

Tuning the Graphene Band Gap by Thermodynamic Control of Molecular Self-Assembly on Graphene

Mariana Hildebrand

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1st supervisor : Prof. Dr. Nicholas Harrison

2nd supervisor: Prof. Dr. Peter Haynes

In memory of my dearest grandmother, Dr. Luzie Brem-Rupp.

Abstract

Recent interest in functionalised graphene has been motivated by the prospect of creating a two-dimensional semiconductor with a tuneable band gap. Various approaches to band gap engineering have been made over the last decade, one of which is chemical functionalisation. However, the patterning of molecular adsorption onto graphene has proved to be difficult, as grown structures tend to be stochastic in nature.

In the first part of this work, a predictive physical model of the self-assembly of halogenated carbene layers on graphene is suggested. Self-assembly of the adsorbed layer is found to be governed by a combination of the curvature of the graphene sheet, local distortions, as introduced by molecular adsorption, and short-range intermolecular repulsion. The thermodynamics of bidental covalent molecular adsorption and the resultant electronic structure are computed using Density Functional Theory. It is predicted that a direct band gap is opened that is tuneable by varying coverages and is dependent on the ripple amplitude. This provides a mechanism for the controlled engineering of graphene's electronic structure and thus its use in semiconductor technologies.

In the second part of this work, the formation of intrinsic ripples in graphene sheets under isotropic compression is examined. An isotropic compression of graphene is shown to induce a structural deformation on the basis of Density Functional Perturbation Theory. Static instabilities, indicated by imaginary frequency phonon modes, are induced in the high symmetry $\Gamma - K$ (zigzag) and $\Gamma - M$ (armchair) directions by an isotropic compressive strain of the graphene sheet. The wavelength of the unstable modes (ripples) is directly related to the

magnitude of the strain and remarkably insensitive to the direction of propagation in the 2D lattice. These calculations further suggest that the formation energy of the ripple is isotropic for lower strains and becomes anisotropic for larger strains. This is a result of graphene’s elastic property, which is dependent on direction and strain. Within the quasi harmonic approximation this is combined with the observation that molecular adsorption energies depend strongly on curvature to suggest a strategy for generating ordered overlayers in order to tune the functional properties of graphene.

Based on the results of this work, we can conclude that (pre-)rippled graphene sheets can be used to direct molecular adsorption in order to form specific patterns by tuning the thermodynamic equilibrium of the addition reaction of small (organic) molecules.

Preface

This dissertation presents work carried out between October 2015 and August 2019 in the Computational Materials group at Imperial College London under the supervision of Professor Dr. Nicholas Harrison and Professor Dr. Peter Haynes. Several sections and chapters presented here include work that has been published or is currently being prepared for publication. The relevant chapters and publications are as follows:

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This dissertation is a result of my own work and includes nothing that is the outcome of work done in collaboration except as declared in the Preface and specified in the text. This dissertation is not substantially the same as any that I have submitted, or is being concurrently submitted, for a degree or diploma or other qualification at Imperial College London or any other university or similar institution, except as declared in the Preface and specified in the text. I further state that no substantial part of my dissertation has already been submitted, or is being concurrently submitted for any such degree, diploma or other qualification at Imperial College London or any other university or similar institution, except as declared in the Preface and specified in the text.

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Mariana Hildebrand

London, September 2019

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Chapter I

Background Information

I.1 About Graphene

Graphene consists of a monoatomic layer of carbon atoms, arranged in a planar, two-dimensional, hexagonal "honeycomb" lattice. One method of obtaining graphene is from graphite via exfoliation. [1]. Since 2004 [2], graphene has received a large amount of attention and publicity due to its unique properties; its ultrahigh charge carrier mobility and monoatomic thickness make graphene very interesting for semiconductor technologies such as CMOS or MOSFET devices [1, 3–7]. Other remarkable properties of graphene are its extremely high thermal and electrical conductivity as well as its elasticity and mechanical stiffness [8]. The discovery of graphene and its remarkable properties led to a hunt for other two-dimensional materials. Apart from graphite, other layered materials can potentially be exfoliated [1]. Most common examples include hexagonal-Boron-Nitride sheets, Transition Metal Oxides (such as titania nanosheets) or Transition Metal Dichalcogenides (see Figure I.1).

2-D NANOMATERIALS

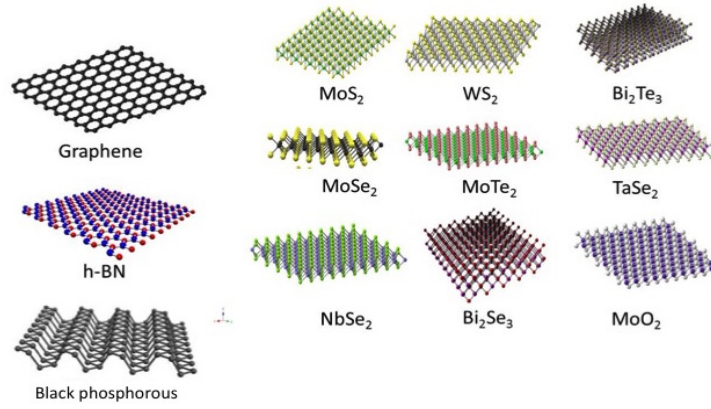


Figure I.1: Different two-dimensional nanomaterials, with kind permission of Toby Sainsbury

Properties of Graphene - the Electronic Structure

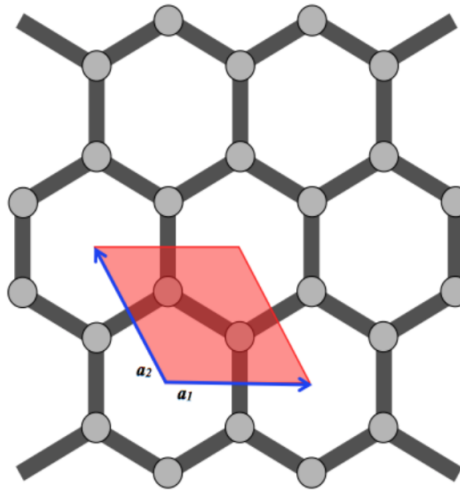


Figure I.2: A hexagonal graphene honeycomb lattice with a unit cell (red shade) defined by the real-space unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, with kind permission of Faris Abualnaja

As previously stated, graphene consists of a hexagonal "honeycomb" lattice as is illustrated above. A graphene unit cell consists of two atoms, arranged at a distance of $1.42 \text{ \AA}$ apart. Each carbon atom is connected to its three nearest neighbours within the graphene lattice via strong covalent bonds; we

commonly refer to these bonds as σ -bonds. These in-plane σ -bonds are formed by electrons from the $2s$, $2p_x$ and $2p_y$ valence orbitals. The neighbouring atom's $2p_z$ orbitals overlap and form the delocalised so-called π valence (half-occupied) and π^* conduction (unoccupied) bands. The π valence band is a half-filled band because each carbon atom contributes one electron.

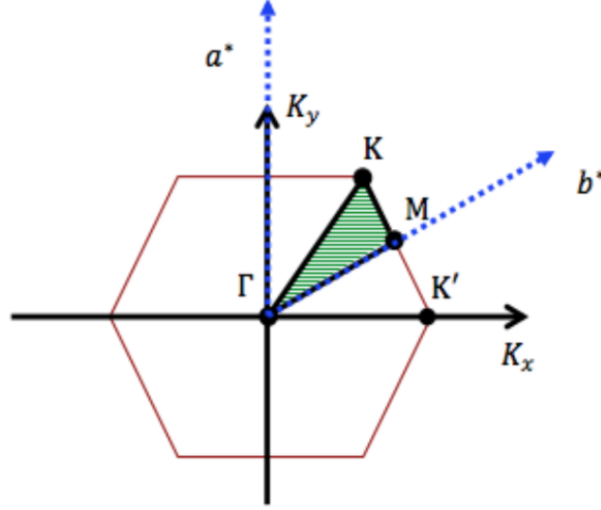


Figure I.3: Schematic description of the 1st Brillouin Zone of graphene; symmetry irreducible area is shown in green, with kind permission of Faris Abualnaja

Figure I.3 shows graphene's 1st Brillouin Zone. The π valence and π^* conduction bands meet in the K (and K') high symmetry point at the Fermi level, forming the so-called Dirac-cone (see Figure I.4). This particular feature gives rise to the famous dispersion-relation [9]

$$E(\mathbf{k}) = \pm \hbar v_F |\mathbf{k} - \mathbf{K}| \quad (\text{I.1})$$

where $\mathbf{k} = (k_x, k_y)$ and the Fermi velocity $v_F = \sqrt{3\gamma_0 a}/2\hbar \approx 10^6 \text{ ms}^{-1}$. There is a linear relationship between energy, $E(\mathbf{k})$ and momentum, $\mathbf{k}$, near the Fermi level where charge carriers (holes or electrons) are massless Dirac Fermions, moving with a group velocity of v_F . The graphene dispersion will be discussed in more detail in the theoretical background section. In the Figure below, we can see that the Density of States (DOS) vanishes at the Fermi level.

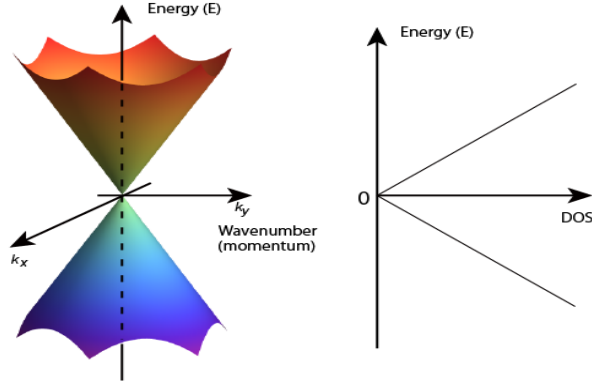


Figure I.4: Schematic description of the Dirac cone [10]

Due to this particular feature, graphene is commonly referred to as a semi-metal. Figure I.5 illustrates graphene's electronic structure in comparison to metals, semiconductors and insulators.

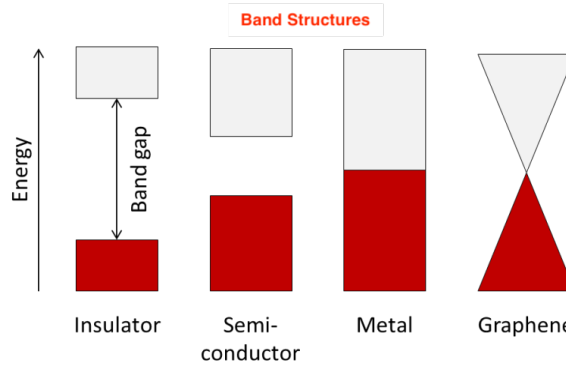


Figure I.5: Schematic description of different electronic structures [11]

Of course, in order to make graphene applicable for semiconductor technologies, it is crucial to open a band gap. Consequently, this issue has been the object of intense research activities over the last decade and many different methods and mechanisms to open a band gap have been suggested.

I.1.1 Band Gap Engineering of Graphene

In order for the remarkable electronic properties of graphene to be fully exploited, a method for opening a band gap in a controlled way must be developed. The physi- and chemisorption of various types of molecules on graphene has been studied extensively, a reason being the possible modification of graphene's

electronic structure to make it applicable for semiconductor technologies as mentioned in the previous section. [1, 3–7, 12–16]. In order to open a band gap, the inversion (or sublattice) symmetry of graphene must be broken, i.e. by implementing different on-site energies on both sublattices [1, 17]. Covalent functionalisation of graphene sheets is expected to result in large changes to the electronic structure as it actively disturbs the sp^2 -backbone thus breaking the sublattice symmetry [18–21]. An alternative approach is to interface graphene with layers of hexagonal Boron-Nitrides [22–24]. For example, Cohen *et al.* demonstrate that the band structure of a combined graphene/h-BNN system is a superposition of the band structures of both systems. Depending on different stacking geometries, different band gaps can be obtained [24].

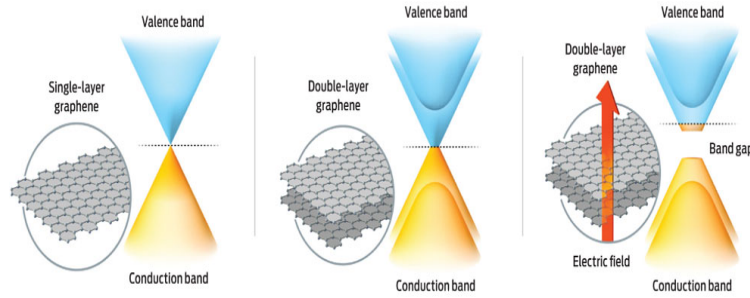


Figure I.6: Schematic description of band gap opening of double layer graphene through application of an electric field [25]

Another possible approach is the application of electric fields in order to open a band gap as is illustrated in Figure I.6 [25, 26]. The application of an electrical field perpendicular to the graphene plane electrostatically varies the on-site energies on both sublattices, thus breaking the inversion symmetry and opening a band gap [17]. The band gap is tuneable with the applied gate voltage [17]. Strain engineering poses another possibility to modify graphene's electronic structure – for example, the adsorption of graphene on a substrate such as silicon carbide (SiC) induces strain on the graphene lattice through the inherent lattice mismatch [27] and ripples may be created, partly changing the sp^2 to sp^3 -hybridisation.

I.1.2 Strain Engineering of Graphene

An important factor to be considered when examining covalent functionalisation of graphene is the adsorbate-induced rippling of the graphene sheet and how specific rippling patterns may influence molecular adsorption. Goler *et al.* [27] examined the adsorption of hydrogen molecules on rippled graphene on a SiC substrate using STM experiments and Density Functional Theory (DFT). They observed that hydrogen molecules preferentially bind to regions with convex curvature. Boukhvalov *et al.* [28] also studied hydrogen adsorption on rippled graphene sheets and conclude that local curvature also influences the chemical activity of the sheet. It has been suggested that highly curved areas are more catalytically active than flat regions due to a higher chemical potential of electrons: this is due to the higher strain energies of distorted graphene sheets, indicating that these areas may be more likely to react with nearby chemical species [27,29,30]. This is also in accordance with studies that have shown that Carbon-Nanotubes (CNT's) are more catalytically active than flat graphene sheets due to their enhanced curvature and that small organic molecules prefer to form covalent bonds at the outer convex areas of the CNT [31,32]. Using DFT, Cho *et al.* showed that convexly curved areas of carbon-based nanostructures are more reactive towards chemisorption than flat areas, suggesting that increased curvature results in increased sp^3 -contributions to binding [33]. The magnitude of curvature and thus the reactivity of CNTs can be controlled by the diameter size [34–36]. Pan *et al.* [37] examined the influence of pre-rippled (curved) graphene sheets with a wavelength of 25 Å on the adsorption of small molecules (H_2 , N_2 , NO and CO) using DFT and found that the binding energy can be significantly decreased with an increasing compression and therefore enhanced curvature of the sheet. They also find that chemisorption of small organic molecules occurs preferentially with convex curvature whereas physisorption is preferred in concave regions. Chen *et al.* [38] used DFT calculations to study ripple wavelengths of 25 Å. They conclude that the introduction of curvature (and the resulting deviation from planarity) leads to a variation

in bond lengths and thus distorted rings in the rippled graphene sheets. This suggests that ripples can be created and used to direct molecular adsorption. A variety of methods for generating sheets with static ripples have been suggested. As already mentioned, adsorption on a SiC (0001) substrate is a common way to generate strain and thus rippled graphene sheets because of the inherent lattice mismatch [27]. Rossi *et al.* compared the DFT calculation results of corrugated graphene on a SiC substrate to STM experiments [39]. It was found that a compressive strain of 5% gives a similar corrugation pattern to that obtained in experiments. Katsnelson *et al.* [40] examined the influence of temperature on rippling, finding that heating of graphene on a SiC substrate can effectively be used to generate periodic ripples with different wavelengths [40]. Experiments and atomistic Monte Carlo simulations done by Katsnelson *et al.* show that ripples in unsupported sheets spontaneously occur at ripple wavelengths of 80 Å [40] due to thermal fluctuations. The deviation from planarity leads to bond length variations of 1.3 to 1.5 Å and thus distorted rings inside the sheet. By contrast, Marder *et al.* [41] find that rippling of graphene is rather a consequence of adsorbed molecules than of thermal fluctuations. Previous work by Meyer *et al.* [42] shows that the broadening of experimentally observed Bragg peaks contradicts the formation of ripples based on thermal fluctuations as thermal vibrations can only reduce the intensity but not broaden diffraction peaks [42–44]. This leads to the conclusion that the formation of static ripples through molecular adsorption as suggested by Marder *et al.* is more likely. Furthermore, Marder *et al.* can prove that the Mermin-Wagner theorem is not relevant on the scale of microns, thus rendering the analysis of Katsnelson *et al.* irrelevant. The Mermin-Wagner theorem states that a true two-dimensional crystal only exists at zero temperature [45,46]. If it remains completely planar, the two-dimensional crystal will undergo rotations at large distances which will result in a breakdown of long-range order. The scale l at room temperature for which this process occurs can be expressed as

$$l \sim a \exp[Ga^2/k_B T]. \quad (\text{I.2})$$

Here, a is the lattice spacing and G is graphene's shear modulus [41]. The bulk shear modulus $\mu \approx G/a$ of graphite is 440 GPa [47], whereas the lattice spacing is greater than $a > 1 \text{ \AA}$, leading to a scale of $l > 10^{30} \text{ m}$ [41]. Marder *et al.* argue that this renders angular rotation irrelevant on the scale of microns.

Another topic to be considered for strain engineering of graphene is the direction and strain dependence of graphene's elasticity. Various studies have shown that the elasticity of graphene varies with direction (see Figure I.7) [48–50]. For example, previous studies demonstrated that armchair graphene nanoribbons (GNRs) have a higher Young's Modulus, tensile fracture stress and strain than zigzag GNRs of the same size [48, 49]. The increased stiffness of the graphene sheet in armchair direction would be expected to result in a lower $\Delta z \uparrow$ (out-of-plane) distortion than that in the zigzag direction under the application of isotropic strain. The nonlinear in-plane elastic properties of graphene have also been studied by Wei *et al.* using DFT [50], where a Taylor expansion of graphene's elastic strain energy density, up to 5th order in the strain, is used to describe the thermodynamically favoured elastic response of graphene. Their results suggest a nonlinear behaviour at 5% strain and a noticeable anisotropy in elastic behaviour at $>5\%$ strain. It is therefore expected that the elastic behaviour of graphene will significantly influence the ripple formation process.

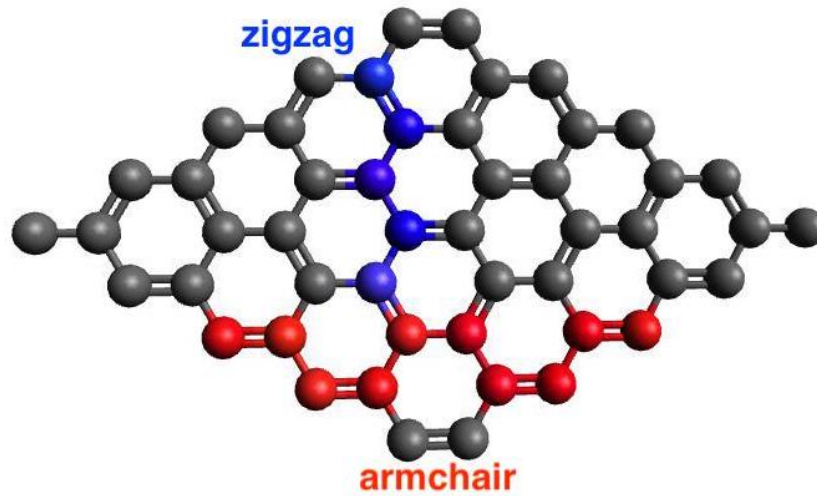


Figure I.7: A graphene sheet indicating both the armchair (red) and zigzag (blue) directions

Summarising we can say that the formation of ripples in strained graphene and how the introduced curvature can be used to direct molecular adsorption is of general interest in a variety of possible systems.

I.1.3 Objectives and Aims

The purpose of the second (and main) chapter of this work is to develop a predictive model of the adsorption energetics on a graphene sheet, and to validate it with respect to DFT calculations, for the bidentate binding of a class of simple organic molecules, the halogenated carbenes [14, 20, 21]. We compare two kinds of halogenated carbenes: Dichlorocarbene (DCI) and Dibromocarbene (DBr).

Halogenated carbenes are of interest for the modification of graphene’s electronic structure because their substituents are easily replaceable, therefore offering the possibility to control the size of the band gap depending on the attached substituent. Furthermore, graphene’s sp^2 -backbone is highly stable and inert; consequently, highly reactive molecules are required in order for chemisorption to take place and covalent bonds to form. As they are a highly reactive species, carbenes therefore offer a very reasonable means of graphene functionalisation. The reactivity of the carbene can be influenced by the attached substituent, i.e through mesomeric effects. One purpose for the model will be to assess the conditions under which self-assembly of patterned overlayers can be achieved by exploiting the tendency of the graphene sheet to form ripples.

Carbenes, as highly reactive intermediates, are also likely to change the electronic properties of graphene upon adsorption. Even though carbenes are highly reactive, the molecular structure of graphene is maintained as has been shown in various experiments and carbenes have proven to be an excellent means of functionalising graphene [14]. Varying the carbene concentration and arrangement may allow for tuneable properties via trends in chemical, geometric and charge transfer mechanisms. The induced changes of properties are readily analysed within the context of DFT calculations. We understand that free-standing

graphene generally is a hypothetical system and that real systems for applications are supported on substrates. However, for the application of theory to identify trends in the behaviour of the graphene sheet a free-standing sheet is often used in the literature [20,21,27,28,37]. Here we wish to study the physics of adsorption to a graphene sheet loosely interacting with a substrate.

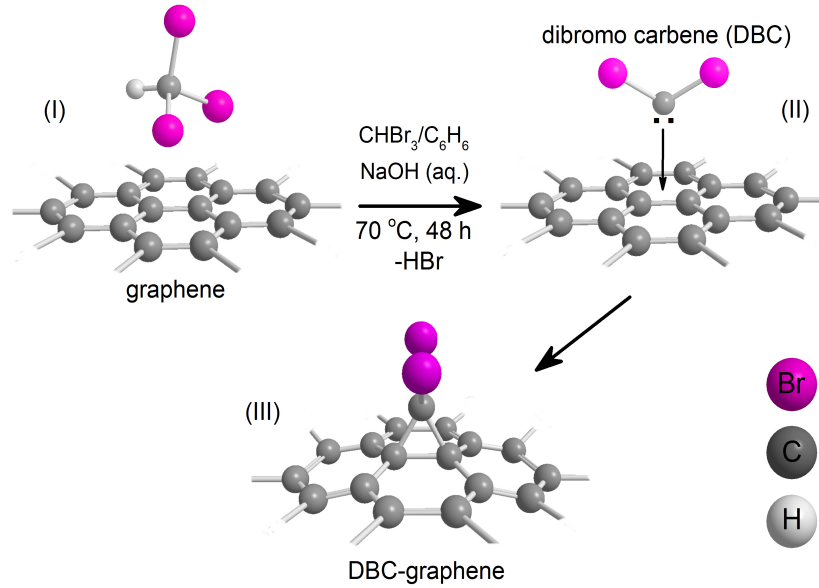


Figure I.8: Scheme for addition of Dibromocarbene (DBr) on graphene; reprinted with permission from Sainsbury, T.; Passarelli, M.; Naftaly, M.; Gnanih, S.; Spencer, S.J.; Pollard, A.J. Covalent Carbene Functionalization of Graphene: Towards Chemical Band-Gap Manipulation, *Appl. Mater. Interfaces*, **2016**, 8, 4870-4877, Copyright 2016 American Chemical Society

Figure I.8 shows the reaction mechanism of Dibromocarbene on graphene - the carbene undergoes a cycloaddition reaction, binding in a bridge position (Figure I.9). The covalent bond formed through the chemisorption process is likely to change the sp^2 to sp^3 -hybridisation and therefore pulls the atoms out of plane, thus inducing a rippling of the sheet.

The third chapter of this work focuses on the structural characteristics and energetics of graphene under isotropic compression established using Density Functional Perturbation Theory (DFPT) calculations. We discuss the structural instabilities induced by strain, report on the energy of formation for various ripples and examine the influence of graphene's elasticity on the ripple formation.

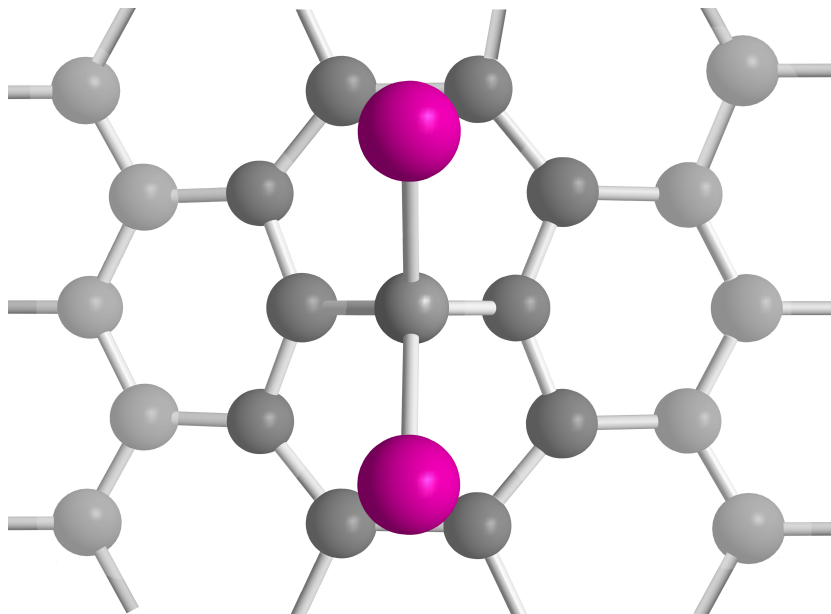


Figure I.9: Scheme for addition of Dibromocarbene (DBr) on graphene; reprinted with permission from Sainsbury, T.; Passarelli, M.; Naftaly, M.; Gnaniah, S.; Spencer, S.J.; Pollard, A.J. Covalent Carbene Functionalization of Graphene: Towards Chemical Band-Gap Manipulation, *Appl. Mater. Interfaces*, **2016**, 8, 4870-4877, Copyright 2016 American Chemical Society

I.2 Theoretical Background

In the following section, Hartree atomic units (a.u.) are used. In the Hartree units, the reduced Planck constant ($\hbar$), the magnitude of the electronic charge ($|e|$), the rest mass of the electron (m_e) and the permittivity of free space multiplied by 4π are set equal to one, so that

$$\hbar = |e| = m_e = 4\pi\epsilon_0 = 1. \quad (\text{I.3})$$

I.2.1 The Many-Body Problem

The Many-Body Schroedinger Equation

In order to understand and obtain the static properties of a collection of atoms, it is necessary to find solutions to the time-independent Schroedinger equation

$$\hat{H}\Psi_n = E\Psi_n. \quad (\text{I.4})$$

Here, $\hat{H}$ is the Hamiltonian operator for a system of M nuclei and N electrons in state n , Ψ_n is the wavefunction and E is the energy. Essentially, solving the Schroedinger equation means finding the eigenvalues and eigenfunctions of the Hamiltonian operator $\hat{H}$. This procedure enables us to at least formally predict the properties of any quantum mechanical system until relativistic effects become important [51]. However, for systems that contain more than two particles, the Schroedinger equation is no longer analytically solvable; therefore it must be solved numerically. Due to the complexity and dimension of solid state or molecular systems, approximations that simplify the problem become necessary. Under neglect of relativistic and magnetic effects, the general Hamiltonian operator $\hat{H}$ of any system of atoms can be defined as

$$\begin{aligned} \hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{e-e} + \hat{V}_{n-n} + \hat{V}_{e-n} = & - \sum_i \frac{1}{2} \nabla_i^2 - \sum_\alpha \frac{1}{2m_\alpha} \nabla_\alpha^2 + \\ & \sum_i \sum_{j \neq i} \frac{1}{2|\mathbf{r}_i - \mathbf{r}_j|} + \sum_\alpha \sum_{\beta \neq \alpha} \frac{Z_\alpha Z_\beta}{2|\mathbf{R}_\alpha - \mathbf{R}_\beta|} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}. \end{aligned} \quad (\text{I.5})$$

Here, the indices i, j run over all electrons whereas the indices α, β run over all nuclei. $\mathbf{r}_i$ and $\mathbf{R}_\alpha$ stand for the position of the i th electron and α th nucleus. m_α and Z_α indicate the mass and the atomic number of the α th nucleus. In the order shown above, the terms represent the following: the electron kinetic energy, the nuclear kinetic energy, the electron-electron Coulomb interaction, the nucleus-nucleus Coulomb interaction and the electron-nucleus Coulomb interaction.

The Born-Oppenheimer Approximation

If we consider the fact that nuclei are significantly heavier than electrons ($m_{\text{nucleus}}/m_{\text{electron}} \simeq 1836$), we can assume that electrons move significantly faster than nuclei and react to any motion of the nuclei instantaneously [52,53].

Therefore, we can neglect the kinetic energy of the nuclei. Furthermore, we can assume that the Coulomb repulsion between the nuclei can be held constant [52,53]. As a consequence, the electrons are always in the instantaneous ground- state of the nuclear configuration; this is the Born-Oppenheimer approximation. We can thus simplify the Hamiltonian operator $\hat{H}$ (see equation I.5) and write the electronic Schroedinger equation as

$$\left[-\sum_i \frac{1}{2} \nabla_i^2 + \sum_i \sum_{j \neq i} \frac{1}{2|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right] \Psi_{n,\text{el}} = E \Psi_{n,\text{el}}. \quad (\text{I.6})$$

The following sections will discuss methods for solving the electronic problem shown in equation I.6.

I.2.2 How to Determine the Electronic Wavefunction

The Variational Principle

If dealing with an N-electron system, the N-body eigenfunctions of the electronic Hamiltonian cannot be found exactly because of the electron-electron interaction term. Consequently, we are obliged to turn to approximate approaches in order to find the electronic ground state. The so-called variational principle states that, given a Hamiltonian $\hat{H}$ and a wavefunction Ψ , the expectation value of the Hamiltonian over this wavefunction gives an upper limit to the ground state energy of the system. This can be expressed as (in bra-ket notation)

$$\langle \Psi | \hat{H} | \Psi \rangle \geq E_0. \quad (\text{I.7})$$

Here, E_0 is the ground state energy. Furthermore, the wavefunction Ψ is assumed to be normalised and does not necessarily have to be an eigenfunction of the Hamiltonian. This means that given a set of trial wavefunctions obtained by a procedure of our choice, the linear combination of those trial wavefunctions that minimises the expectation value of the Hamiltonian provides an estimate of the ground state energy. Additionally, it provides an estimate of the true

ground state wavefunction. This implies that we can obtain a good estimate of the ground state energy E_0 from wavefunctions that do not correspond to and are significantly different from the true ground state wavefunction.

Hartree products, Slater Determinants and the Hartree Fock Method

In order to apply the variational principle, we must use an appropriate set of trial wavefunctions.

One possibility is to approximate the electronic wavefunction $\Psi_{n,\text{el}}$, as a Hartree product. A Hartree product refers to a simple product of single-particle wavefunctions $\chi = \psi_1(\mathbf{r}_1) \dots \psi_N(\mathbf{r}_N)$, that is a product of one-electron functions $\psi_i(\mathbf{r}_i)$ [54,56]. While the Hartree product has the advantage of being a simple approximation, it does not fulfil the Pauli exclusion principle (the indistinguishability of electrons). Furthermore, it does not include the correlation between electrons as introduced by the electron-electron interaction term.

In order to fulfill the Pauli exclusion principle, the Hartree product needs to be antisymmetrised. This can be realised by using a Slater determinant instead of a simple product, leading to the so-called Hartree-Fock method. [54] As it is not directly relevant to this work, further details shall be omitted in this context.

The Linear Combination of Atomic Orbitals (LCAO) or Tight Binding Approach

In the previous sections, we discuss many-electron wavefunctions, constructed as antisymmetrised products of one electron functions. These one electron molecular functions are in turn constructed as superpositions of single-particle atomic wavefunctions: atomic orbitals. This leads to the so-called Linear Combination of Atomic Orbitals (LCAO) or Tight Binding approach.

The Linear Combination of Atomic Orbitals essentially refers to a quantum superposition of atomic orbitals ; x atomic orbitals combine to form x molecular orbitals from $i = 1$ to x. The single particle electronic wavefunction is thus described as a linear expansion of the form

$$\phi_i = C_{1i}\psi_1 + \dots + C_{xi}\psi_x = \sum_{\mathbf{r}} C_{\mathbf{r}i}\psi_{\mathbf{r}}. \quad (\text{I.8})$$

Here, ϕ_i is a molecular orbital which is represented as the sum of x atomic orbitals $\psi_{\mathbf{r}}$; each atomic orbital is multiplied by a corresponding coefficient $C_{\mathbf{r}i}$ and $\mathbf{r}$ (1 to x) indicates which atomic orbital is combined in the term. Consequently, the (molecular) orbitals are expressed as a linear combination of basis functions with the basis functions being single-particle orbitals. The coefficients $C_{\mathbf{r}i}$ and the ground state energy E can then be found by solving the electronic Schrodinger equation (equation I.6), using the variational principle (equation I.7) [54], which is the basis of most computational algorithms used today. Different choices of atomic orbitals are available for computations, the most widely used being Slater-Type (STO) or Gaussian-Type Orbitals (GTO) [54]. The single-particle functions may also be expressed as *plane waves* rather than atomic orbitals. This is discussed in section I.2.6. Furthermore, the electronic structure of graphene can be well-described with a tight-binding approach which is demonstrated in the following section.

I.2.3 The Dispersion Relation of Graphene¹

As previously mentioned, the electronic structure of graphene can be well-described with a tight-binding approach. As we already discussed in the introduction, in Figure I.2 we can see that a graphene unit cell consist of two atoms, each having one p_z orbital, $\phi(\mathbf{r})$. The C-C bond length a_{C-C} within the graphene sheet is 1.42 Å [1]. In this context, we label the positions of the two atoms within the unit cell as $\mathbf{T}_j$ and the unit cell itself as $\mathbf{R}$. First of all, we construct the basis functions as

$$\Phi_{\mathbf{k}j}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \phi(\mathbf{r} - \mathbf{T}_j - \mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}. \quad (\text{I.9})$$

¹This section is based on the lecture notes and course work exercises of Dr. Johannes Lischner for the *Electronic Structure and Materials Course I*, **2015/16**, Imperial College London

We may now express the the Schroedinger equation (equations I.4 and I.6) in terms of the following functions:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_j C_{\mathbf{k}j} \Phi_{\mathbf{k}j}(\mathbf{r}). \quad (\text{I.10})$$

Now we can determine the coefficients $C_{\mathbf{k}j}$ by projecting the Schroedinger equation onto equation I.9 and can thus write it (in bra-ket notation) as

$$\sum_j C_{\mathbf{k}j} \langle \Phi_{\mathbf{k}l} | \hat{H} | \Phi_{\mathbf{k}j} \rangle = \epsilon_{\mathbf{k}} \sum_j C_{\mathbf{k}j} \langle \Phi_{\mathbf{k}l} | \Phi_{\mathbf{k}j} \rangle \quad (\text{I.11})$$

The matrix elements in equation I.11 can be expressed and evaluated as :

$$\begin{aligned} \langle \Phi_{\mathbf{k}l} | \hat{H} | \Phi_{\mathbf{k}j} \rangle &= \sum_{\mathbf{R}} \langle \phi_l(0) | \hat{H} | \phi_j(\mathbf{R}) \rangle e^{i\mathbf{k} \cdot \mathbf{R}} \approx \langle \phi_l(0) | \hat{H} | \phi_j(0) \rangle + \\ &\sum_{\mathbf{R}=\mathbf{d}_{NN}} \langle \phi_l(0) | \hat{H} | \phi_j(\mathbf{R}) \rangle e^{i\mathbf{k} \cdot \mathbf{R}} = \epsilon_j \delta_{jl} + \sum_{\mathbf{R}=\mathbf{d}_{NN}} t_{lj} e^{i\mathbf{k} \cdot \mathbf{R}} \end{aligned} \quad (\text{I.12})$$

where $\mathbf{d}_{NN}$ represents the vector to the unit cell that contains the nearest-neighbour (NN) atoms and

$$\begin{aligned} \langle \Phi_{\mathbf{k}l} | \Phi_{\mathbf{k}j} \rangle &= \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}'} \langle \phi_l(\mathbf{R}') | \phi_j(\mathbf{R}) \rangle e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} = \sum_{\mathbf{R}} \langle \phi_l(0) | \phi_j(0) \rangle e^{i\mathbf{k} \cdot \mathbf{R}} \approx \\ &\sum_{\mathbf{R}} \delta_{\mathbf{R},0} \delta_{lj} e^{i\mathbf{k} \cdot \mathbf{R}} = \delta_{lj}. \end{aligned} \quad (\text{I.13})$$

We may now project onto the two basis functions per unit cell which leads to the following two equations:

$$C_{\mathbf{k}A} \epsilon_p + C_{\mathbf{k}B} \epsilon_p + \sum_{\mathbf{d}_{NN}} t e^{i\mathbf{k} \cdot \mathbf{d}_{NN}} = \epsilon_{\mathbf{k}} C_{\mathbf{k}A} \quad (\text{I.14})$$

and

$$C_{\mathbf{k}B} \epsilon_p + C_{\mathbf{k}A} \epsilon_p + \sum_{\mathbf{d}_{NN}} t e^{i\mathbf{k} \cdot \mathbf{d}_{NN}} = \epsilon_{\mathbf{k}} C_{\mathbf{k}B}. \quad (\text{I.15})$$

Here, the unit cells (corresponding to the graphene sublattices) are denoted by A and B.

By taking equations I.14 and I.15 and assuming that $\epsilon_p = 0$, we can define a matrix equation in order to find the (expansion) coefficients $C_{\mathbf{k}j}$ as

$$t \begin{bmatrix} 0 & f_{\mathbf{k}} \\ f_{\mathbf{k}}^* & 0 \end{bmatrix} \vec{C}_{\mathbf{k}} = \epsilon_{\mathbf{k}} \vec{C}_{\mathbf{k}}. \quad (\text{I.16})$$

Here, the function $f_{\mathbf{k}} = \sum_{\mathbf{d}_{NN}} e^{i\mathbf{k} \cdot \mathbf{d}_{NN}}$. The vectors $\mathbf{d}_{NN}$ can be written as

$$d_1 = 0, \quad (\text{I.17})$$

$$d_2 = a_{C-C} \sqrt{3} \hat{e}_y, \quad (\text{I.18})$$

and

$$d_3 = a_{C-C} \left(-\frac{3}{2} \hat{e}_x + \frac{\sqrt{3}}{2} \hat{e}_y \right). \quad (\text{I.19})$$

Therefore, by absorbing a_{C-C} into $\mathbf{k}$, we obtain the function $f_{\mathbf{k}}$ as

$$f_{\mathbf{k}} = 1 + e^{i\sqrt{3}\mathbf{k}_y} + e^{-i\frac{3}{2}\mathbf{k}_x} e^{i\frac{\sqrt{3}}{2}\mathbf{k}_y}. \quad (\text{I.20})$$

Now, in order to find the energies $\epsilon_{\mathbf{k}}$, it is necessary to find the eigenvalues of the Hamiltonian matrix (see equation I.11), for example as:

$$0 = \det(\hat{H} - \epsilon_{\mathbf{k}}) = \epsilon_{\mathbf{k}}^2 - t^2 |f_{\mathbf{k}}|^2 \quad (\text{I.21})$$

$$\epsilon_{\mathbf{k}} = \pm t |f_{\mathbf{k}}|. \quad (\text{I.22})$$

The K and K' Dirac (high symmetry) points (as mentioned in the introduction) are defined as $\text{K} = (2\pi/(3a_{C-C}); 2\pi/(3\sqrt{3})a_{C-C})$ and $\text{K}' = (2\pi/(3a_{C-C}); -2\pi/(3\sqrt{3})a_{C-C})$ [1, 9]. At the Dirac points, we find that $f_{\mathbf{K}} = f_{\mathbf{K}'} = 0$ thus showing the degeneracy at the two high symmetry points [1, 9, 55]. The resulting electronic

structure is shown in Figure I.10.

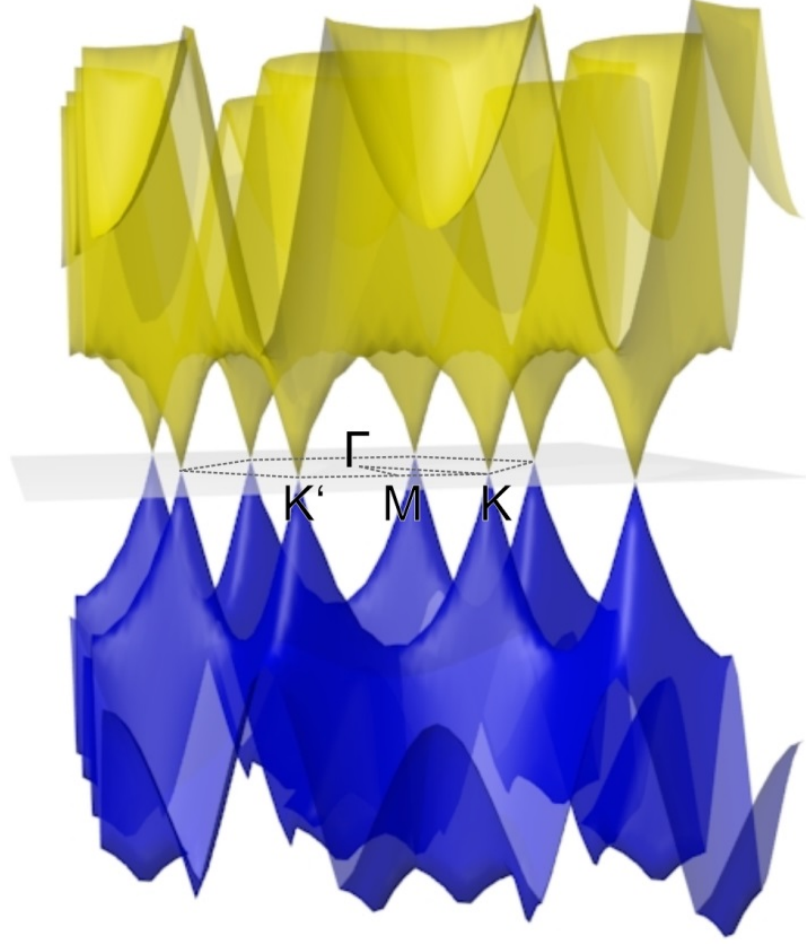


Figure I.10: Illustration of the K and K' high symmetry (Dirac) points resulting from the dispersion relation of graphene [55]

I.2.4 Density Functional Theory (DFT)

As we already established, the Schrodinger equation cannot be solved analytically for a system that contains more than two particles/one electron. Therefore, in order to calculate the properties of larger systems (i.e. solid states or molecules), we require a method that provides an acceptable degree of accuracy. The basic idea of *Density Function Theory* (DFT) is that the energy is considered as a functional of the density of electrons which is defined as

$$n(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}). \quad (\text{I.23})$$

Instead of the wavefunction, we use the density as a variable in this context which drastically reduces the size and complexity of the problem [56]. The concept of DFT was suggested by Kohn, Hohenberg and Sham in 1964, 1965. However, the general idea to use the electron density instead of the wavefunction was already proposed by Thomas Fermi in 1927 [57–59].

The Hohenberg-Kohn Theorems

The concept of DFT is based on the two Hohenberg-Kohn theorems. The Hohenberg-Kohn theorems state the following:

- 1 : the wavefunction, energy and other (ground state) properties are uniquely defined by the electron density, meaning that the total energy is a functional of the density
- 2 : the electron density that minimises the energy of the overall energy functional is the true electron density of the ground state [54]

This allows us to find the ground state density and energy by applying the variational principle; the electron density needs to be varied until the energy of the functional is minimised [54, 56].

The Kohn-Sham Equations

One major challenge in DFT is that the exact form of the functional is not known and therefore, approximate forms must be used. To find a reasonable approximation for the kinetic energy functional is rather difficult. Therefore (in 1965), in order to address this problem, Kohn and Sham invented a reference-system of non-interacting fermions, which has the same ground-state density as the interacting system [54, 56].

We can write the energy functional - as defined by the Hohenberg- Kohn theorems in the previous section - in terms of orbitals which describe the electron density $n(\mathbf{r})$ [54,56]. It then takes the following form:

$$E[\{\psi_i\}^2] = E_{known}[\{\psi_i\}^2] + E_{XC}[\{\psi_i\}^2] \quad (\text{I.24})$$

where the term E_{known} is defined as

$$\begin{aligned} E_{known}[\{\psi_i\}^2] = & -\frac{1}{2} \sum_{i=1}^N \int \psi_i^* \nabla_i^2 \psi_i d^3\mathbf{r} + \sum_i \int V_{e-n}(\mathbf{r}_i) n(\mathbf{r}_i) d^3\mathbf{r} \\ & + \sum_i \sum_{j \neq i} \int \int \frac{n(\mathbf{r}_i) n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d^3\mathbf{r}_i d^3\mathbf{r}_j + E_{ion}. \end{aligned} \quad (\text{I.25})$$

"Here, the terms on the right stand for the kinetic energies of the non-interacting system, the Coulomb interactions between the electrons and the nuclei, the classical contributions to the Coulomb interactions between pairs of electrons and the Coulomb interactions between pairs of nuclei." [60] The E_{XC} term represents the so-called *exchange-correlation functional*. It shall be discussed in detail in the next section. Summarising the above, we can conclude the following: in order to obtain the ground state energy, we need to define the ground state electron density which means we must find the minimum energy solutions of the total energy functional [54]. The Kohn-Sham equations make it possible to find the ground-state electron density by solving a set of equations in which each equation involves a single electron [54], defined as

$$\left[-\frac{1}{2} \nabla^2 + V_{e-n}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})\right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (\text{I.26})$$

Here, V_H stands for the Hartree potential. V_{XC} is defined as a functional derivative of the exchange-correlation energy. The $\psi_i(\mathbf{r})$ are commonly known as the *Kohn-Sham (KS) states*. The ε_i are the KS energy eigenvalues. The

Hartree potential V_H is defined as

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \quad (\text{I.27})$$

"The Hartree product specifies the classical contribution to the Coulomb repulsion between one electron and the total electron density that is expressed by all electrons included in the problem". [60] [54, 56]. It is obvious that the formalism described above leads to a circular problem. In order to solve the Kohn-Sham equations, we require the Hartree potential. On the other hand, the electron density is required in order to define the Hartree potential and other contributions to the energy. This means that a self-consistent procedure is needed in order to circumvent this problem. We can summarise the *Self-Consistent-Field (SCF) algorithm* as follows [54]:

1. Make an initial guess for the electron density $n_{guess}(\mathbf{r})$
2. Use the initial trial electron density $n_{guess}(\mathbf{r})$ in order to solve the KS equations and obtain the KS states $\psi_i(r)$
3. Take the KS wavefunctions and calculate a new electron density $n_{new}(\mathbf{r})$
4. Compare the initial $n_{guess}(\mathbf{r})$ and the new electron density $n_{new}(\mathbf{r})$. If they are the same within a certain tolerance threshold, the SCF procedure is complete. If not, update the trial electron density using $n_{new}(\mathbf{r})$ and repeat the procedure from step 2 until self-consistency is achieved.

Different schemes can be used in order to update the density in the last SCF step. Throughout this work, the Broyden method is used [61]. The Broyden method utilises information from previous steps in the SCF procedure in order to define the $n_{new}(\mathbf{r})$, thus resulting in much faster convergence.

The final energy obtained by the SCF procedure is given in the following form [62]:

$$E = \sum_i \varepsilon_i + E_{XC}[n(\mathbf{r})] - \int d\mathbf{r} V_{XC}(\mathbf{r})n(\mathbf{r}) - \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{2|\mathbf{r} - \mathbf{r}'|} \quad (\text{I.28})$$

Even though the KS eigenvalues ε_i are a mathematical construct, they can have some physical meaning. For example, the highest occupied energy KS state corresponds to the Fermi energy in metals [63,64] (or the first ionisation energy in molecules). Therefore, the KS eigenvalues are commonly used to obtain the electronic band structure of a material [63]. Mostly, this offers a good approximation, however, it does lead to some accuracy issues of the obtained band structures based on the choice of exchange correlation functional as will be discussed in the following section.

I.2.5 The Exchange Correlation Functional

As we saw in the previous section (equations I.24 and I.28), we need to define the so-called *exchange-correlation functional* $E_{XC}[n(\mathbf{r})]$ within the DFT formalism. The exchange-correlation functional contains corrections to all other exact terms, such as exchange-correlation effects. Its exact form is not known, which requires us to treat it approximately. The form we choose in order to treat the exchange-correlation functional is the key approximation and consequently the key limitation of the DFT method. The following three sections shall discuss different possibilities of approximating the exchange-correlation functional.

The Local Density Approximation (LDA)

The first approximation to the exchange-correlation functional was made by Kohn and Sham themselves in their initial paper - it is commonly known as the *Local Density Approximation* (LDA). The LDA assumes a uniform electron gas where the electron density is constant at all points in space and where the functional is numerically known to great precision [56]. It can be described by the following expression:

$$E_{XC}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{XC}[n(\mathbf{r})] \quad (\text{I.29})$$

Here, ϵ_{XC} stands for the exchange-correlation energy per electron in a uniform interacting electron gas with a density $n(\mathbf{r})$ [65]. It is possible to obtain ϵ_{XC} by parametrising highly accurate quantum Monte Carlo simulations [66, 67]. This method also allows for a highly accurate computation of $E_{XC}[n(\mathbf{r})]$. The most common parametrisation for the LDA has been suggested by Perdew and Zunger [68] and shall be used throughout this work for all computations where the LDA is applied.

The Generalised Gradient Approximation (GGA)

As the name implies, the *Generalised Gradient Approximation* (GGA) utilises the gradient in the electron density in addition to the local density and can be expressed as

$$E_{XC}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{XC}[n(\mathbf{r})] F_{XC}[n(\mathbf{r}), \nabla n(\mathbf{r})]. \quad (\text{I.30})$$

Here, ϵ_{XC} follows the same definition as for the LDA. $F_{XC}[n(\mathbf{r}), \nabla n(\mathbf{r})]$ is the so-called enhancement factor. It can exist in different forms thus leading to different GGA functionals [67, 69–71]. Throughout this work, the PBE functional [69] (named after its three creators) shall be used where the GGA is applied.

Beyond LDA and GGA

As mentioned previously, it is common to use the KS eigenvalues in order to calculate the electronic band structure of a system. Even though the shape of these DFT band structures generally gives a good approximation if compared with experimentally measured band structures, when dealing with semiconducting or insulating materials, the band gap is severely underestimated. This

is particularly true for using local- or semi-local functionals such as LDA or GGA [56]. We can explain this short-coming of local and semi-local exchange-correlation functionals with the so-called *Self Interaction Error* (SIE). The SIE arises because an electron interacts with a potential $V(N)$ with N being the number of electrons. In reality, it should be interacting with a potential $V(N-1)$ as to not interact with itself. Due to this self-interaction, the occupied energy levels are shifted upwards, thus leading to an underestimation of the band gap. Hartree-Fock theory on the other hand shows the opposite effect. Here, energy levels are over-corrected and band gaps are overestimated. The Hartree-Fock method includes the exact exchange term but does not treat electron correlation explicitly. Based on this knowledge, Becke *et al.* invented the so-called *Hybrid Functionals* in 1993 [72]. Hybrid functionals include varying amounts of Hartree-Fock exchange in the DFT exchange-correlation functional (e.g. the B3LYP functional contains 20% Hartree-Fock exchange) and give a reasonable prediction of band gaps that agrees well with experimental results. In this work, we are mainly interested in the trend in band gap size, not its exact value. Particularly for plane-wave DFT (which will be discussed in the following sections), the increased accuracy of these more complex functionals comes at a significant computational cost and is not computationally feasible. Therefore, we use LDA and GGA functionals throughout this work (in both chapter II and chapter III).

I.2.6 Plane Wave Density Functional Theory and Pseudopotentials

After establishing the basics of the DFT formalism, we shall now discuss a method for solving the KS equations. All DFT calculations conducted in chapter II and III were done using the QUANTUM ESPRESSO code [73] which is a plane wave pseudopotential DFT code.

Plane Waves

In order to solve the KS equations, we must choose a basis set in which we can express our wavefunctions. As we previously discussed, this can be done in the form of atomic orbitals that are centred on the nuclei of the system within the LCAO approach. However, when studying solid state systems, we are looking at a system of a periodic nature where a unit cell is repeated many times in space. Therefore, for this particular case it is more feasible to describe the system by using the unit cell in question and introducing periodic boundary conditions. This suggests a different choice of basis set - plane waves. The Bloch theorem states that in a system with periodic boundary conditions we may write the KS states in the following form:

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Upsilon}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r}) \quad (\text{I.31})$$

with Υ being the number of unit cells in the simulated system. i enumerates the bands whereas $\mathbf{k}$ is the wave vector. The values of $\mathbf{k}$ are constrained by the chosen boundary conditions. The first term of the equation composes the so-called plane wave, which means we can define a plane wave as $\varepsilon_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Upsilon}} e^{i\mathbf{k}\cdot\mathbf{r}}$. $u_{i\mathbf{k}}(\mathbf{r})$ stands for a function that has the same periodicity as the crystalline system.

$u_{i\mathbf{k}}(\mathbf{r})$ is defined as

$$u_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_n C_{in}(\mathbf{k}) e^{i\mathbf{G}_n\cdot\mathbf{r}} \quad (\text{I.32})$$

Here, Ω is the volume of the unit cell, $\mathbf{G}_n$ are reciprocal lattice vectors of the periodic crystal, and the C_{in} are expansion coefficients. We can now apply the KS Hamiltonian operator to the wavefunction in equation I.31, substitute in equation I.32 and solve the resulting matrix system in order to obtain the KS eigenvalues ε_i as well as the expansion coefficients C_{in} . This then leads us directly to the KS states ψ_i . Because the resulting KS states ψ_i have the same periodicity as the reciprocal lattice by definition, we can restrict the wave

vectors $\mathbf{k}$ to the *first Brillouin Zone* (BZ) of the reciprocal lattice. A plane wave $\varepsilon_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ can be associated with a momentum $\mathbf{k} + \mathbf{G}$ and thus with a kinetic energy $E = \frac{|\mathbf{k}+\mathbf{G}|^2}{2}$. Consequently, it must have an associated length scale of the form $\lambda \propto \frac{1}{\sqrt{E}}$. This means that we need to include plane waves of an increasingly high energy in order to accurately describe variations in our wavefunction, and thus the density which as a consequence significantly increases the cost of our simulations. However, we can also conclude that if we simply require our calculations to be accurate within a certain tolerance threshold, it is only necessary to include plane waves up to a certain energy cut-off value (E_{cut}). Therefore, we can simply systematically improve a plane wave basis-set by increasing E_{cut} until the properties of interest remain constant within the tolerance threshold. Finding the converged E_{cut} value is part of the benchmarking process ; results must be converged with respect to the energy cut-off and the k-point sampling of the first BZ. This shall be discussed in the computational details section.

Pseudopotentials

In all methods described so far, all electrons of the system are considered, including the core electrons. In practice, the number of plane waves required to describe a system (including all its electrons) beyond the size of small atoms would exceed practical limits. Therefore, pseudopotentials have been invented. Since the largest contribution to bonding (and other properties of the system) comes from the valence electrons, we can assume the core electrons to be mostly inactive. This is commonly referred to as the *frozen core-approximation* [74,75]. Furthermore, the wavefunctions of the valence electrons oscillate rapidly within the core region, leading to a very high kinetic energy which almost entirely cancels out the potential energy arising from the electron-nucleus interaction in the same region [76]. Therefore, based on the two statements above, we can replace the potential arising from the nuclei V_{ext} with an effective pseudopotential in order to describe the core regions and only treat the valence electrons explicitly in our calculations. This significantly reduces the required

cut-off energy and thus makes the calculations less computationally expensive. In this work, two types of pseudopotentials shall be used: norm-conserving and ultrasoft pseudopotentials [77].

I.2.7 Phonons - The Calculation of Vibrational Properties

Phonons refer to a quantised collective oscillation of atoms at a single frequency [79,80]. As discussed in the previous sections, DFT provides the means to accurately solve the electronic Hamiltonian. However, in order to obtain vibrational properties, we must solve the nuclear (or vibrational) Schroedinger equation

$$\left[-\sum_{p\alpha} \frac{1}{2m_{p\alpha}} \nabla_{p\alpha}^2 + E_{elec}(\{\mathbf{R}\}) \right] \chi(\{\mathbf{R}\}) = \hat{H}_{vib} \chi(\{\mathbf{R}\}) = E_{vib} \chi(\{\mathbf{R}\}). \quad (\text{I.33})$$

The eigenvalue E_{elec} for a given configuration of nuclei is obtained by solving the electronic Schroedinger equation (equation I.6). It defines the potential energy surface on which the nuclei move [81]. χ are expansion coefficients that depend on the nuclear positions. Equation I.33 allows for the use of supercells, thus allowing for a scenario in which atoms in adjacent unit cells move differently; this corresponds to vibrations with non-zero wave numbers. Therefore, α runs over all nuclei within a unit cell, p runs over all unit cells in the supercell, and $\{\mathbf{R}\}$ defines the set of nuclear positions.

The most common approach to simplify the nuclear (or vibrational) Hamiltonian ($\hat{H}_{vib}$) is the *Harmonic Approximation*. Considering that nuclei are relatively heavy, we can assume that they will not move far away from their respective equilibrium positions. Therefore, we can expand E_{elec} as a Taylor series around the equilibrium positions as

$$E_{elec}(\{\mathbf{R}\}) = E_{elec}(\{\mathbf{R}^0\}) + \frac{1}{2} \sum_{p\alpha i; p'\alpha'j} \left. \frac{\partial^2 E_{elec}(\{\mathbf{R}\})}{\partial \mathbf{X}_{p\alpha i} \partial \mathbf{X}_{p'\alpha'j}} \right|_{\{\mathbf{R}^0\}} \mathbf{X}_{p\alpha i} \mathbf{X}_{p'\alpha'j} + \mathcal{O}(\mathbf{X}^3). \quad (\text{I.34})$$

Here, $\mathbf{X}_{p\alpha} = \mathbf{R}_{p\alpha} - \mathbf{R}_{p\alpha}^0$ with $\mathbf{R}_{p\alpha}$ and $\mathbf{R}_{p\alpha}^0$ as the current and equilibrium positions of the α th nucleus in the p th unit cell. Assuming that the $\mathbf{X}_{p\alpha}$ are small enough to neglect the $\mathcal{O}(\mathbf{X}^3)$ terms, equation I.34 produces a quadratic potential [81, 82]. Therefore, neglecting the constant term in the Taylor expansion, the harmonic vibrational potential is expressed as

$$V_{har}(\{\mathbf{R}\}) = \frac{1}{2} \sum_{p\alpha i; p'\alpha' j} \left. \frac{\partial^2 E_{elec}(\{\mathbf{R}\})}{\partial \mathbf{X}_{p\alpha i} \partial \mathbf{X}_{p'\alpha' j}} \right|_{\{\mathbf{R}^0\}} \mathbf{X}_{p\alpha i} \mathbf{X}_{p'\alpha' j} \quad (\text{I.35})$$

All cubic $\mathcal{O}(\mathbf{X}^3)$ and above terms are considered to be *anharmonic*.

At a temperature of 0 K, the harmonic approximation offers a sufficiently accurate description of the vibrational modes in a lattice [83]. However, at higher temperatures the harmonic approximation may fail and an anharmonic approximation may be required.

Normal Modes in a Crystal

In order to obtain the properties of phonons using the *harmonic approximation*, it is required to have information about the force constants acting on the system [88]. We can obtain this information by applying the Hellmann-Feynman theorem. Here, the forces acting on each atom are described as

$$\mathbf{F}_i = -\frac{\partial E}{\partial u_i(\mathbf{R})} \quad (\text{I.36})$$

with $\mathbf{R}$ being the atomic position, $u(\mathbf{R})$ being the atomic displacement and i representing the i th atom [8, 80, 89]. Then, we can obtain the so-called Hessian Matrix of *Interatomic Force Constants* (IFCs) by taking the derivative of the forces with respect to the atomic positions of all atoms within a supercell. The Hessian matrix of IFC's can be written as

$$C_{ij}(\mathbf{R} - \mathbf{R}') = \frac{\partial^2 E}{\partial u_i(\mathbf{R}) \partial u_j(\mathbf{R}')} = -\frac{\partial \mathbf{F}_i}{\partial u_j(\mathbf{R}')} \quad (\text{I.37})$$

Here, $u_i(\mathbf{R})$ [$u_j(\mathbf{R}')$] is the displacement of atom i [j]. "Simply stated, equation I.37 describes the change in force that happens on atom i when there is a

change in the displacement u_j of atom j [8].

Using a plane wave as an ansatz to the harmonic (vibrational) Schroedinger equation, we can express the atomic displacements as

$$u(\mathbf{R}, t) = \epsilon \cdot e^{i(\mathbf{q} \cdot \mathbf{R}) - \omega(\mathbf{q}t)}. \quad (\text{I.38})$$

Here, ϵ is a vector that describes the direction and magnitude of the atoms' movement. It is commonly known as the *polarisation vector* of the normal mode [80] and is the eigenvector of the following 3-dimensional eigenvalue problem

$$M\omega(\mathbf{q})^2 \epsilon = D(\mathbf{q})\epsilon. \quad (\text{I.39})$$

with D referring to the *Dynamical Matrix*. The *Dynamical Matrix* is the mass-reduced Fourier transform of the matrix of IFCs (equation I.37). It is expressed as

$$D_{i\alpha;j\alpha'}(\mathbf{q}) = \frac{1}{N_{\mathbf{p}} \sqrt{m_{\alpha} m'_{\alpha'}}} \sum_{pp'} C_{p\alpha i; p' \alpha' j} e^{i\mathbf{q}(\mathbf{R}_p - \mathbf{R}_{p'})}. \quad (\text{I.40})$$

Here, $N_{\mathbf{p}}$ is the number of unit cells. Equation I.39 shows that the frequencies $\omega(\mathbf{q})^2$ are the eigenvalues of the Dynamical Matrix [80] in addition to being dependent on the wave vector $\mathbf{q}$. The dependence of the frequency ω on the wave vector $\mathbf{q}$ is commonly known as the *Phonon Dispersion Relation* [80]. The eigenvalue problem in equation I.39 can be solved by standard numerical methods. In ab initio lattice dynamics, it is central to determine the elements of the Hessian matrix of IFC's (equation I.37). This can be done using two different methods: the finite placement theory and its relations [84,85] or *Density Functional Perturbation Theory* (DFPT) [86]. In chapters II and III of this work, the DFPT formalism shall be applied.

Phonon Branches

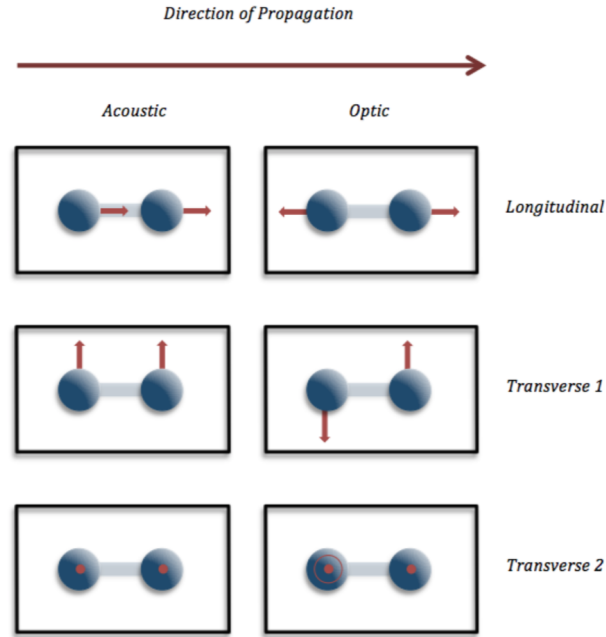


Figure I.11: The direction of wave propagation is shown by the dark red arrow (top). All possible modes in a system that has 2 atoms per unit cell are shown. For acoustic modes (left), both atoms are in phase and can move in either a longitudinal (in plane/compressional) or transverse (out of plane/perpendicular) motion. For optic modes (right), both atoms are out of phase and can move in either a longitudinal or transverse motion, with kind permission of Faris Abualnaja [8]

Phonon dispersion curves of crystals that have at least two atoms per unit cell show two types of branches - the *acoustic* and the *optic* branch [80,87]. In the acoustic branch, the atoms in the same unit cell of the Bravais lattice move in phase with each other (see Figure I.11, left) [80,87]. The optic branch describes a motion in which the atoms in the same unit cell of the Bravais lattice are out of phase by 180° ; the out-of phase movement makes these modes higher-frequency modes (see Figure I.11, right) [87]. For a system with $N \geq 2$ atoms in the primitive cell, there are 3 acoustic modes (LA, TA, ZA) and $3N - 3$ optical modes (LO, TO, ZO) [80,87]. For each of these classes there is one in plane longitudinal mode (LA, LO) and two transverse modes, one in plane and the other in the out of plane z-direction (TA, TO and ZA, ZO respectively, see Figure I.11) [80,87].

I.2.8 Computational Details for this Project

All DFT and DFPT calculations presented in chapters II and III have been performed using the QUANTUM ESPRESSO program [73].

Computational Details for Chapter II²

The effects of electronic exchange and correlation are described using the Perdew-Burke-Ernzerhof (PBE) density functional [69], previously shown to reproduce the binding of carbene-based molecules to graphene and the resulting changes in graphene's electronic structure [20]. Core electrons are represented using Vanderbilt's ultrasoft pseudopotentials [77]. Due to a technical feature of the code it is convenient to compute the phonon modes in the LDA approximation using a Perdew-Zunger (PZ) functional [91] and norm-conserving pseudopotentials [77]. The 1st Brillouin zone is sampled in reciprocal space with the Monkhorst-Pack method [92]. An energy cutoff of 16 Ryd and a k-point mesh of $3 \times 3 \times 1$ k-points is found to produce accurate results for the ultrasoft pseudopotential that is used with the PBE functional. For the norm-conserving pseudopotential that is used with the PZ functional, an energy cutoff of 50 Ryd is recommended. Band structure calculations have been performed on a grid of 132 k-points along the Γ -K-M- Γ path. Initially, a hexagonal unit cell with two atoms in a honeycomb structure has been constructed from the experimental graphene lattice parameter (that is deduced from XRD) of 2.46 Å [93] where the sp^2 -orbitals arrange themselves in a plane at 120 ° angles. Marzari-Vanderbilt cold smearing [95] with a spread value of 0.008 Ryd has been applied. The "Davidson" diagonalisation method with a mixing factor of 0.2 has been chosen for self consistency [96] to solve the Kohn-Sham equations during SCF iteration. The systems have been fully relaxed until the total energy changes less than 10^{-4} Ryd and the force changes less than 10^{-3} Ryd/bohr between two consecutive self consistent steps.

²the following text is reprinted and adapted with permission from M. Hildebrand, F. Abualnaja, Z. Makwana, N.M. Harrison, **Strain Engineering of Adsorbate Self-Assembly on Graphene for Band Gap Tuning**, *The Journal of Physical Chemistry C*, 123, **2019**, 4475-4482, DOI: 10.1021/acs.jpcc.8b09894. Copyright 2019 American Chemical Society

The two-dimensional sheet is modelled as a three-dimensional periodic system with a vacuum space of 10 Å in the z-direction (that is perpendicular to the sheet). This prevents interactions between periodic images and allows sufficient space for the molecules to be adsorbed [94]. The optimised lattice parameter is 2.46 Å which is in accord with that observed in X-ray diffraction (XRD) (2.46 Å, [93]).

Computational Details for Chapter III³

The Quantum Espresso (QE) program [73] has been used for the Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT) calculations of the phonon frequencies reported here. A DFPT approach is favoured when calculating the phonon frequencies as it is less computationally expensive than alternative methods based on finite placements [86]. Exchange-Correlation effects are described within the local density approximation (LDA) using the Perdew-Zunger (PZ) functional [91]. The crystalline orbitals are expanded in a plane-wave basis set and the core electrons are replaced by a norm conserving pseudopotential [73, 77]. A norm-conserving pseudopotential with an LDA functional is preferred when computing phonon calculations because it reduces the probability for producing an error when applying the Acoustic Sum Rule (ASR). In addition, when using a norm-conserving pseudopotential, the phonon acoustic modes can be computed to a numerical precision of 0 cm⁻¹ at the gamma (Γ) point in the QE program. The self consistent field was converged to a strict energy tolerance of 10⁻¹² Ry for the phonon calculations. Moreover, the Brillouin zone (BZ) of the two – dimensional graphene lattice is sampled on a Monkhorst – Pack (MP) grid [92] of 3N x 3N in order to guarantee the correct sampling of the Dirac points, and to ensure an appropriate subdivision of the reciprocal lattice. It was found that an MP grid of 12 x 12 is sufficient for sampling the primitive cell, while an MP grid of 3 x 3 is sufficient for the

³the following text is reprinted and adapted with permission from F. Abualnaja, M. Hildebrand, N.M. Harrison, **Ripples in Isotropically Compressed Graphene**, 173, *Computational Materials Science*, 109422, 2020, DOI: <https://doi.org/10.1016/j.commatsci.2019.109422>

supercells considered in this work. These calculations are then translated into real space using a Fourier transform approach, while applying the ASR [73,86]. The Phonon Dispersion Curves (PDCs) are computed along the Γ -K-M- Γ high symmetry path using a mesh of 147 q-points. The initial geometry was a graphene sheet of lattice constant 2.46 Å [93] in a 3D periodic cell within which 2D periodic sheets are separated by a vacuum region of 10 Å which is sufficient to remove any interaction between periodic images [94]. A Marzari-Vanderbilt cold smearing method [95] with a spread value of 8×10^{-3} Ry is applied. For self-consistency, the Davidson diagonalization procedure [96] with a mixing factor of 0.2 was used and self-consistency was considered to be achieved when the total energy per atom is less than 10^{-4} Ry. Geometry relaxation was terminated when the largest inter-atomic force per atom was less than 10^{-3} Ry/Bohr between two consecutive iterations. Here, the sum over all inter-atomic forces is 0 ensuring a static structure. The optimised lattice constant is 2.46 Å, in excellent agreement with that observed in XRD [93].

Additional Information

Additional information on the benchmarking process for the computational details can be found in Appendix B.1.

Chapter II

Strain Engineering of Adsorbate Self-Assembly on Graphene for Band Gap Tuning¹

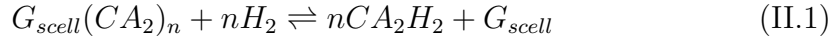
Abstract

In this chapter, a predictive physical model of the self-assembly of halogenated carbene layers on graphene is suggested. Self-assembly of the adsorbed layer is found to be governed by a combination of the curvature of the graphene sheet, local distortions, as introduced by molecular adsorption, and short-range intermolecular repulsion. The thermodynamics of bidental covalent molecular adsorption and the resultant electronic structure are computed using Density Functional Theory. It is predicted that a direct band gap is opened that is tuneable by varying coverages and is dependent on the ripple amplitude. This provides a mechanism for the controlled engineering of graphene's electronic structure and thus its use in semiconductor technologies.

¹the text in this chapter is reprinted and adapted with permission from M. Hildebrand, F. Abualnaja, Z. Makwana, N.M. Harrison, **Strain Engineering of Adsorbate Self-Assembly on Graphene for Band Gap Tuning**, *The Journal of Physical Chemistry C*, 123, **2019**, 4475-4482, DOI: 10.1021/acs.jpcc.8b09894. Copyright 2019 American Chemical Society

II.1 Methodology

Carbenes are highly reactive species and are therefore typically generated in situ by the dissolution of the Chloro-/Bromoform in the presence of the phase-transfer catalyst trihexylamine [14,97]. For the purpose of computing the relative energetics of adsorption however we choose an isolated hydrogen molecule as a well defined reference in the knowledge that this can be adapted to the local chemical potential of hydrogen in any specific experimental conditions. The formal reaction considered is therefore,



where A=Cl, Br, G denotes the graphene sheet, and the subscript *scell* refers to a particular periodic supercell of the graphene primitive unit cell.

The molecular coverage is therefore depicted as;

$$\Theta = n/A_{\text{scell}} \quad (\text{II.2})$$

where A_{scell} = number of maximum adsorption sites per supercell in armchair or zigzag direction, respectively.

The adsorption energy of n carbene molecules to a periodic supercell is,

$$E_{\text{ads}}^{\text{scell}} = (E_{\text{scell}} + n \times E_{\text{H}_2}) - (n \times E_{\text{mol}} + E_{\text{gra}}^{\text{scell}}) \quad (\text{II.3})$$

where $E_{\text{ads}}^{\text{scell}}$: is the energy per supercell of the graphene with n carbene molecules adsorbed, E_{H_2} , E_{mol} and $E_{\text{gra}}^{\text{scell}}$ are the energies of a hydrogen molecule, a carbene molecule and the pristine graphene sheet per supercell, respectively.

The binding energy per molecule is then,

$$E_{\text{bind}} = \frac{E_{\text{ads}}^{\text{scell}}}{n} \quad (\text{II.4})$$

With this reference, binding is always endothermic (the reference energy is discussed further in section II.4).

II.2 Results and Discussion

The choice of a particular periodic supercell for modelling adsorption constrains the ripple wavelengths to those that are commensurate with the cell. Facile ripple wavelengths can be identified within the harmonic approximation by computing the phonon modes of the graphene sheet.

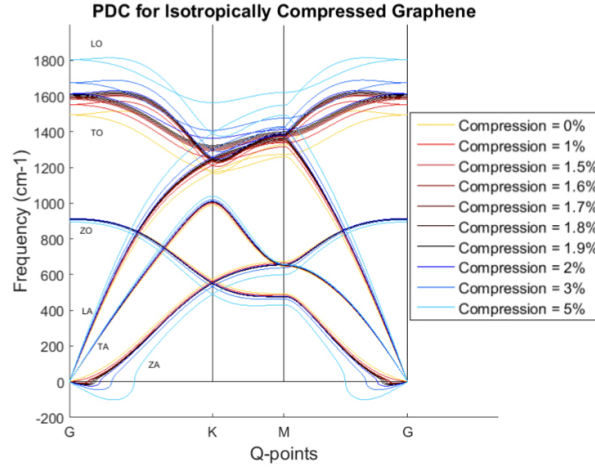


Figure II.1: Phonon Dispersion Curve (PDC) of a graphene unit cell under 0-5% compression

The computed phonon dispersion curves of graphene under 0 to 5% compressive stress are displayed in Figure II.1. For 0% strain, the sheet is harmonically stable. At 1.5% strain, a facile mode at $\frac{1}{5} \frac{\pi}{a}$ is observed where a is defined as the lattice constant. The soft phonon modes along the G-K and G-M directions occur around $|k| = \frac{1}{5} \frac{\pi}{a}$ suggesting the facile formation of a ripple with a wavelength of $\lambda = 10a$ in either zigzag or armchair directions in the lattice. With increasing strain the wavelength of the minimum frequency phonon, and thus that of the most stable ripple, decreases.

In what follows adsorption is therefore modelled in a 5x5 supercell of the primitive cell. Computed geometries for two adsorption patterns of seven and four molecules in a fixed 5x5 supercell (wavelength of 25 Å) and for a single

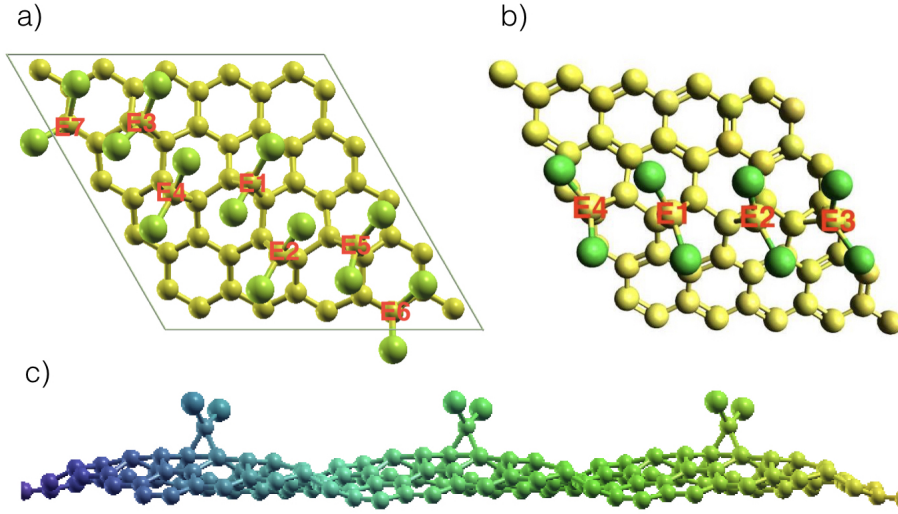


Figure II.2: (a) 7 DCl molecules on 5x5 graphene supercell after optimisation (armchair direction, $\Theta = 28\%$), (b) 4 DCl molecules on 5x5 graphene supercell (zigzag direction, $\Theta = 18.1\%$), (c) Rippled structure corresponding to adsorption site E_1 in armchair direction (compare Figures II.5a and b)

molecule in the same cell are displayed in Figure II.2. Figure II.2 shows that the Dichlorocarbene adsorption introduces curvature and consequently a rippling of the graphene sheet. Therefore, it is expected that molecular adsorption introduces a chemical strain to the graphene sheet. In order to rationalise the chemical strain introduced by the carbene molecules, the lattice parameters have been optimised for the patterns at maximum coverage of $\Theta = 28\%$ in armchair and $\Theta = 18.1\%$ in zigzag orientation (Figures II.3VIII/IX and II.4V/VI). We find that the lattice parameters decrease under carbene adsorption and that a chemical strain of 3% is introduced.

In order to analyse contributions to the binding energy it is useful to define the *distortion energy* [98] of the sheet as the energy difference per periodic supercell between the graphene sheet in the geometry it adopts in the adsorbed system (the *distorted sheet*, $E_{\text{slab|sys}}^{\text{txt}}$, where *txt* indicates the supersell size) and that of the clean planar sheet ($E_{\text{slab}}^{\text{txt}}$), that is;

$$E(\text{dist}) = \frac{(E_{\text{slab|sys}}^{\text{txt}} - E_{\text{slab}}^{\text{txt}})}{n} \quad (\text{II.5})$$

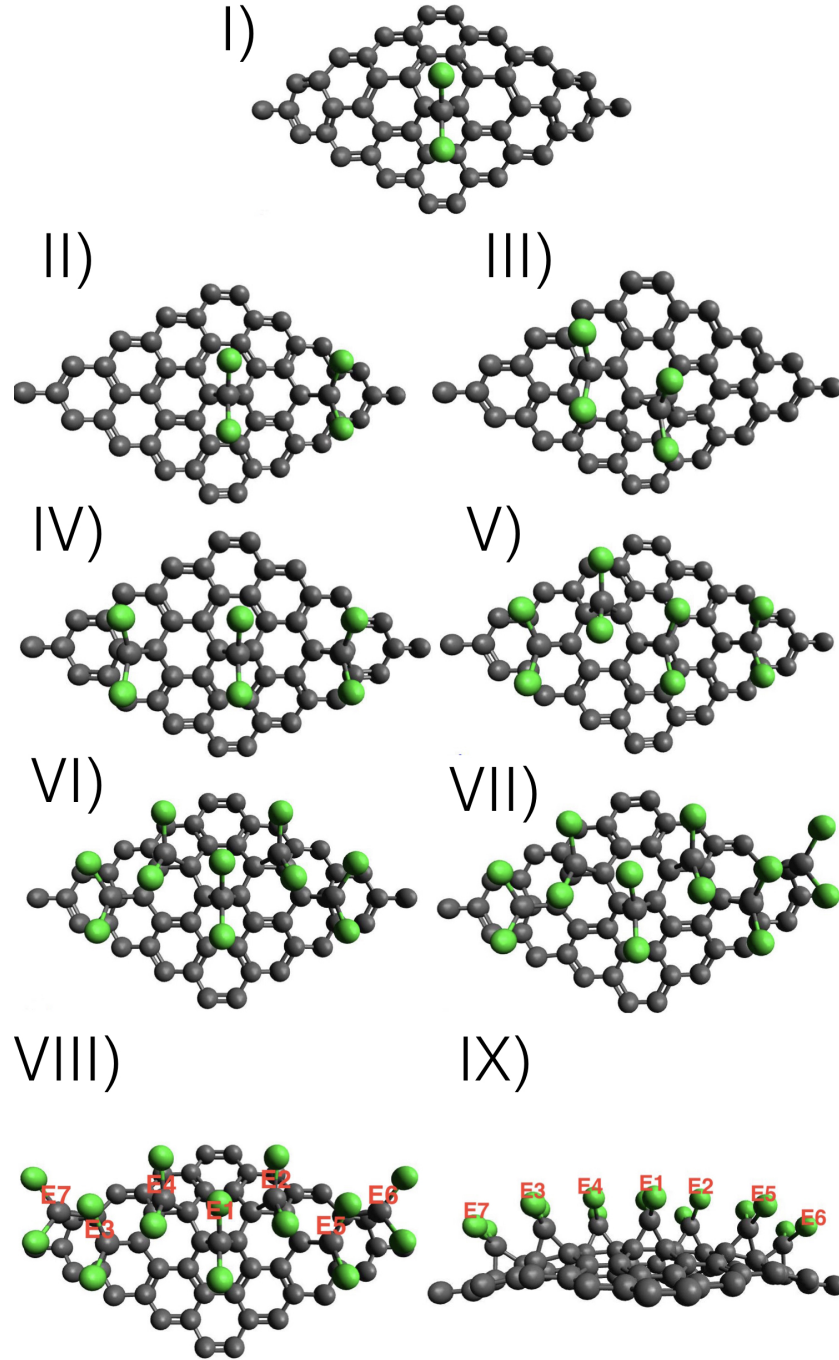


Figure II.3: I) 1 DCl molecule adsorbed ($\Theta = 4\%$) II) 2 DCl molecules adsorbed in armchair direction ($\Theta = 8\%$), III) 2 DCl molecules adsorbed in armchair direction (nearest-neighbours, $\Theta = 8\%$), IV) 3 DCl molecules adsorbed in armchair direction ($\Theta = 12\%$), V) 4 DCl molecules adsorbed in armchair direction ($\Theta = 16\%$), VI) 5 DCl molecules adsorbed in armchair direction ($\Theta = 20\%$), VII) 6 DCl molecules adsorbed in armchair direction, ($\Theta = 24\%$), VIII) 7 DCl molecules adsorbed in armchair direction, ($\Theta = 28\%$), IX) 7 DCl molecules adsorbed in armchair direction, sideview, ($\Theta = 28\%$)

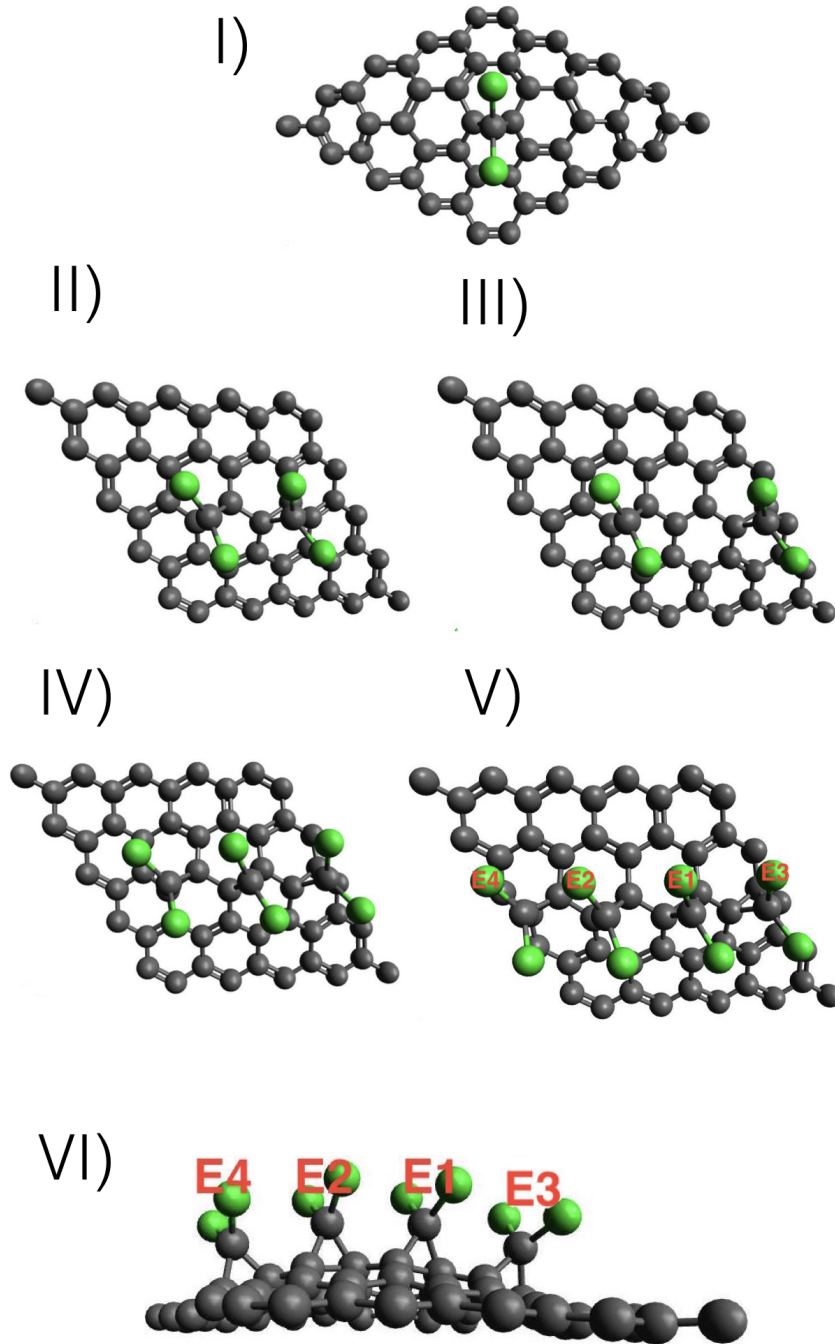


Figure II.4: I) 1 DCI molecule adsorbed ($\Theta = 4.5\%$) II) 2 DCI molecules adsorbed in zigzag direction (nearest-neighbours, $\Theta = 9\%$), III) 2 DCI molecules adsorbed in zigzag direction ($\Theta = 9\%$), IV) 3 DCI molecules adsorbed in zigzag direction ($\Theta = 13.6\%$), V) 4 DCI molecules adsorbed in zigzag direction ($\Theta = 18.1\%$), VI) 4 DCI molecules adsorbed in zigzag direction, sideview, ($\Theta = 18.1\%$)

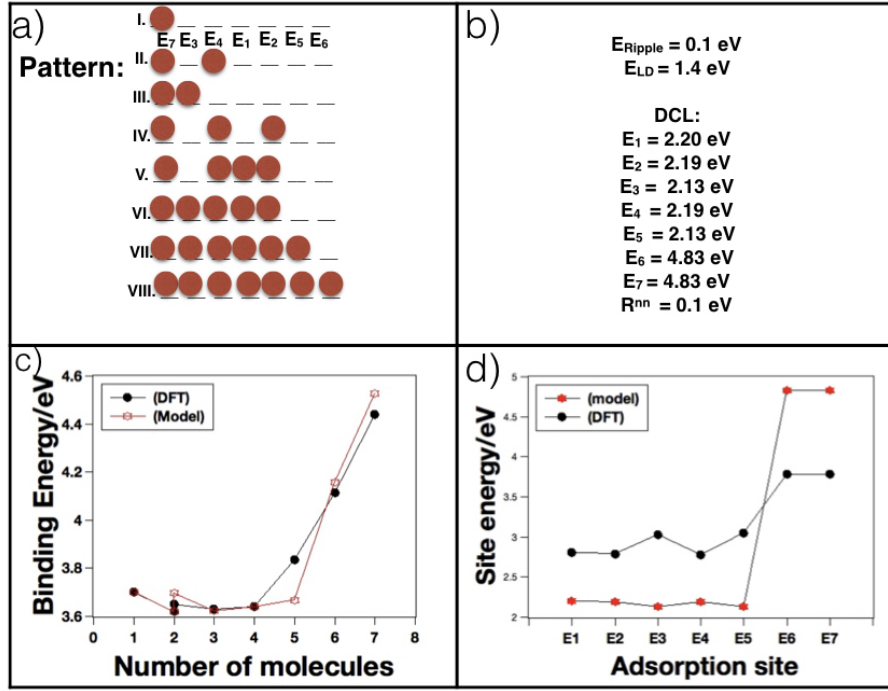


Figure II.5: a) Pattern of molecules for adsorption in armchair direction (compare Figure II.3), b) Site energies and nearest- neighbour interaction term as obtained with equation II.6, c) Model and DFT binding energies vs coverage (DCl), d) Model and DFT site energies in dependence of the adsorption site (DCl)

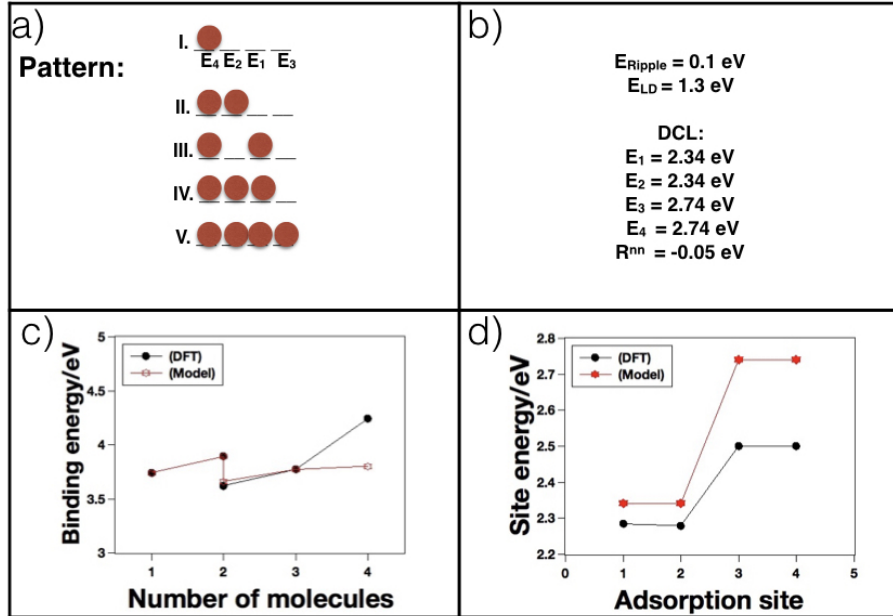


Figure II.6: a) Pattern of molecules for adsorption in zigzag direction (compare Figure II.4), b) Site energies and nearest- neighbour interaction term as obtained with equation II.6, c) Model and DFT binding energies vs coverage (DCl), d) Model and DFT site energies in dependence of the adsorption site (DCl)

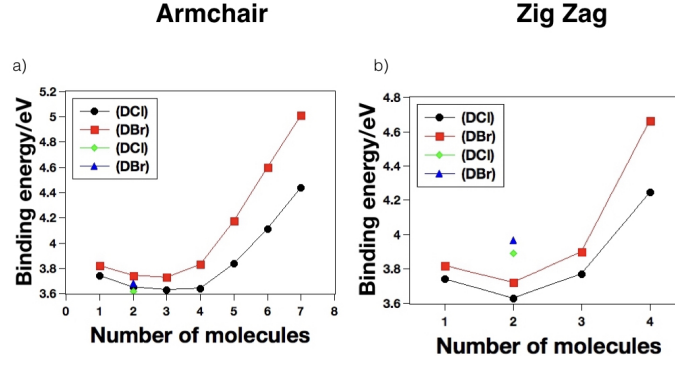


Figure II.7: (a) Binding energy as a function of coverage (armchair direction) (b) Binding energy as a function of coverage (zigzag direction) ; two molecules adsorbed show two data points as the adsorption energy has been computed for two different patterns at this coverage (compare Figures II.3II and III and II.4II and III; the green and blue dots refer to two molecules adsorbed next to each other as shown in Figures II.3III and II.4II)

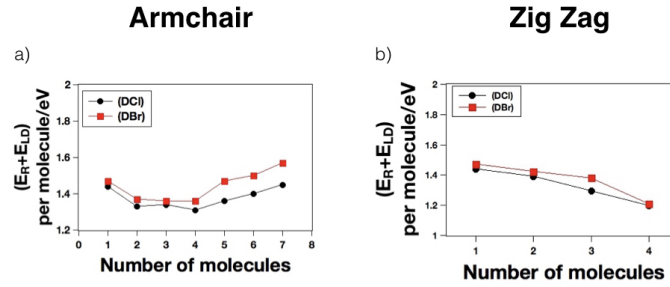


Figure II.8: (a) ($E_R + E_{LD}$) per molecule as a function of coverage (armchair direction) (b) ($E_R + E_{LD}$) per molecule as a function of coverage (zigzag direction)

where n is the number of adsorbed molecules. The adsorption and distortion energies were computed for the symmetry irreducible adsorption patterns depicted in Figures II.3, II.4, II.5a and II.6a. We distinguish between local coordination of the molecules along the armchair and zigzag directions in the sheet (see Figure II.2). In this cell there are 25 (22) potential adsorption sites in the armchair (zigzag) orientations. The zigzag orientation shows fewer potential adsorption sites than the armchair orientation in this particular cell for steric reasons (compare Figure II.2a and b).

For a single molecule the minimum energy geometry corresponds to a binding energy of ~ 3.7 eV (Figure II.7). Examining this geometry in Figure II.2 it is

clear that the sheet has spontaneously formed a ripple for which the distortion energy (equation II.5) is ~ 1.44 eV. Considering the distortion energy to be made up of an energy to form the ripple E_R and a local distortion to accommodate adsorption, E_{LD} , we suggest a simple model of the adsorption energy, E_{ads} ,

$$E_{ads} = E_R + \sum_i E_{LD}^i + \sum_i E_i + \sum_i R^{nn} \quad (\text{II.6})$$

where each adsorption site is characterised by a local distortion energy (E_{LD}^i) that represents the distortion of the sheet local to the adsorption site and a site energy, ($E_i^{ac/zz}$) that may differ for armchair (ac) and zigzag (zz) orientations. The final term, R^{nn} , accounts for a direct nearest-neighbour inter-molecular interaction. The computed binding energy and the sum of ripple energy and local distortion energy ($E_R + E_{LD}^i$) per molecule for all configurations are displayed in Figures II.7 and II.8. Considering adsorption in the armchair orientation the data in Figure II.8a suggests two facts that enormously simplify the application of this model. Firstly, the ripple forms at a cost of $\sim 0.1(\pm 0.1)$ eV per supercell with the adsorption of a single molecule and this is largely unchanged by subsequent adsorption. Secondly, that the local distortion at each site costs $\sim 1.4(\pm 0.1)$ eV and is largely independent of the site (the data in Figure II.8a shows that the values for $(E_R + E_{LD}^i)$ converge to a value of ~ 1.4 eV). These two facts lead to an initial distortion energy of ~ 1.44 eV for single molecular adsorption and a consistent increment of $\sim 1.4(\pm 0.1)$ eV for each additional molecule adsorbed (Figure II.8a) so that $E_{LD}^i = E_{LD} \approx 1.4$ eV. There is a similar behaviour for adsorption in the zigzag orientation (Figure II.8b).

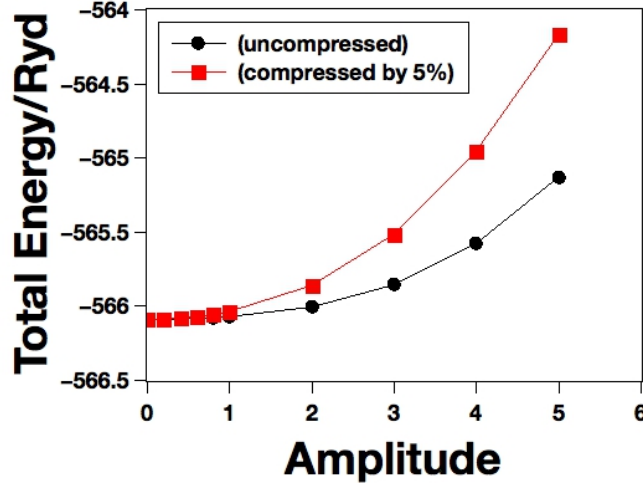


Figure II.9: Energy profile of the phonon mode (at $\sim 136.39 \text{ cm}^{-1}$) which has largest overlap with molecule-induced ripples

In order to better understand the nature of the induced ripple, the molecule-induced ripples have been projected onto the phonon eigenvectors. A large overlap (~ 0.7) is found for a rather soft ripple mode of $\sim 136.39 \text{ cm}^{-1}$. The computed energy profile for the distortion along this mode for 0 and 5% compression is displayed in Figure II.9. The harmonic distortion energy for forming this ripple with an amplitude of 0.7 in the uncompressed sheet is 0.1 eV per supercell which is close to the computed distortion energy. This suggests a further simplification; that the ripple distortion energy for a variety of wavelengths is reliably predicted within the harmonic approximation. These simplifications suggest that it is the site energies - which depend on local curvature of the graphene sheet, local distortions, as introduced by molecular adsorption, and short-range intermolecular repulsion - that determine the overall energy for any particular pattern of adsorption. The terms E_i and R^{nn} are then obtained by solving a set of linear equations: using the DFT adsorption energies for each adsorption pattern and by inserting E_{LD} and E_R into equation II.6. An additional simplification can be made by considering symmetry-relations of the adsorption sites. Figure II.3 (VIII and IX) shows that $E_2 = E_4$, $E_3 = E_5$ and $E_6 = E_7$ considering their positions on the ripple. (Similarly, for adsorption in zigzag direction, $E_1 = E_2$ and $E_3 = E_4$ (Figure II.4V and VI).)

Fitting these terms in equation II.6, to the computed energies for each of the adsorption patterns considered (see Figures II.3 and II.4) leads to the values presented (Figures II.5 and II.6). The predictions of the model for any symmetry-inequivalent adsorption pattern are then compared to the DFT results (in Figure II.5c and d, Figure II.6c and d). The simplified model produces an excellent representation of the computed adsorption energetics. Two different tests have been done in order to verify the accuracy of the model. Firstly, the obtained parameters have been re-inserted into equation 6 and are expected to give an identical answer to the DFT adsorption energies initially used to solve equation 6 as a set of linear equations. Therefore, considering the simplifications made by taking symmetry-relations between adsorption sites into account, the model excellently reproduces the DFT energies as a function of the number of adsorbed molecules (see Figures II.5c and II.6c). Secondly, the energies of the adsorption sites have been computed independently using DFT. This has been done by locally relaxing the immediate environment of the adsorption site and by relaxing the molecule on the adsorption site. The close agreement in Figures II.5d and II.6d suggests that the separation of the terms in the model provides an accurate representation of the computed adsorption energies. We note that in the armchair orientation, the energies of 8 symmetry-distinct DFT energies fit to a model with 5 parameters (5 symmetry-distinct DFT energies fit to a model with 3 parameters in the zigzag orientation). An analysis of Dibromocarbene adsorption produces a model of similar accuracy (more detailed information in section II.4).

Referring to Figure II.5, in the armchair orientation, the site energies do not vary significantly for adsorption sites E_1 to E_5 whereas adsorption sites E_6 and E_7 are significantly higher in energy (~ 2.6 eV/ ~ 59.9 kJ/mol, Figure II.5b). In the zigzag orientation E_1 and E_2 are slightly lower in energy than E_3 and E_4 (~ 0.4 eV/ 9.2 kJ/mol, Figure II.6b). This indicates that the bidentate carbene molecules bind more readily to convex areas of the rippled sheet (Figures II.5b, II.3VIII and IX, Figures II.4 and II.6) while concave areas are not preferred for covalent binding (chemisorption). A change from sp^2 to sp^3 -hybridisation

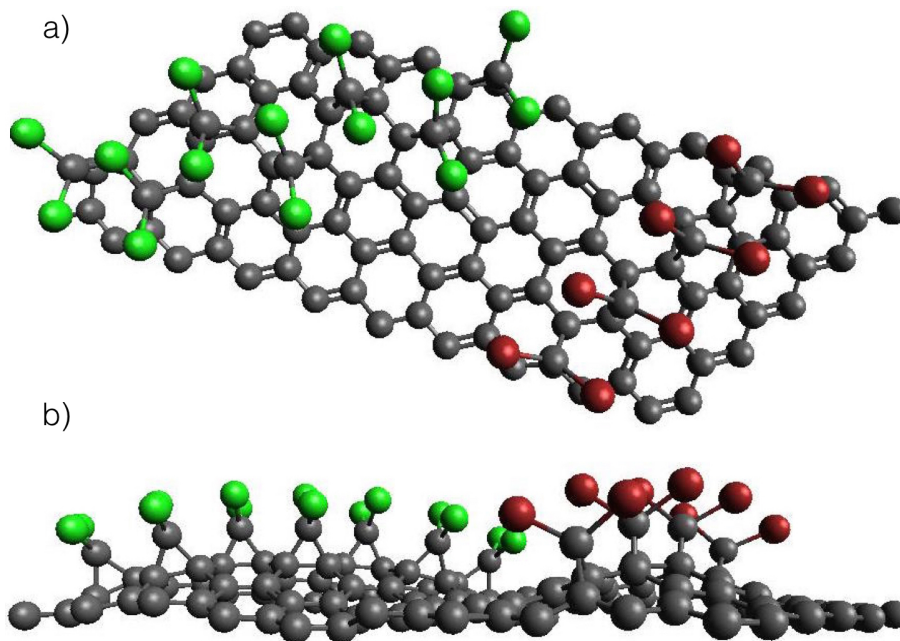


Figure II.10: a) Eggbox structure top view - green halogens denote armchair orientation, red halogens denote zigzag orientation, b) Eggbox structure side-view

through covalent bonding can also be confirmed by a change in C-C bond length from ~ 1.42 Å to ~ 1.54 Å within the graphene sheet through bidentate binding (more detailed information in section II.4). Adsorption sites E_6 and E_7 in armchair direction are significantly higher in energy than adsorption sites E_3 and E_4 in zigzag direction (see Figures II.5b and II.6b) - this anisotropy arises because adsorption sites E_3 and E_4 in zigzag direction sit in a more convex region of the sheet (compare Figures II.3 and II.4).

In recent theoretical studies on the chemi- and physisorption of hydrogen, it has been demonstrated that physisorption induces concave curvature [27, 37]. This is due to repulsive interactions between the approaching hydrogen molecule and the p-electron system of the sp^2 -hybridised graphene sheet, leaving the sp^2 -bonds intact but introducing curvature. Chemisorption on the other hand induces convex curvature by changing sp^2 to sp^3 -hybridisation through covalent bonding.

This observation and the model site energies for Dichlorocarbene are consistent with the general notion that the convex curvature increases the sp^3 -nature of

the C-C bonds, favouring covalent interactions (chemisorption).

The intermolecular interaction R^{nn} is negligibly small for the adsorption of Dichlorocarbene (Figures II.5b and II.6b). However, Dibromocarbene shows a slightly higher intermolecular repulsion as expected given that the ionic radius of bromine (1.96 Å [99]) is significantly larger than the ionic radius of chlorine (1.81 Å [99]) (see section II.4, Figure II.13b).

The small energy difference between the armchair (E_1 to E_5) and zigzag (E_1 and E_2) adsorption sites (~ 0.1 eV/9.6 kJ/mol, Figures II.5b and II.6b) strongly suggests that in most chemical environments both orientations coexist, so two-dimensional periodic "egg box" structures are favourable (Figure II.10). Furthermore, the binding energies (Figure II.7a and b) and model parameters (Figures II.5 and II.6) indicate that if the chemical potential of the reactants is tuned to an equilibrium so that $G_{scell}(CA_2)_n + nH_2 = nCA_2H_2 + G_{scell}$ (equation II.1), the system will equilibrate to a coverage of $\Theta = 8\%$ ($\Theta = 9\%$ zigzag orientation), corresponding to pattern II in Figure II.3 (pattern II in Figure II.4 for zigzag orientation) where the molecules preferably sit in convex areas of the sheet. The chemical potential and therefore the coverage and adsorption pattern are in principle tuneable by changing the reactant concentrations (i.e. by controlling the rate of carbene generation). Another consequence of the model is that (pre-)rippled graphene sheets may be used to direct molecular adsorption in order to form arrays of well-ordered adsorbates.

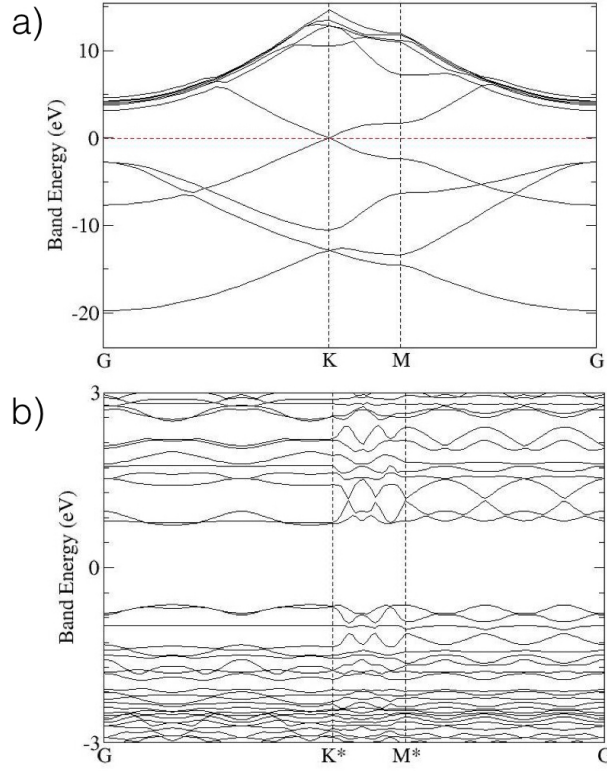


Figure II.11: a) Band structure of graphene unit cell b) Supercell band structure corresponding to $\Theta = 28\%$ for DCl in armchair orientation as shown in Figure II.3VIII; gap opening of ~ 1.5 eV ; Fermi level at 0 eV

Halogenated carbene adsorption leads to a significant change in the electronic structure of the graphene sheet. A direct band gap opens (see Figure II.11). The perturbation of the sublattice symmetry as well as the disturbance of the sp^2 - backbone through covalent molecular adsorption (chemisorption), result in a band gap opening. Previous research within our group has shown that defects may be used to open a band gap in graphene [100,101]. The predicted band gap varies significantly with coverage with the largest band gap opening at $\Theta = 28\%$ for armchair orientation ($\Theta = 13.6\%$ zigzag orientation, Figure II.12a and b). In general, the band gap is sensitive to the attached halogen but only at $\Theta = 24$ and 28% for armchair orientation, a significant difference between Dichloro- and Dibromocarbene adsorption can be observed with Dichlorocarbene opening a larger band gap (Figure II.12a). For adsorption in the armchair direction, a band gap can only be formed for coverages of 16% and higher (see Figure II.12a). This indicates that the thermodynamic equilibrium (equation II.1) must

be tuned in favour of higher coverages in order to obtain a significant band gap opening. The computed band gap is a strong function of ripple amplitude, growing as the amplitude increases (see Figure II.12c and d).

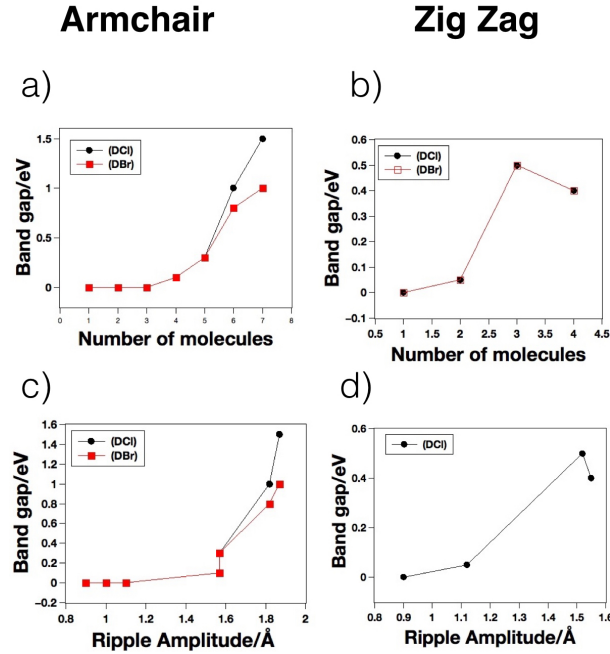


Figure II.12: a) Band gap vs coverage (armchair direction), b) Band gap vs coverage (zigzag direction), c) Band gap vs Ripple amplitude (armchair direction), d) Band gap vs Ripple amplitude (zigzag direction)

II.3 Summary and Conclusion

In summary, a generic physical model has been presented for the self-assembly of bidentally binding molecules on graphene surfaces dependent on the curvature of the graphene sheet, local distortions, as introduced by molecular adsorption and intermolecular nearest-neighbour repulsions. We predict that only a small perturbation is required to generate specific rippling patterns and that this species of molecules preferentially binds in convex areas of the rippled sheet due to the covalent nature of the binding (chemisorption). Physisorption based on van der Waals interactions rather occurs in concave areas of the rippled sheet. For 0% strain, the sheet is harmonically stable ; spontaneous rippling occurs at 1.5% strain. Molecular adsorption also introduces spontaneous rip-

pling which subsequently directs the adsorption pattern. We can conclude that rippled graphene sheets can be used to direct molecular adsorption in order to form specific patterns by tuning the thermodynamic equilibrium of the addition reaction. A direct band gap can be opened which offers the possibility of effective band gap engineering by controlling molecular patterns. The band gap shows a strong dependency on ripple amplitude and a larger band gap is formed with increasing ripple amplitude in case of chemisorption.

II.4 Additional Information

The Model for Dibromocarbene

The figures below show the model for Dibromocarbene in armchair and zigzag orientations, respectively.

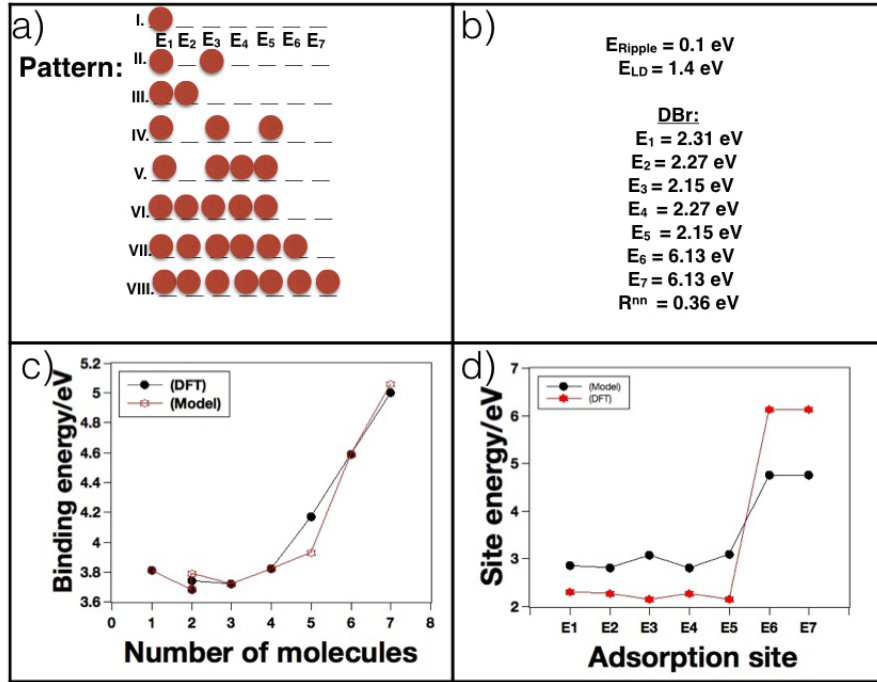


Figure II.13: a) Pattern of molecules for adsorption in armchair direction (compare Figure II.3), b) Site energies and nearest-neighbour interaction term as obtained with equation 6 (main text), c) Model and DFT binding energies vs coverage (DBr), d) Model and DFT site energies in dependence of the adsorption site (DBr)

It is obvious that the model for the adsorption of Dibromocarbene shows the same trend and accuracy as for the adsorption of Dichlorocarbene (compare Figures II.5 and II.6). As already mentioned, Dibromocarbene shows a slightly higher intermolecular repulsion which is expected given that the ionic radius of bromine (1.96 Å [99]) is significantly larger than the ionic radius of chlorine (1.81 Å [99]).

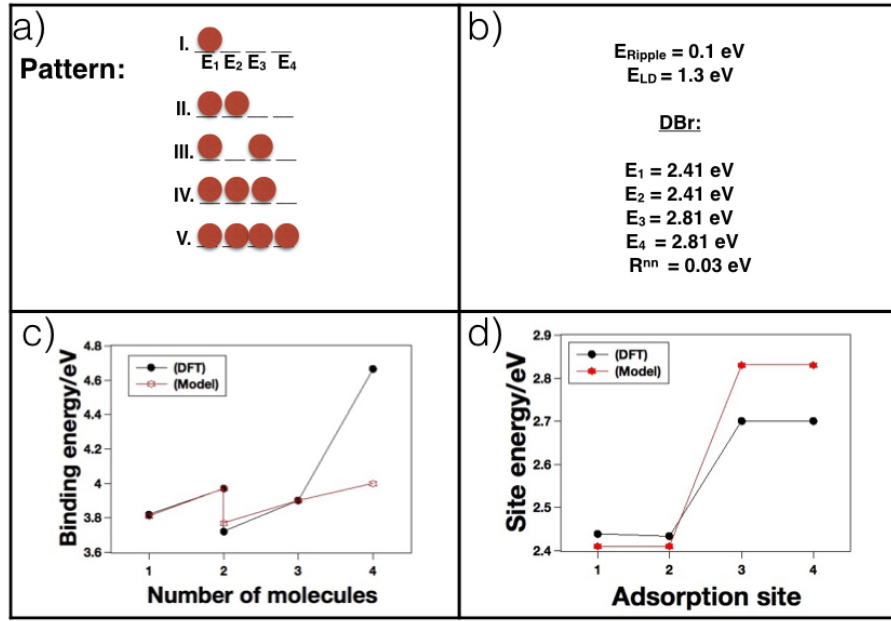


Figure II.14: a) Pattern of molecules for adsorption in zigzag direction (compare Figure II.4), b) Site energies and nearest-neighbour interaction term as obtained with equation 6 (main text), c) Model and DFT binding energies vs coverage (DBr), d) Model and DFT site energies in dependence of the adsorption site (DBr)

Structural Parameters²

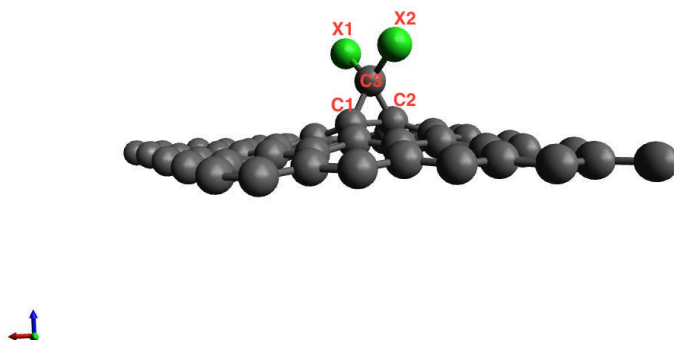


Figure II.15: 1 DCl molecule adsorbed on 5x5 graphene supercell after optimisation

As already mentioned, Dichloro- and Dibromocarbene have been adsorbed with increasing coverage. Because the carbenes undergo a cycloaddition reaction [5], they have been studied in bridge position (see Figure II.15). The covalent bonding disturbs the sp^2 -backbone and leads to sp^3 -hybridisation, therefore the sheet begins to ripple. In Table II.1 the bond lengths and angles after adsorption are shown. C1 and C2 refer to the carbon atoms of the sheet upon which the molecules are adsorbed (see Figure II.15), C3 refers to the carbon atom of the molecule (see Figure II.15) and X1 and X2 refer to the molecule's halogens (see Figure II.15).

²DCl = Dichlorocarbene, DBr = Dibromocarbene

Table II.1: Bond lengths and bond angles after adsorption

	C1-C2/Å	C1/C2-C3/Å ¹	C3-X1/X2/Å ¹	C3-X1-X2 angle ¹	C1-C2-C3 angle ¹
Dichlorocarbene					
armchair					
E ₁ ² /armchair	1.55	1.57	1.76	113°	58°
E ₂ /armchair	1.55	1.57	1.76	111°	58°
E ₃ /armchair	1.55	1.57	1.76	108°	58°
E ₄ /armchair	1.55	1.57	1.76	111°	58°
E ₅ /armchair	1.55	1.57	1.76	108°	58°
E ₆ /armchair	1.52	1.62	1.77	103°	58°
E ₇ /armchair	1.52	1.62	1.77	103°	58°
zigzag					
E ₁ /zigzag	1.55	1.58	1.77	111°	59°
E ₂ /zigzag	1.55	1.58	1.77	111°	59°
E ₃ /zigzag	1.54	1.56	1.75	112°	58°
E ₄ /zigzag	1.54	1.56	1.75	112°	58°
Dibromocarbene					
armchair					
E ₁ /armchair	1.55	1.58	1.92	109°	59°
E ₂ /armchair	1.56	1.58	1.99	109°	59°
E ₃ /armchair	1.55	1.59	1.90	106°	59°
E ₄ /armchair	1.56	1.58	1.99	109°	59°
E ₅ /armchair	1.56	1.58	1.99	109°	59°
E ₆ /armchair	1.52	1.59	1.95	99°	56°
E ₇ /armchair	1.52	1.59	1.95	99°	56°
zigzag					
E ₁ /zigzag	1.55	1.58	1.93	109°	58°
E ₂ /zigzag	1.55	1.58	1.93	109°	58°
E ₃ /zigzag	1.54	1.55	1.90	112°	58°
E ₄ /zigzag	1.54	1.55	1.90	112°	58°

¹ C1, C2, C3, X1 and X2 as defined in Figure II.15² adsorption sites E as defined in Figure II.2a and b

Experimentally, a C-C double bond length of 1.42 Å and a C-C single bond length of 1.54 Å can be found [1]. The C1/C2-C3 bond lengths for DCl adsorbed on a 5x5 graphene supercell vary around 1.5 Å and the C3-X1/X2 bond lengths vary around 1.7 Å (DCl) (1.9 Å for DBr) (see Table II.1). The C3-X1-X2 bond angles vary between 103° and 112° (DCl) (99° and 112° for DBr). The C1-C2-C3 bond angles vary around 60° for all systems (see Table II.1). Because the two atoms upon which the molecules are adsorbed are pulled out of plane (see Figures II.2 and II.15), the hexagonal rings inside the sheet show varying bond lengths of 1.3 to 1.5 Å. This differs from the expected C-C bond length of 1.42 Å in a planar pristine graphene sheet. These results indicate that the covalent molecular adsorption is distorting the sheet by changing sp²- to sp³-hybridisation.

Adsorption Energetics

Carbene radicals are a highly reactive species which is why we have chosen to represent the adsorption and binding energies with a physically sensible reference in the main text as presented in the previous section.

In the previous section we say that the adsorption energy of n molecules to a

periodic supercell is,

$$E_{\text{ads}}^{\text{scell}} = (E_{\text{scell}} + n \times E_{\text{H}_2}) - (n \times E_{\text{mol}} + E_{\text{gra}}^{\text{scell}}) \quad (\text{II.7})$$

where $E_{\text{ads}}^{\text{scell}}$ is the energy per supercell of the graphene with n carbenes adsorbed, E_{H_2} , E_{mol} and $E_{\text{gra}}^{\text{scell}}$ are the energies of a hydrogen molecule, a carbene molecule and the pristine graphene sheet per supercell, respectively.

The binding energy per molecule is then,

$$E_{\text{bind}} = \frac{E_{\text{ads}}^{\text{scell}}}{n} \quad (\text{II.8})$$

With this reference, binding is always endothermic (positive, compare Figure II.7).

To make clear that carbenes are indeed a highly reactive species, in Table II.2 we show the adsorption and binding energies with respect to the carbene radical as

$$E_{\text{ads}} = E_{\text{adsorbate/sheet}} - (E_{\text{adsorbate}} + E_{\text{sheet}}) \quad (\text{II.9})$$

with $E_{\text{adsorbate/sheet}}$ as the energy of the combined graphene/molecule system, $E_{\text{adsorbate}}$ as the energy of the free carbene radical and E_{sheet} as the energy of the clean graphene sheet [14]. The negative (exothermic) adsorption energies show that the addition of a carbene radical is a highly favourable reaction.

Table II.2: Adsorption and Binding Energies with respect to carbene radicals

	Adsorption energy/eV	Binding energy/eV
1 DCl	-0.25	-0.25
1 DBr	-0.17	-0.17
armchair		
2 DCl	-0.67	-0.33
2 DCl (nn) ¹	-0.61	-0.30
3 DCl	-0.97	-0.32
4 DCl	-1.26	-0.31
5 DCl	-0.60	-0.12
6 DCl	0.93	0.15
7 DCl	3.36	0.48
2 DBr	-0.63	-0.31
2 DBr (nn) ¹	-0.51	-0.25
3 DBr	-0.81	-0.27
4 DBr	-0.68	-0.17
5 DBr	0.86	0.17
6 DBr	3.59	0.59
7 DBr	7.07	1.01
zigzag		
2 DCl	-0.12	-0.06
2 DCl (nn)	-0.61	-0.30
3 DCl	-0.55	-0.18
4 DCl	1.15	0.28
2 DBr	-0.05	-0.02
2 DBr (nn)	-0.55	-0.27
3 DBr	-0.29	-0.09
4 DBr	2.65	0.66

¹ nn refers to the two molecules being adsorbed as nearest-neighbours (see Figures II.3 and II.4)

Figure II.16 shows the binding energy as a function of coverage in armchair orientation when calculated as referenced in equation II.9. We can see that in comparison to Figure II.7 in the previous section, the binding energy follows the same trend but shows exothermic behaviour. Adsorption for higher coverages becomes endothermic ($\Theta = 24\%$ and 28% for DCl and $\Theta = 20\%$, 24% and 28% for DBr).

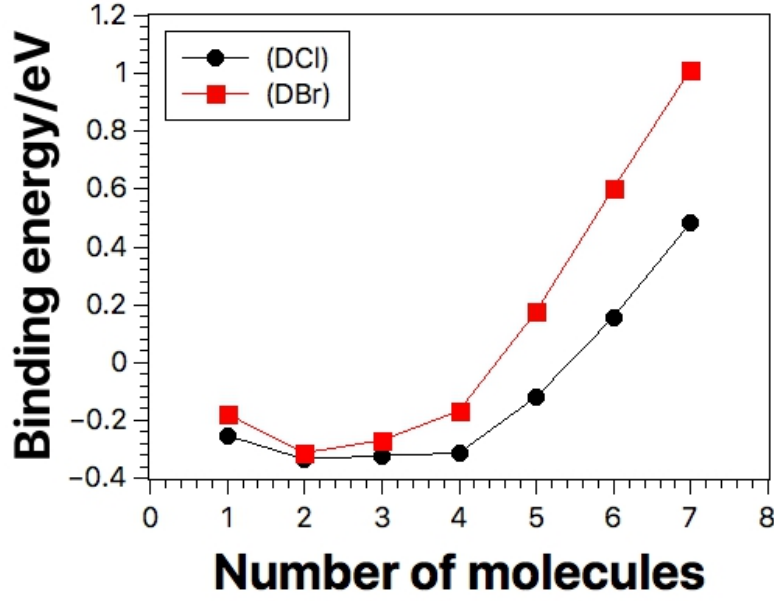


Figure II.16: Binding energy as a function of coverage for armchair orientation when calculated as referenced in equation II.9

Löwdin Charges and Charge Transfer

The direction of the charge transfer for the adsorbed molecules has been defined as

$$\Sigma = \sigma(\text{molecule}/s_{(\text{after adsorption})}) - \sigma(\text{molecule}/s_{(\text{before adsorption})}) \quad (\text{II.10})$$

with Σ : the charge difference of the molecule/s,

$\sigma(\text{molecule}/s_{(\text{after adsorption})})$: the overall charge on the molecule/s after adsorption and

$\sigma(\text{molecule}/s_{(\text{before adsorption})})$: the overall charge on the molecule/s before adsorption.

The results are given in units of millielectrons in Table II.3.

Considering the fact that the charge difference is given in units of millielectrons, no significant charge transfer can be observed. Therefore, band gap opening is most likely to be caused by molecule-induced rippling of the graphene sheet or

Table II.3: Change in electronic charge of molecules through molecular adsorption

	charge difference on molecule/s Σ /millielectrons ¹
1 DCl/graphene sheet ²	25.366
2 DCl/armchair ³	22.566
3 DCl/armchair ³	22.222
4 DCl/armchair ³	19.966
5 DCl/armchair ³	18.740
6 DCl/armchair ³	17.661
2 DCl/zigzag ⁴	21.033
3 DCl/zigzag ⁴	22.200
4 DCl/zigzag ⁴	20.416
1 DBr/graphene sheet ²	25.200
2 DBr/armchair ³	22.900
3 DBr/armchair ³	-13.422
4 DBr/armchair ³	17.325
5 DBr/armchair ³	14.926
6 DBr/armchair ³	11.477
2 DBr/zigzag ⁴	-10.733
3 DBr/zigzag ⁴	-8.233
4 DBr/zigzag ⁴	-15.375

¹ calculated as defined in Formula II.10² 1 molecule adsorbed on 5x5 graphene sheet³ 2-6 molecules adsorbed in armchair direction on 5x5 graphene sheet⁴ 2-4 molecules adsorbed in zigzag direction on 5x5 graphene sheet

a net dipole effect of the adsorbed molecules - not by charge transfer effects.

Chapter III

Ripples in Isotropically Compressed Graphene¹

Abstract

In this chapter, the formation of intrinsic ripples in graphene sheets under isotropic compression is examined. An isotropic compression of graphene is shown to induce a structural deformation on the basis of Density Functional Perturbation Theory. Static instabilities, indicated by imaginary frequency phonon modes, are induced in the high symmetry $\Gamma - K$ (zigzag) and $\Gamma - M$ (armchair) directions by an isotropic compressive strain of the graphene sheet. The wavelength of the unstable modes (ripples) is directly related to the magnitude of the strain and remarkably insensitive to the direction of propagation in the 2D lattice. These calculations further suggest that the formation energy of the ripple is isotropic for lower strains and becomes anisotropic for larger strains. This is a result of graphene's elastic property, which is dependent on direction and strain. Within the quasi harmonic approximation this is combined with the observation that molecular adsorption energies depend strongly on curvature to suggest a strategy for generating ordered overlayers in order to tune the

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functional properties of graphene.

III.1 Results and Discussion

The computed phonon band structure for an unperturbed graphene sheet is presented in Figure III.1 (solid black lines). The six phonon modes can be classified as optical (O) or acoustic (A). There are 3 acoustic modes (LA, TA, ZA) and $3N - 3$ optical modes (LO, TO, ZO), where $N = 2$ is the number of atoms in the primitive cell. For each of these classes there is one in-plane longitudinal mode (LA, LO) and two transverse modes, one in-plane (TA, TO) and one out-of-plane (ZA, ZO) [80]. Under zero strain all of the vibrational mode frequencies are positive indicating that the sheet is harmonically stable. Isotropic compressive strain is modelled by reducing the cell parameters under the constraint that the sheet retains the periodicity of the primitive cell.

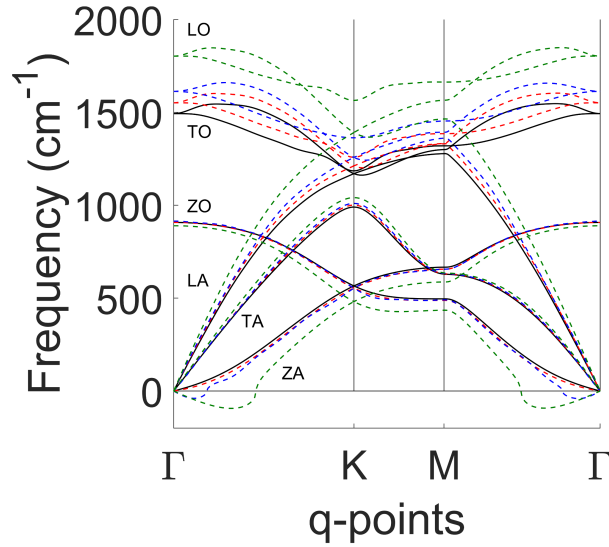


Figure III.1: Phonon dispersion curve (PDC) of a graphene unit cell under 0% (black solid line), 1% (dashed red lines), 2% (dashed blue lines), and 5% (dashed green lines) isotropic compression. Strains greater than 1% induce imaginary frequencies for the ZA mode.

In Figure III.1, the phonon band structures for 1%, 2% and 5% isotropic compressive strains are displayed as red, blue and green dashed curves respectively.

The in-plane transverse and longitudinal mode frequencies generally increase as the C - C bonds are compressed. However, the out-of-plane transverse mode frequencies are significantly reduced. In certain q-point regions (Γ - K and Γ - M) the calculated frequency becomes imaginary, which is shown as negative in Figure III.1. This negative behaviour is apparent only for the ZA mode. These out-of-plane distortions in the strained graphene sheet illustrate the unstable geometry and static ripple formations that may be modelled using the harmonic approximation. At 1% compressive strain (dashed red lines in Figure III.1) the sheet is harmonically stable, while compressions greater than 2% (dashed blue and green lines in Figure III.1) show sheet instabilities. These instabilities increase with greater strain as can be seen by the increased negativity at 5% compressive strain (dashed green lines in Figure III.1). The imaginary (negative) frequencies are along the high symmetry Γ - K (zigzag) and Γ - M (armchair) directions, for both compressive strains. The q-vector corresponding to the most negative frequency ($\vec{q}_{min}$) for each strain provides an estimate of the wavevector of the distortion induced by the harmonic instability; the computed $|q_{min}|$ is a strong function of strain but a remarkably weak function of direction. This is further explored by plotting a higher resolution map of the calculated frequency of the ZA mode for the central region of the Brillouin zone (the region Γ - A - B - Γ where A and B are the locations where the frequencies start to become negative with A in Γ - K (zigzag) and B in Γ - M (armchair) direction, displayed for a strain of 5% in Figure III.2). The fact that $|q_{min}|$ is, to a very good approximation, isotropic is immediately apparent.

At 2% strain, $|q_{min}|$ corresponds to a phonon wavelength that is along both the zigzag and armchair directions and is closely approximated by a ripple commensurate with a 10 x 10 supercell of the primitive graphene unit cell. Similarly, for 5% strain, $|q_{min}|$ corresponds to a phonon wavelength along the zigzag and armchair directions that are both closely approximated by a ripple commensurate with a 5 x 5 supercell of the primitive graphene unit cell. Using these commensurate supercells, the energy of phonon modes along the Γ - K (zigzag) and Γ - M (armchair) directions can be computed as a function of am-

plitude Δz . These energy profiles are presented in Figure III.3. The minimum energy (or depth of the well) of the computed energy profiles (Figure III.3) corresponds to the energetically most favoured Δz distortion (amplitude) and thus the preferred rippling configuration (or *stable ripple amplitude*).

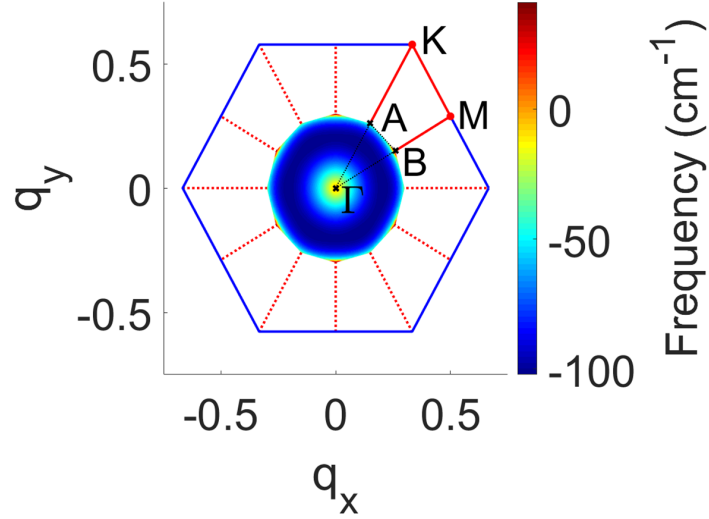


Figure III.2: Phonon modes in the first Brillouin zones of an isotropically compressed graphene sheet by 5% giving imaginary (shown as negative) frequencies within a smaller region defined by the path $\Gamma - A - B - \Gamma$.

At 2% strain, the armchair and zigzag modes have a similar stable ripple amplitude of $\sim 0.19 \text{ \AA}$ (Figure III.3a). At 5% strain, stable amplitudes are significantly different, $\sim 0.29 \text{ \AA}$ in the armchair direction and $\sim 0.63 \text{ \AA}$ in the zigzag direction. The distinctive difference in Δz distortion at 5% compressive strain (and the lack thereof at 2% compressive strain) can be explained by the simple notion that graphene's elasticity becomes anisotropic for both armchair and zigzag directions as a function of strain [48–50]. The anisotropic behaviour of the $\Gamma - K$ (zigzag) and $\Gamma - M$ (armchair) directions at 5% compressive strain (and the lack thereof at 2% compressive strain) furthermore suggests that the ripple formation process under isotropic compression is based on two competing effects, a) the energy gain through out-of-plane Δz distortions (*rippling*) and b) the elasticity of the sheet, which varies with direction and strain [48–50]. Based on the formalism suggested by Wei *et al.* [50], we can therefore express

the ripple formation energy as

$$E_{strain} - E_0 = E_{Ripple} = -\frac{1}{2}k(\Delta z \uparrow)^2 + C_{IJ}\Omega_I\Omega_J \quad (\text{III.1})$$

where E_{strain} is the energy of the strained graphene sheet, E_0 is the energy of the unstrained, flat graphene sheet, E_{Ripple} is the ripple formation energy, k is related to the force constant of the ZA phonon mode and Δz is the displacement along it, C_{IJ} are the elastic constants and $\Omega_I\Omega_J$ are the Lagrangian stresses. At small compressive strains, the difference in elastic constants for both armchair and zigzag directions is negligibly small, and the sheet shows isotropic behaviour, thus rippling unfavourably in any direction. At higher compressive strains (5% and more), the difference in elastic constants for both directions increases significantly, thus leading to anisotropic behaviour with the sheet preferably distorting in the zigzag direction.

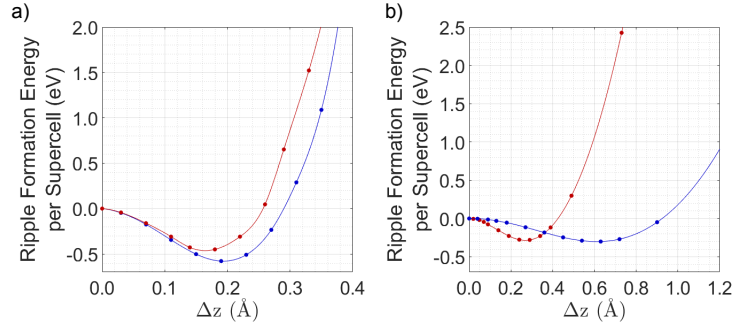


Figure III.3: (a) Energy profiles of two phonon modes (armchair (red) and zigzag (blue) direction) under 2% compression at the minimum frequency of $\sim -24 \text{ cm}^{-1}$ (minimum of dashed blue line in Figure II.1, computed in a 10x10 supercell). (b) Energy profiles of two phonon modes (armchair (red) and zigzag (blue) direction) under 5% compression at the minimum frequency of $\sim -100 \text{ cm}^{-1}$ (minimum of dashed green line in Figure II.1, computed in a 5x5 supercell).

The harmonic distortion energy for forming ripples at the stable ripple amplitudes in both $\Gamma - K$ (zigzag) and $\Gamma - M$ (armchair) directions is comparable at both strains (Figure III.3). At 2% strain the harmonic distortion energy for both modes (and thus directions) at the stable ripple amplitudes ($\sim 0.19 \text{ \AA}$) is $\sim 0.5 \text{ eV}$ per supercell (Figure III.3a). 5% strain shows a harmonic distortion energy

of ~ 0.3 eV per supercell for both modes (and thus directions) at the stable ripple amplitudes (~ 0.29 Å and ~ 0.63 Å, Figure III.3b). However, overall, the zigzag direction is slightly lower in energy (~ 0.1 eV) for both strains and thus inconsiderably energetically favoured (blue curves in Figure III.3a and III.3b). The difference in energy between both Γ - K (zigzag) and Γ - M (armchair) directions is small enough that in a chemical environment, a combination of both ripple orientations is more likely for the compressive strains reported in this work. This has also shown to be true in our previous work on the chemisorption of halogenated carbenes, which suggests the likely formation of an eggbox-type (containing both armchair and zigzag ripple formations) structure (see chapter II, section II.2, Figure II.10). However, in accordance with the results of Wei *et al.* [50], we expect a more significant difference in ripple formation energy and thus an increased anisotropy between the Γ - K (zigzag) and Γ - M (armchair) directions at strains of $> 5\%$ [50].

III.2 Summary and Conclusions

In this chapter we have demonstrated a theoretical analysis of isotropically compressed graphene for the facilitation of chemical adsorption. Using Density Functional Perturbation Theory to examine a uniformly compressed graphene sheet, we find that the sheet is harmonically stable at 0 and 1% compressive strain. At 2 and 5% strain, two symmetric soft phonon modes along the Γ - K (zigzag) and Γ - M (armchair) directions are observed, suggesting a facile formation of periodic ripples in either direction. These lattice distortions have an associated ripple formation energy cost that is isotropic for smaller strains but becomes anisotropic for larger strains due to a direction and strain dependence of graphene's elasticity. The small energy difference between the armchair and zigzag directions for the strains reported here further suggests the formation of eggbox-type structures. These results will allow for controllable and well-defined molecular patterning by exploiting the curvature as induced by isotropic strain.

Chapter IV

Summary and Outlook

IV.1 Summary

In this thesis, various methods to obtain well-ordered overlayers on graphene to tune its functional properties have been suggested. The patterning of molecular adsorption onto graphene has proved to be difficult, as grown structures tend to be stochastic in nature. We have moved towards a more detailed understanding of the ripple formation process under isotropic compression and how curvature can be exploited to direct molecular adsorption.

In chapter II, we suggested a generic physical model for the self-assembly of bidentally binding (organic) molecules on graphene surfaces. Using Density Functional Theory, we demonstrated that the self-assembly is dependent on the curvature of the graphene sheet, local distortions, as introduced by molecular adsorption, and intermolecular nearest- neighbour repulsions. We predict that only a small perturbation is required to generate specific rippling patterns and that this species of molecules preferentially binds in convex areas of the rippled sheet due to the covalent nature of the binding (chemisorption). Molecular adsorption introduces spontaneous rippling, which subsequently directs the adsorption pattern. Therefore, we can conclude that (pre-)rippled graphene sheets can be used to direct molecular adsorption in order to form specific patterns by tuning the thermodynamic equilibrium of the addition reaction. The small

energy difference between the armchair and zigzag adsorption sites suggests that the sheet typically ripples in both directions, leading to the formation of eggbox-type structures. A direct band gap can be opened and is tuneable with, a) molecular coverage, b) the ripple amplitude and c) the chemical nature of the attached halogen. This offers the possibility of effective band gap engineering by controlling molecular adsorption patterns. This paves the way to potentially making graphene applicable in semiconductor technologies.

In chapter III we presented a theoretical analysis of isotropically compressed graphene for the facilitation of chemical adsorption. Using Density Functional Perturbation Theory to examine a uniformly compressed graphene sheet, we find that the sheet is harmonically stable at 0 and 1% compressive strain. At 2 and 5% strain, two symmetric soft phonon modes along the $\Gamma - K$ (zigzag) and $\Gamma - M$ (armchair) directions are observed, suggesting a facile formation of periodic ripples in either direction. These lattice distortions have an associated ripple formation energy cost that is isotropic for smaller strains but becomes anisotropic for larger strains due to a direction and strain dependence of graphene's elasticity. This anisotropy can particularly be seen in the difference of $\Delta z \uparrow$ (out-of-plane) distortions in the armchair and zigzag directions at larger strains ($\geq 5\%$). We can conclude that the ripple formation process under isotropic compression is based on two competing effects a) the energy gain through out of plane $\Delta z \uparrow$ distortions and b) the elasticity of the sheet which varies with direction and strain. The small energy difference between the armchair and zigzag directions for the strains reported here further suggests the formation of eggbox-type structures which is in accordance with the results in chapter II. These results will allow for controllable and well-defined molecular patterning by exploiting the curvature as induced by isotropic strain.

IV.2 Outlook and Future Work

Using the work presented in this thesis, several possible avenues of future research present themselves. To conclude, we will briefly discuss these possibilities.

Although the work presented in both chapters II and III constitutes a novel approach to addressing the issue of obtaining well-ordered overlayers, it is theoretical in nature. Therefore, we suggest experiments exploring the avenues suggested here. One possible way of doing this would be to use (pre-)rippled graphene sheets on SiC substrates or graphene/hexagonal Boron Nitride heterostructures in a tuneable equilibrium reaction with small (organic) molecules. The chemical potential and therefore the coverage and adsorption pattern are in principle tuneable by changing the reactant concentrations in deposition from solution. The resulting adsorption patterns could be readily characterised with X-ray diffraction (XRD) and Scanning Tunnelling Microscopy (STM) experiments.

Furthermore, the model and the results in chapter II focus on the chemisorption of small (organic) molecules. Physisorption is expected to follow a slightly different adsorption process with the molecules rather binding to concave than to convex regions. We therefore suggest that dispersion corrected Density Functional Theory calculations be performed on small physisorbed molecules in order to develop a generic model describing the self-assembly of physisorbed molecules.

Finally, even though graphene's elasticity is discussed in chapter III, a more detailed analysis of the elastic properties is required. For example, using Density Functional Perturbation Theory, the elastic constants in both armchair and zigzag directions could be computed at different (isotropic) strains in order to have a more detailed understanding of the change in elasticity with direction and strain.

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Appendix A

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Figure A.1: Copyright permission for Figures in chapter I

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Figure A.2: Copyright permission for Figures in chapter II

Appendix B

Methodology

B.1 Benchmarking of Computational Details

Benchmarking of GGA Functional

In chapter II, the effects of electronic exchange and correlation are described using the Perdew-Burke-Ernzerhof (PBE) density functional [69], previously shown to reproduce the binding of carbene-based molecules to graphene and the resulting changes in graphene's electronic structure [20]. Core electrons are represented using Vanderbilt's ultrasoft pseudopotentials [77]. Figures B.1 and B.2 show the benchmarking of the aforementioned functional and pseudopotential for a primitive graphene cell in order to define the parameters required to achieve sufficient convergence of the calculations.

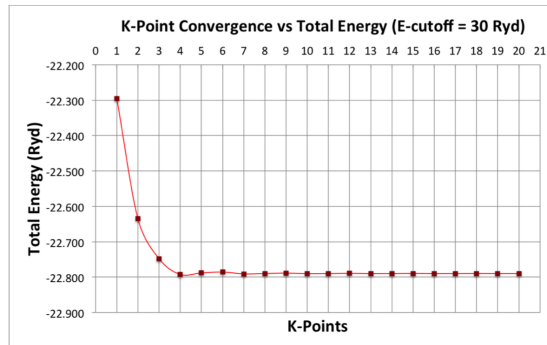


Figure B.1: The total energy of the system begins to converge at roughly a 3x3 k-point mesh with an error of 0.1%.

Figure B.1 shows that convergence is reached with a $\sim 3 \times 3 / 4 \times 4$ k-point mesh. For increased accuracy, calculations of the primitive cell have been performed with a 12×12 k-point mesh. Calculations of 5×5 supercells have been performed with a 3×3 k-point mesh. This is justified by the simple notion that expanding the graphene unitcell to a 5×5 supercell reduces the graphene Brillouin Zone to $G-K/5-M/5-G$ with $K/5$ and $M/5$ being the absolute values of K and M in reciprocal space divided by the expansion factor of the unitcell. Therefore, less k-points are needed for accurate sampling. Band structure calculations are computed along the $\Gamma-K-M-\Gamma$ high symmetry path using a mesh of 132 k- points.

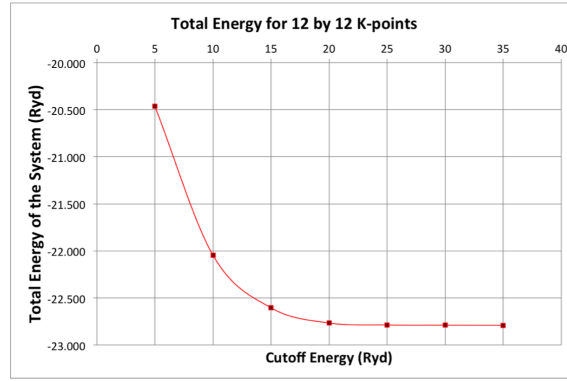


Figure B.2: The total energy of the system begins to converge at ~ 15 Ryd for a 12×12 k-point mesh with an error of about 1%.

Figure B.2 shows that convergence is reached with an energy cutoff of ~ 15 Ryd; throughout chapter II an energy cutoff of 16 Ryd has been used.

Benchmarking of LDA Functional

Phonon modes throughout chapter II and III have been computed with the LDA approximation using a Perdew-Zunger (PZ) functional [91] and norm-conserving pseudopotentials [77]. Figures B.3 and B.4 show the benchmarking of the aforementioned functional and pseudopotential for a primitive graphene cell in order to define the parameters required to achieve sufficient convergence of the calculations.

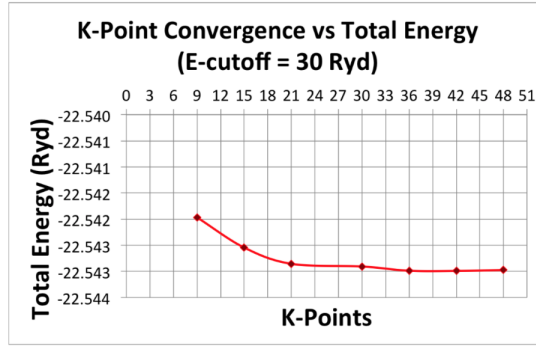


Figure B.3: The total energy of the system begins to converge at roughly a 12x12 k-point mesh with an error of 0.1%.

Figure B.3 shows that convergence is reached with a $\sim 12 \times 12 / 15 \times 15$ k-point mesh. Phonon Dispersion Curves (PDCs) are computed along the Γ –K–M– Γ high symmetry path using a mesh of 147 q-points. 5x5 and 10x10 supercells have been computed using a 3x3 k-point mesh (as has been justified in the previous section).

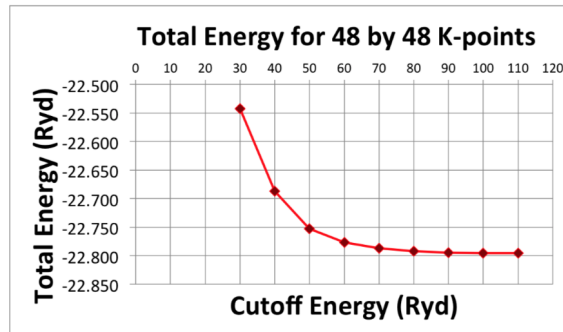


Figure B.4: The total energy of the system begins to converge at ~ 50 Ryd for a 48x48 k-point mesh with an error of about 1%

Figure B.4 shows that convergence is reached with an energy cutoff of ~ 50 Ryd; throughout chapter II and III an energy cutoff of 50 Ryd has been used.

Benchmarking of Phonon Dispersion

Figure B.5 shows the phonon dispersion of uncompressed graphene. Figure B.5a shows the phonon dispersion curve of a primitive graphene cell computed by us as described in the previous section, using a PZ functional with a norm-

conserving pseudopotential. Figure B.5b shows both a computed [103] (also with a PZ functional and a norm-conserving pseudopotential) and experimental [104] phonon dispersion curve. The circles in Figure B.5b indicate results obtained by Inelastic Neutron Scattering (INS) whereas the triangles indicate results obtained by Inelastic X-ray Scattering (IXS). The black line in Figure B.5b was obtained computationally. We can see that our phonon dispersion curve is in excellent agreement with that found in literature.

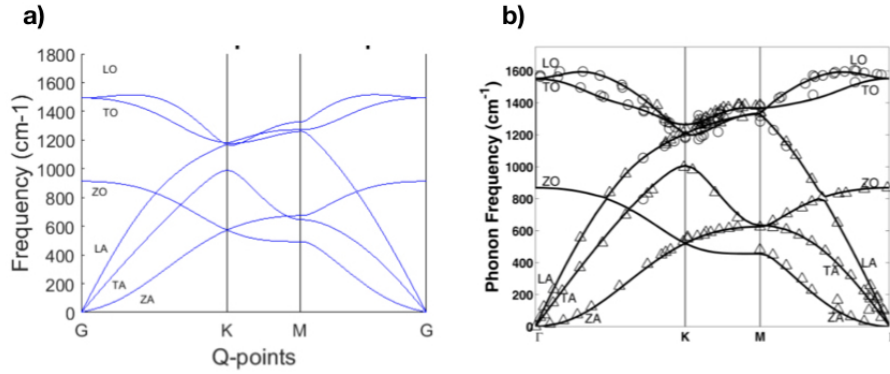


Figure B.5: a) Phonon Dispersion Curve as obtained in this work, b) Phonon Dispersion Curve as obtained in literature [103,104] with the black line obtained computationally [103], the circles obtained by INS [104] and the triangles obtained by IXS [104].

B.2 Computational Details - Input files

All calculations presented in chapters II and III have been done with **QUANTUM ESPRESSO** version 4.3.1. The following two images show the input files of a singlepoint (scf) calculation for a graphene unit cell and a 5x5 graphene supercell, respectively (Figures B.6 and B.7). Other possible calculations are: 'relax' which allows for a structural optimisation and 'vc-relax' (variable cell) which allows for an optimisation of the lattice and structure simultaneously.

```

&control
  calculation='scf'
  restart_mode='from_scratch',
  pseudo_dir = '/Users/mh5213/bin/espresso-5.0.2/pseudo',
  prefix='graphene',
  tprnfor = .true.
  tstress=.true.
  nstep=50000
  etot_conv_thr=1.0D-4
  forc_conv_thr=1.0D-3
  verbosity='high'
  disk_io='default'
/
&system
 ibrav = 4,
  celldm(1) = 4.66,
  celldm(3) = 15.725,
  nat=2, ntyp= 1, ecutwfc = 16, ecutrho = 128,
  occupations='smearing', smearing='mp', degauss=0.01,
  nbnd = 10,
/
&electrons
  diagonalization='david'
  electron_maxstep=1000
  conv_thr = 1.0e-8
  mixing_beta = 0.3
/
&ions
/
&cell
  cell_factor=4.0D0
  press=0.0
  press_conv_thr=0.1
/
ATOMIC_SPECIES
C 12.01 C.pbe-rrkjus.UPF
ATOMIC_POSITIONS crystal
C      0.666666666  0.333333333  0.000000000
C      0.333333333  0.666666666  0.000000000
K_POINTS (automatic)
30 30 1  0 0 0

```

Figure B.6: Input file for a singlepoint calculation of a graphene unit cell

```

&control
  calculation='scf'
  restart_mode='from_scratch',
  pseudo_dir = '/home/mh5213/bin/upf_files',
  prefix='graphene',
  tprnfor = .true.
  tstress=.true.
  nstep=50000
  etot_conv_thr=1.00-4
  forc_conv_thr=1.00-3
  verbosity='high'
  disk_io='default'
  wf_collect=.TRUE.

/
&system
  ibrav = 4,
  cellldm(1) = 23.3,
  cellldm(3) = 15.725,
  nat=50, ntyp= 1, ecutwfc = 16, ecutrho = 128,
  occupations='smearing', smearing='cold', degauss=0.008,
  nbnd = 150,

/
&electrons
  diagonalization='david'
  electron_maxstep=1000
  conv_thr = 1.0e-8
  mixing_beta = 0.3

/
&ions
/
&cell
  press=0.0
  press_conv_thr=0.1
/
ATOMIC_SPECIES
C 12.01 C.pbe-rrkjus.UPF
ATOMIC_POSITIONS (angstrom)
C      1.25415      0.72408      0.00000
C      0.00000      1.44817      0.00000
C     -0.00000      2.89633      0.00000
C     -1.25415      3.62042      0.00000
C     -1.25415      5.06858      0.00000
C     -2.50830      5.79267      0.00000
C     -2.50830      7.24083      0.00000
C     -3.76245      7.96492      0.00000
C     -3.76245      9.41308      0.00000
C     -5.01660      10.13717      0.00000
C      3.76245      0.72408      0.00000
C      2.50830      1.44817      0.00000
C      2.50830      2.89633      0.00000
C      1.25415      3.62042      0.00000
C      1.25415      5.06858      0.00000

/
C      0.00000      5.79267      0.00000
C     -0.00000      7.24083      0.00000
C     -1.25415      7.96492      0.00000
C     -1.25415      9.41308      0.00000
C     -2.50830      10.13717      0.00000
C      6.27075      0.72408      0.00000
C      5.01660      1.44817      0.00000
C      5.01660      2.89633      0.00000
C      3.76245      3.62042      0.00000
C      3.76245      5.06858      0.00000
C      2.50830      5.79267      0.00000
C      2.50830      7.24083      0.00000
C      1.25415      7.96492      0.00000
C      1.25415      9.41308      0.00000
C      0.00000      10.13717      0.00000
C      8.77905      0.72408      0.00000
C      7.52490      1.44817      0.00000
C      7.52490      2.89633      0.00000
C      6.27075      3.62042      0.00000
C      6.27075      5.06858      0.00000
C      5.01660      5.79267      0.00000
C      5.01660      7.24083      0.00000
C      3.76245      7.96492      0.00000
C      3.76245      9.41308      0.00000
C      2.50830      10.13717      0.00000
C      11.28735      0.72408      0.00000
C      10.03320      1.44817      0.00000
C      10.03320      2.89633      0.00000
C      8.77905      3.62042      0.00000
C      8.77905      5.06858      0.00000
C      7.52490      5.79267      0.00000
C      7.52490      7.24083      0.00000
C      6.27075      7.96492      0.00000
C      6.27075      9.41308      0.00000
C      5.01660      10.13717      0.00000
K_POINTS (automatic)
3 3 1 0 0 0

```

Figure B.7: Input file for a singlepoint calculation of a graphene 5x5 supercell

Band structures have been calculated along the G-K-M-G high symmetry path. The fractional coordinates along that path are as follows: G (0 ; 0), K (1/3 ; 1/3) , M (1/2 ; 0). In order to generate the k-point mesh along the high symmetry path, a python script has been used [102]. The relevant input files for that script for the graphene unit- and 5x5 supercells are shown below (Figures B.8 and B.9). Due to a technical feature of QUANTUM ESPRESSO, the high symmetry points are give in cartesian coordinates of the lattice parameter a. It should be noted that expanding the graphene unitcell to a 5x5 supercell reduces the graphene Brillouin zone to G-K/5-M/5-G with K/5 and M/5 being the absolute values of K and M in reciprocal space divided by the expansion factor of the unitcell.

```

! hexagonal
!
! First the unit cell (in atomic units = Bohr)
1.000000  0.000000  0.000000
-0.500000  0.866025  0.000000
0.000000  0.000000  15.726000
!then the number of points along the 1st special path
20

! then the special kpoints and their labels
G  0.00000  0.00000  0.00000 K  0.33333333  0.57735027  0.00000
K  0.33333333  0.57735027  0.00000 M  0.50000000  0.28867513  0.00000
M  0.50000000  0.28867513  0.00000 G  0.00000  0.00000  0.00000

```

Figure B.8: Input file to generate k-point mesh along the G-K-M-G path in cartesian coordinates of the lattice parameter a for the graphene unitcell

```

! hexagonal
!
! First the unit cell (in atomic units = Bohr)
5.000000  0.000000  0.000000
-2.500000  4.330125  0.000000
0.000000  0.000000  15.726000
!then the number of points along the 1st special path
60

! then the special kpoints and their labels
G  0.00000  0.00000  0.00000 K*  1.66666665  2.88675135  0.00000
K*  1.66666665  2.88675135  0.00000 M*  2.50000000  1.44337565  0.00000
M*  2.50000000  1.44337565  0.00000 G  0.00000  0.00000  0.00000

```

Figure B.9: Input file to generate k-point mesh along the G-K-M-G path in cartesian coordinates of the lattice parameter a for the 5x5 graphene supercell

In the following Figures, various input files in order to obtain phonon dispersion curves and/or phonon frequencies in the gamma point are shown.

```

Phonon Dispersion of graphene
&inputph
recover=.true.
tr2_ph=1.0d-16
ldisp=.true.
nq1=12 nq2=12 nq3=1
prefix='graphene'
amass(1)=12.01
fildyn='graphene.dyn'
/

```

Figure B.10: Input file for phonon dispersion calculation with the QUANTUM ESPRESSO ph.x executable

```

&input
fildyn='graphene.dyn', zasn='simple', flfrc='graphene.fc'
/

```

Figure B.11: Input file for phonon calculation with the QUANTUM ESPRESSO q2r.x executable in order to calculate the Interatomic Force Constants

```

|
&input
asr='simple'
amass(1)=12.01
flfrc='graphene.fc'
flfrq='graphene.freq'
/
219
0.000000 0.000000 0.000000 1.0
0.003333 0.005774 0.000000 1.0
0.006667 0.011547 0.000000 1.0
0.010000 0.017321 0.000000 1.0
0.013333 0.023094 0.000000 1.0
0.016667 0.028868 0.000000 1.0
0.020000 0.034641 0.000000 1.0
0.023333 0.040415 0.000000 1.0
0.026667 0.046188 0.000000 1.0
0.030000 0.051962 0.000000 1.0
0.033333 0.057735 0.000000 1.0
0.036667 0.063509 0.000000 1.0
0.040000 0.069282 0.000000 1.0
0.043333 0.075056 0.000000 1.0
0.046667 0.080829 0.000000 1.0
0.050000 0.086603 0.000000 1.0
0.053333 0.092376 0.000000 1.0
0.056667 0.098150 0.000000 1.0
0.060000 0.103923 0.000000 1.0
0.063333 0.109697 0.000000 1.0
0.066667 0.115470 0.000000 1.0

```

Figure B.12: Input file for phonon calculation with the QUANTUM ESPRESSO matdyn.x executable in order to calculate phonon frequencies at a generic wave vector using the Interatomic Force Constants file calculated by q2r.x

```

Normal modes for graphene
&inputph
  tr2_ph=1.0d-14,
  prefix='graphene',
  amass(1)=12.010,
  outdir='/work/mh5213/espresso_calc/PhD/graphene_test/tests/bands_dos/Faris/phonons_5x5/no_strain'
  epsilon=.false.,
  fildyn='dmat.5x5'
/
0.0 0.0 0.0

```

Figure B.13: Input file for phonon calculation in the gamma point with the QUANTUM ESPRESSO ph.x executable

```

■
&input fildyn='dmat.5x5', asr='simple',
/

```

Figure B.14: Input file for phonon calculation in the gamma point with the QUANTUM ESPRESSO dynmat.x executable ; "applies various kinds of Acoustic Sum Rules" [73]