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Ab-initio studies of adsorbate-surface interactions

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***Ab-initio* studies of adsorbate-surface interactions**

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Co-Advisor: Prof. Dr. Juarez L. F. Da Silva

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To my Mother, Maria Cecilia, Davi Ricardo and Linda

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ABSTRACT

RÊGO, C. R. C. **Ab-initio studies of adsorbate-surface interactions.** 2017. 141p. Thesis (Doctor in Science) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2017.

This thesis supplies a contribution to the understanding of the interaction between carbon-carbon surfaces, atoms with carbon-surfaces, and atoms with metallic surfaces. It is well established that the surface-surface and atom-surface interactions are interesting, important and challenging for reasons that vary from industrial interest up to the academic necessity of understanding it deeply.^{1,2} Currently, there are many measurements and simulations for the geometric and electronic properties of Graphite, these differ by more than 40%.³⁻⁷ This implies that our understanding of the nature of this material is quite poor. The interaction between small transition-metals clusters with a Graphene sheet is another example where our knowledge is very limited. There are many theoretical studies in the literature that describe the interaction between these clusters with a Graphene sheet, but they agree and disagree on many points,⁸⁻¹⁶ which calls for systematic study of this issue. In this thesis we will focus our efforts on studying the surface-surface and atom/clusters-surface interactions. This thesis is split into three projects. The first aims to contribute to the understanding of the interlayer interactions of the bulk Graphite. In the second, we intend to shed some light on comprehending the interaction of an adatom with a Graphene sheet. Both of these projects, are studied within DFT framework with the inclusion of the van der Waals (vdW) corrections. In the Graphite project, we found that the electronic and geometric properties depend on the vdW correction employed in the calculation. In the adatom supported on Graphene project, we combined a modified Anderson-Newns model to describe the coupling between the adatom with Graphene. In addition, we found the existence of competition between quantum and classical forces, which determine the type of site in which the adatom prefers to adsorb. The last project is a dynamical study of an atom that impinges upon a metallic surface. In this project, we focus on the calculation of the sticking coefficient, a measure of the amount of nuclear density attached to the metal surface after collision. At this time the project is not one 100% ready, but our preliminary results indicates that, a small part of the nuclear density stays stuck on the metal.

Keywords: Density Functional Theory. Graphite. van der Waals corrections. Graphene. Sticking coefficient.

RESUMO

RÊGO, C. R. C. **Estudos *Ab-initio* das Interações de Superfícies adsorvidas.** 2017. 141p. Tese (Doutorado em Ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2017.

Esta tese ajuda a entender as interações entre duas superfícies de carbono. A natureza da interação de átomos ou aglomerados atômicos adsorvidos sobre uma superfície de carbono. Além disso, visa esclarecer a dinâmica de um átomo sendo adsorvido sobre uma superfície metálica. As interações superfície-superfície e átomos-superfícies são importantes por razões que variam desde o interesse industrial até a necessidade acadêmica para compreendê-la profundamente.^{1,2} Entendê-las ainda é um desafio. Diversos trabalhos apresentam medidas experimentais e simulações para as propriedades geométricas e eletrônicas do grafite. Tais medidas diferem em mais de 40% umas da outra.³⁻⁷ Isso mostra que nossa compreensão sobre a natureza desse material ainda é bastante pobre. A interação entre pequenos grupos de metais de transição com uma folha de grafeno é outro exemplo em que nosso conhecimento é limitado. Existem muitos estudos teóricos na literatura que descrevem a interação desse tipo de aglomerado com uma folha de grafeno, porém há numerosas discordâncias.⁸⁻¹⁶ Tais controvérsias parecem suplicar por um estudo sistemático. Nesta tese focamos nossos estudos nas interações superfície-superfície e de átomos ou aglomerados atômicos com superfícies de carbono e de um metal. A tese foi dividida em três projetos. O primeiro visa compreender melhor a interação entre as camadas do grafite. No segundo, pretendemos lançar alguma luz no entendimento da interação de átomos e aglomerados atômicos com uma folha de grafeno. Esses dois projetos, são estudados à luz da Teoria do Funcional da Densidade com a inclusão das correções van der Waals (vdW). No Projecto sobre o grafite, mostramos que as propriedades eletrônicas e geométricas dependem do tipo de correção de vdW empregada no cálculo. No projeto sobre átomos e aglomerados atômicos adsorvidos no grafeno, combinamos um modelo modificado de Anderson-Newns para descrever o acoplamento entre um átomo adsorvido e o grafeno. Além disso, encontramos uma competição entre forças quânticas e clássicas, a qual determina o tipo de sítio no qual o átomo prefere ser adsorvido. O último projeto é um estudo dinâmico de um átomo colidindo contra uma superfície metálica. Nesse projeto o foco é posto no cálculo do coeficiente de aderência, o qual mede a taxa de densidade nuclear presa na superfície metálica após a colisão. Resultados preliminares indicam que, uma pequena parte da densidade nuclear permanece aderida ao metal depois da colisão.

Palavras-chave: Teoria do funcional da densidade. Grafite. Correções de van der Waals. Grafeno. Coeficiente de aderência.

LIST OF FIGURES

Figure 1	– Potential energy curve representing the electronic ground state S_0 and the first excited state S_1 of a diatomic molecule. The horizontal red and blue lines are the vibrational levels of the molecule associated to the S_0 and S_1 states, respectively. The black lines represent the rotational levels for the molecule in relation to the ground state S_0 .	
	Source: By the author	29
Figure 2	– Energy level avoided crossing structure of a two-level system for the eigenstates $ \epsilon_+\rangle$ (blue) and $ \epsilon_-\rangle$ (red). One should note, that the gap size of the avoided crossing is proportional to the factor ω . The full blue and red lines without symbols represent the original states, and they touch each other at the degenerate point $z = 0$.	
	Source: By the author	34
Figure 3	– Many body electronic systems concept in which the wavefunction has $3N$ variables, thought of in terms of the electron density with 3 variables.	
	Source: By the author	35
Figure 4	– One-to-one correspondence between external potentials $v_i(\vec{r}) = v_i$, ground state wave functions $\psi[v_i] = \psi_i$, and ground state densities $\rho[v_i] = \rho_i$.	
	Source: By the author	36
Figure 5	– Left side: interacting system with density ρ . Right side: Kohn-Sham system generating the same density ρ that is generated by the interacting system.	
	Source: By the author	38
Figure 6	– Schematic self consistent procedure to solve the Khon Sham equations.	
	Source: By the author	40
Figure 7	– One dimensional model for the harmonic oscillator representing H_2 molecule.	
	Source: By the author	45
Figure 8	– Schematic representation for the augmentation (orange), and interstitial (green) regions with the existence conditions for $ \tilde{\varphi}_i^b\rangle$, $ \varphi_i^b\rangle$, and $ \tilde{p}_j^b\rangle$. The interstitial region is expanded in terms of plane waves.	
	Source: By the author	51
Figure 9	– Crystalline structure of Bernal graphite with ABA stacking. The primitive unit cell is hexagonal with dimensions $a = 2.46 \text{ \AA}$ and $a = 6.71 \text{ \AA}$.	
	Source: By the author	57

Figure 10 – Convergence test for the cutoff energy and total number of k -points in the Brillouin zone. The filled circles represent the relative deviations from the experimental values for the planar and interlayer lattice parameters a and c , respectively. The solid lines are guides to the eye. (a) Relative deviations as functions of the cutoff energy. Each plot corresponds to the indicated combination of the PBE exchange-correlation functional with a van der Waals correction and with the following k mesh: $21 \times 21 \times 5$ (PBE only), $21 \times 21 \times 7$ (PBE+TS), and $21 \times 21 \times 7$ (PBE+TS+SCS). (b) Relative deviations as functions of the number of k points at fixed cutoff energy (900 eV), for the indicated combinations of the PBE functional with van der Waals corrections.

Source: By the author 58

Figure 11 – Total energy per unit cell (four atoms) as a function of volume, for graphite. The blue open circles, red open squares, black open diamonds, magenta open triangles, green solid stars, and yellow solid hexagons represent the PBE, PBE+TS, PBE+TS+SCS, D2, D3 and D3-BJ calculations, respectively. Near each minimum, a solid line fits Eq. (3.2) to the computed energies. The expanded vertical scale in the inset brings out the shallow minimum of the PBE curve.

Source: By the author 60

Figure 12 – Graphite interlayer binding energy as a function of the interlayer lattice parameter c . Shown are the $E_b(c)$'s calculated with PBE+D2 (magenta open triangles), PBE+D3 (green solid stars), PBE+D3-BJ (yellow solid hexagons), PBE+TS (red open squares), and PBE+TS+SCS (black open diamonds), and the experimental binding energies (cyan filled circle). The solid lines represent the Chebyshev interpolation described in Appendix A. The inset compares the PBE+TS+SCS (black open diamonds) and RPA (open blue circles) binding energies to the experimental data (cyan open circle).

Source: By the author 61

Figure 13 – The band structures of graphene ($a_0 = 2.46 \text{ \AA}$), calculated with the standard PBE functional, and bulk graphite ($a_0 = 2.46 \text{ \AA}$, $c = 20.1 \text{ \AA}$), calculated with the TS+SCS scheme. The symmetries of the most important bands (σ_s , σ_{xy} , π_z) are indicated.

Source: By the author 64

Figure 14 – Layer-separation dependence of the π_z -level splitting. The symbols are the results of the indicated computational methods at the equilibrium separations. The solid curve represents the PBE splitting as a function of c . The cyan filled circle and square show the experimental splittings at the experimental equilibrium separation.	
Source: By the author	65
Figure 15 – Lattice structure of graphene. (Right) The basis vectors that form the unit cell in the real space are $\vec{a}_1$ and $\vec{a}_2$. (Left) The Brillouin zone defined by the reciprocal vectors b_1 and $\vec{b}_2$.	
Source: By the author	69
Figure 16 – Valence (positive term of Eq. (4.2)) and conduction (negative term of Eq. (4.2)) band of Graphene. The margenta lines are outlining the cone Dirac.	
Source: By the author	70
Figure 17 – Molecular dynamics simulations to generate the putative global minimum configurations for Pt ₆ . In this optimization procedure, the temperature is varying from 2000 K to 0 K, and all the carbon atoms positions are kept frozen.	
Source: By the author	71
Figure 18 – Top view of the graphene (6×6) supercell, where the high-symmetry adsorption sites are indicated, namely, the one-fold top (T), two-fold bridge (B), and six-fold hollow (H) sites.	
Source: By the author	72
Figure 19 – Convergence test for the Graphene planar lattice parameter. The filled circles represent the points from DFT using PBE, PBE+TS, and PBE+TS+SCS. The solid lines are square polynomial interpolations.	
Source: By the author	73
Figure 20 – Putative global minimum configurations for the neutral TM _n clusters (TM = Ni, Pd, and Pt; $n = 2 - 6$) in the gas phase, obtained with the PBE functional.	
Source: By the author	74
Figure 21 – Lowest-energy DFT-PBE configurations for neutral transition-metal clusters (TM _n ; TM = Ni, Pd, and Pt; $n = 1 - 6$) on graphene, computed with a (6×6) supercell.	
Source: By the author	75

Figure 22 – Adsorption energies computed from Eq. (4.5) for all the lowest-energy configurations for neutral transition-metal clusters (TM_n ; $\text{TM} = \text{Ni}, \text{Pd}$, and Pt ; $n = 1 - 6$) on graphene. DFT (balls) and DFT+vdW corrections (triangles).	
Source: By the author	78
Figure 23 – Binding energies computed from Eq. (4.6) for all the lowest-energy configurations for neutral transition-metal clusters (TM_n ; $\text{TM} = \text{Ni}, \text{Pd}$, and Pt ; $n = 1 - 6$) on graphene. DFT (balls) and DFT+vdW corrections (triangles).	
Source: By the author	79
Figure 24 – Densities of states for a single TM atom adsorbed on graphene. The top panel depicts Gr, while the second, third, and fourth refer to Ni_1/Gr , Pd_1/Gr , and Pt_1/Gr , respectively. The vertical dashed yellow line marks the Fermi level, from which energies are measured.	
Source: By the author	82
Figure 25 – Fits of the LDOS in Figure 24 with the spectral density for the Anderson-Newns model described in the text. The open circles describe the adatom LDOS for the indicated systems, and the solid lines represent Eq. (4.15) with the parameters in Table 5. The insets show that, in contrast with numerical data, the right-hand side of Eq. (4.15) vanishes at zero energy. The vertical dashed line marks the Fermi level, from which energies are measured.	
Source: By the author	84
Figure 26 – Incidence of hydrogen atom upon a metallic surface. Left side: chemically unbound. Right side: chemically bound.	
Source: By the author	90
Figure 27 – Electronic energy states for H^- . The black line is the Ground state, red, blue and magenta are 1st, 2nd, and 3th excited states, respectively. The insertion shows that the electronic states are very close to each other. These states were constructed using a binary notation as presented in Figure 28.	
Source: By the author	98
Figure 28 – Here we are using binary notation: a one 1 for occupied and a zero 0 for unoccupied. The blue lines (levels) with black circles (electrons) are occupied, while the empties are unoccupied. In this example, the binary number 0011 number represent the GS, while 0101 is the 1st excited state.	
Source: By the author	98

Figure 29 – Projection, $(_{z+\Delta z}\langle \ell \ell' \rangle_z - 0.999)$, for the Ground state, $\ell = \ell'$, of the Hamiltonian, Eq. (5.34), at positions z and $z + \Delta z$ with different values for N . Here, the energetic scale is around $\Lambda^{-(N/2)(\Delta\delta(z)/\pi)^2}$, where $\tan(\delta(z)) = -\pi W(z)/D$ is the lag of the conduction band related to $W(z)$.	
Source: By the author	101
Figure 30 – Flowchart connecting the NRG with the Exact Factorization approach. The states $\Phi_z(\ell', 0)$ are obtained via NRG, while $\chi(z, 0)$ is a Gaussian wave packet.	
Source: By the author	105
Figure 31 – Sticking coefficient (black squares) $\int_0^{z_0} \chi(z, t) ^2 dz$ computed at different moments. The insertion on the RHS shows the exact nuclear density (full red lines) started at $z_0 = 20(a_0)$ (blue dashed lines) plotted at the three different times indicated in the panels. The insertion with blue circles shows the sticking coefficient for all the times. The yellow bar in the end of this panel indicates that after 1300(fs) the sticking coefficient does not change further.	
Source: By the author	106
Figure 32 – The lowest and higher energy isomers for Ni_n $n = 1 - 6$. The numbers below correspond to the relative total energy (eV) of the clusters.	
Source: By the author	125
Figure 33 – The lowest and higher energy isomers for Pd_n $n = 1 - 6$. The numbers below correspond to the relative total energy (eV) of the clusters.	
Source: By the author	126
Figure 34 – The lowest and higher energy isomers for Pt_n $n = 1 - 6$. The numbers below correspond to the relative total energy (eV) of the clusters.	
Source: By the author	127
Figure 35 – The lowest and higher energy isomers for Ni_n/Gr $n = 1 - 6$. The numbers below correspond to the relative total energy of the clusters.	
Source: By the author	128
Figure 36 – The lowest and higher energy isomers for Pd_n/Gr $n = 1 - 6$. The numbers below correspond to the relative total energy of the clusters.	
Source: By the author	129
Figure 37 – The lowest and higher energy isomers for Pt_n/Gr $n = 1 - 6$. The numbers below correspond to the relative total energy of the clusters.	
Source: By the author	130
Figure 38 – The local density of states for TM_1/Gr	
Source: By the author	131

Figure 39 – The local density of states for TM_2/Gr	
Source: By the author	132
Figure 40 – The local density of states for TM_3/Gr	
Source: By the author	133
Figure 41 – The local density of states for TM_4/Gr	
Source: By the author	134
Figure 42 – The local density of states for TM_5/Gr	
Source: By the author	135
Figure 43 – The local density of states for TM_6/Gr	
Source: By the author	136
Figure 44 – Adatom (filled circle) interacting with all degrees of freedom of a continuous conduction band with constant density of states ρ .	
Source: By the author	138
Figure 45 – Discretization of the conduction band using a logarithmic mesh with resolution $\Lambda > 1$. Here, the impurity couples to the many degrees of freedom of all energy scales.	
Source: By the author	139
Figure 46 – The conduction band is approximated by a single state per interval. These states are represented by red points.	
Source: By the author	139
Figure 47 – Wilson chain, where the impurity coupled via hybridization V to the first site. Hopping term falling off exponentially with $\Lambda^{-n/2}$.	
Source: By the author	140

LIST OF TABLES

Table 1 – Bulk properties of graphite: equilibrium lattice parameters a_0 and c_0 , bulk modulus B_0 , bulk modulus and its first derivative B' , curvature C_{333} and curvature derivative C_{333} of the interlayer binding energy, cohesive energy E_{coh} , and the interlayer binding energy E_b computed with distinct dispersion corrections. For comparison, the last row lists the average experimental results and the only available theoretical estimate for C_{333} .	59
Table 2 – Per-atom binding energy $-E_b$, average effective coordination number ECN, relative to the number of nearest-neighbors, average bond length d_{av} , and total magnetic moment m_T of the neutral Ni_n , Pd_n , and Pt_n clusters in the putative global-minimum configurations for gas-phase clusters.	73
Table 3 – Structural, energetic, and magnetic properties of transition-metal clusters (TM_n ; $\text{TM} = \text{Ni}, \text{Pd}, \text{and Pt}$; $n = 1 - 6$) on graphene, calculated with the PBE and PBE+TS-SCS functionals. Listed are the most stable adsorption sites, the number N_b of TM atoms bound to the graphene sheet, the adsorption energy $-E_{ad}$ per TM atom, the cohesive energy $-E_{coh}$, the minimum distance d_{min} between the TM_n cluster and the graphene sheet, the changes ΔECN in the average effective coordination number and in the average bond lengths Δd_{av} due to the adsorption on the graphene layer, and total magnetic moment.	76
Table 4 – Effective Bader charges in the TM_n/Gr systems, in units of the electronic charge e , calculated from $\Delta Q^{\text{TM}-\text{C}} = Z_{val} - Q^{\text{Bader}}$. Here ΔQ^{TM_b} and $\Delta Q^{\text{TM}_{unb}}$ are the effective charges on the TM atoms bound to and unbound from C atoms, respectively. ΔQ^{C_b} and $\Delta Q^{C_{unb}}$ are the total effective charges in C atoms bound to and unbound from TM atoms, respectively.	80
Table 5 – Adjustable parameters on the right-hand side of Eq. (4.15) . E_d^j and α_1 define the frequency and width of each resonance, while β_j defines the strength of the resonance.	86

LIST OF ABBREVIATIONS AND ACRONYMS

vdW	van der Waals
PBE	Perdew-Burke-Erzerhof
DFT	Density Functional Theory
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
RPA	Random Phase Approximation
QMC	Quantum Monte Carlo
TS	Tkatchenko-Scheffler
TS+SCS	Tkatchenko-Scheffler Self Consistent Screening
VASP	Vienna <i>Ab-initio</i> Simulation Package
D2	Method of Grimme
D3	D2 zero damping
D3-BJ	D3 Becke-Jonson Damping
Gr	Graphene
TM	Transition Metal
BO	Born and Oppenheimer
KS	Khon Sham
GEA	Gradient Expansion Approximation
PW	Plane Waves
PAW	Projected Augmented Wave
BZ	Brillouin Zone
PES	Potential Energy Surface
TISE	Time independent Schrödinger Equation
TDSE	Time Dependent Schrödinger Equation

TDPES	Time Dependent PES
NRG	Numerical Renormalization Group
RHS	Right-Hand Side
LHS	Left-Hand Side
PNC	Partial Normalization Condition

CONTENTS

1	INTRODUCTION	23
2	METHODOLOGY	27
2.1	Many Body Problem	27
2.2	Born-Oppenheimer approximation	28
2.3	Density functional theory	33
2.3.1	The Hohenberg-Kohn Theorems	34
2.3.2	Kohn Sham Equations	37
2.4	Exchange and Correlation Functionals	41
2.4.1	LDA and GGA	42
2.5	van der Waals corrections	45
2.6	Projector Augmented Wave (PAW)	49
2.6.1	PAW Method	49
2.7	Plane Waves (PW)	51
2.8	Bader Analysis of Charge Density	52
2.9	Vienna ab initio simulation package (VASP)	53
3	GRAPHITE	55
3.1	Computational details and Convergence tests	56
3.2	Equilibrium lattice parameters	57
3.3	Cohesive energy	58
3.4	Interlayer binding energy	60
3.5	Bulk modulus and its first derivative	61
3.6	Curvature of the interlayer binding energy	62
3.7	Band structure analysis	63
3.8	Graphite: Conclusions	66
4	GRAPHENE	67
4.1	Graphene Properties	68
4.2	Computational Details	69
4.3	Effective coordination number and average bond length	71
4.4	Graphene and Gas-Phase Clusters	72
4.5	Graphene	72
4.6	Gas-Phase Clusters	72
4.7	TM _n Clusters Supported on Graphene	75
4.8	Lowest Energy TM _n /Gr Configurations	77

4.9	Adsorption and Binding Energies	77
4.10	Effect of van der Waals Corrections	80
4.11	Bader Charge	80
4.12	Density of states	81
4.13	TM adatoms on Graphene	81
4.14	Conclusion: Graphene	87
5	STICKING COEFFICIENT	89
5.1	Exact Factorization	90
5.2	Connection between NRG and Exact Factorization	96
5.3	Computational Details	97
5.3.1	Computing $\hat{U}_{en}^{coup}$ matrix element	101
5.3.2	Crank-Nicolson method	103
5.4	Preliminary results	104
5.5	Conclusion: Sticking coefficient	105
6	CONCLUSION AND OUTLOOKS	107
6.1	Conclusion	107
6.2	Outlook	107
	BIBLIOGRAPHY	109
	APPENDIX	121
	APPENDIX A – NUMERICAL COMPUTATION OF THE ELAS- TIC CONSTANTS C_{33} AND C_{333}	123
	APPENDIX B – HIGHER-ENERGY STRUCTURES	125
	APPENDIX C – DENSITY OF STATES	131
	APPENDIX D – NUMERICAL RENORMALIZATION GROUP	137

1 INTRODUCTION

The computational quantum mechanics simulation has a very important role in the understanding of many geometric and electronic properties of atoms, molecules, and solids. The Time-Independent Schrödinger Equation (TISE) is one of the most fundamental equations of quantum mechanics. There are many cases for which the TISE can be solved analytically, e.g., harmonic oscillator, hydrogen-like atoms and some others simple systems. However for more complex multi-electron systems, calculating the exact solution is not feasible even using numerical methods. In such cases, we have to resort to others formalisms or approaches, e.g., Molecular Dynamics, Numerical Renormalization Group, Quantum Phase Approximation, Quantum Monte Carlos methods, Hartree Fock methods or Density Functional Theory, to name a few. In this thesis, many of these methods or combinations of them will be used to tackle the problems that we wish to solve. This thesis is divided into three projects. The first one aims to improve our understanding about the interlayer interactions of the bulk graphite. In the second, we wish to improve our comprehension of the interaction of an adatom with a graphene one sheet. The last project is a dynamical study of an atom that impinges upon a metallic surface. In this part, we intend to measure the amount of the nuclear charge that gets stuck on a metallic surface after a negatively charged Hydrogen atom collides with it.

Since graphene's advent in 2004,¹⁷ the determination of interactions of adatoms with surfaces has attracted much attention in recent years due to catalytic processes involved. For example, the combination of the density functional theory (DFT) framework^{18,19} with current computational power, allow us to calculate accurately many of the ground-state geometric and electronic properties of an adatom interacting with a surface.^{20,21}

The technological importance of carbon materials such as graphite, fullerenes, nanotubes, and graphene has steadily grown in last decades^{22,23} due to their wide range of applications, which includes solid lubricant, energy storage, adsorbents, batteries, microelectronics, biomedicine, etc.^{17,24-26} The resulting research on supported graphene layers on metals and semiconductor surfaces has revived interest in the weak interaction between carbon monolayers and solid surfaces, as well as in the weak interactions within carbon compounds.^{25,27,28} Among carbon materials, graphite is special due to the presence of covalent (in plane) and weak van der Waals (vdW) interactions between the graphene layers with honeycomb symmetry and has hence been widely employed as a testbed for theoretical developments.

Both theoretically and experimentally, our understanding of the nature and strength of the graphitic interlayer binding is limited. Not even the spatial dependence of the interlayer interaction has been firmly determined, an uncertainty that raises doubts

concerning the vdW interactions in graphitic systems.^{29,30} There are many measurements and simulations for geometric and electronic properties that have yielded results that differ by more than 40%.³⁻⁷ Many of these properties depends on the curvature of the interlayer binding energy curve. Thus, to improve our understanding of the bulk properties of graphite, we are going to investigate the shape of the curvature of the interlayer binding energy in the DFT scope, taking into account the vdW corrections.

Graphene presents properties which go beyond those of graphite. Even graphite being used to reinforce steel, it can not be employed as a structural material due to the interlayer interaction. (Rewrite previous sentence meaning unclear) Graphene is stronger than diamond and steel. It also has a much higher electrical conductivity than graphite.^{23,25} The number of unusual features in its physical properties, transport coefficients and absorption spectrum (Gr)^{31,32} makes the two-dimensional material graphene unique among solids. The adsorption properties of the material being likewise extraordinary, transition-metal (TM) clusters on Gr support emerge as promising candidates for a wide range of applications, from catalysis to spintronics. For example, in many reactions the catalytic activity of TM atoms and nanoparticles adsorbed on Gr is much higher than that of standard catalysts, such as methanol oxidation,³³ or hydrogenation of 1,3-Butadiene.³⁴ Vacancies in Gr sheets supporting adsorbed TM clusters enhance their stability and chemical activity⁹ and increase their hydrogen-storage capacity.^{35,36} Yet another example is the large magnetic anisotropy of certain TM's, such as Co, adsorbed on Gr.³⁷

Even though, many theoretical studies have been conducted to describe the geometrical and electronic properties of (TM) clusters on Gr support, they agree and disagree on many points.⁸⁻¹⁶ To our knowledge, the dependence of structural and adsorption properties on cluster size has never been systematically studied from a theoretical perspective. These limitations, complexity, and controversies call for systematic study of TM_n clusters on Gr sheet, to identify trends and classify the interactions between TM clusters and Gr. In this thesis, we present a DFT investigation of the structural, adsorption, and magnetic properties of the TM_n (TM = Ni, Pd, Pt; $n = 1 - 6$) clusters on a Gr monolayer.

The dynamical processes defines one of the busiest frontiers in theoretical Condensed-Matter Physics. The number of atomic-scale problems of interest is very large. Examples are; electron exchange and transport in nanosystems, the interaction of short laser pulses with atoms, the scattering of electrons from atoms and small molecules, and the exchange of electrons during collisions with metallic surfaces.³⁸ Despite the number of publications dedicated to such collisions, the physics of charge transfer between ions and surfaces still defies theoretical treatment.³⁹ Most common among the various approaches is the numerical solution of the Time-Dependent Schrödinger Equation (TDSE) in the Born-Oppenheimer approximation. Likewise that TISE, accurate solutions of the TDSE are rare and available only for very simple cases.⁴⁰

A time-dependent study of an atom interacting with a surface seems to be a natural continuation of the TM clusters on Gr problem. However, this problem has to overcome two conceptual physical challenges. The first is to give a suitable treatment for the atom and metal interaction, i.e., take account of the large number of low-energy electron-hole excitations, which are generated by the atom when it approaches the metallic surface. To get around this point we turn to the Numerical Renormalization Group (NRG).^{41,42} The second challenge is to accurately describe the coupling between nuclear and electronic movement. In many cases the Born-Oppenheimer approximation is used to solve this challenge, under the assumption that the electronic motion is characterized by time scales much shorter than those of nuclear motion. In the problem at hand, however, the time scales associated with the particle-hole excitations are large and comparable to the time scale for the nuclear displacement. Therefore a more recently proposed approach, exact factorization, emerges as an attractive alternative.^{43,44} Here, the system wavefunction is exactly factored into a function of the nuclear coordinates and another function dependent on the electronic coordinates.

In the part of the thesis dedicated to this problem, we propose to explore the dynamics of a negative ionized Hydrogen atom impinging on a solid surface within the new avenue of the Exact Factorization approach. Investigating this problem is important because, even though we know that the Hydrogen atom colliding against a metallic surface has a huge technological applications and importance for many fields of science^{45–47}, we still do not have a deep knowledge of how this phenomenon happens.⁴⁸ This investigation is also instructive, as yet, no practical application of the newly developed formalism has been presented, although the method of exact factorization has been used to compute the time-dependence potential energy surfaces for problems that can be solved, either analytically or numerically, by alternative procedures.

The whole thesis contains six chapters. Chapter 2 describes the DFT methodology as well as the tools involved in the analysis of the data. In Chapter 3 we present the results and discussion of the graphite bulk properties obtained via DFT calculations. Chapter 4 is dedicated to the results and discussion of the adatom supported on Gr project. Chapter 5 is devoted to explain, how the sticking coefficient is computed through the combination of NRG and Exact Factorization approaches. Finally in, Chapter 6, we present our conclusions and possible further work from this thesis.

2 METHODOLOGY

Since ancient Greece, scientists have employed much effort into the characterization of physical and chemical properties of matter. In this age the term *átomo* arose, this means indivisible, since then matter has been understood as a set of atoms. The Greek atom concept evolved from systematic Mendeleyev's studies in the XVII century, empirically sorting the elements of the periodic table by atomic masses.⁴⁹ Nowadays, it is well known that atoms are composed of protons, neutrons and electrons. Protons and neutrons are located at the center of the atom and they have approximately the same mass. They are heavier than electrons and the ratio between the electronic and protonic masses is $1/1836$. The electrons make up a cloud orbiting the nucleus with a radius in the order of 10^4 times larger than the nuclei. Such concepts are analogous with the gravitational and electrostatic forces and this model was introduced by Rutherford.

In 1913, there were many experimental results⁵⁰ incompatible with the idea of an orbiting electron, according to electromagnetism electrons should emit light and naturally slow down towards to the nuclei. Evidently, this would make matter unstable. In that time, such problems led scientists to consider the possibility that the laws of classical physics break down at the atomic scale. Today, this difficulty is termed as Quantum Mechanics. The first approximation to Quantum Mechanics was proposed by Bohr.⁵⁰ In the Rutherford-Bohr theory that electrons are moving along circular trajectories with quantized angular momentum. The model successfully described the energy levels of the hydrogen atom and the Balmer series. These new ideas, about the unknown nature of atomic scale, started a scientific race to advance the field of quantum mechanics. In a few decades, the core mathematical tools to deal with this new science were developed.

The Schrödinger equation published in 1926 was soon applied to small molecules and atoms. It is well known that the numerical solution of the Schrödinger equation when it is applied to solids, molecules, or atoms with more than ten electrons is unfeasible, even when electronic and nuclear movement is decoupled. To solve this problem, we can use many techniques, such as Quantum Monte Carlo, Hartree-Fock, Tight binding, Density Functional Theory (DFT) and others. Among all these methods DFT presents a good compromise between accuracy and computational cost for determining the electronic and geometric properties of atoms, molecules and solids. The description of DFT as well as the explanation of its mathematical apparatus are the aims in this chapter.

2.1 Many Body Problem

A certain quantity of matter can be thought of as a collection of atoms interacting mutually. In the absence of electric or magnetic fields, the electron-electron, electron-

nucleus and nucleus-nucleus interactions are described by the following non relativistic Hamiltonian.

$$\begin{aligned} \hat{H} = & - \sum_{I=1}^P \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 + \frac{e^2}{8\pi\epsilon_0} \sum_{I=1}^P \sum_{J \neq I}^P \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \\ & + \frac{e^2}{8\pi\epsilon_0} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} - \frac{e^2}{4\pi\epsilon_0} \sum_{I=1}^P \sum_{i=1}^N \frac{Z_I}{|\vec{R}_I - \vec{r}_i|}, \end{aligned} \quad (2.1)$$

Here the sets $\vec{R} = \{\vec{R}_I\}$, $I = 1, \dots, P$ and $\vec{r} = \{\vec{r}_i\}$, $i = 1, \dots, N$ denote the collective nuclear and electronic coordinates. M_I and m are nuclear and electronic masses, while $Z_I e$ and e are their charges, respectively. The two first terms in Eq. (2.1) describe the kinetic energy operators for nuclei $\hat{K}_n$ and electrons $\hat{K}_e$. The remaining ones describe the Coulomb interactions, nuclear repulsion, $\hat{V}_{nn}$, electronic repulsion, $\hat{V}_{ee}$, and electron-nuclear attraction, $\hat{V}_{en} = \hat{V}_{ext} = \sum_{i=1}^N v_{ext}$, respectively.

As mentioned above, in the atomic regime the Schrödinger equation is a tool used for the analysis of matter properties. However, for the system described by Eq. (2.1) the exact analytical solution without approximation is feasible only for hydrogenoid atoms or for a simple molecule, e.g., H_2^+ . In order to get around this problem, we are going to present in the next section the Born-Oppenheimer (BO) approximation,⁵¹ which is probably the most basic approximation used to decouple the nuclear and electronic movement from the Schrödinger equation. This method was developed by Max Born and Julius Robert Oppenheimer.

2.2 Born-Oppenheimer approximation

The BO approximation is widely used in condensed matter physics to decouple the nuclear and electronic movements, which in turn simplifies the calculation of the full wavefunction reducing from $6N$ to $3N$ variables. It is well known from experimental observation that the time scale of nuclear movement is smaller than that associated with electrons and this is evident when we compare the electron and proton masses, $1/1836$. Some condensed matter physics books explain this mass difference as the physical explanation validating the BO approximation⁵¹ and unfortunately this misconception has been propagated throughout the years. In spite of this the BO approximation is a very useful tool in the electronic structure field.

In this section, we are going to give the right explanation for the Born-Oppenheimer approximation as well as explain from where this misunderstanding comes from.

Before we present the BO approximation, we must introduce the notion of Potential Energy Surface (PES). The PES is an important concept in electronic structure calculations. A PES describes in mathematical terms the relationship between the energy of an atom, molecule or solid and its spatial configuration (geometry). For one dimensional problems

Figure 1 – Potential energy curve representing the electronic ground state S_0 and the first excited state S_1 of a diatomic molecule. The horizontal red and blue lines are the vibrational levels of the molecule associated to the S_0 and S_1 states, respectively. The black lines represent the rotational levels for the molecule in relation to the ground state S_0 .
Source: By the author

the PES is called the potential energy curve, and is shown in Figure 1 where we present the ground and first excited state of a diatomic molecule.

Now, we are ready to explain the basis of the misunderstanding that the BO approximation is based on the nuclear and electronic mass difference. To start we will study the energetic analysis of a diatomic molecule with one electron as shown in Figure 1. For the large internuclear separation the two nuclei are weakly interacting. As the internuclear separation becomes smaller, the interaction becomes stronger. Then, the interatomic potential energy curve takes a large negative value, and we say that a bond is formed between the atoms. At very small internuclear separations the repulsion is very strong. Such that, the potential energy curve increases sharply in that region. The lines over the potential energy curve for the ground and first excited states represent the vibrational levels of the molecule, while the magnified black lines are the rotational levels.

The diatomic molecule spectrum is discrete and its electronic motion can be modelled as a particle in a box. Thus, the energetic order of the electronic motion of a molecule is proportional to the magnitude of the ground state energy of an electron in a box. For this case, the uncertainty principle states that the magnitude of the momentum associated with electrons must be around $p = \hbar/b$. For that reason, the electronic energy can be approximated by $E_e \approx p^2/m \approx \hbar^2/(mb^2) \approx 1$ (eV), where b is the distance between the atoms in the molecule. The quantum nuclear vibration energy within the

harmonic approximation is given by $E_v = \hbar\omega$. Then, the energy necessary to dissociate the nuclei can be estimated by the classical harmonic oscillator as $E_e \approx M\omega^2 b^2$. Replacing b^2 from the previous equation to dissociate the nuclei, the vibrational energy becomes $E_v \approx (m/M)^{1/2} E_e$. The rotational energy of a molecule, E_r is defined as $E_r = L^2/I$, where I is the moment of inertia of the molecule and is proportional to Mb^2 , L is the rotational angular momentum, which is quantized in units of $\hbar$ according to $L^2 = l(l+1)\hbar$, this leads to $E_r \approx \hbar^2/Mb^2$. Replacing the terms b^2 from E_e in the last expression, $E_r \approx (m/M)E_e$.

The numerical estimate for the rotational and vibrational energies, in terms of (m/M) are in the order of magnitude of $E_r \approx 10^{-4}(\text{eV})$, and $E_v \approx 10^{-2}(\text{eV})$. According to uncertainty principle, the time scale related to these energies is $t_e \approx 10^{-16}(\text{s})$, $t_v \approx 10^{-14}(\text{s})$, and $t_r \approx 10^{-12}(\text{s})$. This example says that $E_e < E_v \approx (m/M)^{1/2} E_e < E_r \approx (m/M) E_e$ and a superficial analysis could lead the unwary to the conclusion that the validity of the BO approximation is based on the nuclear mass differences. If this was the case, the BO approximation would always be true, assuming these mass differences remain, however we know that the BO approach fails for many cases. In the continuation of this section, we are going to show mathematically why the BO approximation fails and introduce an example of when it happens.

When the time scales of the electronic and nuclear motions are very different, then the BO approximation will be valid. From a physical point of view, this means that the electronic and nuclear degrees of freedom can be decoupled, which is equivalent to turning off the nuclear kinetic energy term, $\hat{K}_n = 0$ and $\hat{V}_{nn} = \text{const}$. Hence, the Hamiltonian of Eq. (2.1) can be rewritten as,

$$\hat{H}_{el} = \hat{K}_e + \hat{V}_{ee} + \hat{V}_{ext}. \quad (2.2)$$

From now on, the electronic and nuclear motion will be treated separately. In the literature such decoupling is termed as the Born-Oppenheimer or adiabatic approximation.⁵¹⁻⁵³ The Eq. (2.2) is the Hamiltonian of N interacting nonrelativistic electrons, which is frequently termed as the electronic hamiltonian. Now our many body problem consists of finding solutions for the static Schrödinger equation using the electronic hamiltonian,

$$\hat{H}_{el}\psi_j(\vec{r}_1, \dots, \vec{r}_N) = E_j\psi_j(\vec{r}_1, \dots, \vec{r}_N), \quad (2.3)$$

where $E_j = E_j(\vec{R})$ is the corresponding eigenvalue associated with the j th $\psi_j(\vec{r}; \vec{R}) = \psi_j(\vec{r}_1, \dots, \vec{r}_N)$ wave function for a given nuclear configuration, i.e., the electronic wave is parametrically dependant on the nuclear positions. Here, the values of $E_j(\vec{R})$ constitute a PES associated to the electronic state ψ_j . From now on, the atomic units will be used throughout this thesis i.e., $e = m = \hbar = 1$.

The full Hamiltonian of (2.1) can be recovered by adding again the nuclear kinetic energy to the $\hat{H}_{el}$ Hamiltonian, i.e., $\hat{H} = \hat{H}_{el} + \hat{K}_n$ such that,

$$\hat{H}\Psi = \epsilon\Psi \quad (2.4)$$

An exact solution for $\Psi(\vec{r}, \vec{R})$ can be expressed by using a product expansion of an infinite set of the nuclear $\{\chi_j(\vec{R})\}$ and electronic wave functions $\{\psi_j(\vec{r}; \vec{R})\}$.

$$\Psi(\vec{r}, \vec{R}) = \sum_j \psi_j(\vec{r}; \vec{R}) \chi_j(\vec{R}), \quad (2.5)$$

where those wave functions must obey the following normalization conditions,

$$\sum_j \langle \chi_j | \chi_j \rangle = 1 \text{ and } \langle \psi_j | \psi_{j'} \rangle = \delta_{jj'}. \quad (2.6)$$

In most cases it is still possible to obtain a very precise solution using just some of the conditions. In this sense, the total wavefunction is expanded using the electronic wave functions for a previously selected set of nuclear wavefunctions. Such procedure requires the introduction of expansion coefficients,

$$\Psi(\vec{r}, \vec{R}) = \sum_{jl} b_{jl} \psi_j(\vec{r}; \vec{R}) \chi_{jl}(\vec{R}), \quad (2.7)$$

The nuclear wave function equation is obtained by placing (2.5) into the time-independent Schrödinger equation. This yields a set of coupled equations for the nuclear wave functions,

$$\hat{H} \sum_{j'} \psi_{j'} \chi_{j'} = \epsilon \sum_{j'} \psi_{j'} \chi_{j'}, \quad (2.8)$$

Here, if we multiply the above equation from left by ψ_j^* and integrate over the electronic coordinates we have,

$$\epsilon \chi_j = \sum_{j'} \left(\langle \psi_j | \hat{H}_{el} | \psi_{j'} \rangle + \langle \psi_j | \hat{K}_n | \psi_{j'} \rangle \right) \chi_{j'}, \quad (2.9)$$

in the above equation, the summation of the LHS is eliminated due to the electronic normalization condition. However, due to the nuclear kinetic energy operator, this is not possible for the second term in the RHS. Using the chain rule combined with the identity $\langle \nabla_n \psi_j | \psi_j \rangle = 0$, the expansion of the last term turns out to be,

$$\begin{aligned} \langle \psi_j | \hat{K}_n | \psi_{j'} \rangle \chi_{j'} &= \sum_n \frac{-1}{2M_n} \left(\nabla_n^2 \chi_j + \chi_j \langle \psi_j | \nabla_n^2 \psi_j \rangle \right) \\ &\quad - \sum_n \sum_{j \neq j'} \frac{1}{2M_n} \left(2 \langle \psi_j | \nabla_n \psi_{j'} \rangle \cdot \nabla_n \chi_{j'} + \chi_{j'} \langle \psi_j | \nabla_n^2 \psi_{j'} \rangle \right). \end{aligned} \quad (2.10)$$

Thus Eq. (2.9) becomes,

$$\begin{aligned} &\left[\hat{K}_n + \sum_n \left(\frac{-1}{2M_n} D_{jj} \right) + E_j - \epsilon \right] \chi_j = \\ &- \sum_{j \neq j} \left[U_{jj'} + \sum_n \left(\frac{-1}{2M_n} \right) (2d_{jj'} \nabla_n + D_{jj'}) \right] \chi_{j'}, \end{aligned} \quad (2.11)$$

where the compact notations below are defined as non-adiabatic coupling terms, which are responsible for the coupling between different electronic states, $|\psi_j\rangle$ and $|\psi_{j'}\rangle$, through the nuclear kinetic energy operator,

$$\begin{aligned} d_{jj'} &= \langle \psi_j | \nabla_n \psi_{j'} \rangle \\ D_{jj'} &= \langle \psi_j | \nabla_n^2 \psi_{j'} \rangle. \end{aligned} \quad (2.12)$$

Supposing for some physical reason, that it is possible to neglect the non-adiabatic coupling terms $d_{jj'}$ and $D_{jj'}$ thereby obtaining the BO nuclear eigenvalue problem for the electronic state $|\psi_j\rangle$,

$$(\hat{K}_n + E_j) \chi_j = \epsilon \chi_j, \quad (2.13)$$

and the corresponding full solution for the Schrödinger equation of each electronic state $|\psi_j\rangle$ will be a single product of the nuclear and electronic wave functions,

$$\Psi(\vec{r}, \vec{R}) = \psi_j(\vec{r}; \vec{R}) \chi_j(\vec{R}). \quad (2.14)$$

The Eq. (2.14) is the so called Born-Oppenheimer approximation. However, this approximation is not always suitable. Thus, arises the question, when is it possible to use? To properly answer this question it is necessary to evaluate the non-adiabatic coupling terms and observe when it is and is not possible neglect them. In the following, it will be proved that the nonadiabatic coupling terms $d_{jj'}$ diverge when two PES's get closer to each other.

The first-order coupling terms $d_{jj'}$ for $j = j'$ vanish since $\langle \nabla_n \psi_j | \psi_{j'} \rangle = 0$. Thus, we only have to worry about the terms with $j \neq j'$. Applying the ∇_n operator to the off-diagonal matrix element of the $\hat{H}_{el}$ we have,

$$\begin{aligned} \nabla_n \langle \psi_j | \hat{H}_{el} | \psi_{j'} \rangle &= \langle \nabla_n \psi_j | \hat{H}_{el} | \psi_{j'} \rangle + \langle \psi_j | \nabla_n \hat{H}_{el} | \psi_{j'} \rangle + \langle \psi_j | \hat{H}_{el} | \nabla_n \psi_{j'} \rangle \\ &= (E_{j'} - E_j) \langle \psi_j | \nabla_n \psi_{j'} \rangle + \langle \psi_j | \nabla_n \hat{H}_{el} | \psi_{j'} \rangle. \end{aligned} \quad (2.15)$$

We have to keep in mind that the following equalities hold, $\langle \psi_j | \hat{H}_{el} | \psi_{j'} \rangle = E_j \delta_{jj'}$, $\nabla_n \langle \psi_j | \hat{H}_{el} | \psi_{j'} \rangle = 0$, and $\langle \nabla_n \psi_j | \psi_{j'} \rangle = -\langle \psi_j | \nabla_n \psi_{j'} \rangle$. These identities give us the following expression for $d_{jj'}$,

$$d_{jj'} = \langle \psi_j | \nabla_n \psi_{j'} \rangle = \frac{\langle \psi_j | \nabla_n \hat{H}_{el} | \psi_{j'} \rangle}{(E_j - E_{j'})}. \quad (2.16)$$

Using the chain rule in the term $\nabla_n d_{jj'}$ combined with the completeness relation $\sum_i |\psi_i\rangle \langle \psi_i|$, we obtain the relationship between the first and the second derivative of the non-BO coupling terms,

$$D_{jj'} = \nabla_n d_{jj'} + \sum_i d_{ji}^* d_{ij'}. \quad (2.17)$$

For a given system the non-adiabatic coupling terms will have an important role when $E_j \approx E_{j'}$ but not because of the nuclear mass, i.e., non-adiabatic coupling terms cannot

be neglected when the PES E_j and $E_{j'}$ are close to each other. In such cases, the Eq. (2.14) will not be valid anymore. The so called avoided crossings is an example where the non-adiabatic coupling terms cannot be neglected. To explain this case, let us consider a two-level system. The Hamiltonian for this system with eigenvalues $\{\epsilon_1 z, \epsilon_2 z\}$, and eigenstates $\{|1\rangle, |2\rangle\}$ is written as,

$$\hat{F} = \begin{pmatrix} \epsilon_1 z & 0 \\ 0 & \epsilon_2 z \end{pmatrix}. \quad (2.18)$$

Plugging an external perturbation $\hat{W}$, with only 'off' diagonal elements the Hamiltonian changes to,

$$\hat{F}' = \hat{F} + \hat{W} = \begin{pmatrix} \epsilon_1 z & 0 \\ 0 & \epsilon_2 z \end{pmatrix} + \begin{pmatrix} 0 & \omega \\ \omega^* & 0 \end{pmatrix}. \quad (2.19)$$

The eigenvalues that come from the diagonalization of the new Hamiltonian are the following,

$$\begin{aligned} \epsilon_+ &= \frac{1}{2} \left((\epsilon_1 + \epsilon_2)z + \sqrt{(\epsilon_1 - \epsilon_2)^2 z^2 + 4|\omega|^2} \right) \\ \epsilon_- &= \frac{1}{2} \left((\epsilon_1 + \epsilon_2)z - \sqrt{(\epsilon_1 - \epsilon_2)^2 z^2 + 4|\omega|^2} \right). \end{aligned} \quad (2.20)$$

Figure 2 shows that the addition of the perturbation matrix $\hat{W}$ changes these states. Even when $\epsilon_1 = \epsilon_2$, they are still different from their original values. This happens because these two states have the same symmetry, as shown by the squares and circles in Figure 2. In this case, only their linear combinations are solutions to the Schrödinger equation. When they have different symmetries they will be independent solutions to the Schrödinger equation. In such situations, crossings are allowed, as depicted with the full red and blue lines in Figure 2. In this figure z variable must be understood as a nuclear separation. The term ω is responsible for the coupling between the states ϵ_+ and ϵ_- , and the strength of the separation between those levels is proportional to the amplitude of ω .

In this section, we have learned that the BO approximation reduces the number of variables to be evaluated from $6N$ to $3N$. Additionally, we give an explanation of the validity of this approximation, illustrated with the avoided crossing example. In the Chapter 5 the non-adiabatic coupling terms will play an important role for the approximation to perform the Density functional theory calculations.

2.3 Density functional theory

Here we wish to obtain the electronic properties for a real systems, but even after the Born-Oppenheimer approximation the Hamiltonian in Eq. (2.2) is still far too hard to solve. The way to get around this problem is to make other approximations. Here, DFT is the methodology chosen for such a task. In this chapter we will review some of the fundamental aspects of DFT, as described by Hohenberg and Kohn¹⁸ and Kohn and Sham.¹⁹

Figure 2 – Energy level avoided crossing structure of a two-level system for the eigenstates $|\epsilon_+\rangle$ (blue) and $|\epsilon_-\rangle$ (red). One should note, that the gap size of the avoided crossing is proportional to the factor ω . The full blue and red lines without symbols represent the original states, and they touch each other at the degenerate point $z = 0$.
Source: By the author

2.3.1 The Hohenberg-Kohn Theorems

Working independently, both Thomas (1927) and Fermi (1928) proposed writing the energy of a many body system in terms of electronic density, $\rho(\vec{r})$.⁵² Figure 3 perspective when we move from the many body electronic wave function $\psi(\vec{r}_1, \dots, \vec{r}_N)$ ($3N$ variables) to the electronic density $\rho(\vec{r})$ concept with 3 variables.

However, their approach was unable to describe bound states. Following this idea, in 1964 Hohenberg and Kohn¹⁸ gave a demonstration of theorems that gave the Thomas-Fermi formalism a solid mathematical basis. The advantage of such an idea relies on the fact that $\rho(\vec{r})$ is only dependent on three variables, whereas the wavefunction becomes significantly more complicated as the number of electrons increases.

Theorem 2.1 *In a finite, interacting electronic system there is bijective dependence between the external potential $\hat{v}_{ext}$ and the ground state density $\rho_0(\vec{r})$. This means that the density $\rho_0(\vec{r})$ of a non-degenerate ground state uniquely determines the external potential $\hat{v}_{ext}$, apart from an additive constant.*

Here the proof is done via *reductio ad absurdum*. Let us assume that the solution of the Schrödinger equation using a set of potentials $\mathcal{V}$ leads to a set of non-degenerate ground states Ψ . Then, we are only accounting for non-degenerate ground states, then each

Figure 3 – Many body electronic systems concept in which the wavefunction has $3N$ variables, thought of in terms of the electron density with 3 variables.
Source: By the author

potential $v(\vec{r}) \in \mathcal{V}$ specifies the ground state wave function $|\psi[v]\rangle \in \Psi$ up to a trivial phase factor $e^{-i\alpha}$. Therefore, we must have the following mapping $\mathcal{P} : \mathcal{V} \rightarrow \Psi$, which is invertible $\mathcal{P}^-$.⁵⁴ This means, that two potentials $v_1(\vec{r}), v_2(\vec{r}) \in \mathcal{V}$ differing by more than a constant a , $v_1(\vec{r}) \neq v_2(\vec{r}) + a$, cannot take to the same ground states, i.e., $|\psi[v_1]\rangle \neq e^{-i\alpha}|\psi[v_2]\rangle$. Therefore, different potentials have to have distinct ground states.⁵⁵

If we consider $\mathcal{D}$ as the set of the densities that comes from the set of nondegenerate ground states Ψ via the expectation value of the density operator $\hat{\rho}$,

$$\rho(\vec{r}) = \langle \psi | \hat{\rho} | \psi \rangle = N \sum_{\sigma_1, \dots, \sigma_N} \int d\vec{r}_2 \dots \int d\vec{r}_N |\psi(\vec{r}\sigma_1, \dots, \vec{r}_N\sigma_N)|^2. \quad (2.21)$$

Consequently, a second mapping arises $\mathcal{Q} : \Psi \rightarrow \mathcal{D}$. To prove the theorem we have to demonstrate that the mapping $\mathcal{Q}$ is invertible $\mathcal{Q}^-$, and this proof is done through *reductio ad absurdum* technique.

Let us assume that we can find two different potentials, v_1 and v_2 such that they have the same ground state density ρ_0 . Let ψ_1 and $E[v_1] = \langle \psi_1 | \hat{H}_{el}[v_1] | \psi_1 \rangle$ be the ground state wave function and ground state energy of $\hat{H}_{el}[v_1]$. The same previous procedure is applied for the v_2 potential such that, the ground state wave function is ψ_2 and $E_2 = \langle \psi_2 | \hat{H}_{el}[v_2] | \psi_2 \rangle$. Using the variational principle we have:

$$\begin{aligned} E[v_1] &< \langle \psi_1 | \hat{H}_{el}[v_2] | \psi_1 \rangle = \langle \psi_1 | \hat{H}_{el}[v_1] | \psi_1 \rangle + \langle \psi_1 | \hat{H}_{el}[v_2] - \hat{H}_{el}[v_1] | \psi_1 \rangle \\ E[v_1] &< \langle \psi_1 | \hat{H}_{el}[v_2] | \psi_1 \rangle = E[v_1] + \int \rho(\vec{r})[v_2(\vec{r}) - v_1(\vec{r})]d\vec{r}. \end{aligned} \quad (2.22)$$

Applying the same reasoning, one can get

$$\begin{aligned} E[v_2] &< \langle \psi_2 | \hat{H}_{el}[v_1] | \psi_2 \rangle = \langle \psi_2 | \hat{H}_{el}[v_2] | \psi_2 \rangle + \langle \psi_2 | \hat{H}_{el}[v_1] - \hat{H}_{el}[v_2] | \psi_2 \rangle \\ E[v_2] &< \langle \psi_2 | \hat{H}_{el}[v_1] | \psi_2 \rangle = E[v_2] + \int \rho(\vec{r})[v_1(\vec{r}) - v_2(\vec{r})]d\vec{r}. \end{aligned} \quad (2.23)$$

The addition of the two inequalities Eqs.(2.22) and (2.23) leads to the contradiction,

$$E[v_1] + E[v_2] < E[v_1] + E[v_2]. \quad (2.24)$$

Figure 4 – One-to-one correspondence between external potentials $v_i(\vec{r}) = v_i$, ground state wave functions $\psi[v_i] = \psi_i$, and ground state densities $\rho[v_i] = \rho_i$.
Source: By the author

Consequently, two different nondegenerate ground states, $|\psi[v_1]\rangle \neq e^{-i\alpha}|\psi[v_2]\rangle$, originate different densities $\rho[v_1]$ and $\rho[v_2]$. This proves that, the mapping $\mathcal{Q}$ is invertible, which in turn also proves the Hohenberg-Kohn theorem. Figure 4 illustrates this formalism in terms of one-to-one correspondence.

Essentially the above theorem states that, the expectation value of any physical observable,

$$O[\rho] = \langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle, \quad (2.25)$$

of a given electronic system is a unique functional of the electron density ρ . The Hohenberg and Kohn¹⁸ paper contains another important theorem, relating the total energy observable

$$E_{v_0}[\rho] = \langle \Psi[\rho] | \hat{K}_e + \hat{V}_{ee} + \hat{V}_{ext} | \Psi[\rho] \rangle. \quad (2.26)$$

This new theorem states the following,

Theorem 2.2 *The ground state energy E_0 is the minimum of the total energy functional at the ground state density $\rho[v_0]$.*

The proof of Theorem 2.2 is very simple, because it is a consequence of variational principle. Theorem 2.1 says that, for an arbitrary ground state density there exists a nondegenerate wave function and vice-versa. Then, defining the universal functional of the density

$$F_{HK}[\rho] = \langle \Psi[\rho] | \hat{K}_e + \hat{V}_{ee} | \Psi[\rho] \rangle, \quad (2.27)$$

where the label HK is the shorthand for Hohenberg-Kohn. F_{HK} is universal because, $\hat{V}_{ee}$ it does not depend on the external potential $v(\vec{r})$. Thus, the energy functional above is rewritten as

$$E_v[\rho] = F_{HK}[\rho] + \int \rho(\vec{r})v(\vec{r})d\vec{r}. \quad (2.28)$$

Suppose that the ground state density ρ_1 corresponds to the potential v_1 then the ground state energy is $E_1[\rho_1]$. This implies that, for any other ground state density ρ_i we can write the expression for $E_1[\rho_1]$ as,

$$\begin{aligned} E_1[\rho_i] &= F_{HK}[\rho_i] + \int \rho_i v(\vec{r}) d\vec{r} \\ &= \langle \Psi[\rho_i] | \hat{K}_e + \hat{V}_{ee} + \hat{V}_1 | \Psi[\rho_i] \rangle. \end{aligned} \quad (2.29)$$

Eq. (2.29) states that, $E_1[\rho_1]$ will be equal to $E_1[\rho_i]$ only for $i = 1$, otherwise $E_1[\rho_i] > E_1[\rho_1]$. This means that, without use Schrödinger equation, the ground state energy E_1 can be found by minimization of the functional $E_1[\rho_1]$,

$$E_1 = \min_{\rho \in \mathcal{D}} \left[F_{HK}[\rho] + \int \rho v_1(\vec{r}) d\vec{r} \right]. \quad (2.30)$$

To find the correct ground state density ρ_0 , the inputs of the densities of the variational principle Eq. (2.30) must belong to the set $\mathcal{D}$, otherwise the functionals $F_{HK}[\rho_1]$ and $E_1[\rho_1]$ will be undefined. A given density ρ that belongs to the set $\mathcal{D}$ is said to be v -representable. The procedure to identify if a given density ρ belongs to $\mathcal{D}$ is unknown, and this difficulty is termed as v -representability problem. However, in order to overcome this shortcoming Levy and Lieb^{54,56,57} have proposed an alternative method which only requires the densities to be N -representable. The density that is built from the antisymmetric wavefunction is said to be N -representable.

Those two theorems provide the mathematical basis to replace the $3N$ variable wave function by the 3 variable ground state density. Unfortunately, the universal functional $F[\rho]$ is unknown in DFT. Despite this, much progress has been made in understanding its properties and finding reliable approximations.^{18,52,55}

2.3.2 Kohn Sham Equations

The practical scheme that is currently used for most applications of DFT was invented by Kohn and Sham (1965).¹⁹ Their innovative proposal is based on the idea of writing the v -representable density, $\rho(\vec{r})$, of a system of interacting particles as the same v -representable density,

$$\rho(\vec{r}) = \sum_{i=1}^{N_{occ}} |\phi_i|^2, \quad (2.31)$$

computed from occupied orbitals ϕ_i of an auxiliary system of non-interacting particles Figure 5. Here the index i counts the wavefunctions in order of increasing energy.

The ground-state antisymmetric wave Functions $\psi(\vec{r}_1, \dots, \vec{r}_{N_{occ}})$ corresponding to the system of non-interacting particles is written as a Slater determinant of single-particle orbitals, where ϕ_i satisfies the time independent Schrödinger equation,

$$\left(-\frac{\nabla^2}{2} + v_{eff}(\vec{r}) \right) \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}). \quad (2.32)$$

Figure 5 – Left side: interacting system with density ρ . Right side: Kohn-Sham system generating the same density ρ that is generated by the interacting system.

Source: By the author

In mathematical terms, the total energy functional for the above equation termed here as $E_{KS}[\rho]$, is written as,

$$E_{KS} = K_{KS}[\rho] + \int \rho(\vec{r}) v_{eff}(\vec{r}) d\vec{r}, \quad (2.33)$$

v_{eff} is a effective local single-particle potential to be determined self-consistently. Here, $K_{KS}[\rho]$ is the kinetic energy functional for the non-interacting electronic system, which has the same electronic density as the real system, and it is computed from single-particle orbitals according to

$$K_{KS} = - \sum_i^{N_{occ}} \langle \phi_i | \frac{\nabla^2}{2} | \phi_i \rangle. \quad (2.34)$$

The ground-state energy density of the non-interacting electronic system is obtained from the minimisation of the functional given in Eq.(2.33) with respect to density,

$$\frac{\delta E_{KS}[\rho]}{\delta \rho(\vec{r})} = \frac{\delta K_{KS}[\rho]}{\delta \rho(\vec{r})} + v_{eff} = \mu, \quad (2.35)$$

where the Lagrange multiplier μ specifies the correct number of particles.

The interacting total energy functional Eq.(2.28) associated to the potential v_{ext} can be rewritten as a summation of the non-interacting kinetic energy operator, Hartree energy and an unknown term called the exchange correlation energy,

$$\begin{aligned} E_{v_{ext}}[\rho] &= F_{HK}[\rho] + \int \rho(\vec{r}) v[\rho]_{ext} d\vec{r} \\ E_{v_{ext}}[\rho] &= K_{KS}[\rho] + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}') d\vec{r} d\vec{r}'}{|\vec{r} - \vec{r}'|} + \int \rho(\vec{r}) v[\rho]_{ext} d\vec{r} + E_{xc}[\rho]. \end{aligned} \quad (2.36)$$

Essentially, the exchange correlation energy, $E_{xc}[\rho]$, nothing less than a measurement of our ignorance, and everything that we do not know how to represent is put on inside of this term,

$$E_{xc}[\rho] = (K_e[\rho] - K_{KS}[\rho]) + \left(V_{ee}[\rho] - \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}') d\vec{r} d\vec{r}'}{|\vec{r} - \vec{r}'|} \right), \quad (2.37)$$

Eq.(2.37) considers all the energy contributions that are absent in the previous terms. The first parentheses on the right-hand side contains the kinetic energy of the interacting system

that is missing in the non-interacting electronic system, and the second parentheses, is the contribution of the quantum-mechanical electron-electron interaction to the ground-state energy that is not captured by the classical electron-electron interaction. In particular, the latter parentheses is correct for the self-interaction component of the classical energy.

Applying the same reasoning used in Eq. (2.35) to Eq. (2.36) gives us the following equation for the Lagrange multiplier on the RHS of Eq. (2.35):

$$\frac{\delta E_{v_{ext}}[\rho]}{\delta \rho(\vec{r})} = \frac{\delta K_{KS}[\rho]}{\delta \rho(\vec{r})} + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = \mu \quad (2.38)$$

By comparing Eqs. (2.38) and (2.35), we can immediately see that the two equations are equivalent only if ,

$$v_{eff} = v_{ext} + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{xc}[\rho](\vec{r}) \quad (2.39)$$

where, $v_{xc}[\rho](\vec{r})$ is a functional derivative of the exchange correlation energy given by,

$$v_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}. \quad (2.40)$$

Usually, the exchange correlation potential has a small contribution to the total energy. However, it plays an important role in the binding energy, in some cases up to 100%.⁵⁸ Eq. (2.39) allows us to rewrite Eqs. (2.32) as

$$\left(-\frac{\nabla^2}{2} + v_{eff}[\rho](\vec{r}) \right) \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}), \quad (2.41)$$

where the ground state density ρ_0 is written in same way as Eq. (2.31), i.e.,

$$\rho_0(\vec{r}) = \sum_{i=1}^{N_{occ}} |\phi_i|^2. \quad (2.42)$$

The subtle difference between Eq. (2.41) and Eq. (2.32) is that now v_{eff} is a functional of the density, and consequently its orbitals are too, i.e., $\phi_i[\rho](\vec{r})$. From Eq. (2.41) the kinetic energy functional can be rewritten as the follows,

$$\begin{aligned} K_{KS}[\rho_0] &= - \sum_i^{N_{occ}} \langle \phi_i | \frac{\nabla^2}{2} | \phi_i \rangle \\ K_{KS}[\rho_0] &= \sum_{i=1}^{N_{occ}} \epsilon_i - \int \rho(\vec{r}) v_{eff}[\rho_0] d\vec{r}. \end{aligned} \quad (2.43)$$

Replacing Eqs. (2.39) and (2.43) into Eq.(2.36) we get the following ground state energy for physical system in terms of the Kohn-Sham eigenvalues, ϵ_i , of the noninteracting electronic system,

$$E_{KS}[\rho_0] = \sum_{i=1}^{N_{occ}} \epsilon_i - \frac{1}{2} \int \frac{\rho_0(\vec{r}) \rho_0(\vec{r}') d\vec{r} d\vec{r}'}{|\vec{r} - \vec{r}'|} - \int \rho_0(\vec{r}) v_{xc}[\rho_0] d\vec{r} + E_{xc}[\rho_0]. \quad (2.44)$$

In order to extend the Khon Sham method to spin polarized systems, we set up the ground state electronic density composed of two spin densities,

$$\rho_0(\vec{r}) = \rho_0(\vec{r})_{\uparrow} + \rho_0(\vec{r})_{\downarrow} = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_{occ,\sigma}} |\phi_{i\sigma}(\vec{r})|^2, \quad (2.45)$$

and naturally the Khon Sham equations with spin, will assume the following form,

$$\left(-\frac{\nabla}{2} + v_{eff}[\rho_{\uparrow}, \rho_{\downarrow}](\vec{r})\right) \phi_{i,\sigma}(\vec{r}) = \epsilon_{i,\sigma} \phi_{i,\sigma}(\vec{r}), \quad (2.46)$$

where $v_{eff}[\rho_{\uparrow}, \rho_{\downarrow}]$ is represented by the following equation,

$$v_{eff}[\rho_{\uparrow}, \rho_{\downarrow}] = v_{ext,\sigma}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{xc,\sigma}[\rho_{\uparrow}, \rho_{\downarrow}](\vec{r}), \quad (2.47)$$

and $v_{xc,\sigma}[\rho_{\uparrow}, \rho_{\downarrow}](\vec{r})$ is redefined in following way,

$$v_{xc,\sigma}[\rho_{\uparrow}, \rho_{\downarrow}](\vec{r}) = \frac{\delta E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]}{\delta \rho_{\sigma}(\vec{r})}. \quad (2.48)$$

The set of equations $\{(2.42), (2.41), (2.39), (2.40)\}$ is known in the literature as the Khon Sham equations. It is important to stress here that the input for the K-S equations is an initial density ρ_j and after one iteration the output is another ρ_{j+1} . This means that the density associated with the Kohn-Sham orbitals must be reached via the self consistent procedure. Figure 6 shows the self-consistent procedure used to solve the K-S equations throughout this thesis. The self-consistent procedure is stopped, when the old and new densities differ by no more than a convergence factor ϵ_{tol} . The convergence is sped up adopting a mixing scheme for the densities.

Figure 6 – Schematic self consistent procedure to solve the Khon Sham equations.
Source: By the author

The accuracy of DFT depends on the choice of exchange correlation potentials, v_{xc} , which sometimes may contribute up to 100% of the binding energy, as in the case of Graphite's layers.⁵⁸ In next subsection we will shed a bit of light on this issue, in order to understand its strong and weak points.

2.4 Exchange and Correlation Functionals

The Hohenberg-Kohn theorem defines the existence of the universal functional $F[\rho]$. However, it remains unknown and consequently the exchange correlation energy functional, Eq. (2.37), must be approximated. Before, we start to discuss how this approximation is designed and which properties it must satisfy, we should introduce one the most popular models in condensed matter physics, the so-called homogeneous electron gas model, which is used as the start point to build exchange correlation energy functionals. Such models represent N electrons that interact with one another characterized by their density ρ , where the atomic nuclei are represented by a uniform background of positive charge.⁵⁹ The exchange and correlation energy of this model ε_{xc}^h per unit volume can be computed separately into exchange ε_x^h , and correlation ε_c^h parts, where the exchange is derived analytically and is given by the expression,

$$\varepsilon_x^h(\rho, \xi) = \varepsilon_x^h(\rho, 0) + [\varepsilon_x^h(\rho, 1) - \varepsilon_x^h(\rho, 0)]g(\xi), \quad (2.49)$$

ξ is set as spin polarization,

$$\xi = \frac{\rho_{\uparrow} - \rho_{\downarrow}}{\rho}. \quad (2.50)$$

The exchange energy for unpolarized ($\varepsilon_x^h(\rho, 0)$) and totally polarized ($\varepsilon_x^h(\rho, 1)$) homogeneous electron gas as well as the function ($g(\xi)$) that interpolates these two regimes is given by the following expressions^{55, 59}

$$\varepsilon_x^h(\rho, 0) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho^{4/3}, \quad (2.51)$$

$$\varepsilon_x^h(\rho, 1) = -\frac{3}{4} \left(\frac{6}{\pi} \right)^{1/3} \rho^{4/3}, \quad (2.52)$$

$$g(\xi) = \frac{(1 + \xi)^{4/3} + (1 - \xi)^{4/3} - 2}{(2^{4/3} - 2)}. \quad (2.53)$$

Unlike the ε_x the exact form of the correlation energy (ε_c^h) for the homogeneous electron gas is known only analytically in the high and low density limits. For nonpolarized gas $\xi = 0$, the expressions for high ($r_s \rightarrow 0$) and low ($r_s \gg 1$) densities are,⁶⁰

$$\varepsilon_c(r_c, 0) = \begin{cases} 0.311 \ln(r_s) - 0.048 + r_s(A \ln(r_s) + C) + \dots & r_s \rightarrow 0 \\ \frac{a_1}{r_s} + \frac{a_2}{r_s^{3/2}} + \frac{a_3}{r_s^2} & r_s \gg 1, \end{cases} \quad (2.54)$$

where the parameters $a_{n=1,2,3}$, A, C can be found in the reference,⁶¹ and $r_s = (3/4\pi\rho)^{1/3}$ is the Wigner-Seitz radius.

The analytic expression for the correlation, in the interval between the two high and low density regimes has been obtained from fits of accurate numerical quantum Monte Carlo calculations,⁶²⁻⁶⁴ The Perdew Wang⁶³ interpolation is one of the most widely used parameters in the current literature and it is represented by the following equation,

$$\tilde{\varepsilon}_c^h(r_s, \xi) = \tilde{\varepsilon}_c^h(r_s, 0) + \alpha_c(r_s) \frac{g(\xi)}{g''(0)} (1 - \xi^4) + [\tilde{\varepsilon}_c^h(r_s, 1) - \tilde{\varepsilon}_c^h(r_s, 0)] g(\xi) \xi^4, \quad (2.55)$$

here $\tilde{\varepsilon}_c^h = \rho \varepsilon_c^h$ is the correlation energy per particle. The undefined variables $\tilde{\varepsilon}_c^h(r_s, 0)$, $\tilde{\varepsilon}_c^h(r_s, 1)$, and $\alpha_c(r_s)$ are appropriately parameterized by the following analytic expression,

$$G(r_s, A, \alpha_1, \beta_1, \beta_2, \beta_2, \beta_3, \beta_4) = -2A(1 + \alpha_1 r_s) \times \ln \left[1 + \frac{1}{2A(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)} \right]. \quad (2.56)$$

The numerical values of the parameters $A, \alpha_1, \beta_1, \beta_2, \beta_2, \beta_3, \beta_4$ can be found in the reference.⁶³ The above parameter is commonly used in current DFT literature, as we shall see in the next section, where the LDA (Local Density Approximation) and GGA (Generalized Gradient Approximation) will be addressed.

2.4.1 LDA and GGA

The local density approximation (LDA) or local spin density approximation (LSDA) is the most famous approximation for the exchange correlation energy. This functional was developed in 1965 by Kohn and Sham.¹⁹ The idea behind the LDA is to consider an inhomogeneous electronic system formed by infinite locally homogeneous points, and use the exchange correlation energy of the homogeneous electron gas to represent each of these points. The equation for $E_{xc}[\rho]$ as well as for $v_{xc}(\rho)$ within the LDA is given by the following,

$$E_{xc}[\rho] \approx E_{xc}^{LDA}[\rho] = \int \varepsilon_{xc}^h(\rho) d\vec{r} \quad (2.57)$$

$$v_{xc}^{LDA}(\vec{r}) = \frac{\delta \varepsilon_{xc}^h(\rho)}{\delta \rho}.$$

The LDA (LSDA) is a very simple approximation and one would expect that it is only valid in a slowly varying density regime. But surprisingly, this approximation accurately describes the electronic properties for many different systems, even those with very inhomogeneous densities. The unexpected success of the LDA is due to the fact that many of the sum rules and scaling property conditions are met by this functional.⁶⁵ In comparison with the Hartree-Fock method the LDA or LSDA are almost always computationally less expensive. Besides, LDA (LSDA) is often successful in giving the right physical trends and in many cases it is more precise than Hartree-Fock.⁶⁶

The natural way to improve the LDA or LSDA exchange correlation energy is to relax the local condition of uniformity density. This can be done if the functionals take into account the gradient of the density $\nabla\rho$ or its norm $|\nabla\rho|$. The first attempt to use those new quantities was named as Gradient Expansion Approximation (GEA), which writes the exchange correlation energy as truncated Taylor series in terms of the reduced density gradient (s), here defined as,

$$s(r) = \frac{|\nabla\rho(\vec{r})|}{2\rho(\vec{r})k_F(r)}, \quad (2.58)$$

where, $k_F = (3\pi^2\rho)^{1/3}$ is the Fermi wave vector.

The GEA for $E_{xc}[\rho]$ is written as,

$$\begin{aligned} E_{xc}^{GEA}[\rho] &= \int \varepsilon_{xc}^h(\rho) F_{xc}[\rho(\vec{r}), \nabla\rho(\vec{r}), \nabla^2\rho(\vec{r})] d\vec{r} \\ E_{xc}^{GEA}[\rho] &= \int (\varepsilon_{xc}^h(\rho(\vec{r})) + C_{xc}^2(\rho)s^2 + \dots) d\vec{r} \end{aligned} \quad (2.59)$$

where F_{xc} is an extension function accounting for the variation of the density around a given point. C_{xc}^2 is determined by the density which reduces to a constant. In the case $F_{xc} = 1$, it turns out that this function returns to the original LDA form. Since the GEA considers non-local terms of the density, one might assume that the properties of the atoms, molecules, and solids are better than LDA (LSDA). Unfortunately this is not true, and in many cases the results are worse. This happens, because GEA breaks many important sum rules that are satisfied by LDA (LSDA).^{19,65}

In order to overcome the problems associated with GEA, Perdew and other researchers proposed to replace the Taylor expansion in the Eq.(2.59) by a damping function $F_{xc}(\rho, s)$, in such a way that the $\vec{r} \rightarrow \infty$. F_{xc} remains finite, and $F_{xc} = F_{xc}(\rho, \nabla\rho)$ is chosen so that it satisfies the sum rules as well the scaling property conditions. This new procedure is called Generalized Gradient Approximations (GGA). Thus, the general form for $E_{xc}^{GEA}[\rho]$ using GGA is written as,

$$E_{xc}^{GGA}[\rho] = \int \varepsilon_{xc}^h(\rho) F_{xc}(\rho, s) d\vec{r}. \quad (2.60)$$

Eq. (2.59), F_{xc} stems from a Taylor expansion, a uniquely defined procedure. Here, however, one is free to choose the constraints that the new F_{xc} must obey. Hundreds of alternatives have been proposed.^{63,67-71} The Perdew-Burke-Ernzerhof (PBE) functional is among the most popular and used currently to simulate properties of matter.⁶⁹ The PBE exchange part is described by,

$$E_x^{PBE}[\rho] = \int \varepsilon_x^h(\rho) \left[1 + \kappa - \frac{\kappa}{(1 + \beta\pi^2 s^2/3\kappa)} \right] d\vec{r}, \quad (2.61)$$

where $\kappa = 0.804$ and $\beta = 0.066725$. The spin polarized variant for E_x^{PBE} is obtained using a spin scaling relationship as described in reference,⁷² which is given by

$$E_x^{PBE}[\rho] = \frac{1}{2}E_x[2\rho_\uparrow] + \frac{1}{2}E_x[2\rho_\downarrow]. \quad (2.62)$$

The PBE correlation part is given by,

$$E_c^{PBE}[\rho] = \int \left[\varepsilon_c^h(\rho, \xi) + \rho c_0 f(\xi)^3 \ln \left\{ 1 + \frac{(1 + At^2)\beta t^2/c_0}{1 + At^2 + A^2 t^4} \right\} \right] d\vec{r}. \quad (2.63)$$

Here, $t = |\nabla \rho|/2k_s\rho$ is a dimensionless density gradient, with the screening wave number $k_s = \sqrt{4k_F/\pi}$ and $f(\xi) = [(1 + \xi)^{2/3} + (1 - \xi)^{2/3}]/2$ is a spin scaling factor. The function A is given by the following expression,

$$A = \frac{\beta/c_0}{\exp\{[-\varepsilon]_c^h(\rho, \xi)/c_0 f(\xi)^3\} - 1}, \quad (2.64)$$

with $c_0 = 0.031091$.

The PBE functional satisfies many sum rules, all parameters are expressed in term of fundamental constants. The main sum rules and scaling property conditions, that an exchange correlation functional should obey are the following;

$$\int d\vec{r}' [g(\vec{r}, \vec{r}') - 1] \rho(\vec{r}') = -1, \quad (2.65)$$

where $g(\vec{r}, \vec{r}')$ is a normalized probability of finding an electron at $\vec{r}'$ given that another electron is at $\vec{r}$. The exact exchange energy is strictly negative $E_x[\rho]$, while the correlation part is non-positive $E_c[\rho] \leq 0$. The Lieb-Oxford bound⁷³ is other important property that the exchange correlation functional in principle should satisfy,

$$E_x[\rho] \geq E_{xc}[\rho] \geq -1.68 \int \rho(\vec{r})^{4/3} d\vec{r}, \quad (2.66)$$

this property is satisfied by LDA and some GGAs like PBE functionals. Levy and Perdew⁵⁷ have introduced coordinate scaling conditions,

$$\begin{aligned} E_x[\rho_\lambda] &= \lambda E_x[\rho] \\ E_c[\rho_\lambda] &> \lambda E_c[\rho], \quad \lambda > 1 \\ E_x[\rho_\lambda] &< \lambda E_c[\rho], \quad \lambda < 1. \end{aligned} \quad (2.67)$$

where $\rho_\lambda(\vec{r}) = \lambda^3 \rho(\lambda \vec{r})$ is a scaled density.

The meta-GGAs are the next step in development beyond GGAs. These functionals include new semi-local features via kinetic energy density. The main advantage of them in comparison with GGAs, is that they are partially free of self-interaction.⁷⁴ On the other hand, they are computationally more expensive than GGAs. A further improvement on the meta-GGA is given by hybrid functionals. This class of functionals is built by mixing a part of the exact Hartree-Fock exchange energy with other GGAs or LDAs, the parameter responsible for this mixing is adjusted empirically.⁷⁵ The GGA-PBE functional presents a good compromise between accuracy and computational time demand, in many cases it is equivalent or better than the BLYP functional.⁷⁶ Due to this, in the present work the PBE functional as proposed originally will be used in our calculations.⁶⁹

Dispersion forces are essentially due to long-range electron correlation effects which due to their construction are absent in LDA and GGAs functionals. The non-locality is an intrinsic character of the dispersive interactions, which emerge due to charge fluctuations on one system, which in turn induce a dipole on the other. Thus, for any system where such effect has an important role in electronic properties some corrections are needed. In order to clarify this issue in the next section we are going to explain how to calculate some of these corrections.

2.5 van der Waals corrections

If we consider two neutral atoms or molecules we will see that they attract each other. This attraction is not surprising if we consider they can have electric dipole moment. However, Johannes Diderik van der Waals conducted a study which showed that this force still exists between two helium atoms which are spherically symmetric and lack any permanent multipole moment. The nature of such force must be derived taking into account quantum mechanical effects. In 1930, London and Eisenschitz applying a quantum mechanical treatment found that the potential between two neutral atoms is given by $-C/R^6$, where R is the separation between the atoms and the constant C is positive.⁷⁷ This kind of van der Waals force is widely used in Condensed Matter Physics, in particular as *a posteriori* corrections for the DFT total energies. In this section we will derive the dispersion relation $-C/R^6$, and present within the *a posteriori* framework the most used vdW corrections for DFT calculation.

To illustrate the physical idea behind the van der Waals force, we are going to use a one dimensional atomic system, where two harmonic oscillators are mimicking the dynamic of the H_2 molecule. We are aware that the vdW are caused by quantum fluctuations in the polarization of the particles and because of that the Hamiltonian below must be thought as snapshot of the system in the moment of the fluctuation. In this sense, the model Figure 7 shows that the electrons are bound to the protons separated by the R distance.

Figure 7 – One dimensional model for the harmonic oscillator representing H_2 molecule.
Source: By the author

The full hamiltonian that describes the system shown in Figure 7 is modelled by the unperturbed $\hat{H}_0$ and Coulombic interactions $\hat{H}_1$, i.e., $\hat{H} = \hat{H}_0 + \hat{H}_1$, where

$$\hat{H}_0 = \frac{1}{2}p_1^2 + \frac{1}{2}\omega_0^2x_1^2 + \frac{1}{2}p_2^2 + \frac{1}{2}\omega_0^2x_2^2 \quad (2.68)$$

and

$$\hat{H}_1 = \left(\frac{1}{|R|} + \frac{1}{|R + x_1 - x_2|} - \frac{1}{|R + x_1|} - \frac{1}{|R - x_2|} \right). \quad (2.69)$$

Considering that the internuclear distance is much larger than the atomic size, i.e., ($R \gg x_1, x_2$) one can approximate $\hat{H}_1$ by,

$$\hat{H}_1 \approx -2 \frac{x_1 x_2}{R^3}. \quad (2.70)$$

Adding $\hat{H}_1$ with $\hat{H}_0$, and applying the transformations $x_{\pm} = (x_1 \pm x_2)/\sqrt{2}$ and $p_{\pm} = (p_1 \pm p_2)/\sqrt{2}$ we arrive at,

$$\hat{H} = \frac{p_+^2}{2} + \frac{1}{2} \left(\omega_0 - \frac{2}{R^3} \right)^2 x_+^2 + \frac{p_-^2}{2} + \frac{1}{2} \left(\omega_0 + \frac{2}{R^3} \right)^2 x_-^2, \quad (2.71)$$

The above equation states that the new frequencies for the coupled oscillators are,

$$\omega_{\pm} = \sqrt{\left(\omega_0^2 \mp \frac{2}{R^3} \right)} \approx \omega_0 \mp \frac{1}{\omega_0 R^3} - \frac{1}{2m^2 \omega_0^3 R^6} + \dots \quad (2.72)$$

If we taken into account only the first three terms in the expansion and compute the difference in energy before and after coupling, the final result is

$$E^{\text{vdW}} = \frac{1}{2}(\Delta\omega_+ + \Delta\omega_-) \approx -\frac{1}{2\omega_0^3 R^6} = -\frac{C_6}{R^6}. \quad (2.73)$$

This equation states that the attractive dependence of $1/R^6$ is one of the most important contributions to the vdW forces. The C_6 constant also known as the dispersion coefficient is the main issue within the vdW corrections methods, and generally each family of correction is associated with the approach used to estimate it.

Our total-energy DFT calculations rely on the PBE exchange correlation functional. To accurately describe the interlayer distance in graphite, we have added vdW corrections to the dispersion forces, the vdW-corrected DFT total energy E_{tot} being obtained as follows:

$$E_{\text{tot}} = E_{\text{tot}}^{\text{DFT}} + E_{\text{tot}}^{\text{vdW}}, \quad (2.74)$$

where $E_{\text{tot}}^{\text{DFT}}$ is the DFT-PBE total energy, and $E_{\text{tot}}^{\text{vdW}}$ is the correction to the total energy due to the vdW interactions, which is given by the following equation:

$$E_{\text{tot}}^{\text{vdW}} = E^{(2)} + E^{(3)}. \quad (2.75)$$

The first term on the right-hand side of Eq. (2.75) stems from the dipole-dipole interactions induced by quantum fluctuations in the electron density, while $E^{(3)}$ comes from the triple dipole dispersion term found in the third-order perturbation treatment of three atoms ijk .^{78,79} Within this framework, the accuracy depends on the dispersion coefficients C_6^{AB} , which determine $E^{(2)}$, and/or C_9^{ABC} , which determines $E^{(3)}$, where A , B , and C

indicates the chemical species. The two coefficients can be extracted from experimental data, or they can be computed, a number of theoretical approaches having been proposed. Of special interest here are the TS, TS+SCS, D2, and D3 corrections as implemented in VASP, upon which our computations are based.

Since the dipolar interactions diverge with the separation $R \rightarrow 0$, the corrections $E^{(2)}$ and $E^{(3)}$ include a multiplicative factor $f_{\text{damp}}(R, R_0, s, d)$ to insure correct behaviour at small distances. The damping function is defined by three parameters; R_0 , s , and d . More specifically, $f_{\text{damp}}(R, R_0, s, d)$ vanishes (approaches unity) at very small (large) distances, and the transition from $f_{\text{damp}}(R \rightarrow 0) = 0$ to $f_{\text{damp}}(R \rightarrow \infty) = 1$ is controlled by R_0 , s , and d .^{7,80} Roughly speaking, one expects the transition to occur at a distance scale set by the sum R^0 of the vdW radii of the two interacting species AB. The scaling factor s , which depends on the employed exchange correlation functional only, defines more precisely the transition point: $f_{\text{damp}}(R, R^0, s, d)$ rises sharply from zero to unity around $R = sR^0$. Finally, the parameter d , also dependent on the XC functional only, defines the abruptness of the transition. Different ways to calculate the damping function have recently been proposed, among them a procedure defined within the Many-Body Dispersion (MBD) method.⁸¹ To investigate the effect of the damping functions on the accuracy of the results, we probed a few expressions for $f_{\text{damp}}(R, R_0, s, d)$, such as the zero and Becke-Johnson dampings implemented in the D3-correction approach, denoted D3 and D3-BJ, respectively.

In the D2 scheme,⁸²

$$E^{(2)} = -\frac{1}{2} \sum_{ij} f_{\text{damp},2}(R_{ij}) \frac{C_6^{AB}}{R_{ij}^6}, \quad (2.76)$$

while the second term on the right-hand side of Eq. (2.75), $E^{(3)}$, is zero. The C_6^{AB} coefficients are found from the equation

$$C_6^{AB} = \sqrt{C_6^A C_6^B}, \quad (2.77)$$

and

$$C_6^A = 0.05 N I_p^A \alpha^A, \quad (2.78)$$

where the atomic ionization potentials I_p and static dipole polarizabilities α were obtained from PBE0⁸³ calculations with $N = 2, 10, 18, 36$, and 54 for atoms in rows 1 – 5 of the periodic table.

In the D3 scheme,⁷⁹ both terms on the right-hand side of Eq. (2.75) are nonzero, and

$$E^{(3)} = \gamma \sum_{ijk} f_{\text{damp},3}(\bar{R}_{ijk}) \frac{C_9^{ABC}}{(R_{ij} R_{jk} R_{ki})^3}. \quad (2.79)$$

Here, the constant γ depends on the internal angles of the triangle formed by R_{ij} , R_{jk} and R_{ki} ,⁷⁸ and the ternary coefficients C_9^{ABC} are obtained from the binary dispersion coefficients C_6^{AB} as follows. The binary coefficients are given by the modified Casimir-Polder

integral⁸⁴:

$$C_6^{AB} = \frac{3}{\pi} \int_0^\infty d\omega \frac{1}{m} [\alpha^{A_m H_n}(i\omega) - \frac{n}{2} \alpha^{H_2}(i\omega)] \quad (2.80)$$

$$\times \frac{1}{k} [\alpha^{B_k H_l}(i\omega) - \frac{l}{2} \alpha^{H_2}(i\omega)] , \quad (2.81)$$

which takes the polarizabilities of simple molecules with well-defined electronic structures into account, instead of free-atom polarizabilities.

When the polarizabilities of the sample molecules are substituted on the right-hand side of Eq. (4.9), an interpolation procedure yields the chemically reasonable coordination numbers for the system under study and determines the dispersion coefficients. The ternary dispersion coefficients C_9^{ABC} are then obtained from the expression

$$C_9^{ABC} \approx -\sqrt{C_6^{AB} C_6^{AC} C_6^{BC}} . \quad (2.82)$$

In the TS and TS+SCS schemes, the analytical form for $E^{(2)}$ is almost the same as in the D2 and D3 schemes, while $E^{(3)}$ is null. To determine the dispersion coefficients C_6^{AA} , a different concept is exploited. In the TS approach, the parameters C_6^{AB} are obtained from the expression

$$C_6^{AB} = \frac{2C_6^{AA}C_6^{BB}}{\left(\frac{\alpha_0^B}{\alpha_0^A}C_6^{AA} + \frac{\alpha_0^A}{\alpha_0^B}C_6^{BB}\right)}, \quad (2.83)$$

and the dispersion coefficients from the equality

$$C_6^{AA} = \left(\frac{V_{\text{eff}}^A}{V_{\text{free}}^A}\right)^2 (C_6^{AA})^{\text{free}}, \quad (2.84)$$

where the ratio $V_{\text{eff}}^A/V_{\text{free}}^A$ between the effective and free (noninteracting) atomic volumes are obtained from the Hirshfeld partitioning of the computed electronic densities for the interacting system and free atom, and α_0^A and α_0^B are the static polarizabilities.⁷

The TS approach disregards the screening of the electrostatic interaction between distant dipoles, which has no effect upon the polarizabilities of free atoms. This approximation is less adequate to compute the polarizabilities of atoms in large molecules or condensed phases. To account for screening, the TS+SCS approach treats the environment as a dipole field,⁸⁵ and substitutes a set of quantum harmonic-oscillator densities for the atomic densities, so that the spatial dependence can be integrated out. The solution of the resulting SCS equation determines the frequency-dependent screened polarizabilities $\alpha_{SCS}^A(i\omega)$,⁸⁵ where the homonuclear dispersion coefficients C_6^{AA} are computed from the Casimir-Polder formula⁸⁴

$$C_6^{AA} = \frac{3}{\pi} \int_0^\infty \left(\alpha_{SCS}^A(i\omega)\right)^2 d\omega . \quad (2.85)$$

An improved version of the TS method recently developed by Tkatchenko *et. al.* includes electrodynamic response (TS + SCS) and many-body (TS + MBD) effects.⁸¹ The latter has been proven equivalent to an RPA computation of dispersion energies.⁸⁶ Additional details on the D2, D3, TS, and TS+SCS vdW corrections can be found elsewhere.^{7,27,79,80,82,85,87–89}

2.6 Projector Augmented Wave (PAW)

We have solved the Kohn-Sham equations with the all electron Projected Augmented Wave (PAW) method. As it is well known, the wave function in the core regions exhibit an oscillating behavior, which needs a large set of plane waves to be appropriately modelled, making it particularly expensive and time consuming. A possible solution is the use of pseudopotentials, but this method takes into account only valence electrons in the solution of KS equations. The pseudopotential framework offers an inaccurate description of properties strongly dependent on the behaviour of wavefunctions close to the nuclei. Therefore, another method is needed to describe the physics around the nucleus. To overcome this problem, in 1994 Bloch⁹⁰ proposed an approach based on the true all electron Kohn Sham single particle wave function. However, this approach suffers from ghost states arising, which causes difficulties in the construction of PAW datasets for a number of elements.⁹¹ With the view to circumvent this problem, in 1999 Kresse⁹² modified slightly the PAW total energy functional. In this section, we are going to present a brief overview of the PAW method and Plane Waves (PW) basis set.

2.6.1 PAW Method

The PAW technique allows the DFT calculations to be performed with greater computational efficiency. This method is based on a linear transformation $\hat{T}$, which uses an pseudo wave function $|\tilde{\psi}_n\rangle$ to map the true all electron Kohn-Sham single particle wave function,

$$|\psi_n\rangle = \hat{T}|\tilde{\psi}_n\rangle, \quad (2.86)$$

where n is a quantum label for band index, spin, and $\vec{k}$ vector.

Applying this transformation to the KS hamiltonian $\hat{H}_{KS}$, one can get the ground state for a smooth wave function,

$$\hat{T}^\dagger \hat{H}_{KS} \hat{T} |\tilde{\psi}_n\rangle = \epsilon_n \hat{T}^\dagger \hat{T} |\tilde{\psi}_n\rangle, \quad (2.87)$$

where $\hat{H}_{KS}$ is the term between parentheses on the left side of Eq.(2.41). To define $\hat{T}$, we must take into account that the true wave functions are already smooth beyond a certain distance from the core. Thus, $\hat{T}$ must only modify the wave function close to the nuclei. For this reason we define,

$$\hat{T} = \mathbb{1} + \sum_b \hat{T}^b, \quad (2.88)$$

where b is a label for each atomic species, $\hat{T}^b$ is an atom centred operator, which acts only inside the augmentation region $|\vec{r} - \vec{R}^b| < r_c^b$. The cut off radii r_c^b is defined in such way that there is no overlap among the augmentation spheres.

Inside the augmentation spheres the true wave function $|\psi_n\rangle$ is expanded in terms of partial waves $|\varphi_i^b\rangle$, where for each $|\varphi_i^b\rangle$ there exists a corresponding auxiliary smooth partial wave $|\tilde{\varphi}_i^b\rangle$, such that they must satisfy the following relationship,

$$|\varphi_i^b\rangle = (\mathbb{1} + \hat{T}^b)|\tilde{\varphi}_i^b\rangle \leftrightarrow \hat{T}^b|\tilde{\varphi}_i^b\rangle = |\varphi_i^b\rangle - |\tilde{\varphi}_i^b\rangle. \quad (2.89)$$

The above requirement defines the transformation $\hat{T}$ in terms of $|\varphi_i^b\rangle$ and $|\tilde{\varphi}_i^b\rangle$. As $\hat{T}^b$ is only defined inside the augmentation region $|\vec{r} - \vec{R}^b| < r_c^b$, then outside of this limit each partial wave and its associated auxiliary smooth partial wave must be the equal, i.e., $|\varphi_i^b\rangle = |\tilde{\varphi}_i^b\rangle$.

The construction of $|\tilde{\varphi}_i^b\rangle$ must form a complete set inside the augmentation region. Thus, the smooth wave functions can be expanded as,

$$|\tilde{\psi}_n\rangle = \sum_i \gamma_{n,i}^b |\tilde{\varphi}_i^b\rangle, \quad (2.90)$$

where the expansion coefficients $\gamma_{n,i}^b$ are to be determined. Once $|\varphi_i^b\rangle = \hat{T}|\tilde{\varphi}_i^b\rangle$, we realize that the following expansion inside the augmentation region,

$$|\psi_n\rangle = \hat{T}|\tilde{\psi}_n\rangle = \sum_i \gamma_{n,i}^b |\varphi_i^b\rangle, \quad (2.91)$$

exhibit the same coefficients $\gamma_{n,i}^b$. Since $\hat{T}$ should be linear, the expansion coefficients $\gamma_{n,i}^b$ can be determined as scalar products of the smooth wave function $|\tilde{\psi}_n\rangle$, that is,

$$\gamma_{n,i}^b = \langle \tilde{p}_i^b | \tilde{\psi}_n \rangle = \int \tilde{p}_i^{*b}(\vec{r} - \vec{R}^b) \tilde{\psi}_n d\vec{r}, \quad (2.92)$$

where $|\tilde{p}_i^b\rangle$ are localized functions termed smooth projector functions. As mentioned above, overlap between the augmentation regions are not allowed, then we expect the smooth wave function, $|\tilde{\psi}_n\rangle = \sum_i |\tilde{\varphi}_i^b\rangle \langle \tilde{p}_i^b | \tilde{\psi}_n \rangle$ to reduces to $|\tilde{\psi}_n\rangle$ itself in the limit $|\vec{r} - \vec{R}^b| < r_c^b$. Thus, $|\tilde{\varphi}_i^b\rangle$ and the projectors must satisfy the completeness relation,

$$\begin{aligned} \sum_i |\tilde{\varphi}_i^b\rangle \langle \tilde{p}_i^b| &= \mathbb{1} \\ \langle \tilde{p}_i^b | \tilde{\varphi}_j^b \rangle &= \delta_{i,j} \end{aligned} \quad (2.93)$$

Now we have all elements to define the $\hat{T}$ operator. Using Eq. (2.93) combined with Eq. (2.89) we arrive at,

$$\hat{T}^b = \hat{T}^b \sum_i |\tilde{\varphi}_i^b\rangle \langle \tilde{p}_i^b| = \sum_i \hat{T}^b (|\varphi_i^b\rangle - |\tilde{\varphi}_i^b\rangle) \langle \tilde{p}_i^b|, \quad (2.94)$$

then the final form for the $\hat{T}$ operator is written as,

$$\hat{T} = \mathbb{1} + \sum_{b,i} \left(|\varphi_i^b\rangle - |\tilde{\varphi}_i^b\rangle \right) \langle \tilde{p}_i^b|, \quad (2.95)$$

From the above equation is easy to see that the full wavefunction $|\psi_n\rangle$ is given by,

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle - \sum_{b,i} \left(|\varphi_i^b\rangle - |\tilde{\varphi}_i^b\rangle \right) \langle \tilde{p}_i^b | \tilde{\psi}_n \rangle, \quad (2.96)$$

where the pseudo wave function $|\tilde{\psi}_n\rangle$ the variational quantity of the PAW method and is computed by solving the eigenvalue problem in Eq. (2.87). It is expanded in plane waves in the interstitial region as depicted in the Figure 8.

The above relation fixes the oscillations and smooth components of the wave function in a specific parts of the space. The sets of functions that appear in Eq. (2.96) are $|\varphi_i^b\rangle$, $|\tilde{\varphi}_i^b\rangle$ and the projectors $\tilde{p}_i^b$ must be constructed obeying the closure relation in Eq. (2.93). The quantities $|\varphi_i^b\rangle$ are constructed as numerical solutions of the Schrödinger equation for the isolated atom, and used as basis set to build the true wave function $|\psi_n\rangle$, which can conveniently be previously calculated for each atomic specie of the periodic table. The projectors connect auxiliary smooth partial waves from the smooth wave function $|\tilde{\psi}_n\rangle$ with true wave function $|\psi_n\rangle$. Figure 8 shows where each function of the PAW methods resides in the interstitial and augmentation regions.

Figure 8 – Schematic representation for the augmentation (orange), and interstitial (green) regions with the existence conditions for $|\tilde{\varphi}_i^b\rangle$, $|\varphi_i^b\rangle$, and $|\tilde{p}_j^b\rangle$. The interstitial region is expanded in terms of plane waves.

Source: By the author

2.7 Plane Waves (PW)

The solution of the Schrödinger equation for periodic systems, e.g., solids, is achieved via Bloch's theorem, which states that the wave function of an electron within a

periodic potential may be expressed as,

$$\psi(\vec{r})_{n,\vec{k}} \equiv \psi_{n,\vec{k}} = u_n(\vec{r}) \exp(i\vec{k} \cdot \vec{r}), \quad (2.97)$$

where $\exp(i\vec{k} \cdot \vec{r})$ is a phase factor and $u_n(\vec{r})$ represents the periodicity of the system that should satisfy $u_n(\vec{r}) = u_n(\vec{r} + \vec{L})$, here $\vec{L}$ is a unit cell vector, n is the band index, and $\vec{k}$ is a wave-vector confined to the first Brillouin Zone (BZ). Expanding $u_n(\vec{r})$ in terms of a Fourier series,

$$u_n(\vec{r}) = \sum_{\vec{G}=0}^{\infty} C_{n,\vec{G}} \exp\{i\vec{G} \cdot \vec{r}\}, \quad (2.98)$$

where $\vec{G}$ has to satisfy the identity $\exp(i\vec{G} \cdot \vec{R}_j) = 1$, i.e., $\vec{G} \cdot \vec{a}_j = 2\pi m$, with m and $(j = 1, 2, 3)$ being integer numbers. It means that, $\vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$, where $\vec{b}_j$'s ($\vec{b}_i$'s) are the real (reciprocal) lattice vectors, respectively. Thus, the wave function may therefore be written as a linear combination of PW,

$$\psi_{n,\vec{k}} = \frac{\exp\{i\vec{k} \cdot \vec{r}\}}{\sqrt{\Omega}} \sum_{\vec{G}=0}^{\infty} C_{\vec{k}} \exp\{i\vec{G} \cdot \vec{r}\}, \quad (2.99)$$

here Ω is the volume of the unit cell.

The above equation introduces naturally the PW basis set, written on this basis set, the Schrödinger equation is reduced to the matrix eigenvalue problem

$$\sum_{\vec{G}'} \left(\frac{1}{2} |\vec{k} + \vec{G}|^2 \delta_{\vec{G},\vec{G}'} + V_{eff}(\vec{G} - \vec{G}') \right) C_{j\vec{k}}(\vec{G}') = \epsilon_{j\vec{k}} C_{j\vec{k}}(\vec{G}), \quad (2.100)$$

where $V_{eff}(\vec{G} - \vec{G}')$ are the Fourier coefficients of v_{eff} .

Bloch's theorem implies that is necessary for an infinite number of PW to represent the true wave function with absolute precision. However, the Fourier coefficients $C_{\vec{k}}(\vec{G})$ of a given wave decrease with increasing $|\vec{k} + \vec{G}|$. In practice, the expansion must be truncated. This may be achieved by adopting a cut off energy E_{cut} for the PW, such that only the PWs satisfying the condition $\frac{1}{2} |\vec{k} + \vec{G}|^2 \leq E_{cut}$ are taken into account in the Eq.(2.99).

2.8 Bader Analysis of Charge Density

The partial charge for atoms, molecules, and solids can be estimated by different methods. The method, which is used in this work was developed by R. Bader.⁹³

The partial charge for atoms, molecules, and solids can be simulated in many different ways. Here we are using the Bader analysis. Its concept is very intuitive and is based on the idea of dividing the space into volumes and then computing the integrals of the charge density over these volumes. Each one of these volumes encloses an atom by a surface $S(\vec{r})$ and must satisfy the zero flux surfaces $S(\vec{r})$ condition

$$\nabla \rho(\vec{r}) \cdot \hat{n}(\vec{r}) = 0, \quad (2.101)$$

where $\hat{n}(\vec{r})$ is the unit normal vector to the surface $S(\vec{r})$.

Essentially the Bader analysis divides a molecule or solid into atoms based on the charge density ρ . The Bader charge for each atom is calculated by,

$$Q^{Bader} = \int_{V_s} \rho(\vec{r}) dV, \quad (2.102)$$

V_s is the volume enclosed by the surface $S(\vec{r})$.

2.9 Vienna ab initio simulation package (VASP)

In the previous sections, we had our theoretical framework which was connected through the VASP code. In this section we describe the computational details involved in the calculations.

The generalized gradient approximation, with the exchange correlation functional by Perdew-Burke-Erzerhof (PBE)⁶⁹ was used for all calculations performed here. We have solved the Kohn-Sham equations with the all-electron projected augmented wave (PAW) method,^{90,92} as implemented in VASP code (*Vienna Ab-initio Simulation Package*),⁹⁴ which uses plane waves under periodic boundary conditions as its basis set. We have considered the PAW projectors, as provided within VASP,⁹² employing for C = $2s^2 2p^2$, Ni = $[\text{Ar}] 3d^8 4s^2$, Pd = $[\text{Kr}] 4d^{10}$, and Pt = $[\text{Xe}] 4f^{14} 5d^9 6s^1$ valence electrons. To obtain the equilibrium volumes, we have calculated the stress tensor and minimized the stress and atomic forces.

To take account the magnetic character of the metallic atoms, all calculations used Ni, Pd, and Pt atoms, and have been performed with the spin-polarized approach. The k-point sampling for the Brillouin zone was performed using the Monkhorst-Pack scheme.⁹⁵ To improve the self-consistent electronic convergence, we employed a Gaussian smearing with small value. In next chapters, we are going to introduce a section termed as, Computational Details, to give more information with respect to the convergence procedures involved in each project.

3 GRAPHITE

It has long been known that the intralayer chemical binding in graphite is much stronger than the interlayer vdW interaction.^{3–5} The short bond lengths resulting from the intralayer binding are well described by density functional theory (DFT)^{18,19} in the Perdew-Burke-Erzerhof (PBE)⁶⁹ generalized-gradient approximation (GGA)⁶⁸ for the exchange-correlation (XC) functional. The binding between layers is governed by nonlocal long-range dispersion forces,³ which are poorly described by DFT within local²⁰ or semilocal XC functionals.^{96,97} *Ab initio* calculations using multireference configuration interaction with a double-zeta plus polarization basis set have yielded 1.36 eV per C atom as the correlation-energy contribution to the cohesive energy of a graphite layer.⁹⁸ Alternative numerical procedures have also been employed, such as the quantum Monte Carlo (QMC)^{99,100} method and random-phase approximation (RPA).^{101,102}

For example, QMC calculations by Spanu *et al.*¹⁰³ have yielded $E_b = -56$ meV/atom for graphite AB, close to the experimental value reported by Zacharia *et al.* (52 meV/atom).⁵ RPA-based methods can be combined with DFT computations to exploit the translational symmetry of the system. A good example is the study by Lèbegue *et al.*,¹⁰² which found $E_b = -48$ meV/atom and comparably accurate elastic constants. Unfortunately, both QMC and RPA calculations require enormous computational efforts, which limits the range of applications. Few periodic layered materials are within the reach of either method.

To overcome these problems, different GGA functionals combined with nonlocal correlations or direct functionals for the vdW nonlocal correlation^{79,104–106} have recently been proposed. The resulting binding energies for graphite^{105,106} are significantly improved with respect to the binding energies from PBE or hybrid meta-GGA calculations, which are too small to satisfy stability requirements.^{79,104,105} To date, several corrections to plain DFT have been proposed to accurately describe the vdW corrections at lower computational cost, namely the Tkatchenko-Scheffler (TS) correction without⁷ and with⁸⁵ self-consistent screening (TS+SCS), and the D2 and D3 corrections put forward by Grimme.^{79,82} Gobre and Tkatchenko employed the TS and TS+SCS corrections, as implemented in the Fritz-Haber Institute *ab-initio* molecular simulation (FHI-aims) package,¹⁰⁷ to study vdW interactions in single- and multilayer graphene, fullerenes, single-wall carbon nanotubes and graphene nanoribbons.²⁷ They found that the TS+SCS correction yields good results for the interlayer binding energies and reliably describes rare-gas solids, the acid test of vdW corrections.

In a parallel study, Grimme *et al.* considered numerous systems and found that the D3 correction constitutes an improvement over D2, for layered materials in particular.⁷⁹ Recently, Bučko *et al.* applied the TS, TS+SCS, and D2 corrections to the PBE functional,

as implemented in the Vienna *Ab-initio* Simulation Package (VASP),^{94,108} to study a wide range of systems, including layered materials,⁸⁰ molecular solids,⁸⁷ and ionic surfaces.⁸⁹ For graphite, the target of the present work, Bučko *et al.*,⁸⁰ Grimme *et al.*,⁷⁹ and Gobre and Tkatchenko²⁷ focused on the interlayer binding energy and bulk modulus. Finer details, such as the curvature of the interlayer binding energy and the splitting between levels in the band structure, were not discussed in those studies, even though they impose demanding checks on the accuracy resulting from vdW corrections. Furthermore, the D3 correction and its variants with different damping functions have not been applied to graphite.

To compare the performance of different vdW corrections (TS, TS+SCS, D2, D3, D3-BJ), we have calculated the lattice parameters, bulk modulus, cohesive energy, interlayer binding energy, curvature of the interlayer binding energy (second and third derivatives), and band structure of graphite. In addition, we have given special attention to a feature of the computed band structures, the π_z -splitting at the Γ -point. The most important results are summarized in Table 1 along with theoretical and experimental findings. We have only included previous theoretical studies for which the graphite properties were calculated at the equilibrium lattice constants optimized by total energy calculations. As benchmarks, we have chosen the precise experimental data for the equilibrium geometry and cohesive energy,^{109–113} except for the interlayer binding energy, for which we use the theoretical, high-level RPA results.¹⁰²

3.1 Computational details and Convergence tests

As depicted in Figure 9 the Bernal graphite contains four carbon atoms per unit cell, crystallized in a hexagonal lattice. The experimental lattice constants are $a_{exp} = 2.46 \text{ \AA}$ (planar) and $c_{exp} = 6.71 \text{ \AA}$ (interlayer).¹⁰⁹ To optimize the agreement between numerical results and experimental data for the bulk properties while minimizing computational cost, we have performed convergence tests using stress tensor calculations to find the equilibrium volume, further detail about the stress tensor formalism can be found in reference.¹¹⁴ More specifically, the tests determined the best cutoff and total number of k -points or mesh in the Brillouin zone. Our calculations were carried out with PBE, PBE+TS, and PBE+TS+SCS.

Figure 11 presents relative deviations of the computed planar and interlayer lattice constants from the experimental values as functions of the cutoff energy [panel (a)] and of the k -mesh size [panel (b)] for PBE, PBE with TS van der Waals corrections, and PBE+TS+SCS with TS+SCS van der Waals corrections. Comparison among the vertical scales on the three bottom plots in the two panels shows that the van der Waals corrections stabilize the computation of the lattice parameter c , a first indication that, by itself, the PBE functional is inadequate to describe interlayer binding. From a more practical viewpoint, given the convergence at high energies in both panels, we adopted a 900 eV

Figure 9 – Crystalline structure of Bernal graphite with ABA stacking. The primitive unit cell is hexagonal with dimensions $a = 2.46 \text{ \AA}$ and $a = 6.71 \text{ \AA}$.
Source: By the author

cutoff and a $21 \times 21 \times 7 = 3087$ -point k -mesh in our computations of the stress tensor.

The calculated equilibrium lattice parameters, a_0 and c_0 are compared with experimental data in Table 1. While the planar parameter a_0 is practically independent of the van der Waals corrections, the interlayer parameter resulting from the PBE computation is in striking disagreement with the experimental value. The TS and TS+SCS corrections yield substantial improvement. A deviation of less than 1% from the former van der Waals correction seems fortuitously small.

3.2 Equilibrium lattice parameters

Table 1 lists the equilibrium lattice parameters a_0 (in the graphite plane) and c_0 (perpendicular to the graphite plane), compared with experimental and previous theoretical results. As expected, the PBE estimate for a_0 is accurate, only 0.16% above the experimental value. Another expected result, given the attractive nature of the interactions, is that the vdW corrections reduce a_0 . In particular, the D2, D3, D3-BJ, and TS+SCS vdW corrections bring a_0 into closer agreement with the experimental result: the relative error ranges from -0.04% to 0.08% . By contrast, the absolute value of the -0.16% relative deviation resulting from the TS computation equals that of the PBE computation.

To compute c_0 , we have fitted the c -dependent binding energies to Chebyshev polynomials and identified the separation at which the first derivative equals zero, as detailed in Appendix A. As reported in previous studies,^{79,80,87,102,103} the PBE functional yields a result larger than the experimental value, a deviation commonly attributed to the absence of non-local long-range correlations in the PBE functional. The local density approximation (LDA) yields $c_0 = 6.57 \text{ \AA}$, which underestimates the lattice parameter by 2%.²⁰ The vdW corrections provide substantial improvement over the PBE estimate. The

Figure 10 – Convergence test for the cutoff energy and total number of k -points in the Brillouin zone. The filled circles represent the relative deviations from the experimental values for the planar and interlayer lattice parameters a and c , respectively. The solid lines are guides to the eye. (a) Relative deviations as functions of the cutoff energy. Each plot corresponds to the indicated combination of the PBE exchange-correlation functional with a van der Waals correction and with the following k mesh: $21 \times 21 \times 5$ (PBE only), $21 \times 21 \times 7$ (PBE+TS), and $21 \times 21 \times 7$ (PBE+TS+SCS). (b) Relative deviations as functions of the number of k points at fixed cutoff energy (900 eV), for the indicated combinations of the PBE functional with van der Waals corrections. Source: By the author

resulting relative errors are 3.9 % (D2), -3.8 % (D3), -0.5 % (D3-BJ), 0.6 % (TS), and 1.1 % (TS+SCS). Only the D3-BJ, TS, and TS+SCS corrections yield a_0 and c_0 estimates under the 2.0 % relative-error limit, typical of local and semilocal-functional computations for metals and semiconductors.¹¹⁵

3.3 Cohesive energy

From the equilibrium total energy and C free-atom total energy, we have calculated the graphite cohesive energy. PBE yields -7.85 eV/atom, 6.5 % larger than the experimental value (-7.37 eV/atom^{113,118}), a result whose accuracy is comparable to that of PBE cohesive-energy computations for metals and semiconductors.^{76,119,120} Our estimate deviates from previous DFT results, -7.55 eV/atom,¹²¹ and -7.34 eV/atom.¹²² Part of the error is due to the standard PAW C projector in our computation, which yields less accurate

Table 1 – Bulk properties of graphite: equilibrium lattice parameters a_0 and c_0 , bulk modulus B_0 , bulk modulus and its first derivative B'_0 , curvature C_{33} and curvature derivative C'_{33} of the interlayer binding energy, cohesive energy E_{coh} , and the interlayer binding energy E_b computed with distinct dispersion corrections. For comparison, the last row lists the average experimental results and the only available theoretical estimate for C_{33} .

Procedure	a_0 (Å)	c_0 (Å)	B_0 (GPa)	B'_0	C_{33} (GPa)	$-C'_{33}$ (GPa)	$-E_{\text{coh}}$ (eV/atom)	$-E_b$ (meV/atom)	Refs.
PBE	2.466	8.755	1.6	15.70	0.55	4	7.85	1.2	This work
PBE+D2	2.461	6.444	40.2	13.02	22.04	178	7.96	55.04	This work
PBE+D3	2.464	6.965	23.8	4.81	13.09	90	7.93	47.30	This work
PBE+D3-BJ	2.464	6.745	30.1	10.13	17.16	115	7.99	52.36	This work
PBE+TS	2.458	6.665	56.1	10.05	34.61	188	7.98	81.34	This work
PBE+TS+SCS	2.461	6.633	40.5	12.77	26.79	184	7.97	53.76	This work
RPA	2.46	6.68			36			48	102
ACFD-RPA	2.46	6.68				530			112
QMC	2.46	6.852						56	103
LDA	2.46	6.66			29.5			24	102
LDA	2.46	6.75			29.9			24.78	105
PBE	2.46	7.809			1.2			1.05	105
PBE	2.47	8.84	1				7.99		87
PBE	2.466	9.62	0.8					0.6	104
revB86B	2.47	6.72						55.17	106
C09 (vdw)	2.47	6.54						70.67	106
cx13 (vdw)	2.47	6.65						60.42	106
optPBE (vdW)	2.47	6.98						59.63	106
optB88 (vdW)	2.47	6.76						65.94	106
optB86B(vdW)	2.47	6.72						65.15	106
vdW-DF	2.47	7.52	12		13			24	116
DF1	2.46	7.199			23.0			49.65	105
DF2	2.46	6.944			33.5			48.94	105
DF1(PBE)	2.46	6.892			35.6			67.44	105
VV10	2.46	6.777			46.1			71.11	105
PBE+D2	2.46	6.740			44.0			55.56	105
PBE+D2	2.46	6.45	38				8.10		87
PBE+D2	2.466	6.43	46.5					54.1	104
PBE+TS	2.46	6.68	59					82	80
PBE+TS	2.46	6.604						87.83	27
PBE+TS+SCS	2.46	6.604						50.54	27
PBE+TS+SCS	2.46	6.75	43					55	80
PBE+TS+SCS+MBD	2.46	6.70						48	81
Experiment	2.46							52±5	5
Experiment	2.462	6.707	35.8±1.6						109
Experiment	2.463	6.712			38.7				111
Experiment								31±2	6
Experiment	2.46	6.70						35	4
Experiment								42.64	3
Experiment	2.603	6.706	33.8	8.9					110
Experiment							7.37		113
Experiment					36.5				117
Reference datum	2.462	6.707	35.6	8.9	37.6	530	7.37	48	102, 109–113

Source: By the author

total energies than the hard PAW C projectors, i.e., about 0.10 eV/atom. Nonetheless, the chief contribution to the error in the calculated cohesive energy comes from overbinding in the intralayer interactions, which is a shortcoming of the PBE calculations that the vdW corrections cannot remedy. In fact, given their attractive contribution to the total energy, all the vdW corrections magnify the relative error in the cohesive energy. With the D3-BJ correction, for instance, the relative error grows from 6.5 % to 8.4 %.

Figure 11 – Total energy per unit cell (four atoms) as a function of volume, for graphite. The blue open circles, red open squares, black open diamonds, magenta open triangles, green solid stars, and yellow solid hexagons represent the PBE, PBE+TS, PBE+TS+SCS, D2, D3 and D3-BJ calculations, respectively. Near each minimum, a solid line fits Eq. (3.2) to the computed energies. The expanded vertical scale in the inset brings out the shallow minimum of the PBE curve.

Source: By the author

3.4 Interlayer binding energy

One of the key energetic properties of graphite is the binding energy between the honeycomb layers, i.e., the interlayer binding energy,^{80,105,105,116} which differs from the exfoliation energy³ (i.e., the energy required to remove one graphite sheet from a semi-infinite film), or the interaction energy of two graphene sheets.⁷⁹ Accordingly, we have computed the interlayer binding energy per atom E_b as a function of the interlayer separation ($c/2$) at fixed $a = 2.466 \text{ \AA}$. The interlayer binding energy is defined by the equation

$$E_b(c) = -\frac{E_{tot}(c) - E_{tot}(c = \infty)}{4}, \quad (3.1)$$

where $E_{tot}(c)$ is the total energy.

We have computed the right-hand side of Eq. (4.6) in the interval $c_{exp}/2 \leq c \leq 3 \times c_{exp}$, with $3c_{exp} = 20.1 \text{ \AA}$ substituted for $c = \infty$. Figure 12 shows the resulting interlayer binding energies for the vdW corrections under study, compared to the experimental data. For visual convenience, the RPA binding energies¹⁰² (blue open circles) are shown in the inset, compared with the PBE+TS+SCS (black open diamonds) and experimental binding energies (cyan open circles). Table 1 compares the binding energy at the equilibrium distance c_0 for each computational approach with the experimental data, which spread

Figure 12 – Graphite interlayer binding energy as a function of the interlayer lattice parameter c . Shown are the $\bar{E}_b(c)$'s calculated with PBE+D2 (magenta open triangles), PBE+D3 (green solid stars), PBE+D3-BJ (yellow solid hexagons), PBE+TS (red open squares), and PBE+TS+SCS (black open diamonds), and the experimental binding energies (cyan filled circle). The solid lines represent the Chebyshev interpolation described in Appendix A. The inset compares the PBE+TS+SCS (black open diamonds) and RPA (open blue circles) binding energies to the experimental data (cyan open circle). Source: By the author

from $-31(2)$ meV/atom to $-52(5)$ meV/atom.^{3–6} The RPA¹⁰² and QMC¹⁰³ results are closer to the upper limit, $-52(5)$ meV/atom. The D2, D3, D3-BJ, TS, and TS+SCS corrections overestimate the reference binding energy (-48 meV/atom by 14.7 %, 1.45 %, 9.08 %, 69.45 %, and 12.01 %, respectively). Thus, except for the TS method, the vdW corrections yield great improvement over the PBE functional (1.2 meV/atom). Comparison with the high-level RPA results and with the experimental data shows that the D3 correction yields the smallest error.

3.5 Bulk modulus and its first derivative

Another ground-state property for comparison with experimental data is the equilibrium curvature of the total energy as a function of volume, i.e., the bulk modulus B_0 and its first derivative B'_0 . To compute the volume dependence of the total energy,

we have considered a set of equally spaced volumes, with a and c optimised for each of these. To calculate B_0 and B'_0 , we have fitted the symbols representing the calculated total energies in Figure 11 with the Birch-Murnaghan equation of state (solid lines),¹²³

$$E_{tot}(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \gamma^3 B'_0 - \gamma^2 [4\gamma - 2] \right\}, \quad (3.2)$$

where $\gamma = (V_0/V)^{2/3} - 1$, $B'_0 = (\partial B/\partial P)_{V_0}$, and V_0 indicates the equilibrium volume. Table 1 lists the resulting B_0 and B'_0 . The experimental results for B_0 are spread in the interval from 33.8 to 37.4 GPa^{109–111,124} (average 35.6 GPa), while the only available experimental datum for B'_0 is 8.9.¹¹⁰

The PBE computation yields $B_0 = 1.6$ GPa, far below the experimental range obtained from room-temperature measurements. Inspection of the blue open circles in Figure 11 traces the poor agreement back to the unreasonable flatness of the potential-energy surface resulting from the PBE computation. The vdW corrections clearly improve the results, but the agreement is imperfect. The D3 ($B_0 = 23.8$ GPa, -33.2% deviation), and D3-BJ ($B_0 = 30.1$ GPa, -15.5% deviation) results underestimate the average experimental bulk modulus, while the D2 ($B_0 = 40.2$ GPa, 12.9% deviation), TS ($B_0 = 56.1$ GPa, 57.6% deviation), and TS+SCS ($B_0 = 40.5$ GPa, 13.8% deviation) results overestimate it. The PBE+D3-BJ, PBE+D2 and PBE+TS+SCS functionals yield bulk moduli in best agreement with the average experimental value.

When comparison with experimental data, the PBE+D3 correction underestimates B'_0 , while the other functionals overestimate it. The PBE estimate, $B'_0 = 15.7$, overshoots the experimental value by 76.4% . The vdW corrections improve the agreement, but the results are still far from the experimental value: D3 yields $B'_0 = 4.8$, 46.0% below, D2 yields $B'_0 = 13.0$, 46.0% above, D3-BJ yields $B'_0 = 10.1$, 13.5% below, PBE+TS yields $B'_0 = 10.0$, 12.4% above, and PBE+TS+SCS yields $B'_0 = 12.7$, -42.7% above the measured derivative. The PBE+D3-BJ and PBE+TS functionals yield the B'_0 value in best agreement with the experiment.

3.6 Curvature of the interlayer binding energy

We now try to identify the source of the discrepancies between the calculated bulk moduli and the experimental data. To this end, we recall that the bulk modulus is related to elastic constants C_{11} , C_{12} , C_{13} , and C_{33} by the following equation¹²⁵:

$$B_0 = \frac{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}{(C_{11} + C_{12}) + 2C_{33} - 4C_{13}}. \quad (3.3)$$

We will here focus our discussion on the second and third order elastic constants C_{33} and C_{333} , respectively, which are chiefly dependent on the interlayer interactions. The elastic

constants can be obtained from the equalities

$$C_{33} = \frac{c_0^2}{V_0} \left. \frac{\partial^2 E_b(a, c)}{\partial c^2} \right|_{c_0} = c_0 \left. \frac{d^2 E_b(c)}{dc^2} \right|_{c_0}, \quad (3.4)$$

and

$$C_{333} = \frac{c_0^3}{2V_0} \left. \frac{\partial^3 E_b(a, c)}{\partial c^3} \right|_{c_0} = \frac{c_0^2}{2} \left. \frac{d^3 E_b(c)}{dc^3} \right|_{c_0}. \quad (3.5)$$

Although the third and second derivatives on the right-hand side might be estimated from finite-difference formulas, small oscillations superimposed on the minima in Figure 12 would introduce relatively large numerical deviations. We therefore prefer a spectral method, the Chebyshev differentiation procedure detailed in Appendix A. The results are presented in Table 1. For comparison, experimental data for C_{33} are also tabulated, which range from 36.5 GPa to 37.8 GPa.^{111,117}

The TS value for C_{33} is closer to the measured elastic constant than the TS+SCS result, just like the TS value for B_0 is closer to the measured bulk modulus than the TS+SCS result. While it yields more accurate binding energies, screening degrades the TS estimate for the curvature of the potential-energy surface. The D3 and D3-BJ data in Table 1 clearly show that the curvature of the interlayer binding energy critically depends on the damping function. We conclude that the development of more reliable damping functions may warrant better agreement with experimental data. Among the studied vdW corrections, the TS, TS+SCS, and D2, in that order, yield the best estimates for C_{33} . We next compare the C_{333} coefficients from vdW corrections with the RPA result, 530 GPa.¹¹² This value is substantially larger than the $-C_{333}$ resulting from the vdW corrections. The RPA tends to underestimate the binding energy at short distances, a trend that is expected to affect its derivatives in the vicinity of the equilibrium separation. Nonetheless, the resulting deviations are unlikely to account for the sizable discrepancies between the RPA and the vdW results in the $-C_{333}$ column of Table 1. D3, which includes long-range screening, yields the poorest agreement, but even the other corrections come to only third of the RPA value.

3.7 Band structure analysis

As explained in Section 4.8, for given atomic configuration, i.e., for fixed geometry, the vdW corrections simply shift the DFT-PBE total energy. At fixed lattice and atomic parameters, the electron density and the band structure are independent of the E_{tot}^{vdW} . The corrections nevertheless change the equilibrium lattice parameters and hence indirectly affect the band structure. Figure 13 shows the PBE band structures for two lattice structures, namely the equilibrium graphite PBE+TS+SCS structure ($a_0 = 2.466$ Å, $c = 20.1$ Å) and a graphene layer ($a_0 = 2.466$ Å). The two band structures are very similar,

Figure 13 – The band structures of graphene ($a_0 = 2.46 \text{ \AA}$), calculated with the standard PBE functional, and bulk graphite ($a_0 = 2.46 \text{ \AA}$, $c = 20.1 \text{ \AA}$), calculated with the TS+SCS scheme. The symmetries of the most important bands (σ_s , σ_{xy} , π_z) are indicated. Source: By the author

except for differences due to interlayer interactions. For example, the π_z - and σ_s -bands are degenerate in graphene, but the same bands are split at the Γ -point in graphite, due to the interlayer interactions. The very small σ_s splitting depends on intralayer states. By contrast, the π_z -band splitting is substantial (for the PBE+TS+SCS structure, $\Delta\pi_z = 2.14 \text{ eV}$) as one would expect, since the π bands come from the p_z states perpendicular to the honeycomb layers. We therefore discuss the results for the π_z band in more detail.

We have calculated $\Delta\pi_z$ as a function of the interlayer distance for the PBE functional. The solid line in Figure 14 depicts the results. Also shown in the figure are the splittings $\Delta\pi_z$ for the D2, D3, D3-BJ, TS, and TS+SCS structures and the available

Figure 14 – Layer-separation dependence of the π_z -level splitting. The symbols are the results of the indicated computational methods at the equilibrium separations. The solid curve represents the PBE splitting as a function of c . The cyan filled circle and square show the experimental splittings at the experimental equilibrium separation.
Source: By the author

experimental data.^{126,127} The $\Delta\pi_z$ resulting from the vdW-corrected calculations vary from 0.56 eV at $c = 8.32$ Å to 2.38 eV at $c = 6.45$ Å). Experimentally, at $c = c_0$, $\Delta\pi_z = 2.4$ eV¹²⁶ or $\Delta\pi_z = 2.6$ eV.¹²⁷

The solid curve in Figure 14 is very well reproduced by the fit $\Delta\pi_z = A_1 \exp(-B_1 c)$ with $A_1 = 436.74$ eV and $B_1 = 0.76$ Å⁻¹. This decay of the π_z -band splitting mirrors the exponential reduction of the overlap between carbon orbitals in neighboring layers as the layer separation grows. The blue open circle representing the PBE result in Figure 14 lies far from the experimental points, because the functional manifestly overestimates the interlayer separation. The vdW corrections improve the agreement. For the PBE+TS+SCS vdW correction, in particular, the relative error is 10.6 %. Nonetheless, even at the experimental distance $c_0 = 6.707$ Å, the solid curve lies significantly below the experimental splittings. The plot in Figure 14 therefore shows that the vdW corrections are insufficient to determine $\Delta\pi_z$ with less than 10 % deviation. The XC functional will have to be improved before more accurate description of the graphite band structure can be achieved.

For the experimental lattices constants $c_0 = 6.707$ Å and $a_0 = 2.462$ Å, the hybrid functional PBE0 yields the band splitting $\Delta\pi_z = 2.20$ eV. Since $\Delta\pi_z$ at fixed lattice parameters is insensitive to the vdW corrections, we can see that this computationally more demanding functional offers no significant improvement upon the PBE estimate for the band splitting.

3.8 Graphite: Conclusions

We have studied the properties of graphite in the DFT-PBE framework with several vdW corrections, namely D2, D3, D3-BJ, TS, and TS+SCS. We have computed several properties for which experimental results are available: the equilibrium lattice parameters a_0 and c_0 , cohesive energy E_{coh} , interlayer binding energy E_b , bulk modulus B_0 , curvature of the interlayer binding energy C_{33} , C_{333} , and π_z -splitting at the Γ -point. The TS+SCS correction, which self-consistently accounts for dynamic screening, yields results in fair to good agreement with the experimental data.

Nonetheless, even the TS+SCS correction leaves room for improvement, a conclusion that is highlighted by the 29% relative error in the calculated elastic constant C_{33} and the striking disagreement with the RPA result for C_{333} . The other studied vdW corrections (D2, D3, D3-BJ, and TS) yield relatively large disagreement with the experimental data for one (D3-BJ), or two (D2, D3, TS) of the selected properties. In practical terms, our results and analysis indicate that the TS+SCS correction is the preferred method for the vdW corrections, but in case that convergence or computational cost be a problem, we recommend the D3-BJ correction. We have also shown that the damping function controls the accuracy of the results for the elastic constant C_{33} .

4 GRAPHENE

Various experimental approaches have recently yielded several stable TM adatoms, clusters and nanoparticles on Gr sheets.^{33,128–130} The resulting samples have been characterized via X-ray diffraction (XRD) and spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and transmission electron microscopy (TEM).^{129,130} For example, stable Ru and Rh nanoparticles on Gr in the 2 nm to 3 nm range resulted from decomposition of metal carbonyl precursors under rapid microwave irradiation of a graphene suspension in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate.¹²⁸ Another work described the formation of 5 to 40 atom Pt subnanoclusters on Gr nano-sheets, which started with the ethanol reduction of H_2PtCl_6 and yielded compounds containing Pt^{2+} with particle sizes in the 2 nm to 7 nm range. Subsequent immersion in a H_2 atmosphere at 400 °C generated Pt subnano-clusters.¹²⁹ In a morphological study of atomic Co and Fe adsorption on Gr, STM measurements showed that Co monomers adsorb on top.¹³⁰ Unfortunately, displacement of the adatom by the tip defeated the effort to determine the Fe adsorption site.

On the theoretical front, notwithstanding the number of reports, the influence of the Gr support on the properties of the TM clusters is poorly understood. Most DFT investigations of Gr-supported TM clusters have been focused on the structure of TM-atom or small TM_n -cluster adsorption on Gr, with $n = 1 - 4$ or 5 atoms, and $\text{TM} = \text{Co}$,^{37,131} Au ,¹³² Pt ,^{12,13,133} Pd ,^{10,11,134} Pt-Au alloys,⁸ and 3d TM atoms ($\text{TM} = \text{Fe}$, Co , Ni).^{37,131,135,136} The TM-adatom adsorption site on Gr has been found to depend strongly on the TM. For example, 3d adatoms bind on the hollow sites,^{37,131,135} while Pd and Pt adatoms bind on the bridge sites.^{10–13} Rudenko *et. al.*¹³¹ have identified two stable states of Co adatoms on Gr: the high-spin configuration ($3d^7 4s^2$, with $S = 3/2$), which is physisorbed, and the low-spin configuration ($3d^9$, with $S = 1/2$), associated with chemical bonding, i.e., strong orbital hybridization. For small clusters (e. g., Pt), the Pt-Pt binding has been found to be much stronger than the Pt-C binding, so that the cluster structure is preserved upon adsorption on Gr, while the magnetic moments, local spins, orbital moments and magnetic-anisotropy energies of the adsorbed Pt clusters are much smaller than in the gas-phase clusters.¹²

To our knowledge, the cluster-size dependence of structural and adsorption properties has never been systematically studied. In the case of Ni, for instance, only single-atom¹³⁵ and large-cluster ($n = 6 - 9$)⁹ adsorptions have been considered. Moreover, different authors have reported contradictory findings on the cluster structure on Gr sheet. For example, Ji *et. al.*⁸ and Cabria *et al.*¹¹ have found the Pd_2 dimer to bind by one atom, perpendicularly to the Gr sheet, while Thapa *et al.*¹⁰ have shown that each Pd atom binds to a bridge site,

so that the dimer axis is parallel to the sheet.

The findings by Blonski *et al.*¹² and Fampiou *et al.*¹³ on the Pt₂ and Pt₃ structures on Gr are similar, both describing an upright dimer and an upright triangle with one edge parallel to the sheet, respectively. By contrast, their reports on the structure of the Pt₄ cluster are distinct: a bent rhombus was found by Ref.¹² and a trigonal pyramid by Ref.¹³ Only the following larger-size clusters have been investigated: Pd-Au with $n = 7$;¹³⁷ Co,¹³⁸ Pt,¹⁴ Fe, Co, Ni,¹⁶ and MPd₁₂ (M = Fe, Co, Ni, Cu, Zn, Pd),¹⁵ and Au₄₉.¹³⁹

These limitations, complexity, and controversies call for systematic study of TM_{*n*} clusters on Gr sheet, to identify trends and classify the interactions between TM clusters and Gr. Here, we present a density-functional investigation of the structural, adsorption, and magnetic properties of the TM_{*n*} (TM = Ni, Pd, Pt; $n = 1 - 6$) clusters on a Gr monolayer. To accurately describe the effect of van der Waals interactions on the geometry and electronic structure of the studied systems, we add vdW corrections to the ground-state energies.

To probe the interactions we carry out Bader-charge and density-of-states analyses. On the basis of the results, we propose a theoretical model that improves our understanding of the interaction between the TM and graphene atoms.

4.1 Graphene Properties

Here we are going to give a brief introduction to the geometric and electronic properties of Graphene.

Geim and Novoselov used the Scotch Tape method have experimentally isolated a new 2D material termed as Graphene. Their finding is today considered an important step for the development of new electronic devices. Graphene is a stable hexagonal structure formed by a single atomic layer, where each carbon is bound to its nearest neighbors via the sp^2 or σ hybridization. These σ states form the covalent bonds and give rise to the hexagonal shape of Graphene as shows in Figure 15. The carbon atoms have valence of four, with one remaining state. It is called π state and is perpendicular to the hexagonal plane. These π states are responsible for the high mobility on Graphene, because their electrons are weakly bounded and can hop to other carbons.²³

Graphene is composed of a honeycomb arrangement of carbon atoms in two sublattices. In Figure 15 the sublattices are represented in blue and red colors with two carbon atoms per unit cell. The lattice constant is $a = 2.46 \text{ \AA}$ and the interatomic distance between the red and blue carbons is $d \approx 1.42 \text{ \AA}$. In the real space, the structure of the unit cell is generated by the translation of the vectors $\vec{a}_1 = a(\sqrt{3}/2, 1/2)$ and $\vec{a}_2 = a(\sqrt{3}/2, -1/2)$. The atomic positions are $\vec{r}_1 = (0,0)$ and $r_2 = a_1/3 + a_2/2 = d(1/\sqrt{3}, 0)$. In the reciprocal space the vectors are $\vec{b}_1 = 2\pi(1/\sqrt{3}, 1)$ and $\vec{b}_2 = 2\pi(1/\sqrt{3}, -1)$.

Figure 15 – Lattice structure of graphene. (Right) The basis vectors that form the unit cell in the real space are $\vec{a}_1$ and $\vec{a}_2$. (Left) The Brillouin zone defined by the reciprocal vectors $\vec{b}_1$ and $\vec{b}_2$.
Source: By the author

The right side of Figure 15 shows that the Brillouin zone presents some very important high symmetry points: the point is located at the hexagon center with $\vec{k} = 0$ and in the middle of them is the M point. The two inequivalent K and K' are the points where the valence and conduction bands intersect, this is called Dirac point. Around of this point, the electronic spectrum has a conical shape, the so-called Dirac cones. The tight binding Hamiltonian in the nearest neighbors approximation is,

$$H_{Gr} = -t \sum_{\langle i,j \rangle} (a_i^\dagger b_j + \text{H. c.}) \quad (4.1)$$

, where t is the hopping parameter, a_i and b_j are annihilation operators for blue and red sublattices respectively. The resulting energy bands associated with this Hamiltonian are:

$$\epsilon(\vec{k}) = \pm t [1 + 4 \cos^2(k_y a/2) + 4 \cos(k_y a/2) \cos(\sqrt{3} k_x a/2)]^{1/2} \quad (4.2)$$

Eq. (4.2) as depicted in Figure 16 states that the positive and negative bands are symmetric in the vicinity of the Dirac point and allow us to linearise Eq. (4.2) according to,

$$\epsilon(\vec{k}) = \pm v_F |\vec{k}| \quad (4.3)$$

, where v_F is the Fermi-velocity. This linear dispersion relation is the Graphene fingerprint that distinguishes it from other materials.^{25,140}

4.2 Computational Details

Our total energies spin-polarized calculations were computed with a 500 eV plane-wave cutoff, which is 17% higher than the largest recommended energy among the C (414 eV), Ni (357 eV), Pd (251 eV), Pt (249 eV) PAW projectors. To improve the self-consistent electronic convergence, we employed a Gaussian smearing of 0.01 eV. The Brillouin-zone (BZ) integrations for the TM_n clusters in the gas phase used only the

Figure 16 – Valence (positive term of Eq. (4.2)) and conduction (negative term of Eq. (4.2)) band of Graphene. The margenta lines are outlining the cone Dirac.
Source: By the author

Γ -point. For TM_n on Gr, using a (6×6) supercell, the integrations ran over a $3 \times 3 \times 1$ $\mathbf{k}$ -point mesh.

To model the neutral TM_n ($\text{TM} = \text{Ni}, \text{Pd}, \text{Pt}, n = 1 - 6$) clusters in the gas phase, we employed a $16 \text{ \AA}$ cubic box. The resulting separation between clusters was at least $10 \text{ \AA}$, which insured that the interaction between each cluster and its nearest image be negligible.

To study the adsorption properties of the TM_n clusters on Gr, we employed the hexagonal (6×6) supercell with 72 C atoms depicted in Figure 18. Consecutive Gr layers were separated by a $16 \text{ \AA}$ -wide vacuum region. For each TM_n cluster, either supported or unsupported, several atomic configurations were calculated to obtain a putative lowest-energy configuration. Molecular dynamics simulations helped us identify the cation in the putative global minimum configurations (pGMC), an expedient that proved especially important for larger clusters, such as presented in Figure 17 for case of the TM_6 cluters. To determine all equilibrium PBE configurations we required the atomic force on every atom to be smaller than $0.025 \text{ eV/\AA}$, and the total energy to converge within of $1 \times 10^{-6} \text{ eV}$. We re-optimized the lowest-energy configurations with the PBE+TS-SCS functional.

Figure 17 – Molecular dynamics simulations to generate the putative global minimum configurations for Pt_6 . In this optimization procedure, the temperature is varying from 2000 K to 0 K, and all the carbon atoms positions are kept frozen.
Source: By the author

4.3 Effective coordination number and average bond length

Before we start the discussion about the clusters properties, we should introduce the concepts of Effective coordination number (ECN) divided by the number NNN of nearest-neighbors and average bond lengths $d_{av}(\text{\AA})$, which are used to characterize some geometrical properties of the free and adsorbed clusters.

The average ECN and d_{av} for a given cluster with N atoms are calculated by solving the set of equations,

$$\begin{aligned} \text{ECN} &= \frac{1}{N} \sum_{i=1}^N \text{ECN}_i, \quad d_{av} = \frac{1}{N} \sum_{i=1}^N d_{av}^i, \\ \text{ECN}_i &= \sum_j \exp \left[1 - \left(\frac{d_{ij}}{d_{av}^i} \right)^6 \right], \quad d_{av}^i = \frac{\sum_j d_{ij} \exp \left[1 - \left(\frac{d_{ij}}{d_{av}^i} \right)^6 \right]}{\sum_j \exp \left[1 - \left(\frac{d_{ij}}{d_{av}^i} \right)^6 \right]}, \end{aligned} \quad (4.4)$$

where d_{ij} is the distance between atom i and j . d_{av}^i is computed self-consistently within the convergence parameter $|d_{av}^i(\text{new}) - d_{av}^i(\text{old})| < 0.0001$. The smallest bond length between the atom i and all j atoms d_{min}^i is used as start point for d_{av}^i . Self-consistent solution of this cycle yields the ECN_i

The power 6 of the exponential term in Eq. (4.4) is used in order to recover ECNs equal to the standard coordination number for lattices systems like simple cubic, face-centered cubic, and undistorted high-symmetric icosahedral configurations.^{141,142}

Figure 18 – Top view of the graphene (6×6) supercell, where the high-symmetry adsorption sites are indicated, namely, the one-fold top (T), two-fold bridge (B), and six-fold hollow (H) sites.

Source: By the author

4.4 Graphene and Gas-Phase Clusters

4.5 Graphene

For the (6×6) Gr supercell, binding energies of -7.854 eV/atom, -7.857 eV/atom, and -7.858 eV/atom resulted with $2\times 2\times 1$, $3\times 3\times 1$, and $6\times 6\times 1$ $\mathbf{k}$ -point meshes, respectively. We therefore selected the $3\times 3\times 1$ mesh, which provides the best compromise between accuracy and computational cost, for the subsequent calculations.

The computed in-plane lattice parameter showed excellent agreement with experiment. We obtained $a_0 = 2.471$ Å (PBE) for the graphene (1×1) lattice, only 0.37 % larger than the experimental value (2.462 Å).¹⁰⁹ The strong localized covalent C–C sp^2 bond (2.6 eV/bond) makes the equilibrium distance insensitive to the vdW TS-SCS correction. Our result for a_0 is therefore consistent with the values in previous studies.^{58,80,143}

4.6 Gas-Phase Clusters

Figure 20 shows the pGMC's for Ni_n , Pd_n , and Pt_n clusters in the neutral state. The most important higher-energy isomers are described in the Appendix B. Table 2 lists the binding energies per atom E_b , measured from the free atom energies, the effective coordination numbers (ECN), relative to the number of nearest neighbors (NNN),^{142,144} the average weighted bond lengths d_{av} , and the magnetic moments m_T .

For both Ni_n and Pd_n , compact structures, ranging from a perfect triangle for $n = 3$ (ECN = 2 NNN) to a bipyramidal structure for $n = 6$ (ECN = 3.97 NNN) proved to be most stable. By contrast, the studied Pt_n clusters showed strong preference for planar

Figure 19 – Convergence test for the Graphene planar lattice parameter. The filled circles represent the points from DFT using PBE, PBE+TS, and PBE+TS+SCS. The solid lines are square polynomial interpolations.

Source: By the author

structures with smaller ECN's. The same behavior has been reported in small Au_n ($n < 14$) clusters. Given that relativistic effects tend to lower the energy of the $6s$ -orbitals and raise that of the $5d$ electrons, and that the hybridization is stronger in the planar structures, it has been argued that such relativistic effects account for the planar structure of small Au and Pt clusters.^{145–149} More recently, detailed analysis of the planar-to-globular transition in small gold clusters has convincingly questioned that argument.¹⁵⁰ The planar structures for Pt_n ($n = 4 - 6$) in Figure 20, which resulted from nonrelativistic computations, support the conclusions in Ref.¹⁵⁰

Table 2 – Per-atom binding energy $-E_b$, average effective coordination number ECN, relative to the number of nearest-neighbors, average bond length d_{av} , and total magnetic moment m_T of the neutral Ni_n , Pd_n , and Pt_n clusters in the putative global-minimum configurations for gas-phase clusters.

n	$-E_b$ (eV)			ECN (NNN)			d_{av} (Å)			m_T (μ_B)		
	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt
2	1.41	0.66	1.90	1.00	1.00	1.00	2.08	2.46	2.32	2.0	2.0	2.0
3	1.81	1.28	2.46	1.99	2.00	2.00	2.20	2.57	2.48	2.0	0.0	2.0
4	2.14	1.69	2.76	2.93	2.98	2.49	2.27	2.59	2.50	4.0	2.0	2.0
5	2.39	1.82	3.02	3.19	3.60	2.39	2.28	2.63	2.46	6.0	2.0	0.0
6	2.61	1.97	3.27	3.97	3.98	2.89	2.31	2.64	2.47	8.0	2.0	2.0

Source: By the author

Figure 20 – Putative global minimum configurations for the neutral TM_n clusters (TM = Ni, Pd, and Pt; $n = 2 - 6$) in the gas phase, obtained with the PBE functional.
Source: By the author

The average bond lengths and average effective coordination numbers grow with the cluster size n . Inspection of Table 2 reveals the following ordering of average bond lengths: $d_{av}^{\text{Ni}} < d_{av}^{\text{Pt}} < d_{av}^{\text{Pd}}$. To explain this sequence, we have to examine the two inequalities separately. To see that the first inequality mirrors the difference between the atomic radius of Ni and the radii of the other two atoms, we only have to recall that the separation in bulk Ni (3.52 a.u.) is nearly 10% smaller than those in bulk Pd (3.89 a.u.) or Pt (3.92 a.u.).¹¹³

The same argument cannot explain the second inequality, however. The difference between the separations in bulk Pd and Pt is less than 1%. Moreover, the bulk data indicate that Pd is smaller than Pt, not larger. The inequality $d_{av}^{\text{Pt}} < d_{av}^{\text{Pd}}$ must therefore be due to a feature of the clusters not found in the bulk: the planarity of small Pt clusters. Had we considered clusters with larger sizes than the n in Table 2, the Pt structure would have changed to globular, and the ordering in the bulk systems would have prevailed: $d^{\text{Ni}} < d^{\text{Pd}} < d^{\text{Pt}}$. The results for d_{av} in Table 2 are in good agreement with previous results for Ni,^{151,152} Pd,^{153,154} and Pt^{147,149} clusters, with the glaring exception of Ni_5 .^{155–157}

The computed magnetic moments for the Pd_n and Pt_n clusters are equal to $2 \mu_B$, except that the moment vanishes for Pd_3 and Pt_5 . The Ni_n clusters possess larger magnetic moments, as expected, in the $2 - 8 \mu_B$ range. The magnetic moment is proportional to the number of unpaired d electrons and can be labelled by the multiplicity $2S + 1$ of the total spin S . Our calculations show that Ni_n is in a triplet state for $n = 2 - 3$, and in quintet, septet, and nonet states for $n = 4, 5$, and 6 , respectively. Song *et al.*¹⁵¹ report an heptet for $n = 6$, but otherwise our results agree well with their findings. In particular,

the magnetic moments in our computations for $n = 3$ and $n = 5$ agree with theirs, rather than with the earlier computations in Ref.¹⁵⁸

We identified singlet states for Pd $n = 2, 3$ and triplets for $n = 4 - 6$, in disagreement with the Ref.,¹⁵⁹ which found triplets for $n = 2, 5, 6$, and quintuplets for $n = 3, 4$. For Pt $_n$, we identified triplets for $n = 2, 3, 4, 6$, and a singlet for $n = 5$, in disagreement with Kumar *et al.*,¹⁴⁷ notwithstanding the agreement between the structures computed in Ref.¹⁴⁷ and here.

4.7 TM $_n$ Clusters Supported on Graphene

Figure 21 – Lowest-energy DFT-PBE configurations for neutral transition-metal clusters (TM $_n$; TM = Ni, Pd, and Pt; $n = 1 - 6$) on graphene, computed with a (6×6) supercell.
Source: By the author

Table 3 – Structural, energetic, and magnetic properties of transition-metal clusters (TM_n ; $\text{TM} = \text{Ni}, \text{Pd}, \text{and Pt}$; $n = 1 - 6$) on graphene, calculated with the PBE and PBE+TS-SCS functionals. Listed are the most stable adsorption sites, the number N_b of TM atoms bound to the graphene sheet, the adsorption energy $-E_{ad}$ per TM atom, the cohesive energy $-E_{coh}$, the minimum distance d_{min} between the TM_n cluster and the graphene sheet, the changes ΔECN in the average effective coordination number and in the average bond lengths Δd_{av} due to the adsorption on the graphene layer, and total magnetic moment.

TM	n	site	N_b	$-E_{ad}$ (eV)	$-E_{ad}^{\text{vdW}}$ (eV)	$-E_b$ (eV)	$-E_b^{\text{vdW}}$ (eV)	d_{min} (Å)	d_{min}^{vdW} (Å)	ΔECN (%)	$\Delta\text{ECN}^{\text{vdW}}$ (%)	Δd_{av} (%)	$\Delta d_{av}^{\text{vdW}}$ (%)	m_T (μ_B)	m_T^{vdW} (μ_B)
Ni	1	top		1.16	1.43	1.16	1.43	2.02	1.84	0.00		0.00		0.0	0.0
	1	bridge		1.24	1.51	1.24	1.51	2.09	1.93	0.00		0.00		0.0	0.0
	1	hollow		1.47	1.81	1.47	1.81	2.11	2.11	0.00	0.00	0.00	0.00	0.0	0.0
	2	hollow	1	0.52	0.81	1.92	2.22	2.22	2.21	0.00	0.00	+3.37	+2.94	2.0	2.0
	3	bridge	2	0.55	0.83	2.37	2.64	2.05	2.04	+0.50	0.00	+2.27	-2.07	2.0	1.9
	4	bridge	3	0.48	0.73	2.62	2.87	2.03	2.02	+2.39	+1.59	+2.20	+2.21	2.4	0.0
Pd	5	bridge	3	0.29	0.56	2.67	2.95	2.11	2.01	+11.91	-0.12	+2.63	+1.52	4.0	4.0
	6	bridge	3	0.16	0.41	2.77	3.05	2.03	2.02	+0.50	+0.33	+1.30	+1.32	2.2	2.2
	1	hollow		0.92	1.14	0.92	1.14	2.39	2.43	0.00		0.00		0.0	
	1	top		1.10	1.28	1.10	1.28	2.07	2.08	0.00		0.00		0.0	
	1	bridge		1.14	1.34	1.14	1.34	2.09	2.17	0.00	0.00	0.00	0.00	0.0	0.0
						1.09 ^{a,b}		2.22 ^a							
Pt	2	bridge	2	0.73	0.92	1.39	1.59	2.13	2.14	0.00	0.00	+3.47	+8.13	0.0	0.0
						1.28 ^a		2.26 ^a							
						1.10 ^c		1.78 ^c							
						1.29 ^d	2.48 ^d								
	3	bridge	2	0.29	0.46	1.58	1.75	2.23	2.23	0.00	0.00	+4.05	+3.54	1.6	1.6
						1.44 ^a		2.29 ^a							
Pt	4	bridge	2	0.23	0.40	1.93	2.09	2.28	2.27	-1.01	-0.97	+0.39	+0.22	1.8	1.8
						1.84 ^a		2.43 ^a							
	5	bridge	2	0.21	0.35	2.04	2.19	2.22	2.18	-1.67	-0.95	+0.76	+1.02	1.6	1.6
						1.93 ^a		2.43 ^a							
	6	bridge	2	0.14	0.27	2.12	2.25	2.19	2.19	-0.50	+0.74	+0.76	+0.45	1.6	1.6
	1	hollow		0.88	1.19	0.88	1.19	2.40	2.39	0.00		0.00		0.0	
Pt	1	top		1.42	1.68	1.42	1.68	2.02	2.02	0.00		0.00		0.0	
	1	bridge		1.62	1.88	1.62	1.88	2.09	2.09	0.00	0.00	0.00	0.00	0.0	0.0
						1.54 ^e		1.54 ^e		2.11 ^e					
						1.57 ^f				2.10 ^f					
	2	bridge	1	0.48	0.71	2.37	2.60	2.23	2.23	0.00	0.00	+1.72	+1.31	1.8	1.8
				0.48 ^e		2.38 ^e									
Pt	3	bridge	2	0.48	0.73	2.94	3.17	2.23	2.23	-0.50	0.00	0.00	+1.09	0.0	0.0
				0.47 ^e		2.95 ^e									
				0.45 ^f		2.49 ^f									
	4	bridge	2	0.38	0.60	3.12	3.35	2.22	2.21	+19.28	+16.23	+3.20	+3.38	1.8	1.8
				0.31 ^e		3.03 ^e									
				0.28 ^f				2.60 ^f							
Pt	5	bridge-hollow	2	0.31	0.52	3.33	3.55	2.14	2.14	-0.42	-0.54	+1.22	+1.23	2.0	2.0
				0.16 ^e		3.20 ^e									
Pt	6	bridge	2	0.11	0.30	3.38	3.59	2.15	2.15	-0.69	+0.74	+1.61	+1.84	2.0	2.0

^aGGA-PW91;¹¹ ^bGGA-PW91;¹³⁴ ^cGGA-PBE;¹⁰ ^dGGA-PBE;⁸ ^eGGA-PW91;¹² ^fGGA-PBE.¹³

Source: By the author

The lowest energy PBE and PBE+TS-SCS configurations for $\text{TM}_n/\text{graphene}$ are nearly the same, i.e., only minor differences distinguish the computed structures. We hence present only the PBE results in Figure 21. The higher-energy structures and their total energies can be found in the Appendix B. The most important structural parameters, adsorption energies, and magnetic properties for both the PBE and PBE+TS-SCS functionals are summarized in Table 3 and will be discussed in Sec. 4.8.

4.8 Lowest Energy TM_n/Gr Configurations

Our results show that Ni adatoms are most stable at the sixfold hollow sites. By comparison, binding to a single C atom at a top site raises the binding energy by 0.31 eV. In contrast, Pd and Pt adatoms bind to the graphene bridge sites, with the binding to the top and hollow sites being less stable and higher in energy by 0.22 eV and 0.74 eV, respectively.

The energy differences favoring adsorption at the top site, relative to the hollow site, are -0.31 eV, 0.18 eV, and 0.54 eV for Ni, Pd, and Pt, respectively. Larger the adatom radius, the more stable the top site. Our results are in good agreement with previous findings.^{10,12,13,135} In the lowest-energy configurations of the TM_2 diatomic molecules, Ni_2 and Pt_2 bind perpendicularly to the graphene plane on the hollow and bridge sites, respectively. Only one of the two TM atoms binds to the surface. By contrast, Pd_2 binds parallel to the graphene plane with each Pd atom on a bridge site. Our results for Pd_2 agree with the results by Ji *et al.*⁸ and Cabria *et al.*,¹¹ but disagree with another study,¹⁰ which concluded that the Pd_2 stands upright on the graphene sheet. Our results for Pt_2 agree well with those by Blonski *et al.*,¹² and Fampiou *et al.*¹³

For $\text{TM}_3/\text{graphene}$, the triangular clusters bind perpendicularly to the plane, at the bridge sites. More specifically, in the most stable configuration two of the three atoms bind to the plane. Configurations with the triangle flat on the Gr sheet have higher energy.

For $n = 4$, the TM_n tetrahedral clusters bind to the graphene with three, two, or two TM atoms for Ni_4 , Pd_4 , and Pt_4 , respectively. We found the same numbers of bound atoms for Ni_n , Pd_n , and Pt_n with $n = 5$ and $n = 6$. The number of atoms that bind to the graphene sheet therefore remains fixed as the cluster size grows, an invariance that will be discussed below. For Pt_n ($n = 3 - 6$), our results are similar to those reported by Blonski *et al.*¹² For Pd_n ($n = 3 - 6$), there is clear disagreement with the results by Cabria *et al.*¹¹.

For most clusters, the ECN and d_{av} are practically identical to those in the gas-phase clusters, the differences ranging from -1.67% to 2.39% . There are a few exceptions, however. For instance, upon adsorption the ECN's for Ni_5 and Pt_4 rise roughly 12% and 19% , i.e., from 3.19 NNN and 2.49 NNN to 3.57 NNN and 2.97 NNN, respectively. As these examples show, the cluster-graphene interaction tends to enhance the average coordination. Nonetheless, the bond lengths change by less than $0.1 \text{ \AA}$ upon adsorption.

4.9 Adsorption and Binding Energies

To monitor the strength of the cluster-graphene interaction we calculated the adsorption energy per atom E_{ad} and the binding energy per atom E_b . Both E_{ad} and E_b are

measured from the energies of the (infinitely separated) Gr sheet and gas-phase clusters:

$$E_{ad} = \frac{1}{n}(E_{tot}^{TM_n/Gr} - E_{tot}^{Gr} - E_{tot}^{TM_n}) , \quad (4.5)$$

and

$$E_b = \frac{1}{n}(E_{tot}^{TM_n/Gr} - E_{tot}^{Gr} - nE_{tot}^{TM}) , \quad (4.6)$$

where $E_{tot}^{TM_n/Gr}$, E_{tot}^{Gr} , $E_{tot}^{TM_n}$, and E_{tot}^{TM} are the total energies of the TM_n/Gr system, Gr plane, gas-phase TM_n cluster, and TM free atom, respectively, $E_{tot}^{TM_n/Gr}$ and E_{tot}^{Gr} being computed with the same unit cell. Table 3 lists the results.

Figure 22 – Adsorption energies computed from Eq. (4.5) for all the lowest-energy configurations for neutral transition-metal clusters (TM_n ; $TM = Ni, Pd, \text{ and } Pt$; $n = 1 - 6$) on graphene. DFT (balls) and DFT+vdW corrections (triangles).

Source: By the author

In Figure 22 one can observe that with either the PBE or the PBE+vdW functionals, the magnitude $|E_{ad}|$ of the adsorption energy is reduced as the cluster size grows. The PBE computation of the adsorption energy for Ni_n , for instance, went down from 1.47 eV/atom ($n = 1$) to 0.16 eV/atom ($n = 6$). The reduction in the per-atom adsorption energy can be easily understood, since the number of TM atoms directly bound to the Gr sheet tends to saturate as n grows. However, the per-cluster adsorption energy nE_{ad} , a quantification of the cluster-graphene interaction, tends to decrease with n . This trend is due to the increased coordination of the TM atoms bound to the graphene, i.e., as the sharing of electrons increases, the adsorption energy decreases.

In contrast with the adsorption energy, Figure 23 shows that the binding energy per atom rises in magnitude with n . For Ni_n our PBE computation showed that, in

Figure 23 – Binding energies computed from Eq. (4.6) for all the lowest-energy configurations for neutral transition-metal clusters (TM_n ; $\text{TM} = \text{Ni}, \text{Pd}, \text{and Pt}$; $n = 1 - 6$) on graphene. DFT (balls) and DFT+vdW corrections (triangles).
Source: By the author

analogy with the binding energies of the gas-phase clusters, $|E_b|$ grows with n , from 1.47 eV/atom ($n = 1$) to 2.77 eV/atom ($n = 6$). Relative to the binding energies in Table 2, the binding energies of the supported clusters are slightly larger. For $n = 6$, for instance, the binding energy in Table 2 is 2.61 eV/atom, while the corresponding energy in Table 3 is 2.77 eV/atom ($n = 6$). On intuitive grounds, in analogy with the reasoning that explains the binding energies of metallic systems, one would expect the binding energy to decrease upon adsorption, since the valence electrons of the n TM atoms are now shared among a larger number of bonds. The enhanced binding energies in Table 3 indicates that the adsorption also redistributes the valence electrons of the carbon bonds in the vicinity of the adsorption sites.

Comparison with the literature shows good agreement with the data for Pd_n/Gr and Pt_n/Gr . For example, our calculated E_b for Pd_n/Gr ($n = 1, 2$) lie in the range of the published binding energies, which ranges from $-1.09 \text{ eV}^{11,134}$ to -1.18 eV^{10} for Pd_1/Gr , and from -1.10 eV^{10} to -1.29 eV for Pd_2/Gr .^{8,11} Our results slightly overestimate the energies obtained by Cabria *et al.*¹¹ with the GGA-PW91 functional, e. g., $|E_b| = 1.44, 1.84, \text{ and } 1.93 \text{ eV}$ for $\text{Pd}_3/\text{Gr}, \text{Pd}_4/\text{Gr}, \text{ and } \text{Pd}_5/\text{Gr}$, respectively. Our findings for Pt_n/Gr ($n = 1 - 6$) agree very well with the data by Blonski *et al.*¹² ($|E_b| = 2.38 \text{ eV}$ to 3.20 eV and $|E_{ad}| = 1.54 \text{ eV}$ to 0.16 eV for Pt_n/Gr), while slightly overestimating the results of Fampiou *et al.*¹³

Table 4 – Effective Bader charges in the TM_n/Gr systems, in units of the electronic charge e , calculated from $\Delta Q^{TM-C} = Z_{val} - Q^{\text{Bader}}$. Here ΔQ^{TM_b} and $\Delta Q^{TM_{unb}}$ are the effective charges on the TM atoms bound to and unbound from C atoms, respectively. ΔQ^{C_b} and $\Delta Q^{C_{unb}}$ are the total effective charges in C atoms bound to and unbound from TM atoms, respectively.

n	ΔQ^{TM_b}			$\Delta Q^{TM_{unb}}$			ΔQ^{C_b}			$\Delta Q^{C_{unb}}$		
	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt	Ni	Pd	Pt
1	+0.525	+0.235	+0.056	0.000	0.000	0.000	-0.486	-0.149	-0.087	-0.039	-0.086	+0.032
2	+0.336	+0.359	+0.111	-0.133	0.000	-0.249	-0.479	-0.199	-0.126	+0.276	-0.159	+0.264
3	+0.564	+0.262	+0.355	-0.122	-0.141	-0.248	-0.382	-0.215	-0.224	-0.059	+0.094	+0.117
4	+0.865	+0.339	+0.352	-0.116	-0.119	-0.173	-0.578	-0.250	-0.258	-0.172	+0.030	+0.079
5	+0.802	+0.278	+0.331	-0.125	-0.058	-0.295	-0.573	-0.246	-0.259	-0.104	+0.025	+0.223
6	+0.762	+0.265	-0.105	-0.023	-0.025	+0.091	-0.597	-0.221	-0.228	-0.141	-0.018	+0.242

Source: By the author

4.10 Effect of van der Waals Corrections

In most cases, the addition of vdW corrections to the total DFT energy has virtually no effect on the cluster structures in the gas phase, with the average bond lengths and the ECN's changing by less than 0.01 Å and 0.01 NNN, respectively. There are two exceptions. First is Ni_5 which becomes more compact, with its ECN growing from 3.19 to 3.58 NNN, and its average bond length, from 2.28 Å to 2.31 Å. The second is Pd_2 , whose average ECN decaying from 2.59 to 2.47 NNN.

The TM_n clusters supported on graphene displayed a similar trend. The vdW corrections changed their ECNs and average bond lengths by less than 1 %. The minimal distances d_{min} separating the clusters from the Gr sheet varied within the 0.00 % to 0.50 % range. Again, two exceptions were found: Ni_5 and Pd_5 , for which d_{min} changed by 4.7 % and 1.8 %, respectively.

As expected, the vdW correction enhances the adsorption energies. The enhancement grows with the cluster size, but it has weaker dependence on the TM element. $|E_{ad}|$, for example, is enhanced by a factor ranging from 1.23 to 2.56 for Ni_n as the size grows from $n = 1$ to $n = 6$. For Pd_n , the enhancement varies from 1.18 to 1.93 in the same range, and for Pt_n , from 1.16 to 2.37.

4.11 Bader Charge

We relied on Bader-charge analysis to determine the nature of the interaction between the TM_n clusters and graphene. To compute the Bader charge Q^{Bader} for every atom in each TM_n/Gr system we employed VASP high-density grids.¹⁶⁰ We calculated the average effective charge $\Delta Q^{TM-C} = Z_{val} - Q^{\text{Bader}}$, where Z_{val} and Q^{Bader} are the number of valence electrons and Bader charge on each atom, respectively. Table 4 presents the average effective charge on the TM atoms bound with C atoms, on the remaining TM atoms, and on the C atoms bound to TM atoms.

Our results show that the binding to the Gr sheet displaces a small electronic charge away from the TM atoms bound to the C atoms. The TM atoms therefore acquire positive charge, while negative charge is transferred to the C atoms directly bound to the cluster and to the other cluster atoms, the ones that are unbound from the C atoms. For example, in the Pt_n/Gr systems ($n = 1 - 5$) the charge on the TM atoms directly bound to C atoms lies in the 0.06 to $0.36e$ range. Charges of the C atoms bound to the TM atoms are in the -0.09 to $-0.26e$ range.

The transfer is due to the unequal electronegativities,¹⁶¹ (1.91 for Ni, 2.28 for Pt, 2.20 for Pd, and 2.55 for C). The effective Bader charges ΔQ^{TM_b} and ΔQ^{C_b} in Table 4 correlate well with the electronegativity differences. The remaining charges, $\Delta Q^{TM_{unb}}$ and $\Delta Q^{C_{unb}}$, reflect redistributions imposed by two physical constraints: (i) overall, the TM_n/Gr system must have zero charge; and (ii) far from the adsorption site the electronic density must approach that of the Gr sheet.

4.12 Density of states

To describe the electronic properties of studied systems we calculated the local densities of states (LDOS) for the C and TM atoms for pure Gr, gas-phase TM_n ($n = 2 - 6$) clusters, and TM_n/Gr ($n = 1 - 6$). Figure 24 displays the LDOS for TM_1/Gr . Results for TM_n/Gr ($n = 2 - 6$) can be found in Appendix C.

The top panel of Figure 24 displays the LDOS for a pure Gr sheet, showing C s -states and C $p_x + p_y$ -states lying deeply in the valence band, while the C p_z states, represented by the green line, are close to the Fermi level, which controls the binding of the TM_n clusters. Upon adsorption of TM_n clusters, small peaks associated with C p_z -states arise, while the overall C p_z peak amplitude decreases, as shown by the three lower panels, which display the LDOS for TM_1/Gr [TM=Ni (second panel), Pd (third panel), and Pt (bottom panel)]. The d -state LDOS in the three bottom panels display prominent peaks in the vicinity of the Fermi level and are similar to each other, even though the blue curve in the second panel is more tightly concentrated around the Fermi level than the purple and gray curves in the third and bottom panels, respectively. The d -states hybridize weakly with the C p_z states.

4.13 TM adatoms on Graphene

Our results for Ni_1/Gr show preference for the hollow site, followed by the bridge and top sites. The bridge site is the lowest-energy configuration for Pd_1/Gr and Pt_1/Gr , followed by the top and hollow sites. These results agree with previous findings.^{10,12,13,135}

The small adsorption energies in Table 3 are typical of physisorption. The covalent bonds between the p_z orbitals of Carbon and the d_{z^2} , d_{xz} , and d_{yz} orbitals of the TM

Figure 24 – Densities of states for a single TM atom adsorbed on graphene. The top panel depicts Gr, while the second, third, and fourth refer to Ni₁/Gr, Pd₁/Gr, and Pt₁/Gr, respectively. The vertical dashed yellow line marks the Fermi level, from which energies are measured.

Source: By the author

are weak. The tabulated energies show that $|E_{\text{ad}}^{\text{Pt}}| > |E_{\text{ad}}^{\text{Ni}}| > |E_{\text{ad}}^{\text{Pd}}|$. The relatively small energy gained from adsorption at the bridge site in Pd₁/Gr is only 0.04 eV higher than the energy from on-top adsorption. Given this small barrier separating two neighboring adsorption sites, we expect Pt to be mobile on Gr. The barriers between the hollow and bridge sites in Ni₁/Gr and between the bridge and top sites in Pt₁/Gr, approximately 0.2 eV each, are sufficiently high to pin the adsorbates to the most stable sites.

The binding to the hollow site distinguishes Ni/Gr from the other two systems. Whether the hollow or the bridge site is more favorable it is determined by the competition between quantum and classical forces: the tendency to form chemical bonds and the

image-charge attraction from the Gr layer. The latter pulls the adsorbed atom towards the plane through the Gr lattice sites and hence tends to bring small atoms to the open space surrounded by six C atoms.

Two factors therefore combine to favor Ni adsorption at the hollow site. The charge $0.525e$ on the Ni atom enhances the image-charge potential, and the small radius of the transition metal allows accommodation close to the lattice plane, which further strengthens the electrostatic attraction. From the data in Table 3 and the C atomic radius, simple geometry yields a distance $d = 2.0 \text{ \AA}$ between the a Ni atom and the plane, which corresponds to an 0.94 eV image-charge energy, a large fraction of the Ni_1 adsorption energy. As the cluster size n grows the charge transferred to the bonded Ni atoms decreases. For $n > 2$ it becomes preferable to bind two or three atoms at bridge sites instead of having a single atom at a hollow site.

By contrast with Ni, neither the transferred charges nor the atomic radii favor adsorption of Pd or Pt at hollow sites. The two atoms are bigger and the transferred charges, listed in Table 4 are $0.235e$ (Pd) and $0.056e$ (Pt). Even for $n = 1$, therefore, Pd_n/Gr and Pt_n/Gr are more stable at bridge sites.

The decay of the E_b and E_{ad} presented in Figures 22 and 23 indicates that the nature of the binding for TM_1 and $\text{TM}_{n \neq 1}$ are controlled by different mechanisms. In an effort to describe the TM d -orbital LDOS's in Figure 24 in more detail, we now compare the numerical results with the predictions of a simple theoretical model. Traditionally, the adsorption of atoms on metallic surfaces has been described by the Anderson-Newns model,^{162,163} in which the metal is represented by a non-interacting, structureless, half-filled band, and the adatom, by a single level coupled to the conduction band. Prior to discussing generalizations of the model to describe adsorption on Gr, brief recapitulation of its characteristics seems warranted.

Mathematically, the Anderson-Newns model is expressed by the Hamiltonian

$$H = E_d d^\dagger d + \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \sum_{\mathbf{k}} (V_{\mathbf{k}} d^\dagger c_{\mathbf{k}} + \text{H. c.}), \quad (4.7)$$

The adatom energy E_d is shifted, relative to the atomic level, by the image potential induced on the metal by the ionized particle. In Eq. (4.7), the Fermi operator c_d ($c_{\mathbf{k}}$) annihilates an electron at the adatom level (at a conduction level with momentum k). The first and second terms on the right-hand side represent the adatom and the metal, respectively, and the last term is the momentum-dependent coupling between the two subsystems. The energies $\epsilon_{\mathbf{k}}$ define the dispersion relation for the metal.

The single-particle Hamiltonian in Eq. (4.7) is easily diagonalized. The LDOS ρ_{dd} for the c_d level can be obtained from the expression

$$\rho_{dd}(\omega) = -\frac{1}{\pi} \text{Im}[G^R(\omega)], \quad (4.8)$$

Figure 25 – Fits of the LDOS in Figure 24 with the spectral density for the Anderson-Newns model described in the text. The open circles describe the adatom LDOS for the indicated systems, and the solid lines represent Eq. (4.15) with the parameters in Table 5. The insets show that, in contrast with numerical data, the right-hand side of Eq. (4.15) vanishes at zero energy. The vertical dashed line marks the Fermi level, from which energies are measured.

Source: By the author

where $G^R(\omega)$ is the retarded Green's function

$$G^R(\omega) = \frac{1}{\omega - E_d - \Sigma_d(\omega)}. \quad (4.9)$$

Here $\Sigma_d(\omega)$ is the c_d -level self-energy, due to the hybridization between the adatom and conduction levels.

The self-energy is given by the expression

$$\Sigma_d(\omega) = \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{\omega - \epsilon_{\mathbf{k}} + i\eta}, \quad (4.10)$$

where η is a positive infinitesimal.

The real part $\Sigma_R(\omega)$ of the self-energy shifts the adatom energy E_d , while its imaginary part $\Delta_d(\omega)$ broadens E_d . Substitution of Eq. (4.9) on the right-hand side of Eq. (4.9) yields the following expression for the c_d -level LDOS:

$$\rho_{dd}(\omega) = \frac{1}{\pi} \frac{\Delta_d(\omega)}{\left(\omega - E_d - \Sigma_R(\omega)\right)^2 + \Delta_d^2(\omega)}. \quad (4.11)$$

Margulis and Muryumin¹⁶⁴ have extended the Anderson-Newns model to discuss hydrogen adsorption on Gr. In essence, the extension amounts to (i) substituting two bands with the Gr dispersion relation for the second term on the right-hand side of Eq. (4.7); and (ii) defining the momentum-dependent couplings V_k to describe binding to a bridge (B), hollow (H), or top (T) site. For each site, the self-energy can then be computed from Eq. (4.10), with the following results:

$$\Delta_d^B(\omega) = \alpha_1 2|\omega| \left(1 - 0.5J_0(\omega)\right), \quad (4.12a)$$

$$\Delta_d^H(\omega) = \alpha_1 6|\omega| \left(1 - J_0(\omega)\right), \quad (4.12b)$$

$$\Delta_d^T(\omega) = \alpha_1 |\omega|, \quad (4.12c)$$

$$\Sigma_R^B(\omega) = \alpha_2 \omega \left(2g_c \ln \left|\frac{\omega}{\omega_c}\right| - (\pi/2)N_0(|\omega|)\right), \quad (4.13a)$$

$$\Sigma_R^H(\omega) = \alpha_2 \omega \left(6g_c \ln \left|\frac{\omega}{\omega_c}\right| - 3N_0(\sqrt{3}|\omega|)\right), \quad (4.13b)$$

$$\Sigma_R^T(\omega) = \alpha_2 g_c \omega \ln \left|\frac{\omega}{\omega_c}\right|. \quad (4.13c)$$

Here $\alpha_1 = \sqrt{3}|V_0|^2/|V_{pp\pi}|$, and $\alpha_2 = 2\alpha_1/\pi$, where $V_{pp\pi} = -3.03$ eV is the π -electron transfer integral for clean Graphene. J_0 and N_0 are the zero-order Bessel and Neumann functions, respectively. V_0 is an adjustable parameter defining the strength of the hybridization.^{162,163} The cut-off energy ω_c is equal to $0.30\pi/\sqrt{3}$, and the cutoff function $g_c(\omega)$ is the Lorentzian

$$g_c(\omega) = \frac{\omega_c^2}{\omega^2 + \omega_c^2}. \quad (4.14)$$

Description of TM adsorption on Gr calls for additional modification. The electronic configurations of the metals in our computation, Ni = [Ar]3d⁸4s², Pd = [Kr]4d¹⁰, and Pt = [Xe]4f¹⁴5d⁹6s¹, all with ten electrons in the valence band, are poorly described by the LDOS in Eq. (4.8), which covers a unit area.

We have therefore fitted our numerical results with a combination of LDOS's analogous to (4.8), i.e., with the generalized form

$$\rho_{dd}(\omega) = \sum_{j=1}^N \frac{\beta_j \Delta_d^j(\omega)/\pi}{\left(\omega - E_d^j - \Sigma_R^j(\omega)\right)^2 + \left(\Delta_d^j(\omega)\right)^2}, \quad (4.15)$$

where $N = 5$, the β_j and E_d^j are adjustable parameters, and the $\Sigma_R^j(\omega)$ [$\Delta_d^j(\omega)$] are given by one of Eqs. (4.12) [Eqs. (4.13)], according to the adsorption site, with adjustable coefficients α_1^j substituted for the α_1 on the right-hand sides.

Table 5 – Adjustable parameters on the right-hand side of Eq. (4.15) . E_d^j and α_1 define the frequency and width of each resonance, while β_j defines the strength of the resonance.

TM	Adsorption site	j	β_j	E_d^j	$ V_0^j $
Ni	hollow	1	0.77	-4.59	0.15
		2	0.79	-1.62	0.45
		3	0.01	-1.06	0.28
		4	0.43	-1.87	0.24
		5	0.65	-6.41	0.16
Pd	bridge	1	0.91	-6.27	0.32
		2	1.00	-5.48	0.35
		3	0.69	-6.98	0.25
		4	0.23	-14.69	0.37
		5	0.49	-7.55	0.22
Pt	bridge	1	0.78	-6.17	0.31
		2	0.78	-4.48	0.29
		3	0.30	-15.00	0.43
		4	0.50	-3.94	0.31
		5	0.71	-6.95	0.26

Source: By the author

Figure 25 shows the resulting fits. The fitting parameters are listed in Table 5. As the main plots show, the model LDOS reproduce the peak positions and widths, but miss the marked dips around $\epsilon = -0.6$ eV and $\epsilon = -1.2$ eV in the Ni/Gr dotted curves in the first panel of Figure 25. The peaks represent the resonances resulting from the coupling between each adatom level and the Gr states. The discrepancies in the top panel indicate that the two dips are due to destructive interference between the resonances associated with the coupling of the Ni adatom and the C adatom around the hollow site, a partial cancellation that the superposition of spectral densities on the right-hand side of Eq. (4.15) cannot reproduce. No comparable interference is observed at the bridge sites, as indicated by the better agreement, in the same energy range, between the numerical and the analytical Pd/Gr and Pt/Gr curves in the second and third panels, respectively.

The insets in Figure 25 are magnifications of the regions around the Fermi level. While the analytical LDOS vanish at $\epsilon = 0$, the dotted lines representing the numerical data have positive minima at positive energies. For the Anderson-Newns model, which represents a single adatom adsorbed on an infinite Gr monolayer, $\rho_{dd}(\epsilon = 0)$ must be zero, because the Gr density of states vanishes at the tip of the Dirac cones. In the DFT computation, by contrast, the charge transferred from the periodic array of TM adatoms to the C atoms raises the Fermi level to an energy above the Dirac singularity. The minimum

LDOS in each panel is therefore controlled by the charge transferred between the adsorbed atom and the C atoms. The progressively smaller inset minima agree well with transferred charges in Table 4, which shrink from $0.53e$ (Ni/Gr) to $0.24e$ (Pd/Gr) and $0.06e$ (Pt/Gr) as one moves down from the top to the bottom panels in Figure 25.

4.14 Conclusion: Graphene

We have carried out an *ab initio* density-functional investigation of the structural, energetic and magnetic properties of one to six-atom Ni, Pd and Pt clusters on Gr. With a few exceptions, adsorption preserves the structure of the gas-phase clusters. As n grows, the interaction between the TM_n clusters and Gr weakens. The interaction is strongest for Ni and weakest for Pd and hence weakens as the d -orbital occupation grows. The van der Waals correction in our study had little effect upon the TM_n cluster structures, either in the gas phase or adsorbed on Gr. Nonetheless, as expected, the corrections raise the adsorption energy. Our results show that, like the adsorption energy itself, the van der Waals contribution to the adsorption energy grows with cluster size and with the decrease of the number of d -electrons.

Adsorption results in charge transfer between the TM_n clusters and Gr. The charge transfer from the TM atoms directly coupled to C atoms is controlled by the electronegativity difference. Typically, the charge transfer between Ni and C is twice (three times) as large as the transfer between Pd (Pt) and C. In almost all studied systems, negative charge is transferred from the bound TM atoms to the C atoms. The exception is Pt_6 , in which Pt acquires a small negative charge. In all cases, the charge on the remaining cluster atoms partially compensates for the charge lost by the bound TM atoms.

In order to further explore the physics involved in adsorption of the TM_n on Gr, we have used a modified Anderson-Newns model to describe the coupling between the two. Analysis of the agreement between the c_d -level LDOS resulting from the model and the DFT computations identified destructive interference between the resonances resulting from (Ni) adsorption on hollow sites, but no interference when the TM atom is adsorbed on bridge sites (Pd_1/Gr or Pt_1/Gr).

5 STICKING COEFFICIENT

Central to the study of nuclear motion is the concept of a Time-Dependent PES (TDPES),¹⁶⁵ which has proved extremely useful in the interpretation of dynamic phenomena.⁴⁴ As explained in Chapter 2, the BO approximation breaks down when two PES get close to one another. In 2012 Abedi *et al*^{43,44} showed that the electron-nuclear Schrödinger equation allows for exact solutions comprising of a rigorous separation of the electronic and nuclear motions. In this formalism, named as Exact Factorization, the BO expansion of infinity PES is replaced by a single product of a time-dependent electronic and nuclear wavefunctions.

We aim in this chapter is to show how to compute the sticking probability, i.e., the amount of nuclear probability that gets stuck on a metallic surface after an initially negatively charged hydrogen collides against it. In Figure 26 we have an illustration for the unbound and bound cases. Such a phenomenon requires a good treatment of electron-hole excitations, and the way those excitations decay depends critically on the description of the nuclear motion and its correlation with the dynamics of electrons.^{166–168}

The ground-state energies for H and for its anion H^- are (-13.6 eV) and (-14.3 eV), respectively. Therefore the ground state is negatively charged, and we will consider the collision of an H^- ion with the surface. In other words, we envision an H^- ion initially moving with a small kinetic energy towards the metallic surface. Once the atom is negatively charged, the nucleus is violently attracted to the surface by the image potential. In this scenario, we approximate the nuclear wavefunction as a gaussian wave packet i.e., a linear combination of states with different momenta, which contains the momenta for many excited states of H^- as well of the neutral hydrogen.

Essentially, this problem has to overcome two conceptual challenges. The first is give a suitable treatment of the atom-metal interaction, i.e., it takes account of the large number of low-energy electron-hole excitations, which are generated by the atom when it approximates the metallic surface. To get around this point, let us empoly the Numerical Renormalization Group (NRG).^{41,42,169,170} Describing accurately the coupling between nuclear and electronic movement is the second challenge, and it can be overcome within the Exact Factorization framework.

The strategy we follow to compute the sticking probability is described in the following sections. In the Section 5.1, we derive in detail the Exact Factorization equations, which are important to describe the interplay of nuclear and electron dynamics. In Section 5.2 we explain the connection between NRG and Exact Factorization. The NRG method is described in Appendix D and it will be responsible for generating the electronic basis set.

Figure 26 – Incidence of hydrogen atom upon a metallic surface. Left side: chemically unbound. Right side: chemically bound.
Source: By the author

In the remaining sections, we present our numerical procedure to calculate the sticking coefficient S , and our preliminary results.

5.1 Exact Factorization

The non-relativistic Hamiltonian under the influence of electronic, V_{ext}^e , and nuclear, V_{ext}^n , external fields, describes a system of interacting electrons and nuclei,

$$\hat{H} = \hat{H}'_{BO} + \hat{T}_n + V_{ext}^n. \quad (5.1)$$

$\hat{T}_n = \frac{-\sum_n \nabla_n^2}{2M_n}$ is the nuclear kinetic energy term. $\hat{H}'_{BO} = \hat{H}_{BO} + V_{ext}^e$, and $\hat{H}_{BO}$ denotes the Born-Oppenheimer electronic Hamiltonian. It contains the kinetic energy $\hat{T}_e$ operator, electron-electron, nucleus-nucleus as well as electron-nucleus Coulomb potentials. In general our aim in analysing quantum time-dependent systems is to solve the time-dependent Schrödinger equation (TDSE),

$$i\partial_t \Psi(\vec{r}, \vec{z}, t) = \hat{H} \Psi(\vec{r}, \vec{z}, t). \quad (5.2)$$

Here the collective electronic and nuclear coordinates are represented by $\vec{r} = \{r_i\}$, $\vec{z} = \{z_n\}$, where the labels i and n indicate the electron and nuclei, $i = 1, \dots, N_e$ and $n = 1, \dots, N_n$, respectively. Abedi *et al.*, 2012 and Abedi *et al.*, 2010 have shown that the exact full wavefunction without spin, $\Psi(\vec{r}, \vec{z}, t)$ solution of the TDSE can be factorized as a product,

$$\Psi(\vec{r}, \vec{z}, t) = \Phi_z(\vec{r}) \chi(\vec{z}), \quad (5.3)$$

of the nuclear wavefunction $\chi(\vec{z})$ and the electronic wavefunction $\Phi_z(\vec{r})$ where the latter is a conditional electronic wavefunction depending parametrically on the nuclear position.^{43,44} This factorization, is termed Exact Factorization (EF) and it is based on two theorems. Next we present their proofs and discuss their implications.

The proof of the first theorem requires the use of a quantum mechanical stationary action $\mathcal{S}$. The action $\mathcal{S}$ is defined as a functional of the many-body wavefunction $\Psi(\vec{r}, \vec{z}, t)$ between an initial time t_i and a final time t_f . In the Frenkel form $\mathcal{S}$ is the integral

$$\mathcal{S}[\Psi, \Psi^*] = \int_{t_i}^{t_f} dt \langle \Psi | \hat{H} - i\partial_t | \Psi \rangle. \quad (5.4)$$

The optimal $\Psi(t)$ solution for the TDSE Eq. (5.2) is obtained for $\delta_{\Psi^*} \mathcal{S} = 0$ only when $\delta\Psi_{t_i}$ and $\delta\Psi_{t_f}$ vanish at the boundaries of the time interval, i.e., $\delta\Psi_{t_i} = \delta\Psi_{t_f} = 0$. The identity $\delta_{\Psi^*} \mathcal{S} = 0$ means that the ideal $\Psi(\vec{r}, \vec{z}, t)$ should minimize the deviation given by Eq. (5.4) in a given time interval.¹⁷¹

Theorem 5.1 (a): *The exact solution of Eq. (5.2) can be written as a single product $\Psi(\vec{r}, \vec{z}, t) = \Phi_z(\vec{r}, t)\chi(\vec{z}, t)$, where $\Phi_z(\vec{r})$ satisfies the Partial Normalization Condition (PNC)*

$$\langle \Phi_z | \Phi_z \rangle = 1, \quad (5.5)$$

for any fixed nuclear configuration $\vec{z}$, at any time t .

(b): *The wavefunctions $\Phi_z(\vec{r}, t)$ and $\chi(\vec{z}, t)$ satisfy*

$$(\hat{H}_{el}(\vec{r}, \vec{z}, t) - \epsilon(\vec{z}, t)) \Phi_z(\vec{r}, t) = i\partial_t \Phi_z(\vec{r}, t) \quad (5.6)$$

$$\left(\sum_n \frac{1}{2M_n} (-i\nabla_n + \vec{A}(\vec{z}, t))^2 + V_{ext}^n + \epsilon(\vec{z}, t) \right) \chi(\vec{z}, t) = i\partial_t \chi(\vec{z}, t), \quad (5.7)$$

where the electronic Hamiltonian is

$$\hat{H}_{el}(\vec{r}, \vec{z}, t) = \hat{H}'_{BO}(\vec{r}, \vec{z}, t) + \hat{U}_{en}^{coup}[\Phi_z, \chi]. \quad (5.8)$$

Here, the electron-nuclear coupling potential $\hat{U}_{en}^{coup}[\Phi_z, \chi]$, scalar potential $\epsilon(\vec{z}, t)$, and vector potential $\vec{A}(\vec{z}, t)$ terms are

$$\hat{U}_{en}^{coup}[\Phi_z, \chi] = \sum_n \frac{1}{2M_n} \left[(-i\nabla_n - \vec{A}_n(\vec{z}, t))^2 + 2 \left(\frac{-i\nabla_n \chi(\vec{z}, t)}{\chi(\vec{z}, t)} + \vec{A}_n(\vec{z}, t) \right) \cdot (-i\nabla_n - \vec{A}_n(\vec{z}, t)) \right], \quad (5.9)$$

$$\epsilon(\vec{z}, t) = \langle \Phi_z(\vec{r}, t) | \hat{H}_{el} - i\partial_t | \Phi_z(\vec{r}, t) \rangle_{\vec{r}}, \quad (5.10)$$

$$\vec{A}_n(\vec{z}, t) = \langle \Phi_z(\vec{r}, t) | -i\nabla_n | \Phi_z(\vec{r}, t) \rangle_{\vec{r}}, \quad (5.11)$$

where $\langle \dots | \dots | \dots \rangle_{\vec{r}}$ denotes an inner product over all spatial electronic variables only.

To prove part **(a)** we must replace Ψ by the right-hand side of Eq. (5.3) in the action principle (Eq. (5.4)). It follows that

$$\begin{aligned} \mathcal{S}[\Phi_z(\vec{r}), \Phi_z^*(\vec{r}), \chi(\vec{z}), \chi^*(\vec{z})] = \int_{t_i}^{t_f} dt \int d\vec{z} \int d\vec{r} |\chi|^2 \Phi_z^* \left(\hat{H}'_{BO} + \hat{T}_n - i\partial_t \right) \Phi_z + \\ |\Phi|^2 \chi^* \left(\hat{T}_n + V_{ext}^n - i\partial_t \right) \chi + |\chi|^2 \Phi_z^* \sum_n \frac{1}{M_n} \left(\frac{i\nabla_n \chi}{\chi} \right) \cdot (-i\nabla_n \Phi_z). \end{aligned} \quad (5.12)$$

In order to prove the PNC, it is necessary to add a Lagrange multiplier $\mu(\vec{z}, t)$ to Eq. (5.12). $\mathcal{S}$ then turns into

$$\tilde{\mathcal{S}} = \mathcal{S} + \int d\vec{z} \mu(\vec{z}, t) \langle \Phi_z | \Phi_z \rangle. \quad (5.13)$$

Now, we must replace $\mathcal{S}$ by $\tilde{\mathcal{S}}$ in the minimization procedure, i.e., we must evaluate

$$\begin{aligned} \frac{\delta \tilde{\mathcal{S}}[\Phi_z(\vec{r}, t), \Phi_z^*(\vec{r}, t), \chi(\vec{z}, t), \chi^*(\vec{z}, t)]}{\delta \Phi_z^*(\vec{r}, t)} = 0 \\ \frac{\delta \tilde{\mathcal{S}}[\Phi_z(\vec{r}, t), \Phi_z^*(\vec{r}, t), \chi(\vec{z}, t), \chi^*(\vec{z}, t)]}{\delta \chi^*(\vec{z}, t)} = 0. \end{aligned} \quad (5.14)$$

After a few algebraic steps, the first term in Eq. (5.14) leads to an equation of motion for $\Phi_z(\vec{r}, t)$,

$$\left(\hat{H}'_{BO} + \hat{T}_n - i\partial_t + \frac{\mu}{|\chi|^2} \right) \Phi_z + \sum_n \frac{1}{M_n} \left(\frac{-i\nabla_n \chi}{\chi} \right) \cdot (-i\nabla_n \Phi_z) = - \frac{(\hat{T}_n + V_{ext}^n - i\partial_t) \chi}{\chi} \Phi_z, \quad (5.15)$$

and the equation of motion for $\chi(\vec{z}, t)$ is obtained from the second Eq. (5.14),

$$\frac{\langle \Phi_z | \hat{H}'_{BO} + \hat{T}_n - i\partial_t | \Phi_z \rangle + \sum_n \frac{1}{M_n} \left(\frac{-i\nabla_n \chi}{\chi} \right) \cdot \vec{A}_n}{\langle \Phi_z | \Phi_z \rangle} = - \frac{(\hat{T}_n + V_{ext}^n - i\partial_t) \chi}{\chi}. \quad (5.16)$$

Substituting the LHS of Eq. (5.16) on the RHS of Eq. (5.15) one obtains,

$$\begin{aligned} \left(\hat{H}'_{BO} + \hat{T}_n - i\partial_t + \frac{\mu}{|\chi|^2} \right) \Phi_z + \sum_n \frac{1}{M_n} \left(\frac{-i\nabla_n \chi}{\chi} \right) \cdot (-i\nabla_n \Phi_z) = \\ \left(\langle \Phi_z | \hat{H}'_{BO} + \hat{T}_n - i\partial_t | \Phi_z \rangle + \sum_n \frac{1}{M_n} \left(\frac{-i\nabla_n \chi}{\chi} \right) \cdot \vec{A}_n \right) \frac{\Phi_z}{\langle \Phi_z | \Phi_z \rangle}. \end{aligned} \quad (5.17)$$

The PNC appear naturally when Eq. (5.17) is multiplied by Φ_z^* and integrated over the electronic coordinates $\vec{r}$. This procedure shows that $\mu(\vec{z}, t) = 0$, which implies that the PNC conserves the norm of Φ_z . It means that Φ_z will evolve through time with a constant norm.^{172, 173}

Now we have all the tools to demonstrate part **(b)** of the Theorem 5.1, i.e., Eqs (5.6) and (5.7). The Theorem 5.1 states that, if the electronic wavefunction starts with

a state $\Phi_z(\vec{r},0)$ with unitary norm, i.e., $\langle \Phi_z(\vec{r},0) | \Phi_z(\vec{r},0) \rangle = 1$, then the norm will be conserved during the time evolution. This allow us to rewrite the Eq. (5.17) as,

$$\begin{aligned} & \left(\hat{H}'_{BO} + \hat{T}_n - i\partial_t \right) \Phi_z + \sum_n \frac{1}{M_n} \left(\frac{-i\nabla_n \chi}{\chi} \right) \cdot (-i\nabla_n \Phi_z) = \\ & \left(\langle \Phi_z | \hat{H}'_{BO} + \hat{T}_n - i\partial_t | \Phi_z \rangle + \sum_n \frac{1}{M_n} \left(\frac{-i\nabla_n \chi}{\chi} \right) \cdot \vec{A}_n \right) \Phi_z. \end{aligned} \quad (5.18)$$

In order to obtain Eq. (5.6) we subtract and add some terms in the above equation, so that

$$\begin{aligned} & \left(\hat{H}'_{BO} - i\partial_t + \mathcal{D} \right) \Phi_z = \langle \Phi_z | \hat{H}'_{BO} - i\partial_t | \Phi_z \rangle \Phi_z \\ & + \sum_n \frac{1}{2M_n} \langle \Phi_z | -\nabla_n^2 - 2i \left(\frac{\nabla_n \chi}{\chi} \right) \cdot \vec{A}_n | \Phi_z \rangle \Phi_z, \end{aligned} \quad (5.19)$$

where $\mathcal{D}\Phi_z$ is defined by,

$$\begin{aligned} \mathcal{D}\Phi_z &= \sum_n \frac{1}{2M_n} \left(-\nabla_n^2 - 2(\nabla_n \chi / \chi) \cdot \nabla_n \right) \Phi_z \\ \mathcal{D}\Phi_z &= \sum_n \frac{1}{2M_n} \left(-\nabla_n^2 + i\nabla_n \vec{A}_n - i\nabla_n \vec{A}_n + i\vec{A}_n \nabla_n - i\vec{A}_n \nabla_n + \vec{A}_n^2 - \vec{A}_n^2 \right. \\ & \quad \left. - 2(\nabla_n \chi / \chi) \cdot \nabla_n \right) \Phi_z \\ \mathcal{D}\Phi_z &= \sum_n \frac{1}{2M_n} \left((-i\nabla_n - \vec{A}_n)^2 - i\nabla_n \vec{A}_n - 2i\vec{A}_n \nabla_n - 2\vec{A}_n^2 - 2(\nabla_n \chi / \chi) \cdot \nabla_n \right. \\ & \quad \left. + i\vec{A}_n \nabla_n + \vec{A}_n^2 + 2i(\nabla_n \chi / \chi) \cdot \vec{A}_n - 2i(\nabla_n \chi / \chi) \cdot \vec{A}_n \right) \Phi_z \\ \mathcal{D}\Phi_z &= \sum_n \frac{1}{2M_n} \left((-i\nabla_n - \vec{A}_n)^2 + 2(-i(\nabla_n \chi / \chi) + \vec{A}_n) \cdot (-i\nabla_n - \vec{A}_n) \right) \Phi_z \\ & \quad + \sum_n \frac{1}{2M_n} \left(-i\nabla_n \vec{A}_n + i\vec{A}_n \nabla_n + \vec{A}_n^2 - 2i(\nabla_n \chi / \chi) \cdot \vec{A}_n \right) \Phi_z \\ \mathcal{D}\Phi_z &= U_{en}^{coup} \Phi_z + \sum_n \frac{1}{2M_n} \left(-i\nabla_n \vec{A}_n + i\vec{A}_n \nabla_n + \vec{A}_n^2 - 2i(\nabla_n \chi / \chi) \cdot \vec{A}_n \right) \Phi_z. \end{aligned} \quad (5.20)$$

Replacing the RHS of Eq. (5.20) in the LHS of Eq. (5.19) we arrive at,

$$\begin{aligned} & \left(\hat{H}_{el} - i\partial_t \right) \Phi_z = \langle \Phi_z | \hat{H}'_{BO} - i\partial_t | \Phi_z \rangle \Phi_z \\ & \quad + \sum_n \frac{1}{2M_n} \langle \Phi_z | -\nabla_n^2 + i(\nabla_n \vec{A}_n) - \vec{A}_n^2 | \Phi_z \rangle \Phi_z \\ & \left(\hat{H}_{el} - i\partial_t \right) \Phi_z = \langle \Phi_z | \hat{H}'_{BO} - i\partial_t | \Phi_z \rangle \Phi_z \\ & \quad + \sum_n \frac{1}{2M_n} \langle \Phi_z | (-i\nabla_n - \vec{A}_n)^2 | \Phi_z \rangle \Phi_z, \end{aligned} \quad (5.21)$$

To complete the proof that Eq. (5.23) is equivalent to Eq. (5.6), we have to show that when using the vector potential definition Eq. (5.11), the second term of $\hat{U}_{en}^{coup}$ vanishes because $(-i\nabla_n - \vec{A}_n)$ becomes zero inside the integral of Eq. (5.10), according to the

following derivation,

$$\begin{aligned}
\langle \Phi_z | \left(\frac{-i\nabla_n \chi(\vec{z}, t)}{\chi(\vec{z}, t)} + \vec{A} \right) \cdot (-i\nabla_n - \vec{A}_n) | \Phi_z \rangle &= \\
\left(\frac{-i\nabla_n \chi(\vec{z}, t)}{\chi(\vec{z}, t)} + \vec{A}_n \right) \langle \Phi_z | (-i\nabla_n - \vec{A}_n) | \Phi_z \rangle &= \\
\left(\frac{-i\nabla_n \chi(\vec{z}, t)}{\chi(\vec{z}, t)} + \vec{A}_n \right) \langle \Phi_z | (-i\nabla_n - \vec{A}_n) | \Phi_z \rangle &= 0.
\end{aligned} \tag{5.22}$$

Therefore, replacing the above identity on the LHS of Eq. (5.23) we show that it reproduces Eq. (5.10),

$$\begin{aligned}
(\hat{H}_{el} - i\partial_t) \Phi_z &= \langle \Phi_z | \hat{H}'_{BO} - i\partial_t | \Phi_z \rangle \Phi_z \\
&\quad + \sum_n \frac{1}{2M_n} \langle \Phi_z | (-i\nabla_n - \vec{A}_n)^2 | \Phi_z \rangle \Phi_z \\
(\hat{H}_{el} - i\partial_t) \Phi_z &= \langle \Phi_z | \hat{H}_{el} - i\partial_t | \Phi_z \rangle \Phi_z \\
(\hat{H}_{el}(\vec{r}, \vec{z}, t) - \epsilon(\vec{z}, t)) \Phi_z(\vec{r}, t) &= i\partial_t \Phi_z(\vec{r}, t).
\end{aligned} \tag{5.23}$$

Using the same reasoning, one can demonstrate that Eq. (5.14) leads to Eq. (5.7).

Eq. (5.10) is an exact Time-Dependent generalization of the adiabatic BO Potential Energy Surface (TD PES), a concept that has proven very important for the understanding of the time-dependent phenomena.^{43,174} According to Eq. (5.22) only the term $(-i\nabla_n - \vec{A}_n)^2$ contribute for the expectation value of $\hat{U}_{en}^{coup}$, i.e.,

$$\langle \Phi_z(\vec{r}, t) | \vec{U}_{en}^{coup} | \Phi_z(\vec{r}, t) \rangle = \sum_n \frac{1}{2M_n} \langle \Phi_z | (-i\nabla_n - \vec{A}_n)^2 | \Phi_z(\vec{r}, t) \rangle. \tag{5.24}$$

To demonstrate, we are going to use the relation $\nabla_n \cdot \langle \Phi_z | \nabla_n | \Phi_z \rangle = \langle \nabla_n \Phi_z | \nabla_n \Phi_z \rangle + \langle \Phi_z | \nabla_n^2 | \Phi_z \rangle$, which leads to

$$\begin{aligned}
\langle \Phi_z(\vec{r}, t) | (-i\nabla_n - \vec{A}_n)^2 | \Phi_z(\vec{r}, t) \rangle &= \langle \Phi_z(\vec{r}, t) | -\nabla_n^2 + i\vec{A}_n \cdot \nabla_n + \vec{A}_n^2 + i\nabla_n \cdot \vec{A}_n | \Phi_z(\vec{r}, t) \rangle \\
&= -\langle \Phi_z | \nabla_n^2 | \Phi_z \rangle + \langle \Phi_z | (\nabla_n \cdot \vec{A}_n) | \Phi_z \rangle + i\langle \Phi_z | \vec{A}_n \cdot \nabla_n | \Phi_z \rangle \\
&= -\langle \Phi_z | \nabla_n^2 | \Phi_z \rangle + (\nabla_n \cdot \vec{A}_n) - \vec{A}_n^2 \\
&= \langle \nabla_n \Phi_z | \nabla_n \Phi_z \rangle - \vec{A}_n^2.
\end{aligned} \tag{5.25}$$

From which it follows that $\epsilon(\vec{z}, t)$ is,

$$\epsilon(\vec{z}, t) = \langle \Phi_z(\vec{r}, t) | \hat{H}'_{BO} - i\partial_t | \Phi_z(\vec{r}, t) \rangle + \sum_n \left(\frac{\langle \nabla_n \Phi_z(\vec{r}, t) | \nabla_n \Phi_z(\vec{r}, t) \rangle}{2M_n} - \frac{\vec{A}_n^2}{2M_n} \right). \tag{5.26}$$

The $\hat{U}_{en}^{coup}$ is a non-Hermitian operator, such non-hermiticity is due to the $\nabla_n \chi / \chi$ term, which has a real and an imaginary component, which usually are non-zero. Thus, it gives rise to $(\nabla_n \chi / \chi) \cdot \nabla_n$; such a term is a kind of a momentum operator, $\vec{p} = -i\nabla$,

divided by the imaginary unit, i.e., $\tilde{p} = -\nabla$. Even though $\hat{U}_{en}^{coup}$ is non-Hermitian, its expectation value is real, as follows from Eq. (5.25), which shows that $\langle \Phi_z | U_{en} \Phi_z \rangle \in \mathbb{R}$.

It is important to observe that the TD PES given in Eq. (5.26) contains a time derivative term $\langle \Phi_z(\vec{r}, t) | -i\partial_t | \Phi_z(\vec{r}, t) \rangle$. This term is intimately related with the gauge transformation of the Eqs (5.6)-(5.11), and will be an important ingredient to prove the second theorem.

Theorem 5.2 (a): *Equations (5.6)-(5.11) are form invariant within the gauge-like transformation*

$$\begin{aligned}\tilde{\Phi}(\vec{r}, t) &:= e^{i\theta(\vec{z}, t)} \Phi_r(\vec{r}, t), \\ \tilde{\chi}(\vec{r}, t) &:= e^{-i\theta(\vec{z}, t)} \chi(\vec{r}, t),\end{aligned}\tag{5.27}$$

$$\begin{aligned}\vec{A}_n(\vec{z}, t) &\rightarrow \tilde{\vec{A}}_n(\vec{z}, t) = \vec{A}_n(\vec{z}, t) + \nabla_n \theta(\vec{z}, t), \\ \epsilon(\vec{z}, t) &\rightarrow \tilde{\epsilon}(\vec{z}, t) = \epsilon(\vec{z}, t) + \partial_t \theta(\vec{z}, t).\end{aligned}\tag{5.28}$$

(b) *The wavefunctions $\Phi_z(\vec{r}, t)$ and $\chi(\vec{z}, t)$ are unique within the $(\vec{z}, t)$ dependent phase transformation, Eq. (5.27)*

The proof of part **(a)** is straightforward, we have just to substitute Eq. (5.27) and Eq. (5.28) into Eqs (5.6)-(5.11). To prove part **(b)** we assume that $\Phi_z(\vec{r}, t)\chi(\vec{z}, t)$ and $\tilde{\Phi}_z(\vec{r}, t)\tilde{\chi}(\vec{z}, t)$ are two different solutions of the $\Psi(\vec{z}, \vec{r}, t)$, which satisfy the PNC, i.e.,

$$\Psi(\vec{z}, \vec{r}, t) = \Phi_z(\vec{r}, t)\chi(\vec{z}, t) = \tilde{\Phi}_z(\vec{r}, t)\tilde{\chi}(\vec{z}, t).\tag{5.29}$$

From the very last equation follows that,

$$\frac{\tilde{\Phi}_z(\vec{r}, t)}{\Phi_z(\vec{r}, t)} = \frac{\tilde{\chi}(\vec{z}, t)}{\chi(\vec{z}, t)} =: a(\vec{z}, t),\tag{5.30}$$

and

$$|\tilde{\Phi}_z(\vec{r}, t)|^2 = |a(\vec{z}, t)|^2 |\Phi_z(\vec{r}, t)|^2.\tag{5.31}$$

Thus, using the PNC one finds that $|a(\vec{z}, t)|^2 = 1$. Therefore, we conclude that $a(\vec{z}, t)$ must be a exponential phase factor, the phase depending on z and t :

$$a(\vec{z}, t) = e^{i\theta(\vec{z}, t)}.\tag{5.32}$$

The product of the electronic, $\Phi_z(\vec{r}, t)$, and nuclear, $\chi(\vec{z}, t)$, wavefunctions is an exact solution for the TDSE. The quantity $|\Phi_z(\vec{r}, t)|^2 = |\Psi_z(\vec{r}, \vec{z}, t)|^2 / |\chi(\vec{z}, t)|^2$ measures the conditional probability of having the electrons at $\vec{r}$ when the nuclei are in the $\vec{z}$ configuration, and the probability of finding a given nuclear configuration $\vec{z}$ for a given

time is, $\langle \Psi_{\vec{z}}(\vec{r}, \vec{z}, t) | \Psi_{\vec{z}}(\vec{r}, \vec{z}, t) \rangle_{\vec{r}} = |\chi(\vec{z}, t)|^2$. The TDPEs, $\epsilon(\vec{z}, t)$ and the phase that is transferred from electrons to the nuclei or vice-versa, here are represented by the vector potential $\vec{A}(\vec{z}, t)$, together with the electron-nuclear coupling potential $\hat{U}_{en}^{coup}$ which are responsible for the connection between the electronic and nuclear wavefunctions. In the next sections, we introduce the numerical procedures used to compute $\chi(z, t)$, from which we will determine the sticking coefficient.

5.2 Connection between NRG and Exact Factorization

The aim of this section is to explain the connection between the NRG (Appendix D) and Exact Factorization approach. We are considering a normal collision of a hydrogen atom with a flat metallic surface. Our simplified model is defined by the following Hamiltonian:

$$\hat{H} = \hat{H}_{BO} + \hat{K}_n, \quad (5.33)$$

here the nuclear kinetic energy term is given by $\hat{K}_n = -\nabla_n^2/2M_n$, where M_n is the nuclear mass. The physics of this phenomenon is dominated by the electron-hole excitation, which will cause one PES be close to the other PES.

The truncated form for the electronic Hamiltonian is given by,

$$\begin{aligned} \hat{H}_{BO} = & \sum_{n=0}^N t_n (f_n^\dagger f_{n+1} + H.c.) + \epsilon_a n_a + U n_{a\uparrow} n_{a\downarrow} \\ & + \sqrt{2}V(z)(f_0^\dagger c_a + H.c.) - W(z)f_0^\dagger f_0 [1 - (n_{a\uparrow} - n_{a\downarrow})^2], \end{aligned} \quad (5.34)$$

where ϵ_a is the energy of the atomic orbital associated with the operator c_a . U is the electron-electron repulsive interactions, $V(z)$ is the coupling term between the atomic orbital and the metal surface, which decays rapidly as the distance z grows. The operator $f_n^\dagger$ in Eq. (5.34) is defined as $f_n^\dagger = \frac{1}{\sqrt{N}} \sum_k c_k^\dagger$, where N is the number of states in the conduction band, that are subject to a charge image potential $W(z)$, which is nonzero only when the atom is charged, i.e., $n_a = 0$ or $n_a = 2$. As mentioned in the beginning, we are considering the case where the atom is negatively charged, i.e., H^- . The energy splitting between the ground states of H^- and H being much larger than the coupling V , the latter can be safely neglected. The occupation n_a is then conserved, and $\hat{H}_{BO}$ reduces to a single-particle Hamiltonian, whose diagonalization is straightforward. The two spin channels are moreover decoupled; for simplicity, we will consider only one of the two

channels. Thus, the Hamiltonian $\hat{H}_{BO}$ in matrix notation becomes,

$$H_{BO} = \begin{pmatrix} 2\epsilon_a + U & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -2W & t_0 & 0 & 0 & 0 & 0 \\ 0 & t_0 & 0 & t_1 & 0 & 0 & 0 \\ 0 & 0 & t_1 & 0 & t_2 & 0 & 0 \\ 0 & 0 & 0 & t_2 & \ddots & \ddots & 0 \\ 0 & 0 & 0 & 0 & \ddots & 0 & t_N \\ 0 & 0 & 0 & 0 & 0 & t_N & 0 \end{pmatrix}. \quad (5.35)$$

If we neglect, for a moment the kinetic energy of the nucleus, then z becomes a fixed parameter in the Hamiltonian $\hat{H}_{BO}$. If a z grid is defined, $\hat{H}_{BO}(z)$ can be diagonalized at each grid site. Plotted as functions of z , the resulting eigenvalues make up PES $E_j(z)$, where $j = 0, 1, \dots$ indexes the eigenvalues and hence the surfaces. In the BO approximation, one would simply solve the Schrödinger equation for the nuclear motion driven by each energy surface, project an initial nuclear wavepacket onto the resulting eigenvectors and determine the subsequent evolution of the packet. But in this problem such approximation is not allowed, because when H^- gets close to the surface the image charge potential $W(z)$ grows very quickly, and considering that the decay of electron-hole excitations depend on nuclear movement, the PES's must be significantly coupled, which is depicted in Figure 27. For this reason, we use the Exact Factorization instead of the BO approximation.

Figure 27 shows that the PES's are very close to each other. As discussed in Chapter 1, when two or more PES's are close to each other the non-adiabatic dynamics plays an important role in the system studied. Thus, almost all the necessary physics to trap part of the nuclear density on the metal surface can be found in that region. In next section, we are going to show to how the discretization procedure should be conducted and which constraints must be satisfied.

5.3 Computational Details

Here, we introduce the discretization needed to solve the Exact Factorization equations. In addition, we give a brief overview of the algorithm that describes the time evolution of the TDSE. The so called Crank-Nicolson method.

The electronic wave function $|\Phi\rangle_z^t$ is defined by the following basis set,

$$|\Phi\rangle_z^t = \sum_{\ell'} \beta_{\ell',z}^t |\ell'\rangle_z = \sum_{\ell'} \beta_{\ell',z}^t |\ell'\rangle_z = \sum_{\ell'} |\beta_{\ell',z}^t| e^{i\theta_{\ell'}(z,t)} |\ell'\rangle_z, \quad (5.36)$$

where $|\ell'\rangle_z$'s are the real eigenfunctions calculated via NRG at a given position z for the Hamiltonian given by Eq. (5.34).

The PNC implies that $\sum_{\ell'} \beta_{\ell'} \beta_{\ell'}^* = 1$. In order to simplify the notation in some situations, we will write $\beta_{\ell',z}^t$ as $\beta_{\ell'}^t$. It will prove useful to define a column vector β

Figure 27 – Electronic energy states for H^- . The black line is the Ground state, red, blue and magenta are 1st, 2nd, and 3th excited states, respectively. The insertion shows that the electronic states are very close to each other. These states were constructed using a binary notation as presented in Figure 28.

Source: By the author

Figure 28 – Here we are using binary notation: a one 1 for occupied and a zero 0 for unoccupied. The blue lines (levels) with black circles (electrons) are occupied, while the empties are unoccupied. In this example, the binary number 0011 number represent the GS, while 0101 is the 1st excited state.

Source: By the author

containing all the $\beta_{\ell'}$'s, where

$$\beta^\dagger = (\beta_{1,z_1}, \beta_{2,z_1}, \dots, \beta_{1,z_2}, \beta_{2,z_2}, \dots, \beta_{N,z_M}). \quad (5.37)$$

In order to evaluate, the first term on the RHS of Eq. (5.26), it is necessary to compute the time derivative of $|\Phi\rangle_z^t$. Then, using $\beta_{\ell'} = |\beta_{\ell'}| e^{i\theta_{\ell'}(z,t)}$ and recalling that the

normalization imposed by the PNC is time independent we have,

$$\begin{aligned}
\partial_t \sum_{\ell'} \beta_{\ell'} \beta_{\ell'}^* &= 0 \\
\sum_{\ell'} [(\partial_t \beta_{\ell'}) \beta_{\ell'}^* + \beta_{\ell'} (\partial_t \beta_{\ell'}^*)] &= 0 \\
\sum_{\ell'} (\partial_t \beta_{\ell'}) \beta_{\ell'}^* &= - \sum_{\ell'} \beta_{\ell'} (\partial_t \beta_{\ell'}^*) \\
\sum_{\ell'} [|\partial_t \beta_{\ell'}| |\beta_{\ell'}| + i |\beta_{\ell'}|^2 \partial_t \theta_{\ell'}] &= \sum_{\ell'} [-|\partial_t \beta_{\ell'}| |\beta_{\ell'}| + i |\beta_{\ell'}|^2 \partial_t \theta_{\ell'}] \\
\sum_{\ell'} [|\partial_t \beta_{\ell'}| |\beta_{\ell'}|] &= \sum_{\ell'} [-|\partial_t \beta_{\ell'}| |\beta_{\ell'}|].
\end{aligned} \tag{5.38}$$

From the last expression we see that

$$\sum_{\ell'} |\partial_t \beta_{\ell'}| |\beta_{\ell'}| = 0. \tag{5.39}$$

If we repeat the above procedure for the spatial derivative with respect to the nuclear position, i.e., $\nabla_n \sum_{\ell'} \beta_{\ell'} \beta_{\ell'}^* = 0$, we get the following identity:

$$\sum_{\ell'} |\beta_{\ell'}| \nabla_n |\beta_{\ell'}| = 0. \tag{5.40}$$

Now we have all the ingredients to evaluate the first term on the RHS of Eq. (5.26). For this, we are going to use the definition of $|\Phi\rangle_z^t = \sum_{\ell'} \beta_{\ell',z} |\ell'\rangle_z$ combined with Eq. (5.43) and replace into the below equation. Therefore,

$$\begin{aligned}
\langle \Phi_z(\vec{r}, t) | \vec{H}^{BO} - i \partial_t | \Phi_z(\vec{r}, t) \rangle &= \left(\langle \Phi_z(\vec{r}, t) | \vec{H}^{BO} \Phi_z(\vec{r}, t) \rangle - i \sum_{\ell'} \langle \Phi_z(\vec{r}, t) | (\partial_t \beta_{\ell'}) |\ell'\rangle \right) \\
\langle \Phi_z(\vec{r}, t) | \vec{H}^{BO} - i \partial_t | \Phi_z(\vec{r}, t) \rangle &= \langle \Phi_z(\vec{r}, t) | \vec{H}^{BO} \Phi_z(\vec{r}, t) \rangle + \sum_{\ell'} \left(-i (\partial_t \theta_{\ell'}) |\beta_{\ell'}|^2 + |\beta_{\ell'}| \partial_t |\beta_{\ell'}| \right) \\
\langle \Phi_z(\vec{r}, t) | \vec{H}^{BO} - i \partial_t | \Phi_z(\vec{r}, t) \rangle &= \langle \Phi_z(\vec{r}, t) | \vec{H}^{BO} \Phi_z(\vec{r}, t) \rangle + \sum_{\ell'} |\beta_{\ell'}|^2 \partial_t \theta_{\ell'}.
\end{aligned} \tag{5.41}$$

For the computation of the vector potential, as defined in Eq. (5.11), we have to replace Eq. (5.40) in the expression for $\langle \Phi_z^t | \nabla_n \Phi_z^t \rangle$,

$$\begin{aligned}
\langle \Phi_z^t | \nabla_n \Phi_z^t \rangle &= \sum_{\ell'} \left(|\beta_{\ell'}| \nabla_n |\beta_{\ell'}| + i |\beta_{\ell'}|^2 \nabla_n \theta_{\ell'} \right) + \sum_{\ell, \ell'} \beta_{\ell}^\dagger \beta_{\ell'} \langle \ell | \nabla_n \ell' \rangle \\
\langle \Phi_z^t | \nabla_n \Phi_z^t \rangle &= i \left[\sum_{\ell'} |\beta_{\ell'}|^2 \nabla_n \theta_{\ell'} + 2 \sum_{\ell, \ell'} |\beta_{\ell}| |\beta_{\ell'}| \sin(\theta_{\ell'} - \theta_{\ell}) |\langle \ell | \nabla_n \ell' \rangle| \right],
\end{aligned} \tag{5.42}$$

and consequently the above equation combined with the definition of vector potential Eq. (5.11) shows that $\vec{A} \in \mathbb{R}$. The second part in RHS of Eq. (5.42) has been proved using the properties $\langle \ell' | \nabla_n \ell \rangle = -\langle \ell | \nabla_n \ell' \rangle$ and $\mathcal{Z} - \mathcal{Z}^* = 2i \text{Im}(\mathcal{Z})$, where $\mathcal{Z} \in \mathbb{C}$.

Next, applying the ∇_n over the normalization condition for the real $|\ell'\rangle_z$ we get the following relationship:

$$\begin{aligned}\nabla_n \langle \ell | \ell' \rangle &= 0 \\ -\langle \ell' | \nabla_n \ell \rangle &= \langle \nabla_n \ell' | \ell \rangle,\end{aligned}\tag{5.43}$$

here $\ell, \ell' = (1, 2, \dots, N)$. Taking into account that $|\ell'\rangle_z \in \mathbb{R}$, we may rewrite the RHS of the above equation as

$$\langle \ell | \nabla_n \ell' \rangle = \tau_{\ell, \ell'},\tag{5.44}$$

where $\tau_{\ell, \ell'}$ is the element of $N \times N$ matrix. The diagonal elements of the τ matrix are null, because $|\ell'\rangle_z$ are real functions. To illustrate the previous idea, we are going to consider the τ matrix for the two states case, with $|\ell'\rangle_z$ and $|\ell\rangle_z$ defined as,

$$|\ell'\rangle_z = \begin{pmatrix} \cos(s(z)) \\ -\sin(s(z)) \end{pmatrix}, \quad |\ell\rangle_z = \begin{pmatrix} \sin(s(z)) \\ \cos(s(z)) \end{pmatrix},\tag{5.45}$$

using Eq. (5.44) the τ matrix from becomes,

$$\tau = \begin{pmatrix} 0 & \tau_{\ell, \ell'} \\ -\tau_{\ell, \ell'} & 0 \end{pmatrix},\tag{5.46}$$

usually matrix is defined as the electronic nonadiabatic coupling term.

From now on, all the discretization procedure will be conducted within the finite differences framework. The term ${}_z \langle \ell' | \nabla_n \ell \rangle_z$ appears frequently in the Exact Factorization approach. Such terms, in the scope of finite differences give rise to the projections ${}_{z+\Delta z} \langle \ell | \ell' \rangle_z$. Because of this, the computation of these projections has an important role in the connection of NRG and the Exact Factorization approach. Figure 29 shows the projection $({}_{z+\Delta z} \langle \ell | \ell' \rangle_z - 0.999)$ for the ground state with different values of N .

In order to satisfy the identity given in Eq. (5.43) and others, we have to add weights γ in the element of τ , because in any discretization method always there is an error associated with the size of the mesh. Thus,

$$\begin{aligned}{}_z \langle \ell' | \nabla_n \ell \rangle_z &= -{}_z \langle \ell | \nabla_n \ell' \rangle_z \\ \gamma^+ {}_z \langle \ell' | \ell \rangle_{z+\Delta z} - \gamma^- {}_z \langle \ell' | \ell \rangle_{z-\Delta z} &= -\gamma^+ {}_z \langle \ell | \ell' \rangle_{z+\Delta z} + \gamma^- {}_z \langle \ell | \ell' \rangle_{z-\Delta z} \\ \frac{\gamma^+}{\gamma^-} &= \left(\frac{{}_z \langle \ell' | \ell \rangle_{z-\Delta z} + {}_z \langle \ell | \ell' \rangle_{z-\Delta z}}{{}_z \langle \ell' | \ell \rangle_{z+\Delta z} + {}_z \langle \ell | \ell' \rangle_{z+\Delta z}} \right) = \alpha\end{aligned}\tag{5.47}$$

where, $\gamma^+ = \sqrt{\alpha}$ and $\gamma^- = 1/\sqrt{\alpha}$. One can note that, in the limit of $\Delta z \rightarrow 0$, we get $\alpha = 1$ and we observe that its analytical condition is recovered.

Figure 29 – Projection, $(z + \Delta z \langle \ell | \ell' \rangle_z - 0.999)$, for the Ground state, $\ell = \ell'$, of the Hamiltonian, Eq. (5.34), at positions z and $z + \Delta z$ with different values for N . Here, the energetic scale is around $\Lambda^{-(N/2)(\Delta\delta(z)/\pi)^2}$, where $\tan(\delta(z)) = -\pi W(z)/D$ is the lag of the conduction band related to $W(z)$.
Source: By the author

5.3.1 Computing $\hat{U}_{en}^{coup}$ matrix element

For $\vec{A} = 0$, the operator $\hat{U}_{en}^{coup}$ is given by,

$$\hat{U}_{en}^{coup}[\Phi_z(\vec{r}, t), \chi(\vec{z}, t)] = \hat{U} = -\frac{1}{2M} [\nabla_n^2 + 2\xi \cdot \nabla_n], \quad (5.48)$$

where $\xi = \nabla_n \chi / \chi = f(z) + ig(z)$

Here the matrix representation of $\hat{U}$ will be evaluated on the following basis set $|\Phi\rangle_z = \sum_{\ell'} \beta_{\ell',z}^t |\ell'\rangle_z$, where ${}_z\langle \ell | \ell' \rangle_z = \delta_{\ell\ell'}$ and $|\ell'\rangle_z$ are the BO states for the initial time.

Consider the action of $\hat{U}$ on $|\Phi_z\rangle$,

$$\hat{U}|\Phi_z\rangle = \sum_{\ell'} U \beta_{\ell'} |\ell'\rangle_z. \quad (5.49)$$

We write this equation as a matrix $\hat{U}$ acting on a column vector β . For $\hat{U}$ acting on $|\Phi_z\rangle$ and calculating the gradient by finite differences, we get

$$\begin{aligned} \hat{U}|\Phi\rangle_z &= \sum_{\ell'} [(\nabla_n^2 \beta_{\ell',z}) |\ell'\rangle_z + 2(\nabla_n \beta_{\ell',z})(\nabla_n |\ell'\rangle_z) + \beta_{\ell',z}(\nabla_n^2 |\ell'\rangle_z) \\ &\quad + 2\xi((\nabla_n \beta_{\ell',z}) |\ell'\rangle_z + \beta_{\ell',z}(\nabla_n |\ell'\rangle_z))] \end{aligned} \quad (5.50)$$

Considering an internal product with ${}_z\langle\ell|$ in the above equation, we have

$${}_z\langle\ell|\hat{U}\Phi\rangle_z = \sum_{\ell'} U, \quad (5.51)$$

where

$$\begin{aligned} U = & \nabla_n^2 \beta_{\ell',z} \delta_{\ell,\ell'} + 2(\nabla_n \beta_{\ell',z})_z \langle\ell|\nabla_n \ell'\rangle_z + \beta_{\ell',z} ({}_z\langle\ell|\nabla_n^2 \ell'\rangle_z) \\ & + 2\xi(\nabla_n \beta_{\ell',z} \delta_{\ell,\ell'} + \beta_{\ell',z} \langle\ell|\nabla_n \ell'\rangle_z). \end{aligned} \quad (5.52)$$

For the β 's the shape of U operator is a block diagonal matrix,

$$U = \left(\begin{array}{c|c|c|c|c} V_{\ell,\ell'}(z_1) & 0 & 0 & \dots & 0 \\ \hline 0 & V_{\ell,\ell'}(z_2) & 0 & \dots & 0 \\ \hline 0 & 0 & V_{\ell,\ell'}(z_3) & \dots & 0 \\ \hline \vdots & \vdots & \vdots & \ddots & \vdots \\ \hline 0 & 0 & 0 & \dots & V_{\ell,\ell'}(z_M) \end{array} \right) \begin{pmatrix} \beta_{\ell',z_1} \\ \beta_{\ell',z_2} \\ \beta_{\ell',z_3} \\ \vdots \\ \beta_{\ell',z_M} \end{pmatrix} \quad (5.53)$$

where,

$$V_{\ell,\ell'}(z) = \delta_{\ell,\ell'} \nabla_n^2 + 2{}_z\langle\ell|\nabla_n \ell'\rangle_z \nabla_n + {}_z\langle\ell|\nabla_n \ell'\rangle_z + 2\xi(\delta_{\ell,\ell'} \nabla_n + {}_z\langle\ell|\nabla_n \ell'\rangle_z). \quad (5.54)$$

The use of finite differences to discretize the $\beta_{\ell',z}$ gives rise to other two off-diagonal matrices. These matrices are denoted by $R_{\ell,\ell'}$ and $L_{\ell,\ell'}$, and their expressions are presented below.

$$U = [R_{\ell,\ell'} \beta_{\ell',z+\Delta z} + C_{\ell,\ell'} \beta_{\ell',z} + L_{\ell,\ell'} \beta_{\ell',z-\Delta z}] \quad (5.55)$$

where,

$$\begin{aligned} R_{\ell,\ell'} &= \left[\frac{\delta_{\ell,\ell'}}{(\Delta z)^2} + \frac{1}{(\Delta z)} ({}_z\langle\ell|\nabla_n \ell'\rangle_z + \xi \delta_{\ell,\ell'}) \right] \\ C_{\ell,\ell'} &= \left[\frac{-2\delta_{\ell,\ell'}}{(\Delta z)^2} + {}_z\langle\ell|\nabla_n^2 \ell'\rangle_z + 2\xi {}_z\langle\ell|\nabla_n \ell'\rangle_z \right] \\ L_{\ell,\ell'} &= \left[\frac{\delta_{\ell,\ell'}}{(\Delta z)^2} - \frac{1}{(\Delta z)} ({}_z\langle\ell|\nabla_n \ell'\rangle_z + \xi \delta_{\ell,\ell'}) \right] \end{aligned} \quad (5.56)$$

To illustrate the structure of the matrix U , we are going to use a finite basis of

nuclear coordinates. Thus, the full U matrix form is,

$$U = \begin{pmatrix} C_{\ell,\ell'}(z_1) & R_{\ell,\ell'}(z_2) & 0 & \dots & \dots & 0 \\ L_{\ell,\ell'}(z_1) & C_{\ell,\ell'}(z_2) & R_{\ell,\ell'}(z_3) & 0 & \dots & 0 \\ 0 & L_{\ell,\ell'}(z_2) & C_{\ell,\ell'}(z_3) & R_{\ell,\ell'}(z_4) & 0 & 0 \\ \vdots & 0 & L_{\ell,\ell'}(z_{x-1}) & C_{\ell,\ell'}(z_x) & R_{\ell,\ell'}(z_{x+1}) & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\ 0 & 0 & 0 & 0 & L_{\ell,\ell'}(z_{M-1}) & C_{\ell,\ell'}(z_M) \end{pmatrix} \begin{pmatrix} \beta_{\ell',z_1} \\ \beta_{\ell',z_2} \\ \beta_{\ell',z_3} \\ \vdots \\ \beta_{\ell',z_{M-1}} \\ \beta_{\ell',z_M} \end{pmatrix}. \quad (5.57)$$

5.3.2 Crank-Nicolson method

One of most used algorithms to perform the time evolution of TDSE is the Crank-Nicolson method, which is based on finite difference. Such a scheme combines stability and accuracy through the average between the implicit and explicit Forward Time Centered Space (FTCS) schemes. It also conserves probability, and is $O(\Delta t)^3$ accurate in time. Here we introduce the Crank-Nicolson method, which will be used to describes the time evolution of our electronic $\hat{H}^e$ and nuclear $\hat{H}^n$ Hamiltonians. Where such Hamiltonians are defined from Eqs (5.6) and (5.7) as,

$$\hat{H}^e = \hat{H}_{el} - \epsilon(\vec{z}, t) \quad (5.58)$$

$$\hat{H}^n = \frac{1}{2M}(-i\nabla_n + \vec{A}[\Phi_z(\vec{r}, t)])^2 + \epsilon(\vec{z}, t). \quad (5.59)$$

The Crank-Nicolson scheme at time t is represented by the following expression,

$$|\Psi\rangle_z^{t+1} = (\mathbb{1} + i\gamma\hat{H}_z^\eta)^{-1} (\mathbb{1} - i\gamma\hat{H}_z^\eta) |\Psi\rangle_z^t. \quad (5.60)$$

This matrix formula can be simplified by noting that

$$(\mathbb{1} + i\gamma\hat{H}_z^\eta)^{-1} (\mathbb{1} - i\gamma\hat{H}_z^\eta) = \hat{B}^{-1} - \mathbb{1}, \quad (5.61)$$

where $\gamma = \Delta t/2$, and $\hat{B} = 0.5(\mathbb{1} + i\gamma\hat{H}_z^\eta)$. Eq. (5.61) can be proved from the identity,

$$\hat{B}^{-1} - \mathbb{1} = \hat{B}^{-1} (\mathbb{1} - \hat{B}), \quad (5.62)$$

where $|\Psi\rangle$ and $\hat{H}^\eta$ can be understood as the wave function and Hamiltonian for electrons or nuclei,

$$|\Psi\rangle_z^{t+1} = \left[2 (\mathbb{1} + i\gamma\hat{H}_z^\eta)^{-1} - \mathbb{1} \right] |\Psi\rangle_z^t. \quad (5.63)$$

The notation $|\Phi\rangle_z^t$ will henceforth describe the electronic state on site z at time step t as a linear combination of ℓ' states, where ℓ' represents the excited states as well

as the ground state ($\ell' = 0$) for the electronic Hamiltonian $\hat{H}^e$. Therefore, we write the expansion,

$$|\Phi\rangle_z^t = \sum_{\ell'} \beta_{\ell',z}^t |\ell'\rangle_z, \quad (5.64)$$

Thus, replacing Eq. (5.64) into Eq. (5.60) it becomes,

$$\sum_{\ell'} \beta_{z,\ell'}^{t+1} |\ell'\rangle_z = \sum_{\ell'} (\hat{B}^{-1} - \mathbb{1}) \beta_{z,\ell'}^t |\ell'\rangle_z. \quad (5.65)$$

Sometimes it is useful to use a column vector β , which contains all the $\beta_{\ell'}$'s, where

$$\beta^\dagger = (\beta_{z_1,1}, \beta_{z_1,2}, \dots, \beta_{z_2,1}, \beta_{z_2,2}, \dots, \beta_{z_M,N}). \quad (5.66)$$

The coefficients $\beta_{\ell',z}$ at step time $t + 1$ are determined by taking the inner product of ${}_z\langle\ell|$ with Eq. (5.65), where we should use the following conditions,

$${}_z\langle\ell|\ell'\rangle_z = \delta_{\ell,\ell'} \text{ and } {}_z\langle\ell|\ell'\rangle_{z\pm\Delta z} \neq 0. \quad (5.67)$$

So, Eq. (5.67) and Eq. (5.65) read,

$$\begin{aligned} \sum_{\ell'} \beta_{z,\ell'}^{t+1} {}_z\langle\ell|\ell'\rangle_z &= \sum_{\ell'} {}_z\langle\ell| (\hat{B}^{-1} - \mathbb{1}) \beta_{z,\ell'}^t |\ell'\rangle_z \\ \beta_z^{t+1} &= \beta_z^t (\hat{B}^{-1} - \mathbb{1}). \end{aligned} \quad (5.68)$$

Figure 30 presents a flowchart, connecting the NRG with the Exact Factorization approach to get the sticking coefficient S . In this figure, the initial electronic $\Phi_z(\ell', 0)$ comes from the NRG solution, while the nuclear wave functions are represented by a Gaussian wave packet. The solution of the TDSE will determine the wavepacket for long times, and the integrated long-time probability density in the vicinity of $z = 0$ will determine the sticking probability S .

5.4 Preliminary results

Our preliminary results are based on a BO expansion basis set. This expansion is used instead of the Exact Factorization formalism because the non-Hermiticity associated to the $\hat{U}_{en}$ operator interferes in the convergence of the calculations. We are still working on that issue in order to satisfy the Exact Factorization conditions.

Figure 31 shows the preliminary results related to the sticking coefficient project. This figure presents a time-dependent evolution for a gaussian wave packet representing the nucleus of H^- , which is under influence of the charge image potential $W = -1/(2z^2)$. The initial nuclear packet is written as,

$$\chi(z, t = 0) = \left(\frac{1}{2\pi\sigma^2} \right)^{1/4} \exp \left\{ \left(-\frac{(z - z_0)^2}{4\sigma^2} \right) \right\} \exp(ik_0 z), \quad (5.69)$$

Figure 30 – Flowchart connecting the NRG with the Exact Factorization approach. The states $\Phi_z(\ell',0)$ are obtained via NRG, while $\chi(z,0)$ is a Gaussian wave packet.
Source: By the author

where $\sigma = 1.0(a_0)$, $k_0 = 5(1/a_0)$, and $z_0 = 20(a_0)$. The first factor on the RHS of Eq. (5.69) localizes a wave function centred on z_0 with a width of σ , while the second factor gives it a initial momentum of k_0 . We use σ large enough to enclose several oscillations of the wave function, and the momentum k_0 always had kinetic energy sufficient to create excited states in the H^{-1} configuration.

The insert to the right side of Figure 31 displays on the top panel the packet (full red lines) close to the initial position (blue dashed lines). In the middle panel, we observe the packet starting the collision against the metallic surface, in this stage the formation of rapid oscillations occurs caused by the attractive potential. The last panel shows the packet far away from its initial position with a value of σ larger than the initial one. The insertion with blue circles shows the sticking coefficient for all the times with initial momentum equal to $k_0 = 5$. The yellow bar in the end of this panel indicates that after 1300(fs) the sticking coefficient does not continue to change, which allows the measurement of the sticking coefficient. The black squares are the measurements for $\int_0^{z_0} |\chi(z,t)|^2 dz$ computed for incidence momenta. One can note in the last curve shows that the sticking coefficient decays exponentially.

5.5 Conclusion: Sticking coefficient

Those results presented in Figure 31 point out that a small part of the nuclear density of an initially negatively charged Hydrogen H^{-} thrown with an initial momentum

Figure 31 – Sticking coefficient (black squares) $\int_0^{z_0} |\chi(z,t)|^2 dz$ computed at different moments. The insertion on the RHS shows the exact nuclear density (full red lines) started at $z_0 = 20(a_0)$ (blue dashed lines) plotted at the three different times indicated in the panels. The insertion with blue circles shows the sticking coefficient for all the times. The yellow bar in the end of this panel indicates that after 1300(fs) the sticking coefficient does not change further.
Source: By the author

k_0 against a metallic surface gets stuck on the metal. This means that the electron-hole excitation plays an important role in this collision process. We still are working on this project, and we expect the proposal to yield results providing new insight both on scientific and methodological aspects of dynamical problems.

6 CONCLUSION AND OUTLOOKS

6.1 Conclusion

This thesis supply a contribution to the understanding of the interaction between carbon-carbon surface, atom with carbon-surface, and atom with a metallic surface. This thesis was splitting into three projects. In the graphite project, we found that the electronic and geometric properties depend on the vdW correction employed in the calculation. In the adatom supported on graphene project, we combined a modified Anderson-Newns model to describe the coupling between the adatom with Graphene. Beside this, we found the existence of competition between quantum and classical forces, which determines the type of site in which the adatom prefer to adsorbing. In the last project. In this project, we found that the electron-hole excitation plays an important role in the calculation of the sticking coefficient for an initially negatively charged Hydrogen H^- thrown with an initial momentum k_0 against a metallic surface. Our preliminary results indicate that a small part of the nuclear density gets stuck on the metal.

6.2 Outlook

The possible spin-off products of this thesis are:

(1) Explore new avenues using the Time-Dependent DFT (TDDFT) point of view for an TM that impinges upon a Gr sheet, investigate the weekness of TDDFT and propose corrections based on the Exact Factorization.

(2) Relate the Exact Factorization scheme to mixed quantum-classical simulations and explore a possible connection between the non-Hermiticity of $U_{en}[\chi, \Phi]$ and the so-called electronic friction tensor.¹⁷⁵

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Appendix

APPENDIX A – NUMERICAL COMPUTATION OF THE ELASTIC CONSTANTS C_{33} AND C_{333}

As Eqs. (3.4) and (3.5) show, the elastic constant C_{33} and C_{333} can be computed from the interlayer-separation dependence of the binding energy E_b . In practice, the binding energies are only known at a set of discrete separations c_j ($j = 1, 2, \dots, J$), and a numerical procedure is required to compute the second and third derivatives d^2E_b/dc^2 and d^3E_b/dc^3 at the equilibrium separation c_0 . Given that the c dependences contain small oscillations superimposed on the broad minima—the oscillations are difficult to discern at the scale of the figure, but become visible under magnification—, to compute the derivatives, spectral methods are superior to finite-difference methods. Spectral methods are more accurate because they rely on information drawn from a relatively large number of data points, while finite-difference methods extract the derivatives from much smaller data sets. Were the binding-energy curves periodic, Fourier series would be the most recommended approach. Since the curves are not periodic, projection upon Chebyshev polynomials is preferable.

To optimize the computation of the curvature and its derivative at the equilibrium position, we first have to choose the interval defining the projection. To this end, given a sequence of symbols defining a curve in Figure 12, we choose the interval ranging from the smallest $c_j = c_{jmin}$ such that $E_b < 0$ to c_J . We then linearly scale the c axis so that the interval $c_{jmin} \leq c \leq c_J$ maps onto the interval $-1 \leq x \leq 1$. Next, to choose the (nonuniform) mesh that will define the projection, we pick the number N of mesh points so that each mesh point is (approximately) one of the roots of the N th order Chebyshev polynomial $T_N(x)$. More specifically, N is the largest integer such that no two roots of $T_N(x)$ lie between two successive points along the uniform mesh of the c_j in Figure 12.

Once the mesh is defined, we write the binding-energy curve as a $N - 1$ order Chebyshev series

$$E_b(x) = \sum_{n=0}^{N-1} c_n T_n(x), \quad (\text{A.1})$$

i.e., project $E_b(x)$ upon the basis of the Chebyshev polynomials $T_n(x)$ ($n = 0, \dots, N - 1$). Since each derivative $dT_n^{(m)}(x)/dx^m$ ($m = 1, 2, \dots$) is a linear combination of the $n - m$ first Chebyshev polynomials, it is then a simple matter to numerically compute $dE_b(x)/dx$, $d^2E_b(x)/dx^2$, and $d^3E_b(x)/dx^3$. The equilibrium parameter c_0 is then determined as the c value linearly mapped onto the root of $dE_b(x)/dx$, and the derivatives $[dE_b^2(x)/dx^2]_{c_0}$ and $[dE_b^3(x)/dx^3]_{c_0}$ needed to compute C_{33} and C_{333} from Eqs. (3.4) and (3.5) can be easily evaluated.

Figure 33 – The lowest and higher energy isomers for Pd_n $n = 1 - 6$. The numbers below correspond to the relative total energy (eV) of the clusters.
Source: By the author

Figure 34 – The lowest and higher energy isomers for Pt_n $n = 1 - 6$. The numbers below correspond to the relative total energy (eV) of the clusters.
Source: By the author

Figure 35 – The lowest and higher energy isomers for Ni_n/Gr $n = 1 - 6$. The numbers below correspond to the relative total energy of the clusters.
Source: By the author

1

top
	Pd1	Pd1	Pd1	Pd2	Pd2	Pd2	Pd2	Pd2	Pd2	Pd2
side
ΔE (eV)	0.2214	0.0440	0.0000	0.6984	0.4751	0.3867	0.3801	0.3611	0.3594	0.3585
top
	Pd2	Pd2	Pd2	Pd2	Pd3	Pd3	Pd3	Pd3	Pd3	Pd3
side
ΔE (eV)	0.2901	0.0868	0.0221	0.0000	0.2211	0.1732	0.0639	0.0607	0.0563	0.0496
top
	Pd3	Pd3	Pd3	Pd3	Pd4	Pd4	Pd4	Pd4	Pd4	Pd4
side
ΔE (eV)	0.0314	0.0065	0.0019	0.0000	0.3602	0.2272	0.1804	0.1402	0.0516	0.0508
top
	Pd4	Pd4	Pd4	Pd5	Pd5	Pd5	Pd5	Pd5	Pd5	Pd5
side
ΔE (eV)	0.0418	0.0380	0.0000	0.1133	0.1021	0.0945	0.0883	0.0593	0.0099	0.0029
top
	Pd5	Pd5	Pd6	Pd6	Pd6	Pd6	Pd6	Pd6	Pd6	Pd6
side
ΔE (eV)	0.0003	0.0000	0.3382	0.3272	0.1631	0.0650	0.0481	0.0159	0.0011	0.0000

Figure 36 – The lowest and higher energy isomers for Pd_n/Gr $n = 1 - 6$. The numbers below correspond to the relative total energy of the clusters.
Source: By the author

Figure 37 – The lowest and higher energy isomers for Pt_n/Gr $n = 1 - 6$. The numbers below correspond to the relative total energy of the clusters.
Source: By the author

APPENDIX C – DENSITY OF STATES

Here we present the densities of states for the TM_n atom adsorbed on graphene with $n = 1 - 6$.

Figure 38 – The local density of states for TM_1/Gr .
Source: By the author

Figure 39 – The local density of states for TM₂/Gr.
Source: By the author

Figure 40 – The local density of states for TM_3/Gr .
Source: By the author

Figure 41 – The local density of states for TM₄/Gr.
Source: By the author

Figure 42 – The local density of states for TM₅/Gr.
Source: By the author

Figure 43 – The local density of states for TM₆/Gr.
Source: By the author

APPENDIX D – NUMERICAL RENORMALIZATION GROUP

In the simplest description, quantum adsorption of an atom on a metallic surface is modeled by the Hamiltonian,

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{imp} + \hat{\mathcal{H}}_{bath} + \hat{\mathcal{H}}_{int}, \quad (\text{D.1})$$

where $\hat{\mathcal{H}}_{imp}$ represents the degrees of freedom of the impurity and its properties, $\hat{\mathcal{H}}_{bath}$ describes the free conduction band, and $\hat{\mathcal{H}}_{int}$ describes the coupling between the two. Traditionally, the adsorption of atoms on metallic surfaces has been described by the well known Anderson impurity model,^{162,163} whose Hamiltonian is divided in the following way

$$\begin{aligned} \hat{\mathcal{H}}_{imp} &= \sum_{\sigma} \epsilon_d d_{\sigma}^{\dagger} d_{\sigma} + U n_{d,\uparrow} n_{d,\downarrow} \\ \hat{\mathcal{H}}_{bath} &= \sum_{\sigma} \sum_{\vec{k}} \epsilon_{\vec{k}} c_{\vec{k},\sigma}^{\dagger} c_{\vec{k}\sigma} \\ \hat{\mathcal{H}}_{int} &= \sum_{\sigma} \sum_{\vec{k}} V_{\vec{k}} \left(c_{\vec{k},\sigma}^{\dagger} d_{\sigma} + c_{\vec{k},\sigma} d_{\sigma}^{\dagger} \right). \end{aligned} \quad (\text{D.2})$$

In Eq. (D.2), the Fermi operators c_d and $c_{\vec{k}}$ annihilates an electron at the ad-atom level and at a conduction level with momentum $\vec{k}$, respectively. ϵ_d is the adatom energy and U is the Coulomb repulsion energy. The energies $\epsilon_{\vec{k}}$ define the dispersion relation for the metal. The strength of the coupling between the conduction band (bath) and the impurity is given by the hybridization term $V_{\vec{k}}$.

The NRG approach was designed to treat quantum impurity systems, and is therefore suitable to diagonalize the Anderson Hamiltonian.¹⁶⁹ Here we are going to discuss the meaning of the NRG steps only, and not to prove its mathematical aspects. In this thesis, we are considering the hybridization term $V_{\vec{k}}$ as independent of $\vec{k}$, such that $V_{\vec{k}} = V$. In this approximation, the renormalization group theory states that only the s-wave states are important in the scattering process of an electron from the impurity. The other states start to be important when their energies get closer to the energy of the bandwidth. Beside this, we assume the dispersion relation to be linear, i.e., $\epsilon_{\vec{k}} = v_F |\vec{k}|$, which implies a constant density of state $\rho = 1/2D$, with the band defined in the range from $-D$ to D , where the dimensionless energy parameter is defined as $\epsilon = \epsilon/D$. Then Eq. (D.1) can be conveniently written as,

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{imp} + \sum_{\sigma} \int_{-1}^1 d\epsilon b_{\epsilon\sigma}^{\dagger} b_{\epsilon\sigma} + \sqrt{\frac{\Gamma}{\pi}} \sum_{\sigma} \int_{-1}^1 d\epsilon (b_{\epsilon\sigma} d_{\sigma} + d_{\sigma}^{\dagger} a_{\epsilon\sigma}), \quad (\text{D.3})$$

in the above equation we have changed $\vec{k}$ to ϵ and $c_{\vec{k}\sigma}$ to $b_{\epsilon\sigma}$, where the last operator satisfies the fermionic commutation, $[b_{\epsilon\sigma}^{\dagger}, b_{\epsilon'\sigma'}] = \delta(\epsilon - \epsilon') \delta_{\sigma,\sigma'}$.⁴² Eq. (D.3) says that the

adatom interacts with all degrees freedom of a continuous conduction band with constant density of states, a behavior represented in Figure 44.

Figure 44 – Adatom (filled circle) interacting with all degrees of freedom of a continuous conduction band with constant density of states ρ .
Source: By the author

In the solution of strongly correlated impurity systems, the low-energy excitations around of the fermi level ϵ_F are especially important, and this region must be described with high energetic resolution. This problem was tackled by K.G. Wilson in his seminal paper,⁴¹ which formulated the NRG method. The NRG approach is a non-perturbative method that defines a renormalization group transformation of allowing numerical diagonalization of the effective Hamiltonians.¹⁶⁹

The NRG can be divided into five steps. Step (1): the discretization of the conduction band D could in principle be thought in terms of a uniform mesh of size $\delta = D/N = const$, where N is the number of intervals. In strongly correlated impurity systems, the most interesting scale energy lies around the fermi level and uniform mesh automatically define a minimum energy $\epsilon_{min} = \Delta$, which would restrict the computations only when the energy of interest was large than Δ . Because of that, the number of states in the band with an uniform mesh would be very large, which in turn would create an astronomical number of the many-body states generated from them. Once we wish to have access to the very tiny energy scale, a logarithmic mesh, i.e., $\Delta = \ln(\epsilon_{m+1}) - \ln(\epsilon_m) = \ln(\Lambda)$ reduces the computational cost, since with few sites the diagonalization procedure will be feasible.

Here, the dimensionless parameter $\Lambda > 1$ controls the size of the intervals with an error in the order of $\exp(-\pi^2/\ln(\Lambda))$.¹⁷⁰ The discretization of the conduction band $[-D < \epsilon_k < D]$ is divided into energy intervals $-\Lambda^{-m}, \Lambda^{-(m+1)}, \dots$ and $[\Lambda^{-m}, \Lambda^{-(m+1)}, \dots]$ for positive and negative parts respectively, with $\epsilon_F = 0$ and $m = 0, 1, \dots$. In this thesis, we adopt $\Lambda = 3$. and Figure 45 shows a scheme of this discretization.

In the step (2) a transformation is performed over the operators $b_{\epsilon\sigma}$, this operation replaces an infinite set of states for each interval by a single state that is a linear combination of all $b_{\epsilon\sigma}$, which interacts with the impurity, i.e., the continuous Hamiltonian given in

Figure 45 – Discretization of the conduction band using a logarithmic mesh with resolution $\Lambda > 1$. Here, the impurity couples to the many degrees of freedom of all energy scales.

Source: By the author

Eq. (D.3) is exchanged by a discrete one. After of the discretization, this is the second approximation that appears in NRG. In Figure 46 we show a sketch of this transformation for a logarithmic discretization of the conduction band.

Figure 46 – The conduction band is approximated by a single state per interval. These states are represented by red points.

Source: By the author

The step (3) changes basis of the system from b_ϵ to f_n , which leads to the so called Wilson chain. In such change of basis, the impurity couples via the hybridization V only to one site. In order to take account of the remaining terms a Lanczos transformation is performed, this transformation resulting in a chain Hamiltonian with only nearest neighbor hopping t_n , where t_n , Eq. (D.4), fall off exponentially with the distance from the impurity.^{170,176}

$$t_n = \Lambda^{-n/2} \frac{(1 - \Lambda^{-(n+1)})}{(1 - \Lambda^{-(2n+1)})^{1/2} (1 - \Lambda^{-(2n+3)})^{1/2}} \frac{(1 - \Lambda^{-1})}{\log(\Lambda)}. \quad (\text{D.4})$$

This transformation allow us to rewrite the Hamiltonian Eq. (D.3) as,

$$\begin{aligned}\hat{\mathcal{H}} &= \hat{\mathcal{H}}_{imp} + \sqrt{\frac{\Gamma}{\pi}} \sum_{\sigma} \left(f_{0\sigma}^{\dagger} d_{\sigma} + d^{\dagger} f_{0\sigma} \right) \\ &+ \frac{\Lambda}{2} \sum_{\sigma} \sum_{n=0}^{\infty} t_n \left(f_{n\sigma}^{\dagger} f_{n+1\sigma} + f_{n\sigma} f_{n+1\sigma}^{\dagger} \right),\end{aligned}\quad (\text{D.5})$$

where the operator $f_{n\sigma}^{\dagger}$ act creating an electron on site n . Figure 47 shows that the hopping matrix fall off exponentially with $\Lambda^{-n/2}$.

Figure 47 – Wilson chain, where the impurity coupled via hybridization V to the first site. Hopping term falling off exponentially with $\Lambda^{-n/2}$.
Source: By the author

In the step (4) we use renormalization group transformation to truncates the Hamiltonian of Eq. (D.5), which now is viewed as a series of Hamiltonians $\hat{\mathcal{H}}_N$ with ($N = 0, 1, 2, \dots$), where

$$\begin{aligned}\hat{\mathcal{H}}_N &= \Lambda^{(N-1)/2} \left(\hat{\mathcal{H}}_{imp} + \sqrt{\frac{\Gamma}{\pi}} \sum_{\sigma} \left(f_{0\sigma}^{\dagger} d_{\sigma} + d^{\dagger} f_{0\sigma} \right) \right. \\ &\left. + \frac{\Lambda}{2} \sum_{\sigma} \sum_{n=0}^{N-1} t_n \left(f_{n\sigma}^{\dagger} f_{n+1\sigma} + f_{n\sigma} f_{n+1\sigma}^{\dagger} \right) \right).\end{aligned}\quad (\text{D.6})$$

The original system, Eq. (D.5), is recovered in the limit $\Lambda = 1$ and $N \rightarrow \infty$, i.e.,

$$\hat{\mathcal{H}} = \lim_{N \rightarrow \infty} \Lambda^{-(N-1)/2} \hat{\mathcal{H}}_N. \quad (\text{D.7})$$

The factors $\Lambda^{-(N-1)/2}$ and $\Lambda^{(N-1)/2}$ that appear in above equations are chosen such that at each iteration N the energies of $\hat{\mathcal{H}}_N$ are of the order 1.

$\hat{\mathcal{H}}_N$ can be solved iteratively by starting from $\hat{\mathcal{H}}_0$ and iteratively adding the next site. As $t_n \propto \Lambda^{-n/2}$ decays exponentially as n grows, then each new site added to the system can be thought as a perturbation of order $\Lambda^{-n/2}$, which changes the states of the previous iteration, and therefore the energy scales of the $\hat{\mathcal{H}}_N$ are improved as the chain size grows. The renormalization group recursion relations for two neighbor Hamiltonian are expressed as,

$$\begin{aligned}\hat{\mathcal{H}}_{N+1} &= \sqrt{\Lambda} \hat{\mathcal{H}}_N + \sum_{\sigma} t_N \left(f_{N\sigma}^{\dagger} f_{N+1\sigma} + f_{N+1\sigma}^{\dagger} f_{N\sigma} \right) \\ \hat{\mathcal{H}}_0 &= 1/\sqrt{\Lambda} \left(\hat{\mathcal{H}}_{imp} + \hat{\mathcal{H}}_{int} \right)\end{aligned}\quad (\text{D.8})$$

Step (5) says how to use the iterative diagonalization procedure to get the eigenvalues and eigenvectors via NRG. Usually to prevent the rapid growth of the Fock space the states with energies above of $E_{cut}\Lambda^{-1/2}$ are discarded, and only the states with lowest many-particle energies are kept, typically $E_{cut} \approx 20 \times D$.¹⁶⁹ After this, the number of iteration, N , is incremented up to reach the maximum size of the Wilson chain, N_{max} , where typical values are between 60 and 80.^{169,170} Finally, with the eigenvector and eigenvalue converged the properties of the system can be analyzed.