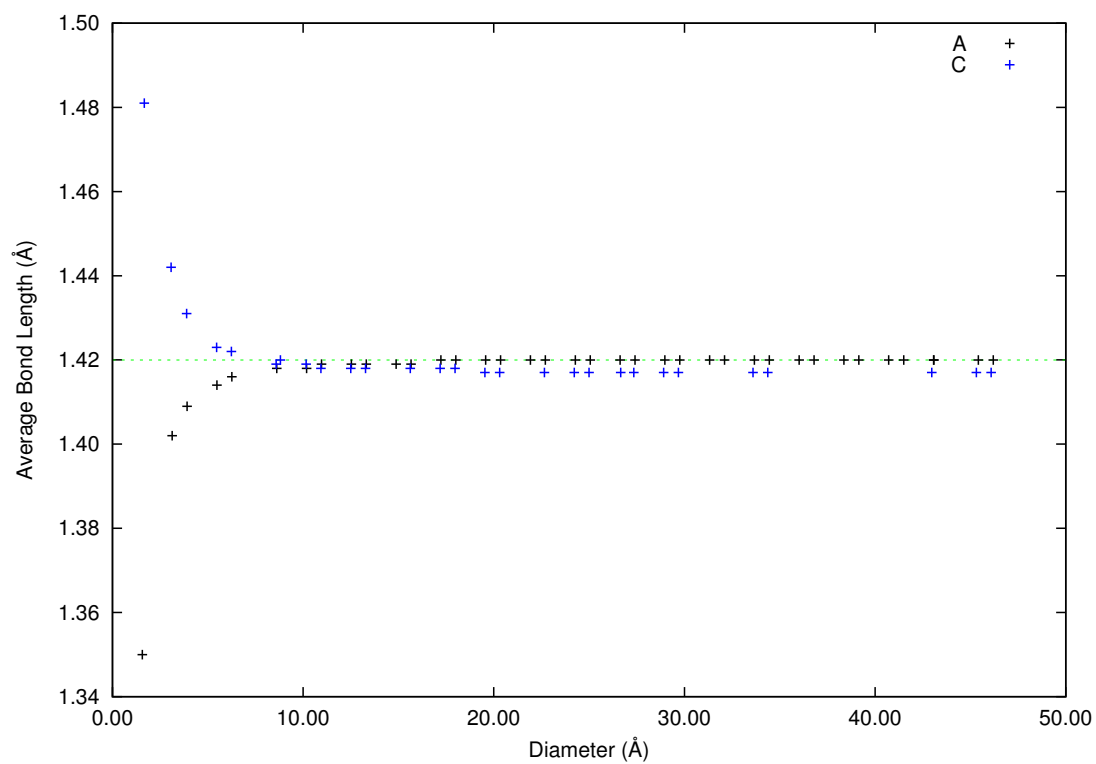


Figure 4.15: Comparison between the average bond length and nanotube diameter for a range of $(m,0)$ nanotubes, at two different geometries - graphene (**A**) and m-def2-QZVP optimised (**C**), using B3LYP.

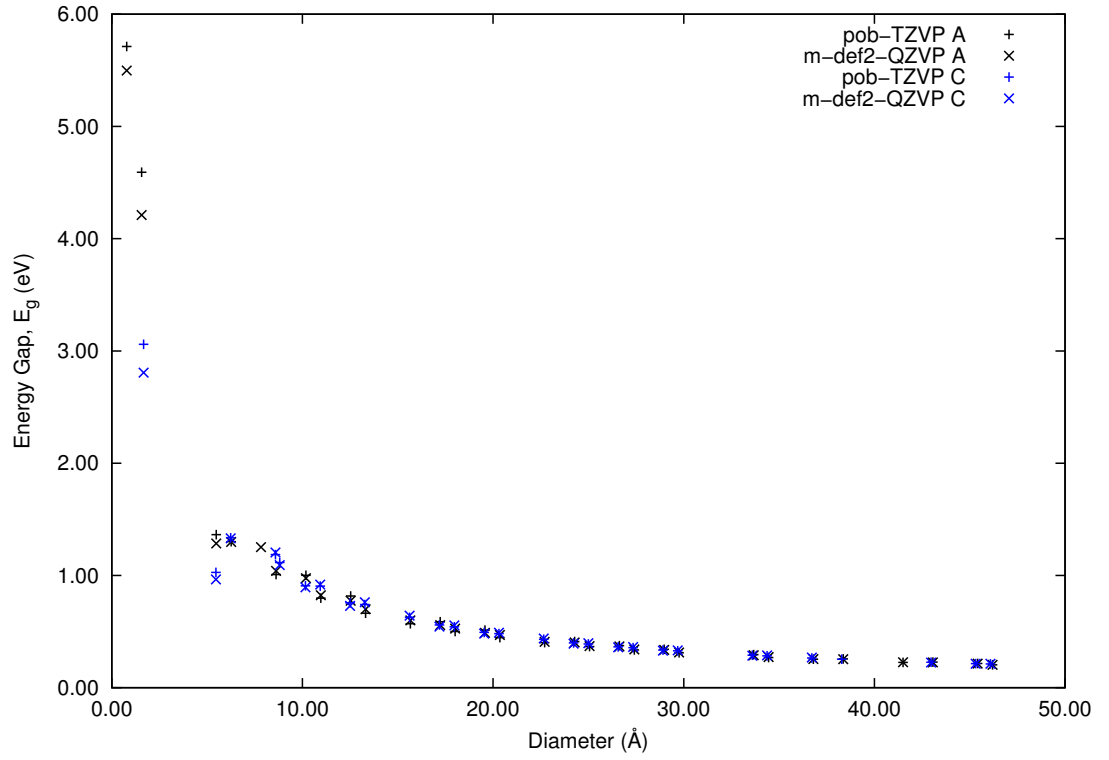


Figure 4.16: Comparison between the diameter and E_g for a range of $(m,0)$ nanotubes, at two different geometries (**A**, **C**) and basis sets (pob-TZVP, m-def2-QZVP), using B3LYP.

with a notable disagreement between the qualitative nature of the (7,7), (8,8) and (9,9) nanotubes studied with HF theory.

A comparison of the E_g and smallest optically-allowed gap (E_g^*), from this B3LYP study (using geometry **C** and the m-def2-QZVP basis set) and GW calculations [153, 169] can be found in Table 4.10. Whilst the B3LYP calculations of the (3,3) and (5,0) SWCNTs predict metallicity, we have provided the smallest longitudinal ($\Delta m = 0$, $E^\parallel$) gaps through a direct analysis of eigenvalues. Values of E_o obtained through optical absorption studies [161] are given for comparison, in lieu of experimental values of E_g , which are non-trivial to deduce.

We see that for the subset of nanotubes given in Table 4.10, B3LYP calculates values of E_g beneath that of GW for the semiconducting nanotubes, and above GW for the metallic (5,0) nanotube. When comparing the single-particle lowest optically-allowed gaps, the (3,3) value is larger for B3LYP than GW, whilst for the other two systems, the B3LYP value is smaller than the GW value, and quantitatively we find that GW and B3LYP vary by 0.23 eV to 1.66 eV. Neither method provides values of the single-particle lowest optically-allowed gap that are consistently in good agreement with experimental values of E_o .

The DOS of a wide range of nanotubes has been studied, and this study has shown that by increasing the diameter of SWCNTs, we both restore symmetry of the van Hove singularities and change the nature of the electronic DOS towards that of graphene 4.2.

An infinitely large SWCNT can be thought to be a layer of (metallic) graphene, and by studying the qualitative nature of E_g for the larger range of SWCNTs (< 46 Å diameter), we show that the gap tends towards zero slowly, indicating that the $\sigma - \pi$ hybridisation is still present in larger diameter nanotubes.

Ind.	E_g (eV)
(1,0)	5.498
(2,0)	4.218
(4,0)	-
(5,0)	-
(7,0)	1.288
(8,0)	1.298
(10,0)	1.258
(11,0)	1.048
(13,0)	0.978
(14,0)	0.828
(16,0)	0.778
(17,0)	0.698
(19,0)	nc
(20,0)	0.608
(22,0)	0.558
(23,0)	0.528
(25,0)	0.488
(26,0)	0.468
(28,0)	nc
(29,0)	0.408
(31,0)	0.408
(32,0)	0.378
(34,0)	0.368
(35,0)	0.338
(37,0)	0.338
(38,0)	0.318
(40,0)	nc
(41,0)	nc
(43,0)	0.298
(44,0)	0.278
(46,0)	nc
(47,0)	0.258
(49,0)	0.258
(50,0)	nc
(52,0)	nc
(53,0)	0.228
(55,0)	0.228
(56,0)	nc
(58,0)	0.218
(59,0)	0.208

Table 4.7: E_g^Γ for a set of zone-folding semiconducting $(m,0)$ nanotubes, calculated with B3LYP and the m-def2-QZVP basis set. A dash represents a metallic system ($E_g = 0$), whilst the notation “nc” denotes systems which are affected by linear dependence of the basis set.

Ind.	Diam. Å	Avg. CC Å	$E_g^{pob-TZVP}$	$E_g^{m-def2-QZVP}$
(1,0)	0.784	1.239	5.713	5.498
(2,0)	1.566	1.350	4.592	4.211
(4,0)	3.132	1.402	-	-
(5,0)	3.916	1.409	-	-
(7,0)	5.482	1.414	1.363	1.285
(8,0)	6.264	1.416	1.301	1.298
(10,0)	7.830	1.417	1.287	1.252
(11,0)	8.614	1.418	1.008	1.040
(13,0)	10.180	1.418	1.001	0.975
(14,0)	10.962	1.419	0.797	0.824
(16,0)	12.528	1.419	0.816	0.775
(17,0)	13.312	1.419	0.664	0.699
(19,0)	14.878	1.419	nc	nc
(20,0)	15.660	1.419	0.570	0.600
(22,0)	17.226	1.420	0.587	0.558
(23,0)	18.010	1.420	0.501	0.527
(25,0)	19.576	1.420	0.513	0.489
(26,0)	20.358	1.420	0.446	0.470
(28,0)	21.924	1.420	nc	nc
(29,0)	22.708	1.420	0.402	0.408
(31,0)	24.274	1.420	0.411	0.403
(32,0)	25.056	1.420	0.366	0.371
(34,0)	26.622	1.420	0.374	0.367
(35,0)	27.406	1.420	0.336	0.340
(37,0)	28.972	1.420	0.342	0.337
(38,0)	29.754	1.420	0.310	0.314
(40,0)	31.320	1.420	nc	nc
(41,0)	32.104	1.420	nc	nc
(43,0)	33.670	1.420	0.294	0.289
(44,0)	34.452	1.420	0.269	0.272
(46,0)	36.018	1.420	nc	nc
(47,0)	36.802	1.420	0.253	0.255
(49,0)	38.368	1.420	0.257	0.253
(50,0)	39.150	1.420	0.238	nc
(52,0)	40.716	1.420	nc	nc
(53,0)	41.500	1.420	0.225	0.226
(55,0)	43.066	1.420	0.228	0.225
(56,0)	43.085	1.420	0.213	nc
(58,0)	45.416	1.420	0.216	0.214
(59,0)	46.198	1.420	0.203	0.204

Table 4.8: Diameter, average bond length and E_g^Γ for a range of (m,0) SWCNTs studied with the pob-TZVP and m-def2-QZVP basis sets, at the initial graphene geometry. A dash represents a metallic system ($E_g = 0$), whilst the notation “nc” denotes systems which are affected by linear dependence of the basis set.

Ind.	Diam. Å	Avg. CC Å	$E_g^{pob-TZVP}$	$E_g^{m-def2-QZVP}$
(2,0)	1.666	1.481	3.059	2.807
(4,0)	3.078	1.442	-	-
(5,0)	3.888	1.431	-	-
(7,0)	5.466	1.423	1.027	0.965
(8,0)	6.240	1.422	1.335	1.331
(10,0)	8.812	1.420	1.115	1.092
(11,0)	8.588	1.419	1.186	1.204
(13,0)	10.156	1.419	0.907	0.894
(14,0)	10.932	1.418	0.905	0.919
(16,0)	12.500	1.418	0.756	0.729
(17,0)	13.276	1.418	0.741	0.761
(19,0)	nc	nc	nc	nc
(20,0)	15.622	1.418	0.627	0.642
(22,0)	17.188	1.418	0.559	0.544
(23,0)	17.966	1.418	0.543	0.555
(25,0)	19.532	1.417	0.492	0.482
(26,0)	20.308	1.417	0.481	0.490
(28,0)	nc	nc	nc	nc
(29,0)	22.654	1.417	0.431	0.438
(31,0)	24.220	1.417	0.399	0.392
(32,0)	24.998	1.417	0.390	0.396
(34,0)	26.564	1.417	0.364	0.359
(35,0)	27.342	1.417	0.357	0.362
(37,0)	28.906	1.417	0.335	0.330
(38,0)	29.684	1.417	0.328	0.333
(40,0)	nc	nc	nc	nc
(41,0)	nc	nc	nc	nc
(43,0)	33.594	1.417	0.289	0.285
(44,0)	34.372	1.417	0.283	0.287
(46,0)	nc	nc	nc	nc
(47,0)	36.716	1.417	0.265	0.268
(49,0)	38.282	1.417	0.254	0.252
(50,0)	nc	nc	nc	nc
(52,0)	nc	nc	nc	nc
(53,0)	nc	nc	nc	nc
(55,0)	42.970	1.417	0.227	0.224
(56,0)	nc	nc	nc	nc
(58,0)	45.314	1.417	0.215	0.213
(59,0)	46.090	1.417	0.211	0.213

Table 4.9: Diameter, average bond length and E_g^Γ for a range of (m,0) SWCNTs studied with the pob-TZVP and m-def2-QZVP basis sets, at the B3LYP-optimised geometry **C**. A dash represents a metallic system ($E_g = 0$), whilst the notation “nc” denotes systems which are affected by linear dependence of the basis set.

	E_g (eV)		E_g^* (eV)		E_o (eV)
	B3LYP	GW	B3LYP	GW	Expt.
(3,3)	0.58	-	4.92	3.26	3.1 [161]
(5,0)	1.57	1.30 [169]	1.57	2.54 [153]	1.37 [161]
(7,0)	0.96	1.82 [169]	3.49	-	-
(8,0)	1.33	-	1.57	1.80 [153]	1.60 [157]

Table 4.10: Lowest energy B3LYP and GW-calculated eigenvalue gaps (E_g) and optically-allowed eigenvalue gaps (E_g^*) of a range of SWCNTs, in comparison to experimental values of E_o .

	3-21G		pob-TZVP		m-def2-QZVP		Expt. [161]	GW-BSE. [153]
	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$		
E_g (eV)	11.90	5.49	9.11	6.56	10.31	6.52	-	3.26
E_o (eV)	6.67	2.17	5.44	3.21	5.28	3.16	3.1	3.17
E_b (eV)	5.23	3.32	3.67	3.35	5.03	3.36	-	0.09

Table 4.11: Energy gap (E_g), optical gap (E_o) and exciton binding energy (E_b) for the (3,3) SWCNT, using HF and three different basis sets at the optimised geometry **C**. Experimental and GW-BSE values have been supplied for comparison.

4.6.7 Optical Gaps of SWCNTs

We have shown that B3LYP used with the energy and polarisation converged basis sets m-def2-QZVP and pob-TZVP can reproduce ground state quantities such as bond lengths and density of states, with good agreement with previously published experimental and theoretical work for small diameter SWCNTs. We now extend our **k**-coupled TD-DFT and TD-HF methods towards studying the excited states of similar small diameter nanotubes.

(3,3)

The polarisability of a (3,3) SWCNT with infinite length was studied with B3LYP and HF, using the 3-21G, pob-TZVP and m-def2-QZVP basis sets, and the optimised structure **C**. The data for the lowest-energy asymptotes is given in Table 4.11 for HF, and Table 4.12 for B3LYP, along with experimental values and those from previous computational studies.

Using the 3-21G basis set, the first pole in the polarisability originates from perturbation through the axis of the nanotube, $E_o^{\perp} = 2.17$ eV for HF theory. This is an unexpected observation, as the polarisability against the axis of the nanotube is

known to be suppressed, due to the depolarisation seen in experimental and theoretical studies [160,161]. We do observe, however, that the polarisability against the nanotube axis is generally one order of magnitude beneath that of the polarisability along the axis, until the polarisability along the axis nears an asymptote, when the difference can increase to two orders of magnitude. The second asymptote is from perturbations along the axis of the nanotube, at an energy three times that of the first pole, $E_o^{\parallel} = 6.67$ eV. When using the 3-21G basis set with the HF method, the (3,3) SWCNT is predicted to be metallic during the SCF of **CRYSTAL**, meaning that the use of E_g to calculate the exciton binding energies of these transitions is not trivial.

Numerical analysis of the eigenvalue gaps shows that conduction and valence bands do not touch in reciprocal space, leading to the lowest-energy HF eigenvalue gap at 0.25 eV, which is an E^{11} transition. This is qualitatively similar to the DOS for the (3,3) nanotube studied with B3LYP, and this gap separation has been predicted and seen in other work [150,168], and is another effect of curvature on the electronic structure. The lowest-energy E_{22} is 9.39 eV, and the lowest crosswise gaps are $E_{21} = 5.49$ eV and $E_{12} = 5.73$ eV.

Through analysis of the transition probabilities of the optical matrix, we find that the first optically allowed excitation is E_{21} at 5.49 eV, whilst the first optically allowed axial excitation of $E_{44} = 11.90$ eV, rather than E_{22} as suggested by the single-particle DOS. This analysis of the optical matrix leads to an axial exciton binding energy of $E_b^{\parallel} = 5.23$ eV, and a perpendicular exciton binding energy of $E_b^{\perp} = 3.32$ eV.

Similar to the study using the 3-21G basis set, there is a non-zero value of E_g around E_F for the pob-TZVP basis set in HF theory, which represents the E_{11} transition, but is not optically allowed. The first optically allowed axial transition is $E_{11} = 9.11$ eV, and the first optically allowed perpendicular transition is $E_{21} = 6.56$ eV. We find $E_o^{\perp} = 3.21$ eV and $E_o^{\parallel} = 5.44$ eV, resulting in $E_b^{\perp} = 3.35$ eV and $E_b^{\parallel} = 3.67$ eV.

For the m-def2-QZVP basis set, we find the lowest axial and perpendicular energy gaps with non-zero transition intensities to be $E_{22} = 10.31$ eV and $E_{21} = 6.52$ eV. We find $E_o^{\perp} = 3.16$ eV and $E_o^{\parallel} = 5.28$ eV, resulting in $E_b^{\perp} = 3.36$ eV and $E_b^{\parallel} = 5.03$ eV.

It is interesting to note that by changing the basis set within the HF method, $E_b^{\perp}$ varies by only 0.04 eV, whilst $E_b^{\parallel}$ varies by 1.56 eV. This implies that the excitations which are perpendicular to the nanotube axis do not require a good description of diffuse orbitals. The large change in $E_b^{\parallel}$ is not caused solely by a similar variation in $E_o^{\parallel}$, but by a 2 eV decrease in $E_g^{\parallel}$ for the pob-TZVP basis set. This is because the optical matrix shows a strong transition at E_{11} for the pob-TZVP basis set, but not for the other basis sets.

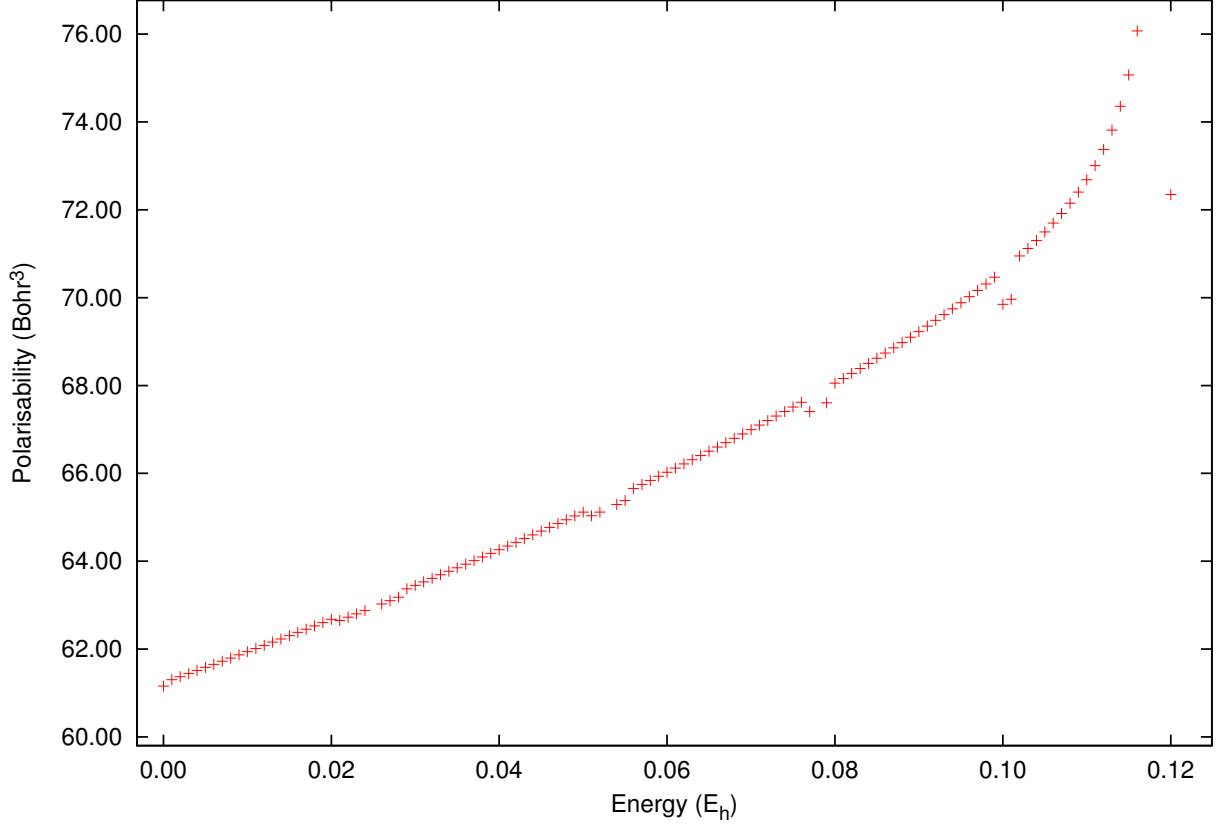


Figure 4.17: Polarisability tensor of the (3,3) nanotube perpendicular to the nanotube axis, calculated with the m-def2-QZVP basis set and the HF method.

By studying the character of the perpendicular polarisability for the (3,3) nanotube, using the pob-TZVP and m-def2-QZVP basis sets within the HF method, we see that the polarisability alternates between two curves, with less than 20 percent of the points falling on the lower curve, as shown in Figure 4.17.

In comparison to the experimental and GW-BSE results we find that HF overestimates the axial excitation as expected, creating exciton binding energies far greater than the GW-BSE results.

As seen previously for the 3-21G basis set with the HF method, E_{11} has zero transition probability when the B3LYP functional is used, with the lowest axial gap at $E_{33} = 4.80$ eV. In addition, the lowest crosswise gap is $E_{21} = 2.86$ eV, with $E_o^{\parallel} = 4.27$ eV and $E_o^{\perp} = 2.08$ eV, which leads to $E_b^{\parallel} = 0.53$ eV and $E_b^{\perp} = 0.78$ eV. However

	3-21G		pob-TZVP		m-def2-QZVP		Expt. [161]	GW-BSE. [153]
	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$		
$E_g(\text{eV})$	4.80	2.86	4.93	3.52	4.92	3.50	-	3.26
$E_o(\text{eV})$	4.27	2.08	3.67	2.42	3.62	2.42	3.1	3.17
$E_b(\text{eV})$	0.53	0.78	1.26	1.12	1.30	1.08	-	0.09

Table 4.12: Energy gap (E_g), optical gap (E_o) and exciton binding energy (E_b) for the (3,3) SWCNT, using B3LYP and three different basis sets at the optimised geometry C. Experimental and GW-BSE values have been supplied for comparison.

for the perpendicular excitation we find that at a resolution of $1 * 10^{-4} E_h$, the polarisability does not reach an asymptote, but instead is unable to converge, at a low polarisability gradient. Previous crosswise polarisabilities (*i.e.* $0.0766 E_h$) only require 10 self-consistent cycles to converge, but at $0.0767 E_h$ the polarisability is divergent and oscillating.

The optical matrix from the pob-TZVP calculations using B3LYP show that the axial $E_g = E_{22} = 4.93$ eV, and the crosswise $E_g = E_{21} = 3.52$ eV. As $E_o^{\parallel} = 3.67$ eV and $E_o^{\perp} = 2.42$ eV, $E_b^{\parallel} = 1.26$ eV and $E_b^{\perp} = 1.12$ eV.

When using the m-def2-QZVP basis set, the lowest optically-allowed transition in each direction is $E_{21} = 3.50$ eV and $E_{22} = 4.92$ eV, and the first optical gaps are $E_o^{\parallel} = 3.62$ eV and $E_o^{\perp} = 2.42$ eV. The resulting exciton binding energies are $E_b^{\perp} = 1.08$ eV and $E_b^{\parallel} = 1.30$ eV, which are in agreement with the pob-TZVP values.

In comparison of all three basis sets to the experimental and theoretical data, we find that our TD-B3LYP calculations of the (3,3) nanotube all overestimate E_o , with the 3-21G basis set overestimating by ~ 1 eV, and the optimised basis sets overestimating by ~ 0.5 eV. The GW-BSE value of E_b is 0.09 eV, from the LDA-based calculations of Spataru *et al.* [153], whereas the 3-21G, pob-TZVP and m-def2-QZVP basis sets calculate E_b to be 0.53, 1.26 and 1.30 eV respectively.

When we compare the B3LYP results to those from HF theory, we find that the HF-calculated E_g , E_o and E_b are always larger. This is identical to the findings of the alkali halide study (Chapter 3), and is in agreement with the general expectations of HF theory, such as the large fundamental gap (due to no electronic self-interaction error) and large E_o due to the correct treatment of exchange/Coulomb interactions. For the optimised basis sets, the crosswise optical gaps are < 1 eV greater than B3LYP values, whilst the exciton binding energies in HF are ~ 2 eV larger.

	3-21G		pob-TZVP		m-def2-QZVP		Expt. [161]	GW-BSE. [153]
	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$		
$E_g(\text{eV})$	1.10	2.22	1.59	0.91	1.57	0.82	-	1.3
$E_o(\text{eV})$	1.06	1.82	1.44	0.76	1.44	0.71	1.37	1.33
$E_b(\text{eV})$	0.04	0.40	0.15	0.15	0.13	0.11	-	0.03

Table 4.13: First energy gap (E_g), optical gap (E_o) and exciton binding energy (E_b) for the (5,0) SWCNT, using (B3LYP) and three different basis sets at the optimised geometry **C**. Experimental and GW-BSE values have been supplied for comparison.

(5,0)

The polarisability of a (5,0) SWCNT with infinite length was studied with B3LYP, using the 3-21G, pob-TZVP and m-def2-QZVP basis sets, and the m-def2-QZVP/B3LYP optimised structure. The data for the asymptotes is given in Table 4.13, along with experimental values and those from previous computational studies.

With the 3-21G basis set, we find that E_{11}^{Γ} is degenerate with E_{22}^{Γ} and E_{21}^{Γ} , with a value of 1.10 eV. However, the first perpendicular excitation is observed at 1.82 eV, and is therefore impossible to have originated from the low-energy E_{21}^{Γ} eigenvalue gap. Additionally, the energy gap $E_{21}^2 = 1.49$ eV has a non-zero transition intensity, yet is not observed in the polarisability spectrum. The lowest-energy optically-allowed gap which is higher than $E_o^{\perp}$ is $E_{42}^{\Gamma} = 2.22$ eV, giving a perpendicular exciton binding energy of $E_b^{\perp} = 1.4$ eV.

In comparison to the experimental and GW-BSE values, we find that E_o is underestimated by ~ 0.3 eV for TD-B3LYP, but there is very good agreement for E_b .

A similar band structure is seen for both the pob-TZVP and m-def2-QZVP basis sets, where the conduction and valence bands touch at the first and second $\mathbf{k}$ -points - we will call this gap E_{00} for clarity. As the zone-folding rule predicts this nanotube to be semiconducting, we believe that the metallic character is due to curvature effects, where the orbital rehybridisation creates a metallic system, but is insufficient to create the gap around E_F as seen for the (3,3) nanotube.

For the pob-TZVP basis set, the first optically-allowed axial transition is $E_{11} = 1.59$ eV, which corresponds to the axial optical gap $E_o^{\parallel} = 1.44$ eV, giving an exciton binding energy of $E_b^{\parallel} = 0.15$ eV. There appear to be multiple poles in the polarisability along the perpendicular direction, at energies beneath $E_o^{\parallel}$. However, there are no optically-allowed transitions between bands whose indices differ by 1 (*i.e.* E_{xy} or E_{yx} , where $|x - y| \leq 1$). Further study of the optical matrix shows that the transition $E_{31} = 0.91$ eV is the lowest-energy optically-allowed option, resulting in an exciton binding energy

	3-21G		pob-TZVP		m-def2-QZVP		Expt. [157]	GW-BSE [153]
	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$	$E^{\parallel}$	$E^{\perp}$		
$E_g(\text{eV})$	1.52	1.52	1.58	2.18	1.57	2.09	-	2.54
$E_o(\text{eV})$	1.50	1.39	1.58	1.42	1.63	1.39	1.60	1.55
$E_b(\text{eV})$	0.02	0.13	0.00	0.76	-0.06	0.70	-	0.99

Table 4.14: Energy gap (E_g), optical gap (E_o) and exciton binding energy (E_b) for the (8,0) SWCNT, using (HF/B3LYP) and three different basis sets at the optimised geometry **C**. Experimental and GW-BSE values have been supplied for comparison.

of $E_b^{\perp} = 0.15$ eV.

Using the m-def2-QZVP basis set for the (5,0) nanotube, the optical matrix shows that the first optically-allowed transition which is parallel to the nanotube axis is $E_{11}^{\Gamma} = 1.56$ eV, which is degenerate with E_{22}^{Γ} . With the axial optical gap of $E_o^{\parallel} = 1.44$ eV, $E_b^{\parallel} = 0.12$ eV. The lowest optically allowed crosswise transition is $E_{20} = 0.82$ eV (where the acceptor band does not appear as a van Hove singularity in the DOS, as it forms the Dirac cone), and the first asymptote in the perpendicular polarisation is at $E_o^{\perp} = 0.71$ eV, giving $E_b^{\perp} = 0.11$ eV.

(8,0)

The polarisability of a (8,0) SWCNT with infinite length was studied with B3LYP, using the 3-21G, pob-TZVP and m-def2-QZVP basis sets, and the m-def2-QZVP/B3LYP optimised structure. The data for the asymptotes is given in Table 4.14, along with experimental values and those from previous computational studies.

The 3-21G basis set gives the first optically allowed E_g as $E_{11}^{\Gamma} = 1.52$ eV, with $E_o^{\parallel} = 1.50$ eV resulting in $E_b^{\parallel} = 0.02$ eV. A study of the optical matrix elements shows that the first optically allowed gaps are degenerate with $E_{11}^{\Gamma} = E_{22}^{\Gamma} = E_{21}^{\Gamma}$, resulting in the crosswise $E_o^{\perp} = 1.39$ giving $E_b^{\perp} = 0.13$ eV.

Using the pob-TZVP basis set for the (8,0) nanotube, we find that the lowest-energy optically-allowed KS gaps are $E_{22}^{\Gamma} = 1.58$ eV and $E_{32}^{\Gamma} = 2.18$ eV. However, $E_o^{\parallel} = 1.58$ eV too, indicating a system with zero exciton binding energy. This is an unexpected observation as the GW-BSE results show a exciton binding of ~ 1 eV, and the three next-largest axial gaps are 1.92, 2.18 and 2.29 eV, none of which would be able to recreate the degree of binding shown in the GW-BSE calculations.

Unusually, the lowest optically allowed axial gap is $E_{22}^{\Gamma} = 1.57$ eV, whilst we observe the first axial asymptote in the polarisability at $E_o^{\parallel} = 1.63$ eV. These values imply a repulsive electron-hole interaction, which can be interpreted as the repulsive exchange

	This work			Ref. [153]			Expt. [157, 170]
	LDA	B3LYP	TD-B3LYP	LDA	GW	BSE	
E_{11} (eV)	1.62	1.58	1.58	1.39	2.54	1.55	1.60
E_{22} (eV)	1.82	1.92	1.87	1.51	2.66	1.80	1.88
E_{22}/E_{11}	1.12	1.22	1.18	1.09	1.05	1.16	1.17

Table 4.15: Comparison of the two lowest optically-allowed transitions of the (8,0) SWCNT calculated in this work using the pob-TZVP basis set, with those from the GW-BSE study of Spataru *et al.* [153].

contribution being larger than the attractive Coulomb interaction, as suggested by Spataru *et al.* [153].

Due to the poor convergence of the polarisability around the first pole, $E_o^\perp$ was extrapolated to be 1.39 eV, giving $E_b^\perp = 0.7eV$.

The work by Spataru and co-workers [153] shows a comparison of E_{11} and E_{22} of the (8,0) SWCNT, calculated with and without the electron-hole coupling. In Table 4.15 we compare our LDA and TD-B3LYP results from the pob-TZVP basis sets to this GW-BSE study and the experimental estimates.

Across all three basis sets, we find that TD-B3LYP greatly underestimates the E_b of the axial excitation, in comparison to the GW-BSE results. However, we also find that TD-B3LYP provides values of the optical gap which are in better agreement with the experimental value than the GW-BSE study.

Conclusions of optical properties

Despite predictions that self-induced depolarisation effects inhibit the observation of excitations perpendicular to the nanotube axis, our calculations show that both HF and B3LYP exhibit bound excitons from perpendicular perturbations. In addition, we observe a markedly decreased polarisability in the direction perpendicular to the nanotube axis for each nanotube studied, which indicates that the computed polarisability may be used as a qualitative gauge of optical absorption intensity. In studying three different systems - a nanotube which is metallic in both zone-folding and B3LYP calculations (3,3), a nanotube which is semiconducting in zone-folding predictions, but metallic due to curvature effects in B3LYP (5,0) and a nanotube which is semiconducting according to both zone-folding and B3LYP calculations, we find it difficult to draw conclusions about the global application of TD-B3LYP to SWCNTs. For the small-diameter (3,3) nanotube, both zone-folding and B3LYP calculations predict a metallic system, and we find that TD-B3LYP overestimates the axial E_o by ~ 0.5 -1.2 eV, which

is both an improvement in relative and absolute deviation, in comparison to TD-B3LYP for the alkali halides. Along with an overestimation of E_o , the exciton binding energy is overestimated in TD-B3LYP, when compared to GW-BSE results, with the optimised basis sets showing an overestimation of ~ 1.1 eV. In moving to the (5,0) nanotube which is semiconducting in the zone-folding model, but metallic in B3LYP due to curvature-induced orbital rehybridisation, B3LYP overestimates E_o by 0.07 eV for the optimised basis sets, with respect to the experimental value, but are in agreement with the GW-BSE optical gap. However, the exciton binding within B3LYP is still overestimated in comparison to LDA-based GW-BSE. For the (8,0) nanotube, which is predicted to be semiconducting by both the zone-folding and B3LYP methods, the optimised basis sets lead to calculated values of E_o which are in very good agreement with the experimental measurement (0.02 eV underestimation). These TD-B3LYP calculations show negligible exciton binding, whereas the GW-BSE calculations suggest that $E_b = 1.0$ eV. This disparity between values of E_b calculated in our work, and those of Spataru *et al.* does not denote a failure or breakdown of our method, as our values of E_b are an estimate and compromise made between single-particle and two-particle methods.

As seen in the study of E_g^Γ , the 3-21G basis set often calculates values of E_g which are generally not in good agreement with the optimised basis sets, yet for the smaller nanotubes, the 3-21G basis set generates bound excitons with the same degree of binding as the larger basis sets. This indicates that small basis sets without diffuse orbitals can describe similar excitation processes in SWCNTs to those basis sets which have been optimised.

5

Conclusions

In this work, we have proven that basis sets for excited state calculations are not reliably quantified nor qualified by their prediction of ground state properties. This is evidenced clearly by the choice of basis set for bulk LiF (Section 3.4.3). For example, the Dovesi-Nada basis set pair reliably calculates the fundamental gap E_g in comparison to the other studied basis sets, yet fails to describe the edge of the conduction bands, creating a system that is not compatible with the widely accepted excitation model of transferring an electron from a fluorine ion to the lithium sublattice. We propose instead to quantify basis sets by their calculations of static mean dynamical polarisability (MDP), a concept studied for molecular systems by Rappoport *et al.* [79], but not yet expanded towards extended or crystalline systems. This basis set convergence criterion is an application of the Hylleraas variational principle, whereby basis sets can be quantified by the calculated maximum of first-order response properties. We show that for LiF and NaF the total energy of a unit cell can be converged at a minimum, yet the MDP remain unconverged. By selecting basis sets which are optimised towards the polarisability, rather than total energy, we believe we reach the basis set limit, and we have used such basis sets to study the optical properties of the alkali halides and single-walled carbon nanotubes (SWCNTs).

We observe that for LiF, calculations with basis sets which are not polarisation-converged provide values of E_o and E_g which are very similar to those from polarisation-converged basis sets. By replicating the basis set study for NaF we find that there is a large variation in the E_g and MDP, caused by the increased polarisability of the alkali cation. However, even with such variations in the MDP and E_g , the calculated exciton binding energies within NaF are in very good agreement with each other. Additionally, we show that the choice of a larger and more-converged basis set will not always provide results closer to experimental values.

We find that TD-LDA and TD-PBE produce no binding of the exciton in LiF, due to the lack of HF exchange in the response kernel. Both TD-HF and global hybrid-exchange TD-B3LYP describe the formation of a bound electron-hole pair, with the pure HF calculations over-binding the exciton, and TD-B3LYP calculations under-binding the exciton. The dependence of the exciton binding on the contribution of HF exchange energy (c_{HF}) to the B3LYP functional is studied, showing that whilst E_g increases linearly with c_{HF} , the optical gap (E_o) does not, and that a single value of c_{HF} is unable to reproduce experimental values of both E_g and E_o for LiF.

In our study of the alkali halide series, we show the dependence of E_o on $\mathbf{k}$ -point coupling, and that all systems exhibit non-negligible exciton binding energies. For the majority of systems, we underestimate the E_b by <0.6 eV, whilst for the rubidium halides we greatly underestimate E_g , E_o and E_b , but by comparison to PBE/VASP calculations, we prove that it is not due to the choice of basis set, but an effect that is being poorly described or missing from both approaches to these heavy-atom systems.

Regarding the ground-state electronic properties of SWCNTs, we find a very good agreement between B3LYP results and the zone-folding method for predicting the metallicity of SWCNTs, even for the unoptimised graphene geometry. By using relaxed structures and optimised basis sets, we observe an even better agreement for the nanotubes studied, with those that fail to obey the zone-folding $((m - n)/3 = \mathbb{Z})$ rule being low-diameter high-curvature systems. Through changing the method to HF or LDA, we find a much poorer qualitative agreement to the zone-folding predictions regarding the metallic or semiconducting nature of the SWCNTs studied, and poor agreement to the quantitative B3LYP results. Using the HF method we overestimate E_g^Γ relative to B3LYP for the majority of nanotubes, with many systems predicted to be metallic by both B3LYP and the zone-folding rule, described as semiconductors by HF. Conversely, the LDA functional describes the majority of studied nanotubes as metals, and underestimates the values of the semiconducting nanotubes. The quantitative nature of the HF and LDA calculations are an expected observation, after our study on the alkali halides.

Our B3LYP band structures and projected density of states show asymmetry of the occupied and unoccupied states above and below E_F , which is not seen by simple TB models. We clearly observe van Hove singularities in the DOS for all studied nanotubes - phenomena which are indicative of the pseudo one-dimensional character of SWCNTs. By studying nanotubes of increasing diameter (and thus decreasing curvature), we observe an increase in symmetry of the van Hove singularities around $(E_{v1} + E_{c1})/2$ (which is E_F for metallic systems), but also an increase in graphene-like nature of the

DOS away from E_F , supporting the theory that the asymmetry of van Hove singularities is an effect of the curvature. Our study on the effect of geometry relaxation on the electronic structure shows that there is both a quantitative and qualitative change in the band structure, which is reduced for higher-diameter nanotubes.

In a quantitative comparison of the fundamental gap at Γ (E_g^Γ) with a variety of basis sets, we observe that the 3-21G basis set is unpredictably often in agreement with the polarisation and energy-optimised pob-TZVP and m-def2-QVZP basis sets, whilst the pob-TZVP and m-def2-QVZP are in a good qualitative and quantitative agreement with each other for the vast majority of systems. Qualitatively we find that the 3-21G basis set is greatly affected by the choice of geometry, where upon relaxation, the metallic or semiconducting character of E_g often changes.

As a nanotube of infinite diameter is indistinguishable from a layer of graphene, it is expected that as we increase the size of each studied SWCNT, we will observe more graphene-like properties and behaviour of the electronic structure. This is proven qualitatively in the change of nature of the DOS, and also in the quantitative nature of E_g , when we study zigzag nanotubes of diameters up to 46 Å.

Due to the two-dimensional nature of SWCNTs, there are two directions along which an electric field can be applied - axially or perpendicular, unlike the bulk alkali halide series. Previous experimental and theoretical work has shown that excitations which arise from perturbations perpendicular to the nanotube are suppressed, due to a self-induced depolarising effect. However, experimental studies have shown that these forbidden excitations are observable [154], and our work proves that both TD-HF and TD-B3LYP can produce strongly bound excitons from perpendicular excitations. In addition, we observe that the optical gaps of the perpendicular excitations vary far less with the choice of basis set, often with E_o^{3-21G} in very good agreement with the values calculated with the polarisation and energy optimised basis sets. However, both a qualitative and quantitative analysis of the perpendicular excitations calculated through TD-B3LYP is hard to achieve against either previous theoretical or experimental work, due to the presumption of the strong depolarisation effect making such excitations unmeasurable.

For the axial optical excitations, which are more commonly seen in experimental studies, this work shows that TD-B3LYP is closer to both the GW-BSE [153] and experimental [157,161] values of the optical properties than TD-HF, with TD-HF strongly over-binding the excitons in the (3,3) nanotube. We have studied the MDP of three nanotubes which exhibit different classes of electronic structure partly due to curvature effects, and as such it is not a trivial task to draw complete conclusions as to

the applicability of TD-B3LYP to all SWCNTs. Overall, we find that the polarisation and energy-optimised basis sets provide calculated values of the optical gap that are in very good agreement with the experimental and GW-BSE values, however TD-B3LYP poorly describes exciton binding energies, in comparison to the GW-BSE calculations. Without an experimental value of E_b for comparison, it is difficult to decide on which method correctly describes the nature of the excitation, when both B3LYP and GW are known to give reliable values of the KS gap in carbon allotropes.

In conclusion, we have found that our *ab initio* global hybrid exchange-correlation TD-B3LYP linear response calculations provide comparable values to the more expensive GW-BSE calculations, providing a competitive option for the calculation of optical gaps of SWCNTs.

Appendix A

Appendix

A.1 CRYSTAL Development

During this work I took on a secondary role as a developer for the **CRYSTAL** software suite. The modifications I made to the code-base include new functionalities and routines to aid with the calculation of optical properties. For example, one major development has resulted in an increased efficiency in the calculation of asymptotes of the MDP, by allowing for multiple frequency-dependent polarisability calculations from a single ground-state energy calculation. My developmental work has also included the expansion of joint density of state (JDOS) calculations to include each irreducible $\mathbf{k}$ -point in the first Brillouin zone. This has allowed me to calculate EELS spectra of LaMnO_3 surfaces accurately, for comparison with experimental measurements. In the original implementation of the $\mathbf{k}$ -uncoupled calculations, the initial unperturbed ground-state calculation was required to have one $\mathbf{k}$ -point, Γ . I've added an option to the TD-DFT module, where the user can instead choose to run a ground-state calculation containing multiple irreducible $\mathbf{k}$ -points, followed by a $\mathbf{k}$ -uncoupled TD-DFT calculation. This addition allows for smaller unit cells to be used for the ground-state calculation, leading to improved efficiencies.

A.2 CRYSTAL DOS

The equation used for the projected density of states within the **CRYSTAL** software suite is

$$\rho_\mu(\epsilon) = \frac{2}{V_B} \sum_j \sum_\nu \sum_{\underline{g}} \int_{BZ} S_{\mu\nu}(\underline{k}) a_{\mu j}(\underline{k}) a_{\nu j}^*(\underline{k}) e^{i\underline{k} \cdot \underline{g}} \delta[\epsilon - \epsilon_j(\underline{k})] d\underline{k}, \quad (\text{A.1})$$

where V_B is the volume of the Brillouin zone, $S_{\mu\nu}$ is the overlap matrix for orbitals μ, ν , and $a_{\mu j}, a_{\nu j}^*$ are the coefficients for the Bloch function $e^{i\mathbf{k}\cdot\mathbf{g}}$ (see Eqn. 2.16).

A.3 Alkali Halide Basis Sets

The following basis sets are in the current **CRYSTAL** format - information regarding the structure of this format can be found in the **CRYSTAL** manual [104] and website [171].

(1) “Dovesi:Nada”

Lithium

Unmodified - Ref. [108]

```

3 3
0 0 6 2 0
700.0 0.001421
220.0 0.003973
70.0 0.01639
20.0 0.089954
5.0 0.315646
1.5 0.494595
0 0 1 1 0
0.5 1.0
0 2 1 0 0
0.6 1.0
```

Fluorine

Unmodified - Ref. [109]

```

9 4
0 0 7 2 0
13770. 0.000877
1590.0 0.00915
326.5 0.0486
91.66 0.1691
30.46 0.3708
```

```

      11.50   0.4165
      4.76   0.1306
0 1 3 7 0
      19.    -0.1094   0.1244
      4.53  -0.1289   0.5323
      1.37   1.0      1.0
0 1 1 0 0
      0.45   1.    1.
0 1 1 0 0
      0.205  1.    1.

```

(2) pob-TZVP

Lithium

Unmodified - Ref . [78]

```

3 5
0 0 6 2 0
6269.262801      0.00020540968826
940.31612431     0.0015916554089
214.22107528     0.0082869829707
60.759840184     0.033856374249
19.915152032     0.11103225876
7.3171509797     0.27449383329
0 0 2 1 0
2.9724674216     0.23792456411
1.2639852314     0.30765411924
0 0 1 0 0
0.50255162       1.
0 0 1 0 0
0.10007462       1.
0 2 1 0 0
0.14507133       1.

```

Fluorine

Unmodified - Ref. [78]

9 8	
0 0 6 2 0	
35479.100441	0.00021545014888
5318.4728983	0.0016700686527
1210.4810975	0.0086733211476
342.8551814	0.035049933175
112.01943181	0.11165320133
40.714740248	0.25988506647
0 0 2 2 0	
16.039678111	0.3942296688
6.503818674	0.24998238551
0 0 1 0 0	
1.44200749	1.
0 0 1 0 0	
0.45977258	1.
0 2 4 5 0	
80.233900483	0.0063685999134
18.594010743	0.04430314353
5.6867902653	0.16867248708
1.9511006294	0.36166346255
0 2 1 0 0	
0.63228452	1.
0 2 1 0 0	
0.19835532	1.
0 3 1 0 0	
0.56312635	1.

(3) m-def2-QZVP**Lithium**

Unmodified - Ref. [105] (Unused)

3 13

0 0 1 2 0	
14853.977085	0.000042711388815
2225.2236477	0.000332353108
504.88739008	0.0017518436649
142.45847548	0.007347799585
46.31559958	0.025899837683
16.655335474	0.076670682431
6.4331186199	0.18276075765
2.6027043858	0.32655434038
1.0897245405	0.37000429828
0 0 1 1 0	
4.4236595971	0.11120987921
1.235639499	0.79987335862
0 0 1 0 0	
0.46067470602	1.
0 0 1 0 0	
0.096617166955	1.
0 0 1 0 0	
0.045915452296	1.
0 0 1 0 0	
0.02114004873	1.
0 2 3 0 0	
3.2605109206	0.0086504749023
0.65003043115	0.047614123736
0.16941671073	0.21001138
0 2 1 0 0	
0.055732343767	1.
0 2 1 0 0	
0.020489959241	1.
0 2 1 0 0	
3.327	1.
0 3 1 0 0	
0.23	1.
0 3 1 0 0	
0.0757	1.
0 4 1 0 0	

0.135 1.

Modified (Used)

3 8

0 0 9 2 0

14853.977085 0.000042711388815

2225.2236477 0.00033235310800

504.88739008 0.0017518436649

142.45847548 0.0073477995850

46.31559958 0.025899837683

16.655335474 0.076670682431

6.4331186199 0.18276075765

2.6027043858 0.32655434038

1.0897245405 0.37000429828

0 0 2 0 0

4.4236595971 0.11120987921

1.235639499 0.79987335862

0 0 1 0 0

0.46067470602 1.

0 0 1 0 0

0.1706202614 1.

0 2 3 0 0

3.2605109206 0.0086504749023

0.65003043115 0.047614123736

0.16941671073 0.21001138

0 2 1 0 0

3.327 1.

0 3 1 0 0

0.23 1.

0 4 1 0 0

0.235 1.

Fluorine

Unmodified - Ref. [105] (Unused)

9 17	
0 0 8 2 0	
132535.97345	0.000047387482743
19758.112588	0.00037070120897
4485.1996947	0.0019450784713
1273.815102	0.0080573291994
418.93831236	0.027992880781
152.55721985	0.082735120175
59.821524823	0.19854169012
24.819076932	0.34860632233
0 0 2 2 0	
100.74446673	0.10505068816
30.10372829	0.94068472434
0 0 1 0 0	
10.814283272	1.
0 0 1 0 0	
4.817288677	1.
0 0 1 0 0	
1.6559334213	1.
0 0 1 0 0	
0.64893519582	1.
0 0 1 0 0	
0.24778104545	1.
0 2 5 5 0	
240.96654114	0.0030389933451
57.020699781	0.024357738582
18.12695212	0.11442925768
6.6457404621	0.37064659853
2.6375722892	0.79791551766
0 2 1 0 0	
1.06382172	1.
0 2 1 0 0	
0.4193256275	1.
0 2 1 0 0	
0.15747588299	1.
0 3 1 0 0	

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5.014	1.
0 3 1 0 0	
1.725	1.
0 3 1 0 0	
0.586	1.
0 4 1 0 0	
3.562	1.
0 4 1 0 0	
1.148	1.
0 5 1 0 0 (g-orbitals are not yet implemented in CRYSTAL)	
2.376	1.

Modified (Used)

9 16	
0 0 8 2 0	
132535.97345	0.000047387482743
19758.112588	0.00037070120897
4485.1996947	0.0019450784713
1273.815102	0.0080573291994
418.93831236	0.027992880781
152.55721985	0.082735120185
59.821524823	0.19854169012
24.819076932	0.34860632233
0 0 2 2 0	
100.74446673	0.10505068816
30.10372829	0.94068472434
0 0 1 0 0	
10.814283272	1.
0 0 1 0 0	
4.817288677	1.
0 0 1 0 0	
1.6559334213	1.
0 0 1 0 0	
0.64893519582	1.
0 0 1 0 0	

0.24778104545	1.
0 2 5 5 0	
240.96654114	0.0030389933451
57.020699781	0.024357738582
18.12695212	0.11442925768
6.6457404621	0.37064659853
2.6375722892	0.79791551766
0 2 1 0 0	
1.06382172	1.
0 2 1 0 0	
0.4193256275	1.
0 2 1 0 0	
0.15747588299	1.
0 3 1 0 0	
5.014	1.
0 3 1 0 0	
1.725	1.
0 3 1 0 0	
0.586	1.
0 4 1 0 0	
3.562	1.
0 4 1 0 0	
1.148	1.

(A) m-def2-SVP**Lithium**

Unmodified - Ref. [105] (Unused)

3 5	
0 0 5 2 0	
266.27785516	0.0064920150325
40.069783447	0.047747863215
9.0559944389	0.20268796111
2.4503009051	0.48606574817
0.72209571855	0.43626977955

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0 0 1 1 0		
	0.052810884721	1.
0 0 1 0 0		
	0.020960948798	1.
0 2 2 0 0		
	1.45	0.2586
	0.3	1.
0 2 2 0 0		
	0.082	1.

Modified (Used)

3 3		
0 0 5 2 0		
	266.27785516	0.0064920150325
	40.069783447	0.047747863215
	9.0559944389	0.20268796111
	2.4503009051	0.48606574817
	0.72209571855	0.43626977955
0 2 2 1 0		
	1.45	0.2586
	0.3	1.
0 2 1 0 0		
	0.082	1.

Fluorine

Unmodified - Ref. [105] (Unused)

9 6		
0 0 5 2 0		
	2894.832599	-0.0053408255515
	435.4193912	-0.039904258866
	98.843328866	-0.17912768038
	27.485198001	-0.46758090825
	8.5405498171	-0.4465313102

```

0 0 1 2 0
    1.0654578038    1.
0 0 1 0 0
    0.33247346748    1.
0 2 3 5 0
    22.696633924    -0.045212874436
    4.9872339257    -0.23754317067
    1.3491613954    -0.51287353587
0 2 1 0 0
    0.34829881977    1.
0 3 1 0 0
    1.4              1.

```

Modified (Used)

```

9 6
0 0 5 2 0
    2894.832599      -0.0053408255515
    435.4193912      -0.039904258866
    98.843328866     -0.17912768038
    27.485198001     -0.46758090825
    8.5405498171     -0.4465313102
0 0 1 2 0
    1.0654578038     1.0
0 0 1 0 0
    0.33247346748     1.0
0 2 3 5 0
    22.696633924     -0.045212874436
    4.9872339257     -0.23754317067
    1.3491613954     -0.51287353587
0 2 1 0 0
    0.34829881977     1.
0 3 1 0 0
    1.4              1.

```

(B) “Merawa:Nada”**Lithium**

Unmodified - Ref. [172] (Used)

3	4		
0	0	5	2 0
	840.0		0.00264
	217.5		0.00850
	72.3		0.0335
	19.66		0.1824
	5.044		0.6379
0	1	1	1 0
	1.478	1.	1.
0	1	1	0 0
	0.479	1.	1.
0	3	1	0 0
	0.6	1.	

Fluorine

See basis set 1.

(C) “Ojamae:Nada”**Lithium**

Unmodified - Ref. [173] (Used)

3	3		
0	0	6	2 0
	840.0		0.00264
	217.5		0.00850
	72.3		0.0335
	19.66		0.1824
	5.044		0.6379
	1.5	1.	
0	1	1	1 0

		0.514	1.	1.
0	1	1	0	0
		0.216	1.	1.

Fluorine

See basis set **1**.

(D) “m-Merawa:Nada”**Lithium**

Unmodified - see basis set **B**. (Unused)

Modified (Used)

3	5			
0	0	5	2	0
		840.0		0.00264
		217.5		0.00850
		72.3		0.0335
		19.66		0.1824
		5.044		0.6379
0	1	1	1	0
		1.85	1.	1
0	1	1	0	0
		0.69	1.	1
0	1	1	0	0
		0.25	1.	1
0	3	1	0	0
		0.600	1.	

Fluorine

See basis set **1**.

(E) m-def2-TZVP**Lithium**

Unmodified - Ref. [105] (Unused)

3 8		
0 0 6 2 0		
6269.262801	0.00020540968826	
940.31612431	0.0015916554089	
214.22107528	0.0082869829707	
60.759840184	0.033856374249	
19.915152032	0.11103225876	
7.3171509797	0.27449383329	
0 0 2 1 0		
2.9724674216	0.23792456411	
1.2639852314	0.30765411924	
0 0 1 0 0		
0.51427489953	1.	
0 0 1 0 0		
0.077030885901	1.	
0 0 1 0 0		
0.028938896433	1.	
0 2 1 0 0		
0.4	1.	
0 2 1 0 0		
0.06	1.	
0 3 1 0 0		
3.327	1.	

Modified (Used)

3 6		
0 0 6 2 0		
6929.262801	0.00020540968826	
940.31612431	0.0015916554089	
214.22107528	0.0082869829707	
60.759840184	0.033856374249	

19.915152032	0.11103225876
7.3171509797	0.27449383329
0 0 2 1 0	
2.9724674216	0.23792456411
1.2639852314	0.30765411924
0 0 1 0 0	
0.51427489953	1.
0 0 1 0 0	
0.077030885901	1.
0 2 1 0 0	
0.4	1.
0 2 1 0 0	
3.327	1.

Fluorine

Unmodified - Ref. [105]

9 11	
0 0 6 2 0	
35479.100441	0.00021545014888
5318.4728983	0.0016700686527
1210.4810975	0.0086733211476
342.8551814	0.035049933175
112.01943181	0.11165320133
40.714740248	0.25988506647
0 0 2 2 0	
16.039678111	0.39422966880
6.503818674	0.24998238551
0 0 1 0 0	
1.5440477509	1.
0 0 1 0 0	
0.61223452862	1.
0 0 1 0 0	
0.24027979698	1.
0 2 4 5 0	

80.233900483	0.0063685999134
18.594010743	0.044303143530
5.6867902653	0.16867248708
1.9511006294	0.36166346255
0 2 1 0 0	
0.66970211298	1.
0 2 1 0 0	
0.2165130041	1.
0 3 1 0 0	
3.107	1.
0 3 1 0 0	
0.855	1.
0 4 1 0 0	
1.917	1.

(F) m-def2-TZVPP**Lithium**

Unmodified - Ref. [105] (Unused)

0 0 6 2 0	
6269.262801	0.00020540968826
940.31612431	0.0015916554089
214.22107528	0.0082869829707
60.759840184	0.033856374249
19.915152032	0.11103225876
7.3171509797	0.27449383329
0 0 2 1 0	
2.9724674216	0.23792456411
1.2639852314	0.30765411924
0 0 1 0 0	
0.51427489953	1.
0 0 1 0 0	
0.077030885901	1.
0 0 1 0 0	
0.028938896433	1.

0 2 1 0 0	
0.4	1.
0 2 1 0 0	
0.06	1.
0 2 1 0 0	
3.327	1.
0 3 1 0 0	
0.1319	1.

Modified (Used)

3 7	
0 0 6 2 0	
6929.262801	0.00020540968826
940.31612431	0.0015916554089
214.22107528	0.0082869829707
60.759840184	0.033856374249
19.915152032	0.11103225876
7.3171509797	0.27449383329
0 0 2 0 0	
2.9724674216	0.23792456411
1.2639852314	0.30765411924
0 0 1 0 0	
0.51427489953	1.
0 0 1 0 0	
0.077030885901	1.
0 2 1 0 0	
0.4	1.
0 2 1 0 0	
3.327	1.
0 3 1 0 0	
0.2319	1.

Fluorine

See basis set **E**

(G) m-Merawa:m1-TRB**Lithium**See basis set **D****Fluorine**

Unmodified - Ref. [81] (Unused)

9 26	
0 0 4 2 0	
37736.	0.0049427358
5867.08	0.036991024
1332.47	0.19661032
369.441	0.82771554
0 0 1 0 0	
116.843	1.
0 0 1 0 0	
40.3488	1.
0 0 1 0 0	
14.9663	1.
0 0 1 0 0	
5.87593	1.
0 0 1 0 0	
1.65334	1.
0 0 1 0 0	
0.610836	1.
0 0 1 0 0	
0.233289	1.
0 0 1 0 0	
0.0933157	1.
0 0 1 0 0	
0.0373263	1.
0 0 1 0 0	
0.0149305	1.
0 0 1 0 0	
0.0059722	1.

0 2 3 6 0		
102.262	0.030118321	
23.9384	0.21546768	
7.52059	0.83369412	
0 2 1 0 0		
2.77246	1.	
0 2 1 0 0		
1.10005	1.	
0 2 1 0 0		
0.446775	1.	
0 2 1 0 0		
0.171870	1.	
0 2 1 0 0		
0.068748	1.	
0 2 1 0 0		
0.0274992	1.	
0 2 1 0 0		
0.0109997	1.	
0 3 1 0 0		
2.19994	1.	
0 3 1 0 0		
0.618732	1.	
0 3 1 0 0		
0.206244	1.	
0 3 1 0 0		
0.068748	1.	
0 3 1 0 0		
0.022916	1.	
0 4 1 0 0		
0.206244	1.	

Modified (Used)

9 21		
0 0 1 2. 1.		
37736.	0.0049427358	

0 0 1 2. 1.	
5867.08	0.036991024
0 0 1 0. 1.	
1332.47	0.19661032
0 0 1 0. 1.	
369.441	0.82771554
0 0 1 0. 1.	
116.843	1.
0 0 1 0. 1.	
40.3488	1.
0 0 1 0. 1.	
14.9663	1.
0 0 1 0. 1.	
5.87593	1.
0 0 1 0. 1.	
1.65334	1.
0 0 1 0. 1.	
0.610836	1.
0 0 1 0. 1.	
0.233289	1.
0 2 1 6. 1.	
102.262	0.030118321
0 2 1 0. 1.	
23.9384	0.21546768
0 2 1 0. 1.	
7.52059	0.83369412
0 2 1 0. 1.	
2.77246	1.
0 2 1 0. 1.	
1.10005	1.
0 2 1 0. 1.	
0.446775	1.
0 2 1 0. 1.	
0.17187	1.
0 3 1 0. 1.	
2.19994	1.

0 3 1 0. 1.	
0.618732	1.
0 3 1 0. 1.	
0.206244	1.

(H) m2-KP:def2-TZVP**Lithium**Unmodified - see basis set **K** (Unused)

Modified (Used)

3 18	
0 0 6 2 0	
108401.4	0.0000035604716764
16230.85	0.000027686065979
3693.639	0.00014561749834
1046.225	0.00061468268460
341.3346	0.0022335453216
123.2364	0.0072237602518
0 0 1 1 0	
48.07162	1.
0 0 1 0 0	
19.93437	1.
0 0 1 0 0	
8.671334	1.
0 0 1 0 0	
3.904202	1.
0 0 1 0 0	
1.800662	1.
0 0 1 0 0	
0.845141	1.
0 0 1 0 0	
0.392653	1.
0 0 1 0 0	
0.1570612	1.
0 2 1 0 0	

55.51916	1.
0 2 1 0 0	
13.17503	1.
0 2 1 0 0	
4.238383	1.
0 2 1 0 0	
1.554368	1.
0 2 1 0 0	
0.602069	1.
0 2 1 0 0	
0.24758	1.
0 3 1 0 0	
4.238383	1.
0 3 1 0 0	
1.554368	1.
0 3 1 0 0	
0.602069	1.

Fluorine

See basis set **E**

(I) Merawa:m2-TRB

Lithium

See basis set **B**

Fluorine

Unmodified - see basis set **K** (Unused)

Modified (Used)

9 16	
0 0 4 2 0	
37736.	0.0049427358
5867.08	0.036991024
1332.47	0.19661032

369.441	0.82771554
0 0 1 2 0	
116.843	1.
0 0 1 0 0	
40.3488	1.
0 0 1 0 0	
14.9663	1.
0 0 1 0 0	
5.87593	1.
0 0 1 0 0	
1.65334	1.
0 0 1 0 0	
0.610836	1.
0 0 1 0 0	
0.233289	1.
0 2 3 5 0	
102.262	0.030118321
23.9384	0.21546768
7.52059	0.83369412
0 2 1 0 0	
2.77246	1.
0 2 1 0 0	
1.10005	1.
0 2 1 0 0	
0.446775	1.
0 2 1 0 0	
0.17187	1.
0 3 1 0 0	
2.19994	1.
0 3 1 0 0	
0.618732	1.
0 3 1 0 0	
0.206244	1.

(J) Merawa:m1-TRB**Lithium**See basis set **B****Fluorine**See basis set **G****(K) m1-Kobayashi-Partridge(KP):m1-TRB****Lithium**

Unmodified - Ref. [174] (Unused)

3 35	
0 0 6 2 0	
108401.4	0.0000035604716764
16230.85	0.000027686065979
3693.639	0.00014561749834
1046.225	0.0006146826846
341.3346	0.0022335453216
123.2364	0.0072237602518
0 0 1 1 0	
48.07162	1.
0 0 1 0 0	
19.93437	1.
0 0 1 0 0	
8.671334	1.
0 0 1 0 0	
3.904202	1.
0 0 1 0 0	
1.800662	1.
0 0 1 0 0	
0.845141	1.
0 0 1 0 0	
0.392653	1.
0 0 1 0 0	
0.097806	1.

0 0 1 0 0		
0.045012	1.	
0 0 1 0 0		
0.020642	1.	
0 0 1 0 0		
0.0082568	1.	
0 0 1 0 0		
0.0033027	1.	
0 0 1 0 0		
0.0013211	1.	
0 2 1 0 0		
55.51916	1.	
0 2 1 0 0		
13.17503	1.	
0 2 1 0 0		
4.238383	1.	
0 2 1 0 0		
1.554368	1.	
0 2 1 0 0		
0.602069	1.	
0 2 1 0 0		
0.24758	1.	
0 2 1 0 0		
0.10973	1.	
0 2 1 0 0		
0.051617	1.	
0 2 1 0 0		
0.02525	1.	
0 2 1 0 0		
0.012398	1.	
0 2 1 0 0		
0.0049592	1.	
0 2 1 0 0		
0.0019837	1.	
0 3 1 0 0		
4.238383	1.	

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0 3 1 0 0	
1.554368	1.
0 3 1 0 0	
0.602069	1.
0 3 1 0 0	
0.24758	1.
0 3 1 0 0	
0.10973	1.
0 3 1 0 0	
0.051617	1.
0 3 1 0 0	
0.02525	1.
0 3 1 0 0	
0.012398	1.
0 3 1 0 0	
0.0049592	1.
0 3 1 0 0	
0.0019837	1.

Modified (Used)

3 14	
0 0 6 2 0	
108401.4	0.0000035604716764
16230.85	0.000027686065979
3693.639	0.00014561749834
1046.225	0.0006146826846
341.3346	0.0022335453216
123.2364	0.0072237602518
0 0 1 1 0	
48.07162	1.
0 0 1 0 0	
19.93437	1.
0 0 1 0 0	
8.671334	1.
0 0 1 0 0	

3.904202	1.
0 0 1 0 0	
1.800662	1.
0 0 1 0 0	
0.845141	1.
0 0 1 0 0	
0.392653	1.
0 2 1 0 0	
55.51916	1.
0 2 1 0 0	
13.17503	1.
0 2 1 0 0	
4.238383	1.
0 2 1 0 0	
1.554368	1.
0 2 1 0 0	
0.602069	1.
0 2 1 0 0	
0.24758	1.

FluorineSee basis set **G****(L) m3-KP:m1-TRB****Lithium**Unmodified - see basis set **K** (Unused)

Modified (Used)

3 15	
0 0 6 2 0	
108401.4	0.0000035604716764
16230.85	0.000027686065979
3693.639	0.00014561749834
1046.225	0.0006146826846
341.3346	0.0022335453216

123.2364	0.0072237602518
0 0 1 1 0	
48.07162	1.
0 0 1 0 0	
19.93437	1.
0 0 1 0 0	
8.671334	1.
0 0 1 0 0	
3.904202	1.
0 0 1 0 0	
1.800662	1.
0 0 1 0 0	
0.845141	1.
0 0 1 0 0	
0.392653	1.
0 2 1 0 0	
55.51916	1.
0 2 1 0 0	
13.17503	1.
0 2 1 0 0	
4.238383	1.
0 2 1 0 0	
1.554368	1.
0 2 1 0 0	
0.602069	1.
0 2 1 0 0	
0.24758	1.
0 3 1 0 0	
0.6	1.

Fluorine

See basis set **G**

(M) m2-KP:def2-QZVP**Lithium**See basis set **H****Fluorine**See basis set **3****m-def2-QZVP basis sets**

All unmodified basis sets are from Ref. [105]

Sodium

Unmodified (Unused)

11 18	
0 0 10 2 0	
379852.20081	0.000020671384468
56886.006378	0.00016070466617
12942.701838	0.00084462905848
3664.3017904	0.0035519026029
1194.7417499	0.012754034468
430.98192917	0.039895462742
167.83169424	0.10720154498
69.30666904	0.23339516913
29.951170886	0.36333077287
13.380791097	0.30544770974
0 0 3 2 0	
121.74011283	0.036142427284
37.044143387	0.28820961687
13.995422624	0.79337384869
0 0 1 1 0	
5.9827797428	1.
0 0 1 0 0	
2.4830455118	1.
0 0 1 0 0	

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1.0452506187	1.
0 0 1 0 0	
0.43875640383	1.
0 0 1 0 0	
0.065595633185	1.
0 0 1 0 0	
0.030561925072	1.
0 0 1 0 0	
0.015509064018	1.
0 2 8 6 0	
690.77627017	0.00037478518415
163.82806121	0.003177544103
52.876460769	0.016333581338
19.812270493	0.059754902585
8.1320378784	0.15879328812
3.4969068377	0.2904936326
1.5117244146	0.36368131139
0.64479294912	0.28195867334
0 2 1 0 0	
0.26145823312	1.
0 2 1 0 0	
0.11704726116	1.
0 2 1 0 0	
0.040494747666	1.
0 2 1 0 0	
0.015666707355	1.
0 3 1 0 0	
2.9	1.
0 3 1 0 0	
0.23	1.
0 3 1 0 0	
0.0757	1.
0 4 1 0 0	
0.135	1.

Modified (Used)

11 12	
0 0 10 2 0	
379852.20081	0.000020671384468
56886.006378	0.00016070466617
12942.701838	0.00084462905848
3664.3017904	0.0035519026029
1194.7417499	0.012754034468
430.98192917	0.039895462742
167.83169424	0.10720154498
69.30666904	0.23339516913
29.951170886	0.36333077287
13.380791097	0.30544770974
0 0 3 2 0	
121.74011283	0.036142427284
37.044143387	0.28820961687
13.995422624	0.79337384869
0 0 1 1 0	
5.9827797428	1.
0 0 1 0 0	
2.4830455118	1.
0 0 1 0 0	
1.0452506187	1.
0 0 1 0 0	
0.43875640383	1.
0 2 8 6 0	
690.77627017	0.00037478518415
163.82806121	0.003177544103
52.876460769	0.016333581338
19.812270493	0.059754902585
8.1320378784	0.15879328812
3.4969068377	0.2904936326
1.5117244146	0.36368131139
0.64479294912	0.28195867334
0 2 1 0 0	
0.26145823312	1.
0 2 1 0 0	

0.11704726116	1.
0 3 1 0 0	
2.9	1.
0 3 1 0 0	
0.23	1.
0 4 1 0 0	
0.235	1.

Potassium

Unmodified (Unused)

19 22	
0 0 11 2 0	
2022075.1391	0.000010144874011
303044.65568	0.000078783500963
69013.93849	0.00041380919674
19559.244615	0.0017427571893
6383.8934901	0.0063004086126
2305.3502858	0.020125347032
899.14418101	0.05696606052
372.59500133	0.13882654093
161.97635247	0.27132285414
73.085553853	0.36383620662
33.595644762	0.24724464776
0 0 4 2 0	
685.49855365	0.0044367463797
211.66163373	0.042502718169
80.851405131	0.18467742018
35.108667236	0.29353173891
0 0 1 2 0	
14.409437283	1.
0 0 1 1 0	
6.8697147262	1.
0 0 1 0 0	

3.2121883687	1.
0 0 1 0 0	
1.2610484365	1.
0 0 1 0 0	
0.61438946301	1.
0 0 1 0 0	
0.27264370973	1.
0 0 1 0 0	
0.077173005207	1.
0 0 1 0 0	
0.040918397569	1.
0 0 1 0 0	
0.017055762425	1.
0 2 9 6 0	
3469.6649718	0.0002134022597
822.02356107	0.0018637844836
266.58406636	0.010211431546
101.28048161	0.040799604728
42.429490761	0.12257473393
18.912083912	0.26405833679
8.701777903	0.38227164575
4.0854567599	0.29998812383
1.866728606	0.078007265591
0 2 5 6 0	
27.544639057	-0.0058222994163
9.2098893609	-0.026787531329
1.7232877425	0.30666847665
0.77969303735	0.66927944165
0.34379047862	0.60376468615
0 2 1 0 0	
0.14346681918	1.
0 2 1 0 0	
0.068	1.
0 2 1 0 0	
0.032	1.
0 2 1 0 0	

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0.0153	1.
0 3 1 0 0	
1.7	1.
0 3 1 0 0	
0.51	1.
0 3 1 0 0	
0.18	1.
0 3 1 0 0	
0.054	1.
0 4 1 0 0	
0.267	1.

Modified (Used)

19 17	
0 0 11 2 0	
2022075.1391	0.000010144874011
303044.65568	0.000078783500963
69013.93849	0.00041380919674
19559.244615	0.0017427571893
6383.8934901	0.0063004086126
2305.3502858	0.020125347032
899.14418101	0.05696606052
372.59500133	0.13882654093
161.97635247	0.27132285414
73.085553853	0.36383620662
33.595644762	0.24724464776
0 0 4 2 0	
685.49855365	0.0044367463797
211.66163373	0.042502718169
80.851405131	0.18467742018
35.108667236	0.29353173891
0 0 1 2 0	
14.409437283	1.
0 0 1 1 0	
6.8697147262	1.

0 0 1 0 0	
3.2121883687	1.
0 0 1 0 0	
1.2610484365	1.
0 0 1 0 0	
0.61438946301	1.
0 0 1 0 0	
0.27264370973	1.
0 0 1 0 0	
0.077173005207	1.
0 2 9 6 0	
3469.6649718	0.00021340225970
822.02356107	0.0018637844836
266.58406636	0.010211431546
101.28048161	0.040799604728
42.429490761	0.12257473393
18.912083912	0.26405833679
8.701777903	0.38227164575
4.0854567599	0.29998812383
1.866728606	0.078007265591
0 2 5 6 0	
27.544639057	-0.0058222994163
9.2098893609	-0.026787531329
1.7232877425	0.30666847665
0.77969303735	0.66927944165
0.34379047862	0.60376468615
0 2 1 0 0	
0.14346681918	1.
0 2 1 0 0	
0.068	1.
0 3 1 0 0	
1.7	1.
0 3 1 0 0	
0.51	1.
0 3 1 0 0	
0.18	1.

0 4 1 0 0	
0.267	1.

Rubidium

Unmodified (Unused)

37 17	
0 0 2 2 0	
7.474461804	0.26999390986
6.7296180594	-0.42624989529
0 0 1 2 0	
2.7822883445	1.
0 0 1 2 0	
0.53494544647	1.
0 0 1 2 0	
0.22522959349	1.
0 0 1 1 0	
0.050765580412	1.
0 0 1 0 0	
0.026940281781	1.
0 0 1 0 0	
0.013051395489	1.
0 2 4 6 0	
5.9998960731	0.05456854967
3.2040784712	-0.26447792498
0.8699197995	0.50033505958
0.44104169728	0.75243449327
0 2 1 6 0	
0.22139898232	1.
0 2 1 6 0	
0.10679039696	1.
0 2 1 0 0	
0.033292658822	1.
0 2 1 0 0	

0.01284700375	1.
0 3 2 10 0	
4.6530655240	-0.0011653388661
0.44914033653	0.15584297068
0 3 1 0 0	
0.1008957719	1.
0 3 1 0 0	
0.027432280711	1.
0 3 1 0 0	
0.095353625581	1.
0 4 1 0 0	
0.85245	1.

Modified (Used)

37 10	
0 0 2 2 0	
7.474461804	0.26999390986
6.7296180594	-0.42624989529
0 0 1 2 0	
2.7822883445	1.
0 0 1 2 0	
0.53494544647	1.
0 0 1 2 0	
0.22522959349	1.
0 2 4 6 0	
5.9998960731	0.05456854967
3.2040784712	-0.26447792498
0.8699197995	0.50033505958
0.44104169728	0.75243449327
0 2 1 6 0	
0.22139898232	1.
0 2 1 6 0	
0.10679039696	1.
0 3 2 10 0	
4.653065524	-0.0011653388661

0.44914033653	0.15584297068
0 3 1 0 0	
0.2008957719	1.
0 4 1 0 0	
0.85245	1.

Chlorine

Unmodified (Used)

17 22	
0 0 10 2 0	
1467459.0095	0.000011478257194
219756.16433	0.000089234299775
50010.770301	0.00046911086186
14164.823918	0.0019762446133
4620.7465525	0.0071419937783
1667.8991635	0.022753219445
650.29199265	0.063959782953
269.38037376	0.15331059238
117.06752106	0.28986952417
52.811766843	0.36348071452
0 0 3 2 0	
461.42769988	0.018019457578
142.12665355	0.16489442314
54.437838768	0.63891587584
0 0 1 2 0	
24.160770219	1.
0 0 1 0 0	
9.7083540306	1.
0 0 1 0 0	
4.5640696733	1.
0 0 1 0 0	
2.1194744832	1.
0 0 1 0 0	
0.75722365394	1.

0 0 1 0 0	
0.33747224597	1.
0 0 1 0 0	
0.13860775149	1.
0 2 8 6 0	
2501.945789	0.0002424261841
592.88059285	0.0021079961749
192.18089186	0.011432693869
72.875710488	0.044956698060
30.43635837	0.13197476145
13.490178902	0.27493639225
6.1478071413	0.38347236372
2.845094482	0.28871943885
0 2 2 5 0	
105.39397936	-0.034311760144
6.7369738513	0.64060818902
0 2 1 0 0	
1.2421095772	1.
0 2 1 0 0	
0.55669714254	1.
0 2 1 0 0	
0.23387801464	1.
0 2 1 0 0	
0.09316449089	1.
0 3 1 0 0	
5.191	1.
0 3 1 0 0	
1.276	1.
0 3 1 0 0	
0.583	1.
0 3 1 0 0	
0.243	1.
0 4 1 0 0	
0.423	1.
0 4 1 0 0	
1.089	1.

0 5 1 0 0 (g-orbitals are not yet implemented in CRYSTAL)
0.827 1.

Bromine

Unmodified (Used)

35 25	
0 0 11 2 0	
10629044.264	0.0000059322104325
1591918.2739	0.000046118980689
362333.98437	0.00024244612378
102643.11141	0.0010231422748
33489.846668	0.0037121984175
12091.24719	0.011978107933
4716.1908789	0.034682692842
1956.159808	0.089068331264
853.08595848	0.19330124567
387.96633666	0.32071144956
182.85156613	0.32996797574
0 0 4 2 0	
3240.4086421	0.006590519407
1000.4631935	0.068439609656
383.37301682	0.34495478668
166.03929698	0.82315542085
0 0 1 2 0	
87.919906994	1.
0 0 1 2 0	
35.675840068	1.
0 0 1 2 0	
17.543657842	1.
0 0 1 0 0	
8.4473660433	1.
0 0 1 0 0	
3.9666180616	1.
0 0 1 0 0	

1.8356815987	1.
0 0 1 0 0	
0.59084778776	1.
0 0 1 0 0	
0.28863218421	1.
0 0 1 0 0	
0.12153380537	1.
0 2 10 6 0	
26566.476579	0.00006207365741
6290.5088566	0.00055131636217
2043.317841	0.003168011098
781.67221007	0.01381659729
331.51078945	0.048018539681
151.09198667	0.13162015183
72.395278166	0.26860052203
35.869510844	0.36827391093
18.139906191	0.27108612944
9.0466688944	0.076215338633
0 2 5 6 0	
253.71822146	-0.0013729169381
97.250818058	-0.010393811185
42.03489796	-0.032204214612
9.9685673555	0.24224770086
4.9395854745	0.53557868398
0 2 1 5 0	
2.4382845475	1.
0 2 1 0 0	
1.18	1.
0 2 1 0 0	
0.51047564965	1.
0 2 1 0 0	
0.21215851928	1.
0 2 1 0 0	
0.08394360499	1.
0 3 7 10 0	
601.44434484	0.00062783723765

180.8571864	0.0057205157153	
69.98680634	0.029002521527	
30.3247103	0.096446989766	
14.027909238	0.2206582587	
6.6511702082	0.33657642375	
3.1354168338	0.34872040582	
0 3 1 0 0		
1.4393591843	1.	
0 3 1 0 0		
0.59350441438	1.	
0 3 1 0 0		
0.23	1.	
0 4 1 0 0		
0.3407	1.	
0 4 1 0 0		
0.8257	1.	
0 5 1 0 0 (g-orbitals are not yet implemented in CRYSTAL)		
0.6491	1.	

A.4 Carbon Nanotube Basis Sets

3-21G

Unmodified - Ref. [175] (used)

6 3		
0 0 3 2 0		
172.256	0.0617669	
25.9109	0.358794	
5.53335	0.911913	
0 1 2 4 0		
3.66498	-0.395897	0.23646
0.770545	1.21584	0.860619
0 1 1 0 0		
0.195857	1.	1.

pob-TZVP

Unmodified - Ref. [78] (Used)

6 8	
0 0 6 2 1	
13575.349682	0.00022245814352
2035.233368	0.0017232738252
463.22562359	0.0089255715314
131.20019598	0.035727984502
42.853015891	0.11076259931
15.584185766	0.24295627626
0 0 2 2 1	
6.2067138508	0.41440263448
2.5764896527	0.23744968655
0 0 1 0 1	
0.4941102	1.
0 0 1 0 1	
0.1644071	1.
0 2 4 2 1	
34.697232244	0.0053333657805
7.9582622826	0.035864109092
2.3780826883	0.14215873329
0.8143320818	0.34270471845
0 2 1 0 1	
0.56624171	1.
0 2 1 0 1	
0.2673545	1.
0 3 1 0 1	
0.87915842	1.

m-def2-QZVP

Unmodified - Ref. [105](unused)

6 17
0 0 8 2 0

A. APPENDIX

67025.071029	0.000038736308501
10039.986538	0.00030107917575
2284.9316911	0.0015787918095
647.1412213	0.0066087087195
211.09472335	0.02336712325
76.177643862	0.070420716898
29.633839163	0.17360344953
12.187785081	0.32292305648
0 0 2 2 0	
53.026006299	0.074897404492
15.258502776	0.76136220983
0 0 1 0 0	
5.2403957464	1.
0 0 1 0 0	
2.2905022379	1.
0 0 1 0 0	
0.69673283006	1.
0 0 1 0 0	
0.27599337363	1.
0 0 1 0 0	
0.10739884389	1.
0 2 5 2 0	
105.12555082	0.00084647553844
24.884461066	0.0066274038534
7.8637230826	0.030120390419
2.8407001835	0.099951435476
1.1227137335	0.23826299282
0 2 1 0 0	
0.46050725555	1.
0 2 1 0 0	
0.18937530913	1.
0 2 1 0 0	
0.075983791611	1.
0 3 1 0 0	
1.848	1.
0 3 1 0 0	

0.649	1.
0 3 1 0 0	
0.228	1.
0 4 1 0 0	
1.419	1.
0 4 1 0 0	
0.485	1.
0 5 1 0 0 (g-orbitals are not yet implemented in CRYSTAL)	
1.011	1.

Modified (used)

6 11	
0 0 8 2 0	
67025.071029	0.000038736308501
10039.986538	0.00030107917575
2284.9316911	0.0015787918095
647.1412213	0.0066087087195
211.09472335	0.02336712325
76.177643862	0.070420716898
29.633839163	0.17360344953
12.187785081	0.32292305648
0 0 1 2 0	
5.2403957464	1.
0 0 1 0 0	
2.2905022379	1.
0 0 1 0 0	
0.69673283006	1.
0 0 1 0 0	
0.27599337363	1.
0 2 5 2 0	
105.12555082	0.00084647553844
24.884461066	0.0066274038534
7.8637230826	0.030120390419
2.8407001835	0.099951435476
1.1227137335	0.23826299282

A. APPENDIX

0 2 1 0 0		
	0.46050725555	1.
0 2 1 0 0		
	0.18937530913	1.
0 3 1 0 0		
	1.848	1.
0 3 1 0 0		
	0.649	1.
0 4 1 0 0		
	1.419	1.

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