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ABSTRACT

Graphene has generated great interest in the scientific community due to its high electron mobility and ease of reversible doping when it is part of a field effect transistor. However, several applications are limited by the lack of a gap in graphene’s electronic structure. Among the methods of opening this bandgap, chemical modification has been deemed plausible theoretically and has been achieved with varying success experimentally.

In this dissertation we cover four main topics regarding graphene chemical modification: i) we model the energetics of adatom bonding with Density Functional Theory (DFT), ii) we use DFT to explore the effect of electronic and hole doping of graphene on adatom bonding and diffusion, iii) we describe the mechanisms behind the interactions between an adatom and graphene with tight-binding models that describe electron correlations beyond mean field approximations, and iv) we present a Monte Carlo model for simulating clustering behavior in partially functionalized graphene. We focus on atomic hydrogen, fluorine, and oxygen in these studies.

In the DFT study of adatom bonding energetics (Chapter 2), we find that hydrogen and fluorine attach directly above carbon atoms with chemisorption energies of -0.8 eV and -1.8 eV respectively. Hydrogen has an attachment barrier of 0.2 eV while fluorine attaches with no barrier. For both monovalent adatoms, the carbon below puckers away from the graphene plane, showing evidence of \( sp^3 \) hybridization. Overlapping partial densities of states between the adatom and the underlying carbon show that the bond is covalent. A net magnetization localized around the adsorption site arises upon the adsorption of hydrogen, though no such polarization is seen for fluorine. The equilibrium position for oxygen on the surface lies above a C–C bond with both neighboring carbon atoms puckering above the plane. Diffusion calculations show energy barriers of 1.2 eV, 0.35 eV, and 0.73 eV for hydrogen, fluorine, and oxygen, respectively. Zero-point
energies turn out to be non-negligible for hydrogen kinetics, though desorption is found to be more likely than diffusion both with and without these corrections.

In the study of charge effects on adatom bonding (Chapter 3), we find a drastic lowering (from 0.74 eV to 0.15 eV) of the diffusion barrier for oxygen on graphene under electron doping ($7.64 \times 10^{13} \text{cm}^{-2}$). Such a large drop in the energy barrier corresponds to an increase in diffusivity of over nine orders of magnitude. Analyzing the partial densities for the atoms involved shows a weakening of the bonds in the equilibrium position and strengthening of bonds in the transition state as evidence for the drop in the energy barrier. In the case of hydrogen, electron doping suppresses the magnetization localized around the adsorption site. Electronic charging of the graphene plane is also found to change the bonding between fluorine and graphene from largely covalent to largely ionic.

In Chapter 4, we present a Hubbard-like tight-binding model for fluorine on graphene that shows that the mechanism of the $sp^2$-$sp^3$ hybridization crossover arises from a competition between electrostatic interactions and C–F hybridization. A similar model is applied to the hydrogen–graphene system; the magnetic moment formation localized around the adsorption site is explained by a balance between hybridization and intra-atomic coulomb interactions. The model is expanded to include correlations within a small cluster around the adsorption site. This Minimal Anderson Hubbard Model (MAHM) explains the dependence of the magnetization in the H–graphene system on the C–H hybridization, the H site energy, and the H Hubbard term; the model reaffirms the results gained from mean-field calculations.

A tight-binding model is proposed in Chapter 5 to explain the paramagnetic response in fluorinated graphene measured in recent experiments. Odd-numbered bare graphene clusters surrounded by fluorinated sites are hypothesized to contribute magnetic moments to the system within this model. Several adsorption models are proposed to simulate graphene fluorination from 1% to nearly 100% coverage. An Ising-like Monte Carlo model including adatom diffusion
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Chapter 1

Introduction

1.1 The Allotropes of Carbon

Carbon is a fascinating element, as materials of widely varied properties can be constructed solely from it. For example, diamond is one of the hardest materials known (on the Mohs scale), is highly abrasive, and is electrically insulating. Conversely, graphite is exceedingly soft, is electrically conductive, and is an efficient lubricant. In addition, low-dimensional forms of carbon have been created in the laboratory.

Carbon tends to form two types of arrangements: a two-dimensional planar \( sp^2 \) arrangement and a three-dimensional \( sp^3 \) cubic structure. By focusing only on the \( sp^2 \) bonded case, we can construct arrangements in any Euclidian space (see Figure 1-1).

<table>
<thead>
<tr>
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<td><img src="image2.png" alt="Carbon Nanotube" /></td>
<td><img src="image3.png" alt="Graphite" /></td>
<td><img src="image4.png" alt="Diamond" /></td>
</tr>
</tbody>
</table>

Figure 1-1 Various dimensionally constrained allotropes of carbon. All structures are made from \( sp^2 \) bonded carbon except for diamond (bottom of the 3D column).
A zero-dimensional carbon allotrope was discovered in 1985, when Kroto et al. synthesized the first Buckminster fullerene, or "Buckyball" [1]. This cage-like arrangement of carbon atoms, mostly in the form of C\textsubscript{60}, marked the beginning of the search for other allotropes of carbon not existing in nature. In 1991, a one-dimensional allotrope, called the carbon nanotube, was discovered by Iijimia [2]. One remarkable aspect of nanotubes was that they can consist of solely hexagonally arranged \textit{sp}\textsuperscript{2} bonded carbon as opposed to the fullerene’s need for pentagonal arrangements within its structure. In essence, the nanotube is simply a rolled up layer of graphene.

After the discovery of nanotubes, it took over a decade for a single sheet of graphene to be isolated. In fact, theoretical calculations from decades earlier concluded that divergent thermal fluctuations for two-dimensional lattices would prohibit the formation of free-standing two-dimensional crystals [3]. This conclusion was experimentally disproven with the discovery of graphene in 2004 [4].

Since its discovery, graphene has incited a great number of experimental and theoretical studies [5]. According Web of Knowledge, publications containing the topic “Graphene” have increased from 157 in 2004 to over 6000 in 2011 (see Figure 1-2). This flurry of research effort stems mainly from graphene’s remarkable electronic properties.
1.2 Physical and Electronic Structure of Graphene

Graphene consists of a honeycomb arrangement of carbon atoms in two sublattices. The sublattices correspond to the two symmetrically equivalent atoms within the unit cell (see Figure 1-3). The lattice constant is 2.46 Å—the same as that of graphite—and corresponds to an interatomic spacing of \( a = 1.42 \text{Å} \). Hence, the unit cell vectors for graphene are

\[
\vec{a}_1 = \left( \frac{3a}{2}, \frac{\sqrt{3}a}{2} \right), \quad \vec{a}_2 = \left( \frac{3a}{2}, -\frac{\sqrt{3}a}{2} \right). \tag{1.1}
\]

In this orientation, the three nearest neighbors of a given carbon atom are

\[
\vec{\delta}_1 = (a, 0), \quad \vec{\delta}_2 = \left( -\frac{a}{2}, \frac{\sqrt{3}a}{2} \right), \quad \vec{\delta}_2 = \left( -\frac{a}{2}, -\frac{\sqrt{3}a}{2} \right). \tag{1.2}
\]
4

Figure 1-3 Schematic of the graphene unit cell. Vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ indicate the unit cell vectors. Red (dotted) arrows indicate the three nearest neighbors of a carbon atom, $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$.

The bond network within the plane corresponds to $sp^2$ hybridization between all the carbon atoms. One unbound $p_z$ electron, visualized in Figure 1-4, still exists for each carbon atom and is responsible for conduction.

Figure 1-4 Isosurface of the carbon $p_z$ orbitals in graphene.

1.2.1 The Tight-Binding Model

A qualitative understanding of the band structure for the $p_z$ electrons in graphene can be gained from the tight-binding model for solid state systems. It is summarized briefly below.

The wavefunction of an electron within a periodic potential, $V(r)$, such as that of a crystal lattice, will have a periodic envelope and obey Bloch’s theorem [6]. Therefore, a linear
combination of orbitals can be constructed to satisfy this condition for periodicity. For a system with N atoms, a periodic wavefunction $\Phi_j(\vec{k}, \vec{r})$ can be constructed from orbitals $\phi_j(\vec{r})$ as

$$
\Phi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{r}} \phi_j(\vec{r} - \vec{R}),
$$

(1.3)

or the Bloch form [6]. Each position $\vec{R}$ corresponds to a lattice site within the entire crystal. The full wavefunction can then be constructed from a linear combination of the electrons in a given unit cell. For $n_b$ electrons in a unit cell, the wavefunction is

$$
\Psi_i(\vec{k}, \vec{r}) = \sum_{j}^{n_b} C_{ij} \Phi_j(\vec{k}, \vec{r}),
$$

(1.4)

where $C_{ij}$ are the weights of each Bloch function, and the sum runs over the number of electrons in the unit cell. Solving the Hamiltonian of the system,

$$
\hat{H} \Psi_i(\vec{k}, \vec{r}) = E_i(\vec{k}) \Psi_i(\vec{k}, \vec{r}),
$$

(1.5)

using (1.3), and (1.4), yields the following system of tight-binding equations:

$$
\sum_{j}^{n_b} C_{ij'} \langle \Phi_{j'} | \hat{H} | \Phi_j \rangle = E_i(\vec{k}) \sum_{j}^{n_b} C_{ij'} \langle \Phi_{j'} | \Phi_j \rangle.
$$

(1.6)

The terms $\langle \Phi_{j'} | \hat{H} | \Phi_j \rangle$ and $\langle \Phi_{j'} | \Phi_j \rangle$ correspond to the transfer integral and wavefunction overlap terms, respectively. The energy bands can then be solved for by finding the generalized eigenvalues $E_i(\vec{k})$ of the $n_b \times n_b$ matrix defined by (1.6). Due to the localized nature of the basis set, and for simplicity, overlaps and transfer integrals are often only calculated for interactions within a single site and those between nearest neighbors.
1.2.2 Tight-Binding \(\pi\)-Bands of Graphene

Since graphene contains two atoms in its unit cell, and we are only interested in the \(p_z\) orbital for each atom, the tight-binding system of equations will be \(2 \times 2\). The diagonal elements \(<\Phi_j|\hat{H}|\Phi_j>\) are denoted by a site energy \(\varepsilon_{p_z}\) and the off diagonal elements each correspond to a sum over nearest neighbors, \(f(\vec{k}) = e^{ikxa} + 2e^{k\sqrt{3}a/2}\cos\left(\frac{k\sqrt{3}a}{2}\right)\), multiplied by the transfer integral term \(<\Phi_{j'}|\hat{H}|\Phi_j>\), hereafter denoted by \(t\). The overlap between the wavefunctions of neighboring lattice sites is considered similarly for the construction of the overlap matrix. The resulting Hamiltonian and overlap matrices are

\[
H = \begin{pmatrix}
\varepsilon_{p_z} & tf(\vec{k}) \\
tf^*(\vec{k}) & \varepsilon_{p_z}
\end{pmatrix}
\quad \text{and} \quad
S = \begin{pmatrix}
1 & sf(\vec{k}) \\
sf^*(\vec{k}) & 1
\end{pmatrix}
\]

respectively. Solving for the energy bands yields

\[
E_i(\vec{k}) = \frac{\varepsilon_{p_z} \pm tw(\vec{k})}{1 \pm sw(\vec{k})}
\]

where \(w(\vec{k}) = \sqrt{|f(\vec{k})|^2}\). The band structure across the Brillouin zone is shown in Figure 1-5.
The most striking property of the band structure is the linear crossing at the $K$ points. In fact, by use of a Taylor series approximation about the Fermi level ($e_{Fz}$ in this case), the graphene electrons can be characterized as Dirac Fermions with energy $E(\vec{k}) = \hbar \vec{k} \cdot c$, where $c \approx 10^6 cm/s$ (see [7] and references therein).

1.2.3 Density Functional Theory Description of Graphene Bands

When plotting the energy bands against the band structure of pristine graphene from DFT, the hopping term and overlap can be fit to the slope of the linearity near the K-point (see Figure 1-6). The hopping term $t = 2.8 eV$ tends to best match the low energy band behavior of the system. We set $s = 0$ for simplicity, as the overlap term introduces an electron-hole asymmetry in the bands, but does not largely affect the low energy dispersion. Further corrections, such as keeping the wavefunction overlap, taking into account second nearest
neighbor or further C–C interactions, or including more than one orbital per atom [8–11] can better approximate the DFT result if necessary. It is rather unusual for such a simple description to reproduce the band structure of a material with so few effective parameters.

**Figure 1-6** DFT bands of graphene (blue dotted) plotted against the $\pi$-bands of graphene (red solid) calculated from the tight-binding model.

### 1.3 Graphene Functionalization

Although graphene’s unusual band structure—yielding an inordinately high theoretical conductivity—has implications for modern electronics, experiments have revealed drawbacks associated with the use of pure graphene. For example, in FETs made from the material, conduction is difficult to suppress due to the lack of a bandgap. Several methods to induce a gap
in graphene have been proposed, including substrate interactions [12, 13], and graphene bilayers [14, 15]. One of the most widely studied methods is that of chemically modifying the graphene surface, which is the focus of this dissertation.

1.3.1 Graphane (Hydrogenated Graphene)

Hydrogen on graphite was studied theoretically and experimentally for decades prior to the isolation of graphene. Early research goals were aimed at understanding interstellar H recombination and deterioration of graphite hulls in fusion experiments (see [16, 17] and references therein).

In 2004, DFT calculations showed that adsorption of dilute atomic hydrogen could open a bandgap in graphene’s electronic structure [18]. A structure for fully hydrogenated graphene was first predicted through a numerical cluster expansion method [19] (see Figure 1-7). In this structure, each carbon is bonded to a hydrogen atom, effectively saturating the carbon’s free electron and changing the bonding structure from $sp^2$ to $sp^3$. The electronic structure of fully hydrogenated graphene was calculated by Sofo, Chaudhari, and Barber in 2007, and the configuration was dubbed graphane [20]. As no conduction electrons remain due to saturation by hydrogen, the material effectively becomes a large bandgap semiconductor (see inset of Figure 1-7). Experimental hydrogenation of a graphene sample was first carried out by Elias et al. in 2009 [21], though the several factors, including a large energy barrier for surface diffusion (see section 2.2.1), have prevented 100% hydrogen coverage.
1.3.2 Fluorographene

Fluorographene, or CF, has a ground state geometry similar to that of graphane. Fluorinated graphite, has in fact been realized in experiment as early as the 1940’s by the reaction of graphite with high temperature fluorine gas [22, 23]. Fluorinated graphene is generated by reacting graphene with XeF$_2$ [24, 25] or F$_2$ [26]. Some groups have also successfully exfoliated fluorographene layers from fluorinated graphite [27]. Since fluorine forms covalent bonds with the carbon atoms, fluorographene’s band structure closely models that of graphane.

1.3.3 Graphene Oxide

Graphite oxide has been studied for quite some time, with its first recorded preparation dating to the 1850s [28]. Experimental sonication of graphite oxide in solution has been shown to result in single layer flakes, which can then be reduced to nearly pristine graphene [29]. In contrast to the theoretically predicted graphane and fluorographene structures, each graphene
oxide layer is intrinsically disordered, with both atomic oxygen and hydroxyl groups bonded to the graphene plane (see Figure 1-8). Nevertheless, graphene oxide shows insulating behavior in its electronic structure, as the oxide groups still inhibit conduction through the quenching of C $p_z$ orbitals [30, 31].

![Figure 1-8](image)

Figure 1-8 Schematic of oxidized graphene. Carbon, oxygen, and hydrogen atoms are shown in grey, red, and white respectively.

1.3.4 Other Adsorbates

The chemical functionalization of graphene planes is not limited to hydrogen, fluorine and oxygen. Carbon atoms themselves can form as defects upon the surface [32, 33]. Transition and alkali metals also show evidence of bonding with the graphene plane [34–37]. Molecules such as H$_2$O and NH$_3$ have been shown to bind weakly to the surface [38]. Theoretical calculations of metal arenes on graphene have shown evidence for greater control of resulting bandgaps in the material by varying the arene type (its metal center) and concentration [39].
1.4 Dissertation Layout

This dissertation focuses on the study of bonding between atomic hydrogen, fluorine, and oxygen on the graphene surface with both ab-initio and analytical methods.

The dissertation is laid out as follows: Chapter 2 describes DFT results for the three chosen adatoms on the graphene surface. We present results on physical, electronic, and magnetic properties of these adatom–graphene systems and compare results with those of the literature, when available. We also present energetics for diffusion of adatoms across the graphene surface. In Chapter 3, we simulated the addition of charge to the adatom–graphene systems and calculate the effect of said charge on adatom bonding. A Hubbard-like tight-binding Hamiltonian is presented in Chapter 4 to elucidate the mechanism of monovalent adatom bonding to the surface and why charge shows such effects as presented in Chapter 3. Three adsorption models for monovalent adatom beyond the dilute limit are presented in Chapter 5. These models are coupled with a proposed model for paramagnetism among bare carbon clusters embedded in functionalized graphene and compared with recent experimental measurements in fluorinated graphene. Lastly, Chapter 6 explores two future studies considering the effect of the substrate on which the graphene sheet is placed on the local charging and subsequent bonding and diffusion effects of adatoms. Work for this dissertation has resulted in the production of four publications; one in Physical Review Letters [40], two in Physical Review B [41, 42], and one in Carbon [43].
Chapter 2

Energetics and Electronic Structure of Adatom Adsorption and Diffusion on Graphene

As discussed in Chapter 1, graphene can be viewed as a macromolecule, ripe with possibilities for chemical functionalization. The degree of modification can also vary significantly, from dilute concentrations of adatoms to systems in which every free C orbital is hybridized, with a continuous range of partial functionalization in between.

In this chapter, dilute impurities on the graphene surface are explored. Sparse adatoms on the surface are of interest for two reasons: i) even at low concentrations, these impurities greatly impact the electronic properties of the system [18, 44] and ii) such impurities are often present even when they are not wanted. Exploring the interaction between a single adatom and the graphene surface can serve both as a way to quantify the effects on the underlying lattice and to control the interaction itself.

This study focuses on the physical, electronic, and magnetic properties of hydrogen, fluorine, and oxygen on the graphene plane. These three species were chosen for several reasons. For example: i) all three species have successfully adsorbed to graphene in experimental studies [21, 24, 29], ii) they have all yielded insulating graphene structures at high adsorbate concentrations [20, 45, 46], and iii) in the dilute limit, they are simple monatomic defects which can be studied in great detail through simulation and analytical models.

Density Functional Theory (DFT) has proven to be a prime candidate for obtaining accurate approximations of both the electronic energetics and any resulting forces on ions within feasible computational time. One example of DFT’s ability is shown in the discussion of graphene’s electronic structure (see section 1.2.3). A more detailed overview of DFT is found in
Appendix A. The simulation studies presented here were carried out within the Vienna Ab-initio
Simulation Package (VASP) [47, 48] and Quantum ESPRESSO [49]. Both of these packages
function similarly, with differences in results mainly stemming from the differing
pseudopotentials [50, see Supplementary Information]. Detailed comparisons between them will
not be explored in this dissertation. In any case, we are more interested in the trends within data
and relative energetics than precise, absolute energies. The details and parameters of each
calculation are presented within each section below.

2.1 Adatom Adsorption

2.1.1 Hydrogen Adsorption

The interaction between H and graphitic surfaces has been of interest since before the
discovery of graphene. This interest was originally spurred by astrophysical studies regarding H₂
recombination in interstellar media [17] and hydrogen-wall interactions in plasma
experiments [16]. Experimentally, hydrogenation of either graphite or graphene is achieved by
hydrogen plasma bombardment [16, 21, 51, 52].

Several DFT studies have been carried out regarding H on graphene surfaces, even when
constrained to the dilute concentrations [17, 18, 53–63]. Here we reaffirm results seen in the
literature for adsorption and discuss the special care needed when calculating diffusion energy
barriers. Having a clear understanding of the physical, electronic and magnetic properties for H–
graphene systems will aid in guiding the construction of tight-binding models for dilute
adsorption presented in Chapter 4.

To explore the adsorption of a single H atom to the graphene plane, several
approximations must be taken. Within planewave-based DFT, a finite repeating cell must be used
for the calculation; hence, we construct a graphene supercell with a single H atom. Calculations
were carried out for supercells containing 32 C to 72 C, corresponding to a ~1-3% H/C concentration on the graphene substrate (see Figure 2-1 for a typical geometry). Although some finite size cell effects can be seen in the rippling of the plane, the adsorption energetics do not change significantly for larger cell sizes. When calculating magnetic moments for carbon atoms neighboring the adsorption site, finite size effects are more apparent. Hence, we focus on the larger supercell calculations in that case. In all cases the planar lattice constant is fixed to correspond to the experimentally determined C–C distance in pristine graphene (1.42 Å). To eliminate interactions between layers, a 20Å spacing perpendicular to the plane was found to adequately separate neighboring images in the z-direction. Further separation of planes resulted in negligible changes in energetics.

Figure 2-1  A typical cell used for H on Graphene adsorption containing 32 C atoms and 1 H atom. The hydrogen atom is shown in white, and the carbon atoms are shown in grey. Note the 20 Å spacing perpendicular to the graphene plane.

The core electrons within the atoms were treated by the Projector Augmented Wave (PAW) method [64, 65]. The Perdew-Burke-Ernzhof (PBE) [66, 67] implementation of the Generalized Gradient Approximation (GGA) was used to treat exchange and correlation effects between electrons. The energy cutoff was chosen to be 273.9eV; we observed a negligible change
in the qualitative trends of results for higher (400eV) energy cutoffs. A 6x6x1 gamma centered k-point grid was used to sample the Brillouin zone. We carried out ionic iterations until the average net force felt by all ions in the system was $<10^{-3}$eV/Å. Electronic iterations were deemed converged when the energy of the system changed by $<10^{-5}$eV. All calculations allowed for spin polarization among the electrons in the system.

When viewing the graphene plane from above, three high symmetry sites immediately become apparent as likely candidates for energetically favorable adsorption: directly on top of a carbon atom (hereafter referred to as the “T” [for top] site), above a bond between two carbon atoms (hereafter referred to as the “B” [for bridge] site), and onto the hollow location centered in a benzene-like ring of six carbon atoms (referred to as the “H” [for hexagon] site). Previous research [16–18, 42, 53–55, 60, 68, 69] has shown the top site to be most energetically favorable for adsorption.

We wish to model the path of an H atom approaching the graphene plane adiabatically to elucidate any possible energy barrier, as well as the energy gained once the H bonds to the substrate. To proceed, we begin by placing an H atom directly above and at a large (10Å for our simulation cell) distance from the T site it will adsorb to. The H and adsorption site C are then both held fixed while the rest of the atoms are allowed to relax. The procedure is then repeated with the H at closer and closer distances to the graphene plane.

The adsorption energy is calculated by taking the difference between the energy of the graphene+H system ($E_{Graph+H}$) and the sum of the graphene plane and H atom energies in isolation ($E_{Graph} + E_{H}$). To control for any effects of the cell size or shape, the graphene and H isolated energies are calculated within identical simulation cells to those of the graphene+H. Hence, the adsorption energy is

$$E_{ads} = E_{Graph+H} - (E_{Graph} + E_{H})$$

(2.1)
and is calculated as a function of the distance between the adsorption site C atom and the H adatom (also referred to as the C–H distance). Figure 2-2 shows a 0.2 eV energy barrier that is crossed at a C–H distance of ~1.8 Å.

Figure 2-2 Binding energy as a function of C–H distance for a Hydrogen atom approaching the graphene surface. The C–H distance is measured from the adsorption site C to the H. The red (solid) curve shows results for a graphene plane allowed to relax (see left inset), whereas the blue (dashed) curve shows results for a graphene plane held fixed (see right inset).

The adsorption site begins in an $sp^2$ hybridization state along with the rest of the graphene lattice. As the H approaches, the energy increases while the adsorption site puckers away from the lattice. Once the lattice is sufficiently distorted, a covalent C–H bond is formed with an adsorption energy of ~0.8eV and the adsorption site’s hybridization has changed from $sp^2$ to $sp^3$. Note that bonding still arises if the graphene plane is held fixed (not allowed to pucker) as can be seen in the dotted (blue) line in Figure 2-2. However, the energy barrier that must be
overcome in the fixed case is double that of the relaxed plane case and the bonded system remains higher in energy than the isolated graphene and hydrogen atom energies. This is because the inability to pucker prevents the adsorption site from becoming $sp^3$ hybridized, therefore forbidding the creation of a covalent bond with the H atom. Vibrational calculations by Huang et al. yielded a 0.2 eV decrease in the desorption barrier due to zero point energy corrections [70](discussed in more detail in section 2.2.1).

The degree of adsorption site puckering away from the graphene plane as the H atom nears is plotted in Figure 2-3. The puckering begins at a C–H distance of approximately 3 Å, the same distance at which the energy of the system begins to rise. At the equilibrium bonding distance of 1.12 Å, the adsorption site is puckered 0.5 Å from the basal plane.

![Figure 2-3](image)

Figure 2-3 Puckering of the adsorption site from the graphene plane as a function of C–H distance. The red (dotted) line corresponds to the equilibrium CH bond distance.
The adsorption energy and carbon puckering compare well with results from other DFT studies. In Table 2-1, the equilibrium carbon pucker distance ($d_{\text{puck}}$), equilibrium bond length ($d_{\text{CH}}$), adsorption barrier ($E_{\text{bar}}$), and chemisorption energy ($E_{\text{chem}}$) are tabulated for various adatom concentrations (denoted by C/H, or the size of a simulation cell) from studies across the literature. While not all studies report all values, one general trend becomes apparent: as the adatom concentration becomes more dilute, the chemisorption energy tends to become stronger (see Figure 2-4).

Table 2-1 Various bonding properties of hydrogen on graphene from various studies, including this work.

<table>
<thead>
<tr>
<th>Study</th>
<th>C/H</th>
<th>$d_{\text{puck}}$ ($\text{Å}$)</th>
<th>$d_{\text{CH}}$ ($\text{Å}$)</th>
<th>$E_{\text{bar}}$ ($\text{eV}$)</th>
<th>$E_{\text{chem}}$ ($\text{eV}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8</td>
<td>0.36</td>
<td>1.14</td>
<td>0.22</td>
<td>0.67</td>
</tr>
<tr>
<td>B</td>
<td>8</td>
<td>0.35</td>
<td>1.13</td>
<td>---</td>
<td>0.71</td>
</tr>
<tr>
<td>C</td>
<td>8</td>
<td>0.33</td>
<td>1.17</td>
<td>0.18</td>
<td>0.67</td>
</tr>
<tr>
<td>D</td>
<td>8</td>
<td>0.36</td>
<td>---</td>
<td>---</td>
<td>0.75</td>
</tr>
<tr>
<td>E</td>
<td>18</td>
<td>0.41</td>
<td>---</td>
<td>0.21</td>
<td>0.76</td>
</tr>
<tr>
<td>C</td>
<td>18</td>
<td>0.42</td>
<td>---</td>
<td>---</td>
<td>0.77</td>
</tr>
<tr>
<td>F</td>
<td>24</td>
<td>0.35</td>
<td>1.15</td>
<td>0.15</td>
<td>0.57</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td><strong>32</strong></td>
<td><strong>0.52</strong></td>
<td><strong>1.12</strong></td>
<td><strong>0.21</strong></td>
<td><strong>0.78</strong></td>
</tr>
<tr>
<td>C</td>
<td>32</td>
<td>0.48</td>
<td>---</td>
<td>---</td>
<td>0.79</td>
</tr>
<tr>
<td>G</td>
<td>32</td>
<td>---</td>
<td>1.11</td>
<td>---</td>
<td>0.76</td>
</tr>
<tr>
<td>H</td>
<td>32</td>
<td>---</td>
<td>1.13</td>
<td>---</td>
<td>0.66</td>
</tr>
<tr>
<td>I</td>
<td>32</td>
<td>---</td>
<td>---</td>
<td>0.15</td>
<td>0.85</td>
</tr>
<tr>
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<td>0.59</td>
<td>---</td>
<td>---</td>
<td>0.84</td>
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<tr>
<td>J</td>
<td>50</td>
<td>---</td>
<td>---</td>
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<td>0.82</td>
</tr>
<tr>
<td>K</td>
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<td>0.45</td>
<td>1.13</td>
<td>0.21</td>
<td>0.865</td>
</tr>
</tbody>
</table>

A: Reference [53]  G: Reference [18]
B: Reference [54]  H: Reference [61]
C: Reference [55]  I: Reference [52]
D: Reference [63]  J: Reference [59]
E: Reference [62]  K: Reference [70]
F: Reference [17]
Figure 2-4 Chemisorption energy as a function of C/H concentration from a literature review. Labeled values correspond to those in Table 2-1. Note the trend toward larger magnitude chemisorption energies for more dilute adatom concentrations.

Further insight into the nature of the C–H bond can be gained by exploring the evolution of the partial density of states for the relevant chemical species as a function of C–H distance. Figure 2-5 shows this evolution, where a given vertical cross-section for each plot denotes the PDOS at a given $d_{ch}$. In the leftmost panel, the occupied and unoccupied 1s orbitals of the H atom approach the Fermi energy monotonically until the C–H distance reaches 1.7 Å. Beyond this point, mixing between the adsorption site $C_0$ and the H atom occur near -8 eV, corresponding to the creation of an $sp$ bond. The hybridization also extends to the nearest neighbor carbon atom to the adsorption site ($C_n$).
Density of states projected onto various atoms as a function of C–H distance. Spin up and spin down projections are plotted on the top and bottom respectively. Darker regions indicate more states per energy unit. Densities plotted are for, from left to right, the hydrogen adatom, the adsorption site, a nearest neighbor carbon (as shown in Figure 2-3), and a far ‘bulk’ carbon atom respectively.
Another phenomenon observed upon H adsorption is the spin polarization created in the system. This behavior is observed in the projections of magnetization onto the neighboring carbon atoms surrounding the adsorption site. Of interest is the more pronounced magnetic moment for the nearest neighbor to the adsorption cite. As H approaches the graphene plane, the adsorption site and its nearest neighbors begin developing magnetic moments (see Figure 2-6). Note that the magnetization is more pronounced and of opposite sign for C_n than C_0.

![Figure 2-6](image)

**Figure 2-6** Magnetization as a function of Graphene-H distance for several relevant atoms. H, C_0, and C_n are those labeled in Figure 2-3. C_m denotes a carbon atom neighboring C_n further away from the adsorption site. The vertical dotted line corresponds to the equilibrium adatom position.

At the equilibrium position, plotting the magnetic moment as a function of carbon index leading away from the adsorption site reveals both the localized trend and the sublattice dependence of the magnetization (see Figure 2-7). The moment is plotted across two high symmetry directions, armchair and zigzag. The moment is strongest at the C_m atom, with an exponential tail for atoms on the opposite sublattice to the adsorption site. On the same sublattice, C atoms show a similar trend, only with an opposite sign and a lower initial magnitude. Differences between the zigzag and armchair directions arise partially from the differences in
radial distance from the adsorption site, but also from finite size effects. These results coincide with other studies [61, 71]. We study the fundamental mechanisms inducing this behavior in more detail in Chapter 4. In short, the phenomenon emerges from the competition between the C–H hybridization and intra-atomic coulomb interactions within the hydrogen and carbon atoms.

![Figure 2-7](image)

**Figure 2-7** Magnetic moment measured for carbon atoms neighboring the adsorption site. The two curves represent two paths beginning from the adsorption site. The discrepancy in magnetic moment beginning at carbon index 3 is exaggerated by the boundary conditions of the supercell.

### 2.1.2 Fluorine Adsorption and Comparison with Hydrogen

The energetics of adsorption for fluorine on graphene contrasts those of hydrogen, mainly in the form of the lack of an adsorption barrier. The barrier is eliminated due to fluorine’s extreme electronegativity (3.98 on the Pauling scale, compared to 2.20 for hydrogen). With such a large electronegativity, the fluorine–graphene system gains more energy through Coulomb attractions; this counteracts the energy cost required to pucker the adsorption site from the lattice. Hence, no energy barrier is seen as the F atom approaches the graphene plane (see **Figure 2-8**). This result serves as evidence that, when compared to hydrogen, fluorine will attach much more easily to the
graphene surface. This indeed seems to be the case, as experimental fluorination of graphene can be achieved through the decomposition of XeF$_2$ at 30-70°C [24–26], whereas hydrogenation requires exposure to an H plasma [21]. This also corroborates historical work on fluorination of graphitic lattices [22].

![Graphene Energetics](image)

**Figure 2-8** Energetics of F on graphene as a function of C–F distance. Data courtesy of Ning Shen.

Despite fluorine’s electronegativity, which could lead to the assumption that the C–F bond will be ionic, the nature of the bond is still predominantly covalent. This can be observed in the form of mixing between the projected densities of states of F and those of the nearby graphene atoms (see **Figure 2-9**). Despite this covalent bonding, which is structurally similar to the C–H bond, no spin polarization is observed for adsorption. This lack of magnetization is due to the balance of contributions from both the interatomic hybridization and intra-atomic coulomb interactions for fluorine compared to hydrogen, and is discussed in more detail in Chapter 4.
Figure 2-9 Partial densities of states for various atoms involved in the F–Graphene system. Atom labels correspond to those in Figure 2-8. Data taken from Figure 1 of reference [41].

2.1.3 Oxygen Adsorption

The theory behind the mechanism of oxygen attachment onto the graphene surface is more contentious than that of hydrogen and fluorine. DFT studies show that the energy barrier required to dissociate and adsorb an oxygen molecule can be ~0.2 eV or ~1.3 eV depending on the state of the oxygen (singlet or triplet) [68], though experimental studies suggest that oxygen only dissociatively adsorbs on graphene edges [72–74]. In any case, the mechanism for the initial attachment of an oxygen atom to the plane is beyond the scope of this dissertation, and we will limit our focus to the mechanism of diffusion.
2.2 Adatom Diffusion

2.2.1 Hydrogen Diffusion

Diffusion of an H atom along a graphene plane has some added complexities due to the covalent nature of the C–H bond. Will the adatom be mobile across the surface, or will the energetics necessary for such diffusion approach or surpass the barrier for desorption? Depending on the energy cost to move from one T site to another, an H atom that is diffusing may just as likely stay in the gas phase and not reattach. Furthermore, present results not only corroborate results seen in the literature [56, 57, 70, 75], but also take into account the effects of the underlying lattice distortion on the barrier.

Our calculations show that the Minimum Energy Path (MEP) for an H atom diffusing from one T site to another crosses through a B site (directly between two bonded carbon atoms). The barrier is estimated through two different approaches: fixed distance calculations such as those in the adsorption study and the Nudged Elastic Band (NEB) method. In short, the NEB method allows for the determination of a MEP for a reaction pathway between two relaxed equilibrium configurations by the use of images connected by fictitious springs. More details of the NEB method can be found in a description by Jónsson et al. [76].

Simulation of H atom diffusion across the graphene lattice is carried out using Quantum ESPRESSO DFT code. A hexagonal simulation cell consisting of 5x5 graphene unit cells (containing a total of 50 C atoms) was chosen to achieve a H/C concentration of 2%. A larger unit cell was chosen to give more space for the lattice distortions created by the mobile adatom. The Perdew-Berke-Erzenhof (PBE) implementation of the Generalized Gradient Approximation (GGA) was used to treat exchange and correlation between electrons [66, 67]. Projector Augmented Wave (PAW) pseudopotentials were used. Ionic relaxations were carried out using a
single gamma point to sample the Brillouin zone. Calculations were deemed converged when the average net force between atoms was less than $10^{-4}$ eV/Å.

In simulation, moving the H atom along the diffusion path and letting the underlying lattice relax results in a tilting of the C–C bond below (see Figure 2-10). Because of this distortion, care must be taken in choosing the minimal energy transition state. The energy cost to twist the C–C bond to a mirrored position, reflecting the continuation of the path towards the final T site, should have a substantial energy cost.

![Diagram of C–C bond tilt](image)

**Figure 2-10** Schematic of the C–C bond tilt when H is halfway across the reaction coordinate. Mirroring the bond tilting yields the same energy.

**Figure 2-11** maps the energetics of the diffusion pathway for an H atom from one T site to another, crossing the B site. The black curve shows energy calculations for three specific constraints: i) the H atom is fixed at a given position in the diffusion path, ii) the graphene lattice as a whole is fixed, and iii) the two underlying C atoms partaking in the reaction are allowed to move. Stopping at the transition state and continuing the path from the mirrored C–C tilt shown in the green curve results in an energy cost of 0.8eV, which could naively be considered to be the barrier for diffusion. In fact, this value (with differences due to the DFT implementation used) has sometimes been reported in the literature [56, 57]. However, the blue curve, consisting of an NEB calculation over the entire diffusion path (using seven images), yields different energetics. In the NEB result, once the H atom nears the center of the path, a large energy cost (0.4 eV) goes
into the tilting of the C–C bond to its mirror image, resulting in a diffusion barrier of 1.2eV. Recalling that the barrier for adsorption is 0.2 eV and the adsorption energy at equilibrium is 0.8eV, a 1.2eV diffusion barrier would be more costly than desorbing the H atom completely. Other studies [52, 61, 70] agree with this conclusion. However, it is not obvious that rotating the C–C bond when H is halfway through the diffusion path will be the most energetically favorable scenario. The energy cost for bond rotation could be less when the H atom is somewhere else along the diffusion path. To test this, we simulated a reaction pathway consisting of only the C–C bond twisting, with the H atom fixed at different points in the lattice (see the red, violet, and green curves in Figure 2-11). The energy cost is indeed smallest when the H atom is halfway along the diffusion path, with the energy costs growing exponentially higher to rotate the C–C bond as the H atom is moved from the symmetric configuration.

Figure 2-11 Nudged Elastic Band (NEB) and fixed atom diffusion calculations for various positions in the reaction coordinate. The inset shows the placement of the reaction coordinates along the C–C bond.
2.2.2 Fluorine Diffusion

Even though fluorine adsorption to the graphene plane lacks an energy cost, there still exists a barrier for diffusion of F atoms across the plane. The diffusion of F is simulated within Quantum ESPRESSO using the same parameters as the H diffusion study above (now with five NEB images, as opposed to seven). As shown in Figure 2-12, a 0.35eV energy barrier arises for a reaction path similar to that of hydrogen diffusion under the same NEB simulation parameters as for hydrogen.

![Figure 2-12 Energetics for fluorine diffusion as a function of NEB images.](image)

2.2.3 Oxygen Diffusion

There has been limited experimental study of oxygen diffusion, especially with regards to comparisons between theory and experiment. In 1981, Yang and Wong carried out seminal work in measuring oxygen diffusion on graphite through the use of etch-decoration transmission
electron microscopy [73, 74]. They estimated a 1.5 eV energy barrier for oxygen diffusion through the use of this technique.

We study the diffusion of oxygen on graphene with the Vienna Ab-initio Simulation Package (VASP) [47, 48]. VASP was chosen as opposed to Quantum ESPRESSO for this study since VASP can calculate partial densities of state for specific orbitals of specific atoms, which proved useful in understanding the reason behind the energetics. This type of calculation is not currently feasible in Quantum ESPRESSO. An orthorhombic supercell identical to those of the H and F diffusion studies was chosen. This allows us to study a system with a 2% O/C concentration and room to include lattice distortions (as in the previous sections for H and F). An energy cutoff of 300 eV was chosen for the plane wave basis set in the calculation. The projector augmented wave (PAW) [64, 65] method was used to treat the core electrons. K-point spacing was set to 0.019 Å⁻¹, resulting in a 5x5x1 Monkhorst-Pack [77] grid. Determination of the diffusion path was carried out using the VASP transition state theory tools (VTST) implementation of the Nudged Elastic Band (NEB) method with 9 nine images [78]. Spring constants between images were set to -5.0 eV/Å.

The main difference between oxygen and the atomic species described above lies in oxygen’s divalent valence shell. Because of this, two bonds are formed between oxygen and the graphene plane. The equilibrium state is then on a B site as opposed to a T site. In this configuration (also known as the epoxy configuration), two carbon atoms pucker from the plane and partially $sp^3$ hybridize. The C–C bond between the adsorption sites is also stretched, (to 1.5 Å as opposed to 1.42 Å in pristine graphene) and agrees with other studies [68, 79]. The stretch is not enough to break the C–C bond, though studies have shown that aligning oxygen atoms on the graphene surface will ‘unzip’ the graphene sheet [80].

The equilibrium position for oxygen leads to a ‘walking’ mechanism for diffusion, in contrast to the ‘hopping’ behavior seen for hydrogen. NEB calculations show a transition state at
the T site, with an energy cost of 0.73 eV (see Figure 2-13). This barrier is in agreement with an unpublished study by Kawai and Miyamoto of O on graphene [81], and lower than what has been calculated for O diffusion on the outer edge of a nanotube [79]. This energy cost is related to the breaking of the C–O bond away from the diffusion path.

![Energy of the graphene oxygen system as a function of configurations over the diffusion path. Energy is calculated relative to that of the equilibrium position. The two configurations displayed show the equilibrium (E) and transition state (T) configurations.](image)

**Figure 2-13** Energy of the graphene oxygen system as a function of configurations over the diffusion path. Energy is calculated relative to that of the equilibrium position. The two configurations displayed show the equilibrium (E) and transition state (T) configurations.

Interestingly, the diffusion barrier is less than half that estimated by the experimental study of Yang and Wong. However, Yang and Wong estimate the diffusion barrier through rather indirect means. In their study, atomic pits are etched into oxygenated graphite and decorated with gold to become visible under transition electron microscopy. The oxygen diffusivity is then estimated by measuring the growth rate of the graphite pits, assuming carbon leaves the system by combining with a single oxygen atom and forming CO. The use of graphite, varying levels of
oxygenation, possible effects due to adsorbed gold, and assumptions relating to the connection between pit growth and oxygen diffusion may all greatly affect the estimate for the diffusion barrier.

Further evidence of the C–O bond breaking is elucidated by looking at the projected density of states corresponding to the oxygen atom orbitals in both the B and T sites (see Figure 2-14). On the B site, the projection of the DOS on the oxygen atom near the Fermi level mostly consists of an anti-bonding peak (seen in blue) corresponding to the mixing between the oxygen and carbon $p_z$ orbitals. The $p$ states of the O atom also form a peak at over 2 eV below the Fermi level. As the oxygen moves, the lower $p$ state peak moves up, eventually crossing the Fermi level and mixing with the O atom’s $p_z$ states. The peak formed just above the Fermi level describes the unfilled electronic state corresponding to the broken C–O bond.

![Figure 2-14](image.png)

**Figure 2-14** Total density of states and partial densities for oxygen $p$ orbitals perpendicular ($p_z$) and parallel ($p_x$) to the plane. (Top) Densities for the equilibrium geometry. (Bottoms) Densities for the transition state geometry. Spin up densities are given positive magnitudes while spin down are negative.
In contrast to hydrogen, the diffusion barrier does not require enough energy to completely desorb the oxygen atom into the gas phase. This is intuitively understood by the fact that at least one C–O bond is present at every point in the diffusion process. Comparing the 0.73 eV diffusion barrier to the adsorption energy (calculated similarly to Equation (2.1) for $E_{ads}$) of near 2 eV for oxygen adsorption [68] further reinforces the lack of a high desorption probability.

### 2.2.4 Adatom Diffusivity

Surface diffusivity is derived by first describing the mean squared displacement of a random site-to-site hopping in two dimensions as

$$\langle \Delta r^2 \rangle = vd^2 t,$$

where $v$ is the hopping frequency, $d$ is the hopping distance, and $t$ is time. The hopping distance corresponds to the distance between equilibrium sites, which is 1.42 Å for H and F, and 1.23 Å for O. The diffusivity is then defined as the mean squared displacement over unit time,

$$D = \frac{\langle \Delta r^2 \rangle}{zt} = \frac{vd^2}{z},$$

with $z$ corresponding to the amount of possible hopping choices for each site. For H and F, the number of hopping choices corresponds to the nearest neighboring carbon sites, hence $z = 3$. For oxygen, the nearest neighboring C–C bonds are the hopping choices, resulting in $z = 4$. The exponential dependence is introduced as part of the hopping frequency, which we construct using transition state theory [82], yielding

$$v = v_0 e^{\frac{E_{diff}}{k_B T}},$$

where $v_0$ is a vibrational attempt frequency and $E_{diff}$ is the diffusion energy barrier. The diffusivity is then expressed as
To find the vibrational attempt frequency, $v_0$, we calculate the vibrational modes of the system in the equilibrium and transition states. This attempt frequency is defined as the ratio of the products of vibrational modes in the equilibrium state over the vibrational modes product in the transition state,

$$v_0 = \frac{\prod_{i=1}^{N} v_i}{\prod_{i'=1}^{N-1} v_{i'}}$$  \hspace{1cm} (2.6)

Previous studies approximate the attempt frequency to be on the order of $\sim 10 \, THz$ [73, 74], although we calculated this value directly within DFT for the oxygen case for confirmation. Automation of the vibrational mode calculations are carried out within the VASP Transition State Theory (VTST) tools [78]. For the case of oxygen, we find a vibrational prefactor of $26 \, THz$, in good agreement with the estimates by Yang & Wong [74].

Due to its low mass, hydrogen requires special care as quantum mechanical effects are non-negligible regarding its energy barrier and its vibrational prefactor. The quantum corrected diffusion barrier, $E_{\text{diff}}^{\text{QC}}$, includes zero-point energy (ZPE) terms for vibrations in the equilibrium state and the transition state [83],

$$E_{\text{diff}}^{\text{QC}} = E_{\text{diff}} + \frac{1}{2} \sum_{i=1}^{3N-1} \hbar \omega_i^T - \frac{1}{2} \sum_{i=1}^{3N} \hbar \omega_i^E,$$  \hspace{1cm} (2.7)

where $\omega_i^T$ denote the vibrational mode frequencies of the transition state, and $\omega_i^E$ denote the modes of the equilibrium state. The vibrational prefactor is also modified, as the classical approximation by Vineyard no longer holds, yielding [70, 84]:

$$v_0^{QC} = \frac{k_B T}{\hbar} \frac{\prod_{i=1}^{3N} \left( 1 - \exp \left( -\frac{\hbar \omega_i^E}{k_B T} \right) \right)}{\prod_{i=1}^{3N-1} \left( 1 - \exp \left( -\frac{\hbar \omega_i^T}{k_B T} \right) \right)}.$$  \hspace{1cm} (2.8)
Huang et al. calculated both ZPE and vibrational prefactor corrections for hydrogen, deuterium, and tritium diffusion on the graphene surface [70]. Indeed, the ZPE correction is non-negligible, resulting in a $\sim 10\%$ decrease in the diffusion barrier ($\frac{1}{2} \sum_{i=1}^{N-1} \hbar \omega_i^T - \frac{1}{2} \sum_{i=1}^{N} \hbar \omega_i^E = -0.114$ eV). Because the diffusivity depends exponentially on $E_{diff}$ and only linearly on $v_0$, the vibrational prefactor correction turns out to be less important; it is less than one order of magnitude different than the classical term.

In Figure 2-15, diffusivity as a function of inverse temperature is plotted for oxygen, fluorine, and hydrogen with and without ZPE corrections. The exponential prefactor is set to $26$ THz for all diffusivities. At 300K, the diffusivity of oxygen is calculated to be $5.4 \times 10^{-16}$ cm$^2$/s. It is noteworthy to point out that when compared to the Yang and Wong result (at 923K [73, 74]), our result is four orders of magnitude larger ($10^{-7}$ vs $10^{-12}$). The key difference between the experiment and our simulation lies in the directness of the measurement. In the Yang & Wong study, the diffusivity is measured through a more circuitous route, and on a graphite slab as opposed to single layer graphene surface. The experiment involves etching atomically thick pits on a graphite surface and decorating the edges with gold. As oxygen diffuses towards the edges of the pits, it generates CO$_2$ and enlarges the pit diameter. By measuring the increase in pit size, a diffusivity value can be extracted. Since this method involves so many external factors (multiple adatoms, CO$_2$ generation, interactions with gold, etc.), it is not particularly surprising that the diffusivity values differ.
Figure 2-15 Arrhenius plots of diffusivity for O (black solid), F (red dashed), H (green long dashed), H + ZPE corrections (blue dash-dotted) on graphene as well as experimentally measured diffusivity of oxygen on graphite (violet squares). Experimental data \(^{(\text{A})}\) from the study by Yang and Wong [73, 74].

2.3 Conclusions and the Effect of Clustering and Lattice Vibrations

2.3.1 Adatom Conclusions

In conclusion, we report the physical, electronic, and magnetic effects of dilute H, F, and O adsorbates on the graphene surface. For H, we find an adsorption barrier of 0.2 eV and an equilibrium adsorption energy of -0.78 eV, in accordance with previous studies. Hydrogen is found to act as a magnetic impurity, with an oscillatory magnetization localized around the adsorption site. This magnetic character coincides with results from the literature. Fluorine lacks any barrier of attachment, and gains more energy upon bonding \((E_{ads} = -1.76 \text{ eV})\).
In the case of H diffusion, a 1.2 eV barrier is shown, with 0.4 eV of the cost attributed to the twisting of the underlying C–C bond. When zero point energy corrections are considered, which are found to be non-negligible, the barrier for H diffusion still surpasses that of desorption. Although fluorine lacks an adsorption barrier, a 0.35eV diffusion barrier is calculated. Oxygen is found to have a ‘walking’ behavior involving the breaking and reforming of a CO bond along the diffusion path. The PDOS of oxygen orbitals is of special note for understanding the effect of charge on the equilibrium and transition state energetics (see Chapter 3).

2.3.2 Clustering Effects

The simulations presented so far are in no way a fully exhaustive study to recreate the adsorption and diffusion processes that occur in nature. Although these results give a fundamental understanding of the energetics of adsorption in diffusion within dilute and adiabatic limits, many assumptions are taken which may greatly affect the energetics, electronic structure, and morphology of the system.

For example, the energetics of secondary adsorption and clustering of multiple adatoms on the lattice may influence adsorption and diffusion properties. In Chapter 6, we discuss Monte Carlo percolation studies of monovalent adatom adsorption, and include nearest neighbor calculations. In that study we forego detailed ab-initio studies to focus on the effect of correlations between attachment probabilities on cluster growth. A detailed ab-initio analysis of secondary adsorption would require calculating adatom energetics as they approach the graphene plane from both the same and opposite sides of the basal plane compared to the first adsorption site. The effect of distance between adsorption sites will also modify the energetics of adsorption and should be accounted for. Several theoretical studies on double site adsorption have been carried out for hydrogen [51, 57, 85, 86], and experimental results show evidence for hydrogen pairing on the surface [51, 87]. Although some studies have been carried out regarding individual
fluorine adsorption, its barrierless attachment and low diffusion barrier suggest non-negligible interactions between adatoms [88], partly due to the induced rippling of the basal plane. Studies focused solely on the equilibrium adsorption energy of multiple F atoms on the basal plane show evidence of energy gain for clusters of adatoms [88, 89]. In the oxygen case, dissociative adsorption of its molecular form [68] on graphene along with multiple adatom interactions gives a greater understanding of carbon nanotube and graphene ‘unzipping’ [79, 80, 90].

The complexity further increases when moving beyond two site adsorption. One method to study this added complexity would be to explore the adatom adsorption pathway with a graphene plane containing various functionalization configurations. Figure 2-16 shows ten possible nearest neighbor configurations for an already empty adsorption site plus two further configurations regarding possible desorption mechanisms. Here, each configuration is labeled by the number of same-side functionalized neighbors followed by opposite-side functionalized neighbors (for example, state 0-3 has 0 neighbors functionalized on the same side as the incoming H atom and 3 neighbors functionalized on the opposite side). The last two configurations shown correspond to a H atom approaching a site which is already functionalized. These are important to note, as H desorption could be facilitated by incoming H atoms, as defined by the Eley-Rideal mechanism. If we approach these scenarios with the use of DFT studies similar to those detailed above, one complication introduced is the large number of states near the Fermi level. Difficulties in reaching convergence DFT energy calculations arise due to the highest occupied energy states constantly fluctuating above and below the Fermi level. To accurately explore the reaction pathway for these configurations, the energy tolerances and ‘smearing’ of energy level populations must be carefully chosen to improve energetic convergence.
2.3.3 Effect of Lattice Vibrations

Regarding adatom diffusion, one main assumption is the static morphology of the graphene basal plane. In most diffusion studies carried out by NEB methods, this assumption is reasonable, as the surface in question is part of a three-dimensional bulk material which absorbs phonons and keeps the material rigid. The fact that graphene is atomically thin complicates this assumption, as thermal fluctuations may drastically modify the morphology of the surface. One can factor in these morphological fluctuations by quantifying diffusion events within molecular dynamics calculations at finite temperatures. However, using ab-initio methods for this approach would be very costly in terms of computational resources. Another approach would be to model this behavior with a reactive force field method that adequately reproduces DFT results, such as ReaxFF [91]. Conversely, a DFT study could be carried out in which the hybridization interactions are modified so that the energy barriers for diffusion events are lowered, therefore...
increasing the likelihood and frequency of diffusion events per simulation time [92].

Nevertheless, graphene is often affixed to some substrate (such as SiO$_2$) in experimental studies, so assuming that the graphene sheet is a surface of some ‘bulk’ material when phonons are concerned, this approach is not unrealistic.
Chapter 3

The Effect of Charge on Adatom Bonding

With an understanding of adatom adsorption and diffusion developed, the question arises as to what external stimuli may affect these bonding properties. One parameter which could substantially affect the bonding between graphene and adatoms is the charging of the plane due to the application of a gate voltage within a Field Effect Transistor (FET).

When its electronic transport properties are studied experimentally, graphene is often placed on a p-doped silicon wafer containing a 300nm thickness silica (SiO$_2$) surface. In the first electrical characterization of graphene, Geim, Novoselov, and coworkers measured a linear change in doping of the graphene sample with respect to the gate voltage applied in a graphene FET [4]. This relation can be understood by modeling the transistor as a parallel plate capacitor. The plates in this model consist of the p-doped silicon and graphene, and the silica substrate is the dielectric medium sandwiched between the plates (see Figure 3-1 for a schematic of this capacitor model). Starting from the charge on the plates of the surfaces from classical electrostatics, we yield the doping density as a function of gate voltage,

\[ n_{\text{graph}} = \frac{\varepsilon_{\text{SiO}_2} \varepsilon_0}{d} V_g, \]  

(3.1)

The terms $\varepsilon_{\text{SiO}_2}$, $\varepsilon_0$, $A$, $V_g$, $d$, and $n_{\text{graph}}$ are the relative permittivity of the silica dielectric, the permittivity of free space, the area of each surface, the gate voltage applied, the distance between surfaces, and the charge carrier density of the graphene plane, respectively. Given a 300nm silica substrate with a permittivity of 3.9, a linear dependence between graphene charge density and gate voltage arises: $n_{\text{graph}} = \alpha V_g$ with $\alpha \approx 7.2 \times 10^{10} cm^{-2} V^{-1}$ [4]. For the values of gate voltage achievable in an experiment ($V_g \pm 100 \ V$ with a SiO$_2$ dielectric; higher voltages are likely
to burn the sample, see section 3.4), doping densities of up to \( n = 10^{13} \ \text{cm}^{-2} \) can be reached [3]. Because these wide ranges of doping levels can be tuned ‘on the fly’, we wish to explore the effect it will have on adatom adsorption and diffusion.

![Capacitor Model of a graphene FET with graphene atop a doped Si wafer with a 300nm layer of SiO\(_2\). Note the linear relation between gate voltage and graphene charge density.](image)

**Figure 3-1** Capacitor Model of a graphene FET with graphene atop a doped Si wafer with a 300nm layer of SiO\(_2\). Note the linear relation between gate voltage and graphene charge density.

### 3.1 Effect of Doping on Oxygen Diffusion

To model the effect of a gate voltage applied to a graphene FET, we use the same simulation cell (containing 50 C atoms) as discussed in Section 2.2.3. Charging the graphene plane is done by adding charge to the simulation cell and compensating the total charge by a jellium background. Due to the periodic nature of the simulation, this equal but opposite charge must be inserted to neutralize the cell and avoid total energy divergence. Since we have a 20 Å distance between planes, the effect of this background charge on the graphene surface should be minimal, but we can measure this effect quantitatively by measuring the planar averaged electric potential across the z-axis of the simulation cell. Under charging, the planar averaged electrostatic potential shift from graphene to the adatom changes little (<1%).
Within a charged cell, the diffusion energetics are then calculated as was done for the neutral case. Figure 3-2 shows the diffusion energetics for both p-doped (electrons removed) and n-doped (electrons added) cells. For the p-doped case of $7.64 \times 10^{13} \text{ cm}^{-2}$ (equivalent to 1 electron removed from the cell), a 0.16 eV increase, to 0.89 eV, is seen in the diffusion barrier. For the n-doped cases, we see an opposite effect, with the case of $-7.64 \times 10^{13} \text{ cm}^{-2}$ showing a marked drop of 0.6 eV, yielding a barrier of 0.15 eV.

![Figure 3-2](image)

**Figure 3-2** Diffusion energetics for oxygen on graphene for various levels of charge. Equilibrium and transition state geometries are shown above.

Monopole and Dipole corrections were considered to ensure that such interactions did not largely affect the diffusion barriers. While monopole and dipole corrections shifted total energies within both equilibrium and transition state configurations of the system, the energy barrier between the two was largely unchanged (see Table 3-1).
Table 3-1 Diffusion barriers for systems of varying charge with and without dipole corrections

<table>
<thead>
<tr>
<th>Doping Level</th>
<th>+7.64×10^{13}</th>
<th>Neutral</th>
<th>-3.82×10^{13}</th>
<th>-7.64×10^{13}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncorrected Barrier (eV)</td>
<td>0.89</td>
<td>0.73</td>
<td>0.45</td>
<td>0.15</td>
</tr>
<tr>
<td>Dipole Corrected Barrier (eV)</td>
<td>0.92</td>
<td>0.72</td>
<td>0.45</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Through analysis of the bonding geometries we find evidence for a C–O bond weakening in the equilibrium state and a C–O bond strengthening in the transition state (see Table 3-2). As electrons are added to the system, the C–O distance within the equilibrium state increases. This same distance decreases with electronic charge for the transition state. While a change in bond length does not necessarily mean that the bond is weakened, we see further indication of a change in bonding from the C–C distances, which shrink with the addition of electronic charge in the equilibrium state. This lowering suggests that the carbon atoms below are relaxing to the pristine graphene interatomic spacing of 1.42 Å. This shows a tendency toward more ionicity in the equilibrium bond for n-doped cells. In the transition state, the C–C distance rises with n-doping, corresponding to a further deviation from the pristine graphene interatomic distances and showing evidence for a more covalent bond. The bonding angles further reinforce the explanation of a more covalent bond being formed in the transition state.
Select geometric values and energy barriers for varying graphene surface charge densities. The various labeled values are those depicted in Figure 3-2.

| Charge               | Equilibrium State | Transition state | | | | Barrier (eV) |
|----------------------|-------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                      | $d_{puck}$ (Å)   | $d_{puck}$ (Å)   | CO (Å) | CC (Å) | CO (Å) | CC (Å) | $\angle$CCO1 | $\angle$CCO2 | $\angle$CCO3 |                 |
| $+7.64 \times 10^{13} \text{ cm}^{-2}$ | 0.52               | 0.50          | 1.48   | 1.45   | 1.48   | 109.5° | 98.8°   | 97.9°   | 0.89           |
| Neutral              | 0.52               | 0.53          | 1.51   | 1.44   | 1.48   | 108.1° | 101.0°  | 99.9°   | 0.73           |
| $-3.82 \times 10^{14} \text{ cm}^{-2}$ | 0.52               | 0.60          | 1.50   | 1.43   | 1.49   | 104.8° | 104.7°  | 103.6°  | 0.45           |
| $-7.64 \times 10^{13} \text{ cm}^{-2}$ | 0.56               | 0.67          | 1.52   | 1.43   | 1.49   | 105.6° | 105.5°  | 105.4°  | 0.15           |

The bonding angles become larger as the cell is electron doped. The hybridization of the underlying carbon and hence the ionic versus covalent nature of the bond can be quantified through the bonding angles. In this case, we average the $\angle$CCO bonding angles, which are shown in Table 3-3. Also tabulated are the A values corresponding to the hybridization of the underlying C–C bonds [93]. $A = 0$ corresponds to solely $sp^2$ hybridization whereas $A = 0.5$ corresponds to complete $sp^3$ hybridization. The monotonic increase in $A$ with electronic charge gives yet more evidence that the bond at the transition state is becoming more covalent and, hence, more $sp^3$ in character.

**Table 3-3** Average C–C bonding angles and covalency values (A) for O on graphene in the transition state at various doping levels. $A=0$ corresponds to pure $sp^2$ bonding and $A=1/2$ corresponds to fully $sp^3$ bonding.

<table>
<thead>
<tr>
<th>Charge</th>
<th>Average bonding angle</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+7.64 \times 10^{13} \text{ cm}^{-2}$</td>
<td>102.7°</td>
<td>0.318</td>
</tr>
<tr>
<td>Neutral</td>
<td>103.0°</td>
<td>0.327</td>
</tr>
<tr>
<td>$-3.82 \times 10^{13} \text{ cm}^{-2}$</td>
<td>104.4°</td>
<td>0.363</td>
</tr>
<tr>
<td>$-7.64 \times 10^{13} \text{ cm}^{-2}$</td>
<td>105.5°</td>
<td>0.392</td>
</tr>
</tbody>
</table>
A look at the density of states of the system provides an explanation for this bonding behavior. In Figure 3-3 (a), the total density of states of the O–graphene system as well as the partial densities for the $p_z$ and planar orbitals of oxygen are plotted. The planar orbital shows a large peak just below -2 eV and mixing with the graphene states. This mixing is also seen in the $p_z$ orbital, though with another peak just above the Fermi level. This peak is found to be anti-bonding, as small displacements in the O position lower its energy. Upon electron doping, this anti-bonding state becomes partially occupied (see Figure 3-3 (b)), weakening the C–O bonds within the system. An opposite trend is observed for the transition state (shown in Figure 3-3 (c) and (d)). In the transition state, a C–O bond is broken and the oxygen is on top of a single carbon atom. The bonding state is then a combination of the $p_z$ orbitals of oxygen, the $p_z$ state carbon below, and the $p_z$ orbitals of the three nearest neighboring carbon atoms. This state shows a sharp peak below the Fermi level which is partially occupied in the neutral state. In the transition geometry, the peak above the Fermi level corresponds to the unbound O electron. When charged, the peak above the Fermi level becomes occupied, strengthening the C–O bond. Due to the width of the newly occupied peak, a small magnetic moment of $\sim 0.2\mu_B$ appears. The combination of evidence from the bonding geometries and the density of states presents a clear reason for the change seen in the diffusion barrier.
Due to the nature of the diffusivity (see section 2.2.4), any change in the diffusion barrier corresponds to an exponential effect in the oxygen diffusivity. The diffusivity as a function of temperature is shown in Figure 3-4. For the neutral case and at 300K, the diffusivity is $5.4 \times 10^{-16}$ cm$^2$/s. Assuming the same attempt frequency, the maximally n-doped case gives a diffusivity of $3.0 \times 10^{-6}$ cm$^2$/s, corresponding to an increase of ten orders of magnitude. To put this in perspective, the diffusivity in the normal system at ~700K could be reached at ~400K through a doping of $3.82 \times 10^{13}$ cm$^{-2}$. Even if the vibrational prefactor was greatly influenced by quantum effects, as in Hydrogen [70, 94], a several order of magnitude effect would still be seen in the diffusivity.
**Figure 3-4** Oxygen diffusivity as a function of temperature for varying charges.

With a gate voltage able to quickly change the charge on graphene within a device, switching between fast and slow surface diffusion states could be accomplished experimentally. One possible application of this effect can be to control the aligning of oxygen necessary for ‘unzipping’ graphene, which allows for many possible electronic applications [95, 96]. Once any alignments are in place, a change in gate voltage could then fix the patterns in place or allow a charge more amenable to further adsorption.

### 3.2 $Sp^3$-$Sp^3$ Hybridization Crossover in Fluorine on Charged Graphene

For calculating the effect of charge on C–F hybridization, we use the same DFT and charging parameters as the studies in sections 2.1.2 and 3.1.
In Table 3-4 (with tabulated quantities described in Figure 3-5), the lattice distortion due to the adatom decrease as a function of electron doping is shown. For the neutral case, the distortion corresponds to $A = 0.314$, whereas as a doping level of two electrons per unit cell lowers this to $A = 0.047$, the latter corresponding to almost fully $sp^2$ character. When removing electrons, the effect is reversed; an increase in the $sp^3$ character of the bond is observed.

Table 3-4 Angles and bond lengths for fluorine on graphene with varying charge.

<table>
<thead>
<tr>
<th>Charge</th>
<th>$\phi$</th>
<th>$\theta$</th>
<th>$A$</th>
<th>$d_{F-c_0}$ (Å)</th>
<th>$d_{c_0-c_n}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-1.27 \times 10^{14} cm^{-2}$</td>
<td>115.1°</td>
<td>103.1°</td>
<td>0.329</td>
<td>1.47</td>
<td>1.49</td>
</tr>
<tr>
<td>Neutral</td>
<td>115.5°</td>
<td>102.5°</td>
<td>0.314</td>
<td>1.57</td>
<td>1.48</td>
</tr>
<tr>
<td>$-6.36 \times 10^{13} cm^{-2}$</td>
<td>118.8°</td>
<td>96.3°</td>
<td>0.156</td>
<td>2.00</td>
<td>1.43</td>
</tr>
<tr>
<td>$-1.27 \times 10^{14} cm^{-2}$</td>
<td>119.9°</td>
<td>91.9°</td>
<td>0.047</td>
<td>2.50</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Figure 3-5 Figure showing F on graphene with various qualities labeled.

As in the case of oxygen, the partial density of states for the relevant atoms elucidates more evidence behind this $sp^2$ character. Figure 3-6 shows the partial density of states projected onto the atoms involved in bonding as well as a ‘bulk’ carbon atom far from the adsorption site. For the neutral case, the states projected onto the fluorine $p_z$ orbital are rather broad and overlap
with the $C_0$ states, indicating strong hybridization. As the system is charged, the largest magnitude peak rises towards the Fermi level and becomes narrower. When the cell is charged with two electrons (corresponding to $n \approx 1.27 \times 10^{14} \text{ cm}^{-2}$), the F peak exhibits a nearly delta-like character; any overlaps between $F$ and $C_0$ vanish. A complementary change is revealed for the adsorption site. In the neutral case, the states of $C_0$ differ greatly from those of graphene; a large gap is opened and peaks overlap with those of F. As the electronic doping is increased, the energy gap lessens. Once 2 electrons are added to the system, the $C_0$ PDOS shows a nearly identical character to that of bulk graphene carbon; the only telltale sign of its physical connection to fluorine remains as a small peak just below the Fermi level.

<table>
<thead>
<tr>
<th>Neutral</th>
<th>$n-6.36 \times 10^{13} \text{ cm}^{-2}$</th>
<th>$n-1.27 \times 10^{14} \text{ cm}^{-2}$</th>
</tr>
</thead>
</table>

Figure 3-6 Partial densities for atoms labeled in Figure 3-5 at varying levels of charge.

With such a decoupling between graphene and fluorine, the diffusion barrier is subsequently lowered appreciably. Figure 3-7 shows the diffusion barrier for fluorine on neutral
graphene and electronically charged graphene as calculated within Quantum Espresso (see section 2.2.1). While the graphene below is nearly planar, coulomb interactions prevent fluorine diffusion from being completely barrierless.

![Figure 3-7](image.png)

**Figure 3-7** Energetics of the diffusion of fluorine on neutral (black solid) and electronically charged (red dashed) graphene.

### 3.3 Effect of Charge on Hydrogen Induced Magnetization

As presented in the adsorption studies of section 2.1 hydrogen has many similarities to fluorine in the covalency of the bond formed and the resulting hybridization of the adsorption site. The key difference is that, for hydrogen, a magnetic moment forms in the surrounding carbon atoms upon adsorption to the neutral surface. However, spin polarization and, hence, magnetic moment formation, vanishes upon the addition of charge. A charge of 1 electron per 72 carbon atoms is added (equivalent to a doping level of \( \sim 6.30 \times 10^{13} \text{ cm}^{-2} \)); the partial density of
states for the atoms involved in bonding for the neutral as well as charged system are shown in

**Figure 3-8.** In the charged system, the large narrow peak corresponding to the hydrogen orbital remains near the Fermi level and still mixes with $C_0$ and $C_n$. In contrast to the case of fluorine, the hybridization remains strong, as evidenced by the strong mixing between states and the large gap still seen in the DOS of the adsorption site.

![Graph showing PDOS for neutral and charged carbon atoms](image)

**Figure 3-8** Partial densities for hydrogen and the same graphene atoms as **Figure 3-5**. Results from a neutral cell (left) and charged cell (right) are plotted. Note the lack of polarization under electronic charge.

The lack of a change in hybridization under electronic charging is evidence for possible differences in the effect of charge on diffusion when compared with that of fluorine and oxygen. Huang et al. carried out diffusion calculations of hydrogen on hole and electron doped graphene and found a reverse trend than that of our oxygen study: hole doping lowers the diffusion barrier while electron doping increases it [94]. Interestingly, both hole and electron doping increase the barrier for desorption in their study. Huang et al. therefore found a specific hole concentration ($p$-5 $\times$ 10$^{13}$ cm$^{-2}$) at which hydrogen diffusion becomes possible.
3.4 Conclusions and Comments on Graphene Charging

In summary, we studied the effect of graphene surface charge on oxygen, fluorine, and hydrogen bonding. The diffusion barrier for oxygen was found to drop significantly under n-doping, resulting in a change of nearly ten orders of magnitude in the diffusivity. The bond between fluorine and graphene was found to transform from heavily $sp^3$ to almost completely $sp^2$ with the addition of electronic charge. In the case of hydrogen, less of an effect on bond strength was seen, though spin polarization was found to vanish with electronic charge.

Evidence was presented showing that the jellium background added to neutralize the cell should not have a significant effect on the results. However, other methods of charge redistribution exist in the literature. One example of a charge redistribution technique more similar to the physicality of an actual FET device would be to contain the counter charge in a slab some distance from the graphene plane. However, care is needed in choosing the distance between the countercharged slab and the graphene plane, as unphysical bound states will arise if the countercharge slab is at too low a potential. A related approach recently implemented in certain DFT codes (including Quantum ESPRESSO) is the Effective Screening Medium (ESM) method [97]. In short, this method approximates the volumes beyond the DFT cell using classical electrostatics.

Also of note are the high doping levels simulated in this study compared to what is possible in experiment. When placed on a silica dielectric, as is standard in most electronic characterization studies, graphene can reach charge carrier densities of nearly $10^{13} \text{cm}^{-2}$ by way of a gate voltage before the sample becomes damaged. Damage to the sample at high gate voltages occurs when the dielectric material breaks down and shorts the conducting surfaces. The resultant heating from current flow over the new contacts burns the sample. However, gates made from other materials with higher dielectric constants can further enhance the maximally possible
doping. For example, with the use of electrolytic gates, $n \sim 10^{14} \, cm^{-2}$ charge carrier concentrations in graphene [98, 99] have been reached.
Chapter 4

Electronic and Magnetic Structure of Adatoms from Anderson-Hubbard Tight-Binding Models

In Chapters 2 and 3, modeling of dilute adsorbates has been discussed within the context of DFT. However, by taking into account so many details about the system, the mechanisms responsible for the observed results are hidden behind the veil of the computational ‘black box.’ In this chapter, we propose analytical models which not only reproduce the results seen in DFT but also consider quantum correlations beyond mean field levels. With such models, we can then pinpoint the dependence of the system on the strength of interactions and the interplay between them. The use of tight-binding based Hamiltonians to describe our adatom bonding picture is presented; hydrogen and fluorine adsorbates will be revisited. While the models will require the use of mean field solutions, a small cluster based model is presented that reproduces the solutions of the mean field while exactly taking into account electronic correlations.

4.1 The Tight-Binding Model in Second Quantization

In Chapter 1, the band structure of graphene, with its signature linear behavior near the Fermi level was produced by the tight binding model. In fact, this description of the bands of graphene has been known since as early as 1947 [100]. We revisit the Hamiltonian from chapter 1, now in second quantization,

$$\hat{H}_{\text{Graph}}^{0} = \sum_{\sigma,i} \varepsilon_p c_{i\sigma}^{\dagger} c_{i\sigma} - \sum_{(i,j)\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + H.C.$$  (4.1)
where \( c_{i\sigma}^+ \) creates an electron with spin \( \sigma \) on the graphene lattice and \( t \) defines the ‘hopping’ term, or energy for an electron to hop from one site to another. The first term, \( \epsilon_p \), corresponds to the energy of the \( p_z \) orbital at each lattice site. For pure graphene this corresponds to the Fermi level, and is set to zero in this study, for simplicity. The value of \( t \) can be found from fitting graphene’s linear band dispersion near the K point to DFT results (see section 1.2.3), resulting in a value of \( t_{ij} = t \equiv 2.8 \text{ eV} \).

4.2 Including an Adsorbate and Hubbard Interactions

4.2.1 The Anderson-Hubbard Hamiltonian

The Anderson-Hubbard Hamiltonian [101] for a graphene system coupled to an adsorbate contains three distinct terms,

\[
H = H_{\text{graph}} + H_{\text{imp}} + H_{\text{int}},
\]

which correspond to the graphene bands, the energy of the impurity, and the interaction between the impurity and the plane, respectively. To take into account the possibility of magnetic bound states, we must include an electrostatic repulsion term for double occupation of the graphene sites (within \( H_{\text{graph}} \)) and that of the impurity (within \( H_{\text{imp}} \)). This energy, known as the Hubbard term, can also be included for the carbon atoms in the lattice, as this can aid in recreating the localization of the magnetic moment surrounding the adsorption site in the case of hydrogen impurities. We must also assume that hybridization with an adatom can cause both a change in the energy of the adsorption site as well as the strength of the hopping term with its nearest neighbors. Thus, the Hubbard Hamiltonian for the graphene plane,
\[ H_{\text{graph}} = \sum_{\sigma, i} \varepsilon_{p} c_{i\sigma}^\dagger c_{i\sigma} - \sum_{(ij)\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + H.C. + U_\varepsilon \sum_{i} \left( \hat{n}_{i\uparrow} - \frac{1}{2} \right) \left( \hat{n}_{i\downarrow} - \frac{1}{2} \right) \]  

now contains a site dependent hopping term and an energy cost \( U_\varepsilon \) for double occupation in carbon atoms amongst the graphene lattice. The occupation number is defined as \( \hat{n}_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \).

The shift of each occupation by one half corresponds to a ground state at half-filling (one electron per site).

The adsorbate Hamiltonian will contain a different site energy in relation to the carbon atoms as well as its own Hubbard term. The impurity Hamiltonian is then

\[ H_{\text{imp}} = \sum_{\sigma} \varepsilon_{\text{imp}} d_{\sigma}^\dagger d_{\sigma} + U_{\text{imp}} d_{\uparrow}^\dagger d_{\downarrow}. \]  

The adatom will also hybridize with its adsorption site, which will break the symmetry of the graphene bands. The interaction Hamiltonian is

\[ H_{\text{int}} = \sum_{\sigma} \varepsilon_{0} c_{0\sigma}^\dagger c_{0\sigma} - V \sum_{\sigma} (c_{0\sigma}^\dagger d_{\sigma} + d_{\sigma}^\dagger c_{0\sigma}). \]  

Here, a new site energy, \( \varepsilon_{0} \), is defined for the adsorption site (denoted as site 0) and depends on the “covalency” value \( A \) (see section 3.2) as \( \varepsilon_{0} \approx A^2 (\varepsilon_{s} - \varepsilon_{p}) \) [93], where \( \varepsilon_{s} \sim -8 \text{ eV} \) is the energy level of the C s orbital and \( \varepsilon_{p} \equiv 0 \) is the C p\text{z} orbital. V corresponds to the hybridization between the adsorption site and the adsorbate. The symmetry breaking regarding carbon interactions is introduced by a modification of the hopping term between the adsorption site and its neighbors, \( t_{0j} \neq t_{ij} \) for \( i \neq 0 \).

### 4.2.2 The Hartree-Fock Approximation

The interaction terms on the F and C states in the Hamiltonian described above greatly increase the basis set needed to account for all combinatorics of particle populations, as the
system requires many-body terms. To approximate the many-body effects, we use the Hartree-Fock approximation. This approximation transforms the Hubbard term $U_x n_x n_x$, where $x$ is the impurity or the carbon sites. By expanding about the mean field of the occupation numbers $\langle n_x \rangle \approx \langle n_x \rangle + \delta n_x$, the term $U_x n_x n_x$ is approximated by $U_x \langle n_x \rangle n_x + U_x \langle n_x \rangle n_x + U_x \langle n_x \rangle n_x$.

As the last term only shifts the global energy and does not affect the local moment, it is dropped. With this approximation, the Anderson-Hubbard Hamiltonian is thus single-particle in nature, yet it is very accurate in approximating local moment formation in solids [102].

4.3 Modeling the $sp^2$-$sp^3$ Crossover in Fluorine on Charged Graphene

As discussed in Chapter 3, the bond between fluorine and graphene shifts in character from covalent to highly ionic as a function of electronic charge on the graphene plane. This interaction is modeled using the Hamiltonian described above. To model the charge-dependent bonding, the limiting cases of completely $sp^2$ and $sp^4$ hybridization between the adsorption site and its neighbors are considered.

In the fully $sp^2$ hybridized case, F interacts with the graphene plane as a point charge interacts with a conducting surface. Therefore, a classical electrostatic image potential term $-V_{im}(n_{d\sigma} + n_{d\bar{\sigma}} - 1)^2$ is added to the Hamiltonian. Upon expansion of this term and use of the Hartree-Fock approximation, it becomes clear that this potential shifts the orbital energy ($\tilde{\epsilon}_{imp} = \epsilon_{imp} + V_{im}$) and decreases the intra-atomic repulsion within the adatom ($U_{imp} = U_{imp} - 2V_{im}$). Due to the reduction in the Hubbard term, the image potential favors charging of the F atom. In the fully $sp^4$ hybridized case, the adsorption site transfers charge to F, resulting in another electrostatic term $U_{d,0}(n_{d\sigma} + n_{d\bar{\sigma}} - 1)(n_{0\sigma} + n_{0\bar{\sigma}} - 1)$. 
For the undistorted lattice, $t_{0j} = t$ and $\varepsilon_{imp} = 0$. Assuming an exponential form of the CF hybridization with distance, the change in equilibrium bond distance with charge yields $V = 0.4t$. Results from DFT calculations guide the fitting of the remaining parameters. From fitting to PDOS results, $U_f \approx 2.5t$, $\varepsilon_f \approx 1.8t$, and we set $U_c = t$. The image potential term will dominate for the $sp^2$ case and takes a simple Coulomb form, $V_{im}^{sp^2} = \gamma e^2 / 4d_F C_0$ with $\gamma \sim 0.8$ [103, 104]. In this limit, we assume no charge transfer from fluorine to carbon, so $U_{imp,0}^{sp^2} = 0$.

For the distorted lattice, the covalency value (detailed in Table 3-4), results in an adsorption site energy $\varepsilon_{imp} = -0.3t$. The C–C hopping around the adsorption site and the CF hybridization have been calculated by Ihnatsenka and Kirczenow as $t_{0j} = 0.7t$ and $V = 1.4t$ [105]. The charge transfer term will dominate here, so $V_{im}^{sp^3} = 0$ and $U_{imp,0}^{sp^3} \approx V_{im}^{sp^2}$. The entire Hamiltonian, $H = H_{\text{graph}} + H_f + H_{\text{int}}$, is then solved in the Hartree-Fock approximation to generate partial density of states to compare with those of DFT.

An overlay of the tight-binding and DFT $p_z$ orbital partial density of states for various important atoms in the bonding process is shown in Figure 4-1. The results from the tight-binding calculations are not meant to agree quantitatively with DFT, but many features match up within a qualitative comparison. Note the same reduction of overlap between fluorine and the adsorption site coinciding with a narrowing of the fluorine PDOS width upon electronic charging.
In Figure 4-1, the electronic occupation of the $F$, $C_0$, and $C_n$ orbitals are plotted as a function of electron doping (the crossover area is not plotted as it would necessitate contributions from both $V_{im}$ and $U_{imp,0}$). Note how, in the $sp^2$ configuration (large electron doping), there is an increased charge in the F orbital, and little change in the charging of $C_0$ and $C_n$. All orbitals discharge as the system is hole doped. In the DFT case, a significant charging of the F atom is also observed under large electronic charging, though a small discharging of the $C_0$ atom is also observed. By reintroducing a small intra-atomic coulomb term, $U_{f0}^{sp^2} \approx 0.1t$, the tight-binding model can reproduce this small discharge.
The $sp^2$-$sp^3$ crossover can be further understood in terms of energetics. The preference between one bonding state versus another depends on three main competing factors: i) the hybridization between $F$ and $C_0$, ii) the energy cost for graphene lattice distortion, and iii) the intra-atomic Coulomb interaction energy. When the system is neutral, the energy gain from the $F-C_0$ hybridization is greater than the $\sim 0.4t$ cost of lattice distortion (according to DFT calculations). The lattice distortion energy cost can be assumed to be constant across doping levels, as the process is dominated by $\sigma$ bands which are not taken into account in the tight-binding model. The electronic doping will increase the occupation of $F$ and $C_0$. Due to the interatomic coulomb term, $U_{f0}$, the energy of the system rises with charge, effectively dampening the energy reduction due to the hybridization term; this can be understood by the fact that antibonding orbitals are becoming occupied. The competition between the various terms and the hypothesis laid out above can be quantified by calculating the energy difference between the configurations,
Here, $\lambda$ is a parameter that linear interpolates through the effective parameters of the tight-binding Hamiltonian and the brackets correspond to the Hartree-Fock expected value. For the tight-binding Hamiltonian, $\Delta E \approx 0.4t$ across the hole doping regime, though the value lowers upon electron doping.

In summary, a tight-binding model has shown that the covalency of the $F-C_0$ bond can be tuned via a charge to the graphene plane, which can be accomplished in experiment by a gate voltage across a graphene FET. With enhanced ionic character, fluorinated carbon sites in graphene may no longer act as charge scattering centers, therefore increasing the electronic mobility of fluorinated graphene.

### 4.4 Modeling the Magnetic Structure of Hydrogen on Graphene

The tight-binding model for hydrogen on graphene is constructed in a similar way to the model for fluorine presented above. The principle difference lies in how the interactions are quantified. The interaction Hamiltonian introduced in section 4.2 will not be modified due to the smaller electron cloud present in the hydrogen adatom. This means that hydrogen does not act as a point charge when far from the plane (leading to the elimination of $V_{tm}$) and little direct charge transfer between the H and $C_0$ sites occurs during bonding (leading to the elimination of $U_{f0}$). As in section 4.3, fitting the tight-binding results to those of DFT with H away from the graphene plane results in $\varepsilon_{imp} \approx -1.4t$ and $U_{imp} \approx 2.8t$. With H adsorbed to the plane, the difference in distortion compared to F on graphene yields $t_{0j} = 0.6t$, $\varepsilon_0 = -0.7t$ and $V = 2t$.

In Figure 4-3 a)-c), the tight-binding PDOS for H, $C_0$, and $C_n$ are compared with those from DFT. In both cases, a supercell containing 72 C atoms is used. Qualitative details including,
most importantly, the spin polarization in the system, are reproduced well within the tight-binding model and the effective parameters detailed above.

Figure 4-3 DFT (blue solid) and tight-binding (red dashed) PDOS for various adatoms H, C₀, and C₁. The labels correspond to the atoms denoted in Figure 2-3.

In Figure 4-4, the magnetization of each site is plotted for a supercell containing H and 288 C atoms. The larger unit cell further suppresses finite size cell effects and shows the triangular sublattice-dependent localized pattern formed around the adsorption site (compare with Figure 2-7).
Figure 4.4 Magnetization of carbon sites surrounding a graphene impurity within the tight-binding model for a 288C lattice. Red and black circles correspond to positive and negative moments while circle size corresponds to magnetization magnitude.

4.5 A Minimal Anderson-Hubbard Model

In both DFT and tight-binding calculations, the presence of an H impurity induces a charge redistribution and subsequent magnetic moment creation localized mainly on C atoms nearest to the adsorption site. In fact, this phenomenon can be reproduced by simply considering a small cluster of atoms: the H impurity, the adsorption site, and the three C atoms neighboring the adsorption site. Modeling such a small cluster reduces the numerical complexity of the problem, allows for the inclusion of correlations beyond the mean field, and accurately reproduces results shown in the Hartree-Fock approximated models above.

Because of the hexagonal nature of the underlying lattice, the adsorption site directly couples only to a linear combination of the three neighboring atoms. We introduce a new creation operator $c_{\Delta \sigma}^\dagger = \sum_n c_{n \sigma}^\dagger / \sqrt{3}$ for this symmetric state, where $c_{n \sigma}^\dagger$ are the C creation operators and
the sum runs over the three nearest neighbor of the adsorption site. The terms for the rest of the orbitals remain the same as described in section 4.2, resulting in the following Hamiltonian:

\[
H_{\text{Cluster}} = \varepsilon_{\text{imp}} n_{\text{imp}} + U_{\text{imp}} d_1^\dagger d_1 + \varepsilon_0 n_0 \\
+ U_c \left( n_{01} - \frac{1}{2} \right) \left( n_{01} - \frac{1}{2} \right) + \varepsilon_{\Delta} n_{\Delta} \\
+ \frac{U_c}{3} \left( n_{\Delta1} - \frac{1}{2} \right) \left( n_{\Delta1} - \frac{1}{2} \right) \\
- V \sum_\sigma \left( c_{0\sigma}^\dagger d_{\sigma} + d_{\sigma}^\dagger c_{0\sigma} \right) \\
- \sqrt{3} t \sum_\sigma \left( c_{\Delta\sigma}^\dagger c_{0\sigma} + c_{0\sigma}^\dagger c_{\Delta\sigma} \right).
\]

(4.7)

The Hamiltonian is solved through exact-diagonalization (including many-body effects) and magnetization as a function of both hybridization and impurity site energy \( \varepsilon_{\text{imp}} \) is plotted in Figure 4-5. As in section 4.4, \( U_{\text{imp}} \sim 3t, \varepsilon_{\Delta} = 0 \), and \( U_c = t \). However, we take \( \varepsilon_0 = 0 \) for simplicity so as to avoid the complication of added electron-hole symmetry. For \( -3t < \varepsilon_{\text{imp}} < 0 \), a stable spin-1/2 ground state is always formed. As the hybridization increases, the magnetization is transferred from \( H \), to \( C_0 \) (at \( V \sim 1.5t \)), and eventually to \( C_\Delta \) (at \( V > 2t \)).

Assuming an exponential form for \( V \), a plot of the magnetization as a function of \( -\ln(V/t) \) closely reproduces the magnetization calculated from DFT (compare with Figure 2-6).
Figure 4-5 (top) Magnetization as a function of hybridization $V$ and impurity energy $\varepsilon_H$. (bottom) Magnetization along the dashed lines above ($\varepsilon_H = 1.5t$), with $C_H$ plotted instead of $C_\Delta$. 
Chapter 5

Modeling Mesoscale Fluorine Clustering

The creation of graphene channels within a functionalized lattice [88], graphene quantum dots [88], and seamless graphene based integrated circuits [106] all require knowledge on the behavior of adsorbates across varying concentrations. Long range and short range interactions between adatoms may influence the topology of a partially functionalized graphene surface.

In this chapter, we investigate the mesoscale adsorption of monovalent atoms (such as H and F) using three separate simulation methods: i) a random adsorption percolation model, ii) a correlated probability of attachment model, and iii) an Ising-like energy-based Monte Carlo model. While long range interactions may play a role in many site adsorption, we limit our models to only include nearest neighbor interactions. A comment on longer range multiple adsorption energetics is presented in section 5.5. A model for the mechanism of magnetic moment creation in fluorinated graphene is also presented. Recent experimental results concerning paramagnetic behavior in fluorinated graphene are compared with ‘magnetization’ values derived from the three methods introduced.

5.1 Experimental Connection: Paramagnetic Response in Fluorinated Graphene

The phenomenon of magnetism, in both its pure and functionalized forms, has sparked debate within the literature, as some experimental groups have yielded evidence for ferromagnetic behavior in graphene [107] while others propose that the results are due to defects [108]. In 2012, Nair et al. measured the magnetic response to an applied field across graphene at varying levels of fluorination [109]. The experimental data was fit to a Brillouin function for magnetization,
\[ M(z) = N g J \mu_B \left[ \frac{2J + 1}{2J} \coth \left( \frac{2J + 1}{2J} z \right) - \frac{1}{2J} \coth \left( \frac{z}{2J} \right) \right] \]  

(5.1)

where \( z = \frac{g J \mu_B H}{k_B T} \), \( N \) is the number of spins, \( g \) is the g-factor, and \( \mu_B \) is the bohr magneton. The applied field is \( H \) while \( k_B \) is the Botzmann constant. Nair et al. found that only \( J = \frac{1}{2} \) fit the data closely at all temperatures, while all other values for \( J \) resulted in stark qualitative differences [109]. This serves as evidence that spin \( \frac{1}{2} \) paramagnetic moments are created in graphene upon fluorination. The number of spins, \( N \), was then extracted from the Brillouin fits and plotted as a function of fluorine concentration (see Figure 5-1). The moment concentration rises with the degree of fluorination, plateauing at >90% F/C.

![Figure 5-1](image.png)

**Figure 5-1** Spin concentration versus fluorine concentration extracted from Brillouin function fits of reference [109]. Experimental error in fluorine concentration not shown. Experimental data taken from Figure 3 of the study by Nair et al. [109].

### 5.1.1 Tight-Binding Theory for the Paramagnetic Response of Fluorinated Graphene

In the work by Nair et al., they explained the mechanism for magnetization as being due to the edges of fluorinated clusters inducing magnetic moments in the surrounding graphene.
However, from the tight-binding and DFT calculations described in Chapter 2 and Chapter 4, no theoretical evidence of fluorine induced magnetization in the graphene plane has been found.

Another mechanism for paramagnetism in fluorinated graphene may be due to confinement of the C \( p_z \) electrons when surrounded by fluorinated sites. In the limit of fluorographene (100% F/C) with a single fluorine vacancy, the isolated C \( p_z \) orbital will serve as a single spin ½ magnetic moment. A chain of three bare sites embedded in a fluorinated lattice (see Figure 5-2 a)) will also yield a net magnetic moment. This behavior can be explained by a simple tight-binding Hamiltonian for a linear chain,

\[
H^{3\text{ site}} = \begin{pmatrix}
\epsilon_p & t & 0 \\
t & \epsilon_p & t \\
0 & t & \epsilon_p
\end{pmatrix}
\]  

(5.2)

where the hopping term \( t \) and the carbon site energy \( \epsilon_p \) are those described in Chapter 4. Here, the hybridization with the adatom is taken to the limit of infinite strength, so the bare carbon sites become decoupled from the functionalized sites. The highest occupied energy level from the diagonalization of (5.2) will contain only one electron, therefore giving the three-site chain the same moment as a single isolated site (see Figure 5-2 b)). Even for larger clusters in which connection complexities go beyond linear chains, odd numbered clusters always result in an unpaired electron at the highest occupied energy state. Also, as shown in the models below, small chains and clusters will dominate if fluorine tends to cluster.
Figure 5.2 a) Schematic of a partially fluorinated graphene lattice. Fluorinated sites are shown in red, bare carbon sites are shown in black. A chain of three bare carbon sites is circled in green. b) Energy states of a three site chain (energy values described in the text). Note the unpaired electron at the highest occupied state.

5.2 Random Adsorption: Site Percolation on a Honeycomb Lattice

In simplest terms, monovalent atom adsorption onto graphene can be modeled by the occupation of sites on a honeycomb lattice. For each site, there will be some probability $P$ for the site to be occupied. If an occupation is attempted for all sites with the same probability, the resulting lattice will have a concentration of occupied sites equal to the initial probability. Thus, the adsorbate problem is reduced to site percolation on a honeycomb lattice.

We carry out a simulation of site percolation on the honeycomb lattice using the Newman-Ziff algorithm [110] for keeping track of the number and size of each cluster. A periodic lattice consisting of 300x300 carbon atoms is percolated 20 times at each occupation percentage to account for any statistical fluctuation in the cluster distribution. The large cell minimizes finite size cell effects while still allowing for feasible calculation times. Sites are either occupied or not, with no distinction between adatom attaching from above or below the plane,
though an alternating ‘from above’ followed by ‘from below’ attachment proves to be more favorable for fluorine adsorbates [88]. The number of functionalized and bare carbon clusters as a function of occupation percentage is plotted in Figure 5.3. A peak in the number of carbon clusters is located at 0.67 occupation and the adatom clusters show a mirrored curve with a peak at 0.33 occupation. The peaks tend to coincide to the percolation threshold $p_c = 0.697043$ for sites on a honeycomb lattice [111], beyond which spanning clusters form and the number of clusters therefore drops. However, larger unit cells do not close the gap in accuracy and it is unclear as to whether the near match is purely coincidental.

Figure 5.3 Concentration of functionalized clusters (in red) and bare carbon clusters (in blue) as a function of fluorination. Dotted lines indicate the percolation threshold $p_c = 0.697043$ (in blue) and $1 - p_c$ (in red) for sites on a honeycomb lattice. Error bars are on the order of the line width and are not shown.

For the model introduced in section 5.1.1 to hold, the number of magnetic moments measured by Nair et al. should show qualitative similarities with the number of odd carbon clusters from the percolation model. The comparison between the experimental data and the
percolation model are shown in Figure 5-4. While the general trend of increasing moments with fluorination percentage is seen for both curves, two main differences arise: i) the number of odd clusters is several orders of magnitude larger than the number of magnetic spins seen in measurement and ii) the number of odd clusters peaks at 67% “fluorination” and drop monotonically to zero, whereas the experimental data shows a slight plateau beyond 90% fluorination.

Figure 5-4 Comparison of trends between magnetic moment concentration data by Nair et al. [109] and the number of odd clusters from the percolation model. The left axis corresponds to the experimental data (by Nair et al. [109]) while the right axis corresponds to the percolation data.

A similar study was previously presented by Ezawa [112], but for the case of hydrogenation, and therefore had a different theoretical approach to calculating net magnetism. The previous study also made conjectures as to the conductivity functionalized lattices from electronic states of the system at the Fermi level. However, many states at the Fermi level may be localized, impeding their contribution to conduction. Also, the scattering center nature of adsorbates have been shown to suppress conductivity, even at low concentrations [113].
5.3 A Correlated Percolation Model

The random adsorption model of section 5.2 fails to capture any preferential sticking of one site to another. Indeed, both theory [86, 114] and experiment [52] show a tendency for hydrogen and fluorine to cluster together on graphitic surfaces. To take the effect of clustering within the percolation method defined above into account, each site visited can have its probability influenced by the occupation of its nearest neighbors. Figure 5-5 shows a graphene cell with a single site fluorinated. Two adsorption site candidates are pointed out by arrows. For a candidate with a functionalized neighbor, the probability is enhanced by $dP$ over the probability $P$ of attaching to a site with pristine neighbors. The percolation algorithm then must continuously choose candidate sites until a given occupation percentage is reached as opposed to only visiting each site once. As there is no timescale in this model, the base probability no longer has any significance aside from its difference with the enhancement. Therefore, the parameter chosen to model the effect of enhancements is the ratio of the enhancement over the original probability,

$$P_R = \frac{dP}{P}. \quad (5.3)$$

The size of the cell and number of runs per adatom population are set to the same values as in the random adsorption model discussion of section 5.2.
Figure 5-5 Schematic of graphene with a fluorine adsorbed to the surface. Fluorinated site shown in red. Left arrow corresponds to an adsorption probability for F onto a site with pristine nearest neighbors. Right arrow corresponds to an adsorption probability for F onto a site with a functionalized neighbor.

In Figure 5-6, the adatom and bare carbon cluster concentration curves for various probability enhancement ratios are plotted. Upon the introduction of a probability enhancement, three trends become apparent: i) the magnitudes of concentrations drop, ii) an asymmetry in the curves for adatom and carbon clusters arises, and iii) the peak in cluster concentration shifts outward. The lowering of concentrations is obvious for the adatom clusters, as a tendency for clustering will yield a lower amount of larger clusters in a given simulation cell. With less adatom clusters, there are fewer gaps to construct bare carbon clusters, hence the similar suppression of bare carbon cluster concentrations. The asymmetry is introduced by the preferential nature of site attachment. Since the sites are visited at random, the adatom clusters will grow in a fractal-like manner. This behavior will cause many small bare carbon clusters to appear on the adatom cluster edges, therefore increasing the amount of bare clusters relative to adatom clusters. The mechanism for the shift in peaks of the cluster concentration is less clear. One plausible mechanism for this shift may be its connection with the percolation threshold of the lattice. Indeed, a tendency for clustering should shift the percolation threshold for adatom clusters to a lower occupation concentration.
As in section 5.2, the odd numbered clusters are compared with the magnetic moment concentrations measured by Nair et al. and plotted in Figure 5-7. Note that the cluster concentrations and magnetic moments are now plotted on the same scale. For a probability ratio $P_R = 1.0 \times 10^6$, the odd numbered cluster concentration magnitude reaches that of the magnetic moments, however much of the structure of the curve becomes lost.
Figure 5.7 Moment concentration data from Nair et al. plotted against odd numbered cluster concentration curves for varying probability ratios. (inset) A zoomed view of the same plot showing the comparison of the experimental data with odd clusters for $P_R = 1000000$. Note the near total lack of structure in the simulation data.

5.4 An Ising-Like Monte Carlo Adsorption Model

The loss of structure in the cluster concentration curves of section 5.3 arises mainly from the fractal nature of cluster shapes from the random attachment probabilities. What the models described in sections 5.2 and 5.3 do not take into account is the equilibration of a given adatom concentration from an energetic standpoint. In this section, we present an energy based model based off of the Ising model of magnetic spin ordering. Nearest neighbor interactions that take into account the side of the surface to which an adsorbate attaches are included for each site.

In the Ising model, the energy of a configuration of spins $s_i$ (taking the value +1 or -1) is given by $H^{Ising} = J \sum_{<i,j>} s_i s_j$. The term $J$ serves as a coupling between nearest neighboring spins. In a lattice populated from above and below with adsorbates, we define a new “spin” as the
side of attachment for an adsorbate, \( s_i = \{-1, 0, +1\} \), where 0 corresponds to an unoccupied site and \( \pm 1 \) corresponds to a site occupied from above (+1) or below (-1). The energy of a lattice of such “spins” is

\[
H^{1L} = \sum_{<i,j>} J_{opp} + (J_{same} - J_{opp}) \delta_{s_i s_j} s_i s_j - \mu \sum_i |s_i|,
\]

(5.4)

where \( J_{same} \) is the coupling between sites occupied from the same site (see Figure 5-8 b)), \( J_{opp} \) is the coupling between neighboring sites occupied by above and below (see Figure 5-8 c)), and \( \mu \) is the chemical potential. The coupling between a modified site and an unmodified site is zero (see Figure 5-8 a)).

![Figure 5-8](image)

**Figure 5-8** Energy contributions \( (dE) \) for the three possible nearest neighbor configurations involving at least one adatom. Adatom is labeled F and carbon atoms are labeled C. a) Energy contribution between a functionalized and a free carbon. b) Energy contribution between two carbons modified from the same side. c) Energy contribution between two carbon atoms modified on opposite sides.

A metropolis algorithm [115] determines the dynamics of a lattice exposed to possible adsorbates. Candidate sites are chosen at random and checked as to their occupation (empty, modified from above, or modified from below). The resulting energy change, \( dE \), amongst the nearest neighbors is then calculated for changing the occupation value of the site (desorbing or adsorbing an adatom if the site is occupied or unoccupied, respectively). When \( dE \leq 0 \), the occupation value is immediately changed. When \( dE > 0 \), the site’s occupation value is changed.
with probability equivalent to a Boltzmann factor $e^{-dE/T}$, where $T$ serves as the temperature of the lattice. Once a given fluorine concentration is reached, the algorithm only allows diffusion steps. In a diffusion step, the energy change for moving an occupied site to an empty neighbor is calculated and accepted or rejected based on the criteria described above. These diffusion steps continue until the energy of system reaches a convergence threshold.

Data for clusters was tabulated with the same basic parameters as sections 5.2 and 5.3 (300x300 lattice, average calculated for 50 instances at each percentage in this instance). Fitting the odd cluster concentrations to the data by Nair et al. yielded coupling values $J_{same} = -1.0$, $J_{opp} = +1.0$, a chemical potential $\mu = -1.06$, and a temperature $T = 0.09$. As shown in Figure 5-9, both the orders of magnitude and the qualitative trend of the odd-numbered cluster concentration from the Ising-like model closely follow those of the experimental magnetic moment measurements [116].

![Figure 5-9](image-url)

**Figure 5-9** Odd numbered clusters concentrations from the Ising-like Monte Carlo method plotted against the magnetic moment concentration from Nair et al. [109]. Parameters for this fit are $J_{opp}=-1.0$, $J_{same}=1.0$, $\mu=-1.06$, and $T=0.09$. 
5.5 Conclusions and Comments on Conductivity and Long-Range Interactions

In summary, we propose a model for paramagnetic response to explain recent experimental results in fluorinated graphene. Within this model, odd-numbered bare carbon clusters are responsible for magnetic moments in the system. Three adatom adsorption models are proposed to explore the connection between adatom clustering and paramagnetic bare carbon clusters. An Ising-like model, where “spin” is taken as the side of attachment of the adatom to the lattice, shows close agreement with experimental measurements.

It is worth commenting on the effect of these adatom clusters on the conductivity of the lattice. By definition, single continuous clusters of connected carbon atoms should exist below the bare carbon percolation threshold of the lattice. This may lead to the conclusion that hydrogenating of fluorinating up to ~67% of the lattice would still yield a conductive sample. However, this model does not account for the electron scattering off of the functionalized sites, which will greatly lower conductivity. A model which reintroduces both the finite hybridization strength of graphene sites with the chemisorbed atoms and the coulomb interactions for every site will serve better for studies on conductivity.

The effect of interactions beyond nearest-neighbor may also influence the clustering of adatoms on the surface. DFT calculations of the chemisorption energy $E_{\text{chem}}$, as defined in Chapter 2, show that sublattice dependence outweighs dependence on side of attachment beyond the first nearest neighbor (see Figure 5-10). Introducing quasi-local sublattice dependent interactions may improve the physicality of the Ising-like model for adatom clustering.
Figure 5-10 $E_{chem}$ for a second fluorine adsorbed onto a graphene lattice. The black (solid) line shows energies for the second F atom on the same side of the graphene lattice as the first. The red (dashed) line show energies for opposite side attachment. The carbon indices are those labeled in the inset. The blue (dotted) line at $\approx-1.3$ eV denotes $E_{chem}$ for a single F atom on the surface.
Chapter 6

Future Projects

6.1 Improving Charged Slab Calculations within DFT

In Chapters 2 and 3, we discussed simulation studies done using a charged graphene cell. In plane-wave based DFT codes such as VASP, a counter-charge needs to be added to maintain neutrality. Otherwise, the electric potential will diverge, given the periodic boundary conditions imposed in the calculation. In our case, the counter-charge is added by a jellium model homogenously distributed about the cell. This is usually acceptable in the case of three-dimensional crystals, but in the case of graphene we end up with an unphysical charge distributed about the vacuum surrounding the graphene slab. To remediate this issue, we turn to the experimental methods used to charge graphene and try to approximate this method in simulation.

In a graphene FET, graphene is charged by applying gate voltage. This voltage also gives an opposite charge to the surface of the doped silicon below the insulating silica substrate (see Chapter 3). This counter-charge “slab” could be inserted directly into the graphene simulation cell. This would obviously insert a large dipole into the system, so a dipole correcting layer would be necessary as well. Care would be necessary when adding this countercharge layer, especially when p-doping the cell, as spurious states may end up populating the vacuum near said layer.
6.2 Substrate Mediated Charging of Graphene

6.2.1 Local Charge Defects in Silica Substrates

Silica has been widely studied for electronics, and its properties are coming to be understood relatively well. Experimentally, it is the most studied substrate for graphene. It is an amorphous material and is known to introduce charged defects at its interface with graphene [117]. Silica can be modeled in simulation, where it has been shown to generate a realistic density of defects and hence closely approximate experimental results [118]. Charged defects on the silica surface arise from the passivation of oxygen and silicon dangling bonds by hydrogen and hydroxyls.

The adsorption of H, F, and O on this system will be studied. It is known that defects in graphene, and also in the closely related case of carbon nanotubes, play important roles in making the surfaces more chemically active [119]. However, relatively little work has been done on the role of charged defects in the substrate. In future work, binding energies and electronic properties will be calculated, and the effects on the chemical activity of surfaces will be examined.

The magnetic properties of these systems are also of interest. Recently, they have attracted considerable attention experimentally and theoretically in connection with using graphene in “spin-electronics.” As shown in Chapter 2, we found that H formed local magnetic moments on the graphene surface, whereas F did not [41, 42]. However, it is known that localized electronic states at defects in semiconductors can enhance magnetism [120]. It will be interesting to see whether these substrate defect charges enhance or suppress magnetism for adsorbates on graphene. In particular, it may be that F will give local magnetic moments near such charges.

One goal of this future work is to understand diffusion on these substrate-modified surfaces. Little research has been done on diffusion in this area. The local substrate charges can be probed in microscopic detail to see if they enhance or reduce diffusion of H, F, and O, and
how they change the overall diffusion across the system. For example, it will not be surprising if
the charges often reduce diffusion by trapping adatoms, which could play important roles in
surface functionalization. Comparison between the effects of these localized surface charges with
those from a uniform gating as studied in Chapter 3 will also prove useful, as one method may be
more easily achievable experimentally over the other.

6.2.2 Gate Controlled Doping of Graphene on Inhomogeneous Substrates

In future work we will explore the diffusion of several different adatoms in systems
where the doping can be changed by gating. Also, investigating how spatial variations of
substrate doping can be used to affect adatom binding and diffusion will be of interest. These
results may contribute to a new approach to the formation of high quality lateral patterning of
graphene. Consider a model like that shown in Figure 6-1. The substrate is composed of multiple
layers of materials of different dielectric constants. Graphene will be placed on the top as shown,
and the bottom of the structures will be gated in a capacitor geometry. Because of the differing
dielectric constants of the materials, the gate will induce laterally varying doping charges in
graphene. This model may also provide insight into a different system in which laterally varying
gates give rise to changes in the doping charges in graphene. Modeling gated graphene-substrate
systems of this kind can be done using the recently proposed Effective Screening Medium (ESM)
method [97], or a modified charged slab method like that described in section 3.4. In short, this
method generates a more realistic potential profile within the simulation cell in comparison to the
more common method of adding a homogeneous background countercharge throughout the cell.
Calculations of binding geometries, binding energies, and diffusion barriers will be made for H, F, and O adatoms in this system. These results will give information about binding and diffusion of adatoms on the two substrate models. By mapping the diffusion and adsorption energy barriers spatially across the graphene surface, the charge variations effect on adatom binding and kinetics can be quantified.

The adatom binding energies and diffusion constants are the inputs needed to understand the mesoscale kinetics of how surfaces and surface functionalization form. To understand these features better, these parameters can be inputted to Monte Carlo codes not dissimilar from those described in Chapter 5. They will simulate the formation of several graphene surface structures with varying properties, such as permittivities and doping. Simple examples of adsorbate configurations include quantum dots and nanoribbons. The dependences on temperature, gating, and doping densities will be of particular interest. It is important to note that these structures would be formed without the missing atoms and dangling bonds typical of structures formed from etching or lithography. Thus, they are likely have high quality electronic properties, such as high carrier mobilities.
Appendix A Overview of Density Functional Theory

The problem of the inhomogeneous electron gas in an external potential is largely intractable when taken from the pure, many-body form of the Schrödinger equation. Let us start with the “full” form of the Schrödinger’s Hamiltonian for a system of N electrons:

\[
H_{\text{full}} = -\frac{1}{2} \sum_i^N \left( \nabla_i^2 + \sum_k \frac{Z_k q_i}{|r_i - R_k|} \right) + \sum_{i<j} \frac{q_i^2}{|r_i - r_j|}.
\]  

(A.1)

Of note is the kinetic energy of the electrons (which can also be called \(T\)), the coulomb interaction between electrons (hereafter called \(U\)) and the nuclear-electronic interactions (which will be called \(V\)). Even this form is not without its approximations. We have already excluded interaction and kinetic energy terms of the nuclei. Still, this many-body problem becomes impossibly difficult to solve directly for any number of electrons beyond a mere two or three.

A.1 The Hohenberg & Kohn Theorem

In 1964, Hohenberg & Kohn presented a method to address the challenge of the above many-body Hamiltonian. The idea of their theory was the reduction from working with a 3N-dimensional wavefunction to a three-dimensional density. This can be done by formulating the system energy to be a functional of the electron density. Then, using the variational principle, we can construct a minimization condition for the ground state energy of the system,

\[
E[n_0] = \min_{\Psi \sim n} \langle \Psi | T + U + V | \Psi \rangle,
\]  

(A.2)
where \( \langle \Psi | T + U | \Psi \rangle \) contains the kinetic and coulomb interaction energy of the electrons and 
\( \langle \Psi | V | \Psi \rangle \) contains the system dependent external potential. We can now describe the energy of 
the system as

\[
\] (A.3)

It is important to note that \( F[n] \) is system independent, and 

\[
V[n] = \int d^3r \ n(r) v_{\text{ext}}(r),
\] (A.4)

where \( v(r) = \sum_k \frac{Z_k q_k}{|r-R_k|} \) can be determined for each system.

The construction in (A.3) is in and of itself immensely useful. By calculating the energy 
of systems for varying \( v(r) \) choices we can determine quantities such as the lattice parameter of a 
solid as well as the bulk phonon modes of the system. Also, by differentiating energies with 
respect to atomic lattice positions, we can find the forces on the atoms due to the electrons in the 
system. However, not all observables can be calculated as easily using just the HK theorem. Even 
for quantities that can be calculated directly from minimization of the electron density, it is most 
often not the most numerically efficient procedure. Also, only the form of \( E[n] \) has been 
introduced. We still need to construct explicit solvable forms of \( T[n] \) and \( U[n] \).

**A.2 The Kohn-Sham Equations**

In 1965, Kohn (from the original HK theorem) and Sham added significantly to the 
original Hohenberg-Kohn Theorem. In short, Kohn and Sham developed a way to reformulate 
energy functionals into a single particle form of Schrödinger’s equation.

First, approximations must be made to the kinetic and coulomb terms from equation 
(A.3). The kinetic energy can be split up into two terms,
where $T_s[n]$ can be described as the non-interacting kinetic energy term which can be calculated as a sum over independent orbitals. The non-interacting kinetic energy term is described as

$$T_s[n] = -\frac{1}{2} \sum_{i=1}^{N} \int d^3r \, \phi_i^*(r) \nabla^2 \phi_i(r), \quad (A.6)$$

or, rather, the expectation value of the momentum operator on a set of orbitals (known as the Kohn-Sham orbitals) $\phi_i(r)$. The second term, $T_c[n]$, is described as the correlation energy, which includes the non-independence of true wave functions in the system. This term will be absorbed into a new energy term described later.

We can also apply the Hartree approximation to the inter-electron coulomb interaction term. Splitting the electron-electron interaction gives

$$U[n] = U_H[n] + U_{xc}[n] \quad (A.7)$$

with

$$U_H[n] = \frac{1}{2} \int d^3r \, \int d^3r' \, \frac{n(r)n(r')}{|r - r'|}. \quad (A.8)$$

The $U_H[n]$ term arises from the direct electrostatic interaction of the charge density with itself. The term $U_{xc}[n]$ involves both correlation effects from the interdependence of the true system wavefunctions as well as exchange effects from the Hartree approximation. Although the correlation effects are very nuanced and difficult to describe, the exchange energy can be written exactly as

$$U_x[[\phi_i[n]]]$$
$$= -\frac{1}{2} \sum_{j,k} \int d^3r \, \int d^3r' \, \frac{\phi_j^*(r)\phi_k^*(r')\phi_j(r')\phi_k(r)}{|r - r'|}. \quad (A.9)$$
This formulation is identical to the exchange energy yielded by Hartree-Fock theory, only using the orbitals of Kohn and Sham. Knowing the exact form of the needed exchange correction adds insight to constructing density based versions of it, however the orbital based formulation cannot be implemented practically in a numerical calculation. Now equation (A.3) can be rewritten as

$$E[n] = T_s[[\phi_i[n]]] + U_H[n] + E_{xc}[n] + V_{ext}[n]$$  \hspace{1cm} (A.10)

where $E_{xc}$ consists of the exchange and correlation terms which arose in $T[n]$ and $U[n]$. Due to the nature of the Hohenberg-Kohn theorem, this term can also be formulated as a functional of the density.

With this form of $E[n]$ we can then go through the minimization with respect to density by the functional derivative

$$\frac{\delta E[n]}{\delta n(r)} = \mu = \frac{\delta T_s[n]}{\delta n(r)} + \frac{\delta U_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)} + \frac{\delta V_{ext}[n]}{\delta n(r)}$$

$$= \frac{\delta T_s[n]}{\delta n(r)} + v_H(r) + v_{xc}(r) + v_{ext}(r)$$  \hspace{1cm} (A.11)

where

$$v_H(r) = \int d^3r' \frac{n(r')}{|r - r'|}$$

$$v_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n}$$

$$v_{ext}(r) = \frac{\delta V_{ext}[n]}{\delta n}.$$  \hspace{1cm} (A.12)

The term $\mu$ is the chemical potential, and can be thought of as a Lagrange multiplier needed to keep the particle number fixed. Repeating this minimization for a single particle in an external field $v_{eff}(r)$ gives

$$\frac{\delta E[n]}{\delta n(r)} = \mu = \frac{\delta T_s[n]}{\delta n(r)} + \frac{\delta V_{eff}[n]}{\delta n(r)} + \frac{\delta T_s[n]}{\delta n(r)} + v_{eff}(r).$$  \hspace{1cm} (A.13)
Combining equations (A.11) and (A.13), we see that the same density solves both systems if we define $\nu_{\text{eff}}(r) \equiv \nu_H(r) + \nu_{xc}(r) + \nu_{\text{ext}}(r)$. Hence, the many-body picture can be reduced to the following single body Hamiltonian:

$$\left[-\frac{\nabla^2}{2} + \nu_{\text{eff}}(r)\right] \phi_n(r) = \epsilon_n \phi_n(r). \quad \text{(A.14)}$$

The density can then be reconstructed from equation (A.14) as

$$n(r) = \sum_i f_i |\phi_n(r)|^2 \quad \text{(A.15)}$$

where $f_i$ is the occupancy probability for each orbital. Once a density is constructed, it can be fed back into the Hartree and Exchange-Correlation potentials to yield a new set of orbitals. The process is repeated until the energy of the Kohn-Sham orbital system converges. This method is known as the self-consistent field algorithm. Once converged, the energy of the system can be obtained using the orbital energies from (A.14) in the following equation:

$$E_0 = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2} \int d^3 r \int d^3 r' n_0(r)n_0(r') \frac{n_0(r)n_0(r')}{|r - r'|} - \int d^3 r \nu_{xc}(n)n_0(r) + E_{xc}[n_0]. \quad \text{(A.16)}$$

The last three terms in equation (A.16) are necessary to correct for double counting of the Hartree potential and exchange and correlation effects.

Since (A.14) is a simple single particle Hamiltonian, the entire computationally impossible many-body problem has been reduced to a set of single body equations. Indeed, these equations, along with the density construction from (A.15), are solved for in density functional theory. These are known as the Kohn-Sham equations. The remaining challenge, however, is how to deal with the exchange and correlation functionals. These effects cannot be constructed exactly, so the question arises as to how to approximate them.
A.3 The Local Density Approximation

Historically, the first approximation for the kinetic energy of an electron gas (albeit a homogeneous one) was the Thomas-Fermi approximation,

$$t_s^{homo}(n) = \frac{3}{10} \left(3\pi^2 n\right)^{2/3}. \quad (A.17)$$

If we assume that the density, $n$, is constant for any point $r$ (i.e. slowly varying), equation (A.17) could approximate an inhomogeneous electronic system. However, compared to the orbital construction by Kohn and Sham, this kinetic energy is a very poor approximation except for systems with very homogeneous densities (such as Sodium).

The strength in this approximation arises when treating exchange and correlation energies. For a homogeneous electron gas, the exchange energy can be computed exactly, yielding

$$\nu_x(n) = -\frac{3}{4\pi} \left(3\pi^2\right)^{1/3}. \quad (A.18)$$

While no exact solution is known for the correlation energy Quantum Monte Carlo techniques have yielded a satisfactory approximation for $\nu_c(n)$ [121, 122]. The exchange and correlation energy can then be computed by assuming that $n$ varies slowly as in the Thomas-Fermi approximation, yielding

$$E_{xc}[n] = \int d^3r \ (\nu_x + \nu_c)n(r). \quad (A.19)$$

Even though the original Thomas-Fermi term is a poor choice for calculating the kinetic energy functional, its subsequent exchange and correlation energies have proven to work surprisingly well for many systems.
A.4 Current Exchange-Correlation Functionals

More modern exchange-correlation functionals go beyond the Local Density Approximation by including gradient terms. In Kohn and Sham’s original paper, the exchange-correlation energy was expanded about the local density picture as

\[
E_{xc}[n] = \int d^3r \, A_{xc}(n) \, n^{4/3} + \int d^3r \, C_{xc}(n) \, \frac{\nabla n}{n^{4/3}} + \ldots
\] (A.20)

where the first term can be recognized as the LDA term derived above. The inclusion of gradients was tried with varying success historically [123, 124], but rules relating to the mathematical rigor of the underlying theory would often break down.

In 1986, Perdew et al. introduced the Generalized Gradient Approximation (specifically the PW86 functional) [125, 126]. It was further improved five years later with the introduction of PW91 [127]. The main drawback of these functionals, however, was the need to fit a large parameter space to experiment. Perdew, Burke & Ernzhof minimized the parameter space in 1996 with the PBE functional [66]. This particular functional is immensely useful since it relies almost entirely on physical constants. The revised form of this functional (RPBE [128]), is most commonly used in simulations of solid systems today, and is used throughout the simulations concerning this dissertation.
References

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After graduating from Lawrence High School in 2002, Alejandro attended Rensselaer Polytechnic Institute (RPI) where he received a B.S. in Applied Physics in 2006. During the summer following graduation, he began working with Professor Jorge Sofo at The Pennsylvania State University.

While at Penn State, Alejandro developed a keen interest in outreach and education beyond his academic research interests. He has volunteered for a variety of outreach activities since 2007, including Exploration Day, NanoCamp summer camp for high schoolers, a WISE molecular modeling workshop, THON’s Wish program, and STEM day at Park Forest elementary school. He has also served as a judge for the Pennsylvania Junior Academy of Science, and a moderator for the Penn State McNair Summer Research Conference. He has also mentored undergraduate students as part of the Research Experience for Undergraduates (REU) program and through independent research projects.

Alejandro has received a number of fellowships and awards during his time at Penn State, including the Bunton-Waller Graduate Fellowship (2006-2008), the David C. Duncan Graduate Fellowship (2006-2008, 2010, 2011), and the CarbonEARTH fellowship (2010-1012). Specifically under the CarbonEARTH fellowship, Alejandro worked closely with Tammy Hatcher, a sixth grade teacher in the Harrisburg School District, to bolster her class’s science curriculum through the expertise gained by his research.