DIRECT FLUORINATION OF GRAPHENE: A THEORETICAL AND COMPUTATIONAL STUDY OF ITS FORMATION AND OF THE RESULTING MAGNETIC AND ELECTRONIC PROPERTIES

A Dissertation in
Physics
by
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Abstract

The adsorption of fluorine changes the electronic, mechanical, and magnetic properties of graphene. While graphene is an excellent conductor and a semimetal, fully fluorinated graphene is an insulating wide bandgap semiconductor. The electronic properties of graphene can be modified by controlling the adsorbate concentration to produce conducting, semiconducting or insulating components for nanoscale electronic devices.

The high electronegativity of fluorine makes it very reactive to the graphene sheet resulting in structures that are stable under ambient conditions. Moreover, recent reports of spin 1/2 paramagnetism in graphene has invigorated research efforts in this field due the possibility of spin transport devices.

While there is a lot of speculation about the origin of the spin, no clear theoretical explanation exists in the literature. Semi local DFT functionals predict that the fluorine adatom is non-magnetic, whereas calculations with hybrid functionals indicate a local moment of 1\(\mu_B\). However, neither approaches can explain the trends in the experimentally observed spin concentration as a function of fluorination percentage.

After an introduction in Chapter 1 and an overview of our methods in Chapter 2, in Chapter 3, using density functional theory (DFT) we show that in highly fluorinated graphene, small regions of unfluorinated carbon atoms produce localized magnetic states at the fermi-level. We study the shape and size dependence of these regions on the net spin and find that most odd clusters have a net spin of 1/2 while most even clusters have zero spin. We construct a minimal tight binding model that captures the low energy response of DFT and describes the localized magnetic states produced by the unfluorinated carbon atoms. This model is then solved exactly to include the effect of excited states in the magnetic response and go beyond the mean field predictions of DFT.

The model for magnetic carbon regions, when combined with large scale molecular dynamics methods that simulate the surface configurations formed upon
fluorination, can provide a theoretical description of the magnetic response of partially fluorinated samples. However, commonly used semilocal functionals do not provide a physically correct description of the interaction of dilute fluorine adsorption on graphene. These functionals predict a fractional charge on fluorine at a distance of 10Å from the surface (delocalization error), however at such large distances the fluorine atom should interact with the graphene sheet through weak Van Der Waals forces. Classical potentials that are fit to the incorrect behavior of DFT inherit these errors and produce inaccurate fluorine interactions in dynamical processes. We describe the limitations of these functionals in chapter 4 and provide a physical model that predicts a physically reasonable fluorine interaction behavior as a function of distance from the surface.

In chapter 5, we turn towards a reactive force field method, ReaxFF to simulate the fluorination of graphene. The screening effect of fluorine atoms already adsorbed on the surface causes the charge transfer to fluorine atom to be negligible beyond 5Å from the surface. This is important because the fluorine atoms will not be accelerated over large distances towards the surface. We study the adsorption process and surface configurations formed upon fluorination and find that though initially the attachment starts in a correlated fashion, we do not see the formation of large fluorographene ($CF$) like domains. The fluorine atoms adsorb at multiple sites over the lattice, with not enough time to diffuse and form domains. This creates several small unfluorinated carbon regions and applying the model developed in Chapter 3 overestimates the magnetic response.

In conclusion, the magnetic model developed in Chapter 3 is suitable for describing the magnetic response in highly fluorinated graphene with well defined domains of $CF$ like regions as described in Appendix A. For dynamical simulations that produce non-equilibrated configurations, the unfluorinated carbon atoms are not well localized and their interactions are likely to produce a different spin response. This being said, the classical potentials used to simulate the atomic configuration upon fluorination are dependent on DFT calculations of physical parameters like binding energy, charge, bond lengths, etc. Thus, a self interaction error free exchange correlation functional would provide an updated description of the dynamics and interaction on surfaces.
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Dedication

Dedicated to ..

Aquilles, Bharati, Christian, Petals, and Tito.
Chapter 1

Introduction

Carbon is one of the most abundant naturally occurring element that also forms the chemical basis of all known life forms. Its ability to form different kinds of bonds causes it to exist in different allotropic forms like graphite and diamond. The nature of the bond ($sp_2$ in graphite and $sp_3$ in diamond) determines the distinct physical and chemical properties of these allotropes. While graphite is highly conducting, soft and flaky and comprises of planar layers of carbon atoms stacked on top of each other, diamond has a tetrahedral structure and is one of the hardest known materials.

Imagine peeling off a graphite sheet with a scotch till it is possible to isolate a single layer. This single layer is composed of a hexagonal arrangement of $sp_2$ bonded carbon atoms called graphene. Graphene was first isolated in the laboratory by Andre Giem in 2004 [2]. However, it had existed for ages as a part of the graphite in pencils, for instance. The band structure of graphene already existed as text book examples, since it was first calculated by P. R. Wallace in 1947 as a first step to calculate the band structure of graphite [3]. It took a long time to discover graphene, partly because theoretically the existence of two dimensional crystals was considered impossible (due to diverging thermal fluctuations that makes the
structure thermodynamically unstable) and partly due to experimental challenges involved in observing a single layered structure [4,5].

Graphene is often regarded as the mother for other $sp_2$ bonded allotropic forms of carbon. It can be rolled to form quasi one dimensional cylinders or nanotubes [6], wrapped when combined with pentagonal rings to form zero dimensional point sized structures called "buckyballs" or fullerenes [7], and stacked one on top of the other to form 3D graphite.

An interesting feature in the band structure of graphene is that it has linear bands close to the Fermi level. The low energy excitations can be described by massless Dirac fermions similar to the massless fermions of Quantum Electrodynamics (QED). Thus graphene can act as an experimental test bed for many of the novel physics arising in QED. Moreover the charge carriers in graphene exhibit many interesting electronic effects, like, ambipolar electric field effect that can be continuously tuned by applying an external gate voltage [2,8], and extremely high room temperature carrier mobility compared to traditional electronic devices like Silicon MOSFETS [9].

These unique electronic properties of graphene provide a fertile field for future technological advancements and as such have been the topic of intense research interest since its discovery in 2004.

1.1 Functionalization of Graphene

Despite the linear band characteristics and high electron conductivity, there are several experimental challenges associated with designing graphene based electronics. One such challenge involves switching off the field emission transistor (FET) designed out of it. Because of the absence of a gap in the electronic spectrum of graphene, it becomes difficult to suppress the conductivity of the charge carriers. Several methods
have been tried to introduce a band gap in graphene including substrate interactions [10], quantum confinement in nanoribbons [11] and chemical modification through adsorption of atoms on the surface.

Adsorbed impurities play a very important role in the electronic structure of graphene. On one hand such impurities are more common compared to substitutional impurities due to the structural integrity of the sigma bonds that connect the carbon atoms in a plane. Even dilute concentrations of adsorbed impurities can affect the electronic structure and induce local magnetic moments on the surface [12]. These impurities modify the hybridization of the carbon atom at the binding site from $sp_2$ to $sp_3$ bonding, causing the $\pi$ bands of graphene to change. As the adsorbate concentration increases the material transitions from conducting to insulating through a variety of interesting intermediate states. This provides a means to tune the band gap and associated electronic properties by controlling the adsorbate concentration [13]. Changes in the electrical conductivity upon adsorption also finds useful technological applications for gas sensing on surfaces [14].

Though several kinds of adsorbate impurities have been studied including hydrogen [15, 16], fluorine [13, 17, 18], and oxygen [19], experimental reports of spin 1/2 paramagnetism in partially fluorinated graphene has created a recent stir in the research on fluorinated graphene [1]. Moreover, due to the extreme electronegativity of fluorine, it reacts much more easily with graphene compared to hydrogen. Fluorination has been achieved through a variety of techniques using $XeF_2$ gas [17, 18], $F_2$ gas [13], $CF_4$ plasma [20] and by exfoliating graphite fluoride [21]. The resulting structures are stable under ambient conditions. The versatile synthesis techniques and the promise of spin based nano electronics is a major motivation for research in fluorinated graphene.
1.2 Organization of Thesis

This thesis is laid out as follows. In Chapter 2, we provide an introduction to the theoretical and computational tools used in this study including the tight binding model, density functional theory (DFT), and ReaxFF. In Chapter 3, we study the electronic properties of highly fluorinated graphene in the presence of fluorine vacancies using DFT. We find that the unfluorinated carbon atoms at the vacancy sites have a local moment depending on their shape and size and could contribute to the spin 1/2 response seen in experiments with partially fluorinated graphene [1]. We model the low energy spectrum of DFT with a minimal Hubbard model involving the $p_z$ orbitals of the carbon atoms at the vacancy site. This model is solved exactly to study the effect of correlations beyond the mean field in the magnetic response of the unfluorinated carbon regions.

To obtain the theoretical magnetic response of partially fluorinated graphene, we need to combine the magnetic spin model with large scale simulations that predict the surface configurations formed as a result of the fluorination process. An energetics based Monte Carlo model for graphene fluorination is presented in the Appendix to compute the distribution of unfluorinated regions. The results are combined with the magnetic response from Chapter 3 and compared to experimentally measured spin moments.

The dynamics of fluorine interaction with graphene and the chemistry of bond formation and breaking, play an important role in the surface configurations formed during the fluorination process. Current theoretical structure calculation tools do not do a good job of describing the interaction between a fluorine atom and the graphene sheet, as it approaches the surface. In chapter 4, we present the DFT treatment of dilute fluorine adsorption on graphene and highlight the limitations of
semi-local functionals in describing the carbon fluorine bond as it is stretched. We show that these functionals predict an unphysical charge on the fluorine atom far from the surface. Using the image charge interaction from the surface, treated at the RPA level, we calculate the energy shifts in the electronic levels of the adsorbed fluorine atom. We find that the energy of the ionic state is lowered compared to the neutral state resulting in a neutral to ionic transition at 5Å from the surface.

In chapter 5, we use ReaxFF which is a classical force field to simulate the large scale fluorination of graphene. We analyze the charge transfer to the fluorine atoms during the molecular dynamics simulation and find that the fluorine atom is uncharged beyond a distance of 5Å from the surface. This ensures that the fluorine atom will not have an unphysical attraction to the surface over large distances. We study the adsorption isotherms and the surface configurations produced as a result of the dynamical simulation process. We combine the magnetic model of chapter 3 with the surface configurations produced with ReaxFF to predict the magnetic response and compare with experimentally measured spins. We conclude with Chapter 6 by discussing improvements to our model, summarizing the shortcomings of current electronic structure methods in describing the chemistry of dilute fluorine adsorption on graphene, and suggesting methods for addressing these challenges.
Chapter 2  |  Computational Methods

2.1 Graphene - Basics

Graphene is a two dimensional planar material composed of $sp^2$ hybridized carbon atoms arranged in a honeycomb or hexagonal lattice pattern. The unit cell of graphene is composed of two inequivalent carbon atoms site labelled sublattice A and B. The two sites are inequivalent because the orientation of the nearest neighbors about each site is rotated by $180^\circ$ with respect to each other. The lattice vectors in the unit cell can be represented by,

$$\vec{a}_1 = \left( \frac{3a}{2}, \frac{\sqrt{3}a}{2} \right)$$

(2.1)

$$\vec{a}_2 = \left( \frac{3a}{2}, -\frac{\sqrt{3}a}{2} \right)$$

(2.2)

where $a \sim 1.42\text{Å}$ is the carbon carbon atomic distance. The nearest neighbor distances in this orientation are given by,

$$\vec{d}_1 = \left( \frac{a}{2}, \frac{\sqrt{3}a}{2} \right)$$

(2.3)
\[ \vec{\delta}_2 = \left( \frac{a}{2} - \frac{\sqrt{3}a}{2} \right) \]  

(2.4)

\[ \vec{\delta}_3 = \left( -a, 0 \right) \]  

(2.5)

Figure 2.1. Honeycomb lattice of graphene

Each carbon atom in the lattice has a non-bonded \( p_z \) orbital and the key features in the band structure can be obtained through a tight binding model involving these orbitals.

2.2 Tight Binding Model

Solving the full many body Hamiltonian for \( N \) electrons in a solid is a challenging computational problem. In the case that the electrons are tightly bound to the nuclei at the lattice sites, with a finite probability of jumping to neighboring sites, one can use the Tight Binding model to obtain a fairly accurate description of the
band structure. The Hamiltonian of the crystal is represented by,

\[ H(r) = H_{at} + \Delta U(r) \]  \hspace{1cm} (2.6)

where \( H_{at} \) is the atomic Hamiltonian at a given lattice site and \( \Delta U(r) \) is the deviation from the atomic potential due to the presence of the other nuclei in the crystal. Since this Hamiltonian is periodic on the crystal lattice, its eigen functions should also satisfy the same periodicity condition upon translation by a lattice vector. In other words, the eigen function should be of bloch form. For a crystal lattice with \( N \) unit cells the bloch wave function can be written as,

\[ \Phi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \Phi_j(\vec{r} - \vec{R}) \]  \hspace{1cm} (2.7)

\( \vec{R} \) corresponds to the position vector of a site on the lattice. The total wave function can now be written as a linear combination of atomic orbitals per cell. If there are \( m \) orbitals per cell,

\[ \Psi_i(\vec{k}, \vec{r}) = \sum_{j=1}^{m} c_{i,j}(k) \Phi_j(\vec{k}, \vec{r}) \]  \hspace{1cm} (2.8)

The \( j^{th} \) eigen value can be obtained by solving the following eigen value equation,

\[ E_j(k) = \frac{\langle \Psi_j | H(r) | \Psi_j \rangle}{\langle \Psi_j | \Psi_j \rangle} \]  \hspace{1cm} (2.9)

By substituting equation 2.8 in the above expression,

\[ E_j(k) = \frac{\sum_{i',\nu} c_{j,i'}^{\ast} c_{j,i} \langle \Phi_{i'} | H | \Phi_i \rangle}{\sum_{i',\nu} c_{j,i'}^{\ast} c_{j,i} \langle \Phi_{i'} | \Phi_i \rangle} \]  \hspace{1cm} (2.10)
The terms $\langle \Phi_i | H | \Phi_i \rangle$ and $\langle \Phi_i | \Phi_i \rangle$ correspond to the transfer integral matrix $H_{t,i}$ and the overlap integral matrix $S_{t,i}$, respectively. Minimizing the above energy expression we get,

$$\sum_{i=1}^{m} H_{t,i} c_{j,i} = E_j \sum_{i=1}^{m} S_{t,i} c_{j,i}$$  \hspace{1cm} (2.11)

Writing $\Psi_j = [c_{j_1}, c_{j_2}, \ldots, c_{j_m}]^T$, we get the following matrix equation.

$$H \Psi_j = E_j S \Psi_j$$  \hspace{1cm} (2.12)

and the energy eigen values and hence the band structure can be determined by solving the secular equation,

$$\text{det}(H - ES) = 0$$  \hspace{1cm} (2.13)

### 2.2.1 Tight Binding in monolayer Graphene

Since there are two $sp^2$ bonded carbon atoms per unit cell of graphene, the Bloch wave function can be constructed from a linear combination of the $p_z$ orbitals at site A and site B, respectively.

$$\Psi_i(k, r) = \sum_{j=1,2} c_{ij} \Phi_j(k, r) = c_A \Phi_A(k, r) + c_B \Phi_B(k, r)$$  \hspace{1cm} (2.14)

The transfer matrix elements are as follows,

$$\begin{bmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{bmatrix}$$
The diagonal matrix element corresponding to sub lattice A is given by,

\[ H_{AA} = \frac{1}{N} \sum_{R,R'} e^{ik(R-R')} \langle \Phi_A(r-R') | H | \Phi_A(r-R) \rangle \]  

(2.15)

With the nearest neighbor approximation, the main contribution to this term comes from \( R = R' \),

\[ H_{AA} = \frac{1}{N} \sum_{R} \langle \Phi_A(r-R) | H | \Phi_A(r-R) \rangle = \epsilon_0 \]  

(2.16)

This gives us the onsite energy and for undoped graphene \( H_{AA} = H_{BB} = \epsilon_0 \). The off-diagonal terms describe electron hopping between neighboring sites,

\[ H_{AB} = \frac{1}{N} \sum_{R_A, R_B} e^{ik(R_B-R_A)} \langle \Phi_A(r-R_A) | H | \Phi(r-R_B') \rangle \]  

(2.17)

Using nearest neighbor approximation,

\[ H_{AB} = \frac{1}{N} \sum_{R,i} e^{ik \delta_i} \langle \Phi_A(r-R_A) | H | \Phi(r-R_B) \rangle, \]

\[ = \frac{1}{N} \sum_{R} \sum_{i} \gamma_0 e^{ik \delta_i}, \]

\[ = \gamma_0 f(k_x, k_y) \]  

(2.18)

where \( \gamma_0 = \langle \Phi_A(r-R_A) | H | \Phi(r-R_B) \rangle \), is the strength of the hopping parameter between neighboring sites. The index \( i \) runs over the three nearest neighbor atoms at sublattice A as described in equations (2.3) to (2.5). \( f(k_x, k_y) \) can be explicitly written as follows,

\[ f(k_x, k_y) = e^{i \frac{\pi}{2} k_x a + i \frac{\pi}{2} k_y a} + e^{i \frac{\pi}{2} k_x a - i \frac{\pi}{2} k_y a} + e^{-ik_x a} \]  

(2.19)
Thus the transfer matrix and the overlap matrix can be written as follows,

\[
H = \begin{bmatrix} \epsilon_0 & \gamma_0 f(k_x, k_y) \\ \gamma_0 f^*(k_x, k_y) & \epsilon_0 \end{bmatrix}
\]

\[
S = \begin{bmatrix} 1 & s f(k_x, k_y) \\ s f^*(k_x, k_y) & 1 \end{bmatrix}
\]

Solving the secular equation (2.13), and using the fact the overlap between neighboring sites \( s \) is small,

\[
E(k) = \frac{\epsilon_0 \pm \gamma_0 |f(k_x, k_y)|}{1 \pm s|f(k_x, k_y)|} \quad (2.20)
\]

\[
\simeq \epsilon_0 \pm \gamma_0 |f(k_x, k_y)| \quad (2.21)
\]

The band structure of graphene for \( \gamma_0 = -2.8eV \) and setting the reference energy level at \( \epsilon_0 = 0 \) is show in figure 2.2. The key feature in the band structure is the linear relationship close to the Dirac points: \( K = \left( \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}} \right) \), \( K' = \left( \frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}} \right) \). This can be obtained by expanding the energy dispersion relationship in a Taylor series expansion about either of the Dirac points. Expanding \( E(K+q) \) for small \( q \),

\[
E(q) = \frac{3\gamma_0 a}{2} |q|.
\]
2.3 Density Functional Theory

Density Functional Theory is the most popular quantum mechanics based method used in computational physics and chemistry to obtain the ground state structure and energy of atoms, molecules and condensed matter systems.

2.3.1 Many Body Equations

The electronic structure of many body systems can be obtained by solving the Schrodinger equation,

$$H\Psi(\vec{r}, \vec{R}) = E\Psi(\vec{r}, \vec{R}).$$

(2.22)
where \( \vec{r}, \vec{R} \) represents the coordinates of the \( N \) electrons and \( M \) nuclei comprising the system. The Hamiltonian \( H \) is equal to,

\[
H = T_n + V_{nn} + T_e + V_{ee} + V_{ne},
\]

\[
= -\frac{\hbar^2}{2M_I} \sum_{I=1}^{M} \nabla^2 + \frac{1}{2} \sum_{I=1}^{M} \sum_{J \neq I} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} - \frac{\hbar^2}{2m_e} \sum_{I=1}^{N} \nabla^2 +
\]

\[
\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^{N} \sum_{J=1}^{M} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_J|}.
\]

(2.24)

The first two terms in eq. (2.24), \((T_n, V_{nn})\) represent the total kinetic and coulomb energy of the \( M \) ions, the third and fourth terms \((T_e, V_{ee})\) represent the total kinetic and coulomb interaction energy of the \( N \) electrons and the last term \((V_{ne})\) represents the interaction between the electrons and the ions in the system.

Typically, the mass of the ions is much heavier than that of the electrons. This means that the electrons can move quickly and adiabatically adjust to changes in the ionic configuration. Thus the electrons can be assumed to be moving in a constant energy surface produced by a fixed ionic configuration. This is known as the Born-Oppenheimer approximation [22]. Using this approximation the electronic and ionic degrees of freedom can be separated in the above Hamiltonian. Writing the total wave function as a product of the nuclear and electronic wave function, \( \Psi(\vec{r}, \vec{R}) = \Psi_{e,R}(r)\Psi(R) \), the electronic part of the Schrodinger equation decouples to,

\[
H_{e,R} \Psi_{e,R}(r) = E_{e,R} \Psi_{e,R}(r),
\]

(2.25)

with the electronic Hamiltonian written as,

\[
H_{e,R} = -\frac{\hbar^2}{2m_e} \sum_{I=1}^{N} \nabla^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^{N} \sum_{J=1}^{M} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_J|}.
\]

(2.26)
\[ E_{HK}[n(r)] = T_e[n(r)] + V_{ee}[n(r)] + \int v_{ext}n(r)dr, \]
\[ = F_{HK}[n] + V_{ext}[n]. \] (2.28)

where \( T_e \) is the electronic kinetic energy, \( V_{ee} \) is the repulsive electron-electron coulomb interaction and \( V_{ext}(r, R) \) is the interaction of the electron with the external fixed potential of the nucleus. Note that the first two terms in the above equation are system independent and describe the total energy of a system of \( N \) interacting electrons. The only term that depends on the system is the interaction with the external potential, \( V_{ext}(r, R) \).

Even at this point solving the electronic Hamiltonian involves \( 3N \) degrees of freedom with the added complication of electron electron interactions included in the \( V_{ee} \) term. It is impossible to solve this equation exactly for systems beyond a few electrons in size.

### 2.3.2 Hohenberg Kohn Theorems

In 1964 Hohenberg and Kohn came up with a recipe that significantly reduces the complexity of the above equations [23]. The main idea behind these theorems involve reformulating the Hamiltonian in eq. (2.27) in terms of functionals of the charge density of the electrons. According to the Hohenberg Kohn Theorems, given a system of interacting particles, the ground state charge density uniquely determines the external potential \( v_{ext}(r) \) to an additive constant. Secondly, the total energy of the system can be expressed as the sum of the electron charge density.

\[ E_{HK}[n(r)] = T_e[n(r)] + V_{ee}[n(r)] + \int v_{ext}n(r)dr, \]
\[ = F_{HK}[n] + V_{ext}[n]. \] (2.28)
where $v_{\text{ext}}(r) = \sum_I \frac{Z_{Ie}}{|r-R_I|}$ is the external potential of the ions and $F_{HK}$ is the system independent kinetic and coulomb interaction energy of the electrons. The ground state charge density can be obtained by minimizing the total energy with respect to the charge density using the variational principle,

$$E[n_0] = \min_{\Psi \rightarrow n} \langle \Psi | F_{HK} + V_{\text{ext}} | \psi \rangle.$$  \hspace{1cm} (2.29)

Though the Hohenberg Kohn Theorems guarantees the existence of a three dimensional ground state charge density $n_0(r)$ that minimizes the total energy, and significantly simplifies the original $3N$ dimensional electronic problem, it does not provide an explicitly solvable form for the total energy functional.

### 2.3.3 Kohn Sham Equations

In 1965, Kohn and Sham provided a practical means to compute the ground state energy and charge density by reformulating the energy functionals in eq. (2.28) into a single particle Schrodinger equation [24]. The total kinetic energy of the interacting electron system can be written as

$$T_e[n] = T_s[n] + T_c[n].$$  \hspace{1cm} (2.30)

$T_s[n]$ represents the kinetic energy of $N$ independent electrons and the term $T_c[n]$ includes the correlation effects that a rise from the interdependence of the electrons in the many body system. The single particle kinetic energy can be calculated as,

$$T_s[n(r)] = -\frac{1}{2} \sum_i \int d^3r \Phi'_i(r) \nabla^2 \Phi_i(r),$$  \hspace{1cm} (2.31)
where $\Phi_i(r)$, also known as the Kohn Sham orbitals, are single particle states that solve the Kohn Sham equations described later. Similarly the coulomb interaction between the electrons can be written as,

$$V_{ee}[n] = V_H[n] + V_{xc}[n], \quad (2.32)$$

where, $V_H[n]$ is the hatree potential due to the classical interaction between two charge densities,

$$V_H = \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r - r'|}. \quad (2.33)$$

and $V_{xc}[n]$ includes exchange and correlation effects not included in the Hatree potential due to the interdependence of the true electron wave functions. With these definitions the total energy of the system can be written as

$$E[n] = T_s[n] + V_H[n] + E_{xc}[n] + V_{ext}[n]. \quad (2.34)$$

Here $E_{xc}[n]$ includes the exchange and correlation effects arising from the kinetic energy as well as from the coulomb interaction between the electrons. The exact form of the exchange correlation functionals are not known and success or failure of the theory depends on the kind of approximations that are used to deal with this term in a specific situation. The ground state density can now be found by minimizing the above energy functional using the variational principle and under the constraint of fixed $N = \int d^3r n(r)$,

$$\frac{\delta E[n]}{\delta n(r)} = \lambda = \frac{\delta T_s[n]}{\delta n(r)} + \frac{\delta V_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)} + \frac{\delta V_{ext}[n]}{\delta n(r)}, \quad (2.35)$$

$$= \frac{\delta T_s[n]}{\delta n(r)} + v_H(r) + v_{xc}(r) + v_{ext}(r), \quad (2.36)$$
where,

the Hatree potential, \( v_H(r) = \int d^3r \frac{n(r)}{|r - r'|} \), \( (2.37) \)

the exchange correlation potential, \( v_{xc} = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \), \( (2.38) \)

and the external potential, \( v_{ext}(r) = \sum_I \int d^3r \frac{Z_I e}{|r - R_I|} n(r) \). \( (2.39) \)

\( \lambda \) is the Lagrange multiplier that was introduced through the constraint and acts as the chemical potential of the system. Kohn and Sham proposed that the above equations could be solved by replacing the many body potentials of the interacting system by a single particle effective potential, \( V_{KS}(r) \), that produces the same ground state charge density as the original problem. According to the Hohenberg Kohn Theorems this potential uniquely describes the many body system and produces the correct ground state energy. Thus,

\[
\frac{\delta E[n]}{\delta n(r)} = \lambda \frac{\delta T_s[n]}{\delta n(r)} + v_H(r) + v_{xc}(r) + v_{ext}(r),
\]

\( (2.40) \)

\[
= \frac{\delta T_s[n]}{\delta n(r)} + v_{KS}(r).
\]

\( (2.41) \)

with the Kohn Sham potential \( v_{KS}(r) = v_H(r) + v_{xc}(r) + v_{ext}(r) \). Since minimizing the energy with respect to the charge density is the same problem as solving the Schrödinger equation, all we need to do now is solve the single particle Kohn Sham equation

\[
\left(-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}(r)\right) \Phi_i(r) = \epsilon_i \Phi_i(r)
\]

\( (2.42) \)

where \( n(r) = \sum_i \int d^3r |\phi_i(r)|^2 \). The ground state calculation starts from a set of precomputed orbitals, which are used to determine the starting charge density. These are then used to determine the Kohn Sham potential, \( v_{KS} = v_H + v_{xc} + v_{ext} \).
and solve the single particle Schrodinger equation to obtain a new set of orbitals and charge density. The entire process is repeated till the difference between the final and initial starting densities fall below a numerically defined tolerance. The ground state energy is then calculated from the converged charge density. This process is known as the self consistent field method.

### 2.3.4 Exchange Correlation Functionals

While the exact form of the exchange correlation functionals are unknown, many approximations exist in the current implementations of DFT to deal with the complicated electron electron interactions embodied in them. The first of these approximations known as the Local Density Approximation (LDA) was introduced by Kohn and Sham itself, and comprises of replacing the exchange correlation energy with that of a uniform electron gas with the same density.

\[
E^{LDA}_{xc}[n(r)] = \int d^3r \epsilon^{\text{unif}}_x (r) n(r),
\]

and the exchange correlation potential is given by,

\[
v_{xc}(r) = \frac{\delta E^{LDA}_{xc}[n(r)]}{\delta n(r)} = \epsilon^{\text{unif}}_x [n(r)] + n(r) \frac{\delta \epsilon^{\text{unif}}_x [n(r)]}{\delta n(r)}.
\]

Here \( \epsilon^{\text{unif}}_x \) is the exchange correlation potential of the uniform gas. The analytical expression of the exchange energy of a uniform is given by,

\[
U^x_{\text{unif}} = \frac{-3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int d^3r n(r)^{4/3}.
\]
However, no exact expressions exist for the correlation effects, which are obtained numerically by fitting to highly accurate quantum monte carlo calculations [25]. Based on the parameters of these calculations several LDA exchange correlation functionals were developed, most common of them being Perdew-Zunger (PZ) [26] and Perdew-Wang(PW) [27] functionals. The applications of the LDA functionals are limited by the fact that it assumes a uniform density of the electron gas. In general LDA functionals underestimate the bond lengths and overestimates the bond energies. Further improvements are achieved by including the local gradient of the charge density in the formalism of the exchange correlation functionals. The resulting functionals are called Generalized Gradient Approximations (GGA) and are represented by,

\[
E_{xc}^{GGA}[n(r)] = \int d^3r \epsilon_{xc}^{GGA}[n(r), \nabla n(r)].
\]  

(2.46)

Though several formulations of the above functionals exist, that commonly used for treatment of surfaces as well as in this work is the exchange correlation potentials developed by Perdew, Burke and Ernzerhof [28].

2.4 ReaxFF

ReaxFF is a reactive classical force field originally developed by Adri van Duin, William A. Goddard, III and co-workers to simulate complex chemical reactions in hydrocarbons [29]. Since then it has been extended to include several other elements on the periodic table and its estimated usage is over 125 research groups around the globe (see Fig. 2.3) [30]. It can be used to perform molecular dynamics on systems with over thousands of atoms with a computational cost that is several
orders of magnitude lower than quantum chemistry based methods [30]. The major advantage of ReaxFF over traditional force field based methods [31, 32] is the ability to simulate the chemistry of bond breaking and formation during molecular dynamics simulations. This is accomplished by making bond energies dependent on bond order so as to get a smooth transition from bonded to non-bonded state. Bond orders are calculated based on bond distances for every iteration and also adjusted to compensate for over and under coordination of atoms.

**Figure 2.3.** Current implementation of ReaxFF force fields.

The total energy of the system is obtained as a sum of partial contributions of bonded and non bonded interactions. Long range interactions like Coulomb and Vander-Waals interactions are included in the energy contributions and excessive close range interactions are avoided by using a shielding term in the energy expression[]. Charges are computed using the electronegativity equalization method of Mortier[]. ReaxFF force fields are parametrized against Quantum Chemistry data from density functional calculations on relevant systems. Once the force field has been developed
It can be used to study the dynamics and chemistry under different physical conditions like temperature and pressure. Moreover, new parameters from DFT calculations can be systematically incorporated to make the force fields more robust as research progresses.
Chapter 3
Fluorine Vacancy Induced Magnetism in Fluorographene

3.1 Introduction

Since the discovery of graphene by the Manchester group in UK in 2004, many efforts have been made to modify and tune its electronic properties for the fabrication of nanoscale devices [33]. These efforts include the adsorption of atoms on the surface to open a band gap and control the size of the gap. As the impurity atom bonds with the planar \( sp^2 \) carbon in graphene, it removes the \( p_z \) orbital of the intrinsic material from the Fermi-level through a bonding, anti-bonding scheme. The resulting material transitions from conducting to insulating through a series of interesting intermediate regimes [13,16]. Several adsorbates have been used including oxygen and hydrogen however, fluorine continues to be a practical candidate for band gap manipulation, due to the ease with which it combines with carbon [17,18].

Another interesting effect of the adatom adsorption is the formation of a
localized moment at the adsorption site [34–38]. The magnetic structure of the adsorbed impurity has been studied for hydrogen and fluorine adatoms on graphene using ab-initio calculations and explained through the Anderson-Hubbard impurity model [39,40]. These calculations indicate that unlike hydrogen, the fluorine adatom does not acquire a magnetic moment upon adsorption. Moreover, fully fluorinated graphene or fluorographene is predicted to be a wideband gap semiconductor (band gap $\approx 3.5eV$ at $\Gamma$) and as such expected to be non-magnetic [41–43]. Hence, recent experimental measurements showing that partially fluorinated graphene behaves like a spin 1/2 paramagnet has come as a surprise [1]. While this new discovery has exciting implications for the future of two-dimensional magnetic spin storage and transport devices, it brings with it the challenge of understanding the source of the paramagnetic centers. In the following section, we provide some details about the experiment leading to the discovery of spin 1/2 moments in partially fluorinated graphene followed by a discussion about efforts to understand the origin of these spins.

### 3.2 Background

In the experiment described by Nair et al. in [1], the static magnetization and low temperature susceptibility of partially fluorinated graphene is measured using a SQUID magnetometer. Samples large enough to perform these measurements are obtained by using graphene laminates that are prepared by the ultrasonic cleavage of highly oriented pyrolytic graphite (HPOG). These samples are 1-2cm in diameter and show weak background diamagnetism [44]. They are fluorinated by heating in an atmosphere of xenon-difluoride ($XeF_2$) in a Teflon container at $200^\circ C$. As the fluorine obtained from the decomposition of $XeF_2$ combines with the graphene
laminate, the percentage of fluorination is monitored by the physical color change from metallic grey to yellow. Different levels of fluorination are obtained by simply pulling out the sample at different time intervals. Qualitative and quantitative estimates of the fluorine percentage is obtained by Raman spectroscopy and XPS measurements respectively.

It is found that irrespective of the fluorination percentage the response is always spin 1/2 paramagnetic and no signatures of magnetic ordering between the spins are found down to 2K temperature. The magnetization $M(T, H)$ of $N$ non-interacting spins, with angular momentum $J$, in an externally applied magnetic field $H$ and at a temperature $T$, can be described by the Brillouin function $B_J(T, H)$.

$$M(x) = Ng\mu_B JB_J(x). \quad (3.1)$$

Where,

$$B_J(x) = \frac{2J + 1}{2J} \coth\left(\frac{2J + 1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right), \quad (3.2)$$

with, $x = \frac{g\mu_B J H}{k_B T}$. \quad (3.3)

The symbols $k_B$, $\mu_B$, and $g$ are the Boltzmann constant, Bohr magneton and Lande’s g-factor respectively. The low and high field behavior can be extracted by expanding the hyperbolic function in terms of its argument.

At low fields,

$$x << 1; \ \coth(x) = \frac{1}{x} + \frac{x}{3}, \quad (3.4)$$

$$B_J(x) = \frac{x J + 1}{3} \frac{J}{J}, \quad (3.5)$$

$$M(T, H) = Ng^2\mu_B^2 \frac{J(J + 1)}{3} \frac{H}{k_B T}. \quad (3.6)$$

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At high fields,

\[ x \gg 1; \quad \coth(x) = 1, \]  
\[ M = N g \mu_B J. \]

Thus, the magnetization has a linear dependence on the applied field for low fields, saturating to a constant at higher values. For the magnetization measurements in partially fluorinated graphene, best description of the observed data is obtained for \( J = S = 1/2 \), or for a free electron spin (Figure 3.1). All other values of \( J \) do not agree with the functional form of the observed data, producing sharper changes and quicker saturation.

![Figure 3.1. Magnetization as a function of the externally applied static magnetic field for samples with different fluorination percentages as shown in Figure 2 of [1]](image)

The number of spins \( N_s \), extracted from the magnetization data is plotted as a
function of the fluorination percentage as shown in Figure 3.2. We can see that the concentration of spins is very low: about 1 spin per 1000 fluorine atoms. For fluorine coverages below 50%, the spin concentration barely changes. Thereafter the spin concentration slowly increases before reaching a peak and falling off at the 85% fluorination percentage. As we have mentioned previously, DFT calculations using local density functionals do not attribute a spin to the fluorine adatom. However, non-local approaches using Hybrid functionals show that the fluorine adatom could acquire a spin on being adsorbed [45]. However, if this were the case, the experimental data should have had a linear increase in spin concentration with fluorine coverage at least for low fluorine concentrations. From Figure 3.2 we can see that this is not the case.

![Graph](image)

**Figure 3.2.** The number of spins per fluorine extracted from Brillouin function fits to the magnetization data and plotted as a function of fluorination percentage. Recreated from [1]

Instead of attributing the spins to fluorine adatoms, one can look at the regions of unfluorinated carbon atoms as the source of spins. In the highly fluorinated
regime, it is easy to imagine that there will be regions containing one, two or more unfluorinated carbon atoms. The magnetic properties of such defects have been studied for single hydrogen vacancies in graphane and found to carry a magnetic moment of $1\mu_B$ per defect [46, 47]. Similarly, a single unfluorinated carbon atom attached to surrounding fluorographene, should be $sp_2$ hybridized, have a non-bonded $p_z$ orbital and thus an unpaired spin 1/2 electron. Carrying this analogy forward, an unfluorinated region with odd number of carbon atoms, $n$, could have a total spin between 1/2 to $n/2$.

In this chapter, we explore the relationship between the size and shape of the unfluorinated carbon regions and their resulting spin. Using a first principles approach, we start with ground state electronic calculations and study the net spin of different unfluorinated carbon structures in fluorographene. Later on in this chapter, we map the low energy features of the DFT spectrum pertaining to localized states of the these regions to a minimal tight binding Hubbard model. The Kohn-Sham orbitals of DFT are single particle states that provide a good description of the ground state properties, however fail to describe the excited states well. In the presence of an external magnetic field, these excited states could play an important role in the magnetic response. Since our model is exactly solvable we can find the excited states without using expensive time dependent DFT calculations. In this way we go beyond the mean field calculations of DFT in making predictions about the magnetic response in an externally applied static field. Rules regarding the shape and size dependence of the magnetization per unfluorinated region, when combined with large scale molecular dynamics simulations that enable us to count the shape, size, and number distribution, will help answer questions about the magnetic response of partially fluorinated graphene from a theoretical standpoint.
3.3 Ab-intio calculations

3.3.1 Method

In our study we look at simply connected regions of unfluorinated carbon atoms in fluorographene. Starting from a $5 \times 5$ fluorographene supercell we generate structures of the form $-(C_{50}F_{50-x})-$ by removing $x$ number of fluorine atoms from the cell (see Figure 3.3). All our calculations are performed using the DMOL$^3$ implementation of DFT [48–51], and all structures are properly relaxed so that they are in their equilibrium configuration. We use a vacuum of $20\text{Å}$ in the $z$ direction to prevent interaction between images. We use the PBE functional to treat exchange correlation effects and an all electron treatment of the core electrons with no relativistic effects [28]. Dmol$^3$ uses numerically generated atomic orbitals as basis set in the electronic calculations. We use a double numeric precision plus polarization (DNP) basis set with a cut off radius of $3.7\text{Å}$. To calculate the energy and orbital populations we performed spin unrestricted calculations using a $3 \times 3$ k-points grid. To calculate the density of states and spin density properties we used a much denser $9 \times 9$ grid.

3.3.2 Results

Our calculations show that all structures with an odd number of unfluorinated carbon atoms have a net spin of $1/2$. Not surprisingly most structures with even number of unfluorinated carbon atoms have a net spin of zero. Looking at the spin density map, we can see that the spin is localized on the unfluorinated carbon atoms confirming our assertion that in flurographene, unfluorinated carbon regions contribute to a net spin (see Figure 3.4). The spin density map also shows that
on neighboring carbon atoms the spin is oppositely oriented indicating that the nearest neighbor spin correlation is antiferromagnetic.

The confinement of the non-bonded $p_z$ orbitals of the unfluorinated carbon atoms by the surrounding fluorographene structure, cause these impurity states to be localized within the band gap of fluorographene (See the partial density of states projected onto the unfluorinated carbon atoms in Figure 3.5). For most even structures these localized states are spin paired upto the Fermi level resulting in zero net spin per structure. However, for the odd structures there exists one spin unpaired state at the Fermi level resulting in a net spin of $1/2$ per structure. The only exception is the C50F46star structure. Even though this structure has an even number of unpaired electrons, because of its unique geometry there is a degenerate
Figure 3.4. Spin density map for magnetic structures. Blue and red represent the spin down and spin up density isosurfaces with isovalue of $0.05e/\text{Å}^3$. From left to right, i) Single vacancy ($C_{50}F_{49}$), ii) Three vacancy chain ($C_{50}F_{47}$) iii) Four vacancy star ($C_{50}F_{46}\text{star}$), iv) Five vacancy chain ($C_{50}F_{45}\text{chain}$), v) Five vacancy boat ($C_{50}F_{45}\text{boat}$).

spin unpaired localized state at the Fermi level leading to a net spin of 1.

3.4 Exact Electron Interactions Beyond Mean Field

3.4.1 Set Up of Hubbard Model to Describe Unfluorinated Carbon Atoms

In the previous section we saw that the net magnetic moment due to the unfluorinated carbon region originates from the localization of the non-bonded $p_z$ orbitals close to the Fermi level of the material. Hence we can model the magnetic response of these regions by constructing a simple model involving the $p_z$ orbitals of the unfluorinated carbon atoms alone. We start with a standard tight binding approach describing the nearest neighbor hopping between sites and incorporate an onsite Hubbard term to describe the electrostatic repulsion between electrons occupying the same site.

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c^\dagger_{i \sigma} c_{j \sigma} + c^\dagger_{j \sigma} c_{i \sigma}) + U \sum_i n_{i \uparrow} n_{i \downarrow} \quad (3.9)$$
Figure 3.5. Partial (p-projected) density of states projected onto the unfluorinated carbon atom sites. Black and red colors indicate the spin up and spin down states respectively. Blue dashed line is added to indicate the Fermi level clearly. Peaks in the local density of states close to the Fermi level is associated with the non-bonded $p_z$ orbitals of unfluorinated carbon atoms. From left to right - i) Three vacancy chain, ii) Four vacancy chain, iii) Four vacancy star.

Here $c_i^\dagger / c_i$ represents the creation and annihilation operator at site $i$ and the symbol $< i, j >$ indicates that the sum is carried out over nearest neighbor sites only. $n_i$ is the number operator at site $i$. $U$ and $t$ are model parameters that represent the strength of the onsite Coulomb repulsion and the nearest neighbor hopping, respectively.
3.4.1.1 Method

We extract parameters for our model by comparing with DFT results from the previous section. Since DFT is at the mean field level of theory, we simplify the many body Hubbard term using the Hatree-Fock approximation.

\[ Un_{i\uparrow}n_{i\downarrow} \approx Un_{i\uparrow} < n_{i\downarrow} > + U < n_{i\uparrow} > n_{i\downarrow} - U < n_{i\uparrow} > n_{i\downarrow} > \] (3.10)

The last term in this expression represents a constant energy shift in the energy levels that does not affect the local moment formation and hence is dropped from the calculation. With this approximation the above Hamiltonian can be written like the following single particle operator.

\[ H = -t \sum_{<i,j>} (\bar{c}_{i\sigma} c_{j\sigma} + \bar{c}_{j\sigma} c_{i\sigma}) + U \sum_i n_{i\sigma} < n_{i\bar{\sigma}} > \] (3.11)

To obtain the eigenvalues and eigenvectors of this Hamiltonian, we start with some initial values of the spin up and spin down site occupations, \((n_{i\sigma}, n_{i\bar{\sigma}})\), and plug into the Schrodinger equation,

\[ H_\sigma |\Psi_{n\sigma}\rangle = E_{n\sigma}(\{n_{i\bar{\sigma}}\}) |\Psi_{n\sigma}\rangle, \] (3.12)

with,

\[ |\Psi_{n,\sigma}\rangle = \sum_i c_{n,i\sigma} |i \sigma\rangle \] (3.13)

The new site occupations can be calculated from the density of states (DOS) and local (site projected) density of states (LDOS) as follows,

\[ DOS_\sigma = \sum_n \delta(E - E_{n\sigma}(\{n_{i\bar{\sigma}}\})) \] (3.14)
This process is repeated till the site occupations converge to within a small tolerance. The parameters $U$ and $t$ are extracted from the DFT calculations by using a least square fit technique. We use the distance between the discrete eigenvalues obtained by solving the model and the energies indicated by the localized impurity state peaks in the DFT partial density of states (PDOS) as the fitting criteria.

### 3.4.1.2 Results

Starting from the single vacancy DFT PDOS, we can directly read the value of $U$ from the energy difference between the spin split localized states at the Fermi level (see Figure 3.6). From the double vacancy PDOS we independently determine the value of $U$ and the two site hopping parameter $t$. The extracted value of $U$ is in close agreement with that obtained for the single site. To show the effectiveness of our model in capturing the key features in the low energy DFT spectrum we plot the Tight binding (TB) density of states overlaid with the DFT density of states. The density of states obtained from the TB model (3.14) is plotted using a Gaussian function with an arbitrary broadening.

For structures with more than two unfluorinated sites, the outer carbon atoms have a higher electron population compared to the inner sites. This effect has been reported previously in [52]. In short, the high electronegativity of fluorine atoms cause a significant charge transfer from carbon to fluorine. The positively charged carbon atoms sit at a lower potential energy relative to vacuum as compared to the carbon atoms in graphane. This implies that the edge carbon atoms that are
Figure 3.6. Extracting parameters from DFT. From L to R, i) Shows the DFT DOS (Black and Red for spin up and down respectively) projected onto the single vacancy site overlaid with the total DOS (Light green and blue for spin up and spin down respectively). The height of the PDOS is exaggerated to make the features visible. ii) Shows the PDOS projected on the double vacancy site. Red and Black colors represent the spin up and down states. The TB density of states (dark green) is overlaid to show the fitting and the fitted parameters \((U, t)\) are indicated in the table on the left.

connected to two fluorinated carbon neighbors will be at a lower potential energy compared to the carbon atoms in the interior of the structure that are connected to one to zero fluorinated carbon neighbors. We know that the site occupations can be found from the local density of states using (3.16). When we calculate the occupations from the PDOS projected on the outer and inner unfluorinated carbon sites we obtain roughly a 5% difference in population (see Figure 3.7). This effect in included in our model by a term that produces a lower energy shift for the edge carbons by an amount \(\Delta_{1/0} = E_{edge} - E_{in,1/0}\), compared to the interior
carbon atoms. Specifically for the C50F46 chain a $\Delta_1$ of 0.5eV reproduces this 5% difference in population that is observed in the DFT results (see Figure 3.7).

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
& C1 & C2 & C3 & C4 & Total \\
\hline
DFT & 1.05 & 0.95 & 0.95 & 1.05 & 4 \\
TB(HF) & 1.06 & 0.93 & 0.93 & 1.06 & 4 \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
& C1 & C2 & C3 & C4 & Total \\
\hline
DFT & 1.01 & 0.97 & 1.01 & 1.01 & 4 \\
TB(HF) & 1.02 & 0.94 & 1.02 & 1.02 & 4 \\
\hline
\end{array}
\]

**Figure 3.7.** Shows the DOS obtained from the TB(HF) model (green line) overlaid with the DFT DOS. The spin up and down DFT DOS projected on the carbon vacancy structure is shown in black and red respectively. To show the different populations of the constituent carbon atoms in a structure, the DFT DOS is projected onto the outer (blue) an inner (magenta) carbon sites. The table lists the site populations and local moment obtained with DFT and the model. From left to right, i) Four vacancy chain and ii) Four vacancy star.

In the table below we report our findings for the fitted values of $U$ and $\Delta_{1/0}$ for all the structures enumerated in Figure 3.3. Although we expect the value of $U$ to depend on the local screening environment of each structure, we find that all the
values lie within the range [1.8eV-2.2eV] (see Figure 3.8). The C-C bond length of the optimized structures depend on the geometry of the structure. Since the strength of the hopping parameter depends on the overlap of atomic orbitals on neighboring sites, the extracted values of $t$ show an exponential dependence on the C-C bond length (see Figure 3.9).

<table>
<thead>
<tr>
<th>Structure</th>
<th>U</th>
<th>$\Delta_1$</th>
<th>$\Delta_0$</th>
<th>Structure</th>
<th>U</th>
<th>$\Delta_1$</th>
<th>$\Delta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C50F49</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>C50F46-star</td>
<td>2.2</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>C50F48</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>C50F45-chain</td>
<td>2.0</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>C50F47</td>
<td>1.9</td>
<td>0.4</td>
<td>-</td>
<td>C50F45-boat</td>
<td>2.2</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>C50F46-chain</td>
<td>1.8</td>
<td>0.5</td>
<td>-</td>
<td>C50F45-AC</td>
<td>2.2</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>C50F46-boat</td>
<td>1.9</td>
<td>0.5</td>
<td>-</td>
<td>C50F45-star</td>
<td>2.0</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 3.8. Tight binding (TB) model parameters calculated at the Hartree-fock(HF) level of theory. The table enlists the extracted values of $U$ and $\Delta$ for all the structures enlisted in Figure 3.3.

Using the procedure described in this section, we are able to map the local moments in the low energy DFT spectrum to a simple model involving the unfluorinated carbon atoms with a single orbital per site. For structures with a few number of sites it is possible to solve this model exactly using analytic and numeric techniques [53–55]. With the parameters calculated here, we solve for the fully interacting many body ground state as well as excited states of the unfluorinated carbon structures and thereby calculate their response to an externally applied static magnetic field.
3.4.2 Exact Diagonalization of Hubbard Model

3.4.2.1 Method

Before describing the general procedure to obtain the many body solution of the Hubbard model for all the structures, let’s first look at the explicit calculation for the half filled (one orbital per site) double vacancy structure. Throughout this section we will refer to this structure as the two-site model. Using second quantized notation, the Fock space of the two site model at half filling can be enumerated as follows:
Here $c_{i\sigma}^\dagger$ represents the creation operator at site i with spin $\sigma$. The Hubbard Hamiltonian does not mix the spin subspaces. Thus, it becomes convenient to work in a fixed spin basis set. For our two site model, the total spin S can take values $[0,1]$. The possible states in the S=1 subspace are $|\phi_5\rangle$, $|\phi_6\rangle$, and $|\phi_s\rangle = \frac{1}{\sqrt{2}}(|\phi_3\rangle - |\phi_4\rangle)$ which are all degenerate with an energy of 0. The S=0 subspace has the states, $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_s\rangle = \frac{1}{\sqrt{2}}(|\phi_3\rangle - |\phi_4\rangle)$. The Hamiltonian matrix in this subspace, $([|\phi_1\rangle, |\phi_2\rangle, |\phi_s\rangle])$, can be written as follows,

$$
\begin{pmatrix}
U & 0 & -\sqrt{2}t \\
0 & U & -\sqrt{2}t \\
-\sqrt{2}t & -\sqrt{2}t & 0
\end{pmatrix}
$$

with the resulting eigenvalues and eigenvectors,

$$
E_1 = -2t\sqrt{1 + \left(\frac{U}{4t}\right)^2} - \frac{U}{4t} \quad |\psi_1\rangle = \frac{1}{\sqrt{2}} |\phi_s\rangle + \frac{1}{2}(\sqrt{1 + \left(\frac{U}{4t}\right)^2} - \frac{U}{4t})(|\phi_1\rangle + |\phi_2\rangle)
$$

$$
E_2 = U \quad |\psi_2\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle - |\phi_2\rangle)
$$

$$
E_3 = +2t\sqrt{1 + \left(\frac{U}{4t}\right)^2} + \frac{U}{4t} \quad |\psi_3\rangle = \frac{1}{\sqrt{2}} |\phi_s\rangle - \frac{1}{2}(\sqrt{1 + \left(\frac{U}{4t}\right)^2} + \frac{U}{4t})(|\phi_1\rangle + |\phi_2\rangle)
$$

From Fig. 3.10 we see that the energy of the ground state ($S = 0$), $E_1$, increases as $U$ increases, however the energy of the next excited state, $E_{\text{HighSpin}}$ ($S = 1$) does
Figure 3.10. Shows the variation of the many body energy levels of the two-site as a function of $U/t$.

not change with $U$. For a given set of parameters that describe an unfluorinated carbon structure, an externally applied magnetic field could excite the system to a higher energy state. The response of the system would then depend on the spin of the excited states and could be different from the mean field predictions of DFT.

To explore this further we extend the exact diagonalization scheme presented for the double vacancy to larger structures using the SNEG mathematica package [56]. This package enables us to perform symbolic calculations in the second quantized notation and solve for the exact many body ground and excited states. Once we know the excited states, we can calculate the magnetization of the system in the presence of an external applied field. The system under the influence of this external perturbation is written as,

$$H = H_0 + \sum_i \mu_{zi} B_z,$$

(3.17)
with $\mu_{zi} = \frac{g\mu_B}{\hbar} S_{zi} \text{ and } S_{zi} = \frac{\hbar}{2}(n_i^\uparrow - n_i^\downarrow)$. $H_0$ represents the unperturbed Hamiltonian and the second term is the coupling between the applied magnetic field and the local moment per structure. The symbol $g=2$, represents the lande’s g factor for the electrons.

Since the Hubbard Hamiltonian commutes with the total number of particles and the $z$ component of the total spin, we use a fixed $(N, S_z)$ basis, and diagonalize the above Hamiltonian in each subspace. The partition function is given by,

$$Z = \sum_n \exp(-\beta E_n[\{S_{zi}\}]), \quad (3.18)$$

and the magnetization,

$$M = g\mu_B <S_z> = \frac{1}{Z} \sum_{n,i} S_{zi,n} \exp(-\beta E_n[\{S_{zi}\}]), \quad (3.19)$$

where $\beta = \frac{1}{k_B T}$.

### 3.4.2.2 Results

Analytically, the magnetic response of a spin $\frac{1}{2}$ particle can be calculated as follows,

$$E[\{S_z\}] = \pm \mu_B B_z. \quad (3.20)$$

$$Z = \sum_{s_z=-\frac{1}{2}}^{+\frac{1}{2}} \exp(-\beta E[\{S_z\}]). \quad (3.21)$$

$$M = <\mu_z> = \frac{1}{Z} \sum_{s_z=-\frac{1}{2}}^{+\frac{1}{2}} \mu_z \{S_z\} \exp(-\beta E[\{S_z\}]), \quad (3.22)$$

$$= \mu_B \tanh \beta \mu_B B. \quad (3.23)$$
\[ \chi = \lim_{B \to \infty} \frac{\partial}{\partial B} M = \frac{\mu_B^2}{k_B T}. \] (3.24)

and that for a spin 1 particle,

\[ E[\{S_z\}] = \pm 2\mu_B B_z, \ 0. \] (3.25)

\[ Z = \sum_{S_z = -h,0,+h} \exp(-\beta E[\{S_z\}]). \] (3.26)

\[ M = 2\mu_B \frac{\exp(\frac{2\mu_B}{k_B T}) - \exp(-\frac{2\mu_B}{k_B T})}{1 + \exp(\frac{2\mu_B}{k_B T}) + \exp(-\frac{2\mu_B}{k_B T})}. \] (3.27)

We calculate the magnetization of the unfluorinated carbon structures using exact diagonalization techniques, and compare it to the analytical results for a spin=1/2 and spin=1 particle (see Figure 3.11).

**Figure 3.11.** Shows the exact response of unfluorinated carbon structures (dotted lines). Solid lines are added as guides to show the analytically derived magnetization of spin=0, spin=1/2, and spin=1 particles. The temperature T=1.8K is set to the experimental value used by Nair et al.
We find that odd structures have a spin 1/2 response and most even structures have a spin 0 response except for the four carbon star. Magnetic field strengths of up to 5T is not large enough to excite a higher spin response in the unfluorinated carbon regions within the range of parameters ($U$ and $t$ values) that describe them. Though our results indicate that the mean field treatment is good enough in the current situation, in principle it is possible to excite higher spin states for large enough fields (50,000T). Moreover as the size of the unfluorinated regions grow, these states become accessible at lower magnetic field strengths. Thus, our model provides the means to include the effect of correlations beyond the mean field results of DFT.

### 3.5 Conclusions

To summarize, we use DFT calculations to confirm that unfluorinated carbon regions in fluorographene could be the source of local moments that contribute to the spin 1/2 response seen in the experimental measurements [1]. Our study indicates that structures with odd number of unfluorinated carbon regions have a local moment of 1/2 per structure, and most even structures do not have a local moment. We map the low energy features of DFT using a Hubbard model with 1 orbital per site. We show that this model captures the main features of DFT associated with the local moment formation and then solve it exactly to obtain the magnetic response of these structures.

We expect a statistically significant number of unfluorinated regions of different shapes and sizes to exist in samples of partially fluorinated graphene. Theoretically, the number distribution of such regions can be obtained from large scale classical molecular dynamic simulations. In Appendix we present an energetics based monte
carlo simulation for graphene fluorination developed by Suarez [57].

Based on an Ising like interaction between neighboring fluorine atoms (eq. (.1)), this model predicts that the fluorination of graphene starts from small nucleation sites that grow outwards to form large fluorographene (CF) like domains on the surface. Depending on the direction from which the fluorine atoms attach on a particular graphene sub lattice, two kinds of domains can be identified. In one type of domain the fluorine atoms attach from above of sublattice A and from below on sublattice B, in the other type of domain the attachment is reversed (above on sublattice B and below on sublattice A). The carbon atoms at the boundary between these domains remain unfluorinated as it is energetically unfavorable for fluorine to attach on these sites from either above or below the plane (see Fig..2). These carbon atoms represent the unfluorinated carbon regions that are the topic of discussion in this chapter.

Combining with the results for the magnetic carbon structures obtained in this chapter, the total number of spins is plotted in Fig. .3 and compared to the experimentally obtained results of Nair et al. [1]. The magnetic response at different fluoridation percentages is also shown in the same figure. The parameters that describe the Ising like model and drive the energetics of the fluorination process are not optimized against quantum chemistry calculations. Moreover, they do not include interactions beyond nearest neighbor distances or factors that drive the dynamics on the surface, like charge transfer to the fluorine atom, adsorption and migration barriers to mention a few.

In the following chapters we discuss some of the factors that play an important role in simulating the fluorination of graphene and describe the results obtained with a reactive force field based method (ReaxFF) to simulate graphene fluorination.
Chapter 4  
Dilute Fluorine Adsorption on Graphene

4.1 Introduction

The adsorption of dilute fluorine atom on graphene is an interesting and important problem for many different reasons. Firstly, the charge transfer to the fluorine atom and the adsorption energy as the atom approaches the plane are some of the key physical parameters that are trained in classical potentials used to simulate the fluorination of graphene. The charge transfer in the dilute limit determines the interactions in the presence of other fluorine atoms. Thus a correct theoretical description is necessary to simulate the dynamics of fluorine adsorption on the surface.

Secondly, in studying the DFT description of dilute fluorine adsorption, we expose a severe failing of the semi-local functionals (PBE functional used in this work) in treating this problem. These functionals have a tendency to over delocalize the charge density producing ground states with fractional charges, especially in
situations involving bond dissociations [58]. In the problem of fluorine adsorption, we will see that DFT predicts an unphysical charge on the fluorine atom as the bond is stretched.

In this chapter, we describe the problems associated with the DFT treatment of dilute fluorine adsorption on graphene and provide a simple physical model to describe the charge transfer as the fluorine atom approaches the surface. This model can provide insights into the physics of the problem, once delocalization error free functionals are used to treat dilute fluorine adsorption on graphene.

4.2 Density Functional Theory Treatment of Charge Transfer

In this section, we start with the DFT treatment of the chemical bonding for dilute fluorine adsorption on graphene using GGA PBE (semi-local) functionals. While this functional does a good job of describing the bond length and binding energy at equilibrium, it quickly fails as the bond is stretched. We will show that the problem of fluorine adsorption presents unphysical results for the adsorption energy and charge transfer at large bond lengths.

The electronic structure of the fluorine atom once it is bonded to the surface is well described by DFT. The fluorine adatom adsorbs directly on top of a carbon atom, also referred to as the Top site, forming a covalent bond with it. This was shown through the mixing of the electronic density of states of the fluorine atom with the carbon atom at the adsorption site, as well as with the neighboring sites [39]. The carbon atom at the binding site puckers out of the plane indicating that its hybridization changes from $sp_2$ to $sp_3$ upon bonding.
In the same paper, Sofo et al. show that the nature of this C-F bond can be controlled electrically by doping the graphene sheet. They demonstrate that as the graphene sheet is electron doped, the C-F bond elongates and the carbon atom retracts back into the plane. This is described as the $sp_3$ to $sp_2$ cross over. In the $sp_2$ state, the charge on the fluorine atom is higher compared to the covalently bonded $sp_3$ state and the bond has a predominantly ionic character.

Fluorine adsorption on graphene is a barrier less process requiring little to no activation energy, unlike other adatoms like hydrogen [59]. A possible justification is that the high electronegativity of fluorine facilitates initial bond formation by charge transfer from the surface. Such an ionic bond is stabilized over the neutral state through the image charge interaction with the surface [60].

In this section we will use DFT to study the changes in the C-F bond as it is stretched. We show that for large bond lengths ($d_{C-F} \approx 10\text{Å}$), DFT predicts an unphysical fractional charge and non zero adsorption energy for the fluorine atom. This fractional charge is an indication of the delocalization error of semi-local exchange and correlation functionals [58]. We will talk about other systems where similar unphysical charges have been reported and the functionals that have been used to correct them [61,62].

### 4.2.1 Methods

Fluorine adsorption is studied with the DMOL$^3$ implementation of DFT using a 72 carbon atom graphene cell (F/C concentration of 1.4%). This structure is relaxed (geometry optimization) under the constraint of a fixed C-F bond length upto $d_{C-F} = 5\text{Å}$. Beyond this distance we observe no significant puckering of the bonded carbon atom and hence perform constrained fixed point energy calculations.
to cut down on the calculation cost and time. We use the semi local GGA PBE
functionals to treat the exchange and correlation effects. A $3 \times 3 \times 1$ k-points grid
is found to be sufficient for producing well converged results. To minimize the
effect of periodic image interactions in the $z$ direction, we vary the cell sizes from
$20\AA - 200\AA$, and also extrapolate the results to the asymptotic limit, $z = \infty$.

The adsorption energy is calculated from well converged calculations by taking the
difference between the energies of the graphene+F system and the graphene
and fluorine atom taken in isolation, in a box with the same cell size.

$$E_{\text{adsorption}} = E_{\text{graphene}+F} - (E_{\text{graphene}} + E_F)$$  \hspace{1cm} (4.1)

The charge on the fluorine atom is calculated using Mulliken population analysis [63].

\subsection*{4.2.2 Results}

We observe that as the C-F bond is stretched, the puckered carbon atom retreats
back into the plane, indicating a gradual change in the bond from $sp_3$ to $sp_2$
character. As $d_{C-F}$ increases, the magnitude of the adsorption energy decreases,
indicating that the bond becomes weaker. At a significant distance from the surface
(>10Å) we expect the fluorine atom to be neutral and weakly attracted to the
surface through Van-der-Waals interaction. However, from Fig. 4.1 we see that
adsorption energy is still significant (-0.2 eV) at a distance of 10Å, even after
removing the contributions from periodic interaction between images along the $z$
direction ($z = \infty$ limit).

Fig. 4.2 shows the charge on the fluorine atom as the C-F bond is stretched
for different simulation cell heights. We can see that charge on the fluorine atom
initially increases up to a distance of 2Å from the surface and then starts to decrease
Figure 4.1. Adsorption energy as a function of the distance between the fluorine atom and carbon at the binding site. Different colors indicate the height of the box in the z direction in Angstroms as listed in the legend.

as the bond is stretched further. This implies that, initially stretching the bond, makes it more ionic in character. As the separation increases, the charge decreases implying a decrease in the covalent (smaller overlap of wave functions) as well as ionic character. However, even at a separation of 10Å the charge on the fluorine atom is not zero but a small fraction (-0.22e) of the fundamental electron charge. This is surprising because at these large distances the charge on the fluorine atom should be either zero (bond dissociates with neutral charge on fluorine) or some integer fraction of the electron charge (fluorine atom has a charge of -1e and forms an ionic bond with the surface). The fractional charge implies that there is some sort of overlap of wave functions which is unphysical for such large distances.

The origin of this unphysical charge lies in the semi-local functionals that are
used to approximate exchange and correlation effects and tend to over delocalize the charge density. Similar problems have been seen in DFT predictions for dissociation products of molecules like $H_2, H_2^+, NaCl$ to name a few [58]. In the study of $NaCl$ dissociation, Ruzzinsky et al. show that LDA and GGA functionals can incorrectly dissociate the neutral molecule to fractionally charged fragments ($Na^{+q}...Cl^{-q}$) that have a lower energy compared to ($Na^0...Cl^0$) [61]. In the same article, the authors show that HF functionals produce physically meaningful dissociations products.

With the HF method, as the bond is stretched the charge on each fragment increases to a maximum of $\pm 1e$, before going to zero as the molecule dissociates. The distance at which the fragments transition from an ionic to neutral state is described as the Quantum Phase Transition or ionic cross over.
In the next section, we present a simple physical model, based on the image charge interaction between an atom and a surface, to show the possible existence of such an ionic cross over for fluorine atoms adsorbed on graphene. This model could provide support to the physical predictions of the HF method, once it has been developed for treating fluorine adsorption on graphene.

At the heart of the delocalization error is the problem that semi-local functionals do not extrapolate linearly for fractional charges, as they should [64,65]. Instead it has been shown by Cohen et al. that, these functionals have a convex shape for fractional charges in finite systems (atoms and molecules) [66] and a linear shape with incorrect slope for extended systems(surfaces) [67]. The problem of fluorine adsorption presents a hybrid of these two cases as it represents the interaction between a finite (fluorine) and extended system (graphene). This presents an exciting theoretical challenge for electronic structure methods - one that will better describe the interaction between fluorine adsorbates and graphene.

4.3 Physical Model for Charge Transfer

The expected qualitative behavior of the charge on the fluorine atom as a function of the bond length is sketched in Fig. 4.3. Far away from the surface the fluorine atom is neutral. As the fluorine atom approaches, it transitions to an ionic state through the transfer of 1e charge from the surface. This transition is depicted as distance $d_I$ in Fig. 4.3. The ionic state is stabilized by the image charge interaction from the surface. This interaction lowers the energy of the ionic state over the neutral state and they cross over at the distance $d_I$. Once the atom is close enough to the surface, it transitions to a covalently bonded state through hybridization with the atomic wave functions on the surface. Depending on the type of atom and
the surface, the ionic crossover distance might be smaller than the covalent onset. In this case, the neutral atom will directly transition to the covalent state as it approaches the surface.

![Figure 4.3](image)

Figure 4.3. Qualitative sketch of the charge on the fluorine atom as it approaches the surface. $d_I$ marks the ionic cross over distance. The covalent onset is also marked on the figure.

In this section we use a simple physical model to calculate the ionic crossover distance for a fluorine atom adsorbed on graphene. This model is based on the image charge interaction between the adsorbed atom and the surface. The image charge interaction has been extensively used to study the chemisorption of alkali atoms on metal surfaces [68–71]. More recently, the shift in frontier energy levels (Highest Occupied Molecular Orbital, HOMO, and Lowest Unoccupied Molecular Orbital, LUMO) upon adsorption on a metal surface, calculated using constrained DFT techniques, show good agreement with the predictions of the image charge model [62].

Using this model, we will calculate the ionic crossover distance for fluorine by modeling the response of graphene to an external charge in two ways: i) classical metal and ii) with the linear response theory (Random Phase Approximation,
RPA [72]). To accomplish this, we will calculate the shift in the frontier energy levels of the atom as a function of distance from the surface using the image charge interaction as a perturbation. From the shift in the energy levels we will estimate the shift in the electron affinity of the atom and estimate the distance at which it becomes energetically possible to transfer one electron charge from the surface to the atom.

4.3.1 Image Charge Interaction

Let us start with the simple example of a point charge $q_1$ at a distance $d_1$ above a metal surface. The potential in the region $z > 0$ is uniquely determined and can be found using the method of images. Placing an image charge $-q_1$ at a location $d_1$ inside the metal satisfies the boundary conditions for Laplace’s equation in this region (see Fig. 4.4). The energy of this configuration can be calculated as an integral of the force acting on the point charge $q_1$ as it is brought to the position $d_1$ above the surface.

$$U_1 = -\int_{\infty}^{d_1} F(z)dz,$$

(4.2)

with

$$F(z) = -\frac{q_1^2}{4z^2}.$$

(4.3)

Here $F(z)$ is the force between charge $q_1$ and its image inside the metal. Plugging (4.2) in (4.3) we get,

$$U_1 = -\frac{q_1^2}{4d_1}.$$

(4.4)

We find that the energy of interaction is half of what would be expected for interaction between real charges.

Now, a second charge $q_2$ is brought along a line that is parallel to the $z$ axis and
Figure 4.4. Image charge interaction with a metal surface. Charges $q_1$ and $q_2$ produce images $-q_1$ and $-q_2$ inside the metal surface. The metal is represented in dark gray.

at a distance $\rho$ from it to a point at a height of $d_2$ above the surface. The forces acting on this charge are given by,

\[ F_1(z) = -\frac{q_2^2}{4z^2}, \]  

(4.5)

and

\[ F_2(z) = \frac{q_1q_2}{\rho^2 + (d_1 + z)^2}, \]  

(4.6)

where we have excluded the direct interaction with the charge $q_1$. $F_1$ represents the interaction of charge $q_2$ with its own image and $F_2$ represents the interaction with the image of charge $q_1$. The total energy of this configuration can be found by
integrating the force along the line the charge is brought.

\[ U_2 = U_1 + \frac{q_1 q_2}{\rho^2 + (d_1 - d_2)^2} - \int_{-\infty}^{d_2} F_1 dz - \int_{-\infty}^{d_2} F_2 \cos \theta dz \]

\[ = U_1 + \frac{q_1 q_2}{\rho^2 + (d_1 - d_2)^2} + \int_{-\infty}^{d_2} \left( \frac{q_1 q_2}{4z^2} + \frac{q_1 q_2}{\rho^2 + (d_1 + z)^2} \frac{d_1 + z}{\sqrt{\rho^2 + (d_1 + z)^2}} \right) dz \]

\[ = -\frac{q_1^2}{4d_1} + \frac{q_1 q_2}{\sqrt{\rho^2 + (d_1 - d_2)^2}} - \frac{q_2^2}{4d_2} - \frac{q_1 q_2}{\sqrt{\rho^2 + (d_1 + d_2)^2}} \]

In (4.7), the first and the third term are the image charge interaction between each charge and its own image; the second term is the direct interaction between the two charges; and the last term is the interaction between the charge \( q_2 \) and the image of charge \( q_1 \). Note that (4.7) does not include the interaction between \( q_1 \) and the image of \( q_2 \), as this interaction did not exert any force on \( q_2 \) as it was brought to the position \( d_2 \). To keep the symmetry of the problem we can impose the rule that interaction between real and image charges are to be divided by 2 to get,

\[ U = -\frac{q_1^2}{4d_1} + \frac{q_1 q_2}{\sqrt{\rho^2 + (d_1 - d_2)^2}} - \frac{q_2^2}{4d_2} - \frac{1}{2} \frac{q_1 q_2}{\sqrt{\rho^2 + (d_1 + d_2)^2}} - \frac{1}{2} \frac{q_2 q_1}{\sqrt{\rho^2 + (d_2 + d_1)^2}}. \]

(4.8)

However, this does not produce any quantitative difference in the results obtained. Imagine that the two charges represent a atom on the surface, with the charge \( q_1 \) representing the inner ionic core and the charge \( q_2 \) representing the outermost electron. In the next section we calculate the shift in the energy level of the outermost electron under the influence of the interaction \( U_2 \) described in this section.
4.3.2 Shift in the Frontier Energy Levels

Since we are interested in calculating the shift in the frontier levels of fluorine due to the screening from graphene surface, we will make several simplifying assumptions. We will use the $2p_z$ orbital of fluorine to represent the outermost orbital. We will start by treating the surface of graphene as a perfect metal. Later on in the section we will recalculate the energy shifts using the dielectric response of graphene with linear response theory.

In the absence of the metal surface, the direct interaction

$$H_0 = -\frac{e^2}{\sqrt{\rho^2 + (d_1 - d_2)^2}}, \quad (4.9)$$

between the outermost electron and the positively charged ion core (second term in (4.7)), represents the unperturbed state of the atom with,

$$H_0 \Psi_{2p_z} = E_1^0 \Psi_{2p_z}, \quad (4.10)$$

Here, $E_1^0$ is the unperturbed energy of the singly occupied outermost orbital and $E_1 = -\text{IP}$, where IP is the ionization potential of the atom. The unperturbed wave function, as per our assumption, is given by the $2p_z$ orbital of fluorine $\Psi_{2p_z}(r) = Cze^{-\alpha r}$. $r$ is the position of the electron relative to the ion core. $C$ is a constant that normalizes the wavefunction, and the value of $\alpha = 5.11\text{Å}^{-1}$ is obtained by calculating the electronic orbitals of a single fluorine atom inside a box using DFT and fitting to the HOMO wave function.

In the presence of the metal surface, the energy levels of the atom are perturbed due to the image charge interaction from the surface. Setting the origin of the coordinate system at the location of the ion core, we can write the perturbing
potential due to the image charge interaction as,

$$H' = -\frac{e^2}{4d_1} - \frac{e^2}{4(d_1 + z_1)} + \frac{e^2}{\sqrt{\rho^2 + (2d_1 + z_1)^2}}$$  \hspace{1cm} (4.11)

(4.11) is obtained by substituting $q_1 = +e$, $q_2 = -e$ in (4.7) and dropping the direct interaction term. We have also used $z_1$ as the location of the outermost electron relative to the ion core and $d_2 = d_1 + z_1$. To first order in perturbation theory, the shift in the energy of the frontier level can be calculated using,

$$\Delta E_1 = \frac{\langle \Psi_{2p_z}(r_1) | H'_1 | \Psi_{2p_z}(r_1) \rangle}{\langle \Psi_{2p_z}(r_1) | \Psi_{2p_z}(r_1) \rangle}.$$  \hspace{1cm} (4.12)

Next, consider the ionic crossover state of the fluorine atom. The ionic crossover describes the state of the atom for which a charge has been transferred from the surface to the outer most shell. The unperturbed ionic state is spin paired (Pauli’s exclusion principle) and can be represented by the product wave-function

$$\Psi_I(r_1, r_2) = C z_1 z_2 e^{-\alpha(r_1 + r_2)},$$  \hspace{1cm} (4.13)

where $r_1, r_2$ represents the coordinates of the two electrons relative to the ion core and $z_1, z_2$ are their respective $z$ coordinates. In the presence of the metal surface, the perturbing potential can be found by extending the image charge interaction in (4.7) to the case of three charges.

$$U_3 = -\frac{q_3^2}{4d_3} - \frac{q_2q_3}{\sqrt{(\rho_3 - \rho_2)^2 + (d_2 + d_3)^2}} - \frac{q_1q_3}{\sqrt{\rho_3^2 + (d_1 + d_3)^2}} +$$

$$\frac{q_1q_3}{\sqrt{\rho_3^2 + (d_1 - d_3)^2}} + \frac{q_2q_3}{\sqrt{(\rho_3 - \rho_2)^2 + (d_2 - d_3)^2}} + U_2$$  \hspace{1cm} (4.14)
$U_3$ can be split into terms corresponding to the direct interaction and the image charge interaction. The direct term can be written as,

$$U_{3\text{Direct}} = \frac{q_1 q_3}{\sqrt{\rho_3^2 + (d_1 - d_3)^2}} + \frac{q_1 q_2}{\sqrt{\rho_2^2 + (d_1 - d_2)^2}} + \frac{q_2 q_3}{\sqrt{(\rho_3 - \rho_2)^2 + (d_2 - d_3)^2}},$$

where the first two terms represent the electrostatic attraction between the ion core and each electron and the last term represents the Coulomb repulsion between the two electrons. In the absence of the metal surface, the direct term represents the unperturbed Hamiltonian of the ionic state (with $q_1 = +e, q_2 = -e, q_3 = -e$) with the following eigenvalue equation,

$$H_{\text{Ionic}} \Psi_I(r_1, r_2) = E_{\text{Ionic}}^0 \Psi_I(r_1, r_2)$$

Here, $E_{\text{Ionic}} = 2 \times \text{IP} + U_c$ is the unperturbed energy of the doubly occupied frontier level, where $U_c$ represents the Coulomb repulsion between the electrons in the doubly occupied state. The image charge interaction that perturbs the ionic state in the presence of the metal surface is given by the following Hamiltonian,

$$H'_{\text{Ionic}} = -\frac{e^2}{4d_3} - \frac{e^2}{4d_2} - \frac{e^2}{4d_1} + \frac{e^2}{\sqrt{\rho_3^2 + (d_2 + d_1)^2}} + \frac{e^2}{\sqrt{\rho_3^2 + (d_3 + d_1)^2}} - \frac{2e^2}{\sqrt{(\rho_3^2 - \rho_2)^2 + (d_2 + d_1)^2}}.$$
\[
\frac{e^2}{\sqrt{\rho_2^2 + (2d_1 + z_1)^2}} + \frac{e^2}{\sqrt{\rho_3^2 + (2d_1 + z_1)^2}} - \frac{2e^2}{\sqrt{(\rho_3 - \rho_2)^2 + (2d_1 + z_1 + z_2)^2}}.
\]  
(4.18)

The change in the energy of the ionic state can now be found using,

\[
\Delta E_{Ionic} = \frac{\langle \Psi_I(r_1, r_2) | H'_{Ionic} | \Psi_I(r_1, r_2) \rangle}{\langle \Psi_I(r_1, r_2) | \Psi_I(r_1, r_2) \rangle} 
\]  
(4.19)

Now, the electron affinity A, of a fluorine like atom can be defined as the difference in the energy of the ionic state and the highest occupied molecular orbital.

\[
A = E_{Ionic} - E_1^0 
\]  
(4.20)

\[
= 2IP + U - IP 
\]  
(4.21)

Hence, the shift in the electron affinity of a fluorine like atom can be calculated as follows,

\[
\Delta A = \Delta E_{Ionic} - \Delta E_1
\]  
(4.22)

The shift in the energy levels \(\Delta E_1, \Delta E_{Ionic}\) are plotted in Fig. 4.5. Since \(\Delta E_1\) is the energy shift of the singly occupied frontier level for the neutral atom, we expect this value to be close to zero (see Fig. 4.5). Thus the shift in the energy of the affinity level is equal to the shift in the energy of the ionic state. The work function of free standing graphene is in the range 4.89 eV - 5.15 eV [73]. The average energy that is necessary to remove one electron from the Fermi level of graphene into vacuum is roughly 5.0 eV. The electron affinity of bare fluorine atom is 3.4eV. This is the amount of energy that will be released on the transfer of a single electron to the outermost orbital of the atom. The attractive image charge potential from the
Figure 4.5. Figure shows the shift in the frontier energy levels of the atom due to image charge interaction from the surface. The energy shift of the singly occupied state $\Delta E_1$ is shown in pink; the ionic state $\Delta E_{\text{Ionic}}$ is shown in violet; and the electron affinity is shown in yellow. The back dashed line marks an energy of -1.6eV, representing the point at which the electron affinity of fluorine crosses the Fermi level of graphene.

Surface screens the coulomb repulsion in the ionic state causing the electron affinity to decrease relative to the neutral atom. When the electron affinity dips below the Fermi level of graphene, the neutral atom transitions to the ionic state through the transfer of a single electron from the surface. This happens for an energy dip of 1.6 eV at a distance of 6.5Å from the surface.

Though we have modeled graphene as a perfect metal, quantum mechanically it does not screen perfectly. In fact, Sangzi et al. show that at the linear response level of theory, the electric field on other side of the plane though reduced compared to the bare field is still non-zero [74]. The Fourier transform of the external potential
produced by a charge \( q = q_0 \delta(\rho = 0) \delta(z = 0) \), at the surface \((z = d)\) is given by,

\[
V_{ext}(k, d) = \frac{2\pi}{k} e^{-kd} \tag{4.23}
\]

Assuming linear response, the induced potential at the surface is given by,

\[
V_{\text{ind}}(k, d) = (\frac{1}{\epsilon(k)} - 1)V_{ext}(k, d) \tag{4.24}
\]

where \(\epsilon(k)\) is the static dielectric function of graphene calculated with the Random Phase Approximation (RPA). The induced potential is related to the surface charge \(n_{\text{ind}}\) through Poisson’s equation,

\[
\nabla^2 V_{\text{ind}}(\rho, d) = 4\pi n_{\text{ind}}(\rho) \delta(z = d) \tag{4.25}
\]

Taking the Fourier transform of both sides,

\[
V_{\text{ind}}(k, d) = \frac{2\pi n_{\text{ind}}(k)}{k} \tag{4.26}
\]

Rearranging and transforming back to real space,

\[
n_{\text{ind}}(\rho, d) = q_0 \frac{1}{k} \int d^2k e^{i\rho cos \theta} \frac{k}{2\pi} V_{\text{ind}}(k, d)
\]

\[
= q_0 \frac{1}{2\pi} \int dk (\frac{1}{\epsilon(k)} - 1)k e^{-kd} J_0(k\rho) \tag{4.27}
\]

where \(J_0(k\rho)\) is the zeroth order Bessel function of the first kind. The dielectric function of graphene with RPA is given by \([72, 74–76]\)

\[
\epsilon_{\text{RPA}}(k) = 1 + \frac{4e^2k_F}{\hbar v_F k}, \text{ for } k \leq 2k_F \tag{4.28}
\]
where \( k_F = \sqrt{\pi n} \) is the Fermi wave vector and \( n \) is the carrier density. \( v_F \) is the Fermi velocity and \( \kappa \) is the background dielectric constant (\( \kappa = 1 \)) for suspended graphene. For undoped graphene \( k_F = 0 \) and the RPA dielectric function is simply,

\[
\epsilon_{RPA} = 1 + \frac{\pi e^2}{2 \hbar v_F} = 4.5. \tag{4.30}
\]

Substituting (4.30) in (4.27), the induced charge density is

\[
n_{ind}(\rho, d) = q_0 \left( \frac{1}{\epsilon_{RPA}} - 1 \right) \frac{d}{\sqrt{(d^2 + \rho^2)^3}}. \tag{4.31}
\]

which is the charge density produced by a charge \( q_0 \left( \frac{1}{\epsilon_{RPA}} - 1 \right) \) located at a point \( d \) inside the material. Hence, with the RPA response of graphene the image charge produced is simply 0.77 times the charge produced if graphene were a perfect metal.

With this image charge interaction we can calculate the energy shifts in the frontier levels of fluorine following the same procedure described for the perfect metal response. The resulting shifts are shown in Fig. 4.6. From the shift in the electron affinity level we can now anticipate a ionic cross over distance of 5.0\AA. This distance is large enough to be outside the covalent onset region. Thus our model predicts a charge transfer behavior where we can expect the fluorine atom to be in an ionic bond with the surface as it approaches from the gas phase.
Figure 4.6. Figure shows the shift in the frontier energy levels of the atom due to image charge interaction from the surface within the RPA approximation. The energy shift of the singly occupied state $\Delta E_1$ is shown in pink; the ionic state $\Delta E_{\text{Ionic}}$ is shown in violet; and the electron affinity is shown in yellow. The back dashed line marks an energy of -1.6eV, representing the threshold for which the electron affinity of fluorine crosses the Fermi level of graphene.

4.4 Conclusions and Future Work

In this chapter we demonstrate that semi local functionals fail in describing the desorption of dilute fluorine on graphene. We show that even at a distance of 10Å from the surface, these functionals predict that there is a covalent overlap of wave functions as indicated by the fractional charge of -0.2e on the fluorine atom. With a simple physical model based on the image charge interaction between the adsorbed species and the surface, we predict the existence of an ionic cross over for the fluorine atom on graphene. This can serve a qualitative guide for a physically meaningful charge transfer once delocalization error free functionals are used to describe this problem.

Our model incorporates the dielectric response of graphene at the linear response
level with RPA. The RPA dielectric function is calculated using the linear electronic spectrum arising from the \( \pi \) bands in graphene. However close enough to the surface, the fluorine atom would also produce a distortion in the sigma bands perpendicular to the surface. Going beyond the linear response of RPA would provide a better model for the dielectric response of graphene. Secondly, our model calculates the first order shift in the energy using the unperturbed atomic orbitals of fluorine. In principle the surface induces a finite polarization in the atom. A model that incorporates the effects of polarization of the atom on the electronic wave functions would provide a more precise description of the charge transfer in the future.

The problem of atomic adsorption on a surface is important not only from the practical point of view of applications in gas sensing and detection and describing surface configuration of adsorbates, it poses the added theoretical challenge that at the present moment there are no electronic structure tools that can treat these problems correctly. Moreover, classical potentials for large scale molecular dynamics are being fitted to the existing functionals to reproduce the wrong DFT behavior propagating these errors to the theoretical description of the problem.

Delocalization errors of DFT are pervasive in many other systems, especially while describing dissociation of molecules in finite systems like \( H_2, \ NaCl, \ H_2^+ \) [58,61]. In such systems, exchange correlation functionals do not interpolate linearly between integer occupations. Instead they have a convex shape for fractional charges [66]. In finite systems like surfaces the exchange correlation functionals interpolate correctly but with the wrong slope [67]. The interaction of atomic fluorine with graphene presents an interesting class of system that can be described as the interaction between a finite and an extended system. Development of self interaction error free functionals will significantly improve the current description of charge transfer and
adsorption in such systems.
Chapter 5  
Evolution and Morphology of Graphene Fluorination from an Atomic Gas Source

5.1 Introduction

The electronic, structural, and magnetic properties of partially fluorinated graphene depends on the microscopic configurations formed on the surface upon fluorination. Experimentally, microscopic imagining of the surface shows qualitative differences in the structures formed based on the fluorination technique used. Wang et al. [20] show that fluorinated graphene produced from $CF_4$ plasma using chemical vapor deposition (CVD) graphene shows structural inhomogeneities including highly irregular features such as ripples, multilayer islands, folds, and wrinkles. These features do not get fluorinated thus forming conductive networks for charge transport. Contrastingly, Kashtiban et al. [77] show that their technique of fluorinating CVD graphene using $XeF_2$ produces highly ordered domains of chair like $C_2F$ and
stoichiometric fluorographene $CF$ like regions.

In this chapter, we provide a theoretical description of the surface configurations using ReaxFF to simulate the fluorination of graphene. The advantage of using ReaxFF is two fold. On the one hand we can simulate thousands of atoms at a fraction of the time and computational cost of quantum chemistry based methods like DFT. On the other hand, semilocal functionals of DFT suffer from the problem of unphysical fractional charge on the fluorine atom at large distances from the surface as shown in Chapter 4. In this chapter, we show that in the presence of other fluorine atoms in the simulation cell, the ReaxFF charge on fluorine atoms is negligible beyond a distance of 5Å from the surface. Thus the fluorine atoms are not accelerated to the surface over distances of 10’s of Angstroms. Hence, we can circumvent the problem of the unphysical charge on fluorine atoms that arises from the self interaction error of DFT.

We model the adsorption isotherms of the fluorination process using a modified Langmuir model to explain the kinetics of the fluorination process. Lastly, we analyze the microscopic surface configurations formed as a result of the simulation process and predict the magnetic properties by combining with the magnetic response model developed in Chapter 3.

5.2 Computational Methods

In ReaxFF the force fields that simulate the dynamics are parametrized against DFT calculations of bond lengths, bond angles, torsion, charges, binding energy, diffusion constant, etc. on relevant systems. For our calculations we used the already well parameterized C-C force field [78], however new parameters were developed for C-F force fields by Junkermeier et al. [79]. Older versions of the
C-F force fields \[80,81\] were trained using small Teflon-like molecules making the fluorine atoms more reactive to the graphene sheet. Also, older force fields were not trained against the diffusion barrier of fluorine on graphene. Because of the low diffusion barrier (DFT barrier = 0.23eV), fluorine atoms are expected to migrate at room temperature on graphene leading to possible clustering on the surface \[82,83\].

\[\text{Figure 5.1. Bond dissociation curve of a single fluorine atom adsorbed on coronene using ReaxFF force fields. DFT calculations are shown in red and the version of force field used in this chapter is shown in blue. Older versions of force field are shown in green and brown. The current version of the force field shows much better agreement with DFT energies especially between (2-4)\text{	extdegree}Å distance.}\]

Junkermier et al., used \[2 \times 2\] fluorinated graphene structures reported in \[84\] and performed Quantum Espresso (QE) calculations to find the resulting ground state properties. Some of these structures were then used to train the new C-F force
field and others were used as a test for the predictive ability of the force field [79].

The errors ($error = \sqrt{\left(\frac{v_{ReaxFF}-v_{DFT}}{v_{DFT}}\right)^2}$) in the calculated bond lengths, bond angles, and lattice constants for the structures given in [84] is less than 5%, showing good agreement with DFT calculations. The bond dissociation curve for a single fluorine atom adsorbed on coronene molecule shows better agreement with DFT calculations for Junkermier et al force field compared to earlier versions (see Figure 5.1). The bond dissociation energy is calculated using $E_{diss} = E_{coronene+F} - (E_{coronene} + \frac{1}{2}E_{F_2})$

Another significant improvement of the force field over earlier versions is that it has been trained against the diffusion barrier of a single fluorine atom as calculated with the nudged elastic band method of DFT. Using a $12 \times 12$ rectangular cell of graphene, the diffusion barrier for a single fluorine atom attached to a top site to jump to a neighboring top site was calculated using the climbing-image nudged elastic band implementation in QE (see Fig. 5.2) [79]. A total of 11 images, 9 intermediate and 2 precomputed initial and final configurations were used in the calculation. Since the reaxFF force field optimization routine does not include a nudged band method, the barrier energies were trained using geometry optimization with suitable bond restraints. The diffusion barrier calculated with ReaxFF and DFT is compared in Figure 5.2. Diffusion barriers in the presence of a neighboring fluorine atom was also trained into the forcefield as described in details in [79].
5.3 Simulation Results

We performed room temperature (300K) molecular dynamics simulations for a total time duration of 0.25ns. The time interval between each iteration was 0.25fs. We used a Velocity Verlet+Berendson thermostat. The simulation cell comprised of a 800 carbon atom graphene sheet with different starting percentages \(n_F = \frac{N_F}{N_C}\) of fluorine atoms. Figure 5.3 shows a snapshot of a typical fluorination process at a) 0.25ps and b) 25ps for a starting fluorine concentration of 75%. As more fluorine atoms adsorb on the surface the graphene sheet changes from a planar to a more rippled structure. These changes are consistent with the fact that on bonding with a fluorine atom, the carbon atom changes from \(sp^2\) to \(sp^3\) hybridization, puckering in the direction of fluorine attachment. These changes are also accompanied by changes in the lattice constant as described in [80].

The charge transfer to fluorine atoms plays a key role in describing the surface dynamics correctly. We have seen in Chapter 4 that the DFT description of the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure52.png}
\caption{Diffusion barrier of a single fluorine atom along the path from 1 to 2. Red curve is the barrier calculated with DFT and blue curve with ReaxFF implementation of the Nudged Elastic Band method.}
\end{figure}
Figure 5.3. A typical 800C atom simulation cell with a box height of 50Å. Snapshot taken at a) 0.25ps, b) 25ps.

Charge transfer is plagued with self-interaction error. If this error is manifested in the ReaxFF simulation of the molecular dynamics (MD), fluorine atoms that are several angstroms away from the surface will be attracted towards the plane. This is unlikely to produce reasonable surface configurations. In Figure 5.4 we show the average charge on fluorine atoms from 50-100ps as a function of the z-height from the surface. The color represents the density of fluorine atoms with red representing the highest density and blue the lowest. This figure shows that beyond a distance of 5Å the ReaxFF charge on fluorine atoms is negligible. This means that the shielding effect of the fluorine atoms already adsorbed on the surface prevent an unphysical charge transfer to the fluorine atoms in the gas phase. This screening effect counteracts the delocalization error and produces a more reasonable charge on the fluorine atoms as they approach the surface.
Figure 5.4. The average charge on fluorine atoms as a function of distance from the cell. The color represents the density of fluorine atoms along the $z$ direction of the cell. The DFT charge on a single fluorine atom approaching the graphene sheet is overlaid for comparison (black line).

5.3.1 Adsorption Isotherms

Figure 5.5 shows the occupation of the lattice as a function of time steps for the different starting fluorination percentages. Initially the number of adsorbed atoms increases linearly with time eventually reaching a fixed concentration in the lattice. For the initial starting concentration of $n_F = 25\%$ fluorine in the box, all the fluorine atoms get adsorbed on the surface, however for higher starting concentrations such as 50\%, 75\%, and 100\%, the occupation of the lattice saturates to a much lower value compared to the maximum amount that can be adsorbed on the surface.

We use a simple physical model based on a modification of the kinetic Langmuir model to describe the adsorption process [85]. According to the Langmuir model a fraction of the atoms incident on a surface will stick to it based on the availability of empty sites. The Langmuir model describes adsorption at constant gas pressure
and assumes that a maximum of one adsorbate can attach per site, and that there are no adsorbate adsorbate interactions. Adaptations of this model have been successfully applied in gas sensing applications, to understand the kinetics of adsorption and desorption on surfaces [14]. According to the Langmuir model, the rate of adsorption of a classical ideal gas on a surface is directly proportional to the number of vacant sites.

\[
\frac{dN_a}{dt} = \beta_i (N_c - N_a)
\]  

(5.1)

Here, \(N_a\) is the number of occupied sites and \(N_c\) is the total number of sites. The rate constant \(\beta_i\) is the sticking probability at site \(i\), and depends on number of atoms approaching per unit area of the surface per unit time. In our modified model the gas pressure, \(P = \frac{N_g}{V} k_B T\), is not constant as the number density of the gas

**Figure 5.5.** Shows the adsorption isotherms from four different initial fluorine gas densities. Dark yellow 25%, mauve 50%, blue 75% and green 100%. 

![Graph showing adsorption isotherms from four different initial fluorine gas densities.](image-url)
decreases as more and more fluorine atoms get adsorbed on the surface. Thus even though, \( N_F = N_g + N_a = \text{constant} \), \( N_g \) decreases as \( N_a \) increases with time. Thus the rate constant \( \beta_i \), that depends on the number of fluorine atoms approaching the surface, decreases with time. Let \( f(v)d^{3}v \) represents the probability distribution of atoms with velocity in the range \( v \) and \( v+dv \). Here, \( f(v) = \left( \frac{m}{2\pi k_B T} \right)^{3/2}e^{-\frac{mv^2}{2k_BT}} \) is the Maxwell-Boltzmann distribution of speeds for an ideal gas. Considering a infinitesimally small cylinder of cross section \( dA \) and height \( v \cos \theta \, dt \), the number of atoms in this volume is \( n_g \times v \cos \theta \times dA \times dt \). Here \( n_g = \frac{N_g}{V} \) represents the number density of the gas. The total number of atoms striking an area \( dA \) in time \( dt \) from above is,

\[
\begin{align*}
\frac{d}{dt} = & \int n_g \times v \cos \theta \times f(v)d^3v \\
\ \ = & n_g \int v^3 f(v)dv \int_{0}^{\pi/2} \sin \theta \cos \theta d\theta \int_{0}^{2\pi} d\phi \\
\ \ = & n_g \times 2\pi \times \frac{1}{2} \times \int v^3 f(v)dv \\
\ \ = & \frac{n_g v_{avg}}{4} \\
\end{align*}
\]

Here, \( v_{avg} = 4\pi \int v^3 f(v)dv = \sqrt{\frac{8k_B T}{\pi m}} \). Thus, the number of atoms approaching per unit area per unit time = \( \frac{n_g}{4} \sqrt{\frac{8k_B T}{\pi m}} \). If there are \( N_c \) carbon atoms in area \( A \), and the sticking coefficient at site \( i \) is \( s_i \), then the sticking probability per atom considering fluorine atoms can approach from both sides is,

\[
\beta_i = 2 \times \frac{N_g}{4N_c} \sqrt{\frac{8k_B T}{\pi m}} \times \frac{1}{L_z} \times s_i
\]

Here, \( L_z \) is the height of the simulation cell and \( N_g + N_a = N_F \) is the total number of fluorine atoms. Denoting \( \gamma_i = \sqrt{\frac{2k_B T}{\pi m}} \times \frac{1}{L_z} \times s_i \), the Langmuir rate of adsorption
can be written as,
\[
\frac{dN_a}{dt} = \gamma_i(N_F - N_a)(N_c - N_a)
\]  
(5.7)

Typically the sticking coefficient \( s_i \) ranges between \((0,1)\) and is treated as the model parameter. A sticking coefficient of \( s_i = 0 \) means that none of the incident atoms stick to the surface while \( s_i = 1 \) means that all incident atoms will get stuck to the surface. Dividing by \( N_c \) throughout,
\[
\frac{dn_a}{dt} = \gamma_i(n_F - n_a)(1 - n_a)
\]  
(5.8)

Solving for \( n_a(t) \) we get the following general expression,
\[
n_a = \frac{n_F - n_F e^{(1-n_F)\gamma_it}}{n_F - e^{(1-n_F)\gamma_it}}
\]  
(5.9)

Expanding the exponential for small times, we get the following linear dependence of site occupation with time,
\[
n_a = \gamma_i n_F t
\]  
(5.10)

5.3.1.1 Low Occupation Regime

Figure 5.6 shows the fits obtained using equation (5.9) with a sticking coefficient of \( s_i = 1 \) and \( s_i = 1.67 \). For initial times we see that the data follows the linear trend predicted by the model. However, the model underestimates the rate of adsorption even when every atom that approaches a site gets stuck to it \( (s_i = 1) \). The model fits the data for a much larger sticking coefficient of \( s_i = 1.67 \) per site. This steeper rate of adsorption indicates that the fluorine atoms are not independent of each other but get adsorbed on the surface in a correlated manner. We know that the adsorption of a fluorine atom causes the carbon atom to pucker out of the plane.
making the neighboring sites ideal candidates for fluorine attachment from the opposite side.

![Figure 5.6](image)

**Figure 5.6.** Figure shows the adsorption isotherms for different initial gas densities. Dashed lines are fits obtained with the Langmuir model for sticking coefficient $s_i = 1, 1.67$. Steeper initial rise of lattice occupation indicates correlated adsorption of fluorine.

The higher initial rate of adsorption supports the assertion that fluorine adsorption starts in a correlated fashion. To demonstrate this point we calculate the probability of fluorine attachment from the same and opposite sides, to an already modified site, as a function of the manhattan neighbor distance from this site. The SamePairCorrelation function measures the probability of finding another fluorine atom adsorbed from the same side and the OppositePairCorrelation function measures the probability of finding another fluorine atom attached from the other side at a distance $\delta$ away from this site.

\[
\text{SamePairCorrelation} = \frac{1}{N_a \times N_\delta} \sum_{a,\delta} f_a \times f^{\text{same}}_\delta \\
\text{OppositePairCorrelation} = \frac{1}{N_a \times N_\delta} \sum_{a,\delta} f_a \times f^{\text{opposite}}_\delta
\]  

(5.11) (5.12)

Here $f_a$ represents the side of attachment of fluorine at site $a$ and equals (-1,0,1) corresponding to: the site is modified from below, unmodified, or modified from
above the plane, respectively. $N_δ$ represents the number of neighbors at a manhattan distance of $δ$ from site $a$. Figure 5.7 shows the pair correlation functions plotted upto a Manhattan distance of 3 for different initial starting configurations of fluorine. To compare these numbers, note that for a completely random adsorption process the probability of finding an atom at a neighboring site is equal to $n_a$, the occupation of the lattice. Hence the pair positive and pair negative correlation function for random fluorination upto a site occupation of $n_a$ is equal to $n_a/2$ each, respectively. We can see that there is a higher probability of fluorine adsorbing from the opposite side on nearest neighboring sides for all initial fluorine percentages. However comparing this number to the threshold probability of $n_a/2$ for random adsorption, we see that the negative pair correlation on neighboring sites is significant only upto a site occupation of 25%. For higher occupations (higher initial values of $n_F$) the opposite pair correlation function (-0.4) is at the level of the threshold for random occupation($n_F = 0.5, n_a = 0.47, n_a/2 = 0.25$). Thus initially the fluorine adsorption happens in a correlated manner with preferential nearest neighbor attachment.

### 5.3.1.2 High Occupation Regime

Our model predicts that, asymptotically, the occupation of the lattice should saturate to $n_a = n_f$. Though this is the case for smaller initial gas densities ($n_F = 25\%$), the data does not follow this trend for higher starting concentrations of fluorine. It seems that as more fluorine atoms adsorb on the surface, they form a negatively charged repulsive layer, preventing more atoms from further approaching the surface. This effect can be modeled by considering that beyond a certain lattice population the number of available sites is $(1 - \theta n_a$), where the parameter $\theta > 1$ indicates an average lowering of the number of available sites due to occlusion from
Figure 5.7. Figure shows the same and opposite side pair correlation function as a function of manhattan distance from an already modified site for different initial gas densities.

already modified sites. Thus,

\[ \frac{dn_a}{dt} = \gamma_i (n_F - n_a)(1 - \theta n_a) \quad (5.13) \]

with,

\[ n_a = \frac{n_F - n_F e^{(1-\theta n_F)\gamma_i t}}{n_F \theta - e^{(1-\theta n_F)\gamma_i t}} \quad (5.14) \]

Figure 5.8 shows that for higher lattice populations, on an average, each fluorine atom can be thought of as occupying 1.82 lattice sites, preventing further adsorption onto the lattice. While there is a great deal of evidence that graphene can be fluorinated upto 100% coverage, we do not see that with the ReaxFF force field. One reason could be that the force field predicts \( C_2F \) chair as a more stable configuration compared to \( CF \). Formation energy calculations by Junkermeir et al. show that unlike DFT, the \( C2F \) chair configuration has a lower energy compared to \( CF \) [79]. Another explanation could be that the time scales necessary for fluorine
to diffuse and reach an equilibrium configuration is not accessible within the time scale of typical molecular dynamics simulations.

### 5.3.2 Surface Configurations and Magnetic Response

Recent experimental techniques to image the surface of fluorinated graphene shows the formation of highly ordered sizable (150 nm) domains of $CF$, $C2F$ chair and unfluroinated graphene on the surface. These results were obtained after fluorination of CVD graphene with $XeF_2$ \[77\]. Meanwhile other experimental groups report inhomogeneous and disordered microscopic configurations after fluorination with $CF_4$ plasma. With ReaxFF we provide a theoretical description of the surface configurations using an atomic gas source. From the adsorption isotherms we predict that though initially the adsorption of fluorine starts in a correlated manner, the shower of fluorine atoms causes several sites to get fluorinated with no time in between for the atoms to diffuse and form larger domains. This can be contrasted
to the predictions of the energetics based monte carlo simulations of Chapter 4 where fluorine adsorption proceeds outwards from small nucleation sites to form large domains of fluorinated regions. The shower of fluorine atoms leave many sites unoccupied with not enough time for large ordered domain formation.

Figure 5.9. Shows a simulation cell with $n_a = 25\%$. a) on the left shows occupied sites in blue and red color and unmodified sites in grey color. Blue(Red) triangles represent fluorine attachment from above (below) on sublattice A (sublattice B) and inverted blue (inverted red) triangles represent fluorine attachment from above (below) on sublattice B (sublattice A). b) on the right shows $CF$ like clusters formed on the surface.

To demonstrate this we study the surface configurations upon fluorine adsorption by creating a graphical user interface that displays the graphene lattice at a given time of the MD simulation. Unmodified sites are represented by grey triangles. Sites that are modified from above or below on a particular sub-lattice are indicated by different symbols as shown in Figure 5.9 a). In Figure 5.9b) we delineate $CF$ like clusters on the surface. A $CF$ like cluster is a region on the surface where fluorine atoms attach from opposite sides on neighboring sites. Because the sub lattice symmetry of graphene is broken upon fluorine attachment, we get two topologically distinct $CF$ like clusters. Yellow (Green, Type B) clusters also called Type A
clusters denote fluorinated $CF$ like regions where the fluorine atom adsorbs from above(below) on sublattice A (sublattice B) and below (above) on sublattice B (sublattice A). We can see that small $CF$ like regions are only a few atoms in length and randomly scattered throughout the surface.

![Cluster counts for sizes](image1)

![Cluster counts for sizes](image2)

**Figure 5.10.** Figure shows the distribution of Type A, Type B, and unfluorinated carbon clusters of different sizes with $n_F = 50\%$ for a) $n_a = 25\%$ and b) $n_a = 47.3\%$.

Counting the number of Type A, Type B, and unfluorinated clusters of a given size, we see that as more fluorine adsorbs on the surface the overall distribution of $CF$ like clusters shifts towards larger cluster sizes (see Figure 5.10). However, even the largest sized $CF$ clusters do not extend beyond 5-6 atoms in size. As more fluorine atoms attach on the surface, we see a larger number of unfluorinated carbon regions of smaller sizes. This is to be expected from the shower of fluorine atoms producing small patches of regions that do not get fluorinated.

From the surface configurations we predict the magnetic response of fluorinated graphene following the procedure described in Chapter 3. We count the number of odd unfluorinated carbon atoms at the end of the simulation for each of the starting fluorine concentrations. From Chapter 3, each odd carbon cluster contributes a spin of $1\mu_B$. The total spin concentration per carbon can be calculated as a weighted sum of the spin of each odd cluster. Figure 5.11 shows the spin density as a function
Figure 5.11. Comparison of spin concentrations produced by the surface configurations obtained with ReaxFF with that obtained experimentally as shown in Figure 3 of [1].

of fluorination percentage. The spin concentration measured by Nair is also showed on the same graph. With the configurations generated by ReaxFF we find that the moment concentration is at least two orders of magnitude larger than that obtained experimentally. In the absence of large domains of $CF$ like regions the $p_z$ orbitals of small unfluorinated regions can no longer be considered isolated and would not produce spin polarized localized states at the Fermi level. We need to revise our model to include the effect of interaction between weakly localized spins to describe the magnetic response from the microscopic configurations produced by ReaxFF.

### 5.4 Conclusions and Future Work

In summary, we provide a theoretical description of the microscopic configurations formed on the surface upon fluorination with atomic fluorine using ReaxFF. We find that the screening from fluorine atoms already adsorbed on the surface prevents
an unphysical charge transfer to atoms that are far away from the surface. The current version of the ReaxFF force field has also been parameterized against the DFT barrier for fluorine migration and bond dissociation on graphene, making it more robust compared to older versions.

The surface configurations formed after a 0.25ns duration simulation comprise of small chains of $CF$ like regions interspersed with unfluorinated carbon atom sites. Moreover, the occupation of the lattice saturates at a low fluorine coverage (roughly 50%). This suggests that the timescale of the simulation is not significant to allow for fluorine atoms to diffuse and reach an equilibrium configuration. The fact that the force field predicts a lower energy configuration for $C_2F$ chain compared to $CF$ could also lead to low lattice occupations.

Though the magnetic spin model described in Chapter 3 does well to predict the spin density for highly fluorinated graphene with ordered domain configurations, such as those produced by the monte carlo simulations presented in the Appendix, it needs to be updated for the ReaxFF configurations. The unfluorinated carbon atoms in the ReaxFF configuration are weakly confined and interact with neighboring spins. The effects of this interaction is likely to reduce the net spin per carbon.

In conclusion, we believe that any realistic simulation of graphene fluorination needs to have the correct charge transfer behavior for fluorine adsorption. Current implementations of classical molecular dynamics force fields are based on DFT charges and as such affected by the same self interaction error. Even though the charge on the fluorine atoms seem to go to zero for large distances from the surface, we cannot be sure that this is the correct physical behavior. Our efforts suggest for an urgent and cautious look at theoretical structure calculation methods and emphasizes the need to develop new functionals that will correct the DFT delocalization error.
Chapter 6  
Conclusions and Future Work

The overall conclusions of this dissertation are presented as follows. In Chapter 3, we introduce a theoretical model to explain the origin of spin 1/2 paramagnetism in partially fluorinated graphene observed in experiments. Using DFT we investigate the electronic structure of fluorine vacancy sites in fluorographene. We find that the unfluorinated carbon atoms at these sites produce localized magnetic states in the low energy spectrum of the density of states. Since DFT uses mean field approximation, it does not provide an accurate description of the excited states. In the presence of an external magnetic field that couples to the system, the excited states could play an important role in the response of the system. We construct a minimal Hubbard model that describes the localized states produced by the unfluorinated carbon atoms. Parameters for this model are obtained by fitting to DFT density of states. The model is then solved exactly to obtain the magnetic response of the unfluorinated carbon regions. We find that most odd unfluorinated regions have a spin 1/2 response and most even regions have a spin zero response. The magnetic response from this model is combined with a montecarlo simulation of graphene fluorination provided in the Appendix to predict the overall response of partially fluorinated samples.
The montecarlo simulation is an energetics based model that only includes interactions up to nearest neighbor distances to drive the fluorination process. The chemistry of bond formation, non-bonded interactions etc. are missing from this description. A classical dynamical simulation that incorporates physical parameters such as bond energy, bond length, coulomb interactions, charges on atoms; calculated with quantum chemistry techniques should provide a realistic description of what happens during the fluorination process. Therefore, before going on to the direct fluorination using ReaxFF (a classical force field), we stop to look at the DFT description of dilute fluorine adsorption on graphene.

In Chapter 4, we show that semi-local functionals predict an unphysical binding energy and charge transfer to the fluorine atom as the C-F bond is stretched. The charge on the fluorine atom is -0.2e at 10Å from the surface. This implies that classical potentials that are trained with DFT will reproduce this behavior and the fluorine atoms will be accelerated over large distances to the surface. The unphysical charge predictions of DFT on dissociated fragments is due to the delocalization error of semi local functionals and has been seen in the context of bond dissociation in finite molecules such as NaCl, H₂, etc. Nonlocal functionals like Hartree-fock are self interaction error free and have had success in providing a more physically correct description of the dissociation process in finite systems. While this method is being implemented for fluorine adsorption on graphene, we present a simple model that provides a physically intuitive description of the charge transfer process. Using this model, we predict a transition to an ionic state at a distance of 5Å from the surface.

In Chapter 5, we look at the surface configurations produced in a dynamical simulation of graphene fluorination with atomic fluorine using ReaxFF. In support of using ReaxFF, we show that the charge transfer to fluorine atoms is zero beyond
from the surface due to screening from atoms already adsorbed on the surface. Though initially the adsorption starts in a correlated manner especially on nearest neighbor sites overtime the atomic configurations formed barely extend beyond a few atoms in size. There is no large scale domain formation. Moreover, the fluorine occupation seems to saturate at the 60% limit. The shower of fluorine atoms on the surface causes simultaneous adsorption on several sites with not enough time for the atoms to diffuse towards a more equilibrated configuration. This produces several unfluorinated carbon sites that interact with each other and hence applying the model of Chapter 3 to these configurations overestimates the spin response. It is also important to point out that the ReaxFF force field predicts a lower energy ground state for $C_2F$ structure compared to $CF$. This could also contribute to the observed saturation of surface adsorption concentration at 60%.

There are several future directions that can provide interesting insights into the problem of graphene fluorination. Montecarlo accelerated molecular dynamics techniques could be used to access much longer time scales compared to ReaxFF simulations, producing more equilibrated surface atomic configurations. However, since these methods still rely on DFT calculations, a delocalization error free functional like Hatree-fock is expected to provide a better description of the physics behind the atomic interactions in any dynamical simulations. Implementation of such techniques hold much promise for future research.
Appendix

Energetics Based Monte Carlo Simulation of Graphene Simulation

Our group has been actively working to simulate the fluorination of graphene using large scale molecular dynamics techniques. One of the first methods simulates the fluorination of graphene using an energetics based monte-carlo technique [57]. The probability of fluorine attachment is calculated based off the energies from an Ising like model that describes the nearest neighbor interaction between fluorine atoms on the surface. The Ising model is extensively used to study interacting spins in condensed matter systems. In the Ising like model of fluorine simulation the side from which fluorine attaches represents the spin at site $i$. The spin can take values $s_i = \{-1, 0, 1\}$, where (-1) is for attachment from below the plane, (0) is for an unmodified site, and (+1) is for attachment from above the plane. The
Hamiltonian describing the energetics of this process is written as,

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

(1)

Here, \( J_{\text{opp}} \) represents the coupling between neighboring fluorine atoms attached on the opposite sides of the plane, \( J_{\text{same}} \) represents the coupling for same side attachment, and \( \mu \) represents the energy of adsorption independent of the direction of approach. The hexagonal lattice is populated using a metropolis algorithm [86]. The energy change \( dE \), for each move is calculated using the above Hamiltonian and immediately accepted if \( dE < 0 \). If \( dE > 0 \), the change is accepted with a probability \( \exp(-dE/k_B T) \), where \( T \) is the temperature of the lattice. Once a desired concentration of fluorine is reached no further fluorine addition is made, however the adsorbed fluorine atoms are allowed to diffuse to empty sites, if it is energetically favorable using the same procedure as above, until energy fluctuations drop below a threshold value.

The parameters \( J_{\text{opp}} = -0.3eV \) and \( J_{\text{same}} = +0.3eV \) are selected based of DFT calculations that show that opposite side attachment is favored over same side attachment by an energy of 0.6eV on nearest neighbor sites (see figure .1). The value of \( \mu = -0.318eV \) and \( T = 0.027eV \) are adjusted to fit the experimentally measured spins of Nair et al. [1].
**Figure .1.** Same Vs Opposite side attachment. The adsorption energy of a second fluorine atom is plotted as a function of distance (carbon index) from an already modified site. The black line represents the energy for same side adsorption and red dotted line for opposite site adsorption.

A snapshot of the simulation cell at 90% coverage shows the formation of sizable clusters of fluorinated regions on graphene (see Fig..2). We can see the formation of two distinct fluorinated cluster types, one in which fluorine attaches from above on sub-lattice A (pink regions) and the other where fluorine attaches from above on sub-lattice B (orange regions). The two regions are topographically dissimilar with a distinct boundary separating them. The carbon atoms along this boundary remain unfluorinated as it is energetically unfavorable for fluorine atoms to attach from either above or below the plane at these sites (see Fig..2).
Figure 2. A typical simulation cell containing $300 \times 300$ carbon atoms at 90% fluorination. Pink regions represent CF like domains where the fluorine atom attaches from above on sublattice A and orange regions are domains where the fluorine atom attaches from below on sublattice A. Green regions represent unmodified sites. The inset is a zoom in of the region marked by the circle. It shows the unfluorinated carbon atoms that border the boundary of two domains with opposite fluorine orientation.

The carbon atoms along this boundary are an example of the unfluorinated carbon atoms that are the topic of discussion in chapter 3 of this thesis and play an important role in the magnetic response of partially fluorinated graphene. Since these unfluorinated carbon atoms follow the linear boundary between the two types of fluorinated clusters, they are mostly linear in shape. Hence, we can calculate the magnetic response of partially fluorinated graphene by counting the number of odd unfluorinated carbon structures at each fluorination percentage. From chapter 3, we determined that odd unfluorinated regions have a spin 1/2 response to an externally applied magnetic field. The total response of the sample can then be calculated using $\chi = N \chi_{1/2}$. Figure 3 shows the number of spins per carbon as a function of fluorination percentage calculated with the Ising like model and also the magnetic response for different fluorination percentages. The magnetic response is spin 1/2 paramagnetic and the total number of spins show good agreement with experimentally obtained results.
Figure 3. Magnetization as a function of fluorination percentage. i) Shows the number of spins per carbon atom $N_s$ as a function of fluorination percentage. The experimentally obtained spins from figure 2 of [1] is plotted alongside for comparison. ii) Shows the magnetic response as a function of temperature for different fluoridation percentages. Inset shows the linear relationship between $\frac{1}{X}$ and temperature for spin 1/2 response (Curie’s Law).
Bibliography


Vita
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Piali Mitil Aditya was born in Asansol, India where she did her initial schooling. She completed her Bachelors in Physics from St. Stephens College, Delhi and received a Masters in Theoretical Condensed Matter Physics from Delhi University. She spent a year at the Indian Institute of Technology (IIT), Delhi learning about optoelectronics and optical communications while writing her GRE and applying to graduate school in USA. She joined Pennsylvania State University in fall 2008 and started working in the research group of Dr. Jorge O. Sofo from fall 2010.

During the course of her graduate studies, Piali developed a keen interest in education and outreach. She has taught introductory physics courses to engineering and science majors as well as served as a summer lecturer for several of these courses. She received the physics department award for TA teaching excellence in 2015 and completed a Masters in Physics Education along the way to her Ph.D. She is also passionate towards the cause of improving the representation of women in physics and has served as the Vice-President of the student group Physics and Astronomy for Women.