

UC Riverside

UC Riverside Electronic Theses and Dissertations

Title

Local Density of States in Graphene

Permalink

<https://escholarship.org/uc/item/6q04g8bj>

Author

Yang, Ling

Publication Date

2011

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA
RIVERSIDE

Local Density of States for Single Impurity in Graphene

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Physics

by

Ling Yang

December 2011

Dissertation Committee:

Dr. Shan-Wen Tsai , Chairperson

Dr. Chandra Varma

Dr. Kirill Shtengel

The Dissertation of Ling Yang is approved:

Committee Chairperson

University of California, Riverside

Acknowledgments

First of all, I would like to express my sincere appreciation to my advisor Prof. Shan-Wen Tsai. It has been my honor to be her first Ph.D. student. I appreciate her time, patience, support of my Ph.D study and research. Her guidance, wide knowledge and understanding help me go through tough times in the Ph.D pursuit.

I also would like to thank my collaborators Prof. N. M. R. Peres and Bruno Uchoa for helpful discussions about the analytical calculation of the thesis. I am very grateful to my dissertation committee members Prof. Chandra Varma and Prof. Kirill Shtengel, for serving in my committee, for their insightful comments and hard questions. I especially appreciate Filippas D. Klironomos who taught me to use matlab for my research.

My sincere thank also goes to my colleagues in the Department of Physics and Astronomy, in particular my office mates Hsiang-Ku, Mayra, Kyungwook, Hulya and Vincent for the friendship, stimulating discussions, good advice and for all the fun we have had in the past 6 years.

To my husband, Henry, I send my deepest appreciation and love. He helped with the programming and faithfully supported me during the final stages of my Ph.D. I am also grateful to my parents in law for their support.

Lastly, I would like to express my unlimited gratitude and love to my parents, especially my mother, who gave birth to, raised and supported me with endless love. I also would like to send my sincere respect and appreciation to my aunt who financially supported me all the way to graduate school.

To my parents and family for all the support.

ABSTRACT OF THE DISSERTATION

Local Density of States for Single Impurity in Graphene

by

Ling Yang

Doctor of Philosophy, Graduate Program in Physics
University of California, Riverside, December 2011
Dr. Shan-Wen Tsai , Chairperson

Graphene consists of an atom-thick layer of carbon atoms arranged in a honeycomb lattice, and its low-energy electronic excitations are well described as massless Dirac fermions with spin half and an additional pseudospin degree of freedom. Impurities in graphene can have a significant effect on the local electronic structure of graphene when the Fermi level is near the Dirac point. We study the local electronic spectra and real-space and k-space local density of state (LDOS) maps of graphene with different impurities (diagonal and non-diagonal impurity potential) such as vacancies, substitutional impurities, and adatoms. In the presence of a perpendicular magnetic field, we use a linearization approximation for the energy dispersion and employ a T -matrix formalism to calculate the Green's function. We investigate the effect of an external magnetic field on the Friedel oscillations and impurity-induced resonant states.

Using a multimode description for an scanning tunneling microscope (STM) tip, we calculate STM currents for the substitutional and vacancies case and find that strong resonances in the LDOS at finite energies lead to the presence of steps in the STM current and suppression of the Fano factor. We also describe in detail the theory of scanning tunneling spectroscopy in graphene in the presence of adatoms, magnetic or

not, with localized orbitals of arbitrary symmetry, corresponding to any given angular momentum state. We show that quantum interference effects which are naturally inbuilt in the honeycomb lattice, in combination with the orbital symmetry of the localized state, allow scanning tunneling probes to characterize adatoms and defects in graphene.

Contents

List of Figures	ix
1 Introduction	1
2 Green's function for substitutional impurity	7
2.1 Graphene green's function	7
2.2 Local density of states	13
2.3 STM Tip and current	26
3 Magnetic field effects on the local electronic structure near a single impurity in graphene	36
3.1 Dirac Hamiltonian for a two-dimensional system in the presence of a magnetic field	36
3.2 Continuum Hamiltonian for the graphene in the presence of a magnetic field	41
3.3 Numerical Results and Discussions	46
4 Orbital symmetry fingerprints for adatoms in graphene: theory for scanning tunneling probes	52
4.1 Hamiltonian	55
4.2 Local magnetic moments	58
4.2.1 Local DOS	66
4.3 STM theory	69
4.3.1 Green's functions	72
4.3.1.1 Local DOS	75
4.3.2 Tunneling current	77
4.3.2.1 Differential conductance	81
5 Conclusions	91
Bibliography	94
A	98
A.1 Exact Green's functions	98

List of Figures

2.1	(color on line) Honeycomb lattice of graphene, with an substituting impurity at the A sublattice (the square). The unit cell vector $\mathbf{a}_1$ and $\mathbf{a}_2$ as well as the next nearest neighbors vectors δ_i ($i=1,2,3$) are also represented.	8
2.2	LDOS for $t_0 = t$ at the impurity site. Upper left figure corresponds to $\rho_a(\omega, 0)$, upper right figure to $\rho_a(\omega = 0, \mathbf{r})$, Second row left figure corresponds to $\rho_b(\omega, 0)$, second row right figure to $\rho_b(\omega = 0, \mathbf{r})$	17
2.3	LDOS for the case $t_0 = -0.5t$ and $\epsilon_0 = 0.6t$. Upper left figure corresponds to $\rho_a(\omega, 0)$, upper right figure to $\rho_a(\omega = -2.950, \mathbf{r})$, Second row left figure corresponds to $\rho_b(\omega, 0)$, second row right figure to $\rho_b(\omega = -1.0, \mathbf{r})$. . .	18
2.4	LDOS for the case $t_0 = 0.6t$ and $\epsilon_0 = -0.4t$. Upper left figure corresponds to $\rho_a(\omega, 0)$, upper right figure to $\rho_a(\omega = -0.7t, \mathbf{r})$, Second row left figure corresponds to $\rho_b(\omega, 0)$, second row right figure to $\rho_b(\omega = -1.0, \mathbf{r})$. . .	20
2.5	Local density of states in sublattice A and B as function of $r > 0$. The dashed-dotted line is the density of states of pristine graphene at the energy $\hbar\omega = 0.5$ eV. The point $r = 0$ is excluded. The small wavelength oscillations are due to the cut-off momentum k_c and the large ones are the $2q_F$ Friedel oscillations.	21
2.6	Fourier transform of the local density of states. The first row is the density of states in sublattice A (ρ_a), the second row is the density of states in sublattice B (ρ_b), and the third row is the sum of the two, $\rho_a + \rho_b$. Column (a) is for the case of a vacancy, and $\omega = 0.3$ eV. Column (b): $t_0 = -1$ eV, $\epsilon_i = 1$ eV, $\omega = 0.3$ eV. Column (c): $t_0 = 1$ eV, $\epsilon_i = -1$ eV, $\omega = -1.5$ eV. Column (d): $t_0 = 2$ eV, $\epsilon_i = -1$ eV, $\omega = -0.3$ eV.	23
2.7	Fourier transform of the local density of states for $t_0 = 2$ eV, $\epsilon_i = -1$ eV. The first row is the density of states in sublattice A (ρ_a), the second row is the density of states in sublattice B (ρ_b), and the third row is the sum of the two, $\rho_a + \rho_b$. Column (a) is for $\omega = 0.05$ eV. Column (b): $\omega = 0.15$ eV. Column (c): $\omega = 0.3$ eV. Column (d): $\omega = 0.5$ eV.	25
2.8	(colour online) Representation of the STM tip.	27
2.9	Local density of states, $\rho_b(E)$, at the atoms of the tip given by $n = -1, m = 1, 2$. Left: $V = 2$ eV, $V_\perp = 2$ eV. Right: $V = 2$ eV, $V_\perp = 1$ eV. The multi-mode nature of the tip is clearly seen.	30

2.10	Local density of states, $\rho_x(E)$, for $x = a, b$ at the graphene's unit cell $\mathbf{r} = 0$. We have used $t = 3$ eV. Upper left: density of states of pristine graphene and at the B site close to a vancancy. All other panels: local density of states at A (impurity) and B (next to the impurity) sites for different values of the parameters t_0 and ϵ_i . The values of t_0 and ϵ_i corresponds to different types of impurities.	33
2.11	Transmission probability $T(E)$. The parameters used are (all in electron-volt): $V = 2$, $V_\perp = 1$, $W_1=0.9$, $W_2 = 0.2$, and $\epsilon_0 = 0.2$. The resonances seen in the LDOS in Fig. 2.10 show up in the transmission function. The values of t_0 and ϵ_i are the same used in Fig. 2.10 and the four panels here correspond to the same ones in that figure.	34
2.12	STM current J . The parameters used are (all in electron-volt): $V = 2$, $V_\perp = 1$, $W_1=0.9$, $W_2 = 0.2$, and $\epsilon_0 = 0.2$. The values of t_0 and ϵ_i are the same used in Fig. 2.10. The transmission function was computed at finite bias; the zero bias case is given in Fig. 2.11. The four panels here correspond to the same ones in that figure 2.11.	35
3.1	LDOS without impurity. Upper left figure corresponds to $\rho_0(\omega)$ at $\omega_c = 0.1$, upper right figure to $\rho_0(\omega)$ at $\omega_c = 0.2$. Second row left figure corresponds to $\rho_0(\omega)$ at $\omega_c = 0.6$, second row right figure to $\rho_0(\omega)$ at $\omega_c = 1.0$	48
3.2	LDOS real space distribution with different impurity at $\omega = \omega_c = 0.2$. First row is the LDOS at A site. Second row is the LDOS at B site. First column is LDOS for the Boron like impurity. Second column is LDOS for Nitrogen like impurity. Third column is for vacancy case.	48
3.3	LDOS k space distribution with different impurity at $\omega = \omega_c = 0.2$. First row is the LDOS at A site. Second row is the LDOS at B site. Third row is the total LDOS. First column is LDOS for the Boron like impurity. Second column is LDOS for Nitrogen like impurity. Third column is for vacancy case.	50
3.4	LDOS k space distribution with different magnetic field for Nitrogen like impurity. First row is the LDOS at A site. Second row is the LDOS at B site. Third row is the total LDOS. First column is LDOS for $\omega_c = 0.15$. Second column is LDOS for $\omega_c = 0.30$. Third column is for $\omega_c = 0.6$. . .	51
4.1	Honeycomb lattice in graphene, with two distinct sublattices (black and white circles). a) Adatom siting on top of a carbon atom on sublattice A , and b) sitting in the center of the honeycomb hexagon. Red arrows: nearest neighbor vectors.	57
4.2	Illustration of d -wave and f -wave localized orbitals for an adatom that sits at the center of the honeycomb lattice hexagon. a) $d_{x^2-y^2}$ orbital, that corresponds to hybridization amplitudes $V_{x,1} = V$ and $V_{x,2} = V_{x,3} = -V/2$ with the six nearest neighbor carbon atoms on sublattices $x = a, b$, at the vertexes of the hexagon [see Eq. (4.7), (4.8)]. b) d_{xy} orbital corresponding to $V_{x,1} = 0$ and $V_{x,2} = -V_{x,3} = V$. c) $f_{x(x^2-3y^2)}$ orbital, with hybridization amplitudes $V_{a,i} = -V_{b,i} = V$	58

4.3	C_{3v} invariant orbitals for adatoms sitting in the center of the hexagon, on H sites (top), and in substitutional (S) sites (bottom). On the left: s -wave orbitals, with zero angular momentum ($m = 0$); on the right: in-plane f -wave orbitals ($m = 3$). In the two cases, the adatoms hybridize equally with the carbon atoms on the same sublattice (see text).	63
4.4	Level broadening $\Delta(\omega)$ as a function of energy, ω , for different orbital symmetries. All energies in units of the hopping energy t ($V/t = 1/3$). a) Type I orbitals for adatoms sitting on a top carbon site (light/red solid curve) and for d_{xy} -wave (black line) and d_{zx} -wave orbitals (dashed line) on H sites. b) Type II orbitals on H sites. Solid curve: in-plane f -wave orbital; dashed curve: s -wave orbital. Inset: low energy scaling of the level broadening, $\Delta(\omega) \propto \omega ^3$ for $ \omega /t < 1$ (see text). c) Substitutional s/f -wave orbitals (black curve) and d_{xy} -wave orbital (light curve), on S sites.	64
4.5	Comparison of the LDOS between the two different sublattices. Top panels: Energy integrated LDOS around an adatom (center) sitting on a top carbon adatom site. Scans for a) the same sublattice of the impurity and b) for the opposite sublattice. Lower panels: Energy integrated LDOS around a localized orbital (center) with $m = 0$ ($L_z = 0$) angular momentum state, when the adatom sits in the center of a honeycomb hexagon (H site). c) scans for sublattice A and d) B . The two scans are related by a π -rotation.	67
4.6	LDOS around the adatom (center) at a fixed energy ($\omega = -0.2\text{eV}$) for adatoms on H sites. a) LDOS for a $d_{x^2-y^2}$ orbital and b) for an in-plane f -wave orbital.	85
4.7	Fourier transform of the energy integrated LDOS around the adatom. Solid hexagon line indicates the Brillouin zone. The peaks at the center of the zone correspond to forward scattering processes, whereas the peaks at the corners of the zone (K) points correspond to backscattering between the two valleys. Top panels: adatom on a top carbon site case; Fourier transform of the LDOS for the a) opposite and b) same sublattice of the adatom. c) superposition of the patterns in panels a) and b), for both sublattices. d) s -wave orbital at an H site. Lower panels: e) $d_{x^2-y^2}$ -wave orbital and f) $f_{x(x^2-3y^2)}$ orbital also at H sites. The insets in panels d), e) and f) show the details of the forward scattering peaks at the center of the BZ.	86
4.8	Schematic drawing of the STM tip nearby an adatom (small light [red] circle) on top of graphene. Black and white circles: carbon atoms on sublattices A and B . R is the in-plane distance of the impurity to the tip and z the out of plane distance from the center of the tip to the graphene layer.	87
4.9	Energy integrated LDOS around the adatom (center) in the presence of an STM tip. a) Scans for the same sublattice of the impurity and b) for the opposite sublattice (top carbon site case). Scans for sublattice c) A and d) B , nearby an adatom sitting at the center of a honeycomb hexagon (center).	88

- 4.10 Graphene LDOS at the adatom site (top carbon case) for $t_f/t_a = 0.1, 0.7, 1.1$ and 1.6 , from (a) to (d) ($t_a = t_b = 0.15\text{eV}$). Black curve: $n_\uparrow$; brown: $n_\downarrow$. Total LDOS: $n_\uparrow + n_\downarrow$. The two resonant peaks have energy $\epsilon_0 + n_\downarrow U$ and $\epsilon_0 + n_\uparrow U$, with $\epsilon_0 = -0.5\text{ eV}$ and $U = 1\text{eV}$ (see text) 89
- 4.11 Differential conductance induced by the adatom versus bias, when the adatom sits (left) on top of carbon and (right) in the center of the hexagon. See details in the text. a), b) $t_a = t_b = 0.15\text{eV}$ and $t_f/t_a = 1.6, 1.5, 1.35, 1.1, 0.7, 0.25$ and 0.1 (inset), from top to bottom. c), d) $t_c = 0.02\text{eV}$ and $t_f/t_c = 0.7, 0.25, 0.1, 0.05$ and 0.01 . $t_f/t_c = 0.1$ for all curves in red. . . 90

Chapter 1

Introduction

Graphene [44, 45] consists of a monolayer of covalently bonded carbon atoms forming a two-dimensional honeycomb lattice [42]. Low-energy electronic excitations in graphene are well described as massless Dirac fermions with an additional pseudospin degree of freedom. Because of the Dirac spectrum, impurities can have a strong effect on the local electronic structure of graphene when the Fermi energy is near the Dirac point [4, 9, 23, 47–49, 56]. Impurities in graphene can be in the substrate, in the form of adatoms, or as imperfections in the lattice itself. In one hand, there has been very significant progress in decreasing the amount of disorder introduced in graphene, for example by fabrication of suspended samples [40]. On the other hand, impurity effects have been explored to modify and tailor the electronic, thermal and chemical properties of graphene. Examples of the later include experiments with graphane [16], chemical substitution of some of graphene’s carbon atoms by boron and nitrogen atoms [46, 71], and doping of graphene with metals on top [10, 31].

Since graphene is an atomically thin membrane, it can be easily accessed with Scanning Tunneling Microscopy (STM) measurements. Impurity effects can be studied

with atomic resolution and the local spectrum can be obtained by STM spectroscopy. In addition, atomic manipulation can also be performed with STM. There has been several STM studies of graphene grown epitaxially on SiC [7, 39, 58], mechanically exfoliated graphene on SiO₂ [11, 20, 28, 58, 69], and graphene flakes on graphite [37]. In fact, STM experiments have proved instrumental in mapping the topography of corrugated graphene and determining the existence of charge puddles [72]. Additionally, STM experiments are also able to probe the chiral nature of the electrons in graphene when they scatter from impurities [27]. This experimental work showed that intravalley backscattering is virtually absent in graphene. In particular, the STM experiment showed the lack of the $2q_F$ (q_F is the Fermi momentum) Friedel modulation on the local density of states of graphene. As we show explicitly below, this lack of modulation can be traced to the fact that the local density of states at the A and B sublattices are out of phase by π , an aspect already noted in passing previously [5, 60]. Therefore, the local density of states, when averaged over the unit cell, shows no trace of the $2q_F$ oscillation. Additionally, as we show below, at distances d close to the impurity, $d \ll 1/q_F$, there is a strong departure from the $1/r^2$ spatial dependence [2, 9] of the local density of states. Moreover the form of the density of states close to the impurity is very sensitive to type of disorder: diagonal, non-diagonal, or vacancies.

In Chapter 2, we present calculations of STM currents in locally disordered graphene. We focus on the case of chemical substitution (by boron or nitrogen atoms, for example) and use a multimode description for the STM tip. We obtain exact analytical expressions for the local density of states, and also present results for energies beyond the Dirac cone approximation. We model the substitutional impurity by both an on-site impurity potential and local hopping disorder. We find that inclusion of the hopping disorder term leads to additional higher harmonics oscillations in real space for the

density of states for the sub-lattice that does not contain the impurity. The main oscillations in the two sub-lattices are out-of-phase away from the impurity. For the regime in which the electronic hopping between the impurity and the nearest neighbor carbon atoms is decreased in relation to the hopping between carbon atoms in the clean system, the local density of states presents strong resonances. A vacancy is a extreme case of this regime. These resonances lead to the appearance of steps in the STM current, a signature that should be observable experimentally. These resonances also leads to open channels for tunneling between the STM tip and graphene, and lead to a decrease in the Fano factor.

Another issue addressed in this chapter, relates to the effect of the tip on the measured STM currents. In the usual analysis, the electrons in the tip are represented by jellium model with constant density of states. In this type of model neither the real part of the self-energy due to the tip-system coupling nor the variation of the density of states with energy is included (wide band limit). The tip, however, is not an infinite metal. In fact it has a structure where the number of atoms in the atomic planes reduces as we approach the tip. In a previous publication [51] we have modeled the tip as a one dimensional model (in that work we have also considered the simplification of zero on-site energy at the impurity), which corresponds essentially to the case of a constant density of state too a good approximation. In that case we found the STM current to be symmetric around zero energy. When we generalize to the case of a multimode tip this symmetry is lost, as we show in the first part of my work. Comparing the results of Ref. [51] with those given here it is possible to disentangle the effects due to graphene and to the impurities from those due to the tip. This part shows that some care has to be taken when interpreting the STM currents directly.

The second chapter is organized in the following way: In Section 1, the Green's

function formalism is presented, with analytical results for the Green's function for graphene with a substitutional impurity, and for the STM tip modeled by a multimode system. Local density of states results are presented in Section 2, and results for the STM current are presented in Section 3.

In the third chapter, we discussed the impurity effect on the Friedel oscillations and impurity-induced resonant states in presence of the magnetic field, we will see Landau level for the low energy quasiparticles instead of linear approximation. Here we introduce pseudospinor operator and T matrix formalism to calculate the Green's function. First section of this chapter, the Green's function for pristine graphene is given. The Green's function for graphene with a substitutional impurity in the presence of the magnetic field are presented in the second section. In the third section, numerical results are discussed.

As an open surface, graphene offers a solid playground for the detection and local manipulation of quantum states with scanning tunneling (STM) probes. This perspective is particularly promising for adatoms, which can be dragged with atomic precision [14] and can have their magnetic state monitored and controlled with the application of an external gate voltage [55, 61]. There has been substantial progress in the quality of the STM experiments in graphene in the last few years [11, 21, 26, 29, 37, 54, 58, 67, 70, 72]. Recent experiments reported the observation of Landau levels spontaneously generated by strain on the top of nanobubbles in graphene [36], and the observation of charge polarization effects around a Co adatom [6].

Although the microscopic theory of STM is well understood in metallic hosts [52, 59], in graphene the sublattice quantum numbers play a role in the interference effects that drive the emergence of Fano resonances [17]. Those resonances are the most distinctive feature that characterizes the differential conductance line shapes nearby

adatoms, in the presence of an STM tip. In particular, for adatoms that sit at the center of the honeycomb hexagon (H), destructive interference between the different electronic paths of hybridization within the two different sublattices may give rise to suppression of the Fano resonance of the localized state [32, 63, 65], and also change the scattering rate of the localized electrons in to the presence of the fermionic bath [63].

Graphene is also clearly distinct from conventional metallic hosts due to its low DOS. For instance, some adatoms and simple molecules such as NO_2 are not magnetic when adsorbed on top of metals, but are expected to develop a local magnetic moment in graphene [35], as a result of the low DOS in the host material, which lowers the size of the phase space for electronic transitions between states in the localized level and the bath [61]. This magnetic moment nevertheless can be fragile in the proximity of a large metallic STM probe, which can enhance dramatically the hybridization of the localized state with the extended electronic orbitals of the tip. The local moment in that case can be eventually suppressed by bringing the metallic tip sufficiently close to the magnetic adatom, reflecting in characteristic signatures in the differential conductance (DC) curves. This effect is not unique to graphene and may in principle be observed in other surfaces with low DOS, such as in the surfaces of three dimensional topological insulators [22, 53].

In general, the broadening of a localized state, magnetic or not, is expected to scale as $\Delta(\omega) \propto |\omega|^r$, where r is the scaling dimension of the DOS of the host material, which in graphene is $r = 1$. In graphene, nevertheless, localized orbitals of adatoms located either in substitutional impurity sites (S sites) or in H sites and which also preserve the C_{3v} point group symmetry of each sublattice are effectively damped at low energies by a fermionic bath with $r = 3$ [62, 63], due to quantum interference effects. Such orbitals may therefore belong to a different universality class regarding

the Kondo problem as compared to adatoms on top carbon sites, and also adatoms on S or H sites that explicitly break the sublattice point group symmetry [62], in which case the level broadening scales linearly with the energy ($\Delta(\omega) \propto |\omega|$) near the Dirac points. The purpose of the fourth chapter is not to address the spectroscopy of the Kondo effect [13, 25, 38, 55, 62, 66, 68, 73], which will be addressed somewhere else, but to describe in detail the effect of the localized orbital symmetry into the emergence of local resonances nearby the adatom. We also describe the behavior of the Fano line resonances in the differential conductance in terms of the position of the adatoms in the honeycomb lattice and of the specific symmetry of the localized orbital. Whereas the STM theory for adatoms in graphene has been described by us [63] for the case of s -wave orbitals, here we generalize that theory in order to account for effects of higher angular momentum states.

The outline of the fourth chapter is as follows: in section 1, we describe the generic zero dimensional Hamiltonian of an adatom in graphene; in section 2 we briefly describe the role of the orbital symmetry into the formation of local magnetic moments and we show the manifestation of those orbital symmetries in the local density of states (LDOS), whenever the adatom hybridizes with two or more carbon atoms. In section 3 we develop the STM theory in graphene, where we compute the differential conductance accounting for the symmetry of the localized orbitals and their position with respect to the sublattices.

Chapter 2

Green's function for substitutional impurity

2.1 Graphene green's function

Graphene is a two-dimensional honeycomb lattice which has two carbon atoms per unit cell represented in Figure 2.1, one from A sublattice, one from B sublattice. The unit cell vectors are $\mathbf{a}_1$ and $\mathbf{a}_2$, with magnitudes $|\mathbf{a}_1| = |\mathbf{a}_2| = a$, where $a = \sqrt{3}a_0 \simeq 2.461 \text{ \AA}$, and a_0 is the carbon-carbon distance. Any lattice vector $\mathbf{r}$ can be represented in this basis as $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$, with n, m integers. In Cartesian coordinates, $\mathbf{a}_1 = a_0(3, \sqrt{3}, 0)/2$ and $\mathbf{a}_2 = a_0(3, -\sqrt{3}, 0)/2$, and the reciprocal lattice vectors are given by: $\mathbf{b}_1 = 2\pi(1, \sqrt{3}, 0)/(3a_0)$ and $\mathbf{b}_2 = 2\pi(1, -\sqrt{3}, 0)/(3a_0)$. The vectors connecting any A atom to its nearest neighbors are: $\boldsymbol{\delta}_1 = (\mathbf{a}_1 - 2\mathbf{a}_2)/3$, $\boldsymbol{\delta}_2 = (\mathbf{a}_2 - 2\mathbf{a}_1)/3$, and $\boldsymbol{\delta}_3 = (\mathbf{a}_1 + \mathbf{a}_2)/3$.

We consider here the case where a substituting atom replaces a carbon atom in the A sublattice. When this happens two effects take place: (i) the on-site energy ϵ_0 at the impurity site is different from that at the carbon atoms; (ii) the hopping from and

to the impurity atom, t_i , changes relatively to that of pristine graphene. In the latter case, we model the change in the hopping by introducing an additional non-diagonal term to the Hamiltonian, such that $t_i = -t + t_0$ (see below). Using these definitions the Hamiltonian can be written as: $H = H_0 + V_t + V_i$, where

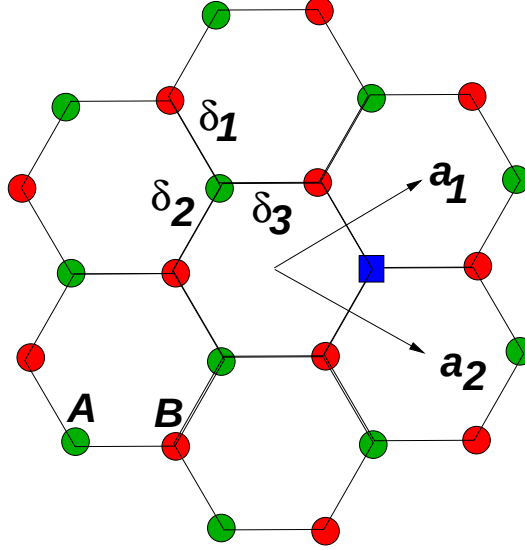


Figure 2.1: (color on line) Honeycomb lattice of graphene, with an substituting impurity at the A sublattice (the square). The unit cell vector $\mathbf{a}_1$ and $\mathbf{a}_2$ as well as the next nearest neighbors vectors δ_i ($i=1,2,3$) are also represented.

$$H_0 = -t \sum_{\mathbf{r}} [b^\dagger(\mathbf{r})a(\mathbf{r}) + b^\dagger(\mathbf{r} - \mathbf{a}_2)a(\mathbf{r}) + b^\dagger(\mathbf{r} - \mathbf{a}_1)a(\mathbf{r}) + \text{h.c.}], \quad (2.1)$$

is the kinetic energy operator and $a^\dagger$, a ($b^\dagger$, b) are fermion creation and annihilation operators in the A (B) sites. The spin index is omitted for simplicity. We consider an isolated impurity located at $\mathbf{r} = (0,0,0)$, on sublattice A, so that its contribution to the Hamiltonian has two terms:

$$V_t = t_0[a^\dagger(0)b(\delta_1) + a^\dagger(0)b(\delta_2) + a^\dagger(0)b(\delta_3) + \text{h.c.}] \quad (2.2)$$

and

$$V_0 = \varepsilon_0 a^\dagger(0) a(0) , \quad (2.3)$$

for hopping and potential disorder, respectively. In the case of zero chemical potential, when the Fermi level crosses the Dirac point, the system is most susceptible to the presence of impurities. In the particular case $t_0 = t$, hopping to the impurity site is completely suppressed, and the scattering term V_t represents a vacancy. It is well known [15] that the formation of a vacancy will lead to some local distortion of the carbon-carbon bonds. This effect is not incorporated in our Hamiltonian, which in that case would not be exactly solvable. The substitution of carbon atoms by boron or nitrogen has the main consequence of changing the local hopping and the onsite energy, both effects included in our description. The particular choice for boron or nitrogen is due to size restrictions imposed by the unit cell of graphene. We note here that replacement of carbon atoms by boron and nitrogen was already experimentally achieved [46]. We first calculate the single particle Green's functions for the system comprised of graphene and a single impurity, described by the Hamiltonian H above. The single particle Green's functions carry sub-lattice indices, and are defined as:

$$G_{aa}(\mathbf{k}, \mathbf{q}, \tau) = - \left\langle T \left[a_{\mathbf{k}}(\tau) a_{\mathbf{q}}^\dagger(0) \right] \right\rangle , \quad (2.4)$$

$$G_{bb}(\mathbf{k}, \mathbf{q}, \tau) = - \left\langle T \left[b_{\mathbf{k}}(\tau) b_{\mathbf{q}}^\dagger(0) \right] \right\rangle , \quad (2.5)$$

$$G_{ab}(\mathbf{k}, \mathbf{q}, \tau) = - \left\langle T \left[a_{\mathbf{k}}(\tau) b_{\mathbf{q}}^\dagger(0) \right] \right\rangle , \quad (2.6)$$

$$G_{ba}(\mathbf{k}, \mathbf{q}, \tau) = - \left\langle T \left[b_{\mathbf{k}}(\tau) a_{\mathbf{q}}^\dagger(0) \right] \right\rangle . \quad (2.7)$$

The equations of motion for the Green's functions are given by:

$$i\omega_n G_{aa}(\omega_n, \mathbf{k}, \mathbf{p}) = \delta_{\mathbf{k}, \mathbf{p}} + \sum_{\mathbf{q}} \left[\lambda_{\mathbf{k}, \mathbf{q}} G_{ba}(\omega_n, \mathbf{q}, \mathbf{p}) + \frac{\epsilon_0}{N_c} G_{aa}(\omega_n, \mathbf{q}, \mathbf{p}) \right] \quad (2.8)$$

$$i\omega_n G_{ba}(\omega_n, \mathbf{k}, \mathbf{p}) = \sum_{\mathbf{q}} \lambda_{\mathbf{q}, \mathbf{k}}^* G_{aa}(\omega_n, \mathbf{q}, \mathbf{p}) \quad (2.9)$$

$$i\omega_n G_{ab}(\omega_n, \mathbf{k}, \mathbf{p}) = \sum_{\mathbf{q}} \left[\lambda_{\mathbf{k}, \mathbf{q}} G_{bb}(\omega_n, \mathbf{q}, \mathbf{p}) + \frac{\epsilon_i}{N_c} G_{ab}(\omega_n, \mathbf{q}, \mathbf{p}) \right] \quad (2.10)$$

$$i\omega_n G_{bb}(\omega_n, \mathbf{k}, \mathbf{p}) = \delta_{\mathbf{k}, \mathbf{p}} + \sum_{\mathbf{q}} \lambda_{\mathbf{q}, \mathbf{k}}^* G_{ab}(\omega_n, \mathbf{q}, \mathbf{p}), \quad (2.11)$$

where

$$\lambda_{\mathbf{k}, \mathbf{p}} = -t\phi_{\mathbf{p}}(\delta_{\mathbf{k}, \mathbf{p}} - t_0/N_c t), \quad (2.12)$$

$$\phi_{\mathbf{p}} = 1 + e^{-i\mathbf{p} \cdot \mathbf{a}_1} + e^{-i\mathbf{p} \cdot \mathbf{a}_2}, \quad (2.13)$$

and N_c is the total number of unit cells in the lattice, and ω_n are fermionic Matsubara frequencies. Note that $\lambda_{\mathbf{p}\mathbf{q}} \neq \lambda_{\mathbf{q}\mathbf{p}}$. This is a consequence of the impurity hopping term V_t , which breaks sub-lattice symmetry. The impurity potential term V_0 also breaks sub-lattice symmetry, and therefore ϵ_0 appears in an asymmetric way in the equations above. The set of equations of motions can be solved exactly. The presence of the scattering term V_t leads to the appearance of the phases $\phi_{\mathbf{k}}$ and a more complex form for the T -matrix than usual. The exact solution for the Green's functions can be written, after a lengthy calculation, in the form [49]:

$$G_{aa}(\mathbf{k}, \mathbf{p}) = \delta_{\mathbf{k}, \mathbf{p}} G_{\mathbf{k}}^0 + g + h [G_{\mathbf{k}}^0 + G_{\mathbf{p}}^0] + G_{\mathbf{k}}^0 T G_{\mathbf{p}}^0, \quad (2.14)$$

$$G_{bb}(\mathbf{k}, \mathbf{p}) = \delta_{\mathbf{k}, \mathbf{p}} G_{\mathbf{k}}^0 + \frac{t\phi_{\mathbf{k}}^*}{i\omega_n} G_{\mathbf{k}}^0 T G_{\mathbf{p}}^0 \frac{t\phi_{\mathbf{p}}}{i\omega_n}. \quad (2.15)$$

where all the terms (G , G^0 , g , h and T) also depend on ω_n (omitted here for brevity).

The terms g , h , and T correspond to sums over infinite series of Feynman diagrams for

impurity scattering, and are given by:

$$g(\omega_n) = t_0^2 \bar{G}^0(\omega_n) / [N_c D(\omega_n)], \quad (2.16)$$

$$h(\omega_n) = t_0(t - t_0) / [N_c D(\omega_n)], \quad (2.17)$$

and

$$T(\omega_n) = -\frac{i\omega_n t_0(2t - t_0) - \epsilon_i t^2}{N_c D(\omega_n)} \quad (2.18)$$

where the denominator $D(\omega_n)$ is defined as

$$D(\omega_n) = (t - t_0)^2 + [i\omega_n t_0(2t - t_0) - \epsilon_i t^2] \bar{G}^0(\omega_n) \quad (2.19)$$

and

$$\bar{G}^0(\omega_n) = \frac{1}{N_c} \sum_{\mathbf{k}} G^0(\omega_n, \mathbf{k}) \quad (2.20)$$

with the diagonal component of the Green's function for the clean system given by ($\hbar = 1$)

$$G_{\mathbf{k}}^0 = G^0(\omega_n, \mathbf{k}) = \frac{i\omega_n}{(i\omega_n)^2 - t^2 |\phi_{\mathbf{k}}|^2}, \quad (2.21)$$

which is translationally invariant. The expressions for the Green's functions, Eqs. (2.14)-(2.19), are exact analytic solutions for graphene with one isolated substitutional impurity, including contributions from both the on-site energy ϵ_0 and the hopping parameter t_0 . Inclusion of the off-diagonal disorder t_0 leads to additional terms, and additional ω -dependence of the graphene Green's function. Since single particle properties, such as local electronic spectra, can be obtained directly from the Green's functions, this ω -dependence has direct experimental consequences, such as for STM spectroscopy mea-

surements.

If we do double Fourier transformation for the Green's function, the physics meaning for the terms in G_{aa} , G_{bb} will be more clear.

$$G_{aa}(\omega_n, \mathbf{R}, \mathbf{R}') = \frac{1}{N_c} \sum_{\mathbf{k}, \mathbf{p}} e^{i\mathbf{k}\mathbf{R} - i\mathbf{p}\mathbf{R}'} G_{aa}(\omega_n, \mathbf{k}, \mathbf{p}), \quad (2.22)$$

$$G_{bb}(\omega_n, \mathbf{R} + \delta_3, \mathbf{R}' + \delta_3) = \frac{1}{N_c} \sum_{\mathbf{k}, \mathbf{p}} e^{i\mathbf{k}(\mathbf{R} + \delta_3) - i\mathbf{p}(\mathbf{R}' + \delta_3)} G_{bb}(\omega_n, \mathbf{k}, \mathbf{p}), \quad (2.23)$$

so the real space Green's function are given by

$$\begin{aligned} G_{aa}(\omega_n, \mathbf{R}, \mathbf{R}') &= G_0(\omega_n, \mathbf{R} - \mathbf{R}') + g\delta_{\mathbf{R},0}\delta_{\mathbf{R}',0} + hG_0(\omega_n, \mathbf{R})\delta_{\mathbf{R}',0} \\ &+ h\delta_{\mathbf{R},0}G_0(\omega_n, \mathbf{R}') + G_0(\omega_n, \mathbf{R})TG_0(\omega_n, \mathbf{R}') \end{aligned} \quad (2.24)$$

$$G_{bb}(\omega_n, \mathbf{R} + \delta_3, \mathbf{R}' + \delta_3) = G_0(\omega_n, \mathbf{R} - \mathbf{R}') + \frac{t}{\omega_n} \tilde{G}_0(\omega_n, \mathbf{R})T\tilde{G}_0(\omega_n, \mathbf{R}') \quad (2.25)$$

where

$$\begin{aligned} G_0(\omega_n, \mathbf{R}) &= \frac{1}{\sqrt{N_c}} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} G^0(\omega_n, \mathbf{k}), \\ \tilde{G}_0(\omega_n, \mathbf{R}) &= \frac{1}{\sqrt{N_c}} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} \phi_{\mathbf{k}}^* G^0(\omega_n, \mathbf{k}) \\ &= G_0(\omega_n, \mathbf{R}) + G_0(\omega_n, \mathbf{R} + \mathbf{a}_1) + G_0(\omega_n, \mathbf{R} + \mathbf{a}_2) \end{aligned}$$

The term $g(\omega_n)$ in G_{aa} only contributes to $G_{aa}(0,0)$, the return amplitude to the impurity site for an electron starting at the impurity site. The factor $1/D(\omega_n)$ contains a sum over an infinite series of intermediate scattering events, but the overall process is bounded and the t_0^2 factor denotes hopping from the impurity to the nearest neighbor B -sites and back to the impurity site. Likewise, an interpretation can be given to the other term which only appears in G_{aa} , namely, $h(\omega_n)G_0(\omega_n, \mathbf{R})$, which contributes

to $G_{aa}(\mathbf{r}, 0)$ and describes the amplitude of propagation between the impurity site and another A site, again with an infinite series of intermediate scatterings. Similarly, the $h(\omega_n)G_0(\omega_n, \mathbf{R}')$ term contributes to $G_{aa}(0, \mathbf{R}')$. No such terms can, of course, appear in G_{bb} when the impurity is at a A site. And no such term can be present when there is only the impurity potential term ϵ_0 . The $G_0(\omega_n, \mathbf{R})T(\omega_n)G_0(\omega_n, \mathbf{R}')$ term, which appears in both G_{aa} and G_{bb} , is the usual term also present in simple on-site impurity potential problems, but in this case the T -matrix contains contributions from both t_0 and ϵ_0 .

2.2 Local density of states

The local density of states(LDOS) in real space can be obtained from the Green's functions (2.24),(2.25) . The local density of states (per spin) at the sub-lattice A and sub-lattice B atoms is defined as

$$\rho_a(\mathbf{R}, \omega) = -\frac{1}{\pi} \text{Im} G_{aa}(\mathbf{R}, \mathbf{R}, \omega) \quad (2.26)$$

$$\rho_b(\mathbf{R} + \boldsymbol{\delta}_3, \omega) = -\frac{1}{\pi} \text{Im} G_{bb}(\mathbf{R} + \boldsymbol{\delta}_3, \mathbf{R} + \boldsymbol{\delta}_3, \omega) \quad (2.27)$$

where R is the position of sub-lattice A. If we set $R = R'$ and $\omega_n \rightarrow \omega + i\delta$. The Green's functions(2.24,2.25) can be simplified as follows,

$$\begin{aligned} G_{aa}(\omega, \mathbf{R}, \mathbf{R}) &= G_0(\omega, 0) + t_0(2t - t_0) \frac{G_0(\omega, 0)}{D(\omega)} \delta_{\mathbf{R},0} - t \frac{(\omega + i\delta)t_0(2t - t_0) - \epsilon_0 t^2}{D(\omega)} [G_0(\omega, \mathbf{R})]^2 \\ G_{bb}(\omega, \mathbf{R} + \boldsymbol{\delta}_3, \mathbf{R} + \boldsymbol{\delta}_3) &= G_0(\omega, 0) - t^2 \frac{(\omega + i\delta)t_0(2t - t_0) - \epsilon_0 t^2}{(\omega + i\delta)^2 D(\omega)} [\tilde{G}_0(\omega, \mathbf{R})]^2 \end{aligned} \quad (2.28)$$

By the Green's function above, we can calculate the density of states beyond the Dirac cone. Here we focus on the properties for density of states for cases such as vacancy, boron impurity and nitrogen impurity and we set energy in the units of t .

For the calculation of the local density of states, the case of a the vacancy where $\epsilon_0 \neq 0$ and $t_0 \neq t$ have to be treated separately. When hopping $t_i = t_0 - t = 0$ is completely suppressed on the impurity the Green's functions in this case can be written as

$$\begin{aligned} G_{aa}^{t_0=1}(\omega, \mathbf{R}, \mathbf{R}) &= G_0(\omega, 0) + \frac{\delta_{\mathbf{R},0}}{\omega - \epsilon_0 + i\delta} - \frac{[G_0(\omega, \mathbf{R})]^2}{G_0(\omega, 0)}, \\ G_{bb}^{t_0=1}(\omega, \mathbf{R} + \delta_3, \mathbf{R} + \delta_3) &= G_0(\omega, 0) - \frac{[\tilde{G}_0(\omega, \mathbf{R})]^2}{(\omega + i\delta)^2 G_0(\omega, 0)}, \end{aligned} \quad (2.29)$$

So if we set $\epsilon_0 = 0$, at $\mathbf{R} = 0$, A site density of states $\rho_a(0, \omega) \propto 1/\delta(\omega)$ in the total DOS which means the density of states due to a vacancy has a strong departure from the pristine value close to Dirac point. And If the vacancy is modeled as infinite on-site potential, so we have $\epsilon_0 \gg t, t_0 = 0$ the Green's function for A site is

$$\begin{aligned} G_{aa}^{\epsilon_0 \rightarrow \infty}(\omega, \mathbf{R}, \mathbf{R}) &= G_0(\omega, 0) + \frac{\epsilon_0}{1 - \epsilon_0 G_0(\omega, 0)} [G_0(\omega, \mathbf{R})]^2 \xrightarrow{\epsilon_0 \gg t} G_0(\omega, 0) - \frac{[G_0(\omega, \mathbf{R})]^2}{G_0(\omega, 0)} \xrightarrow{\omega \rightarrow 0} 0, \\ G_{bb}^{\epsilon_0 \rightarrow \infty}(\omega, \mathbf{R} + \delta_3, \mathbf{R} + \delta_3) &= G_0(\omega, 0) + \frac{\epsilon_0}{1 - \epsilon_0 G_0(\omega, 0)} [G_0(\omega, \mathbf{R})]^2 \end{aligned} \quad (2.30)$$

and the density of states at this limit go to zero. At B site, either suppressed hopping or infinite potential model the density of states are the same. Since,

$$G'_0(\omega, \mathbf{R}) = \frac{1}{N_c} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}} |\phi_{\mathbf{k}}^2| G_0(\omega, \mathbf{k}) = \frac{\omega + i\delta}{t^2} ((\omega + i\delta)G_0(\omega, \mathbf{R}) - \delta_{\mathbf{R},0}), \quad (2.31)$$

From the symmetry of the lattice we use the property

$$\tilde{G}_0(\omega, 0) = \frac{1}{3}G'_0(\omega, 0) = \frac{1}{3}(\omega + i\delta)[(\omega + i\delta)G_0(\omega, 0) - 1] \quad (2.32)$$

Then we can get

$$G_{bb}^{t_0=1}(\omega, \delta_3, \delta_3) = G_0(\omega, 0) - \frac{1}{9} \frac{[(\omega + i\delta)G_0(\omega, 0) - 1]^2}{G_0(\omega, 0)} \xrightarrow{\omega \rightarrow 0} -\frac{1}{9G_0(\omega, 0)} \quad (2.33)$$

$$G_{bb}^{\epsilon_0 \rightarrow \infty}(\omega, \delta_3, \delta_3) = G_0(\omega, 0) + \frac{1}{9} \frac{\epsilon_0}{1 - \epsilon_0 G_0(\omega, 0)} \xrightarrow[\epsilon_0 \gg t]{\omega \rightarrow 0} -\frac{1}{9G_0(\omega, 0)} \quad (2.34)$$

By low frequency $\omega \ll \nu_F k_c$, where $\nu_F = 3ta/2$ and k_c is determined by the conservation of states in the linearized spectrum $|\phi_k| = \nu_F |\mathbf{k}|$ approximation, namely

$$\pi k_c^2 = \frac{(2\pi)^2}{A_c} \Rightarrow k_c^2 = \frac{8\pi}{3\sqrt{3}a^2},$$

where $A_c = 3\sqrt{3}a^2/2$. So in the linear approximation and continuum limit we have

$$\begin{aligned} G_0(\omega, 0) &= \frac{1}{N_c} \sum_{\mathbf{k}} G_0(\omega, \mathbf{k}) = \frac{1}{N_c} \sum_{\mathbf{k}} \frac{\omega}{\omega^2 - \nu_F^2 k^2} \\ &= \omega \frac{A_c}{(2\pi)^2} 2\pi \int_0^{k_c} \frac{k}{\omega^2 - k^2 + i0^+ \text{sign}(\omega)} dk \\ &= \frac{\omega}{2\pi \nu_F^2 k_c^2} [P \int_{\omega^2 - (\nu_F k_c)^2}^{\omega^2} \frac{dx}{x} - i\pi \theta(\nu_F k_c - |\omega|) \text{sign}(\omega)] \\ &= \frac{\omega}{2(\nu_F k_c)^2} \ln \left| \frac{\omega}{\omega^2 - (\nu_F k_c)^2} \right| - \frac{|\omega|}{2(\nu_F k_c)^2} i\pi \theta(\nu_F k_c - |\omega|) \\ &= \frac{\sqrt{3}}{6\pi} \omega \ln \left| \frac{3}{6\pi} \omega^2 \right| - i \frac{\sqrt{3}}{6} |\omega| \end{aligned} \quad (2.35)$$

From the equations above and 2.27, 2.34, 2.34 we can get the local density of states at the nearest neighbor B site is

$$\rho_b(\omega, \delta_3, \delta_3) = \frac{\sqrt{3}}{6\pi} |\omega| \left[1 + \frac{(6\pi)^2}{27\omega^2 [\ln |\sqrt{3}\omega^2/6\pi|]^2} \right] \quad (2.36)$$

with a resonance peak at $\omega = 0$. The full numerical calculations for the whole band width is shown in Figure 2.2.

In the case where there is an enhancement of the hopping amplitude between the impurity and the neighboring atoms (negative t_0). Figure 2.3 shows LDOS at the impurity and the nearest B site for a case with disorder $t_0 = -0.5t$, $\epsilon_0 = 0.6t$. This case would mimic a boron impurity atom. Boron has a larger atomic radius ($R \simeq 0.85\text{\AA}$) than carbon ($R \simeq 0.7\text{\AA}$) and there should be an increase in the absolute value of the hopping amplitude. For the on-site potential disorder, we take the carbon on-site potential to be zero as our reference state and Boron has a smaller atomic number which leads to positive on-site energy. The resonance state of the LDOS at some energies comes from impurity resonance state and van Hove singularities. The real space LDOS plots are at resonance $\omega_0 = -2.950t$ for A sublattice, and $\omega_0 = -1.0t$ which is at the van Hove singularity for B sublattice. The van Hove singularities are more strongly affected at certain directions as shown in Figure 2.3. On B site the van Hove peaks are strongest where the LDOS can be understood as being originated by the three nearest-neighbor B sites of the impurity site and we have star-shaped symmetry in the real space plot at $\omega_0 = -1.0t$ shown in Figure 2.3. The clean system band structure is more like a conventional 2D system close to the band edge, so the resonance peak at $\omega_0 = -2.950t$ has a symmetric spatial distribution as in the first row of Figure 2.3.

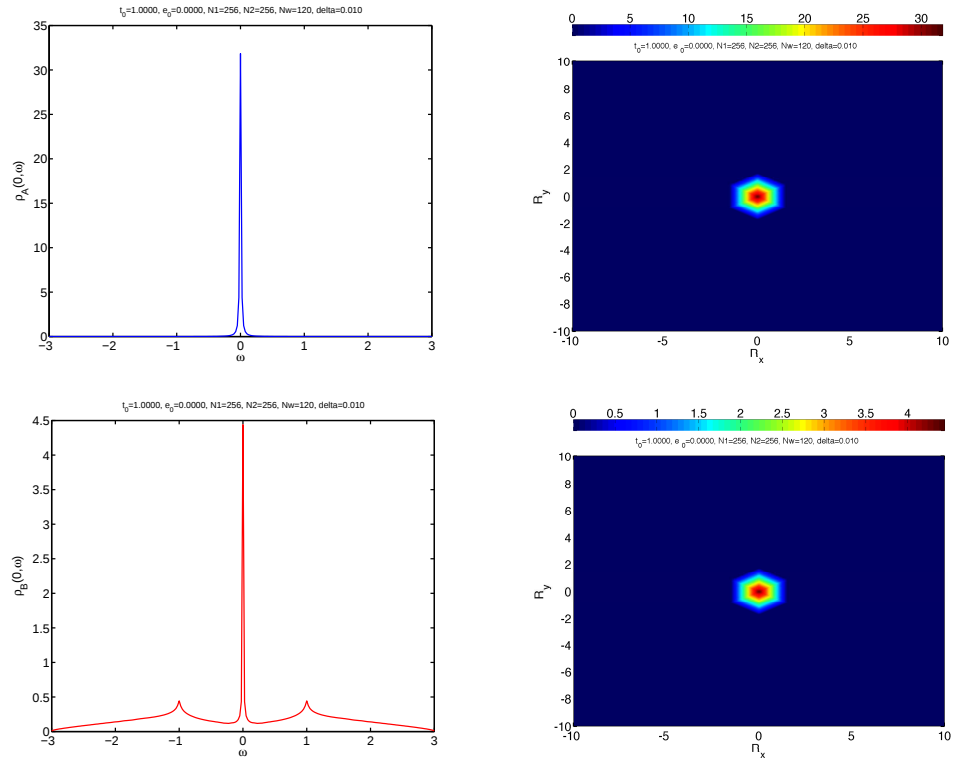


Figure 2.2: LDOS for $t_0 = t$ at the impurity site. Upper left figure corresponds to $\rho_a(\omega, 0)$, upper right figure to $\rho_a(\omega = 0, \mathbf{r})$, Second row left figure corresponds to $\rho_b(\omega, 0)$, second row right figure to $\rho_b(\omega = 0, \mathbf{r})$

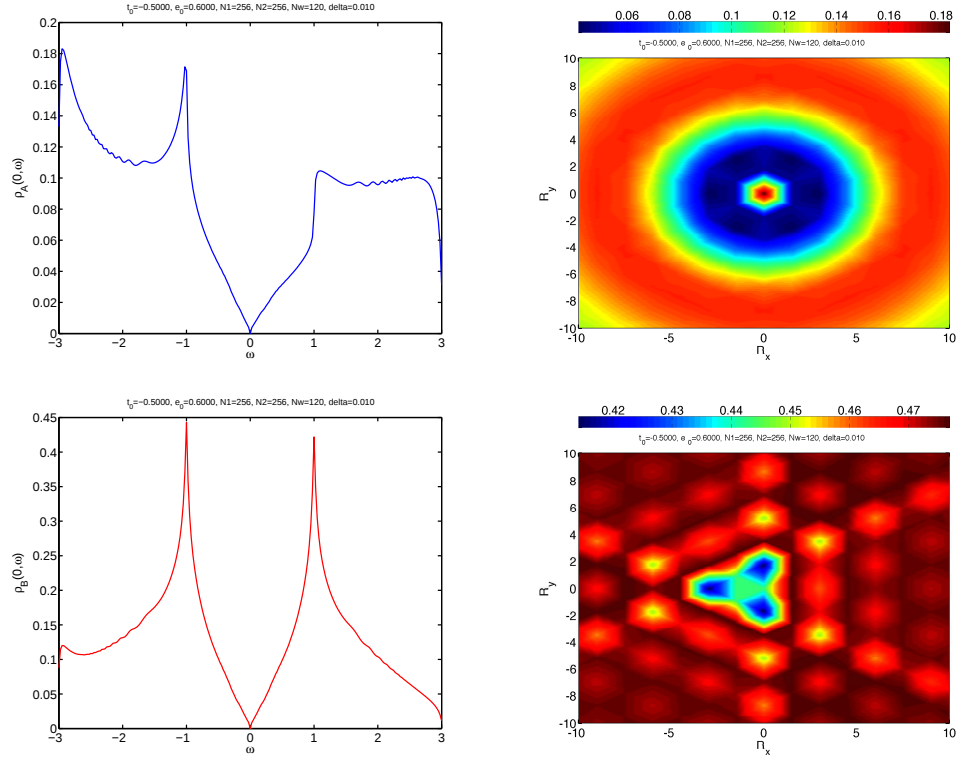


Figure 2.3: LDOS for the case $t_0 = -0.5t$ and $\epsilon_0 = 0.6t$. Upper left figure corresponds to $\rho_a(\omega, 0)$, upper right figure to $\rho_a(\omega = -2.950, \mathbf{r})$, Second row left figure corresponds to $\rho_b(\omega, 0)$, second row right figure to $\rho_b(\omega = -1.0, \mathbf{r})$

In the case of a decreasing of the electron hopping between the impurity and the carbon atoms (positive t_0) the behavior of the density of states is more interesting since resonances start to develop around the Dirac point as in Figure 2.4. Note that the density of the states still goes to zero at the Dirac point. This case would mimic a nitrogen atom. A Nitrogen atom has a smaller atomic radius ($R \simeq 0.65$) than a carbon atom, which gives a smaller hopping amplitude between the Nitrogen impurity and nearest carbon atoms. Also the larger atomic number of Nitrogen atoms leads to a negative on-site potential with respect to the carbon sites.

For $G_{xx}(\mathbf{r}, \mathbf{r}, \omega)$ at position $\mathbf{r}$, we use a linear approximation for $\phi(\mathbf{k})$, which reads $\phi(\mathbf{k}) \simeq 3a_0(k_y - ik_x)/2$. We will get the Green's function from Eq. (2.28)

$$G_{aa}(\mathbf{r}, \mathbf{r}, \omega) = \bar{G}^0(\omega) + T(\omega)[F_0(\omega, r)]^2, \quad (2.37)$$

$$G_{bb}(\mathbf{r}, \mathbf{r}, \omega) = \bar{G}^0(\omega) + \frac{t^2}{\omega^2} T(\omega)[F_1(\omega, r)]^2, \quad (2.38)$$

where $F_n(\omega, r)$ ($n = 0, 1$) is defined as

$$F_n(\omega, r) = \frac{(2n+1)A_c a_0^n}{2^{n+1}\pi v_F^2} \left[\frac{2\omega}{r^n} P \int_0^{k_c r} dx \frac{x^{n+1} J_n(x)}{\alpha^2 - x^2} - i \frac{\pi}{v_F^n} J_n(\alpha) |\omega|^{n+1} \right], \quad (2.39)$$

with $J_n(x)$ the Bessel function of integer order n ; and $k_c = 2\sqrt{\pi}/(\sqrt{3}\sqrt{3}a_0)$, $\alpha = |\omega|r/v_F$, $A_c = 3\sqrt{3}a_0^2/2$, and $v_F = 3ta_0/2$. The Cauchy principal value of the integral in Eq. (2.39) is computed using numerical methods. In Fig. 2.5, we plot the local density of states at both sub-lattices A and B . The typical oscillations due to the presence of the impurity are present. Note that close to the impurity the B sublattice density of states presents higher harmonics as function of r ; these are due to the cut-off momentum

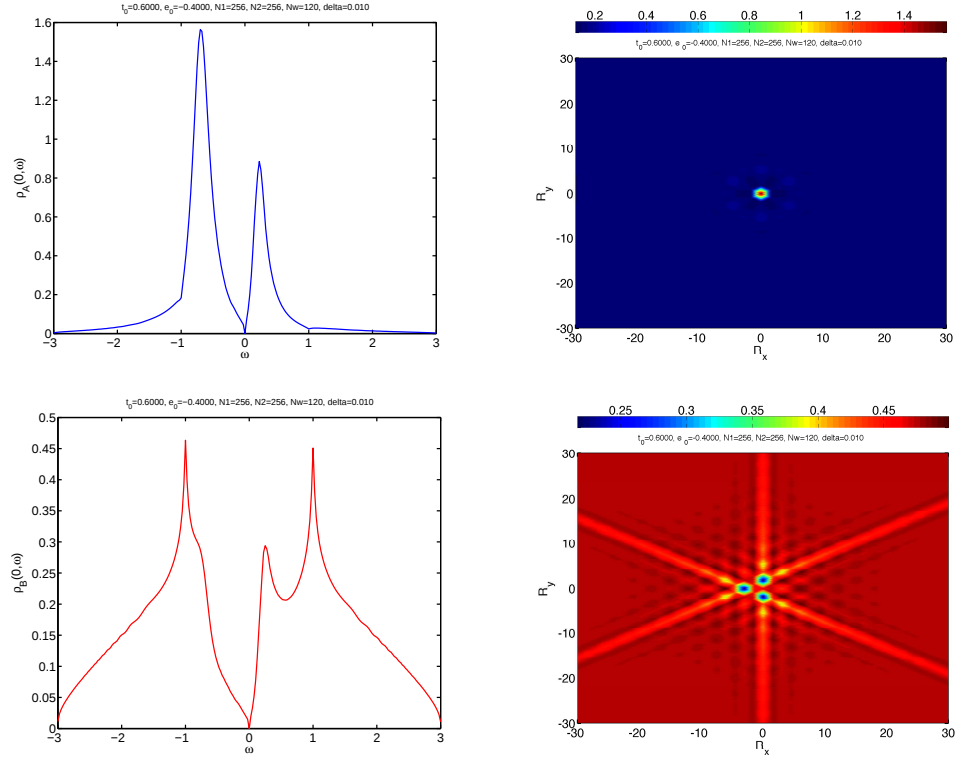


Figure 2.4: LDOS for the case $t_0 = 0.6t$ and $\epsilon_0 = -0.4t$. Upper left figure corresponds to $\rho_a(\omega, 0)$, upper right figure to $\rho_a(\omega = -0.7t, \mathbf{r})$, Second row left figure corresponds to $\rho_b(\omega, 0)$, second row right figure to $\rho_b(\omega = -1.0t, \mathbf{r})$

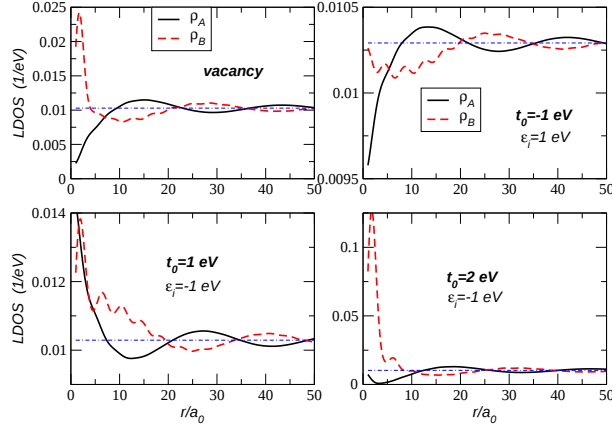


Figure 2.5: Local density of states in sublattice A and B as function of $r > 0$. The dashed-dotted line is the density of states of pristine graphene at the energy $\hbar\omega = 0.5$ eV. The point $r = 0$ is excluded. The small wavelength oscillations are due to the cut-off momentum k_c and the large ones are the $2q_F$ Friedel oscillations.

k_c . On the other hand, the large wavelength oscillations are the $2q_F$ Friedel oscillations: from Fig. 2.5 the wavelength is about $\lambda \simeq 28a_0$; on the other hand, for the energy $\hbar\omega = 0.5$ eV the Fermi momentum is $q_F = 1/(9a_0)$, implying $\lambda \simeq \pi/q_F \simeq 28a_0$. At large values of r the two density of states are out of phase by a factor of π . Therefore, when we average over the unit cell the result is essentially the pristine density of states. This result has strong consequences for STM experiments. If the STM experiment lacks atomic resolution at the A and B sublattices level, the experimental data will show no trace of the $2q_F$ Friedel oscillations. This seems to be the case in the experiments reported in Ref. [27]. Closer to the impurity there is a strong departure from the asymptotic behavior [4]

$$\rho(\mathbf{r}) \propto \frac{1}{r^2} \sin(2r\omega/v_F), \quad (2.40)$$

and the A and B LDOS behave quite differently.

STM measurements of a material surface are ideal for studying real space local features with Atomic resolution. In particular, real space modulation of the STM

intensity can be observed when impurities are present at the surface of a given material. In general, the impurities lead to elastic scattering between the momentum $\mathbf{q}_F$ and $-\mathbf{q}_F$, which is the most efficient process due to phase space restrictions, leading to $2q_F$ Friedel oscillations. In the case of graphene, the chiral nature of its electronic spectrum changes this general behavior. The Fermi surface has disconnected pieces at different points of the Brillouin zone – the $\mathbf{K}$ and $\mathbf{K}'$ points. The Fermi surface consists of circumferences of radius q_F around each $\mathbf{K}$ and $\mathbf{K}'$ points. The scattering process is then characterized by two channels: an intra-cone scattering (within the same $\mathbf{K}$ or $\mathbf{K}'$ points) of momentum change $2q_F$, and an inter-cone scattering (between the $\mathbf{K}$ and $\mathbf{K}'$) points.

A Fourier transform of the real-space STM-intensity currents, proportional to the LDOS, will produce bright spots at the momentum values seen in the real space modulations of the LDOS. When impurities are present, the momentum values characterizing the real space modulation are related to the momentum change associated with a given scattering process. In Ref. [27] it was found that the intra-cone scattering, which would give rise to a bright spot of radius $2q_F$ was absent in the momentum map of the density of states obtained by a Fourier transform of their STM data.

In what follows, we give Fourier transforms of the local density of states of graphene for the different types of impurities discussed previously in the text. We note that our derivation of the Fourier transform of LDOS uses the full Green's functions (2.28) for the calculation of the LDOS, and therefore no approximation has been made in the calculation. The full real-space map of density of states can be obtained numerically from Eqs. (2.26) to Eqs.(2.28), as was done in Ref. [49] and also in the previous text.

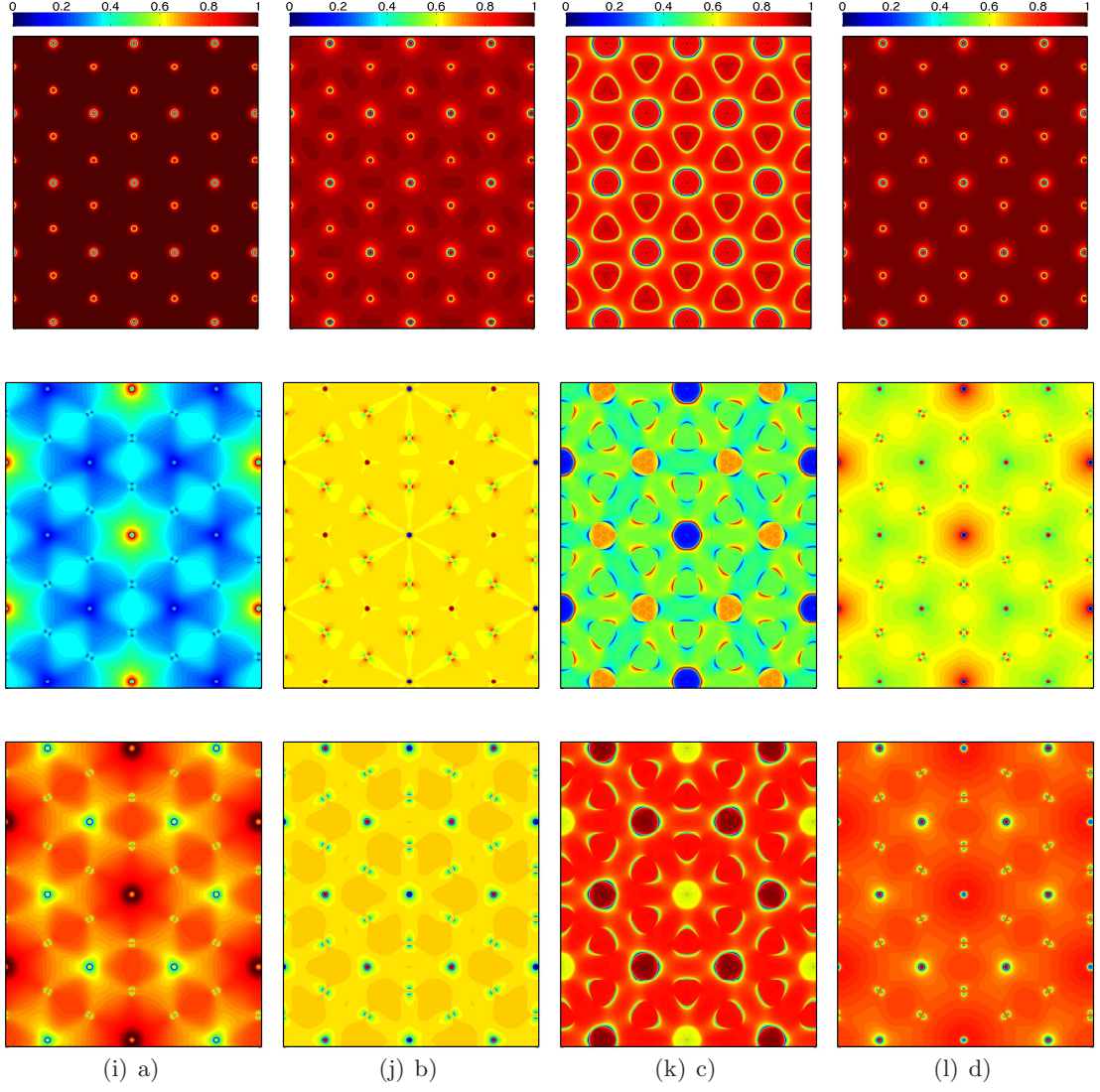


Figure 2.6: Fourier transform of the local density of states. The first row is the density of states in sublattice A (ρ_a), the second row is the density of states in sublattice B (ρ_b), and the third row is the sum of the two, $\rho_a + \rho_b$. Column (a) is for the case of a vacancy, and $\omega = 0.3$ eV. Column (b): $t_0 = -1$ eV, $\epsilon_i = 1$ eV, $\omega = 0.3$ eV. Column (c): $t_0 = 1$ eV, $\epsilon_i = -1$ eV, $\omega = -1.5$ eV. Column (d): $t_0 = 2$ eV, $\epsilon_i = -1$ eV, $\omega = -0.3$ eV.

We now perform a Fourier transform of the density of states,

$$\rho_a(\mathbf{k}, \omega) = \sum_{\mathbf{r}} e^{-i\mathbf{k} \cdot \mathbf{r}} \rho_a(\mathbf{r}, \omega), \quad (2.41)$$

$$\rho_b(\mathbf{k}, \omega) = \sum_{\mathbf{r}} e^{-i\mathbf{k} \cdot (\mathbf{r} + \boldsymbol{\delta}_3)} \rho_b(\mathbf{r} + \boldsymbol{\delta}_3, \omega), \quad (2.42)$$

for $\mathbf{r}$ is the position of sublattice A. The results are shown in Fig. 2.6, where the three rows correspond to $\rho_a(\mathbf{k}, \omega)$, $\rho_b(\mathbf{k}, \omega)$, and the sum $\rho_a(\mathbf{k}, \omega) + \rho_b(\mathbf{k}, \omega)$, from top to bottom; and the four columns correspond to three types of impurities discussed previously. We recall that positive t_0 reduces the hopping from the impurity site to its nearest neighbor carbon atoms – the particular case of $t_0 = t$ represents a vacancy – and negative t_0 increases the hopping of the electrons from the carbon atoms to the impurity site. This latter case would correspond to an atom with a radius larger than carbon, such as boron, leading to an increase of the hopping relatively to the hopping t between nearest neighbor carbons. The column (a) of Fig. 2.6 refers to a vacancy. In this case, it is clear that a $2q_F$ circumference is seen around the $\mathbf{k} = (0, 0)$ point for the ρ_a and ρ_b plots. However, the intensity at the $2q_F$ circle around $\mathbf{k} = (0, 0)$ is suppressed when looking at the $\rho_a + \rho_b$ plot. Features at six spots at a distance $|K|$ around $\mathbf{k} = (0, 0)$ are also seen, these correspond to the K and K' points at the corners of the first Brillouin zone. Additionally, six bright spots at distance $|K + K'|$ are also present. These vectors with modulus $|K + K'|$ are reciprocal lattice vectors $\mathbf{G}$. For a pristine material the local density of states has the periodicity of the underlying lattice, that is, $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R})$, and therefore, the Fourier transform of $\rho(\mathbf{r})$ must show the same intensity at $\mathbf{k} = (0, 0)$ and $\mathbf{k} = \mathbf{G}$. While the presence of an impurity breaks the periodicity of the real-space lattice, the reason for $\mathbf{k} = (0, 0)$ and $\mathbf{k} = \mathbf{G}$ being different is the fact that the impurity

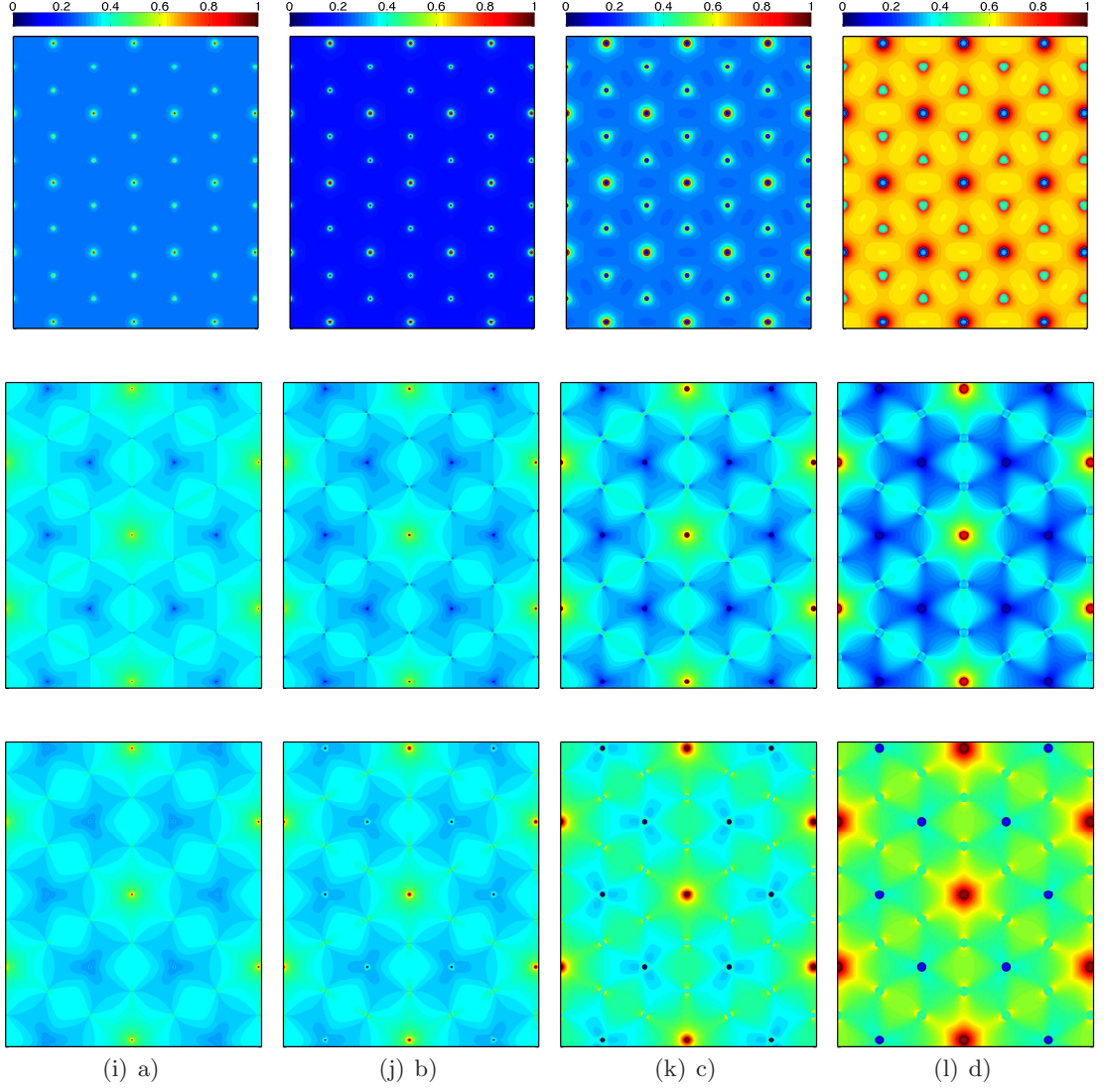


Figure 2.7: Fourier transform of the local density of states for $t_0 = 2$ eV, $\epsilon_i = -1$ eV. The first row is the density of states in sublattice A (ρ_a), the second row is the density of states in sublattice B (ρ_b), and the third row is the sum of the two, $\rho_a + \rho_b$. Column (a) is for $\omega = 0.05$ eV. Column (b): $\omega = 0.15$ eV. Column (c): $\omega = 0.3$ eV. Column (d): $\omega = 0.5$ eV.

considered here is not on a whole unit cell, but on only one of the sites of the unit cell. If there were only one site per unit cell and a single short-range impurity, then the periodicity in k -space would be maintained. In the extreme case, if there was a line of impurities of the vacancy type, this would correspond to cutting the system into half, and $\mathbf{k} = (0, 0)$ and $\mathbf{k} = \mathbf{G}$ would still be the same. Note that in all our cases ρ_A is still periodic in k -space. The impurity on a site A that we consider here, introduces structure within the $\mathbf{R} = 0$ unit cell, therefore, in k -space there is information going beyond the first Brillouin zone. Mathematically this appears because the B-site is located at $\mathbf{R} + \boldsymbol{\delta}_3$, where $\mathbf{R}$ denotes the position of the A sites, and $\boldsymbol{\delta}_3$ is not a lattice vector of triangular Bravais lattice (see Fig. 2.1). When we take the Fourier transform, the periodicity in k -space does not happen at $\mathbf{k} = \mathbf{G}$ anymore, but at larger $\mathbf{k}$. All figures show this signature, which is rather clear in column (c) of Fig. 2.6, since the Fermi surface energy has been chosen as large as $\omega = -1.5$ eV. Inter-cone scatterings, represented by the region around the K and K' points, are highly angular-dependent [5,60], as can be seen particularly in the ρ_b plots. While the scattering around the $\mathbf{G}$ vectors do not have such a strong angular dependence, some trigonal warping is observed in ρ_B . The scatterings around $\mathbf{k} = (0, 0)$ are rotationally symmetric. Fig. 2.7 corresponds to the case $t_0 = 2$ eV and $\epsilon_i = -1$ eV (case (c) of Fig. 2.6), showing how the k -space LDOS map evolves with increasing energy.

2.3 STM Tip and current

Let us consider a model for the STM tip represented by a multimode system. The bulk of the tip is modeled by a square lattice with two atoms in the transverse direction. The end of the tip is represented by a single atom. This choice renders the

system multimode, with two transverse modes. It is as simple to include a truly three dimensional tip, but the current will not be much affected by it. The schematic atomic structure of the tip is represented in Fig. 2.8. The Hamiltonian for the tip can be

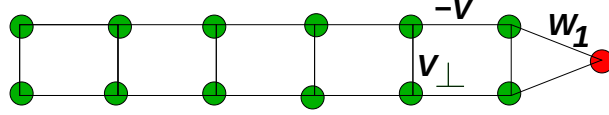


Figure 2.8: (colour online) Representation of the STM tip.

written as $H_t = H_b + H_0$, where H_b represents the bulk of the tip and H_0 the tip's last atom. These two parts of the Hamiltonian are defined as

$$H_b = -V \sum_{n=-\infty}^{-1} \sum_{m=1,2} [c^\dagger(n, m)c(n-1, m) + c(n-1, m)c^\dagger(n, m)] \quad (2.43)$$

$$-V_\perp \sum_{n=-\infty}^{-1} [c^\dagger(n, 1)c(n, 2) + c(n, 2)c^\dagger(n, 1)], \quad (2.44)$$

and

$$H_0 = \epsilon_0 c^\dagger(0)c(0) - W_1 \sum_{m=1,2} [c^\dagger(0)c(-1, m) + c(-1, m)c^\dagger(0)], \quad (2.45)$$

where $c^\dagger$ (c) are creation (annihilation) operators for fermions in the tip. Let us now consider the case of the bulk part of the Hamiltonian's tip, H_b . In the case of a square lattice the wave function is separable and can be written as $|\psi_{l,t}\rangle = |\phi_l\rangle|\phi_t\rangle$, with the longitudinal part of the wave function $|\phi_l\rangle$ given by

$$|\phi_l\rangle = \lim_{N \rightarrow \infty} \sum_{n=-1}^{-N} \sqrt{\frac{2}{N+1}} \sin(n\theta_l) |n\rangle, \quad (2.46)$$

and the transverse part $|\phi_t\rangle$ given by

$$|\phi_t\rangle = \sum_{m=1,2} \sqrt{\frac{2}{3}} \sin(m\alpha_t) |m\rangle. \quad (2.47)$$

In Eqs. (2.46) and (2.47), the states $|n, m\rangle = |n\rangle|m\rangle$ are position states and the numbers θ_l and α_t are given by

$$\theta_l = \frac{\pi l}{N+1}, \quad l = 1, 2, \dots, N, \quad (2.48)$$

and

$$\alpha_t = \frac{\pi t}{3}, \quad t = 1, 2. \quad (2.49)$$

The resolvent for the Hamiltonian H_b is defined as $\hat{G}_b^+ = (E + i0^+ - H_b)^{-1}$, where the $+$ superscript denotes the retarded function. In the eigenstate basis, it has the form

$$\hat{G}_b^+ = \sum_{l,t} \frac{|\psi_{l,t}\rangle\langle\psi_{l,t}|}{E - E_{l,t}}, \quad (2.50)$$

where $E_{l,t}$ are the eigenvalues of H_b , with $H_b|\psi_{l,t}\rangle = E_{l,t}|\psi_{l,t}\rangle$, given by

$$E_{l,t} = -2V \cos \theta_l - 2V_{\perp} \cos \alpha_t, \quad (2.51)$$

For the calcution of the STM current we will need the surface Green's functions defined as

$$G_{diag}(E) = \langle m, -1 | G_b^+ | -1, m \rangle, \quad (2.52)$$

$$G_{offd}(E) = \langle 1, -1 | G_b^+ | -1, 2 \rangle. \quad (2.53)$$

The calculation of (2.52) and (2.53) requires the evaluation of the integral

$$I = \frac{1}{2\pi} \int_0^{2\pi} \frac{d\theta \sin^2 \theta}{E + 2V \cos \theta + jV_\perp}, \quad j = \pm 1, \quad (2.54)$$

which is easily done by contour integration methods [50]. the final results are

$$G_{diag}(E) = \sum_{j=\pm 1} \frac{\beta_j}{2V} - \text{sign}(\beta_j) \frac{1}{2V} \sqrt{\beta_j^2 - 1}, \quad (2.55)$$

$$G_{offd}(E) = \sum_{j=\pm 1} \frac{j\beta_j}{2V} - \text{sign}(\beta_j) j \frac{1}{2V} \sqrt{\beta_j^2 - 1}, \quad (2.56)$$

for $\beta_j^2 > 1$, with $\beta_j = (E + jV_\perp)/(2V)$. In the case $\beta_j^2 < 1$, the Green's functions are obtained from (2.55) and (2.56) by removing the factor $\text{sign}\beta_j$, and choosing the positive sign for the square root of the negative argument:

$$G_{diag}(E) = \sum_{j=\pm 1} \frac{\beta_j}{2V} - i \frac{1}{2V} \sqrt{1 - \beta_j^2}, \quad (2.57)$$

$$G_{offd}(E) = \sum_{j=\pm 1} \frac{j\beta_j}{2V} - ji \frac{1}{2V} \sqrt{1 - \beta_j^2}, \quad (2.58)$$

Using Eq. (2.55), the local density of states at the sites $n = -1, m = 1, 2$ given as usual by $\rho_b(E) = -\frac{1}{\pi} \Im G_{diag}(E)$, is depicted in Fig. 2.9. The multimode nature of the tip is clearly seen in the form of the density of states.

There is a number of ways one can use to describe the tunneling of the electrons between the STM tip and graphene. Here we assume that the coupling is made directly either to the impurity atom or to the next neighbor carbon atom. This choice corresponds to probing the local electronic properties at or around the impurity. More general types of coupling are easily included in the formalism. We write this coupling

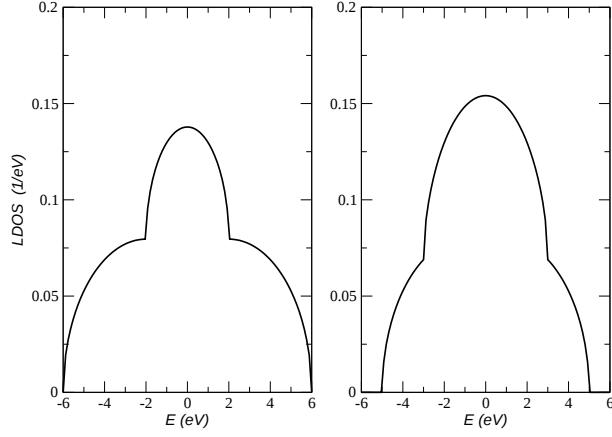


Figure 2.9: Local density of states, $\rho_b(E)$, at the atoms of the tip given by $n = -1, m = 1, 2$. Left: $V = 2$ eV, $V_\perp = 2$ eV. Right: $V = 2$ eV, $V_\perp = 1$ eV. The multi-mode nature of the tip is clearly seen.

as

$$H_T = -W_2[c^\dagger(0)d(0) + d^\dagger(0)c(0)], \quad (2.59)$$

where the operator $d(0)$ can represent either an electron at the impurity atom in the A sub-lattice or at the carbon atom in the B sub-lattice. Since the Hamiltonian of the problem is bilinear we can write it in matrix form as

$$H = \begin{bmatrix} H_b & V_L & 0 \\ V_L^\dagger & H_0 & V_R^\dagger \\ 0 & V_R & H_g \end{bmatrix} \quad (2.60)$$

where the matrices V_L and V_R represent the coupling of the last atom in the tip of the STM microscope to the bulk of the tip and to graphene, respectively, and H_b and H_g stand for the bulk Hamiltonians of the tip and of graphene, respectively. H_g also includes the impurity terms Eqs. (2.2) and (2.3). The matrix H is of infinite dimension

due to H_b and H_g . The matrices $V_L^\dagger$ and $V_R^\dagger$ have the explicit form

$$V_L^\dagger = [\mathbf{0}, -W_1, -W_1], \quad V_R^\dagger = [-W_2, \mathbf{0}], \quad (2.61)$$

where $\mathbf{0}$ represents an infinite dimensional null row vector. The tunneling is a local property, controlled by the coupling of the last atom of the tip to the bulk atoms and to graphene. Since we want to compute local quantities, this is best accomplished using Green's functions in real space. The full Green's function of the system is defined by

$$(\mathbf{1}E + i0^+ - H)G^+ = \mathbf{1}, \quad (2.62)$$

where $\mathbf{1}$ is the identity matrix. The matrix form of the Green's function is

$$G^+ = \begin{bmatrix} G_{bb} & G_{b0} & G_{bg} \\ G_{0b} & G_{00} & G_{0g} \\ G_{gb} & G_{g0} & G_{gg} \end{bmatrix}. \quad (2.63)$$

The quantity of interest is G_{00} , which can be shown to have the form

$$G_{00}^+ = (E + i0^+ - \epsilon_0 - \Sigma_L^+ - \Sigma_R^+), \quad (2.64)$$

where the matrices Σ_L^+ and Σ_R^+ are the self energies and have the form

$$\Sigma_L^+ = 2W_1^2(G_{diag} + G_{offd}), \quad \Sigma_R^+ = W_2^2 G_{xx}^+, \quad (2.65)$$

where G_{xx}^+ is the surface Green's function of the Hamiltonian H_g at the impurity unit cell ($x = a, b$), respectively. Note that the quantity G_{xx}^+ is computed using Eq. (??) and

setting $\mathbf{r} = 0$.

The study of non-equilibrium transport is done using the non-equilibrium Green's function method, or Keldysh formalism. This method is particularly suited to study the regime where the system has a strong departure from equilibrium, such as when the bias potential on the STM tip, V_b , is large. In this work, we consider, however, that the system is in the steady state. Since the seminal paper of Caroli *et al.* on non-equilibrium quantum transport [8], that the method of non-equilibrium Green's functions started to be generalized to the calculation of transport quantities of nanostructures. There are many places where one can find a description of the method [18,24], but a recent and elegant one was introduced in the context of transport through systems having bound states, showing that the problem can be reduced to the solution of an equation similar to a quantum Langevin equation [12]. The general idea of this method is that two perfect leads are coupled to the system, which is usually called the device. In our case the device is defined by the last atom of the tip of the microscope. The Green's function of the device has to be computed in the presence of the bulk of the tip and of graphene. This corresponds to our G_{00}^+ Green's function. Besides the Green's function we need the effective coupling between the last atom of the tip and the bulk atoms as well as that to the graphene atoms, which are determined in terms of the self-energies

$$\Gamma_{L/R} = \frac{i}{2\pi}(\Sigma_{L/R}^+ - \Sigma_{L/R}^-). \quad (2.66)$$

Therefore the effective coupling $\Gamma_{L/R}$ depends on the surface Green's function of the tip and of graphene. According to the general theory, the two systems (bulk of the tip and graphene) are in thermal equilibrium at temperatures $T_{L/R}$ and chemical potential $\mu_{L/R}$ and are connected to the system at some time t_0 . The total current through the

device is then given by

$$J = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E) [f(E, \mu_L, T_L) - f(E, \mu_R, T_R)], \quad (2.67)$$

where the factor of 2 is due to the spin degrees of freedom, $f(x)$ is the Fermi-Dirac distribution and the transmission $T(E)$ is given by

$$T(E) = 4\pi^2 \Gamma_L |G_{00}^+|^2 \Gamma_R. \quad (2.68)$$

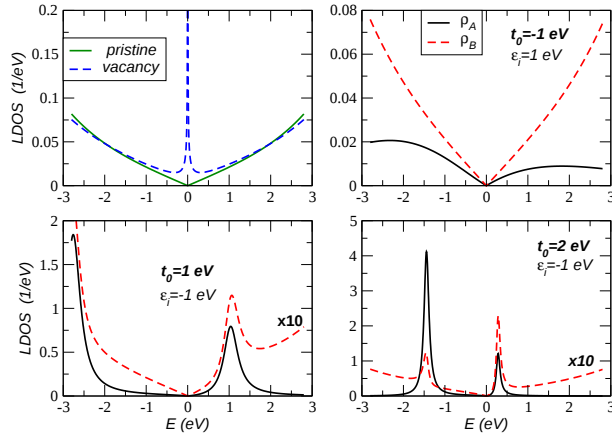


Figure 2.10: Local density of states, $\rho_x(E)$, for $x = a, b$ at the graphene's unit cell $\mathbf{r} = 0$. We have used $t = 3$ eV. Upper left: density of states of pristine graphene and at the B site close to a vacancy. All other panels: local density of states at A (impurity) and B (next to the impurity) sites for different values of the parameters t_0 and ϵ_i . The values of t_0 and ϵ_i corresponds to different types of impurities.

In Fig. 2.11 we depict $T(E)$ in different cases. Note the asymmetry of the density of states which is exhibited even by the pristine case (Fig. 2.11, upper left panel). This asymmetry has a two fold nature: (i) it comes from the fact the bulk of the tip has two transverse atoms but the tip has only one; (ii) the fact that the atom at the tip has a different local energy from those in the bulk. This asymmetry carries

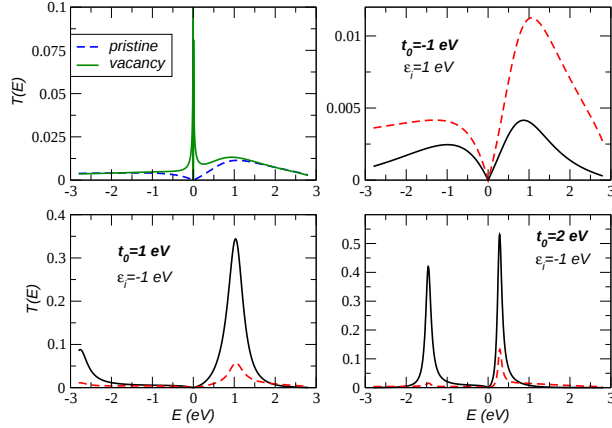


Figure 2.11: Transmission probability $T(E)$. The parameters used are (all in electron-volt): $V = 2$, $V_{\perp} = 1$, $W_1=0.9$, $W_2 = 0.2$, and $\epsilon_0 = 0.2$. The resonances seen in the LDOS in Fig. 2.10 show up in the transmission function. The values of t_0 and ϵ_i are the same used in Fig. 2.10 and the four panels here correspond to the same ones in that figure.

on to the disordered cases. Additionally, for the disordered cases the resonances seen in the local density of states has a strong impact on the transition probability $T(E)$, leading to open transport channels with large values of $T(E)$. This is specially true for the vacancy and for the weakly coupled impurity case, that is, when hopping between impurity and carbon atoms is suppressed in relation to the hopping between carbon atoms, as expected for nitrogen substitution. Since we want to probe the properties of the STM current at zero doping we choose $\mu_L = eV/2$ and $\mu_R = -eV/2$. Also $T_L = T_R = 0$. This renders the calculation of the current to a simple one-dimensional integral of $T(E)$ over the energy. The form of the current will reflect the properties of $T(E)$ as function of energy, and, as we have seen, these are markedly different for the different cases, depending strongly on the value and sign of t_0 . The presence of resonances in $T(E)$ leads to steps in the STM current. This is seen in Fig. 2.12 for the cases of the vacancy and to the case of weak coupling (positive t_0) between the impurity and the neighboring carbon atoms.

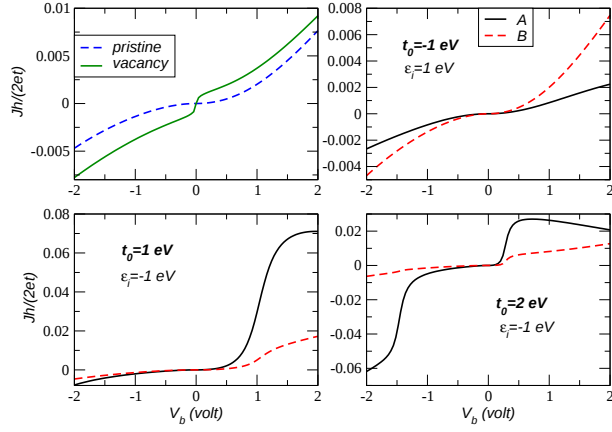


Figure 2.12: STM current J . The parameters used are (all in electron-volt): $V = 2$, $V_{\perp} = 1$, $W_1 = 0.9$, $W_2 = 0.2$, and $\epsilon_0 = 0.2$. The values of t_0 and ϵ_i are the same used in Fig. 2.10. The transmission function was computed at finite bias; the zero bias case is given in Fig. 2.11. The four panels here correspond to the same ones in that figure 2.11.

Chapter 3

Magnetic field effects on the local electronic structure near a single impurity in graphene

3.1 Dirac Hamiltonian for a two-dimensional system in the presence of a magnetic field

The Dirac Hamiltonian in the presence of a magnetic field can be written as:

$$H = H_0 + H_{\text{imp}} , \quad (3.1)$$

with

$$H_0 = v_F [\mathbf{p} + e\mathbf{A}(\mathbf{r})/c] \cdot \boldsymbol{\sigma} , \quad (3.2)$$

and

$$H_{\text{imp}} = (U_1\sigma_0 + U_2\sigma_3 + V\sigma_1)\delta(\mathbf{r}) . \quad (3.3)$$

Here v_F is the Fermi velocity, $\mathbf{p} = (\hbar/i)(\partial/\partial x, \partial/\partial y)$ is the canonical momentum operator in the x - y plane of the graphene layer, $-e$ is the electron charge, $\mathbf{A}$ is the vector potential corresponding to a perpendicular magnetic field B , c is the velocity of light, and σ_0 and σ_i ($i = 1, 2, 3$) are the unit matrix and the three component of Pauli matrix. The quantities U_1 and U_2 represent the strength of the impurity scattering, the combination of which determines the respective strength on two sublattices, while the quantity V represents the strength of the inter-sublattice scattering. In the Landau gauge, we choose the vector potential $\mathbf{A} = (A_x, A_y, A_z) = (-By, 0, 0)$. In the second quantization, the system Hamiltonian can be written as:

$$\begin{aligned}\mathcal{H} &= \int d\mathbf{r} \hat{\Psi}^\dagger(\mathbf{r}) H(\mathbf{r}) \hat{\Psi}(\mathbf{r}) \\ &= \mathcal{H}_0 + \mathcal{H}_{\text{imp}} ,\end{aligned}\tag{3.4}$$

where $\hat{\Psi} = (\phi_\uparrow(\mathbf{r}), \phi_\downarrow(\mathbf{r}))^{\text{Transpose}}$ are two-component pseudospinor operator for two sublattices.

We introduce a 2×2 Matsubara Green's function

$$\mathcal{G}(\mathbf{r}, \tau; \mathbf{r}', \tau') = -\langle T_\tau [\hat{\Psi}(\mathbf{r}, \tau) \hat{\Psi}^\dagger(\mathbf{r}', \tau')] \rangle ,\tag{3.5}$$

where τ is the imaginary time, T_τ is the time-ordering operator, and

$$\hat{\Psi}(\mathbf{r}, \tau) = e^{\mathcal{H}\tau} \hat{\Psi}(\mathbf{r}) e^{-\mathcal{H}\tau} .\tag{3.6}$$

A little algebra leads to the following equation of motion

$$\left[-\frac{\partial}{\partial \tau} - H(\mathbf{r}) \right] \mathcal{G}(\mathbf{r}, \tau; \mathbf{r}', \tau') = \delta(\mathbf{r} - \mathbf{r}') \delta(\tau - \tau') ,\tag{3.7}$$

Similarly, the equation of motion for the Green's function of the clean system is written

as:

$$\left[-\frac{\partial}{\partial \tau} - H_0(\mathbf{r}) \right] \mathcal{G}_0(\mathbf{r}, \tau; \mathbf{r}', \tau') = \delta(\mathbf{r} - \mathbf{r}') \delta(\tau - \tau') . \quad (3.8)$$

By performing the Fourier transform to these Green's function,

$$\mathcal{G}(\mathbf{r}, \tau; \mathbf{r}', \tau') = T \sum_{i\omega_n} \mathcal{G}(\mathbf{r}, \mathbf{r}'; i\omega_n) e^{-i\omega_n(\tau - \tau')} , \quad (3.9)$$

and

$$\mathcal{G}_0(\mathbf{r}, \tau; \mathbf{r}', \tau') = T \sum_{i\omega_n} \mathcal{G}_0(\mathbf{r}, \mathbf{r}'; i\omega_n) e^{-i\omega_n(\tau - \tau')} , \quad (3.10)$$

with T being the temperature, we obtain

$$\begin{aligned} \mathcal{G}(\mathbf{r}, \mathbf{r}'; i\omega_n) &= \mathcal{G}_0(\mathbf{r}, \mathbf{r}') + \mathcal{G}_0(\mathbf{r}, 0; i\omega_n) \\ &\quad \times \mathcal{T}(i\omega_n) \mathcal{G}_0(0, \mathbf{r}'; i\omega_n) , \end{aligned} \quad (3.11)$$

where the single impurity T -matrix is given by

$$\mathcal{T}(i\omega_n) = [\mathcal{S}^{-1} - \mathcal{G}_0(0, 0; i\omega_n)]^{-1} \quad (3.12)$$

and

$$\mathcal{S} = U_1 \sigma_0 + U_2 \sigma_3 + V \sigma_1 . \quad (3.13)$$

The remaining task is to calculate the Green's function of the pure system but in the

presence of magnetic field. For this purpose, we can perform a canonical transformation

$$\begin{aligned}\hat{\Psi}(\mathbf{r}) &= \sum_{\mu} \begin{pmatrix} u_{\mu,1}(\mathbf{r}) & u_{\mu,2}(\mathbf{r}) \\ v_{\mu,1}(\mathbf{r}) & v_{\mu,2}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \gamma_{\mu,1} \\ \gamma_{\mu,2} \end{pmatrix} \\ &= \sum_{\mu,\alpha} \begin{pmatrix} u_{\mu,\alpha}(\mathbf{r}) \\ v_{\mu,\alpha}(\mathbf{r}) \end{pmatrix} \gamma_{\mu,\alpha} ,\end{aligned}\tag{3.14}$$

where the transformation matrix elements are formed by the eigenfunctions to the Hamiltonian H_0 , that is

$$H_0 \begin{pmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{pmatrix} = E \begin{pmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{pmatrix} .\tag{3.15}$$

As such, $\mathcal{H}_0 = \sum_{\mu,\alpha} E_{\mu,\alpha} \gamma_{\mu,\alpha}^\dagger \gamma_{\mu,\alpha}$, and the Green's function can be written as

$$\mathcal{G}_0(\mathbf{r}, \mathbf{r}'; i\omega_n) = \sum_{\mu,\alpha} \frac{\psi_{\mu}(\mathbf{r}) \psi_{\mu}^\dagger(\mathbf{r}')}{i\omega_n - E_{\mu,\alpha}} ,\tag{3.16}$$

where $\alpha = 1, 2$ when $E_{\mu,\alpha} \neq 0$ while $\alpha = 0$ when $E_{\mu,\alpha} = 0$ as will be discussed below, and $\psi_{\mu}(\mathbf{r}) = (u_{\mu}(\mathbf{r}), v_{\mu}(\mathbf{r}))^{\text{Transpose}}$ such that

$$\psi_{\mu}(\mathbf{r}) \psi_{\mu}^\dagger(\mathbf{r}') = \begin{pmatrix} u_{\mu,\alpha}(\mathbf{r}) u_{\mu,\alpha}^*(\mathbf{r}') & u_{\mu,\alpha}(\mathbf{r}) v_{\mu,\alpha}^*(\mathbf{r}') \\ v_{\mu,\alpha}(\mathbf{r}) u_{\mu,\alpha}^*(\mathbf{r}') & v_{\mu,\alpha}(\mathbf{r}) v_{\mu,\alpha}^*(\mathbf{r}') \end{pmatrix} .$$

The eigenfunction to the Hamiltonian can be written in the form:

$$\psi(\mathbf{r}) = \begin{pmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{pmatrix} = \frac{e^{ikx}}{\sqrt{L}} \begin{pmatrix} \chi_1(y) \\ \chi_2(y) \end{pmatrix} ,\tag{3.17}$$

where $k = 2\pi m/L$ with m being an integer and L is linear dimension along the x -

direction. The eigen-problem is then reduced to

$$\begin{aligned}
E \begin{pmatrix} \chi_1(y) \\ \chi_2(y) \end{pmatrix} &= \hbar v_F \begin{pmatrix} 0 & k - y/l_B^2 - \partial/\partial y \\ k - y/l_B^2 + \partial/\partial y & 0 \end{pmatrix} \begin{pmatrix} \chi_1(y) \\ \chi_2(y) \end{pmatrix} \\
&= \frac{\hbar v_F}{l_B} \begin{pmatrix} 0 & -(y - l_B^2 k)/l_B - l_B \partial/\partial y \\ -(y - l_B^2 k)/l_B + l_B \partial/\partial y & 0 \end{pmatrix} \begin{pmatrix} \chi_1(y) \\ \chi_2(y) \end{pmatrix}
\end{aligned}$$

which can be rewritten as

$$E \begin{pmatrix} \chi_1(\xi) \\ \chi_2(\xi) \end{pmatrix} = \hbar \omega_c \begin{pmatrix} 0 & \hat{a} \\ \hat{a}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \chi_1(\xi) \\ \chi_2(\xi) \end{pmatrix}. \quad (3.18)$$

Here the magnetic length $l_B = (\hbar/eB)^{1/2}$, the cyclotron frequency is given by $\hbar \omega_c = \sqrt{2} \hbar v_F / l_B$, and we have defined the dimensionless length scale

$$\xi = y/l_B - l_B k, \quad (3.19)$$

and the creation and annihilation operators

$$a^\dagger = \frac{1}{\sqrt{2}} [-\xi + \partial/\partial \xi], \quad (3.20a)$$

$$a = \frac{1}{\sqrt{2}} [-\xi - \partial/\partial \xi], \quad (3.20b)$$

which obey the canonical commutation relations $[a, a^\dagger] = 1$. The solutions are found to be

$$\begin{pmatrix} \chi_1(\xi) \\ \chi_2(\xi) \end{pmatrix} = \frac{1}{\sqrt{2 - \delta_{n0}}} \begin{pmatrix} (1 - \delta_{n0}) \varphi_{n-1}(\xi) \\ \alpha \varphi_n(\xi) \end{pmatrix}, \quad (3.21)$$

corresponding to the eigenvalue $E = \alpha \hbar \omega_c \sqrt{n}$ with $\alpha = +1$ for $n = 0$ and $\alpha = \pm 1$ for

$n = 1, 2, \dots$. The $\alpha = 1, 2$ mentioned above corresponds to ± 1 here when $n \neq 0$. The function $\psi_n(\xi)$ is the solution of the one-dimensional oscillator,

$$\varphi_n(\xi) = [1/\sqrt{\pi}2^n n!]^{1/2} e^{-\xi^2/2} H_n(\xi) , \quad (3.22)$$

with $H_n(\xi)$ is a Hermite polynomial.

Numerically we can start with the first two functions

$$\varphi_0(\xi) = \frac{1}{\pi^{1/4}} e^{-\xi^2/2} , \quad (3.23a)$$

$$\varphi_1(\xi) = \frac{\sqrt{2}}{\pi^{1/4}} \xi e^{-\xi^2/2} , \quad (3.23b)$$

and then use the following recursion relation

$$\varphi_{n+1}(\xi) = \sqrt{\frac{2}{n+1}} \left[\xi \varphi_n(\xi) - \sqrt{\frac{n}{2}} \varphi_{n-1}(\xi) \right] , \quad (3.24)$$

to calculate all $\varphi_n(\xi)$. Or we may call the standard library for this special function.

3.2 Continuum Hamiltonian for the graphene in the presence of a magnetic field

In the continuum limit, the **proper** Hamiltonian for the graphene with a local short-ranged impurity as considered in arXiv:0906.4867 in the presence of a magnetic field should be as follows:

$$\hat{H} = \hat{H}_0 + \hat{H}_V , \quad (3.25)$$

with

$$\hat{H}_0 = \begin{pmatrix} v_F \hat{\boldsymbol{\sigma}} \cdot (\mathbf{p} + e\mathbf{A}(\mathbf{r})/c) & \hat{0} \\ \hat{0} & v_F \hat{\boldsymbol{\sigma}}^* \cdot (\mathbf{p} + e\mathbf{A}(\mathbf{r})/c) \end{pmatrix}, \quad (3.26)$$

Here the Fermi velocity $v_F = 3ta/2$, and the Pauli matrices $\hat{\boldsymbol{\sigma}} = (\sigma_1, \sigma_2)$ and $\hat{\boldsymbol{\sigma}}^* = (\sigma_1, -\sigma_2)$. and

$$\begin{aligned} \hat{H}_V &= \begin{pmatrix} \epsilon_{A0} & 0 & \epsilon_{A0} e^{i\frac{\theta_2 - \theta_1}{2}} & 0 \\ 0 & 0 & 0 & 0 \\ \epsilon_{A0} e^{-i\frac{\theta_2 - \theta_1}{2}} & 0 & \epsilon_{A0} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \delta(\mathbf{r}) \\ &= \hat{S} \delta(\mathbf{r}). \end{aligned} \quad (3.27)$$

and ϵ_{A0} is the on-site potential disorder, the two angles are defined as $\theta_1 = \pi/6$ and $\theta_2 = 5\pi/6$. In our calculation, we consider one more Hamiltonian which is related to hopping disorder

$$\begin{aligned} H_{\text{hop}} &= \tilde{v}_F \Psi_{1a}^\dagger(\mathbf{0})(p_x - ip_y) \Psi_{1b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} + e^{-i\frac{\theta_2 - \theta_1}{2}} \tilde{v}_F \Psi_{2a}^\dagger(\mathbf{0})(p_x - ip_y) \Psi_{1b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} \\ &+ e^{i\frac{\theta_2 - \theta_1}{2}} \tilde{v}_F \Psi_{1a}^\dagger(\mathbf{0})(p_x + ip_y) \Psi_{2b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} + \Psi_{2a}^\dagger(\mathbf{0}) \tilde{v}_F (p_x + ip_y) \Psi_{2b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} + hc \end{aligned}$$

t_0 the hopping disorder, $\tilde{v}_F = 3t_0/2$

$$\begin{aligned} (p_x - ip_y) \Psi_{1b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} &= -i \left(\frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) \Psi_{1b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} \\ &= -i \left(\frac{\Psi_{1b}(\Delta x) - \Psi_{1b}(-\Delta x)}{2\Delta x} - i \frac{\Psi_{1b}(\Delta y) - \Psi_{1b}(-\Delta y)}{2\Delta y} \right) |_{\Delta x \rightarrow 0, \Delta y \rightarrow 0} \end{aligned}$$

$$\begin{aligned}
(p_x + ip_y)\Psi_{2b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} &= -i\left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\Psi_{2b}(\mathbf{r})|_{\mathbf{r} \rightarrow 0} \\
&= -i\left(\frac{\Psi_{2b}(\Delta x) - \Psi_{2b}(-\Delta x)}{2\Delta x} - i\frac{\Psi_{2b}(\Delta y) - \Psi_{2b}(-\Delta y)}{2\Delta y}\right)|_{\Delta x \rightarrow 0, \Delta y \rightarrow 0}
\end{aligned}$$

From equations above, we define $\Delta x = \Delta y = \tilde{a}$ $\tilde{a}$ is an infinitesimal and we have

$$\begin{aligned}
H_{hop} &= \frac{\tilde{v}_F}{2i\tilde{a}}[\Psi_{1a}^\dagger(0,0)\Psi_{1b}(\tilde{a},0) - i\Psi_{1a}^\dagger(0,0)\Psi_{1b}(0,\tilde{a}) \\
&\quad - \Psi_{1a}^\dagger(0,0)\Psi_{1b}(-\tilde{a},0) + i\Psi_{1a}^\dagger(0,0)\Psi_{1b}(0,-\tilde{a})] \\
&+ e^{-i\frac{\theta_2 - \theta_1}{2}} \frac{\tilde{v}_F}{2i\tilde{a}}[\Psi_{2a}^\dagger(0,0)\Psi_{1b}(\tilde{a},0) - i\Psi_{2a}^\dagger(0,0)\Psi_{1b}(0,\tilde{a}) \\
&\quad - \Psi_{2a}^\dagger(0,0)\Psi_{1b}(-\tilde{a},0) + i\Psi_{2a}^\dagger(0,0)\Psi_{1b}(0,-\tilde{a})] \\
&+ e^{i\frac{\theta_2 - \theta_1}{2}} \frac{\tilde{v}_F}{2i\tilde{a}}[\Psi_{1a}^\dagger(0,0)\Psi_{2b}(\tilde{a},0) + i\Psi_{1a}^\dagger(0,0)\Psi_{2b}(0,\tilde{a}) \\
&\quad - \Psi_{1a}^\dagger(0,0)\Psi_{2b}(-\tilde{a},0) - i\Psi_{1a}^\dagger(0,0)\Psi_{2b}(0,-\tilde{a})] \\
&\quad \frac{\tilde{v}_F}{2i\tilde{a}}[\Psi_{2a}^\dagger(0,0)\Psi_{2b}(\tilde{a},0) + i\Psi_{2a}^\dagger(0,0)\Psi_{2b}(0,\tilde{a}) \\
&\quad - \Psi_{2a}^\dagger(0,0)\Psi_{2b}(-\tilde{a},0) - i\Psi_{2a}^\dagger(0,0)\Psi_{2b}(0,-\tilde{a})]
\end{aligned} \tag{3.28}$$

So the Green's function for the Hamiltonian with impurities is given by

$$\begin{aligned}
G_{\alpha\beta}(\mathbf{r}, \mathbf{r}', i\omega_n) &= G_{\alpha\beta}^0(\mathbf{r}, \mathbf{r}', i\omega_n) + \sum_{I, I'} G_{\alpha\gamma}^0(\mathbf{r}, I, i\omega_n) U_{\gamma\gamma'}(I, I') G_{\gamma'\beta}(I', \mathbf{r}', i\omega_n) \\
G_{\alpha\beta}(I, \mathbf{r}', i\omega_n) &= G_{\alpha\beta}^0(I, \mathbf{r}', i\omega_n) + \sum_{I', I''} G_{\alpha\gamma}^0(I, I', i\omega_n) U_{\gamma\gamma'}(I', I'') G_{\gamma'\beta}(I'', \mathbf{r}', i\omega_n)
\end{aligned} \tag{3.29}$$

This is one closed set of linear equations for $G_{\alpha\beta}(I, \mathbf{r}', i\omega_n)$, I, I' is the position of impurity and four infinitesimal positions $(\tilde{a}, 0), (0, \tilde{a}), (-\tilde{a}, 0), (0, -\tilde{a})$. The indices α and β run $1a, 1b, 2a$ and $2b$. Here we can consider $U_{\mathbf{r}\mathbf{r}'}(I, I')$ are the scattering potential

and we define $I_1 = (\tilde{a}, 0)$, $I_2 = (-\tilde{a}, 0)$, $I_3 = (0, \tilde{a})$, $I_4 = (0, -\tilde{a})$, From the Eq. (3.27) and Eq. (3.28) we have,

$$U(\mathbf{0}, \mathbf{0}) = \hat{S};$$

$$U(\mathbf{0}, I_1) = \begin{pmatrix} 0 & -\tilde{v}_F/2i\tilde{a} & 0 & -e^{i\frac{\pi}{3}}\tilde{v}_F/2i\tilde{a} \\ 0 & 0 & 0 & 0 \\ 0 & -e^{-i\frac{\pi}{3}}\tilde{v}_F/2i\tilde{a} & 0 & \tilde{v}_F/2i\tilde{a} \\ 0 & 0 & 0 & 0 \end{pmatrix};$$

$$U(\mathbf{0}, I_2) = \begin{pmatrix} 0 & \tilde{v}_F/2i\tilde{a} & 0 & e^{i\frac{\pi}{3}}\tilde{v}_F/2i\tilde{a} \\ 0 & 0 & 0 & 0 \\ 0 & e^{-i\frac{\pi}{3}}\tilde{v}_F/2i\tilde{a} & 0 & -\tilde{v}_F/2i\tilde{a} \\ 0 & 0 & 0 & 0 \end{pmatrix};$$

$$U(\mathbf{0}, I_3) = \begin{pmatrix} 0 & \tilde{v}_F/2\tilde{a} & 0 & -e^{i\frac{\pi}{3}}\tilde{v}_F/2\tilde{a} \\ 0 & 0 & 0 & 0 \\ 0 & e^{\frac{\pi}{3}}\tilde{v}_F/2\tilde{a} & 0 & -\tilde{v}_F/2\tilde{a} \\ 0 & 0 & 0 & 0 \end{pmatrix};$$

$$U(\mathbf{0}, I_4) = \begin{pmatrix} 0 & -\tilde{v}_F/2\tilde{a} & 0 & e^{i\frac{\pi}{3}}\tilde{v}_F/2\tilde{a} \\ 0 & 0 & 0 & 0 \\ 0 & -e^{\frac{\pi}{3}}\tilde{v}_F/2\tilde{a} & 0 & \tilde{v}_F/2\tilde{a} \\ 0 & 0 & 0 & 0 \end{pmatrix};$$

$$U(I, 0) = U^\dagger(0, I) \text{ and } U(I, I') = 0 \text{ if } I \neq \mathbf{0} \text{ and } I' \neq \mathbf{0}.$$

Let's define $\mathbf{r}_1 = \mathbf{r} + (\tilde{a}, 0)$, $\mathbf{r}_2 = \mathbf{r} + (-\tilde{a}, 0)$, $\mathbf{r}_3 = \mathbf{r} + (0, \tilde{a})$, $\mathbf{r}_4 = \mathbf{r} + (0, -\tilde{a})$,

$\mathbf{r}'_1 = \mathbf{r}' + (\tilde{a}, 0)$, $\mathbf{r}'_2 = \mathbf{r}' + (-\tilde{a}, 0)$, $\mathbf{r}'_3 = \mathbf{r}' + (0, \tilde{a})$, $\mathbf{r}'_4 = \mathbf{r}' + (0, -\tilde{a})$ If we expand our

Green's function matrix as:

$$\hat{G}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} G(\mathbf{r}, \mathbf{r}',) & G(\mathbf{r}, \mathbf{r}'_1) & G(\mathbf{r}, \mathbf{r}'_2) & G(\mathbf{r}, \mathbf{r}'_3) & G(\mathbf{r}, \mathbf{r}'_4) \\ G(\mathbf{r}_1, \mathbf{r}',) & G(\mathbf{r}_1, \mathbf{r}'_1) & G(\mathbf{r}_1, \mathbf{r}'_2) & G(\mathbf{r}_1, \mathbf{r}'_3) & G(\mathbf{r}_1, \mathbf{r}'_4) \\ G(\mathbf{r}_2, \mathbf{r}',) & G(\mathbf{r}_2, \mathbf{r}'_1) & G(\mathbf{r}_2, \mathbf{r}'_2) & G(\mathbf{r}_2, \mathbf{r}'_3) & G(\mathbf{r}_2, \mathbf{r}'_4) \\ G(\mathbf{r}_3, \mathbf{r}',) & G(\mathbf{r}_3, \mathbf{r}'_1) & G(\mathbf{r}_3, \mathbf{r}'_2) & G(\mathbf{r}_3, \mathbf{r}'_3) & G(\mathbf{r}_3, \mathbf{r}'_4) \\ G(\mathbf{r}_4, \mathbf{r}',) & G(\mathbf{r}_4, \mathbf{r}'_1) & G(\mathbf{r}_4, \mathbf{r}'_2) & G(\mathbf{r}_4, \mathbf{r}'_3) & G(\mathbf{r}_4, \mathbf{r}'_4) \end{pmatrix}, \quad (3.30)$$

The Green's function above can be written as

$$\begin{aligned} \hat{G}(\mathbf{r}, \mathbf{r}'; i\omega_n) &= \hat{G}_0(\mathbf{r}, \mathbf{r}') + \hat{G}_0(\mathbf{r}, 0; i\omega_n) \\ &\quad \times \hat{\mathcal{T}}(i\omega_n) \hat{G}_0(0, \mathbf{r}'; i\omega_n), \end{aligned} \quad (3.31)$$

where the impurity T -matrix is given by

$$\hat{\mathcal{T}}(i\omega_n) = [\hat{U}^{-1} - \hat{G}_0(0, 0; i\omega_n)]^{-1}, \quad (3.32)$$

$$\hat{U} = \begin{pmatrix} U(\mathbf{0}, \mathbf{0},) & U(\mathbf{0}, \mathbf{I}_1) & U(\mathbf{0}, \mathbf{I}_2) & U(\mathbf{0}, \mathbf{I}_3) & U(\mathbf{0}, \mathbf{I}_4) \\ U(\mathbf{I}_1, \mathbf{0},) & U(\mathbf{I}_1, \mathbf{I}_1) & U(\mathbf{I}_1, \mathbf{I}_2) & U(\mathbf{I}_1, \mathbf{I}_3) & U(\mathbf{I}_1, \mathbf{I}_4) \\ U(\mathbf{I}_2, \mathbf{0},) & U(\mathbf{I}_2, \mathbf{I}_1) & U(\mathbf{I}_2, \mathbf{I}_2) & U(\mathbf{I}_2, \mathbf{I}_3) & U(\mathbf{I}_2, \mathbf{I}_4) \\ U(\mathbf{I}_3, \mathbf{0},) & U(\mathbf{I}_3, \mathbf{I}_1) & U(\mathbf{I}_3, \mathbf{I}_2) & U(\mathbf{I}_3, \mathbf{I}_3) & U(\mathbf{I}_3, \mathbf{I}_4) \\ U(\mathbf{I}_4, \mathbf{0},) & U(\mathbf{I}_4, \mathbf{I}_1) & U(\mathbf{I}_4, \mathbf{I}_2) & U(\mathbf{I}_4, \mathbf{I}_3) & U(\mathbf{I}_4, \mathbf{I}_4) \end{pmatrix} \quad (3.33)$$

The Green's function for the pure system $\hat{G}_0$ is expanded the same way as $\hat{G}$

And G_0 is given by

$$G_0(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \mathcal{G}_1(\mathbf{r}, \mathbf{r}'; i\omega_n) & \hat{0} \\ \hat{0} & \mathcal{G}_2(\mathbf{r}, \mathbf{r}'; i\omega_n) \end{pmatrix}. \quad (3.34)$$

It consists of the solution from two independent Dirac equations:

$$\mathcal{G}_{1(2)}(\mathbf{r}, \mathbf{r}'; i\omega_n) = \sum_{\mu, \alpha} \frac{\psi_{1(2), \mu}(\mathbf{r}) \psi_{1(2), \mu}^\dagger(\mathbf{r}')}{i\omega_n - E_{1(2), \mu, \alpha}}. \quad (3.35)$$

When $\epsilon_A = \epsilon_B = 0$, that is, $\epsilon_0 = \epsilon_3 = 0$, we can easily find the following relation:

$$\mathcal{G}_2(\mathbf{r}, \mathbf{r}'; i\omega_n) = \sigma_1 \mathcal{G}_1(\mathbf{r}, \mathbf{r}'; i\omega_n) \sigma_1, \quad (3.36)$$

and

$$\mathcal{G}_1(\mathbf{r}, \mathbf{r}'; i\omega_n) = \mathcal{G}_0(\mathbf{r}, \mathbf{r}'; i\omega_n), \quad (3.37)$$

with $\mathcal{G}_0(\mathbf{r}, \mathbf{r}'; i\omega_n)$ given by Eq. (3.16) in Sec. 3.1.

3.3 Numerical Results and Discussions

The local density of states for each sublattice is given by

$$\begin{aligned} \rho_A(\mathbf{r}) = & -\frac{1}{\pi} \text{Im}[G_{11}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+) \\ & + e^{2i\mathbf{K} \cdot \mathbf{r}} e^{-i\frac{\theta_2 - \theta_1}{2}} G_{13}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+) \\ & + e^{-2i\mathbf{K} \cdot \mathbf{r}} e^{i\frac{\theta_2 - \theta_1}{2}} G_{31}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+) \\ & + G_{33}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+)] , \end{aligned} \quad (3.38)$$

and

$$\begin{aligned}
\rho_B(\mathbf{r}) = & -\frac{1}{\pi} \text{Im}[G_{22}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+) \\
& + e^{2i\mathbf{K} \cdot \mathbf{r}} e^{i\frac{\theta_2 - \theta_1}{2}} G_{24}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+) \\
& + e^{-2i\mathbf{K} \cdot \mathbf{r}} e^{-i\frac{\theta_2 - \theta_1}{2}} G_{42}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+) \\
& + G_{44}(\mathbf{r}, \mathbf{r}; i\omega_n \rightarrow \omega + i0^+)].
\end{aligned} \tag{3.39}$$

The key observation here is that off-diagonal elements of the 4×4 matrix Green's function are involved. These expressions for the local density of states look more complicated but might be more relevant to graphene. The total local density of states is the sum of the projected ones

$$\rho(\mathbf{r}) = \sum_{\alpha} \rho_{\alpha}(\mathbf{r}), \tag{3.40}$$

with $\alpha = A$ and B .

The numerical task is mainly to evaluate $\mathcal{G}_0$ as given in Eq. (3.16). The density of states ρ_0 from $\mathcal{G}_0$ in which case there is no impurity is shown in Fig. 3.1.

Without magnetic field, LDOS real space distribution has Friedel oscillations. In Fig. 3.2, we show the impurity effect on LDOS distribution in real space with magnetic field. The energy we use in this figure is at the first Landau Level.

The Fourier spectrum of the local density of states is defined as

$$\rho_{\alpha}(\mathbf{k}; \omega) = \int d^2\mathbf{r} \rho_{\alpha}(\mathbf{r}; \omega), \tag{3.41}$$

with $\alpha = A$ and B . In Fig. 3.3 we show the impurity effect on LDOS distribution in $\mathbf{k}$ space with magnetic field. First let's set the energy at the first Landau Level. In the

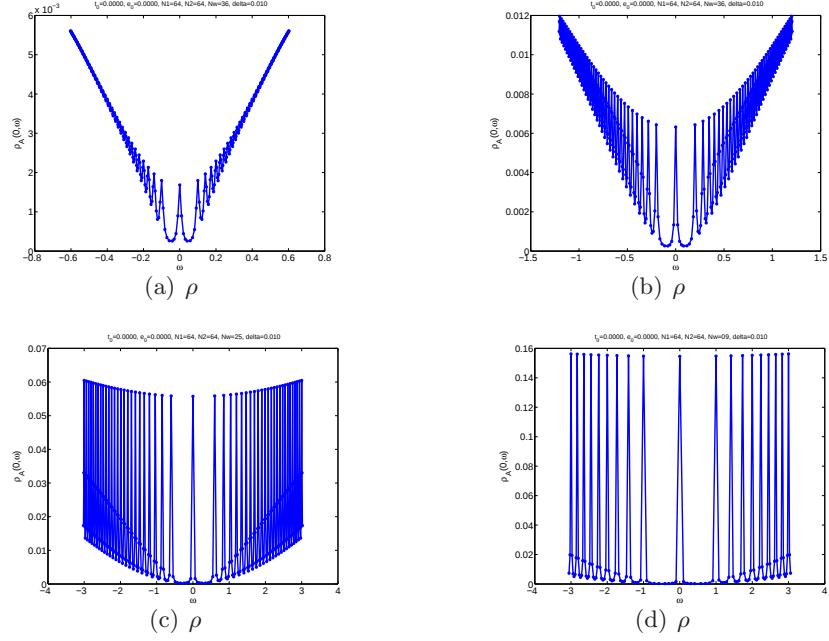


Figure 3.1: LDOS without impurity. Upper left figure corresponds to $\rho_0(\omega)$ at $\omega_c = 0.1$, upper right figure to $\rho_0(\omega)$ at $\omega_c = 0.2$. Second row left figure corresponds to $\rho_0(\omega)$ at $\omega_c = 0.6$, second row right figure to $\rho_0(\omega)$ at $\omega_c = 1.0$.

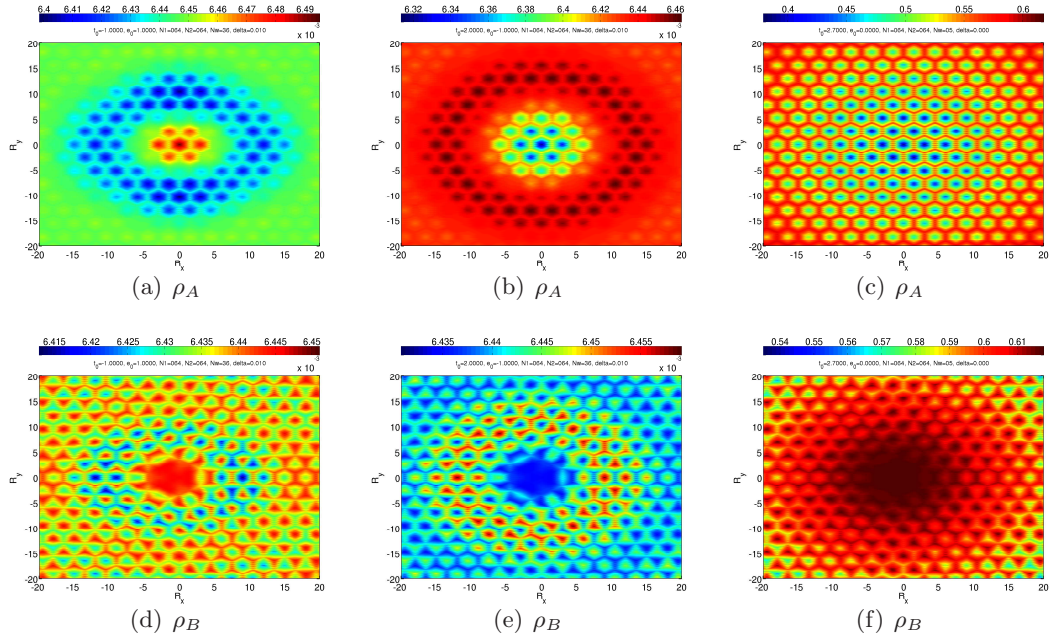


Figure 3.2: LDOS real space distribution with different impurity at $\omega = \omega_c = 0.2$. First row is the LDOS at A site. Second row is the LDOS at B site. First column is LDOS for the Boron like impurity. Second column is LDOS for Nitrogen like impurity. Third column is for vacancy case.

following Fig. 3.4, we will investigate magnetic field effect on the LDOS distribution in k space. In this figure, the intravalley scattering is related to the magnetic length.

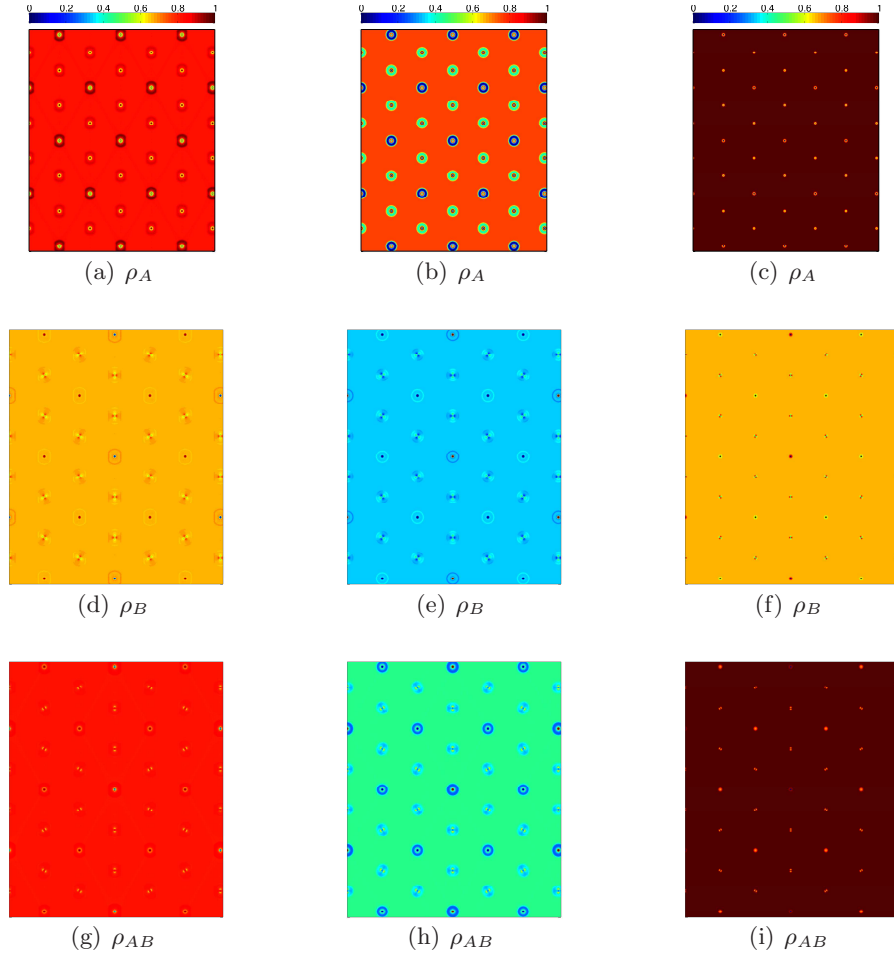


Figure 3.3: LDOS k space distribution with different impurity at $\omega = \omega_c = 0.2$. First row is the LDOS at A site. Second row is the LDOS at B site. Third row is the total LDOS. First column is LDOS for the Boron like impurity. Second column is LDOS for Nitrogen like impurity. Third column is for vacancy case.

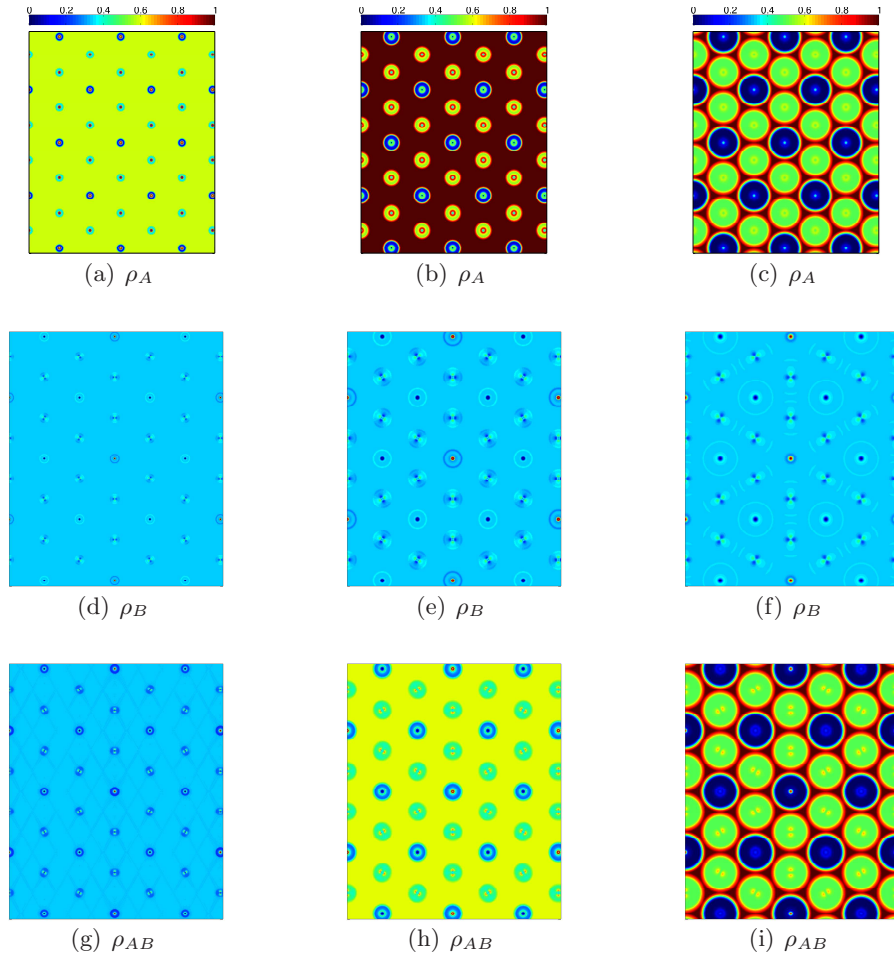


Figure 3.4: LDOS k space distribution with different magnetic field for Nitrogen like impurity. First row is the LDOS at A site. Second row is the LDOS at B site. Third row is the total LDOS. First column is LDOS for $\omega_c = 0.15$. Second column is LDOS for $\omega_c = 0.30$. Third column is for $\omega_c = 0.6$.

Chapter 4

Orbital symmetry fingerprints for adatoms in graphene: theory for scanning tunneling probes

Graphene is a single atomic layer of graphite whose low energy quasiparticles behave as massless Dirac fermions [42,43,70]. As an open surface, graphene offers a solid playground for the detection and local manipulation of quantum states with scanning tunneling (STM) probes. This perspective is particularly promising for adatoms, which can be dragged with atomic precision [14] and can have their magnetic state monitored and controlled with the application of an external gate voltage [55,61]. There has been substantial progress in the quality of the STM experiments in graphene in the last few years [11,21,26,29,37,54,58,67,70,72]. Recent experiments reported the observation of Landau levels spontaneously generated by strain on the top of nanobubbles in graphene [36], and the observation of charge polarization effects around a Co adatom [6].

Although the microscopic theory of STM is well understood in metallic hosts

[52, 59], in graphene the sublattice quantum numbers play a role in the interference effects that drive the emergence of Fano resonances [17]. Those resonances are the most distinctive feature that characterizes the differential conductance line shapes nearby adatoms, in the presence of an STM tip. In particular, for adatoms that sit at the center of the honeycomb hexagon (H), destructive interference between the different electronic paths of hybridization within the two different sublattices may give rise to suppression of the Fano resonance of the localized state [32, 63, 65], and also change the scattering rate of the localized electrons in to the presence of the fermionic bath [63].

Graphene is also clearly distinct from conventional metallic hosts due to its low DOS. For instance, some adatoms and simple molecules such as NO_2 are not magnetic when adsorbed on top of metals, but are expected to develop a local magnetic moment in graphene [35], as a result of the low DOS in the host material, which lowers the size of the phase space for electronic transitions between states in the localized level and the bath [61]. This magnetic moment nevertheless can be fragile in the proximity of a large metallic STM probe, which can enhance dramatically the hybridization of the localized state with the extended electronic orbitals of the tip. The local moment in that case can be eventually suppressed by bringing the metallic tip sufficiently close to the magnetic adatom, reflecting in characteristic signatures in the differential conductance (DC) curves. This effect is not unique to graphene and may in principle be observed in other surfaces with low DOS, such as in the surfaces of three dimensional topological insulators [22, 53].

In general, the broadening of a localized state, magnetic or not, is expected to scale as $\Delta(\omega) \propto |\omega|^r$, where r is the scaling dimension of the DOS of the host material, which in graphene is $r = 1$. In graphene, nevertheless, localized orbitals of adatoms located either in substitutional impurity sites (S sites) or in H sites and which

also preserve the C_{3v} point group symmetry of each sublattice are effectively damped at low energies by a fermionic bath with $r = 3$ [62, 63], due to quantum interference effects. Such orbitals may therefore belong to a different universality class regarding the Kondo problem as compared to adatoms on top carbon sites, and also adatoms on S or H sites that explicitly break the sublattice point group symmetry [62], in which case the level broadening scales linearly with the energy ($\Delta(\omega) \propto |\omega|$) near the Dirac points. The purpose of this work is not to address the spectroscopy of the Kondo effect [13, 25, 38, 55, 62, 66, 68, 73], which will be addressed somewhere else, but to describe in detail the effect of the localized orbital symmetry into the emergence of local resonances nearby the adatom. We also describe the behavior of the Fano line resonances in the differential conductance in terms of the position of the adatoms in the honeycomb lattice and of the specific symmetry of the localized orbital. Whereas the STM theory for adatoms in graphene has been described by us [63] for the case of s -wave orbitals, here we generalize that theory in order to account for effects of higher angular momentum states.

The outline of the paper is as follows: in section II, we describe the generic zero dimensional Hamiltonian of an adatom in graphene; in section III we briefly describe the role of the orbital symmetry into the formation of local magnetic moments and we show the manifestation of those orbital symmetries in the local density of states (LDOS), whenever the adatom hybridizes with two or more carbon atoms. In section IV we develop the STM theory in graphene, where we compute the differential conductance accounting for the symmetry of the localized orbitals and their position with respect to the sublattices. Finally, in section V we present our conclusions.

4.1 Hamiltonian

The Hamiltonian of a magnetic adatom in graphene is described by a sum of four terms,

$$H = H_g + H_f + H_V + H_U , \quad (4.1)$$

where

$$H_g = -t \sum_{\langle ij \rangle} a_{\sigma}^{\dagger}(\mathbf{R}_i) b_{\sigma}(\mathbf{R}_j) + h.c \quad (4.2)$$

is the graphene Hamiltonian in tight-binding, with $t \sim 2.8\text{eV}$ the hopping energy between nearest neighbors sites, a (b) is a fermionic annihilation operator in the A (B) sublattice, with $\sigma = \uparrow, \downarrow$ indexing the spin. In momentum space,

$$H_g = -t \sum_{\mathbf{p}\sigma} \left(\phi_{\mathbf{p}} a_{\mathbf{p}\sigma}^{\dagger} b_{\mathbf{p}\sigma} + h.c. \right) \quad (4.3)$$

where $\phi_{\mathbf{k}} = \sum_{i=1}^3 e^{i\mathbf{k} \cdot \mathbf{a}_i}$ and $\mathbf{a}_1 = \hat{x}$, $\mathbf{a}_2 = -\hat{x}/2 + \sqrt{3}\hat{y}/2$, and $\mathbf{a}_3 = -\hat{x}/2 - \sqrt{3}\hat{y}/2$ are the lattice nearest neighbor vectors. The second term,

$$H_f = \sum_{\sigma} \epsilon_0 f_{\sigma}^{\dagger} f_{\sigma} \quad (4.4)$$

is the Hamiltonian of the localized level with energy ϵ_0 measured from the Dirac point. The third term gives the hybridization Hamiltonian. When the adatoms sit on top of a carbon atom as in the case of H and F atoms, and also simple molecules such as NO_2 ,

$$H_V = V \sum_{\sigma} a_{\sigma}^{\dagger}(0) f_{\sigma} + h.c. ,$$

for adsorption on a given site, say on sublattice A . Adatoms such as transition metals may instead strongly prefer to sit in the hollow site at the center of the hexagon in the honeycomb lattice (see Fig. 1). In that case, the level is coupled to the graphene bath through the hybridization Hamiltonian [63]

$$H_V = \sum_{\sigma} \sum_{i=1}^3 \left[V_{a,i} a_{\sigma}^{\dagger}(\mathbf{a}_i) + V_{b,i} b_{\sigma}^{\dagger}(-\mathbf{a}_i) \right] f_{\sigma} + h.c. \quad (4.5)$$

where $V_{x,i}$ ($x = a, b$) are the hybridization amplitudes of the adatom with each of the nearest neighbors carbon atoms, which are set by the orbital symmetry of the localized estate. In momentum space representation, this Hamiltonian can be written as [62, 63]

$$H_V = \frac{1}{\sqrt{N}} \sum_{\mathbf{p}\sigma} \left(V_{b,\mathbf{p}} b_{\mathbf{p}\sigma}^{\dagger} + V_{a,\mathbf{p}} a_{\mathbf{p}}^{\dagger} \right) f_{\sigma} + h.c., \quad (4.6)$$

where

$$V_{b,\mathbf{p}} = \sum_{\langle j \rangle} V_{b,j} e^{i\mathbf{p} \cdot \mathbf{a}_j} \quad (4.7)$$

$$V_{a,\mathbf{p}} = \sum_{\langle j \rangle} V_{a,j} e^{-i\mathbf{p} \cdot \mathbf{a}_j}, \quad (4.8)$$

with $\langle j \rangle$ representing summation over the hybridization amplitudes of the adatom with the nearest neighbor carbon atoms on a given sublattice, and N is the number of lattice sites in the extended unit cell of the adatom. The discrete sum over momenta can be interchanged by a continuous integration, $\frac{1}{N} \sum_{\mathbf{k}} \longrightarrow A \int d\mathbf{k}$, where $A = 2/D^2$, where $D \approx 7\text{eV}$ is the bandwidth. For notational reasons, we will set $N = 1$ from now on.

For adatoms that sit on top of the carbon atoms, (such as hydrogen), $V_{a,\mathbf{p}} = V$ and $V_{b,\mathbf{p}} = 0$, for adsorption on top of an A site and $V_{a,\mathbf{p}} = 0$ and $V_{b,\mathbf{p}} = V$ for

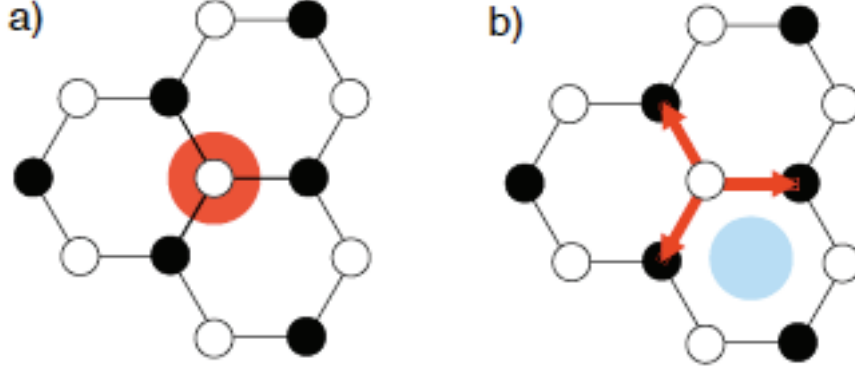


Figure 4.1: Honeycomb lattice in graphene, with two distinct sublattices (black and white circles). a) Adatom sitting on top of a carbon atom on sublattice A , and b) sitting in the center of the honeycomb hexagon. Red arrows: nearest neighbor vectors.

a B site. When the adatom sits at the center of the honeycomb hexagons (H -site), the strengths of hybridization with the six nearest carbon atoms in the tight-binding description depend explicitly on the symmetry of the orbital: for example, for s -wave orbitals, $V_{x,i} \equiv V$ by symmetry, whereas for in-plane f -wave orbitals, the hybridization amplitudes are anti-symmetric on the two sublattices, $V_{a,i} = -V_{b,i} = V$. In the first case (s -wave), $V_{a,\mathbf{p}} = V\phi_{\mathbf{p}}^*$ and $V_{b,\mathbf{p}} = V\phi_{\mathbf{p}}$ whereas in the second (f -wave) $V_{a,\mathbf{p}} = V\phi_{\mathbf{p}}^*$ and $V_{b,\mathbf{p}} = -V\phi_{\mathbf{p}}$. In the case of a $d_{x^2-y^2}$ orbital $V_{x,1} = V$, $V_{x,2} = V_{x,3} = -V/2$, whereas for a d_{xy} orbital, $V_{x,1} = 0$ and $V_{x,2} = -V_{x,3} = V$, and so on, as illustrated in Fig. 4.2. Other interesting cases include for instance substitutional impurities (S -sites) [34], where $V_{a,i} = 0$ for adatoms sitting on A sites and $V_{b,i} = 0$ for substitutional adatoms on B sites. A similar description can be for instance applied for adatoms sitting on bond sites in between two neighbor carbon atoms.

Finally, the last term in Eq. (4.1) is the standard Hubbard U term,

$$H_U = U f_{\uparrow}^{\dagger} f_{\uparrow} f_{\downarrow}^{\dagger} f_{\downarrow},$$

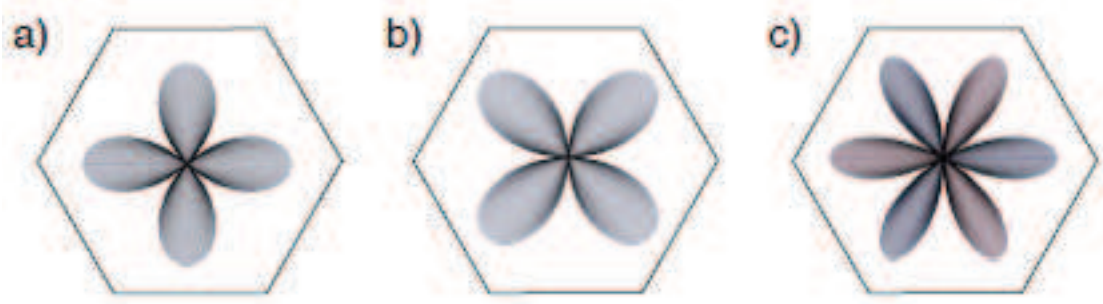


Figure 4.2: Illustration of d -wave and f -wave localized orbitals for an adatom that sits at the center of the honeycomb lattice hexagon. a) $d_{x^2-y^2}$ orbital, that corresponds to hybridization amplitudes $V_{x,1} = V$ and $V_{x,2} = V_{x,3} = -V/2$ with the six nearest neighbor carbon atoms on sublattices $x = a, b$, at the vertexes of the hexagon [see Eq. (4.7), (4.8)]. b) d_{xy} orbital corresponding to $V_{x,1} = 0$ and $V_{x,2} = -V_{x,3} = V$. c) $f_{x(x^2-3y^2)}$ orbital, with hybridization amplitudes $V_{a,i} = -V_{b,i} = V$.

which can be decomposed at the mean-field level into $H_U = U \sum_{\sigma} f_{\sigma}^{\dagger} f_{\sigma} n_{-\sigma}$, where $n_{\sigma} = \langle f_{\sigma}^{\dagger} f_{\sigma} \rangle$ is the occupation of the level, and then absorbed into the definition of the localized energy level in Eq. (4.4),

$$H_f = \sum_{\sigma} \epsilon_{\sigma} f_{\sigma}^{\dagger} f_{\sigma}, \quad (4.9)$$

where $\epsilon_{\sigma} \equiv \epsilon_0 + n_{-\sigma}U$ is the spin dependent renormalized energy of the localized state.

4.2 Local magnetic moments

The formation of local magnetic moments can be addressed by the self consistent calculation of the occupation for up and down spin states, which follows from integrating the DOS from the bottom of the band up to the Fermi level μ , [1, 61]

$$n_{\sigma} = -\frac{1}{\pi} \int_{-\infty}^{\mu} d\omega \operatorname{Im} G_{ff,\sigma}^R(\omega) \quad (4.10)$$

where

$$G_{ff,\sigma}^R(\omega) = [\omega - \epsilon_\sigma - \Sigma_{ff}(\omega) + i0^+]^{-1} \quad (4.11)$$

is the retarded Green's function of the localized electrons, $G_{ff,\sigma}(\tau) = \langle T[f(\tau)f^\dagger(0)] \rangle$, and

$$\Sigma_{ff}(\omega) = \sum_{x,y} \sum_{\mathbf{p}} V_{x,\mathbf{p}}^* G_{xy}^{0R}(\mathbf{p}, \omega) V_{y,\mathbf{p}} \quad (4.12)$$

is the self-energy of the f -electrons, with $x = a, b$. $\hat{G}_{x,y}^{0R}$ are the matrix elements of the retarded Green's function of the itinerant electrons in graphene, $G_{aa,\mathbf{p}}^0(\tau) = -\langle T[a_{\mathbf{p}}(\tau)a_{\mathbf{p}}^\dagger(0)] \rangle$ and so on, which are defined by

$$\hat{G}(\mathbf{p}, i\omega) = \frac{1}{i\omega - \hat{H}}, \quad (4.13)$$

where

$$\hat{H} = -t \begin{pmatrix} 0 & \phi_{\mathbf{p}} \\ \phi_{\mathbf{p}}^* & 0 \end{pmatrix}, \quad (4.14)$$

is the tight-binding Hamiltonian matrix. More explicitly,

$$G_{xy}^{0,R}(\mathbf{p}, \omega) = \frac{1}{2} \sum_{\alpha=\pm} \frac{\mathbf{1} + \alpha \hat{\sigma}_{xy,\mathbf{p}}}{\omega - t\alpha|\phi_{\mathbf{p}}| + i0^+} \quad (4.15)$$

where

$$\hat{\sigma}_{xy,\mathbf{p}} \equiv \frac{\text{Re}(\phi_{\mathbf{p}})\sigma_{xy}^1 - \text{Im}(\phi_{\mathbf{p}})\sigma_{xy}^2}{|\phi_{\mathbf{p}}|}, \quad (4.16)$$

$\mathbf{1}$ is the identity matrix and σ^1 and σ^2 are off-diagonal 2×2 Pauli matrices, namely $\sigma_{ab}^1 = \sigma_{ba}^1 = 1$ and $\sigma_{ab}^2 = -\sigma_{ba}^2 = -i$.

The Green's function of the localized electrons can be written more explicitly

in the following form:

$$G_{ff,\sigma}^R(\omega) = \frac{1}{\omega Z^{-1}(\omega) - \epsilon_\sigma + i\Delta(\omega) + i0^+}, \quad (4.17)$$

where

$$Z^{-1}(\omega) = 1 - \frac{1}{\omega} \text{Re}\Sigma_{ff}(\omega) \quad (4.18)$$

gives the quasiparticle residue and $\Delta(\omega) \equiv -\text{Im}\Sigma_{ff}(\omega)$ is the level broadening of the localized state [62],

$$\Delta(\omega) = V^2 \sum_{\mathbf{p}, \alpha} |\Theta_{\alpha, \mathbf{p}}|^2 \delta(\omega - \alpha |\phi_{\mathbf{p}}|), \quad (4.19)$$

which is defined in terms of the generic tight-binding phases,

$$\Theta_{\alpha, \mathbf{p}} \equiv \frac{1}{\sqrt{2V}} \left(V_{b, \mathbf{p}} + \alpha \frac{\phi_{\mathbf{p}}^*}{|\phi_{\mathbf{p}}|} V_{a, \mathbf{p}} \right), \quad (4.20)$$

where $V \equiv \max(V_{x,i})$.

Those phases depend explicitly on the symmetry of the localized orbital, which reflect in the relative amplitudes of hybridization with the surrounding carbon atoms, and also on the relative position of the adatom with respect to the sublattices, i.e, if the adatom sits on top of a carbon, in the center of the honeycomb hexagon, on a bridge site or else in a substitutional site. This formulation is completely general and can be easily extended to include for instance substitutional impurities in double vacancies.

In the scenario where the adatom sits on top of a carbon atom, the level broadening is given by $\Delta(\omega) = \pi V^2 \rho(\omega)$, where $\rho(\omega) = |\omega|/D^2$ is the DOS in graphene in the linear portion of the spectrum, and therefore $\Delta(\omega)$ scales linearly with energy.

For adatoms that sit on H or S sites, the scaling analysis of the level broadening allows a classification in two symmetry groups, depending on either if the C_{3v} point group symmetry of the honeycomb sublattice is preserved by the adatom or not, as previously mentioned in the introduction. As illustrated in Fig.4.3, when the electrons hop in and out of an adatom sitting on H or S sites, they collect phases which give rise to quantum mechanical interference among the possible hybridization paths. When the amplitudes of hybridization with the three surrounding carbons on the same sublattice are identical, in which case the C_{3v} point group symmetry of sublattice x is preserved, the hopping phases interfere and give rise to an anomalous energy scaling of the hybridization, whose modulus scales now in the same way as the Kinetic energy, $|V_{x,\mathbf{p}}| \propto |\phi_{\mathbf{p}}|$. In that case, the level broadening scales as [62,63]

$$\Delta(\omega) \approx \pi V^2 \rho(\omega) \frac{|\omega|^2}{t^2} \quad (4.21)$$

at low energy, as opposite to the conventional case where this interference is frustrated and $|V_{x,\mathbf{p}}|$ scales to a constant near the Dirac points. In the later, $\Delta(\omega) \propto \rho(\omega)$ corresponds to the standard case, whereas in the former case the damping is super-linear. The first class of orbitals, which we will refer as type II orbitals, include $m = 0$ and $m = 3$ angular momentum states, such as in s and in-plane f -wave orbitals. The standard “ohmic” class (type I) by its turn is described by adatoms on top carbon sites and $m = 1$ and $m = 2$ angular momentum orbitals on H or S sites. To be more concrete, the class of type I orbitals is represented by adatoms that sit on top of a carbon atom, in which case the orbital symmetry is not particularly important, and also by adatoms sitting at H or S sites with localized orbitals in the $E_1(d_{xz}, d_{yz})$ and $E_2(d_{xy}, d_{x^2-y^2})$ representations of d -wave orbitals and also $f_{xz^2}, f_{yz^2}, f_{xyz}, f_{z(x^2-y^2)}$ orbitals in H/S sites.

The class of type II orbitals is described by s , d_{zz} , f_{z^3} orbitals, where $m = 0$, and also by $f_{x(x^2-3y^2)}$, and $f_{y(3x^2-y^2)}$ orbitals ($m = 3$) in H or S sites. The anomalous scaling of the level broadening in Eq. (4.21) has been verified explicitly by *ab initio* methods, in particular for the d_{zz} orbital of Co on graphene [64].

In Fig. 4.4, we show the energy scaling of the level broadening for the different orbital symmetries. Whereas particle-hole symmetry is preserved for adatoms on top carbon sites, where $\Delta(\omega)$ follows the DOS, and also for adatoms on S sites, which effectively hybridize with only one sublattice, for adatoms on H sites, which hybridize with the two sublattices, particle-hole symmetry is explicitly broken in the high energy sector ($|\omega| \gtrsim t$) by the off diagonal matrix elements of the hybridization (at low energy, the off diagonal terms average to zero in the momentum integrals). In particular, $d_{x^2-y^2}$, d_{xy} -wave orbitals (where $V_{a,i} = V_{b,i}$) are strongly damped when the energy of the localized state is far above the Dirac point ($\omega > t$), but otherwise are weakly damped at negative energy states (black solid curve in Fig. 4.4a). Conversely, d_{zx} and d_{zy} -wave orbitals (where $V_{a,i} = -V_{b,i}$) show the opposite trend, in agreement with *ab initio* calculations for Co adatoms in graphene [30, 64]. In the same way, s and in-plane f -wave orbitals, which couple symmetrically and anti-symmetrically with the two sublattices respectively, show a strong particle-hole asymmetry at high energies, as depicted in Fig. 4.4b. In Fig. 4.4c, we show the level broadening for the substitutional case, where particle-hole symmetry is restored. In all cases, the peaks at $|\omega| = t$ are divergences which are reminiscent of the logarithmic singularity of the DOS around the M point of the BZ.

The self-energy of the localized electrons [see Eq. 4.12] can be more explicitly

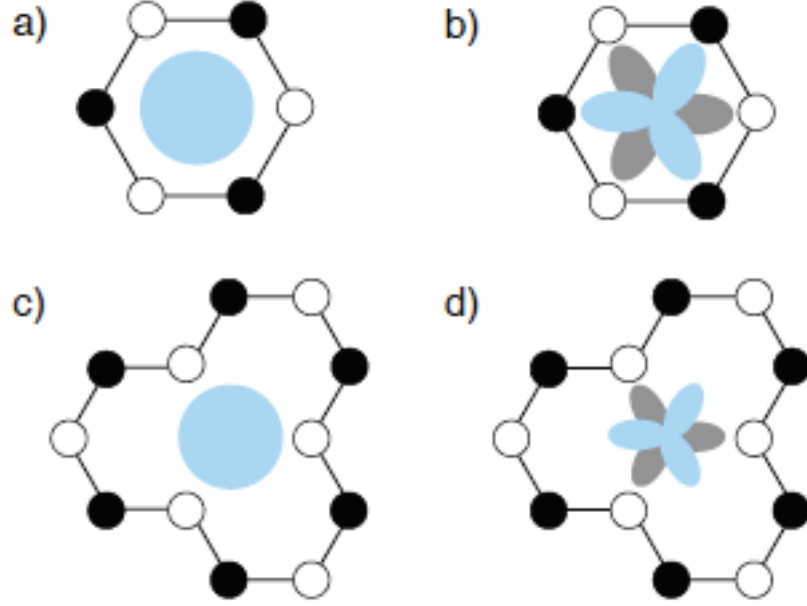


Figure 4.3: C_{3v} invariant orbitals for adatoms sitting in the center of the hexagon, on H sites (top), and in substitutional (S) sites (bottom). On the left: s -wave orbitals, with zero angular momentum ($m = 0$); on the right: in-place f -wave orbitals ($m = 3$). In the two cases, the adatoms hybridize equally with the carbon atoms on the same sublattice (see text).

written in the form

$$\Sigma_{ff}(\omega) = -\omega [Z^{-1}(\omega) - 1] - i\Delta(\omega)\theta(D - |\omega|). \quad (4.22)$$

The density of states of the localized level, $\rho_{ff,\sigma}(\omega) = -1/\pi \text{Im} G_{ff,\sigma}^R(\omega)$ follows from the substitution of Eq. (4.22) into Eq. (4.11),

$$\rho_{ff,\sigma}(\omega) = \frac{1}{\pi} \frac{\Delta(\omega)\theta(D - |\omega|)}{[\omega Z^{-1}(\omega) - \epsilon_\sigma]^2 + \Delta^2(\omega)}. \quad (4.23)$$

As in the original Anderson work [1], the occupation for up and down spin states can be self-consistently calculated at the mean field level from Eq. (4.10). The emergence of a local magnetic moment follows from the appearance of a spin polarized state below the Fermi level, say, at energy $\epsilon_0 + n_\uparrow U$, and a virtual (empty) state at $\epsilon_0 + n_\downarrow U$ for

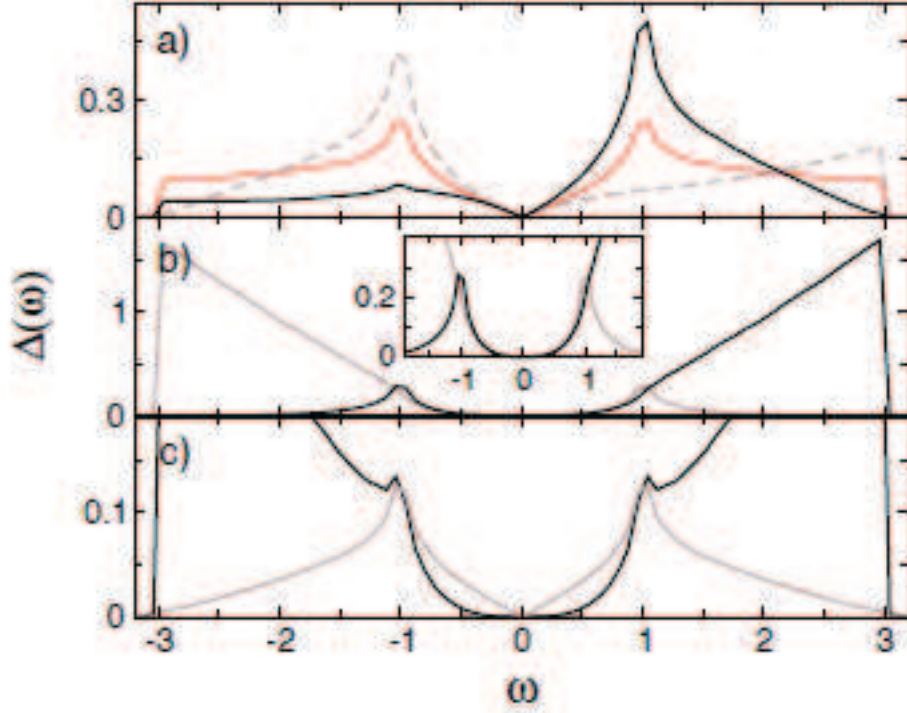


Figure 4.4: Level broadening $\Delta(\omega)$ as a function of energy, ω , for different orbital symmetries. All energies in units of the hopping energy t ($V/t = 1/3$). a) Type I orbitals for adatoms sitting on a top carbon site (light/red solid curve) and for d_{xy} -wave (black line) and d_{zx} -wave orbitals (dashed line) on H sites. b) Type II orbitals on H sites. Solid curve: in-plane f -wave orbital; dashed curve: s -wave orbital. Inset: low energy scaling of the level broadening, $\Delta(\omega) \propto |\omega|^3$ for $|\omega|/t < 1$ (see text). c) Substitutional s/f -wave orbitals (black curve) and d_{xy} -wave orbital (light curve), on S sites.

the majority spin, with $n_\uparrow + n_\downarrow \leq 1$ due to the Pauli principle. Of course, since a single impurity is a zero dimensional system, the presence of local spin polarization ($n_\uparrow \neq n_\downarrow$) does not imply in a true broken symmetry state, as the local moment is allowed to fluctuate freely in any direction of space. In this sense, the original $SU(2)$ symmetry of the problem is preserved.

In the linear cone approximation, where the spectrum is linearized around the Dirac points, $t|\phi_{\mathbf{K}+\mathbf{p}}| \rightarrow vp$ up to the cut-off of the band D , with $v \approx 6\text{eV}\text{\AA}$ as the

Fermi velocity, the level broadening for orbitals of type I is

$$\Delta_I(\omega) \equiv \Delta|\omega| \quad (4.24)$$

at low energies, where $\Delta = \pi(V/D)^2$ is the dimensionless hybridization parameter, and

$$Z_I^{-1}(\omega) = (\Delta/\pi) \ln |1 - D^2/\omega^2|, \quad (4.25)$$

implying that the quasiparticle residue $Z \rightarrow 0$ vanishes logarithmically at low energy.

In the case of super-linear damping, for type II orbitals, the level broadening scales with the *cube* of the energy within the linear cone approximation,

$$\Delta_{II}(\omega) = N_s \Delta |\omega|^3 / t^2, \quad (4.26)$$

and can be orders of magnitude smaller than in the linear case when $|\epsilon_0| \ll t$. $N_s = 1, 2$ correspond to the number of sublattices the adatom effectively hybridizes ($N_s = 2$ for H sites and $N_s = 1$ for S sites, as shown in Fig. 4.3). The quasiparticle residue, Z_σ , in this approximation is given by

$$Z_{II}^{-1}(\omega) = 1 + N_s \Delta / (\pi t^2) [D^2 + \omega^2 \ln |1 - D^2/\omega^2|]. \quad (4.27)$$

The analysis about the formation of local magnetic moments and the zero dimensional phase diagram that comes out has been discussed in detail in ref. uchao for the case of type I orbitals. For type II orbitals, the physics is qualitatively similar, except for the fact that the formation of a local magnetic moment becomes exceedingly easy at small U , due to the fact that the broadening of the level can be negligibly small

when $\epsilon_0/t \ll 1$.

4.2.1 Local DOS

The local DOS around the impurity can be computed directly from the diagonal matrix elements of the electronic Green's function in graphene in the presence of the adatom,

$$\rho_x(\mathbf{r}, \omega) = -\frac{1}{\pi} \text{Im} \sum_{\sigma} \sum_{\mathbf{p}, \mathbf{p}'} G_{xx, \sigma}^R(\mathbf{p}, \mathbf{p}', \omega) e^{i(\mathbf{p} - \mathbf{p}') \cdot \mathbf{R}}, \quad (4.28)$$

where

$$G_{xy, \sigma}(\mathbf{p}, \mathbf{p}', i\omega) = \delta_{\mathbf{p}, \mathbf{p}'} G_{xy}^0(p) + \Lambda_x(p) G_{ff, \sigma}(i\omega) \bar{\Lambda}_y(p'), \quad (4.29)$$

and

$$\Lambda_x(p) \equiv \sum_{y=a,b} G_{xy}^0(p) V_{y, \mathbf{p}} \quad (4.30)$$

$$\bar{\Lambda}_x(p) \equiv \sum_{y=a,b} V_{y, \mathbf{p}}^* G_{yx}^0(p), \quad (4.31)$$

with $V_{a, \mathbf{p}}$ and $V_{b, \mathbf{p}}$ defined in Eq. (4.7) and (4.8).

In Fig. 4.5 we show the topography maps around the impurity, which describe the local DOS integrated in energy. We use the set of parameters $V = 1\text{eV}$, $U = 1\text{eV}$, $\mu = 0.1\text{eV}$ and $\epsilon_0 = -0.5\text{eV}$, which correspond to a spin polarized state with $n_{\uparrow} \approx 0.04$ and $n_{\downarrow} \approx 0.96$. In the case where the adatoms sit on top of a carbon site on a given sublattice (top panels), the maps show a clear asymmetry between the integrated LDOS of the two different sublattices. The pattern on the opposite sublattice of the impurity (Fig. 4.5a) has a lower point group symmetry than in the same sublattice (Fig. 4.5b), what comes from the fact that the adatom in this case has only three nearest neighbor

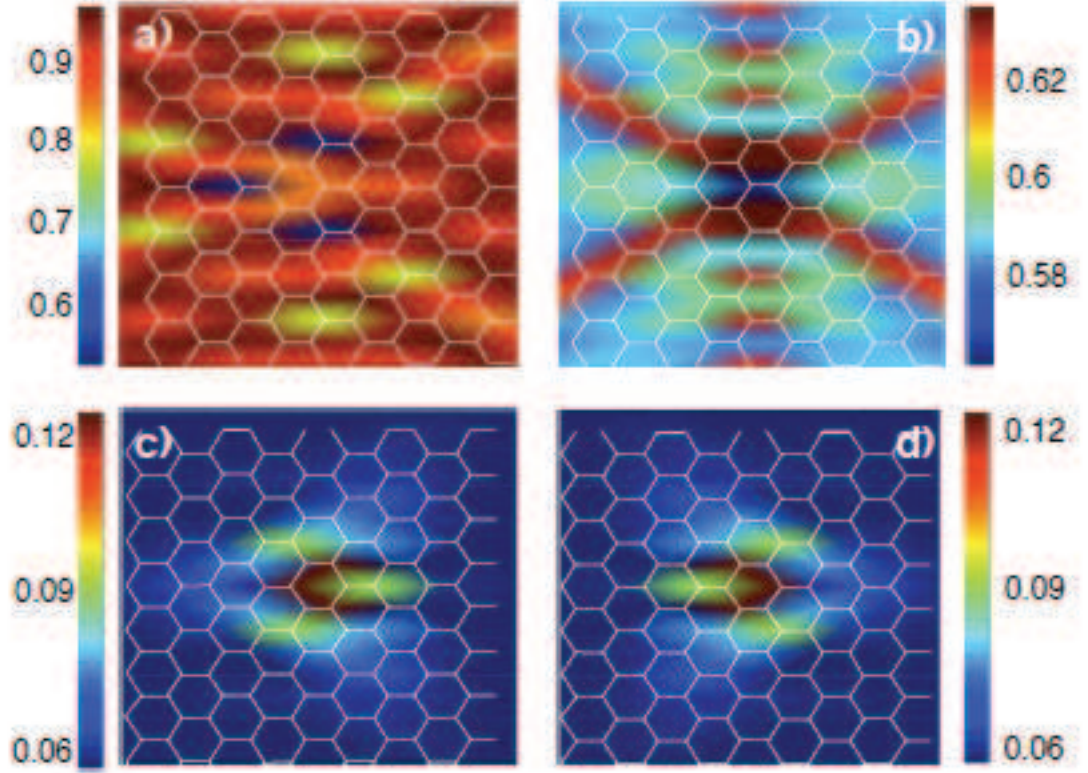


Figure 4.5: Comparison of the LDOS between the two different sublattices. Top panels: Energy integrated LDOS around an adatom (center) sitting on a top carbon adatom site. Scans for a) the same sublattice of the impurity and b) for the opposite sublattice. Lower panels: Energy integrated LDOS around a localized orbital (center) with $m = 0$ ($L_z = 0$) angular momentum state, when the adatom sits in the center of a honeycomb hexagon (H site). c) scans for sublattice A and d) B . The two scans are related by a π -rotation.

carbon sites but six next-nearest neighbor ones. For adatoms sitting in the center of the honeycomb hexagon (lower panels), there is no distinction between the patterns of the two different sublattices, except for a rotation of π . Fig. 4.5c and d depict the integrated LDOS for an s -wave orbital ($m = 0$) sitting on an H site. The intensity of the integrated LDOS maps is also much weaker in the lower panels compared to the upper ones, reflecting the fact that the hybridization for H or S sites is mediated by hopping, and hence weaker than in the top carbon site case for the same set of parameters.

The analysis of the LDOS also permits to identify the symmetry of the local-

ized orbital when the adatom sits either on H or S sites. In Fig. 4.6 we show the LDOS at fixed energy for both a $d_{x^2-y^2}$ orbital (Fig. 4.6a) and a $f_{x(x^2-3y^2)}$ state (Fig. 4.6b). In the former, the orbital d -wave symmetry of the localized state has a clear fingerprint in the induced DOS nearby the adatom. In the case of an in-plane f -wave state, which explicitly preserves the point group symmetry of the sublattices, the fingerprint, although subtle, can be easily characterized by a Fourier analysis of the LDOS, which maps the scattering wavevectors responsible for the emergence of local resonances nearby the adatom.

In Fig. 4.7, we plot the corresponding maps of the energy integrated LDOS in the reciprocal space. The solid hexagonal line indicates the Brillouin zone (BZ). In Fig. 4.7a, we show the maps for the opposite sublattice of the impurity, whereas on Fig. 4.7b, we depict the Fourier transformed maps for the same sublattice of the adatom. The central peaks around the center of the zone (Γ point) indicate forward scattering processes that contribute to the resonant states nearby the adatom, whereas the peaks centered at the K points at the edges the BZ indicate backscattering processes, which connect the different valleys. For the opposite sublattice of the adatom (Fig. 4.7a), the backscattering processes at the K point and the forward scattering ones at Γ are significantly attenuated. In the reciprocal space maps for the *same* sublattice of the impurity (Fig. 4.7b), where unitary scattering should dominate, backscattering processes are strongly enhanced, followed by the presence of subdominant forward scattering peaks. In panel 4.7c, we depict the Fourier transformed map for both sublattices. In those plots (top carbon case), the amount of scattering at the M points, which indicate the position of the Van Hove singularities, is weak compared to the other dominant processes. The shape of the forward scattering peak at the Γ point also reflects the symmetry of the hybridization matrix elements in the Hamiltonian. In the top carbon case, the Γ peak

is isotropic.

In Fig. 4.7d we show the reciprocal space maps for the energy integrated LDOS for an s -wave orbital sitting at an H site. In this case, the height of the central peak is significantly small compared to the dominant peaks around the K points, indicating strong enhancement of the backscattering compared to forward scattering processes. In panel 4.7e we depict the case of a $d_{x^2-y^2}$ -wave orbital also at an H site, whereas in panel 4.7f we show the signature of an $f_{x(x^2-3y^2)}$ orbital (H site) in the reciprocal space. For d and f -wave orbitals, destructive interference leads to attenuation of the backscattering peaks at the K points, in particular in the d -wave case. In the insets of Fig. 4.7d and f we show in detail the features of the forward scattering peaks for s -wave and $f_{x(x^2-3y^2)}$ -wave orbitals, respectively. Both peaks reflect the underlying C_{3v} symmetry of the sublattices, which are incorporated into the hybridization matrix elements of the Hamiltonian for orbitals of type II. For a d -wave orbital (inset of Fig. 4.7e), the forward scattering peak has C_{2v} symmetry.

4.3 STM theory

Let us now consider a problem of more practical interest for tunneling microscopy experiments, where we additionally include an STM tip close to the impurity. The electrons in the metallic tip follow the Hamiltonian

$$H_t = \sum_{\mathbf{p}} \epsilon_{\mathbf{p}} c_{\sigma\mathbf{p}}^\dagger c_{\sigma\mathbf{p}} \quad (4.32)$$

where $\epsilon_{\mathbf{p}} = p^2/2m$ is the electronic dispersion of an electron gas, with m the effective mass. The electrons can tunnel either to the carbon sites in graphene or to the impurity.

In the former case, the tunneling process is described by the Hamiltonian

$$H_{g-t} = \sum_{\langle i \rangle} t_a a_{\sigma}^{\dagger}(\mathbf{R}_i) c_{\sigma}(\mathbf{R}_i - \mathbf{r}) + \sum_{\langle i \rangle} t_b b_{\sigma}^{\dagger}(\mathbf{R}_i) c_{\sigma}(\mathbf{R}_i - \mathbf{r}) + h.c. \quad (4.33)$$

where t_a, t_b are the electronic tunneling energy from the tip to sublattices A , and B in graphene, $\langle i \rangle_t$ denotes sum over the tip nearest neighbor carbon sites ($\mathbf{R}_i$) on a given sublattice, and $\mathbf{r} = (R, z)$ is the position of the center of the tip, where $\mathbf{R}$ is the horizontal distance of the tip to the impurity and z is the distance of the tip to the graphene layer.

The Bloch wave-functions $\psi_{t,\mathbf{p}}(\mathbf{r})$ describing the electronic state at the tip, namely

$$c_{\sigma}(\mathbf{R}_i - \mathbf{r}) = \sum_{\mathbf{p}} \psi_{t,\mathbf{p}}(\mathbf{R}_i - \mathbf{r}) c_{\sigma\mathbf{p}},$$

can be expanded in spherical waves from the center of the tip, $\psi_{t,\mathbf{p}}(r) \propto e^{-\kappa_{\mathbf{p}} r}/r$, where $c_{\sigma\mathbf{p}}$ is a second quantized operator for the tip electrons. The factor [52, 59]

$$\kappa_{\mathbf{p}} = \sqrt{2m(\phi_t - \epsilon_{\mathbf{p}})} \quad (4.34)$$

gives the effective tunneling barrier between the tip and the rest of the system, and is defined by the electronic work function of the tip, ϕ_t . Since the graphene Bloch functions can be expanded in plane waves, $\psi_{g,\mathbf{k}}(\mathbf{R}_i) = e^{i\mathbf{k} \cdot \mathbf{R}_i}$ [59], the Hamiltonian (4.33) becomes

$$H_{g-t} = \sum_{\mathbf{k}\mathbf{p}} \left[t_{a,\mathbf{k}\mathbf{p}}(\mathbf{r}) a_{\sigma\mathbf{k}}^{\dagger} c_{\sigma\mathbf{p}} + t_{b,\mathbf{k}\mathbf{p}}(\mathbf{r}) b_{\sigma\mathbf{k}}^{\dagger} c_{\sigma\mathbf{p}} \right] + h.c., \quad (4.35)$$

where

$$t_{x,\mathbf{k}\mathbf{p}}(\mathbf{r}) \sim \frac{t_x}{z} e^{-\kappa_{\mathbf{p}} z} e^{-i\mathbf{k} \cdot \mathbf{R}} \equiv t_{x,\mathbf{p}}(z) e^{-i\mathbf{k} \cdot \mathbf{R}}. \quad (4.36)$$

describes the spatially averaged hopping matrix elements between the tip and graphene, where the position of each of the carbon atoms underneath the tip is effectively replaced by the in-plane position of the center of the tip with respect to the impurity.

The Hamiltonian for the tunneling from the tip to the impurity is given by:

$$H_{f-t} = t_f f_{\sigma}^{\dagger} c_{\sigma}(\mathbf{r}) + h.c. \quad (4.37)$$

where t_{f-t} is the tunneling energy from the tip to the impurity. In a similar way, we can write

$$H_{f-t} = \sum_{\mathbf{p}} t_{f,\mathbf{p}}(r) f_{\sigma}^{\dagger} c_{\sigma\mathbf{p}} + h.c., \quad (4.38)$$

where

$$t_{f,\mathbf{p}}(r) = t_f \frac{1}{|\mathbf{r}|} e^{-\kappa_{\mathbf{p}}|\mathbf{r}|}. \quad (4.39)$$

where $|\mathbf{r}| = \sqrt{R^2 + z^2}$ measures the center of the tip with respect to the position of the impurity. We will assume that the tip is sufficiently large such that local gating effects due to the proximity of the tip to graphene can be effectively absorbed into the local definition of the chemical potential nearby the adatom [6].

As a brief comment about orders of magnitude for the several quantities, in most materials, the typical work function ϕ_t is of the order of a few eV. In the case where the effective mass m is of the same order of the bare mass of the electron, $\kappa_{\mathbf{p}}^{-1}$ calculated at the Fermi energy translates into a characteristic tunneling length scale with a lower bound of the order 1 nm. Also, since STM tips have a typical radius of the order of 1 nm, z , which accounts for the distance between the center of the tip to graphene is typically a number of the same order. A more detailed description about the characterization of the tip and the surface in the STM problem can be found in Ref. [59].

4.3.1 Green's functions

Now we generalize the original Hamiltonian of the Anderson problem to include Hamiltonian terms (4.32), (4.35) and (4.38),

$$H = H_g + H_f + H_V + H_U + H_t + H_{g-t} + H_{f-t}. \quad (4.40)$$

In the following, we will assume perturbation theory in the hybridization of the tip with the rest of the system, namely t_f and t_x ($x = a, b$) are small compared to the hybridization V of the adatom with the host (graphene). This is not nevertheless a strict requirement at the mean field level, and the 'exact' expressions of the Green's functions are shown in the Appendix. In addition, we will also assume that the system remains in equilibrium in the presence of the STM tip. A detailed calculation of the equilibrium and also out of equilibrium Green's functions in the STM problem for metallic surfaces can be found in Ref. [52].

To further simplify matters, we assume here that $\kappa_{\mathbf{p}} \sim \kappa$ is computed at the Fermi energy and hence is momentum independent, in which case

$$t_{x,\mathbf{k}\mathbf{p}}(\mathbf{r}) \rightarrow t_x(z) e^{-i\mathbf{k}\cdot\mathbf{R}} \equiv t_{x,\mathbf{k}}(\mathbf{r}), \quad (4.41)$$

with $x = a, b$. Since the STM tip is typically large compared to the lattice spacing in graphene, one can further simplify things by assuming $t_{a,\mathbf{p}} = t_{b,\mathbf{p}}$. We will keep the a, b labels below for completeness. A similar assumption will be made for the tunneling matrix element between the tip and the adatom, $t_{f,\mathbf{p}}(r) \rightarrow t_f(r)$.

The matrix elements of the renormalized Green's function in the a, b sublattice basis can be calculated straightforwardly,

$$\begin{aligned}
G_{xy,\sigma}(\mathbf{p}, \mathbf{p}', i\omega) &= \delta_{\mathbf{p}, \mathbf{p}'} G_{xy}^0(p) + \Gamma_x(p, \mathbf{r}) \Lambda_x(p) G_{ff,\sigma}(i\omega) \bar{\Lambda}_y(p') \bar{\Gamma}_y(p', \mathbf{r}) \\
&+ T_x(p, \mathbf{r}) \bar{T}_y(p', \mathbf{r}) \sum_{\mathbf{k}} G_{cc}^0(k),
\end{aligned} \tag{4.42}$$

The quantities $\Lambda_x(p)$ and $\bar{\Lambda}_x(p)$ were defined in Eq. (4.30) and (4.31), whereas

$$T_x(p, \mathbf{r}) \equiv \sum_{y=a,b} G_{xy}^0(p) t_{y,\mathbf{p}}(\mathbf{r}) \tag{4.43}$$

$$\bar{T}_x(p, \mathbf{r}) \equiv \sum_{y=a,b} t_{y,\mathbf{p}}^*(\mathbf{r}) G_{yx}^0(p) \tag{4.44}$$

contain the tunneling amplitudes and phases for the electrons as they hop between the tip and the A, B sublattices. $G_{cc}^0(\mathbf{k}, \tau) = -\langle T[c_{\mathbf{k}}(\tau) c_{\mathbf{k}}^\dagger(0)] \rangle$ is the bare Green's function of the electrons of the tip,

$$G_{cc}^0(p) = \frac{1}{i\omega - \epsilon_{\mathbf{p}}}, \tag{4.45}$$

while Γ and its conjugate form $\bar{\Gamma}$ in Eq. (4.42) define the vertex renormalization due to the presence of the tip,

$$\Gamma_x(p, \mathbf{r}) = 1 + \frac{T_x(p, \mathbf{r})}{\Lambda_x(p)} \bar{t}_f(\mathbf{r}, \omega) \sum_{\mathbf{k}} G_{cc}^0(k) \tag{4.46}$$

$$\bar{\Gamma}_x(p, \mathbf{r}) = 1 + \frac{\bar{T}_x(p, \mathbf{r})}{\bar{\Lambda}_x(p)} t_f(\mathbf{r}, \omega) \sum_{\mathbf{k}} G_{cc}^0(k), \tag{4.47}$$

where the quantities

$$t_f(\mathbf{r}, i\omega) = t_f(r) + \sum_{y=a,b} \bar{\Lambda}_y(-\mathbf{R}, i\omega) t_y(z) \tag{4.48}$$

$$\bar{t}_f(\mathbf{r}, i\omega) = t_f(r) + \sum_{y=a,b} t_y^*(z) \Lambda_y(\mathbf{R}, i\omega), \tag{4.49}$$

give the renormalized tunneling functions between the tip and the adatom, whose bare form, $V_c(r)$, is defined in Eq. (4.39). We also defined

$$\begin{aligned}\Lambda_x(\mathbf{R}) &= \sum_{\mathbf{k}} \Lambda(k) e^{i\mathbf{k}\cdot\mathbf{R}} \\ \bar{\Lambda}_x(\mathbf{R}) &= \sum_{\mathbf{k}} \bar{\Lambda}(k) e^{i\mathbf{k}\cdot\mathbf{R}}\end{aligned}$$

as the Fourier transforms of $\Lambda(k)$ and $\bar{\Lambda}(k)$ [see Eq. (4.30) and (4.31)].

The self-energy correction to the localized electrons, $\Sigma_{ff}(\omega)$, as given in Eq. (4.12), is also dressed by the proximity of the STM tip and assumes the form

$$\Sigma_{ff}(\mathbf{r}, i\omega) = \Sigma_{ff}(i\omega) + \Sigma_{ff}^{(1)}(\mathbf{r}, i\omega) \quad (4.50)$$

where

$$\Sigma_{ff}^{(1)}(\mathbf{r}, i\omega) = t_f(\mathbf{r}) \bar{t}_f(\mathbf{r}) \sum_{\mathbf{k}} G_{cc}(k). \quad (4.51)$$

gives the contribution from the tip to leading order in t_f and t_x . In the presence of the STM tip, the Green's function of the localized electrons depends explicitly on the distance between the tip to the adatom,

$$G_{ff,\sigma}^R(i\omega) = [i\omega - \epsilon_\sigma - \Sigma_{ff}(\mathbf{r}, i\omega)]^{-1}, \quad (4.52)$$

which reflects the influence of the tip into the wavefunction of the localized states.

The imaginary part of the self energy, $\text{Im}\Sigma_{ff}^{(1)}(\mathbf{r}, i\omega)$, renormalizes the level broadening $\Delta(\omega)$, defined in Eq. (4.19), due to the hybridization of the localized electrons with the electrons in the tip. In contrast with metallic hosts, which have a large DOS, in graphene the metallic tip can locally overwhelm the hybridization of the adatom

with the nearby carbon atoms. In the situation where the level broadening becomes large enough as to overcome local correlation effects in the localized state, the tip might eventually lead to suppression of the local magnetism. This effect will be discussed in more detail in sec. IV.B.

Finally, other useful quantities are two off diagonal Green's functions $G_{cx,\sigma}(\mathbf{p}, \tau) = -\langle T[c(\tau)x^\dagger(0)] \rangle$, with $x = a, b$, which are given by

$$G_{cx,\sigma}(\mathbf{p}, \mathbf{p}', i\omega) = G_{cc}^0(p) [T_y^*(p', \mathbf{r}) + \bar{t}_f(\mathbf{r}, i\omega)\bar{\Gamma}_x(p', \mathbf{r}) \times G_{ff,\sigma}(i\omega)\bar{\Lambda}_x(p')], \quad (4.53)$$

and also

$$G_{cf,\sigma}(p) = G_{cc}^0(p)\bar{t}_f(\mathbf{r}, i\omega)G_{ff,\sigma}(i\omega), \quad (4.54)$$

which are required for computing the differential conductance (see sec. IV. B.1).

4.3.1.1 Local DOS

Besides the localized state, the local DOS around the adatom is also affected by the presence of the STM tip. The local DOS nearby the impurity is also indirectly affected by the hybridization of the orbitals of the tip with the adatom localized orbital. For instance, for a magnetic adatom, the DOS is expected to be spin polarized on a given sublattice x ,

$$\rho_{x,\sigma}(\mathbf{r}, \omega) = -\frac{1}{\pi} \text{Im} \sum_{\mathbf{p}, \mathbf{p}'} G_{xx,\sigma}^R(\mathbf{p}, \mathbf{p}', \omega) e^{i(\mathbf{p}-\mathbf{p}') \cdot \mathbf{R}}, \quad (4.55)$$

where the diagonal Green's function $G_{xx,\sigma}(\mathbf{p}, \mathbf{p}', i\omega)$ is explicitly shown in Eq. (4.42).

In a more explicit form,

$$\rho_{x,\sigma}(\mathbf{r}, \omega) = -\frac{1}{\pi} \text{Im} \left[\sum_{\mathbf{p}} G_{xx}^0(p) + [\Gamma_x * \Lambda_x](\mathbf{r}) G_{ff,\sigma}(\omega) [\bar{\Gamma}_x * \bar{\Lambda}_x](\mathbf{r}) + T_x(z) \bar{T}_x(z) \sum_{\mathbf{k}} G_{cc}^0(k) \right] \quad (4.56)$$

gives the local DOS per spin, where

$$[\Gamma_x * \Lambda_x](\mathbf{r}) \equiv \sum_{\mathbf{p}} e^{i\mathbf{p} \cdot \mathbf{R}} \Gamma_x(p, \mathbf{r}) \Lambda_x(p) \quad (4.57)$$

$$[\bar{\Gamma}_x * \bar{\Lambda}_x](\mathbf{r}) \equiv \sum_{\mathbf{p}} e^{-i\mathbf{p} \cdot \mathbf{R}} \bar{\Gamma}_x(p, \mathbf{r}) \bar{\Lambda}_x(p) \quad (4.58)$$

is the Fourier transform convoluted over the the product of the $\Gamma(p, \mathbf{r})$ and $\Lambda_x(p)$ functions (and their respective conjugate forms), as defined in Eq. (4.30), (4.31) and (4.46), (4.47), while $T_x(z, \omega)$ is by definition $T(\mathbf{r}, \omega)|_{\mathbf{R}=0}$ [see Eq. (4.43)], and hence independent of the horizontal distance between the tip and the adatom.

In Fig. 4.9 we show the topography maps for LDOS in the presence of the STM tip for both sublattices in the case of an adatom sitting on top of a carbon atom (top panels) and also for an adatom on an H site (lower panels). In those plots, we use the same set of parameters as before, $V = 1\text{eV}$, $U = 1\text{eV}$, $\mu = 0.1\text{eV}$, $\epsilon_0 = -0.5\text{eV}$, and additionally the parameters $\alpha_D = 4\text{ eV}$ for the band width of the tip and $\epsilon_D = 2\text{eV}$ for the Fermi energy of the tip. The tunneling parameters between the tip and the system where chosen to be $t_f = 0.02\text{ eV}$ and $t_a = t_b = 0.2\text{eV}$. As expected, the plots show basically the same qualitative features as the ones shown in Fig. 4.5 for the actual DOS on graphene in the absence of the STM tip.

The most important feature of the tip in the LDOS can be observed in the

evolution of the magnetic resonances as the STM tip gets close to the adatom. In Fig. 4.10, we show the LDOS measured at the position of an adatom ($\mathbf{R} = 0$) that sits on top of a carbon atom. Using the same set of parameters as before, we show the evolution of the two spin polarized resonant peaks at energy $\epsilon_0 + n_\uparrow U$ and $\epsilon_0 + n_\downarrow U$ as we increase the strength of the hopping amplitude between the tip and the adatom, t_f . As t_f increases (panels 4.10b to d), the peaks are progressively suppressed as the high energy peak for virtual $n_\downarrow$ states is red shifted. As mentioned in the previous section, this effect stems from the fact that due to the low DOS in graphene, the proximity of the metallic STM tip can substantially enhance the broadening of the localized state. For moderate U , this effect may imply in the eventual suppression of the localized moment when the tip is sufficiently close to the adatom, permitting the detection of the local moment with a non-magnetic tip away from the Kondo regime. This effect has also a clear manifestation in the differential conductance curves of STM, which we describe in the next subsection.

4.3.2 Tunneling current

The tunneling current from the tip is defined by:

$$I = -e \left\langle \frac{d\hat{N}_c(t)}{dt} \right\rangle, \quad (4.59)$$

where $\hat{N}_c = \sum_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$ is the number operator for the c electrons in the tip, and e is the electron charge. The motion equation for this operator is

$$\partial_t \hat{N}_c = i [H, \hat{N}_c],$$

where H is the full Hamiltonian defined in Eq. (4.40) including hopping matrix elements between the tip and the system. After a straightforward algebra, the total current follows from the sum of three different contributions that arise from tip tunneling processes to either sublattices A , and B or else to the adatom localized state,

$$I = -2e \operatorname{Im} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left[t_f(\mathbf{r}) \sum_{\mathbf{k}\sigma} iG_{cf,\sigma}^<(\mathbf{k}, \omega) + \sum_{\mathbf{k}\mathbf{p},\sigma} \sum_{x=a,b} t_{x,\mathbf{p}}(z) iG_{cx,\sigma}^<(\mathbf{k}, \mathbf{p}, \omega) \right], \quad (4.60)$$

where

$$G^<(t, t') \equiv i \langle \psi^\dagger(t') \psi(t) \rangle, \quad (4.61)$$

$$G^>(t, t') \equiv -i \langle \psi(t) \psi^\dagger(t') \rangle, \quad (4.62)$$

are real time “lesser” and “greater” Green’s functions, which should be distinguished from retarded (G^R) and advanced (G^A) ones, which are time ordered. If $A(\omega) = B(\omega)C(\omega)$, one may show that [33]

$$A^<(\omega) = B^R(\omega)C^<(\omega) + B^<(\omega)C^A(\omega), \quad (4.63)$$

in which case the total current can be written as

$$I = -2e \operatorname{Im} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \times \sum_{\mathbf{k}} [G_{cc}^{0R}(k) \Sigma_{cc}^<(\mathbf{r}, \omega) + G_{cc}^{0<}(k) \Sigma_{cc}^A(\mathbf{r}, \omega)] \quad (4.64)$$

where

$$\begin{aligned}\Sigma_{cc}(\mathbf{r}, i\omega) = & \sum_{\mathbf{p}} \sum_{x=a,b} t_x(z) \bar{T}_x(z, p) \\ & + t_f(\mathbf{r}) \bar{t}_f(\mathbf{r}) \sum_{\sigma} G_{ff,\sigma}(i\omega)\end{aligned}\quad (4.65)$$

is the self energy correction to the Green's function of the c -electrons in the tip,

$$G_{cc}(\mathbf{p}, \mathbf{p}', i\omega) = [(i\omega - \epsilon_{\mathbf{p}}) \delta_{\mathbf{p}, \mathbf{p}'} - \Sigma_{cc}(\mathbf{r}, i\omega)]^{-1}. \quad (4.66)$$

The first term in Eq. (4.65) gives the self-energy contribution due to the graphene electrons, while the second one is the contribution from the adatom. Using the fluctuation dissipation theorem [33]

$$G^{<}(\omega) = i f(\omega) A(\omega), \quad (4.67)$$

where $A(\omega) = -2\text{Im}G^R(\omega)$ is the spectral function, the total current is given by

$$I(\mathbf{r}, \omega') = 2\pi e t_a^2(z) \int_{-\infty}^{\infty} d\omega \rho_t(\mathbf{r}, \omega) \rho_c(\omega') [f(\omega) - f(\omega')], \quad (4.68)$$

where $f(\omega) = [e^{\omega/T} + 1]^{-1}$ is the Fermi distribution, ρ_c is the DOS at the STM tip,

$$\rho_c(\omega) = -\frac{1}{\pi} \sum_{\mathbf{k}} \text{Im} G_{cc}^0(k), \quad (4.69)$$

and ρ_t is defined as

$$\rho_t(\mathbf{r}, \omega) = -\frac{1}{\pi t_a^2(z)} \text{Im} \Sigma_{cc}^R(\mathbf{r}, \omega). \quad (4.70)$$

This term has units of DOS, and accounts for the phases acquired by the electrons in the tunneling process between the tip and the localized state of the adatom. It can be

conveniently rewritten in the following form:

$$\rho_t(\mathbf{r}, \omega) = \rho_0(\omega) \left\{ \nu(\omega) + \frac{\pi}{2} \rho_0(\omega) V^2 \times \sum_{\sigma} [(\gamma\bar{\gamma} - q\bar{q}) \text{Im} G_{ff,\sigma} + (q\bar{\gamma} + \bar{q}\gamma) \text{Re} G_{ff,\sigma}] \right\},$$

where

$$\nu(\omega) = -\frac{1}{\pi V \rho_0(\omega)} \text{Im} \sum_{x=a,b} \bar{T}_x(\mathbf{R} = 0, \omega). \quad (4.71)$$

$\rho_0(\omega)$ is the bare local DOS of graphene in the absence of the impurity and the tip, and $V \equiv \max(V_{x,i})$, with $V_{x,i}$ the hybridization amplitudes of the adatom with the nearest carbon atoms, as defined in Eq. (4.20). The other parameter, q and its conjugate form, $\bar{q}$ are the Fano factors,

$$q(\mathbf{r}, \omega) = \frac{1}{t_a(z)V} \frac{\text{Re } t_f(\mathbf{r}, \omega)}{\pi \rho_0(\omega)} \quad (4.72)$$

$$\bar{q}(\mathbf{r}, \omega) = \frac{1}{t_a(z)V} \frac{\text{Re } \bar{t}_f(\mathbf{r}, \omega)}{\pi \rho_0(\omega)}, \quad (4.73)$$

while

$$\gamma(\mathbf{r}, \omega) = -\frac{1}{\pi V \rho_0(\omega)} \sum_{x=a,b} \text{Im} \bar{\Lambda}_x(\mathbf{R}, \omega) \quad (4.74)$$

$$\bar{\gamma}(\mathbf{r}, \omega) = -\frac{1}{\pi V \rho_0(\omega)} \sum_{x=a,b} \text{Im} \Lambda_x(\mathbf{R}, \omega) \quad (4.75)$$

gives the corresponding damping factor. These factors characterize the Fano resonances in the differential conductance curves in the vicinity of a localized state.

4.3.2.1 Differential conductance

The Green's function of the localized electrons can be written in a more compact form as:

$$G_{ff,\sigma}^R(\omega) = \frac{\xi_\sigma - i}{\xi_\sigma^2 + 1} \frac{1}{\text{Im}\Sigma_{ff}(\mathbf{r}, \omega)} \quad (4.76)$$

where $\Sigma_{ff}(\mathbf{r}, \omega)$ is the dressed self-energy of the localized electrons due to the proximity of the tip, as defined in Eq. (4.50), and $\xi_\sigma(\omega)$ is defined as

$$\xi_\sigma(\mathbf{r}, \omega) = \frac{\omega - \epsilon_\sigma - \text{Re}\Sigma_{ff}(\mathbf{r}, \omega)}{\text{Im}\Sigma_{ff}(\mathbf{r}, \omega)}. \quad (4.77)$$

The differential conductance follows by computing I/V_b in the limit of $V_b \equiv \omega' - \omega \rightarrow 0$. Since $df(\omega')/d\omega = -\delta(\omega')$ at zero temperature, the differential conductance can be written in the more standard form

$$\begin{aligned} \mathcal{G}(\mathbf{R}, \omega_b) = & 2\pi e \rho_c(0) t_f^2(z) \rho_0(\omega_b) \times \\ & \sum_{\sigma} \left\{ \nu(\omega_b) + \left[\frac{q\bar{q} - \gamma\bar{\gamma} + (q\bar{\gamma} + \bar{q}\gamma)\xi_\sigma}{\xi_\sigma^2 + 1} \right] \right\}, \end{aligned} \quad (4.78)$$

where ω_b is the bias voltage. The first term in parenthesis defines the DC due to the DOS in graphene. The second one is explicitly defined in terms of the Fano parameters and gives the contribution due to the presence of the magnetic adatom.

The experimental detection of a localized state with STM tips is based on the principle of quantum interference between the two different hybridization paths the electrons can take when they tunnel from the impurity to the localized state. In one

way, the electrons can tunnel directly to the localized state. On the other, they can also tunnel to the host material (graphene) and then hybridize with the localized orbital. The signature of such interference appears in the differential conductance curves in the form of a Fano resonance. In graphene, the electrons have additional sublattice quantum numbers which may give rise to additional interference effects, depending on the position of the adatom relative to the two different sublattices. In the case where the adatom sits in the center of the honeycomb hexagon, for a given sublattice, there are three different paths the electrons in graphene take to hybridize with the adatom. Destructive interference between the different paths in a given sublattice can suppress the Fano character of the resonance and change the shape of the DC curves.

When the tip is above the adatom ($R = 0$), the conjugate forms $q = \bar{q}$ and $\gamma = \bar{\gamma}$ in Eq. (4.72)-(4.75) are the same. In the simplest scenario, where an adatom sits on top of a carbon atom, say on site A , the Fano factor is defined explicitly in terms of the self-energy for orbitals of type I, $\text{Re}\Sigma_{ff}^I(\omega) = \omega[Z_I^{-1}(\omega) - 1]$, as given in Eq. (4.25), namely

$$q^A(0, \omega) = \frac{V_c + (t_a(z)/V)\text{Re}\Sigma_{ff}^I(\omega)}{\pi t_a(z)V\rho_0(\omega)}. \quad (4.79)$$

The damping in this case is $\gamma^A = 1$, by noticing that integrals with off diagonal matrix elements of the Green's function, such as $\sum_{\mathbf{k}} G_{ab} = 0$. In a different scenario, for adatoms of type II, which sit either in S or H sites and possess orbitals with C_{3v} point group symmetry, as discussed in Sec. III, the hybridization matrix elements have the form $V_{b,\mathbf{p}} = \pm V\phi_{\mathbf{p}}$ and $V_{a,\mathbf{p}} = V\phi_{\mathbf{p}}^*$, in which case one can easily check that $\Lambda(\mathbf{R} = 0, \omega) = \sum_{x,y=a,b} \sum_{\mathbf{k}} G_{xy} V_{y,\mathbf{p}} = 0$. In that case,

$$q^{II}(0, \omega) = V_c / [\pi t_a(z)V\rho_0(\omega)], \quad (4.80)$$

and $\gamma^{II} = 0$. In the more generic case, for type I orbitals (the ones which are not C_{3v} invariant) that sit on H or S sites, the damping factor γ interpolates between 0 and $N_s = 1, 2$, the number of sublattices the adatom effectively hybridizes.

The shape of the DC curves around the energy of the resonant states of the adatom is driven by the ratio q/γ . When $q/\gamma \gg 1$, the DC curve has the form of a peak, whereas in the opposite limit, for $q/\gamma \ll 1$ it shows a dip. In Fig. 4.11 we show the DC induced by the presence of the adatom in the case where it sits on top of a carbon site (left panels) and also for an type II orbital at an H site (right panels).

In panels a) and b) we assume a fixed set of parameters as in Fig.4.10 and change the ratios t_f/t_a for a given fixed value of $t_a = 0.15\text{eV}$. For $t_f/t_a = 0.1$, the red curve shown in the inset of Fig. 4.11a shows a small dip, which is suppressed when $t_f/t_a \gtrsim 0.2$. By contrast, the curves shown in Fig. 4.11b have a well pronounced peak that persists for all finite values of q^{II} [see inset of Fig.2(b)], what is a consequence of the fact that q^{II}/γ^{II} is always large ($\gamma^{II} = 0$). The red lines correspond to the same ratio $t_f/t_a = 0.1$. Increasing this ratio from $t_f/t_a = 0.25$ up to 1.6, the DC curves show two strongly pronounced peaks which indicate the position of the two magnetic Fano resonances at $\epsilon_0 + n_\uparrow U$ and $\epsilon_0 + n_\downarrow U$. Their width is commensurate with the broadening of the localized state at a given energy. At low energy, those peaks are much sharper for type II adatoms due to the anomalous broadening $\Delta(\omega) \propto |\omega|^3/t^2$ [see Eq. (4.21)]. In panels c) and d) we reexamine the features of the positive bias resonance shown in panels a) and b), but now for $t_a = 0.02\text{ eV}$. The shapes of the curves remain unaltered for the same values of the ratio t_f/t_a , as it can be seen by comparing the red curves between panels a) and c) and also between panels b) and d). All red lines correspond to the same ratio $t_f/t_a = 0.1$. Increasing this ratio from $t_f/t_a = 0.25$ up to 1.6, the

DC curves show two strongly pronounced peaks which indicate the position of the two magnetic Fano resonances at $\epsilon_0 + n_\uparrow U$ and $\epsilon_0 + n_\downarrow U$. For $t_f/t_a < 0.1$, the positive bias peak in the top carbon case, [see Fig. 4.11c] shows an inversion in the structure of the resonance at $t_f/t_c = 0.01$.

The evolution of the separation of the peaks follows the same trend shown before in the LDOS (see Fig. 4.10). The increase of t_f leads to a gradual suppression of the local magnetic moment, and as a consequence to a decrease in the separation of the two peaks. When t_f is large enough, the two DC magnetic peaks eventually merge on top of each other, destroying the local moment completely. Additional fluctuations, which are expected to play a role at very large t_f , should further enhance the suppression of the local moment by the STM tip. The suppression of the local moment can be of course inhibited by strong correlations, at large U , which make the local moment more resilient to the influence of the tip. For instance, a significant suppression of the local moment by the metallic tip is more difficult to achieve in adatoms with a very large U , such as in the case of several transition metals, which typically show a large local moment when hybridized with a metallic host. Gating effects that bring the Fermi level close to the energy of the localized state may on the other hand favor a mixed valence regime state, where the local moment can be destroyed by the tip even at very large U .

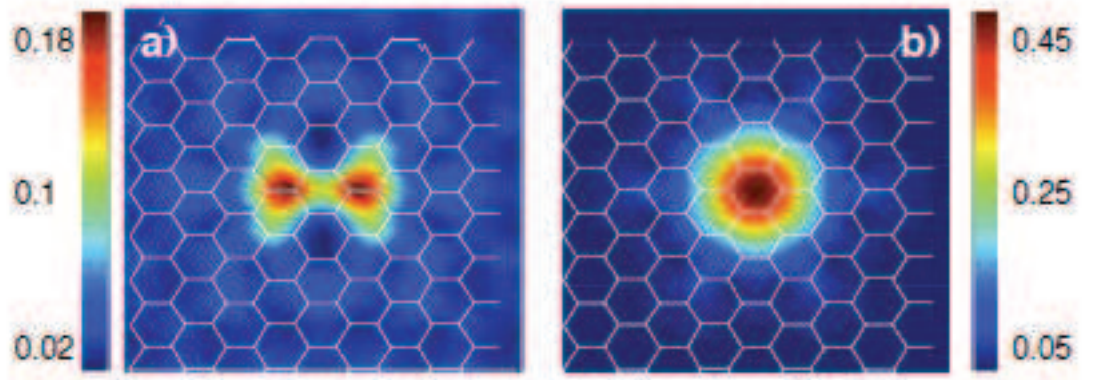


Figure 4.6: LDOS around the adatom (center) at a fixed energy ($\omega = -0.2\text{eV}$) for adatoms on H sites. a) LDOS for a $d_{x^2-y^2}$ orbital and b) for an in-plane f -wave orbital.

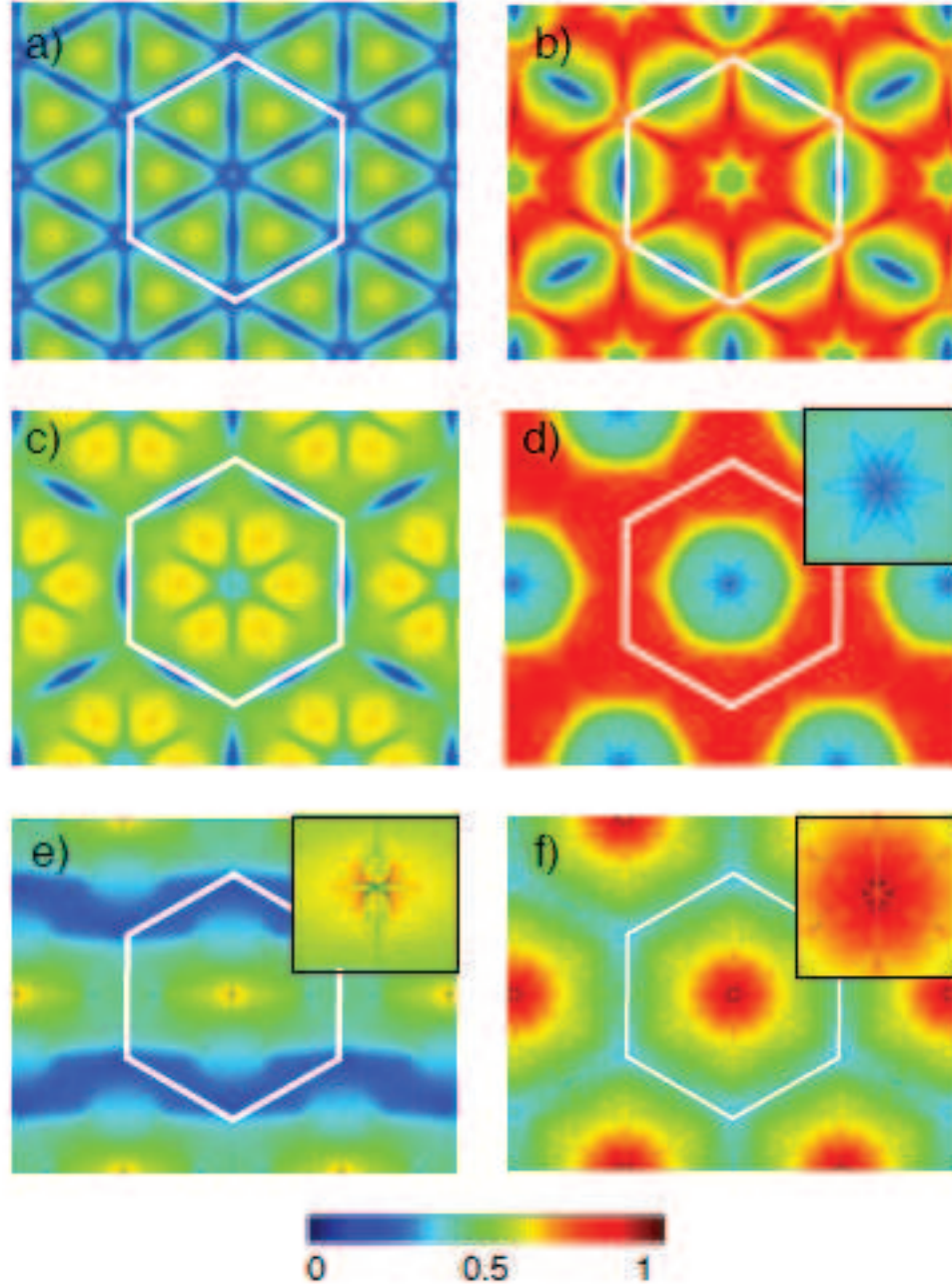


Figure 4.7: Fourier transform of the energy integrated LDOS around the adatom. Solid hexagon line indicates the Brillouin zone. The peaks at the center of the zone correspond to forward scattering processes, whereas the peaks at the corners of the zone (K) points correspond to backscattering between the two valleys. Top panels: adatom on a top carbon site case; Fourier transform of the LDOS for the a) opposite and b) same sublattice of the adatom. c) superposition of the patterns in panels a) and b), for both sublattices. d) s -wave orbital at an H site. Lower panels: e) $d_{x^2-y^2}$ -wave orbital and f) $f_{x(x^2-3y^2)}$ orbital also at H sites. The insets in panels d), e) and f) show the details of the forward scattering peaks at the center of the BZ.

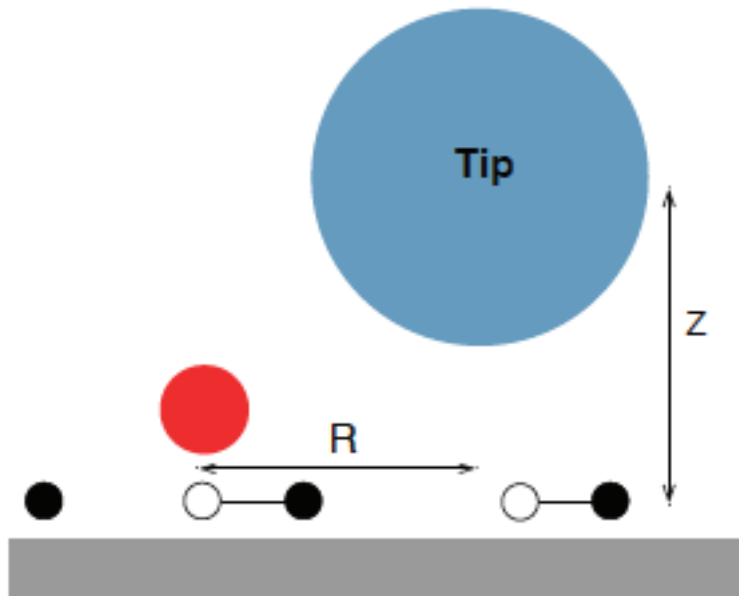


Figure 4.8: Schematic drawing of the STM tip nearby an adatom (small light [red] circle) on top of graphene. Black and white circles: carbon atoms on sublattices A and B. R is the in-plane distance of the impurity to the tip and z the out of plane distance from the center of the tip to the graphene layer.

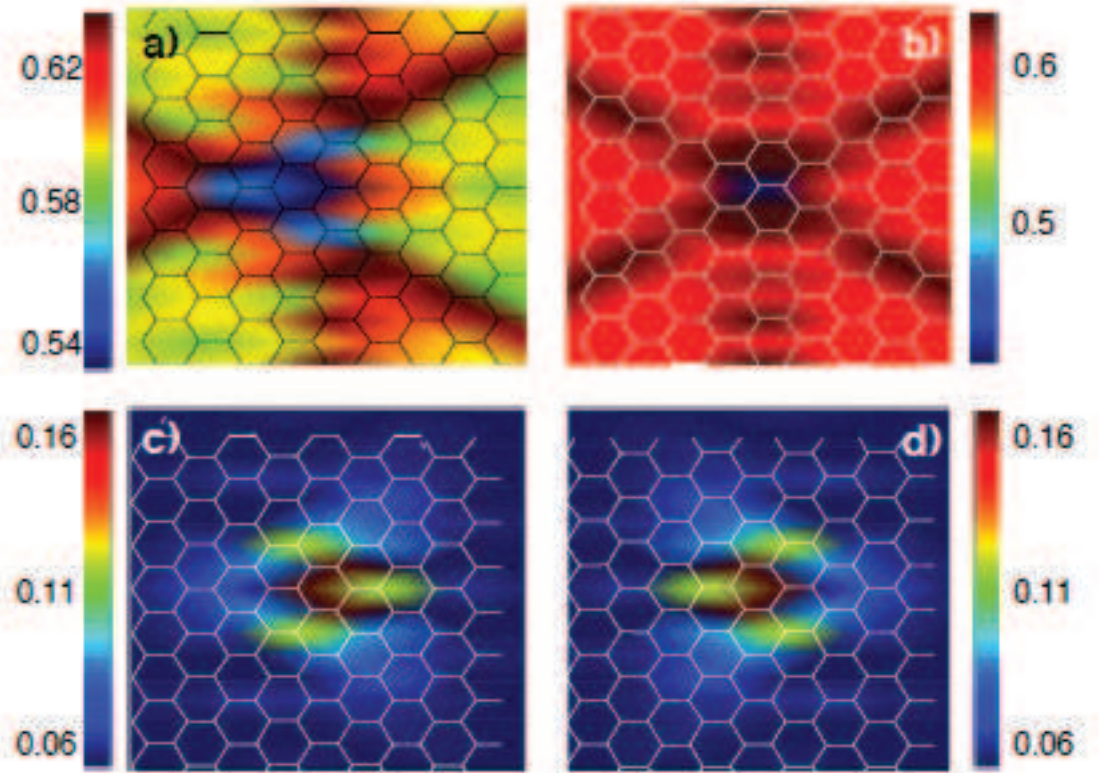


Figure 4.9: Energy integrated LDOS around the adatom (center) in the presence of an STM tip. a) Scans for the same sublattice of the impurity and b) for the opposite sublattice (top carbon site case). Scans for sublattice c) A and d) B , nearby an adatom sitting at the center of a honeycomb hexagon (center).

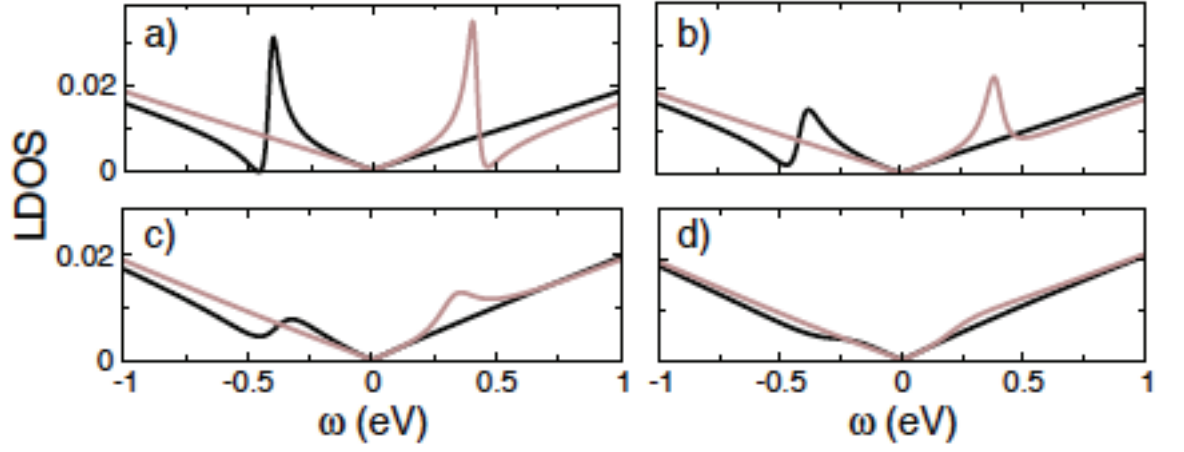


Figure 4.10: Graphene LDOS at the adatom site (top carbon case) for $t_f/t_a = 0.1, 0.7, 1.1$ and 1.6 , from (a) to (d) ($t_a = t_b = 0.15\text{eV}$). Black curve: $n_\uparrow$; brown: $n_\downarrow$. Total LDOS: $n_\uparrow + n_\downarrow$. The two resonant peaks have energy $\epsilon_0 + n_\downarrow U$ and $\epsilon_0 + n_\uparrow U$, with $\epsilon_0 = -0.5\text{ eV}$ and $U = 1\text{eV}$ (see text)

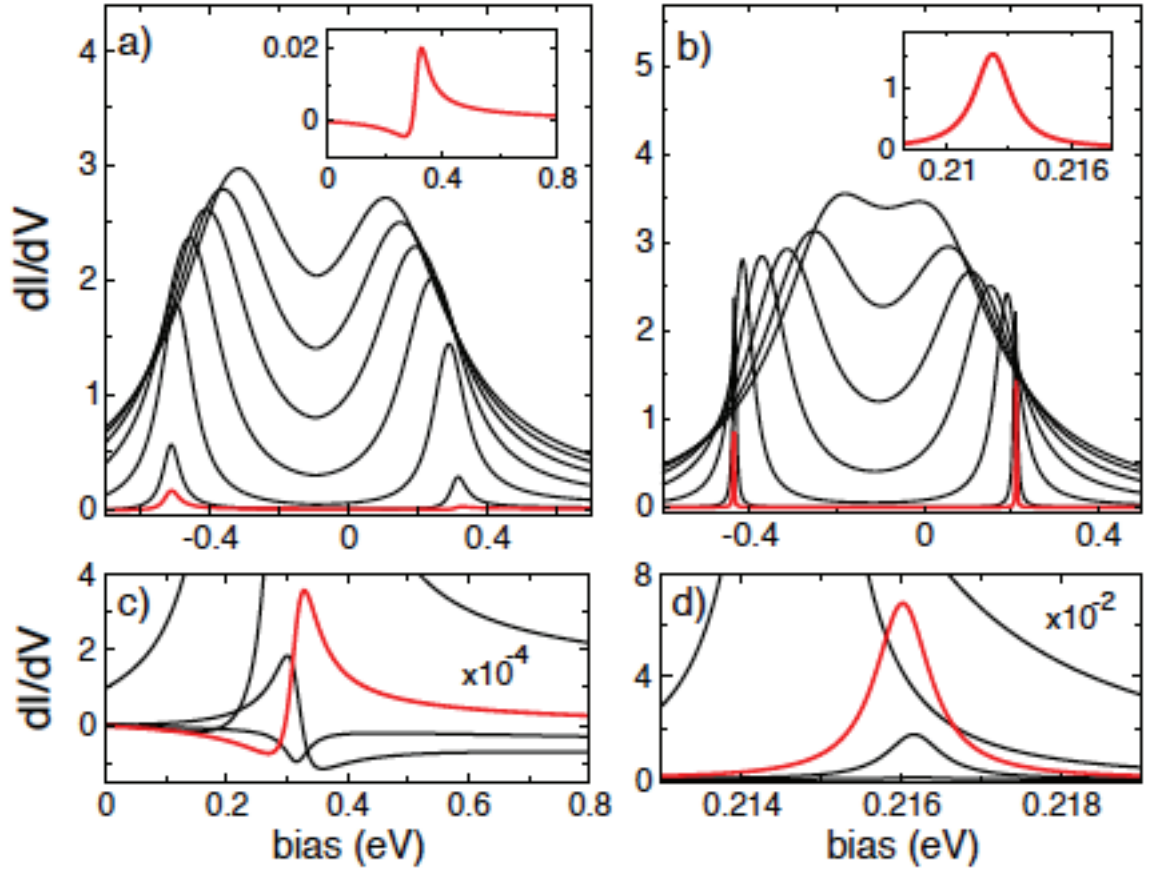


Figure 4.11: Differential conductance induced by the adatom versus bias, when the adatom sits (left) on top of carbon and (right) in the center of the hexagon. See details in the text. a), b) $t_a = t_b = 0.15\text{eV}$ and $t_f/t_a = 1.6, 1.5, 1.35, 1.1, 0.7, 0.25$ and 0.1 (inset), from top to bottom. c), d) $t_c = 0.02\text{eV}$ and $t_f/t_c = 0.7, 0.25, 0.1, 0.05$ and 0.01 . $t_f/t_c = 0.1$ for all curves in red.

Chapter 5

Conclusions

This dissertation has discussed three parts. First, we have studied the STM currents through locally disordered graphene. We have considered a tip with transverse modes. Although the tip is strictly quasi-one-dimensional it still departs from the widely used model of a strictly one-dimensional model. Generalizing now the calculations to a truly three-dimensional tip is reasonably straightforward. The modifications would require introducing a three dimensional square lattice for describing the bulk of the tip, and a decreasing number of atoms for each transverse plane to describe the part of the tip in contact with graphene. This last part of the tip would lead to the most significant change in the calculation, since the device would not be a single atom as in our calculations here, but would be represented by a finite number of them, and therefore the Green's function for the device would be a matrix instead of a c -number. Nevertheless, as long as we take the dispersion of the electrons in the tip to have large bandwidth, the current should not depend much on the local density of states of the tip, since this would be essentially constant. This corresponds to the usual wide band limit.

We have also seen that tunneling through either impurity atoms, or their neigh-

borating carbon atoms, depends on the local density of states of graphene. For certain circumstances – vacancy or weakly coupled impurities – there is a development of resonances at or close to the Dirac point. These resonances lead to a strong enhancement of the tunnelling probability which appear as steps in the tunneling current. It is conceivable that graphene could be locally modified in order to take advantage of these strong resonances developed close to the Dirac point. Clearly the substituting atoms would also locally distort the graphene lattice, an effect not included in our description. How much the STM current would depart from the values computed here would depend on the change in the values of the hopping parameter, and on additional features on the density of states due to the disorder. If future research will pursue the route of modifying graphene locally, our results will be important for the characterization of the surface. Even in the present state of affairs, our results could be used to interpret STM current due to local impurities.

And then, we discussed the impurity effect on the graphene in presence of magnetic field. We use linear approximation in our calculation. For the hopping disorder, we introduce four artificial positions for the impurity site and three nearest neighbor. So we can get the Green's function from T-matrix formula.

At last, we have described the theory of STM for adatoms with inner shell electrons adsorbed in graphene. Unlike the case of metallic hosts, in graphene the symmetry of the localized orbital has fingerprints in the LDOS nearby the adatom whenever the adatom, magnetic or not, hybridizes with two or more carbon atoms. The real and momentum space scanning maps can reveal the position of the adatom with respect to the sublattices and possibly indicate the orbital symmetry of the localized state. The STM tip can be also used to identify the magnetic state of the adatom by taking advantage of the low density of states of graphene, which makes the adatom

localized state more sensitive to tip effects than in conventional metallic hosts.

We have described in detail how sublattice quantum numbers in combination with orbital symmetry effects influence the Fano resonances in the differential conductance nearby the adatom. The formalism is generic for any orbital symmetry state, and can be used in principle to describe any adatom in graphene, provided the different orbitals of interest in the inner shell states are not strongly hybridized among themselves. Additional extensions to describe the multi-orbital case can be included, as well as other effects such as the spin orbit coupling.

Bibliography

- [1] P. W. Anderson. *Phys. Rev.*, 124(41), 1961.
- [2] A. V Balatsky, I Vekhter, and Jian-Xin Zhu. *Rev. Mod. Phys.*, 78(373), 2006.
- [3] C. W. J. Beenakker and C. Schöenberger. *Physics Reports*, 336(1), 2000.
- [4] Cristina Bena. *Phys. Rev. Lett.*, 100(076601), 2008.
- [5] Cristina Bena. *Phys. Rev. B*, 79(125427), 2009.
- [6] V. W. Brar, Regis Decker, H.-M. Solowan, Y. Wang, L. Maserati, K. T. Chan, H. Lee, Caglar O. Girit, A. Zettl, S. G.Louie, M. L. Cohen, and M. F. Crommie. *arXiv*, 1006:1014, 2010.
- [7] V. W. Brar, Y. Zhang, Y. Yayon, T. Ohta, J. L. McChesney, A. Bostwick, E. Rotenberg, K. Horn, and M. F. Crommie. *Appl. Phys. Lett*, 91(122102), 2007.
- [8] C. Caroli, R. Combescot, P. Nozieres, and D. Saint-James. *J. Phys. C:Solid St. Phys.*, 4(916), 1971.
- [9] V. V. Cheianov and V. I. Falko. *Phys. Rev. Lett.*, 97(226801), 2006.
- [10] J. Chen, C. Jang, S. Adam, M. Fuhrer, and E. Williams. *Nat. Phys*, 4(377), 2008.
- [11] A Deshpande, W Bao, F Miao, C. N. Lau, , and B. J Leroy. *Phys. Rev. B*, 79(205411), 2009.
- [12] A. Dhar and D. Sen. *Phys. Rev. B*, 73(085119), 2006.
- [13] B. Dora and P. Thalmeier. *Phys. Rev. B*, 76:115435, 2007.
- [14] D. M. Eigler and E. K. Schweizer. *Nature*, 344(524), 1990.
- [15] A. A. El-Barbary, R. H. Telling, C. P. Ewels, M. I. Heggie, and P. R. Briddon. *Phys.Rev.B*, 68(1):144107, 2003.
- [16] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov. *Science*, 323:610–613, 2009.
- [17] U. Fano. *Phys. Rev.*, 124:1866, 1961.
- [18] D. K. Ferry and S. M. Goodnick. *Transport in nanostructures*. 2001.

- [19] T. Fukuda, H. Oymak, and J. Hong. *Phys. Rev. B*, 75(195428), 2007.
- [20] V. Geringer, M. Liebmann, T. Echtermeyer, S. Runte, M. Schmidt, R. Rückamp, M. Lemme, and M. Morgenstern. *Phys. Rev. Lett.*, 102:076102, 2009.
- [21] V. Geringer, M. Liebmann, T. Echtermeyer, S. Runte, M. Schmidt, R. Rückamp, M. C. Lemme, and M. Morgenstern. *Phys. Rev. Lett.*, 102(076102), 2009.
- [22] K. K. Gomes, W. Ko, W. Mar, Y. Chen, Z.-X. Shen, and H.C. Manoharan. *arXiv*, 0909:0921, 2009.
- [23] V. Meunier Ph. Lambin H. Amara, S. Latil and J.-C. Charlier. *Phys. Rev. B*, 76(115423), 2007.
- [24] H. Haug and A.-P. Jauho. Quantum kinetics in transport and optics of semiconductors. 2008.
- [25] M. Hentschel and F. Guinea. *Phys. Rev. B*, 76:115407, 2007.
- [26] I.Brihuega, P Mallet, C Bena, S Bose, C Michaelis, L Vitali, F Varchon, L Magaud, K Kern, and J. Y Veuillen. *Phys. Rev. Lett.*, 101(206802), 2008.
- [27] I.Brihuega, P.Mallet, S.Bose, C.Michaelis, L.Vitali, F.Varchon, L.Magqud, K.Kern, and J.Y.Veuillen. *Phys. Rev. Lett.*, 101(206802), 2008.
- [28] M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams. *Nano Lett*, 7, 2007.
- [29] M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams. *Nano Lett*, 7(1643), 2007.
- [30] D. Jacob and G. Kotliar. *Phys. Rev. B*, 82:085423, 2010.
- [31] W. Bao Wei Han Y. F. Chiang Yan Li S.-W. Tsai C. N. Lau K. Pi, K. M. McCreary and R. K. Kawakami. *Phys. Rev. B*, 80:075406, 2009.
- [32] I. Paul K. Saha and K. Sengupta. *Phys. Rev. B*, 81:165446, 2010.
- [33] L. P. Kadanoff and G. Baym. Quantum statistical mechanics. 1962.
- [34] A. V. Krasheninnikov, P. O. Lehtinen, A. S. Foster, and P. Pyykkand R. M. Nieminen. *Phys. Rev. Lett.*, 102:126807, 2009.
- [35] O. Leenaerts, B. Partoens, and F. M. Peeters. *Phys. Rev. B*, 77:125416, 2008.
- [36] N. Levy, S. A. Burke, K. L. Meaker, M. Panlasigui, A. Zettl, F. Guinea, A. H. Castro Neto, and M. F. Crommie. *Science*, 329(544), 2010.
- [37] G. Li, A. Luican, and E. Y. Andrei. *Phys. Rev. Lett.*, 102(176804), 2009.
- [38] R. Bulla M. Vojta, L. Fritz. *Europhys. Lett*, 90:27006, 2010.
- [39] P. Mallet, F. Varchon, C. Naud, L. Magaud, C. Berger, and J.-Y. Veuillen. *Phys. Rev. B*, 76(041403(R)), 2007.
- [40] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth. *Nature*, 446(60), 2007.

- [41] V. Mujica, M. Kemp, and M. A. Ratner. *J. Chem. Phys.*, 101(6849), 1994.
- [42] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim. *Rev. Mod. Phys.*, 81(109), 2009.
- [43] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov. *Nature*, 438(197), 2005.
- [44] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. *Science*, 306(666), 2004.
- [45] K. S. Novoselov, D. Jiang, T. Booth, V.V. Khotkevich, S. M. Morozov, and A. K. Geim. *PNAS*, 102(10451), 2005.
- [46] L. S. Panchakarla, K. S. Subrahmanyam, A. Govindaraj S. K. Saha, H. R. Krishnamurthy, U. V. Waghmare, and C. N. R. Rao. Synthesis, structure and properties of boron and nitrogen doped graphene. *Advanced Materials*, 21:4726–4730, Dec 2009.
- [47] V. M. Pereira, F. Guinea, J. M. B. Lopes dos Santos, N. M. R. Peres, and A. H. Castro Neto. *Phys. Rev. Lett.*, 96(036801), 2006.
- [48] N. M. R. Peres, F. Guinea, and A. H. Castro Neto. *Phys. Rev. B*, 73(125411), 2006.
- [49] N. M. R. Peres, F. D. Klironomos, S.-W. Tsai, J. R. Santos, J. M. B. Lopes Dos Santos, and A. H. Castro Neto. *Europhys. Lett*, 80(67007), 2007.
- [50] N. M. R. Peres, T. Stauber, and J. M. B. Lopes dos Santos. *Phys. Rev. B*, 79(035107), 2009.
- [51] N. M. R. Peres, Shan-Wen Tsai, J. E. Santos, and R. M. Ribeiro. *Phys. Rev. B*, 79(035107), 2009.
- [52] M. Plihal and J. W. Gadzuk. *Phys. Rev. B*, 63:085404, 2001.
- [53] P. Roushan, J. Seo, C. V. Parker, Y. S. Hor, D.Hsieh, D. Qian, A. Richardella, M. Z. Hasan, R. J. Cava, and A. Yazdani. *Nature*, 460(2206), 2009.
- [54] G. M. Rutter, J. N. Crain, N. P. Guisinger, T. Li, P. N. First, and J. A. Stroscio. *Science*, 317(219), 2007.
- [55] K. Sengupta and G. Baskaran. *Phys. Rev. B*, 77(045417), 2008.
- [56] Yu. V. Yu. V. Skrypnyk and V. M. Loktev. *Phys. Rev. B*, 73(241402), 2006.
- [57] T. Stauber, N.M.R.Peres, and A.K.Geim. *Phys.Rev.B*, 78:085432, 2008.
- [58] E. Stolyarova, K. T. Rim, S. Ryu, J. Maultzsch, P. Kim, L. E. Brus, T. F. Heinz, M. S. Hybertsen, and G. W. Flynn. *Proc. Natl. Acad.Sci. USA*, 104(9209), 2007.
- [59] J. Tersoff and D. R. Hamann. *Phys. Rev. B*, 31:805, 1985.
- [60] T.Pereg-Barnea and A. H. MacDonald. *Phys. Rev. B*, 78(014201), 2008.
- [61] B. Uchoa, Valeri N. Kotov, N. M. R. Peres, and A. H. Castro Neto. *Phys. Rev. Lett.*, 101(026805), 2008.

- [62] B. Uchoa, T. G. Rappoport, and A. H. Castro Neto. *Phys. Rev. Lett.*, 106:016801, 2011.
- [63] B. Uchoa, L. Yang, S.-W. Tsai, N. M. R. Peres, and A. H. Castro Neto. *Phys. Rev. Lett.*, 103:206804, 2009.
- [64] T. O. Wehling, A. V. Balatsky, M. I. Katsnelson, A. I. Lichtenstein, and A. Rosch. *Phys. Rev. B*, 81:115427, 2010.
- [65] T. O. Wehling, H. P. Dahal, A. I. Lichtenstein, M. I. Katsnelson, H. C. Manoharan, and A. V. Balatsky. *Phys. Rev. B*, 81:085413, 2010.
- [66] D. Withoff and E. Fradkin. *Phys. Rev. Lett.*, 64:1835, 1990.
- [67] J. Xue, J. Sanchez-Yamagishi, D. Bulmash, P. Jacquod, A. Deshpande, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, and B.J.LeRoy. *arXiv*, (1102.2642v1), 2011.
- [68] G.-M. Zhang, H. Hu, and L. Yu. *Phys. Rev. Lett.*, 86:704, 2001.
- [69] Y. Zhang, V. W. Brar, F. Wang, C. Girit, Y. Yayon, M. Panlasigui, A. Zettl, and M. F. Crommie. *Nat. Phys*, 4(627), 2008.
- [70] Y. Zhang, Yan-Wen Tan, Horst L. Stormer, and Philip Kim. *Nature*, 438(201), 2005.
- [71] Yong-Hui Zhang, Ya-Bin Chen, Kai-Ge Zhou, Cai-Hong Liu, Jing Zeng, Hao-Li Zhang, and Yong Peng. *Nanotechnology*, 20(185504), 2009.
- [72] Yuanbo Zhang, Victor W. Brar, Caglar Girit, Alex Zettl, and Michael F. Crommie. *Nat. Phys*, 5:722–726, 2009.
- [73] H.-B. Zhuang, Q. f. Sun, and X. C. Xie. *Europhys. Lett*, 86:58004, 2009.

Appendix A

A.1 Exact Green's functions

At the mean field level, the Green's functions described in sec. IV can be written in an exact form by solving the equations of motion for the fermionic operators $a_{\mathbf{k},\sigma}$, $b_{\mathbf{k},\sigma}$, $c_{\mathbf{p},\sigma}$ and f_σ . After a cumbersome but straightforward algebra, the final expressions are,

$$G_{xy,\sigma}(\mathbf{p}, \mathbf{p}', i\omega) = \delta_{\mathbf{p},\mathbf{p}'} G_{xy}^0(p) + \Gamma_x(p, \mathbf{r}) \Lambda_x(p) G_{ff,\sigma}(i\omega) \bar{\Lambda}_y(p') \bar{\Gamma}_y(p', \mathbf{r}) + \sum_{\mathbf{k}\mathbf{k}'} T_{x,\mathbf{k}'}(\mathbf{r}, p) G_{cc}(\mathbf{k}, \mathbf{k}', i\omega) \bar{T}_{y,\mathbf{k}'}(\mathbf{r}, p'), \quad (\text{A.1})$$

$$G_{cx,\sigma}(\mathbf{p}, \mathbf{p}', i\omega) = \sum_{\mathbf{k}} G_{cc}(\mathbf{p}, \mathbf{k}', i\omega) [\bar{T}_{x,\mathbf{k}}(\mathbf{r}, p') + \bar{t}_{f,\mathbf{k}} \bar{\Gamma}_{x,\mathbf{p}'} G_{ff,\sigma}(i\omega) \bar{\Lambda}_x(p')] , \quad (\text{A.2})$$

and

$$G_{cf,\sigma}(\mathbf{p}', i\omega) = \sum_{\mathbf{p}} G_{cc}(\mathbf{p}, \mathbf{p}', i\omega) \bar{t}_{f,\mathbf{p}}(\mathbf{r}) G_{ff,\sigma}(i\omega) , \quad (\text{A.3})$$

where $p \equiv (\mathbf{p}, i\omega)$. The quantities $\Lambda_x(p)$ and $\bar{\Lambda}_x(p)$ have the same definitions as before [see Eq. (4.30) and (4.31)], whereas

$$T_{\mathbf{p}',x}(\mathbf{r}, p) \equiv \sum_{y=a,b} G_{xy}^0(p) t_{y,\mathbf{p},\mathbf{p}'}(\mathbf{r}) \quad (\text{A.4})$$

$$\bar{T}_{\mathbf{p}',x}(\mathbf{r}, p) \equiv \sum_{y=a,b} t_{y,\mathbf{p},\mathbf{p}'}^*(\mathbf{r}) G_{yx}^0(p). \quad (\text{A.5})$$

The Green's function of the electrons is defined as

$$G_{cc}(\mathbf{p}, \mathbf{p}', i\omega) = [(i\omega - \epsilon_{\mathbf{p}}) \delta_{\mathbf{p}\mathbf{p}'} - \Sigma_{cc,\mathbf{p}\mathbf{p}'}(z, i\omega)]^{-1}, \quad (\text{A.6})$$

where Σ_{cc} is the self-energy for the electrons in the tip due to hybridization effects with the electrons in graphene only,

$$\Sigma_{cc,\mathbf{p}\mathbf{p}'}(z, i\omega) = \sum_{\mathbf{k}} \sum_{x=a,b} t_{x,\mathbf{p}}(z) \bar{T}_{\mathbf{p}',x}(z, k). \quad (\text{A.7})$$

The Green's function of the f -electrons is given by

$$G_{ff,\sigma}(i\omega) = [i\omega - \epsilon_{\sigma} - \Sigma_{ff}(\mathbf{r}, i\omega)]^{-1}, \quad (\text{A.8})$$

where $\Sigma_{ff}(\mathbf{r}, i\omega) = \Sigma_{ff}(i\omega) + \Sigma_{ff}^{(t)}(\mathbf{r}, i\omega)$ is the corresponding self-energy, with

$$\Sigma_{ff}^{(t)}(\mathbf{r}, i\omega) = \sum_{\mathbf{k}\mathbf{k}'} t_{f,\mathbf{k}}(\mathbf{r}) G_{cc}(\mathbf{k}, \mathbf{k}', i\omega) \bar{t}_{f\mathbf{k}'}(\mathbf{r}) \quad (\text{A.9})$$

as the contribution of the tip. The other quantities include the renormalized hybridization of the tip with the adatom,

$$t_{f,\mathbf{p}}(\mathbf{r}, i\omega) = t_{f,\mathbf{p}}(r) + \sum_{\mathbf{k}} \sum_{y=a,b} \bar{\Lambda}_y(k) t_{y,\mathbf{k}\mathbf{p}} \quad (\text{A.10})$$

$$\bar{t}_{f,\mathbf{p}}(\mathbf{r}, i\omega) = t_{f,\mathbf{p}}(r) + \sum_{\mathbf{k}} \sum_{y=a,b} t_{y,\mathbf{k}\mathbf{p}}^* \Lambda_y(k), \quad (\text{A.11})$$

and

$$\begin{aligned} \Gamma_x(p) &= 1 + \sum_{\mathbf{k}\mathbf{k}'} \bar{t}_{f,\mathbf{k}}(\mathbf{r}, i\omega) G_{cc}(\mathbf{k}, \mathbf{k}', i\omega) \frac{T_{\mathbf{k}',x}(\mathbf{r}, p)}{\Lambda_x(p)} \\ \bar{\Gamma}_x(p) &= 1 + \sum_{\mathbf{k}\mathbf{k}'} \frac{\bar{T}_{\mathbf{k}',x}(\mathbf{r}, p)}{\bar{\Lambda}_x(p)} G_{cc}(\mathbf{k}, \mathbf{k}', i\omega) t_{f,\mathbf{k}}(\mathbf{r}, i\omega), \end{aligned}$$

which are vertex corrections that appear in Eq. (A.1) and (A.2).