Electronic and chemical properties of graphene-based structures:
A density functional theory study

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Publication date:
2011

Document Version
Early version, also known as pre-print

Link back to DTU Orbit

Citation (APA):
Electronic and chemical properties of graphene-based structures: A density functional theory study

Ph.D. THESIS

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Abstract

In this thesis several aspects of graphene are investigated using density functional theory (DFT) calculations. Graphene is a two-dimensional sheet of carbon atoms, which was isolated and observed for the first time in 2004.

The binding of graphene on metal surfaces is of great technological and scientific importance. However, theoretical approaches based on DFT do not describe dispersion interactions accurately. A recently developed exchange-correlation functional (vdW-DF), which explicitly includes non-local correlations, is used to investigate the metal–graphene interface, and the results are discussed by comparisons with calculations using standard functionals. The relatively strong binding to Ni, Co and Pd surfaces found in the experiments is not reproduced by the vdW-DF, while it is reproduced by the local density approximation.

Graphene nanoribbons (GNRs) have attracted interest as candidates for future nanoelectronics applications. The stability and electronic properties of standard and reconstructed edges are studied, also with common gas species adsorbed at the edge. It is found that the zigzag edge passivated by atomic oxygen is particularly stable, and its ground state is compared to the well studied hydrogen-passivated zigzag GNR.

Catalytic etching of suspended graphene by silver nanoparticles was observed in-situ in a transmission electron microscope. The channels were shown to be aligned along the zigzag edge. DFT calculations are used to model the reaction path for the gasification of both armchair and zigzag edge atoms on a silver surface. While the removal of armchair atoms proceeds without energy barriers, a barrier is found for the zigzag edge, which reproduces the experimentally determined barrier. This is consistent with the observation of zigzag channels, as the removal of zigzag atoms is the rate-limiting step.

Nanomaterials hold promise as effective catalysts. Metal nanoparticles are already common catalyst for a number of industrial chemical reactions. Graphene is functionalized with porphyrin-like structures and is investigated as catalyst for the electrochemical reduction of CO$_2$ to chemical fuels and
comparisons with transition metals surfaces are made. The functionalization with gallium is found to be the best candidate, even though poisoning of the active site by hydrogen represents a major obstacle.
Resume


Grafén-nanobånd (GNR’er) har tiltrukket opmærksomhed som kandidater til fremtidige anvendelser inden for nanoelektronik. Stabiliteten og de elektroniske egenskaber undersøges for standard- og rekonstruerede kanter, herunder med almindelige gasarter adsorberet på kanten. Det ses at zigzag-kanten passiveret af atomart oxygen er særligt stabil, og grundtilstanden for dette system sammenlignes med den allerede velundersøgte hydrogen-passiverede zigzag-GNR.


Nanomaterialer er lovende som effektive katalysatorer. Metalnanopartikler bruges allerede almindeligt som katalysatorer i flere industrielle kemiske reaktioner. Grafén funktionaliseres med porphyrin-agtige strukturer, og undersøges som katalysator for den elektrokemiske reduktion af CO₂ til kemiske
Preface

This thesis is submitted in candidacy for the Ph.D. degree from the Technical University of Denmark (DTU). It is based on the work carried out at the Center for Atomic-scale Materials Design (CAMD), Department of Physics at DTU from September 2008 to August 2011 under the supervision of Associate Professor Kristian S. Thygesen and Professor Karsten W. Jacobsen. Financial support was provided by DTU.

First of all I would like to thank my supervisors Kristian Thygesen and Karsten Jakobsen for their guidance within the realm of electronic structure theory. I have greatly benefited from their knowledge, ideas and suggestions. I thank Jan Rossmeisl for his advice in the exciting catalysis part, together with Vladimir Tripkovic and Mårten Björketun.

A special acknowledgment goes to my office mates of many years: Mikkel, Egill, Anca, Hai-Jan, Vladimir, Georgios, Jón, Nonni, Jakob and Falko. Thanks also to Carsten, Marcin and Jun for the “relaxing” gym breaks, and to Filippo for the collaboration on the graphene pac-man project.

I am very grateful to Marcin Dulak, Jens J. Mortensen and Ole H. Nielsen from the IT team for making sure that all the CPUs were always up and running. I want to thank Marianne Ærsøe, Helle W. Wellejus, Stavroula G. Nielsen for facilitating all the administrative matters.

A great thanks goes to all the colleagues who commented and proofread part of this thesis: M. Dulak, J. Yan, G. Tritsaris, J. Howalt, Ask. H. Larsen.

Lastly, and most importantly, I would like to thank my family for their continuous love and encouragement throughout my life. A special thanks goes to Silvia, who made my stay in Denmark a wonderful experience beyond academia, and to her family for their loving support.

Copenhagen, August 2011

Marco Vanin
List of Publications

Included Publications

Paper I
Localized atomic basis set in the projector augmented wave method

Paper II
Graphene on metals: A van der Waals density functional study

Paper III
First-principles calculations of graphene nanoribbons in gaseous environments: Structural and electronic properties
M. Vanin, J. Gath, K. S. Thygesen, and K. W. Jacobsen

Paper IV
Mechanism of channelling behaviour of silver nanoparticles on suspended graphene
F. Pizzocchero, M. Vanin, T. Booth, K. W. Jacobsen, P. Bøggild
Submitted to Nano Letters

Paper V
Functionalized graphene as catalyst for CO2 electrochemical reduction
M. Vanin, V. Tripkovic, M. E. Björketun, K.S. Thygesen, K.W. Jacobsen and Jan Rossmeisl
In preparation
Other Publications

Paper VI
Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method
J. Enkovaara et al. (M. Vanin)

Paper VII
Density functional theory based screening of ternary alkali-transition metal borohydrides: A computational material design project
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Chapter 1

Introduction

Even though carbon is one of the most abundant elements in the universe and the basis of organic chemistry and thus of life as we know it, this chemical element has been attracting enormous interests recently. After the discovery of carbon nanotubes and fullerenes in the late 80s and early 90s, the attention has now turned to graphene, a sheet of carbon atoms arranged on a honeycomb lattice. The Nobel prize in Physics of 2010 was awarded to Novoselov and Geim following their isolation of this material for the first time in 2004. Due to the flexibility of its bonding, carbon has a variety of allotropes and for most of them graphene can be considered the basic, two-dimensional ingredient. Carbon nanotubes, one-dimensional systems, can be obtained by rolling graphene along a given direction. Fullerenes, zero-dimensional systems, can be thought as wrapped-up graphene after some pentagons have been introduced. The three-dimensional allotrope, the most common and well known, is graphite, which consists of a stack of weakly interacting graphene layers. In contrast to these $sp^2$-bonded materials, diamond is another three-dimensional carbon allotrope, in which the bonding network is $sp^3$ instead. By peeling off graphite, or alternatively by writing with a pencil, graphene sheets can be produced and occasionally even single layers can be obtained. However, only in recent years experimental tools for manipulating atomic layers and nanostructures in general have become available. This is part of the reason why it has taken so long for graphene to be isolated even though it had been produced before in all probability. The other part of the reason is that no one had actually been looking for it, since two-dimensional crystals had never been observed before, and were believed not to exist, at least in the free-standing form.

Graphene research and publications have developed at a remarkable pace, due to the large variety of properties which make graphene extremely exciting both for fundamental science and for technological applications. In the
1. Introduction

following, a brief overview of graphene properties will be given. For a more comprehensive treatment, the reader is directed to the excellent available review papers[1, 2].

The honeycomb lattice is usually described as consisting of two interpenetrating triangular lattices. The primitive unit cell has two atoms, commonly designated as A and B carbon atoms, as shown in Fig. 1.1. The \( sp^2 \) bonding network leads to the formation of the in-plane \( \sigma \) bond between carbon atoms with a distance of 1.42 Å. This bond is responsible for the strength of the graphitic materials. The remaining \( p \) orbital, perpendicular to the plane, hybridizes to form the \( \pi \) band. Since each \( p \) orbital has one electron, the \( \pi \) band is half filled. The band structure was calculated by Wallace already in 1947[3] using a simple tight-binding approximation, see Fig. 1.1. The key feature is that the two \( \pi \) bands are crossing each other exactly at the Fermi level, giving rise to a conical intersection, known as Dirac point, at the K and K’ points in the Brillouin zone. This peculiar dispersion

\[
E = \hbar v_F |k|
\]

means that the charge carriers in graphene mimic relativistic particles. At low energy the quasiparticles can be described as massless Dirac fermions, where the speed of light in the Dirac equation is replaced by the Fermi velocity \( v_F \). The spin of the relativistic particle is mimicked in graphene by the so called pseudo-spin, which is related to the composition of the wavefunction from the two sublattices. By analogy to quantum electrodynamics (QED) the chirality can also be defined, which basically connects electron states at \( k \) with

Figure 1.1: Left: graphene lattice, with the primitive unit cell containing the A and B carbon atoms. Right: band dispersion for the \( \pi \) bands from the tight binding approximation.
hole states at $-k$ since they belong to the same carbon sublattice. Several exotic effects in graphene can be understood in terms of conservation laws for pseudo-spin and chirality. Examples are the suppression of backscattering and Klein tunneling[4]. Among the most spectacular phenomena reported it is worth mentioning the anomalous quantum Hall effect and the minimum conductivity in the limit of zero carriers. Due to all these unique features, graphene was soon recognized as a material with tremendous potential in the field of post-silicon nanoelectronics. It exhibits remarkable transport properties, with room temperature mobilities up to 15000 cm$^2$V$^{-1}$s$^{-1}$ at ambient conditions[5]. Moreover, being planar, it has significant advantages over carbon nanotubes in terms of fabrication and compatibility with current silicon technology. Field effect transistor behavior was observed already when graphene was first isolated[6].

Despite the fact that the linear band structure is extremely intriguing and interesting, most electronic applications require a band gap in order to operate. Several approaches have been proposed in order to open a band gap in graphene, the most common ones being chemical doping[7, 8], antidot lattices[9], lateral confinement[10] and strain engineering[11]. Recent developments of fabrication techniques have led to the fabrication of graphene nanoribbons (GNRs), which are graphene stripes in which the effect of lateral quantum confinement produces a band gap. Prototype devices have already been demonstrated, in which GNRs are used as semiconducting electronic devices[12]. Challenges in the fabrication and manipulation of these nanostructures still remain, but the experimental achievements have been impressive over the last few years.

Even though the electronic properties have been the most investigated so far, current graphene research also involves a number of other lines. Due to its lightness and stiffness, graphene’s structural properties have been investigated in connection with both fundamental and applied research. Applications in the field of nanoelectromechanical systems (NEMS) are seen as particular promising[13], with particular attention to resonator and sensing applications. Thermal properties have also shown potential for applications, with room-temperature thermal conductivity up to 5000 Wm$^{-1}$K$^{-1}$[14]. The investigation of the chemistry and reactivity of graphene and graphene-based systems is only at the beginning but it is likely to play an important role with respect to precise functionalization and even catalysis[15, 16].

Before concluding this brief overview, a few words have to be said about the current fabrication techniques. The mechanical exfoliation, also known as the scotch-tape method, has been replaced by catalytic growth on metal surfaces[17] with chemical vapour deposition techniques. This method has the potential to be scalable for mass production of large-area graphene flakes.
Methods based on chemical synthesis from graphite, usually via graphene oxides, have also attracted interest recently[18, 19]. The quality and the size of the graphene samples have been improving dramatically over the past few years, but the precise control over the growth mechanism is still challenging. This makes the quest for a cheap and reliable growth method still one of the holy grails in graphene research.

In the present thesis several aspects among the topics mentioned in this introduction have been touched upon. Each chapter deals with the investigation of a different aspect, using first principles calculations to solve the electronic structure problem. In Chapter 2 the theoretical background is presented, with emphasis on the density functional theory (DFT). Chapter 3 reviews the implementation of a localized basis-set within the projector augmented wave method, which is the way of describing the core electrons that is used in the GPAW code[20]. In Chapter 4 the investigation of the binding of graphene on metallic model surfaces is presented. The results from traditional exchange and correlation functionals are compared to the results obtained with a new type of functional, which includes van dew Waals interactions. Relevant comparisons to experimental data are also illustrated, which show that the metal-graphene interface still represents a challenge for DFT-based methods. The stability of GNRs in the presence of common gas species adsorbed at the edge is investigated in Chapter 5. It is pointed out that the saturation of the edges by oxygen atoms is also important to consider, besides the well studied hydrogen passivation. Chapter 6 presents a joint experimental and theoretical study of the mechanism by which suspended graphene is etched by catalytically active silver nanoparticles. The experimental observation of zigzag channels is elucidated by the DFT calculations, which show that the armchair edges are easier to remove and therefore only zigzag edges are left. In Chapter 7 functionalized graphene is investigated as catalyst for the electrochemical reduction of CO2 to chemical fuels and comparisons are made with traditional transition-metal surfaces. The investigated porphyrin-like structures are attractive candidates although issues regarding the poisoning of the active site remain to be addressed.

Outline of the Thesis

This thesis is organized as follows:

Chapter 2 provides a brief theoretical background on the methods that are relevant for this thesis. It also discusses some issues related to the implementation.

Chapter 3 outlines the implementation of a localized basis set within the
projector augmented wave method, and presents a set of benchmark results.

Chapter 4 presents a study about the adsorption of graphene on metallic model surfaces. The results obtained with standard functionals are compared to those obtained with a recently developed functional which includes a non-local term for the treatment of van der Waals interactions. The results are finally compared to experiments.

Chapter 5 presents a study of the stability and electronic properties of graphene nanoribbons with different edge configurations and a number of common gas species adsorbed at the edges.

Chapter 6 presents a joint experimental and theoretical study of the catalytic etching of suspended graphene by silver nanoparticles. Calculations are shown to support the experimental evidence that the channels are etched along the zigzag direction.

Chapter 7 is a first step towards the systematic investigation of porphyrin-like functionalized graphene for catalytic applications. In particular, the electrochemical reduction of CO$_2$ is studied.
Chapter 2

Theory

The results presented in this thesis are based on “ab-initio” (or first-principles) quantum-mechanical calculations. This means that no empirical parameters are used in order to compute the electronic structure properties of a system, but only the atomic numbers and positions are inputs to a calculation. The increase in computer power in the last decades has made it possible to perform ab-initio calculations on larger and more realistic systems, achieving a degree of accuracy which enables direct comparison to experiments.

The aim of this chapter is to give a brief overview of the theoretical methods used in this thesis. Some aspects of the implementation relevant for the work presented in later chapters are also discussed and references are provided to more in-depth literature.

2.1 The Electronic Structure Problem

All properties of matter are in principle described by the well known Schrödinger equation (in the time-independent approximation)

\[ \hat{H}\Psi = \epsilon \Psi. \]  (2.1)

Any observable can be extracted from the many-body wavefunction \( \Psi \), and \( \epsilon \) is the total energy of the system. The Hamiltonian operator \( \hat{H} \) in general depends on both electronic and nuclear degrees of freedoms. The Born-Oppenheimer approximation allows to decouple the electronic and nuclear dynamics due to the large difference in mass between electrons and nuclei, \( m_e/M_n \approx 10^{-3} - 10^{-5} \). The electron problem can thus be reduced to a N-electron Hamiltonian in which the nuclei are assumed to be fixed at some given positions \( \{ \mathbf{R}_i \} \) i.e. they enter as external parameters. In the non-
2. Theory

relativistic approximation it reads

\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_i \sum_{I} \frac{Z_I}{|r_i - R_I|} - \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} \]

(2.2)

where \( r_i \) is the position of electron \( i \) and \( Z_I \) is the atomic number of nucleus \( I \). The first term in (2.2) is the kinetic energy operator, the second term is the electrostatic potential from the ions and the last term is the electron-electron interaction due to the Coulomb repulsion between electrons. Note that \( \hat{V}_{\text{ext}} \) could also include any other external contribution (e.g., applied electromagnetic fields) besides the ionic potential. It should be noted that all the many-body effects are contained in the two-body operator \( \hat{V}_{e-e} \), which is then the most cumbersome term to deal with in realistic calculations.

Solving (2.1) is the fundamental challenge in the theory of the electronic structure of matter, and many ways of attacking the problem have been devised, based on different levels of approximations. For sufficiently small molecules, wavefunction-based methods are feasible and give excellent results. They usually rely on the minimization of a suitable energy functional within the space of a chosen set of approximations for the real wave-function. Many-body perturbation theory is another approach, but extremely expensive numerical methods are required for realistic systems. Quantum Monte Carlo simulations are also computationally very demanding, restricting them only to systems with a few electrons.

A somewhat different approach is provided by the Density Functional Theory (DFT), which has became the basis of much of the computational many-body physics we see today.

### 2.2 Density Functional Theory

DFT is an exact reformulation of the electronic structure problem in terms of the electronic density \( n(r) \) rather than the many-body wavefunction \( \Psi(r_1 \sigma_1, r_2 \sigma_2, ..., r_N \sigma_N) \), which was worth the Nobel Prize in Chemistry in 1998 to Walter Kohn and John Pople. The major strength of this formulation is the fact that it allows to solve the electronic structure problem in an efficient way, thus providing an excellent compromise between accuracy and computational cost. Although in principle exact, the theory requires a universal functional which is in general unknown and must be approximated.
2.2. Density Functional Theory

2.2.1 Hohenberg-Kohn Theorems

The basis of DFT is the work by Hohenberg and Kohn (HK) in 1964 [21]

**Theorem 2.2.1 (Hohenberg-Kohn 1, 1964)** The ground state density $n(r)$ of a many-body quantum system in some external potential $v_{\text{ext}}(r)$ determines this potential uniquely.

which formally enables using the three-dimensional (real) function $n(r)$ instead of the $3N$-dimensional (complex) many-body wave function $\Psi(r_1, r_2, ..., r_N)$ as the basic variable. In other words, all physical properties deriving from a given Hamiltonian through the solution of the time-independent Schrödinger equation are determined by $n(r)$. This includes the ground state energy $E[n(r)]$, among others. More precisely, all physical observables can in principle be expressed as functionals of the electronic charge-density.

The second major ingredient is the existence of a variational principle for the energy functional:

**Theorem 2.2.2 (Hohenberg-Kohn 2, 1964)** For any trial density $n(r)$ it holds $E_0 \leq E[n(r)]$, where $E_0$ is the ground-state energy for the system.

In other words, the minimum value of the total-energy functional $E[n(r)]$ is the ground state energy of the system, and the density which yields its minimum value is exactly the single particle ground-state density.

The explicit form of this energy functional reads

$$E[n] = \int v(r)n(r)dr + F[n],$$  \hspace{1cm} (2.3)

where the universal functional

$$F[n] = \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} dr dr' + G[n],$$  \hspace{1cm} (2.4)

is often separated into the classical Coulomb term due to the charged electrons and the new universal functional $G[n]$.

2.2.2 Kohn-Sham Scheme

Although providing the ultimate theoretical foundation of DFT, the HK work of 1964 does not propose a simple way to solve the many-body problem. Such a scheme was in fact provided by the work of Kohn and Sham in 1965 [22]. For any interacting ground state density $n_0(r)$, a corresponding non-interacting system in some effective potential $V_s$ is constructed such that the
non-interacting Hamiltonian $H_s = T + V_s$ produce the same ground state density $n_0(r)$

$$E_s[n] = T_s[n] + \int v_s(r)n(r)dr. \quad (2.5)$$

We know from the HK theory that

$$E[n] = \int v_{ext}(r)n(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|}drdr' + G[n] \quad (2.6)$$

$$= \int v_{ext}(r)n(r)dr + U_H[n] + G[n], \quad (2.7)$$

and we now write the universal functional as

$$G[n] = T_s[n] + E_{xc}[n]. \quad (2.8)$$

where $T_s[n]$ is the kinetic energy of a system of non-interacting electrons with density $n(r)$ and $E_{xc}[n]$ is the definition of the exchange and correlation energy of the corresponding interacting system which we will discuss later.

The problem of minimizing the functional (2.6) is casted in the form of the Euler-Lagrange equation

$$\delta \left\{ E[n] - \mu \int n(r)dr \right\} = 0, \quad (2.9)$$

where the conservation of electrons is enforced by the Lagrange multiplier $\mu$, fixed so that $\int n(r)dr = N$ Taking the functional derivatives and using (2.6) and (2.8) we obtain an expression for $v_S$

$$v_s(r) = v_{ext}(r) + \int \frac{n_0(r')}{|r-r'|}dr' + v_{xc}([n_0];r), \quad (2.10)$$

where the exchange and correlation potential is

$$v_{xc}([n_0];r) = \frac{\delta E_{xc}[n]}{\delta n(r)} \big|_{n_0}. \quad (2.11)$$

Eq. (2.9) can then be rewritten as

$$\int \delta n(r) \left\{ v_s(r) + \frac{\delta T_s[n]}{\delta n(r)} \right\} dr = 0, \quad (2.12)$$

which takes the same form of an equation applied to a system of non-interacting electrons moving in an effective potential $v_s(r)$. Therefore one
2.2. Density Functional Theory

obtains the sought density $n(r)$ by solving a set of single-particle Schrödinger equations for a given $v_s(r)$

$$\left[-\frac{1}{2}\nabla^2 + v_s(r)\right] \phi_i(r) = \epsilon_i \phi_i(r), \quad (2.13)$$

and computing

$$n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2, \quad (2.14)$$

from which the ground state energy is

$$E_0 = \sum_{j}^{\text{occ}} \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle + \int v_{\text{ext}}(r)n(r)dr + U_H[n] + E_{xc}[n] \quad (2.15)$$

$$= T_s[\{\phi_i\}] + \int v_{\text{ext}}(r)n(r)dr + U_H[n] + E_{xc}[n]. \quad (2.16)$$

As the sum of the eigenvalues in (2.13) is the same of the ground state energy of the non-interacting KS system in (2.5) we can rewrite the kinetic energy term $T_s[\{\phi_i\}]$ as

$$T_s[\{\phi_i\}] = \sum_{j}^{\text{occ}} \epsilon_j - \int v_s(r)n(r)dr, \quad (2.17)$$

which allows to rewrite the ground state energy as

$$E_0 = \sum_{j}^{\text{occ}} \epsilon_j - \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|}drd' + E_{xc}[n] - \int v_{xc}([n_0];r)n(r)dr$$

$$= \sum_{j}^{\text{occ}} \epsilon_j - U_H[n] + E_{xc}[n] - \int v_{xc}([n_0];r)n(r)dr. \quad (2.18)$$

Note that, since the Kohn-Sham potential $v_s(r)$ itself depends on the density, the equations (2.13) are to be solved self-consistently until convergence is reached in the electron density. It is worthwhile mentioning that Kohn-Sham orbital energies do not carry a direct and simple physical meaning, with the exception of the HOMO level which is equal to minus the ionization potential via Koopman’s theorem.

2.2.3 Exchange and Correlation Functionals

The exchange and correlation term in the KS theory appears because the universal functional $F[n(r)]$ contains information beyond the Hartree term
\(U_H[n]\) and the one-body kinetic operator \(T_s[\{\phi_i\}],\)
\[
E_{xc}[n] = F[n(r)] - T_s[\{\phi_i\}] - U_H[n].
\] (2.19)

which is usually separated into exchange and correlation components
\[
E_{xc}[n] = E_x[n] + E_c[n].
\] (2.20)

Several approximations for \(E_{xc}[n]\) have been developed over the years using different approaches, each one providing different accuracy and/or computational cost. Only a brief description of the main types will be given here.

**LDA**

The Local Density Approximation, already introduced by Kohn and Sham in [22], approximates the \(xc\)-energy density with the the \(xc\)-energy density of the homogeneous electron gas with the same density as the the local density of the considered system
\[
E_{LDA}^{xc}[n(r)] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}^{\text{hom}}(\mathbf{r}, [n(\mathbf{r})])
\] (2.21)

The exchange expression for \(\varepsilon_{xc}^{\text{hom}}(\mathbf{r}, [n(\mathbf{r})])\) is known exactly, while the correlation part is fitted to very accurate quantum Monte-Carlo simulations. Several parametrizations exist, the most common ones being the Perdew-Wang[23] and the Perdew-Zunger[24]. The surprisingly good results produced by this simple form are usually attributed to the LDA approximation satisfying many of the constraints of the exact \(xc\) functional. Despite its simplicity, it is still widely used, especially in the solid state community.

**GGA**

The generalized gradient approximations add the dependence on the local density gradient
\[
E_{xc}^{GGA} = \int d\mathbf{r} \varepsilon_{xc}^{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)
\] (2.22)

thus making the functional semi-local. Different GGAs usually differ for the exchange part of \(F_{xc}\), and several of them have been developed. GGAs
2.3 Implementation

functionals are the most commonly used functionals nowadays. The most common versions are by Becke (B88)[25], Perdew and Wang (PW91)[26] and Perdew, Burke and Enzerhof (PBE)[27]. Revised versions of PBE are also widely used, such as revPBE[28] and RPBE[29], which are fitted to databases. In this work the RPBE functional has been used, unless specified otherwise.

vdW-DF

The widely used local and semi-local functionals usually provide an accurate description of covalent and ionic chemical bonds. However, they fail to reproduce nonlocal dispersive forces, in particular van der Waals interactions, which are likely to play an important role in the case of graphene. The vdW-DF[30, 31] was recently developed in order to account for the van der Waals interaction through a non-local correlation term. The functional takes the form

\[ E_{vdw-DF}^{xc} = E_{revPBE}^{xc} + E_{LDA}^{c} + E_{nl}^{c} \]  \hspace{1cm} (2.23)

where \( E_{revPBE}^{xc} \) is the revPBE[28] exchange energy, \( E_{LDA}^{c} \) is the LDA correlation energy and \( E_{nl}^{c} \) is the non-local correction given by

\[ E_{nl}^{c} = \frac{1}{2} \int \int n(r_1)n(r_2)\phi(q_1, q_2, r_{12})dr_1dr_2 \]  \hspace{1cm} (2.24)

where \( r_{12} = |r_1 - r_2| \) and \( q_1 \) and \( q_2 \) are values of a universal function \( q_0(n(r), |\nabla n(r)|) \). Eq. (2.24) is efficiently evaluated by factorizing the integration kernel \( \phi \) and by using fast Fourier transform to compute the self-consistent potential as proposed in Ref. [32].

2.3 Implementation

All the first principle calculations in this thesis have been performed with the GPAW code, which implements DFT within the Projector Augmented Wave formalism. The next sections cover some important aspects of the DFT implementation relevant to the GPAW code. For a detailed account of the GPAW implementation, see [20].

2.3.1 The Projector Augmented Wave Method

When solving the Kohn-Sham equation for condensed matter systems, one of the main concerns is the very different behavior of the wavefunctions close to and far from the nuclei. The rapid oscillations of the wavefunctions in the core region make their representation computationally expensive. In the
pseudopotential approach, the atomic potential is replaced by an effective, smoother, potential which is easier to represent numerically. This pseudopotential is constructed in such a way to reproduce the correct scattering effect on the remaining valence electrons. The drawback of this approach is that the information of the core region wavefunctions is lost. The Projector Augmented Wave (PAW) method allows to use a computationally convenient representation while maintaining the all-electron information available. This is achieved by describing the all-electron wavefunction $|\psi\rangle$ in terms of a smooth pseudo-wavefunction $|\tilde{\psi}\rangle$ in the valence region and a local basis set expansion in the core region, called the augmentation sphere, around each atom $a$. It is thus possible to recover the all-electron wavefunction using the PAW transformation operator $\hat{T}$

$$
|\psi_n\rangle = \hat{T} |\tilde{\psi}_n\rangle
$$

where $n$ is a quantum state label, consisting of a band index and possibly a spin and $k$-vector index. The transformation operator is expressed as

$$
\hat{T} = \sum_a \sum_i (|\phi^a_i\rangle - |\tilde{\phi}^a_i\rangle) \langle \tilde{\phi}^a_i^n |
$$

where $|\phi^a_i\rangle$, $|\tilde{\phi}^a_i\rangle$ and $\tilde{\phi}^a_i$ are atom-dependent partial waves and projector functions which are only non-zero inside the augmentation sphere. The partial waves $|\phi^a_i\rangle$ and $|\tilde{\phi}^a_i\rangle$ are the basis set used to expand $|\psi_n\rangle$ and $|\tilde{\psi}_n\rangle$ respectively. $|\phi^a_i\rangle$ are usually chosen to be the solutions of the Kohn-Sham equations for the isolated atom, and $|\tilde{\phi}^a_i\rangle$ are their smooth continuation inside the augmentation spheres. The projectors $\tilde{\phi}^a_i$ are functions dual to the partial waves $\tilde{\psi}_n$ and can be chosen in order to obtain a rapid convergence of the expansion of the wavefunctions.

Since the core electrons hardly participate in the chemistry, the frozen-core approximation is applied. Within this approximation, the Kohn-Sham orbitals of the core electrons are fixed to the orbitals of the corresponding isolated atoms. The Kohn-Sham equations are thus only solved for the valence electrons.

### 2.3.2 Basis Sets

In order to solve the Kohn-Sham equations, the wavefunctions need to be represented in a computationally convenient way. In the GPAW code, the wavefunctions can be represented using two different basis sets: real-space grids and a localized basis composed of a linear combination of atomic orbitals (LCAO). The latter option has been implemented in order to reduce the
computational cost while keeping an acceptable accuracy. The possibility
to switch seamlessly between the two representations is also a convenient
feature of the code.

**Real Space Grid**

The use of real-space grids for electronic structure calculations is relatively
recent, compared to the more traditional plane-wave basis used by the solid
state community. Real-space techniques provide several advantages over
plane waves. A plane-wave basis inherently imposes periodic boundary con-
ditions, while the grid allows for a flexible treatment of boundary condi-
tions. The Fourier transforms used in plane-wave methods are very difficult
to parallelize efficiently, while the parallelization over real-space domains is
very efficient, requiring only small communication overhead. Similarly to the
plane-wave approach, the accuracy can be systematically tuned by a single
parameter, the grid spacing (in analogy with the kinetic energy cutoff in
plane-wave methods).

In the “grid mode”, the wavefunctions are represented on a three-dimensional
real-space grid. Differential operators, such as the kinetic energy operator,
are represented using finite-difference methods. Well developed grid-based
algorithms can be used, and the Poisson equation is also solved using multi-
grid methods.

**Numerical Atomic Orbitals**

Localized functions, traditionally popular among chemists, provide a very
compact and efficient basis set, suitable for large systems and systems con-
taining a lot of vacuum. This type of basis is also particularly convenient
in combination with Green’s functions-type methods, which make use of the
locality of the representation. A description of the LCAO implementation is
presented in Chapter 3.

### 2.4 Electron Transport Calculations

Non-equilibrium Green’s functions combined with DFT can be used to inves-
tigate electron transport at the atomic scale, within the so called NEGF-DFT
method[33]. Standard DFT calculations provide the structure, the electronic
structure and the Hamiltonian in the LCAO basis (which is then used to
construct the Green’s functions). The transport system is partitioned into
three regions: the two semi-infinite leads (L,R) and the central region (C).
The phase-coherent conductance in the low bias limit is

\[ G(\varepsilon) = G_0 T(\varepsilon_F), \quad (2.27) \]

where \( G_0 = \frac{2e^2}{h} \) is the conductance quantum and \( T(\varepsilon) \) is the transmission function, given by

\[ T(\varepsilon_F) = \text{Tr}[G_L^r(\varepsilon)\Gamma_L(\varepsilon)G_C^a(\varepsilon)\Gamma_R(\varepsilon)]; \quad (2.28) \]

where \( G_L^r \) (\( G_C^a \)) is the retarded (advanced) Green’s function of the central region, and \( \Gamma_\alpha \) is related to the self energies of the leads

\[ \Gamma_{L/R} = i(\Sigma_{L/R} - \Sigma_{L/R}^\dagger). \quad (2.29) \]

and represents the broadening of the states in the central region due to the coupling to the leads. Note that this formulation is totally equivalent to the Landauer-Büttiker formalism[34].

### 2.5 Adsorption

The adsorption energy is often a key quantity, in particular when the interaction between molecules and surfaces is involved. This is especially true in the field of catalysis, where the adsorption energy is a measure of the strength of the bond to the surface, which is a very important descriptor in the investigation of catalytic properties of materials. Since DFT provides total energies, the adsorption energy is calculated as a difference between the energy of the composite system and the energies of the component parts. For example, the adsorption energy of a molecule on a surface is calculated as

\[ \Delta E_{\text{molecule}^\ast} = E_{\text{molecule+surface}} - E_{\text{surface}} - E_{\text{molecule}^\ast}. \quad (2.30) \]

The adsorption energy \( \Delta E \) can be converted into free energy by taking into account the change in zero-point energy \( \Delta ZPE \) and entropy \( \Delta S \) between the composite system and the parts

\[ \Delta G = \Delta E + \Delta ZPE - T\Delta S, \quad (2.31) \]

where \( T \) is the temperature. This is typically the quantity of interest when chemical reactions are considered. The energetics of a chemical reaction pathway is usually investigated by plotting the calculated free energies as a function of a reaction coordinate. In the case of electrochemical processes, due to the presence of the aqueous solution extra terms that take into account the applied potential, the stabilization from the water and the effects of the pH and the electric field should be added[35].
Chapter 3

Localized Atomic Basis Set in the Projector Augmented Wave Method

This chapter is based on Paper I. It discusses the implementation of localized atomic-orbital basis sets within the projector augmented wave (PAW) formalism. Benchmark results are also presented for atomization energies of molecules and equilibrium bulk properties of a variety of solids. An example of structural relaxation is also discussed and compared to the grid result.

3.1 Introduction

As discussed in the previous chapter, the only approximation of DFT is the exchange-correlation functional. However, solving the Kohn-Sham equations involves, besides the challenge of describing the rapid core oscillations as outlined in the PAW section in Chapter 2, the representation of the Kohn-Sham wave functions. Plane waves, wavelets and real-space grids are accurate basis sets which can be systematically improved to achieve better convergence. Relatively less accurate but computationally more efficient are the localized basis sets, such as gaussians or numerical atomic orbitals. The following section will describe the implementation of the localized basis set, which we shall refer to as linear combination of atomic orbitals (LCAO), within the PAW formalism in the GPAW code. A convenient feature of the implementation is the unique possibility of using two different but complementary basis sets within the same formalism and approximations, i.e. the real-space grid and the LCAO basis. This allows to switch seamlessly between the two representations even during a calculation. As an example of this feature, a
Figure 3.1: The pseudo valence states of iron calculated with PAW and the norm-conserving HGH pseudopotentials. Both methods produce smooth wave functions for the delocalized 4s state, but the lack of norm conservation allows the short-ranged 3d state in PAW to be accurately sampled on a much coarser grid.

structural relaxation will be presented where the first steps are performed with the atomic basis while the grid is used for the final steps. In this way adsorption energies, which are typically not very accurate with LCAO methods, can easily be improved in the grid mode. The combination of LCAO and PAW is also unique because compared to norm-conserving pseudopotential methods it allows the use of coarser grids. This is especially important for large systems, where the operations performed on the grid become computationally dominant. As an example, Fig. 3.1 shows the atomic orbitals of iron calculated with the norm-conserving Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials[36] as well as with PAW. The d state is clearly much smoother in PAW.

3.2 Localized Basis Set in PAW

The Kohn-Sham eigenfunctions $|\tilde{\psi}_n\rangle$ are expanded onto atom-centered numerical orbitals $|\Phi_\mu\rangle$

$$|\tilde{\psi}_n\rangle = \sum_\mu c_{\mu n} |\Phi_\mu\rangle,$$  \hspace{1cm} (3.1)

where the expansion coefficients $c_{\mu n}$ are now the variational parameters in the self-consistent loop. The basis orbitals $|\Phi_\mu\rangle$ are chosen as

$$\Phi_{nlm}(r) = \psi_{nl}(r)Y_{lm}(\hat{r}),$$ \hspace{1cm} (3.2)
where $\psi_{nl}(r)$ are strictly localized radial functions, and $Y_{lm}(\hat{r})$ are spherical harmonics. The minimal basis set, called single-zeta, consists of one orbital for each valence state of the considered atom. These orbitals are obtained by solving the radial Kohn-Sham equations for the isolated atom placed in a confining potential well, as proposed in [37]. The cutoff radius is determined by specifying the energy shift $\Delta E$ of the confined orbital compared to the energy of the orbital in the free atom. In this way smaller values of $\Delta E$ correspond to longer-ranged basis orbitals. In order to improve the radial flexibility of the basis set, extra basis functions with the same angular momentum $l$ (multiple zeta) are constructed for each valence state using the split-valence technique [38, 39]. Finally, in order to increase the angular flexibility of the basis set, polarization functions can be added - orbitals with $l$ quantum number corresponding to the lowest unoccupied angular momentum.

In the “LCAO mode”, the matrix elements of the kinetic energy and overlap operators are efficiently calculated in Fourier space using analytical expressions [40]. On the other hand, the matrix elements of the effective potential are still evaluated on the three-dimensional grid, since the density is also evaluated on this grid. All the two-center integrals are calculated only once for a given atomic configuration, before the self-consistent iterations. Since a basis-set calculation involves fewer degrees of freedom compared to a grid-based calculation, the hamiltonian can be directly diagonalized in the space of the basis functions. This significantly lowers the number of iteration to reach self-consistency compared to the iterative minimization approaches used in grid-based calculations. The Hartree potential, which is needed at each self-consistency step, is calculated by solving the Poisson equation in real space using multigrid methods [41].

3.3 Benchmark Results

In this section, selected physical quantities are calculated using the localized basis set. The results are compared to the values obtained using the grid mode, which can be considered as the complete basis-set limit since the same approximations and most implementation is shared.

3.3.1 Molecules

As a first assessment of the accuracy of the LCAO implementation, the atomization energies for the G2-1 data set [42] were calculated. The geometries were taken from MP2(full)/6-31G(d) optimized geometries, and the Perdew-
Burke-Ernzerhof (PBE) functional was employed. The error with respect to the grid results

\[ \Delta E_{LCAO}^{\text{LCAO}} - \Delta E_{\text{grid}}^{\text{grid}} = E_{\text{mol}}^{\text{LCAO}} - \sum_{\text{atoms}} E_{\text{atoms}}^{\text{LCAO}} - \left( E_{\text{mol}}^{\text{grid}} - \sum_{\text{atoms}} E_{\text{atoms}}^{\text{grid}} \right) \]  \hspace{1cm} (3.3)

is shown in Fig. 3.2 for different basis sets. The corresponding mean absolute errors (MAE) are shown in Table 3.1. It can be noted that enlarging the basis set, i.e. adding more orbitals per valence electron, systematically improves the results towards the grid values. The remaining deviations from the grid atomization energies are mostly due to the fact that the orbitals of isolated atoms are long-ranged (in principle infinite), while the basis orbitals are obtained with an artificial confining potential, which produces confined orbitals.
### 3.3. Benchmark Results

#### Table 3.1: Mean Absolute Errors of the LCAO basis set with respect to the grid for the atomization energies from the G2-1 database for $\Delta E = 0.01 eV$

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>MAE [eV]</th>
<th>MAE % [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ</td>
<td>1.71</td>
<td>20.4</td>
</tr>
<tr>
<td>DZP</td>
<td>0.36</td>
<td>4.45</td>
</tr>
<tr>
<td>TZP</td>
<td>0.25</td>
<td>3.02</td>
</tr>
<tr>
<td>TZDP</td>
<td>0.20</td>
<td>2.44</td>
</tr>
</tbody>
</table>

3.3.2 Solids

The equilibrium bulk properties (lattice parameter, cohesive energy and bulk modulus) were calculated for a variety of crystals. Simple metals (Li, Na and Al) were included, as well as semiconductors (AlP, Si and SiC), ionic solids (NaCl, LiF and MgO), transition metals (Fe, Cu and Pt) as well as one insulator (C). The results are shown in Fig. 3.3, where different bars indicate deviations from the grid results for different basis sets. The calculations have been performed for the solids in their most stable crystal structure, using the PBE functional. Spin polarization was included for Fe and for the calculations of the isolated atoms.

The agreement with the real-space grid is excellent, with a mean absolute error of 0.5% in the calculation of lattice constants, 4% in cohesive energies and 6% in bulk moduli using a double zeta polarized (DZP) basis set. In most cases very accurate lattice parameters can be obtained already with a small single zeta polarized (SZP) basis, especially for lattice constants. This is an indication that structure relaxations with the LCAO basis are likely to produce very accurate geometries. The calculations of lattice parameters, in fact, only involve the evaluation of energy differences between similar structures, i.e. not involving references to isolated atoms, thus leading to a more effective error cancellation.

3.3.3 Structure Relaxation

Since LCAO calculations generally reproduce geometries of grid calculations very accurately, they can be used as high-quality initial guesses for grid calculations. This is made possible by the possibility of a seamless switch between basis-set and grid representations. For most systems, an LCAO calculation is 25-30 times faster than a grid calculations, thus making the cost of the LCAO relaxation often negligible. In Fig. 3.4 a performance comparison is shown, for which the atomic positions and the Hessian from the
Figure 3.3: Deviation in lattice parameter, cohesive energy and relative bulk modulus from the grid results. The largest bars have been truncated and are shown with dotted edges.
LCAO relaxation were used in the subsequent grid relaxation. The system is a 38-atom truncated octahedral gold cluster with a CO molecule adsorbed, as shown in the inset of Fig. 3.4. The grid-based relaxation took 223 CPU hours, compared to the 8.4 CPU hours of a LCAO one (with a similar number of relaxation steps). The further grid relaxation took 45 CPU hours, for a total speedup of a factor 4. The speedup is of course system dependent and higher when the initial guess is further away from the converged geometry.

3.4 Summary and Outlook

The implementation of a localized basis in the grid-based PAW code GPAW has been outlined. Test results for atomization and cohesive energies, lattice parameters and bulk moduli have been presented and compared to well converged grid results. The deviations from the grid results have been shown to decrease as the size of the LCAO basis is increased. Since the structural properties are very accurate, it has been demonstrated that the LCAO
relaxation can provide a good initial guess for subsequent grid relaxations. This has been shown to increase the efficiency of grid calculations without compromising the accuracy.
Chapter 4

Graphene on Metals

This chapter is based on the Paper II. It concerns the investigation of the binding of graphene on fcc(111) model metal surfaces. A recently developed exchange-correlation functional has been applied and the results are compared to both standard functionals and to available experiments.

4.1 Introduction

The interaction of graphene with metallic surfaces is an important issue both at the fundamental and at the application level. At the fundamental level it is a very challenging system to study theoretically, since it involves dispersive interactions and a 2D system, which are difficult to describe with standard DFT-based approaches. In the context of applications, catalytic growth of graphene on metal surfaces has become a routine method to produce relatively large graphene samples[17]. Moreover, as a candidate for future nanoelectronics, the contact with metal electrodes definitely plays an important role in the design and fabrication of nano devices. Nevertheless, the nature of the metal-graphene chemical bond is still not well understood. On the experimental side, the lack of control over the details of the metal-graphene interface and the lack of a direct and accurate method to obtain information about the binding distance have made it difficult to investigate the chemical bonding at the interface. On the theoretical side, DFT is well known to have severe limitations when van der Waals interactions are involved. These interactions are likely to play a role in the binding of graphene, due to its closed-shell and planar nature.
4. Graphene on Metals

Figure 4.1: STM image of graphene on single-crystal Cu(111) showing Moiré patterns, from [43]. Graphene growth by CVD has been achieved on most metals.

Figure 4.2: The model for the adsorption of graphene. The left structure (smaller unit-cell) is used for Cu, Ni and Co while the structure on the right is used for Pd, Ag, Au, Pt and Al.

4.2 Computational Details

Two different unit cells were used, in order to obtain commensurate structures without significant strain, as discussed in [44] and shown in Fig. 4.2. The metal slabs were modeled with four atomic layers and the atoms were kept fixed to their experimental lattice parameters, while the carbon atoms in the graphene sheet were relaxed using the DFT forces ($f_{\text{max}} = 0.05 \text{ eV/Å}$). Monkhorst Pack k-point samplings of $6 \times 6 \times 1$ and $4 \times 4 \times 1$ were used respectively for the smaller (Fig. 4.2 left) and the larger (Fig. 4.2 right) orthorhombic unit cells. The wavefunctions were represented on the grid, with a grid spacing of 0.16 Å, and at least 14 Å were added in the direction normal to the surface. The calculations for Ni and Co were spin-polarized.
4.3 Standard DFT and vdW-DF

Local and semi-local functionals usually provide an accurate description of covalent and ionic chemical bonds. On the other hand they notoriously fail to reproduce non local dispersive interaction, in particular van der Waals interactions. Being long-range correlation effects, they cannot be included in any local or semi-local formulation\cite{45}. It is well known that LDA tends to overbind systems where van der Waals forces play a role, while GGAs usually underestimate the binding in these systems.

Since in the case of graphene on metals GGAs, contrary to experiments, predict no binding at all, most theoretical work on these interfaces has heavily relied on LDA. However, the relatively good performances of the LDA functional on these systems are to be considered fortuitous\cite{46, 47}. For this reason, the recently developed vdW-DF functional\cite{30, 31}, described in Chapter 2, has been applied. This functional has proven to improve the results over standard functionals for a number of systems, with particular success in predicting binding energies\cite{48, 49, 50}. A word of caution is in order here, since results involving the application of the vdW-DF functional to metallic systems should be taken with care due to the choice of the response function employed in the construction of the vdW-DF\cite{51}.

4.4 Graphene on fcc(111) Metals

The interaction of graphene on metals was studied on a number of model fcc(111) surfaces: Co, Ni, Pd, Ag, Au, Cu, Pt and Al. The calculated binding energies and distances are reported in Table 4.1. The LDA predicts two classes of metal-graphene interfaces, in good agreement with \cite{44}: Co, Ni and Pd which bind graphene relatively strongly and Ag, Au, Cu, Pt and Al which bind graphene very weakly. The same calculations were also performed with the revPBE\cite{28} functional, and no binding was found for any of the metals. The picture emerging from the vdW-DF functional is that of a weak binding, similar across the different metals. Interestingly, the binding energies for the system that LDA finds weakly bonded are similar to the energies obtained with the vdW-DF. On the other hand, the binding distances are systematically larger in the vdW-DF case. This overestimation of the equilibrium distance has been in fact reported previously\cite{51}.

In the following, the case of graphene on Ni(111) is analyzed. Fig. 4.3 shows the binding curve obtained with the different functionals. It is disappointing to see that different functionals predicts qualitatively different behaviours. The LDA curve has a relatively deep minimum at $\sim 2 \text{Å}$ while
Table 4.1: Binding energies ($E_b$) per carbon atom and binding distances ($d$) of graphene on metal (111) surfaces. Fermi level shift $\Delta E_F$ and charge transfer $\delta Q$ at the vdW-DF equilibrium separation. Negative (positive) $\Delta E_F$ indicates n (p)-type doping. Negative (positive) $\delta Q$ indicates electron transfer to (from) the graphene layer. The charge transfer has been evaluated using the Bader scheme[52]. The revPBE functional yields no binding for all metals.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Ni</th>
<th>Pd</th>
<th>Ag</th>
<th>Au</th>
<th>Cu</th>
<th>Pt</th>
<th>Al</th>
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<tbody>
<tr>
<td>vdW-DF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>3.40</td>
<td>3.50</td>
<td>3.50</td>
<td>3.55</td>
<td>3.57</td>
<td>3.58</td>
<td>3.67</td>
<td>3.72</td>
</tr>
<tr>
<td>$E_b$ (meV)</td>
<td>30</td>
<td>37</td>
<td>39</td>
<td>33</td>
<td>38</td>
<td>38</td>
<td>43</td>
<td>35</td>
</tr>
<tr>
<td>$\Delta E_F$ (eV)</td>
<td>-0.20</td>
<td>0.13</td>
<td>0.65</td>
<td>-0.40</td>
<td>0.21</td>
<td>-0.43</td>
<td>0.66</td>
<td>-0.51</td>
</tr>
<tr>
<td>$\delta Q$ ($10^{-3}e$)</td>
<td>-5.0</td>
<td>-3.0</td>
<td>+5.0</td>
<td>-5.0</td>
<td>+0.4</td>
<td>-4.0</td>
<td>+5.0</td>
<td>-8.0</td>
</tr>
<tr>
<td>LDA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>2.08</td>
<td>2.08</td>
<td>2.33</td>
<td>3.32</td>
<td>3.35</td>
<td>3.21</td>
<td>3.25</td>
<td>3.46</td>
</tr>
<tr>
<td>$E_b$ (meV)</td>
<td>175</td>
<td>123</td>
<td>79</td>
<td>45</td>
<td>31</td>
<td>35</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>1.5-2.2a</td>
<td>2.1b</td>
<td>2.2b</td>
<td>2.1b</td>
<td>5c</td>
<td>-</td>
<td>3.3d</td>
<td></td>
</tr>
<tr>
<td>Hybridization</td>
<td>$s^e$</td>
<td>$s^f$</td>
<td>$s^g$</td>
<td>$s^f$</td>
<td>$w^i$</td>
<td>$w^j$</td>
<td>$w^k$</td>
<td></td>
</tr>
</tbody>
</table>

g Ref. [58]  h Ref. [59]  i Ref. [55]  j Ref. [59]  k Ref. [56]  

the revPBE curve is repulsive. The vdW-DF curve lies in between, and predicts a shallow minimum at 3.5 Å. This large difference in predicted binding distances have a direct impact in the calculated Kohn-Sham bandstructures, which are shown in Fig. 4.3. In isolated graphene, the carbon $p_z$ orbitals placed at A sites ($p_z^A$) are decoupled from the $p_z$ orbitals at B sites ($p_z^B$) at the Dirac point, thus producing two degenerate states (see inset in Fig. 4.3 for the structure). Since in the LDA calculation, the A sites are located directly on top of Ni atoms at a close distance (2.08 Å), a strong hybridization between $p_z^A$ orbitals and Ni$_{3z^2-r^2}$ is observed. This interaction gives rise to an unoccupied antibonding state $\sigma^*$ and two occupied bonding states $\sigma_1$ and $\sigma_2$. The LDA gaps for $\sigma^* - \sigma_1$ and $\sigma^* - \sigma_2$ are 2 eV and 4 eV, respectively. On the other hand, the $p_z^B$ orbitals (occupied in the spin up channel and unoccupied in the spin down channel) hardly interact with Ni $d$ states and therefore remain unchanged. The vdW-DF band structures (because it is calculated at the vdW-DF relaxed distance of 3.50 Å), on the other hand, resemble the free graphene, preserving the Dirac point and only shifting it by +0.13 eV. Similar behavior is found for Co and Pd. For the remaining interfaces both the LDA and vdW-DF bandstructures resemble that of free standing graphene with the Dirac point shifted with respect to the metal Fermi level,
4.4. Graphene on fcc(111) Metals

Figure 4.3: Binding energy ($E_b$) per carbon atom of graphene on the Ni(111) surface calculated with LDA, revPBE and vdW-DF functionals. Graphene is adsorbed in the top-fcc configuration (see inset).

Figure 4.4: LDA (left) and vdW-DF (right) band structures for graphene on Ni(111) in the top-fcc configuration. Larger dots represent larger weight of the carbon $p_z$ orbitals. Only one spin channel is shown, the other being almost identical.
due to the similar binding distances predicted by the two functionals.

Since LDA is known to underestimate band gaps significantly $G_0W_0$ calculations were also performed for the graphene-Ni structures corresponding to the LDA and vdW-DF distances. In both cases no noteworthy differences between the $G_0W_0$ and DFT Kohn-Sham band structures close to the $K$-point were observed.

### 4.5 Comparison to Experimental Data

It is unfortunately very challenging to extract binding energies and binding distances from experiments of a graphene layer on a substrate. The comparison to experimental data is therefore indirect, and relies on different techniques. Recent experimental work on the Ni/graphene interface is based on Angle Resolved Photoemission Spectroscopy (ARPES). The ARPES band structures reveal a band gap at the graphene $K$-point thus suggesting some hybridization between the graphene and Ni orbitals[57, 60]. Earlier LEED measurements found a Ni-graphene bond distance of 2.1Å[54]. Note that both of these results are in line with the LDA calculations. On the other hand LDA is not expected to work well for highly inhomogeneous systems such as the interface structures investigated here. Similar experimental conclusions[53] are found for the Co/graphene interface, using Scanning Tunneling Spectroscopy techniques (STS). These results might indicate a difficulty for the present vdW-DF in describing systems with mixed bonding character, in line with the conclusions of Ref. [61]. It should also be noted that the present calculations are restricted to two specific interface configurations and hence do not take into account the variety of Moiré superstructures observed in experiments. Recent ARPES and LEED data is also available for the Pt/graphene interface[56] which provides clear evidence of weak interaction between graphene and the substrate, with an estimated separation of 3.3Å, in fair agreement with both LDA and our vdW-DF results. STS measurements for graphene on Pd[58] show a band-gap opening of $\sim 0.3$ eV, in contrast with both LDA and vdW-DF predictions. STS experiments on the Au/graphene interface[55], particularly relevant since most electronic contacts consists of gold electrodes, demonstrate a weak interaction between Au and graphene, and a $p$-type doping in agreement with both LDA and vdW-DF results. The available recent experimental data is summarized in the last two rows of Table 4.1.
4.6 Binding from Exchange and Correlation

In order to better characterize the differences in the behaviour of different functionals, it is instructive to look at the exchange contribution to the binding energy. Fig. 4.4 shows the total (full lines) and the exchange-only (dashed lines) binding energy curves for revPBE, PBE and LDA in the case of graphene on Cu(111) (left panel) and on Ni(111) (right panel). The exchange-only energies are calculated by removing the correlation energy term in the exchange-correlation functional and have been evaluated non self-consistently. Clearly, the bonding for the physisorbed graphene on Ag, Au, Cu, Pt and Al originates partially from the exchange term in the LDA xc-functional, as shown for Cu as an example in Fig. 4.4 (left). This is in principle incorrect since the van der Waals interaction is a purely non-local correlation effect. The weak binding energies obtained with the LDA functional are therefore to be taken with caution, since the good agreement with experiments might be fortuitous in most cases. The weak bonding predicted by the vdW-DF functional, similar in magnitude to the LDA results, is produced by the correlation term instead, which is physically correct. Interestingly, this applies to the Ni/graphene system as well, as shown in the right panel of Fig. 4.4. The LDA exchange-only curve shows a broad and weak attractive contribution between 2 Å and 5 Å with two local minima. We note that in a genuine covalent bond the exchange contribution to the binding energy is generally significantly larger than it is in this case. The revPBE and PBE exchange-only curves are repulsive at all separations for both systems. This is exactly the type of behavior which is usually observed in van der Waals bonded dimers or organic molecules on surfaces[30, 62].

4.7 Summary and Outlook

The recently developed vdW-DF functional, which includes explicit non-local correlations, has been applied to study the adsorption of graphene on different metal (111) surfaces and the results have been compared with those from traditional functionals. No binding has been found with GGA functionals. For Ag, Au, Cu, Pt and Al both LDA and vdW-DF predict a weak binding. Nevertheless the binding originates from exchange in the LDA and from correlation in the vdW-DF. A similar weak interaction has also been found for Ni, Co and Pd with the vdW-DF, while the LDA predicts stronger binding and significant hybridization between graphene and metal d states. At the vdW-DF equilibrium distance, the bandstructure is practically unaffected by the underlying metal surface. These results for Ni, Co and Pd appear to
Figure 4.5: Decomposition of the binding energy $E_b$ into exchange-only contributions (dashed lines - only the correlation term is removed) and total binding energy (full lines) for different functionals.

be in conflict with experimental LEED and ARPES data, suggesting that more work is to be done in order to reconcile experiments and theory for the graphene-metal interface. Experiments are currently focusing on obtaining a defect-free interface while theory is improving the description of the energetics, beyond standard DFT\cite{63}. It is particularly crucial to take into account the effect of defects, such as adatoms or step edges, which are likely to play an important role in the binding due to their high reactivity\cite{64}.
Chapter 5

Graphene Nanoribbons in Gaseous Environments

This chapter is based on Paper III. The stability of graphene nanoribbons is investigated taking into account the adsorption of common gas molecules at the edge of the ribbons. Specifically, H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}, CO, CO\textsubscript{2} and H\textsubscript{2}O molecules are considered. The oxygen saturation of the zigzag edge is discussed in more detail and it is compared to its hydrogen-saturated counterpart.

5.1 Introduction

Graphene nanoribbons (GNRs) are stripes of graphene with a finite width. The standard GNRs are either zigzag or armchair, depending on the structure of the two edges. Recent advances in experimental techniques have made it possible to fabricate and characterize graphene-based nanostructures. GNRs have attracted much interest due to their potential role in carbon-based nanoelectronics[12, 65]. The lateral confinement, due to the finite width, opens a band gap, which is a major prerequisite for applications in many nanoelectronic devices such as transistors. Magnetic properties are also very intriguing both from a fundamental perspective, since they involve carbon-based magnetism and from the point of view of potential applications. For example, the zigzag GNR (ZGNR) is theoretically predicted to have a magnetic semiconducting ground state, with spin-polarized edges. This predicted property has attracted great interest in the field of spintronics[66] (see Fig. 5.1).

In order to take advantage of these appealing features, the control over the edge structure is crucial. Theory and experiments have indeed shown that the electronic and transport properties of GNRs are strongly influenced
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Figure 5.1: a) Schematic density of states for a ZGNR in absence of applied electric field. b) An external electric field can be used to turn the ZGNR into a half-metal, for spintronics applications. Adapted from [66].

by the details of the atomic configuration of the edges[67]. Since, contrary to bulk graphene, GNRs edges are very reactive, a detailed knowledge of the stability and properties of the different types of edges is important in order to understand and possibly design GNRs with tailor-made properties.

Most of the previous theoretical work on GNRs concerns only the armchair and the zigzag edges, with or without hydrogen passivation. However, recent calculations have shown that other edge configurations can also exhibit high stability[68]. Non-standard edge configurations have also been recently observed in experiments[69], but they still remain largely unexplored. Besides hydrogen, it is also important to consider the effect of other gas molecules on the edge stability, especially when ambient conditions are relevant. The adsorption of molecules can also be exploited in connection to the functionalization of GNRs[70] in order to manipulate their properties.

5.2 Computational Details

Five different edge configurations[68] were considered, and the unit cell along the periodic direction was chosen to be the smallest possible, see Fig. 5.2. The widths of the nanoribbons were in the range 20-23 Å, wide enough to obtain fully converged results. Periodic boundary conditions were used, and GNRs in neighbouring cells were separated by 10 Å in all directions. All calculations were spin-polarized, and the structures were relaxed until the maximum force was lower than 0.05 eV/Å. A grid spacing of 0.18 Å was used, and a (1 × 1 × 10) Monkhorst-Pack k-point grid was employed to sample the Brillouin zone along the periodic direction of the ribbons.
5.3 Stability

In the following, the stability of five different edge geometries in the presence of H$_2$, O$_2$, N$_2$, CO, CO$_2$ and H$_2$O is investigated. Only the edge carbon atoms were considered as adsorption sites, since these are by far the most reactive sites in GNRs. For example, a H atom on the carbon atom next to the edge atom does not bind, with respect to H$_2$ gas phase.

5.3.1 Adsorption Energies

The adsorption energy of the different molecules for the five edge configurations in Fig. 5.2 were calculated as

$$E_{ads} = E_{ribb+mol} - N_{mol}E_{mol} - E_{ribb},$$

(5.1)

where $E_{ribb+mol}$ is the total energy of the ribbon with the adsorbed gas molecule, $N_{mol}$ is the number of adsorbed molecules and $E_{mol}$ is the total energy of the molecule in the gas phase. Note that, in order to avoid the erroneous DFT description of the O$_2$ molecule, the total energy of gas-phase water and H$_2$ were used as suggested in [35]. The adsorption energies are summarized in Fig. 5.3. It can be seen that atomic oxygen has the highest binding energy in all edge configurations.

Besides the standard zigzag, for which the high reactivity is well established, the ac(56) was also found to be very reactive. This is due, as for the zigzag case, to the spin-polarized peak in the density of states close to the Fermi energy, as shown in Fig. 5.4. Being highly reactive, the pristine zz
Figure 5.3: Adsorption energy per molecule, $E_{\text{ads}}$, for the different molecular species on the different edge configurations in eV. In the case of nitrogen and oxygen we have considered both the molecular and dissociated forms on the edge.

Figure 5.4: Spin-polarized density of states projected onto the edge carbon atom for the ac(56) GNR. The peaks around the Fermi level, similarly to the zigzag case, are responsible for the high reactivity.
5.3. Stability

5.3.1 Edge-formation Energies

The adsorption energies provide information on the strength of the interaction once a given edge configuration has been formed. In order to evaluate the thermodynamic stability of an edge in the presence of gas molecules, the energetic cost of forming the edge itself has to be taken into account. The formation energy of the pristine edges is calculated as

$$E_f = \frac{1}{2L} (E_{\text{ribb}} - N_C E_{\text{bulk}}), \quad (5.2)$$

where $E_{\text{ribb}}$ is the total energy of a ribbon consisting of $N_C$ carbon atoms in the supercell and $E_{\text{bulk}}$ is the total energy per atom in bulk graphene. The calculated energies are shown in the first line of Table 5.1, and are in very good agreement with previous work[68]. Note that for pristine GNRs, the $zz(57)$, also known as rec-zag in the literature, has the lowest edge energy.

The adsorption energy is then converted into free energy with the help of the chemical potential $\mu_{\text{gas}}$ of the gas phase

$$G_{\text{ads}} = \frac{1}{L} E_{\text{ads}} - \rho_{\text{gas}} \mu_{\text{gas}}, \quad (5.3)$$

### Table 5.1: Edge formation free-energy at 0 K and 300 K for the different nanoribbons and adsorbed species in eV/Å. For pristine nanoribbons, i.e. with non-passivated edges, the $zz(57)$ reconstruction is the most stable. This is no longer the case when species are adsorbed at the edge. In this case oxygen and hydrogen passivated edges are lower in energy.

<table>
<thead>
<tr>
<th></th>
<th>$zz(57)$</th>
<th>$ac(56)$</th>
<th>$ac(677)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.46</td>
<td>0.30</td>
<td>0.21</td>
</tr>
<tr>
<td>O</td>
<td>0.00</td>
<td>-0.13</td>
<td>-0.03</td>
</tr>
<tr>
<td>N</td>
<td>0.98</td>
<td>0.93</td>
<td>1.24</td>
</tr>
<tr>
<td>CO</td>
<td>0.90</td>
<td>0.70</td>
<td>0.66</td>
</tr>
<tr>
<td>$N_2$</td>
<td>1.22</td>
<td>1.11</td>
<td>1.20</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.42</td>
<td>0.28</td>
<td>0.82</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>0.59</td>
<td>0.46</td>
<td>0.52</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.89</td>
<td>0.75</td>
<td>0.93</td>
</tr>
</tbody>
</table>

and $ac(56)$ edges also have the highest formation energies, see Table 5.1.
where $\rho_{\text{gas}} = N_{\text{mol}}/L$ is the (linear) density of adsorbed species. The chemical potential at temperature $T$ and partial pressure $P$ is given by

$$\mu = H^0(T) - H^0(0) - TS^0(T) + k_B T \ln \left( \frac{P}{P^0} \right),$$

(5.4)

where $H^0$ and $S^0$ are enthalpies and entropies of the gas phase molecules at $P^0 = 1$ bar. The edge formation free energy is then evaluated as

$$G_{f,\text{ads}} = E_f + G_{\text{ads}}.$$

(5.5)

Fig. 5.5 summarizes the calculated edge formation free energies at 300 K and atmospheric partial pressures for the gas species. The same results are also reported in Table 5.1, where the formation free energies for 0 K are also shown. The edges saturated with oxygen are the most stable, in particular the standard zz and ac, closely followed by the zz(57). Hydrogen saturated edges are also nearly as stable. In addition, the adsorption of CO and $\text{H}_2\text{O}$ is also found to stabilize most edges. The dissociation of $\text{H}_2\text{O}$ is always energetically favored compared to the molecular adsorption. In particular, a water molecule dissociates into OH and H on ac, ac(56), zz(57) and ac(677). On the zz edge, instead, it spontaneously dissociates into oxygen adsorbed and two hydrogen atoms released in the gas phase.
5.4 Oxygen-saturated Zigzag Edge

Since zigzag edges saturated with oxygen atoms are found to be the most stable, in the following the ground state and vibrational properties are investigated and compared to the well studied hydrogen-passivated edge.

5.4.1 Band Structure

The Kohn-Sham band structure for the oxygen saturated GNR is plotted in Fig. 5.6. The ground state, differently from the hydrogen-saturated case, is spin paired and metallic. The two states at the Fermi level are localized at the edges and have weight also on the $p$ orbital of the oxygen atoms. In particular, one state decays into the GNR with weight only on one sublattice (left inset of Fig. 5.6), while the other is almost completely localized on the out of plane $p$ oxygen orbital (right inset of Fig. 5.6). This is different from the hydrogen-saturated case, in which the edge states are localized on the edge carbon atoms only.

5.4.2 Vibrational Properties

It has recently become possible to study differences in the edge orientation of GNRs using Raman spectroscopy[71]. Since vibrational features can be used to determine structural details at the edge, the vibrational properties of the zigzag GNR passivated by oxygen have been calculated.

The phonon frequencies were obtained from the dynamical matrix in real
The vibrational density of states (DOS) of a zigzag ribbon is shown in Fig. 5.7. Overall, both the hydrogen and the oxygen saturated DOS are very similar to the results for bulk graphene. In order to compare the contributions associated with the edge, the edge localized states have been separated out, and are shown in the top of Fig. 5.7. For the hydrogen saturated ribbon, the two peaks are vibrational modes perpendicular to the C-H bond. For the oxygen saturated ribbon only the transverse C-O mode (182 meV) is a truly localized vibration, while the additional peaks in the acoustic part of the spectrum originates from individual normal modes in the longitudinal and out-of-plane series. The localized vibration for the oxygen saturated GNR, being separated in energy from the peaks of the hydrogen saturated GNR, might provide a way to discriminated between the types of saturation in experiments.
5.5 Summary and Outlook

The adsorption of common gas molecules at the edge of different types of GNRs have been studied. In terms of edge formation free energy, the passivation by atomic oxygen is the most stable, closely followed by the hydrogen-passivated GNRs. As for the vibrational properties, the comparable masses of oxygen and carbon lead to a large degree of mixing between localized edge and bulk modes. Only the stretching (transverse) mode of the C-O bond was found to be completely localized at the edge, and decoupled from the normal-mode series. Vibrational patterns might provide a way to distinguish different edges in experiments. It should be noted that the edge formation free energy is not the only quantity which is relevant in order to evaluate stability and to compare to experiments. Energy barriers, for instance, are likely to play a role in the dissociation of the gas molecules and in the structural configuration of the edges.

From the experimental side, the investigation of graphene edges at the atomic level is far from trivial. The effect of the electron beam on the structure is not well understood, and thus represents a major issue in the approaches using transmission electron microscopes[72]. However, the experimental techniques are improving at a very fast pace and are close to achieving atomic resolution even for graphene edges. Interestingly, very recent experiments have been able to resolve edges of graphene on metal surfaces[73]. This represents an important step towards the understanding of the edge stability in the presence of interactions with substrates.
Chapter 6

Mechanism of Channeling Behaviour of Silver Nanoparticles on Suspended Graphene

This chapter is based on Paper IV. It presents a joint experimental and theoretical effort to investigate the catalytic etching of silver nanoparticles on suspended graphene. Environmental transmission electron microscope observations of the channeling behavior of silver nanoparticles on graphene are combined with DFT simulations in order to elucidate the mechanism.

6.1 Introduction

In order to fabricate graphene-based devices, new patterning techniques are needed. Current approaches are in large part adapted from silicon technology which typically involves optical and electron beam lithographies combined with etching. Even though these processes are well developed, they have several limitations when applied to graphene nanostructures. The orientation of lithography with graphene symmetry directions is a major issue, together with the fundamental resolution limits of lithographic techniques. Contamination and impurities from resist treatments also strongly affect the resulting properties of graphene samples.

A potential solution is presented by the catalytic etching, by hydrogenation or oxidation, of graphene via metal nanoparticles[74, 75, 76, 77, 78, 79, 80, 81]. This process, already observed in graphite[82, 83], results in channels of micro-scale length. Most importantly, this etched channels show
a strong tendency to follow the crystal orientation of graphene, and their width is determined by the nanoparticle size. In order to control the process, it is crucial that the phenomena are understood at the atomic level, as the atomic structure of the edges plays an important role in the resulting properties and hence in the future design of nanodevices. The catalytic etching can thus be considered a candidate for precise patterning, besides being an interesting phenomenon of nano-catalysis.

6.2 Observations

The catalytic oxidation of graphene by silver nanoparticles over a temperature range of 600-850 K and with oxygen pressures up to 13 Pa, results in channels parallel to the zigzag direction, as reported in previous work[74]. The use of an environmental transmission electron microscope allowed the in-situ investigation of the dynamical phenomenon, in contrast to previous ex-situ studies which are based on the comparison of “before” and “after” images. A schematic representation of the process is shown in Fig. 6.1(c). The gas-phase oxygen interacts with the silver nanoparticles and, after being adsorbed, it may dissociate. The formed atomic oxygen diffuses on the surface of the particle, eventually reaching the silver-graphene interface where it interacts with the carbon edge atoms. The carbon at the edge reacts with the oxygen at the interface and is gasified as CO, leaving a void which the catalyst particle moves to fill. The reaction takes place as

\[
\alpha C^{graphene} + \beta O_2 \rightarrow \gamma CO + \delta CO_2
\]

(6.1)

where CO production is favored over CO$_2$[84, 85]. An activation energy for the global process is determined to be $E_a = 0.557 \pm 0.016$ eV based on the distribution of nanoparticle velocities.

In a number of cases it was possible to observe the structure of the graphene interface (Fig. 6.1) when nanoparticles etching a bilayer graphene change from removing two layers to just a single layer, or vice versa. The leading edge of a channeling particle always presented two 120 degree separated leading facets, and a corresponding mark was left on graphene.

Bragg reflections from channeling particles were also observed, which suggests that the particles maintain their crystallinity at temperatures exceeding 850 K. In contrast, Bragg reflections were never observed for particles which are stationary at these temperatures, and these particles also show a more spherical shape.

When particles move from the graphene surface to the amorphous carbon support film, they undergo a significant change on morphology and be-
6.2. Observations

Figure 6.1: a-b) TEM images of the transition between monolayer and bilayer etching (and vice versa) within a single channel. These footprints of the interface of the silver particles in the graphene are triangular in shape with edges parallel to the zigzag direction of the graphene lattice. Scale bars 5nm. c) A schematic representation of the catalytic etching process. (i) The oxygen molecules interact with the silver nanoparticles. (ii) After being adsorbed, the oxygen may dissociate. The formed atomic oxygen diffuses on the surface of the particle, reaching the silver-graphene interface where it interacts with the carbon edge atoms. (iii) Carbon at the edge reacts with the oxygen at the interface and is gasified in the molecular form COx leaving a void which the catalyst particle moves to fill. d-e) The triangular front of etching particles is clearly visible in these images. Scale bars 25 nm and 20 nm respectively.
haviour. The Bragg reflections and consistent morphology disappear and the particles rapidly melt, showing a quasi-liquid behavior. The current interpretation is that the weaker and disorganized bonding in the amorphous carbon facilitates the removal of carbon atoms and does not impose any crystalline structure to the particle.

6.3 Computational Details

The graphene/nanoparticle interface was modeled as a Ag(211) stepped surface with a wide graphene nanoribbon (GNR) perpendicular to it, in contact with the silver atoms at the step, see Fig. 6.2. A $4 \times 4 \times 1$ Monkhorst-Pack grid of k-points was used and the structures were relaxed until the forces were lower than 0.05 eV/Å. The wavefunctions were expanded onto the LCAO basis of double-zeta plus polarization type.

For the calculations of the binding energy of a carbon adatom on a silver surface, the Ag(111) surface was chosen. It was modeled as a $3 \times 3$ slab of silver atoms with a thickness of 5 layers. A $8 \times 8 \times 1$ Monkhorst-Pack grid of k-points was used and the structures were relaxed until the forces were lower than 0.05 eV/Å. The wavefunctions were discretized on a real space grid, with a grid spacing of 0.2 Å. The fcc-hollow site was found to be the most stable adsorption site for a carbon adatom on the Ag(111) surface, with an adsorption energy of -3.26 eV.

For the calculations of the binding energy of edge carbon atoms for armchair and zigzag edges, wide ($\sim 28$ Å) graphene nanoribbons in large supercells ($\sim 15$ Å in the periodic direction) were used in order for the vacancy to be considered isolated. A $4 \times 1 \times 1$ Monkhorst-Pack grid of k-points was used and the structures were relaxed until the forces were lower than 0.05 eV/Å. The wavefunctions were discretized on a real space grid, with a grid spacing of 0.2 Å.

6.4 Results

The graphene-silver interface is modeled as a graphene nanoribbon of width equal to 19.8 Å with periodic boundary conditions along its length, placed edge-on to a step in the (211) silver surface, as shown in Fig. 6.2. The calculated carbon-silver equilibrium distance was around 2.25-2.35 Å, depending on the exact position of the carbon atom relative to the closest Ag atoms. In order to apply periodic boundary conditions, the lattice parameter of the graphene or the silver was varied so to have an integer number of both lattice...
Figure 6.2: a) A three dimensional representation of the structure used in the DFT calculation. b-c) Schematic 2D projections of the structure shown in (a). In particular, in (b) the shape of the step is clear, while in (c) the position of the graphene flake with respect to the silver edge is exemplified. d-e) Scale representations in the ZY plane of the actual DFT relaxed graphene-silver interfaces for the armchair and zigzag edges respectively. In (d) two unit cells are shown, with one in (e).
unit cells in the supercell. The lowest energy interface was found when the graphene lattice has negligible stress or strain, see Fig. 6.3, thus suggesting that the first layers of silver atoms are likely to adapt to the graphene C-C bond.

![Graph showing the total energy of the unit cell as a function of the C-C bond length for the case of zigzag edge.](image)

**Figure 6.3:** Total energy of the unit cell as a function of the C-C bond length for the case of zigzag edge. The C-C bond length has been varied by changing the size of the unit cell in all three spatial dimensions.

As shown in Fig. 6.4, the complete cyclic oxidation of rows of interface atoms is considered for both zigzag and armchair edges, returning to an equivalent situation except for the gasified atoms. The zigzag and armchair interfaces are different, since two rows of the zigzag interface have to be removed in order to obtain a zigzag interface again. On the contrary, only one row of interface armchair atoms has to be gasified in order to recover an armchair interface. The removal of zigzag atoms presents an energy barrier of 0.34 eV for the first two steps combined. For the armchair case, instead, the reaction path is downhill in energy. The removal of atoms along the armchair edge is therefore more favorable with respect to the zigzag edge. This suggests that the removal of the zigzag atoms is thus the rate-limiting step for the reaction. This leads to purely zigzag channels, in agreement with the experimental findings. Note that the energy barrier is also in agreement to the experimentally determined barrier of \( E_a = 0.557 \pm 0.016 \) eV, even though transition-state barriers between the intermediates have not been taken into account in the calculations. Accounting for the transition states is likely to result in additional barriers.

In literature, two incompatible theories can be used in order to describe the mechanism of carbon removal by catalytic oxidation and hydrogenation of graphite. The surface model, by Goethel et al.[86], proposes that the car-
Figure 6.4: Energetic path for the modeled etching process for both armchair and zigzag edge. a) In case of the zigzag edge the carbon atoms at the interface are fully oxidized by (b) adding one oxygen atom per undercoordinated carbon atom. c) The newly formed C-O couples are then removed. To obtain the initial situation another line of carbon atoms has to be removed. d) Once these doubly undercoordinated atoms are fully oxidized in a similar manner to (b) and removed (e), the initial state (a) has been recovered except for the gasification of two rows of atoms in graphene. g) For the armchair edge, only one oxidation step is necessary to obtain a complete cycle. h) The interface at the equilibrium is oxidized and then the C-O species are removed, (i). In our calculations the structure is allowed to fully relax at each step, and the total energy is evaluated. (f) A plot of the energy of each of the states (a-e) and (g-i) per CO molecule gasified, i.e. per carbon atom removed at the interface. The reaction in the zigzag case goes uphill with a calculated energy barrier of 0.34eV, while it goes downhill in the armchair case. Both paths end up at the same energy level, which corresponds to the gasification of a “bulk” carbon atom, independent of that atoms position in the lattice.
bon atoms at the graphene-catalyst interface first diffuse into the nanoparticle and then combine with oxygen on the surface, desorbing as CO. The interface model, first introduced by McKee[87], instead proposes that oxygen, adsorbed onto the catalyst surface, diffuses to the interface and here combines with carbon and desorbs. The DFT calculations strongly support the interface model. The calculated binding energies for carbon atoms on the zigzag and armchair edges are respectively 7.7 eV and 5.9 eV. These are much higher than both $k_BT$ and the adsorption energy of a carbon atom on the Ag(111) surface, which is 3.3 eV. This makes the presence of carbon adatoms on the catalyst surface unlikely.

6.5 Summary and Outlook

DFT calculations have been combined with experimental observations to explain the orientation of the channels that are catalytically etched by silver nanoparticles in suspended graphene. The energy barrier determined in the experiments is reproduced and corresponds to the removal of zigzag edge atoms, which is the rate limiting step. This leads to zigzag edges, as observed. Furthermore, both observations and calculations support the interface model. In particular, a carbon atom binds much more strongly to the graphene edge than to the Ag(111) surface. Knowing the energetics of this process is crucial in order to gain full control of the particle motion in technological applications. There are no available methods to date which can produce subnanometer smooth edges in a reliable way.
Chapter 7

Electro-catalysis on Porphyrin-like Functionalized Graphene

This chapter is based on the preprint V. It represents the first step towards a systematic theoretical investigation of functionalized graphene as catalyst nanomaterial. Porphyrin-like functionalized graphene is investigated as catalyst for the electrochemical reduction of CO$_2$ and comparisons are made to traditional transition metal based catalysts.

7.1 Introduction

Catalysis is of key importance to the modern society. Approximately 90% of all products of the chemical industry involve catalytic processes at some stage of their production[88]. Catalysts are materials which increase the rate of a chemical reaction without being consumed during the process. They provide a means to modify the rates at which bonds are broken and formed and thus to control and optimize the yields of the different chemical products. Besides the traditional role in the chemical industry, catalysis now faces a number of new challenges in connection to environmental protection and sustainable energy. This challenge calls for new, improved catalysts, and several new nanosystems have recently been investigated beyond the more traditional transition metal surfaces[89, 90, 91].

Porphyrin-based catalysts are known to be active for a range of chemical reactions. For this reason, combined with the versatility of graphene-based systems, porphyrin-like functionalized graphene, shown in Fig. 7.1, has been investigated here. This type of systems has several potential advantages over
metal catalysts. First, the nature of the active site is totally different. In our material there is only one, isolated, active site, which is in stark contrast to traditional metal-based catalysts where usually several binding sites are available for the intermediate. This feature can be seen as a bridge between a metal-based catalyst and a molecular catalyst and opens up possibilities in terms of controlling and manipulating the active site (this prospect becomes especially appealing when considering that the carbon-based chemistry is well defined compared to that of metallic surfaces). Second, a carbon-based material has significant advantages in terms of price. Third, the limitations imposed by scaling relationships[92, 93] in transition-metal-based catalysis might be less severe in this new type of material.

### 7.2 Computational Details

The unit cell consists of a $4 \times 4$ graphene cell, where two carbon atoms are removed, the active atom is placed and its four neighbours are replaced by nitrogen atoms. This leads to a supercell where different active atoms are separated by 9.9 Å. At least 16 Å of vacuum are present in the non-periodic direction. The calculations were spin-polarized and used a Monkhorst Pack k-point samplings of $(8 \times 8 \times 1)$. All the structures were relaxed until residual forces were lower than 0.04 eV/Å. The wavefunctions were represented on the grid, with a grid spacing of 0.18 Å. In order to evaluate free energies, the corrections for zero-point energies and entropies were taken from Ref. [94]. The gas-phase correction has been calculated with the same procedure of Ref. [94], although for both CO$_2$ and CO.
7.3 Electrochemical Reduction of CO$_2$

The electrochemical reduction of CO$_2$ to chemical fuels has re-gained huge interest in recent years in connection with renewable energy\[95, 96\]. The intermittency of renewable energy sources calls for an efficient energy storage solution\[95\]. The storage of energy in chemical bonds represents an attractive approach, in particular if combined with CO$_2$ capture. This makes the electrochemical reduction of CO$_2$ a very attractive candidate for the production of chemical fuels.

However, in order to have any major impact, the process must be cost-efficient and a key step in realizing that is to find efficient catalysts. Unfortunately, so far no material is known to catalyze this reaction efficiently and with high selectivity. Copper is the only metal that has been experimentally shown to produce significant quantities of hydrocarbons (CH$_4$ and C$_2$H$_4$) from CO$_2$, albeit at a huge voltage cost\[97\]. The origin of the overpotential has remained elusive until recently\[94\], when a complete reaction mechanism was elucidated by employing DFT calculations in conjunction with the computational hydrogen electrode (CHE) method\[35\]. This effort made it possible, for the first time, to construct a free energy diagram for the entire reaction, including potential side reactions, and to identify the potential limiting step. Importantly, the obtained results were in qualitative agreement with experimental data reported by Hori et al.\[97\], and furthermore they explained why hydrocarbons and not methanol, which is commonly produced on copper in gas phase catalysis, are dominant products.

Taking the same approach as in Ref. \[94\], the free energy levels of the intermediates involved in the electroreduction of CO$_2$ have been calculated for the porphyrin-like functionalized graphene for a number of different atoms as central sites in the porphyrin-like structure (Ag, Ru, Ir, Pt, Au, Pd, Co, Rh, Cu, Pd, Al, Ga, Fe, Os and Ni). By analyzing the energy differences of the intermediates the overpotentials required to either reduce CO$_2$ partially to CO/HCOOH or completely to CH$_4$ have been extracted. Additionally, the hydrogen evolution reaction (HER) has also been considered due to the fact that H$^*$ competes with *COOH for the active metal site. In that regard, special attention has been devoted to address selectivity towards the different reaction products. Finally, the scaling relations between different adsorption intermediates have been investigated. This information can be used to predict the potential or fundamental limitations of porphyrin-like functionalized graphene in catalyzing various complex reactions.

As a first issue, the stability of the porphyrin-like structures has been investigated for all the considered active atoms. The stability has been eval-
54 7. Catalysis on Porphyrin-like Functionalized Graphene

Figure 7.2: Stability of the different active sites embedded in the porphyrin-like graphene.

\[ E_{\text{stab}} = E_{\text{porph+atom}} - E_{\text{porph}} - E_{\text{atom}}, \] (7.1)

where \( E_{\text{porph+atom}} \) is the total energy of the porphyrin-like graphene with a given active atom, \( E_{\text{porph}} \) is the total energy of the structure without the active atom and \( E_{\text{atom}} \) is the total energy of the isolated atom. The results are shown in Fig. 7.2. It can be noticed that for most of the active atoms \( E_{\text{stab}} \) is lower than the corresponding cohesive energy of the bulk phase. As an example, the cohesive energy of bulk gallium is -2.81 eV/atom while \( E_{\text{stab}} = -3.7 \) eV. This is an indication of the stability of the structures against sintering.

The free energy diagrams for complete and partial CO\(_2\) reduction on Ga-porphyrin-like functionalized graphene are presented respectively in Fig. 7.3 and Fig. 7.4, along with the free energy diagram for the HER. This system has been chosen since it is the best candidate, among the systems considered, for both the partial and complete CO\(_2\) reduction. In the case of the HER, there are much better catalysts than gallium, however the data for the same system is shown in order to stress the selectivity issue that will be addressed later on. The full reaction path (cf. Fig. 7.3) is the following
7.3. Electrochemical Reduction of CO$_2$

Figure 7.3: Free energy diagram for the complete reduction of CO$_2$ to CH$_4$ on Ga-porphyrin-like functionalized graphene. Energy levels in black are at 0 V, while the red levels correspond to the minimum potential which makes each step downhill in energy.

\[
\begin{align*}
\text{CO}_2 + \text{H}^+ + e^- & \rightarrow \text{COOH}^* \\
\text{COOH}^* + \text{H}^+ + e^- & \rightarrow \text{CO}^* + \text{H}_2\text{O} \\
\text{CO}^* + \text{H}^+ + e^- & \rightarrow \text{HCO}^* \\
\text{HCO}^* + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{CO}^* \\
\text{H}_2\text{CO}^* + \text{H}^+ + e^- & \rightarrow \text{H}_3\text{CO}^* \\
\text{H}_3\text{CO}^* + \text{H}^+ + e^- & \rightarrow \text{O}^* + \text{CH}_4 \\
\text{O}^* + \text{H}^+ + e^- & \rightarrow \text{OH}^* \\
\text{OH}^* + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}.
\end{align*}
\] (7.2)

Typically, when applying the CHE method, the free energy diagram is illustrated at $U = 0$ with respect to the reversible hydrogen electrode (RHE) and at the lowest potential at which all steps are downhill in free energy, i.e. at the overpotential at which all reaction steps become exergonic (red levels in the figures). Fortuitously, in the case of Ga, there are two such steps that occur at the same potential, $U = -0.74$ V, which, by chance, is equal to the onset potential for CH$_4$ production on Cu(211)[94]. The first potential limiting step is the addition of a proton-electron pair to adsorbed CHO to form formaldehyde (H$_2$CO), whereas the second one is protonation of OH to water in the last electrochemical step. For comparison, on Cu(211) protonation of the *CO intermediate was found to be the potential determining step.
Figure 7.4: Free energy diagram for the partial reduction of CO₂ to HCOOH (a) and CO (c) on Ga-porphyrin-like functionalized graphene. The diagram for the HER is shown in (c). Energy levels in black are at 0 V, while the red levels correspond to the minimum potential which makes each step downhill in energy.
In the case of CO evolution (cf. Fig. 7.4c), which is another reaction of interest, Ga-porphyrin-like graphene was also found to be the best catalyst, featuring somewhat lower overpotential, -0.68 V, than for the CO\(_2\) reduction. Note that in this case, in general one also has to take into account the thermodynamical barrier for CO desorption. There is little use of a catalyst if products cannot be removed from the surface\[98\]. To make things worse, CO desorption is a potential independent step and thus little can be done to promote it. This is not a problem for the Ga-porphyrin-like system, since the desorption from the site is energetically favorable. As far as the HER is concerned, the Ga-porphyrin-like structure is a very bad catalyst for the reaction, since almost -0.8 V voltage is needed to evolve hydrogen. The best catalyst should have H\(^*\) binding energy around 0, and the Co-porphyrin-like has been found in this study to be a very good candidate, having \(\Delta H^* = -0.07\) eV.

The lowest possible overpotential is a necessary but not a sufficient condition to have a good CO\(_2\) reduction catalyst. This class of materials has just one catalytically active site per unit cell. This somewhat simplifies the situation because no coverage effects need to be taken into account. On the other hand, the competition for the active sites, i.e. selectivity, enters as a key parameter that determines the overall performance of the catalyst. In other words, if some of the intermediates that are not directly involved in the CH4 production path bind stronger to the surface, they will poison the active site and the reaction will instantly cease. From figures 7.3 and 7.4 it is clear that all the reaction paths considered proceed through formation of *COOH intermediate except for the HER where H\(^*\) formation is the key (only) intermediate step. Consequently, the competition between H\(^*\) and *COOH binding will determine the final product of the reaction. Moreover, since both H\(^*\) and *COOH formation steps involve transfer of one electron and proton pair, the ratio between the two will not be affected by the change of voltage. This finding is contrary to the results obtained on metal surfaces, or more specifically on Cu(211), where the products' yield was strongly influenced by the potential. Particularly, the H\(_2\) yield changed drastically in favour of hydrocarbons as the potential was lowered, which was a clear indication of opening up of *CO formation path, the intermediate that would subsequently repel hydrogen from the surface and enable CO\(_2\) reduction. A similar behaviour would never be observed for the catalysts investigated in this work, since the site blocking by adsorbed hydrogen would never leave a space for CO formation. Hence the CO\(_2\) reduction would be essentially dead. Unfortunately, the unfavourable ratio between COOH and H is not solely restricted to Ga-porphyrin-like graphene, but as seen in Fig. 7.5, a rather general rule that extends to all of the systems studied herein.
Seemingly, these materials are not good catalysts for CO\textsubscript{2} reduction because regardless of the metal atom in the active site, the HER will always prevail against the evolution of the carbon containing gas molecules. However, the reaction diagram in Fig. 7.3 suggests a way to overcome this problem. Namely, if one would reduce CO instead of CO\textsubscript{2} then the weak *COOH binding would no longer present an obstacle for the reduction. The path for CO reduction is the same as for CO\textsubscript{2} except for the missing first two steps. A trade-off between CO and H would thus become a selectivity criterion. The scaling between the CO and H adsorption energy is plotted in Fig. 7.5 (right). Unfortunately, Ga which was found to be the best candidate for CO\textsubscript{2} reduction is, apart from Al, the only material that does not fulfill the selectivity criterion for CH\textsubscript{4} evolution. With the new condition, Co, Rh and Cu also become promising candidates with overpotentials around -0.8 V. Here, it is important to note, that the methane is the only hydrocarbon that can be produced. Making larger hydrocarbon chains would require a Langmuir-Hinshelwood type of reaction, in which two adsorbed carbon containing intermediates join together to form a C-C bond. Since, by design of the catalyst, there is only one active site, this type of reaction can be ruled out.

### 7.4 Scaling Relations

For multi-electron-transfer reactions it is usually difficult to find a good catalyst that can perform the overall reaction at a small overpotential. One of the main reasons for this is that, at least on transition metals, the binding energies of the various reaction intermediates scale with the d-band center
of the surface and therefore they also scale with respect to each other. This means that it is virtually impossible to change the binding energy of one intermediate without also affecting the binding of the other intermediates in a similar fashion. Scaling relations are readily observed on transition metals and alloys for the same class of adsorbates i.e. for the adsorbates that bind to the surface through a same type of atom[92]. The linearity in binding energies on transition metals is usually rationalized through the d-band model[99] and the position of the d-band centre.

The structures studied in this work differ from transition metal surfaces in this respect, as the energy levels are more of atomic character. The difference between the two cases is best seen in Fig. 7.6, where the densities of states have been projected onto the d orbitals of the active atom in the porphyrin-like graphene and onto the d orbitals of a Pt(111) surface. The systems have more sharp peaks compared to the broad features of the d-band for metal surfaces.

The scaling relations are not only confined to metal surfaces, but as it has been recently shown also hold on porphyrin functionalized graphene[100]. The linearity observed in Fig. 7.5 (left) is striking with Au being the only outlier which is explained by the fact that COOH does not bind on Au. On the other hand, there is a much larger scatter in Fig. 7.5 (right). At first glance, the scatter in the two scaling relations seems peculiar. COOH and CO bind through the same atom and therefore one would expect them to scale much better than COOH and H, whereas the opposite is observed. A possible explanation may be found in terms of the orbitals through which COOH, CO

\[ \text{Figure 7.6: Density of states projected onto the d orbitals of a FCC(111) Pt surface (red lower) and of the Pt-porphyrin-like graphene (blue higher). The calculate d-band center is -2.9 eV and -1.4 eV for the fcc(111) and Pt-porphyrin-like respectively.} \]
and H bind to the metal atom. In Fig. 7.7, the HOMO and LUMO orbitals of gas-phase CO and COOH are illustrated. With respect to the vacuum level, the HOMO and LUMO eigenvalues for CO are at -9.1 eV and -2.1 eV, while the HOMO and LUMO for COOH are at -5 eV and -1.4 eV. The Fermi level of the porphyrin-like structures ranges from -0.5 eV to -1.8 eV, depending on which active atom is considered. Being the HOMO level of COOH unpaired and closer to the Fermi level of the surface site, it may contribute more to the binding compared to the HOMO of CO which is much lower in energy. Since the HOMO orbital of COOH is of s-character locally around the carbon atom, the coupling to the active site is similar to the H case, which is of pure s-character. This is only given as a possible explanation, since a more in-depth investigation is needed for a full understanding of the scaling relations in these systems.

7.5 Summary and Outlook

The catalytic activity of the functionalized porphyrin-like structures for the electrochemical reduction of CO$_2$ has been investigated. The results have been carefully compared to the recent findings for the Cu(211) surface, especially in terms of the differences in the active site and its significance for selectivity among reaction products. Gallium functionalized porphyrine-like graphene was found to be the best candidate for CO$_2$ reduction, although the major obstacle was established to be hydrogen poisoning of the active site. Moreover, this turned out to be a general problem regardless of which
metal comprised the active site. The only way to avoid it is to reduce CO rather than CO$_2$ because the first intermediate in the CO reduction path has higher binding energy than hydrogen, whereas in the case of CO$_2$ reduction, COOH binds ca 1 eV more weakly than hydrogen.

This investigation is the first step towards the systematic computational study of functionalized graphene for catalytic applications. Since there has been only little theoretical work has on these systems[101, 102, 103], this is an extremely interesting area to investigate, especially in connection with renewable energy sources. As far as experiments are concerned, modified graphene is being investigated both as support to active nanoparticles[104] and as stand-alone catalyst. In particular, an iron-porphyrin-like functionalized carbon nanotube has recently been synthesized[105] and tested as catalyst for the oxygen reduction reaction.
Appendix A

Van der Waals Interactions in DFT

Dispersive interactions, despite being weak when compared to ionic and covalent bonds, play a very important role in many phenomena in chemistry, biology and materials science. The attractive character comes from the instantaneous dipoles (and possibly higher multipoles) due to the fluctuation of the electron cloud. They are the dominant interaction in regions where there is little or no overlap of electronic densities. This is the basic reason why DFT with local and semi-local functionals cannot describe the van der Waals interaction, which is a long-range correlation effect. Since DFT has become a widely used method in a number of disciplines, there is great interest in describing the van der Waals interaction within the DFT framework.

Several approaches have been devised in order to take into account these interactions. They can be divided into three main groups. The first group of approaches tries to explicitly evaluate the correlation energy within relevant approximations, as for example the Langreth-Lundqvist functional\[30\] (vdW-DF) which has been employed in the present thesis. The second group of approaches adds a pair-wise correction of the form $C_6/R^6$ to the total energy expression. The third group uses semi-local, hybrid or meta functionals that are fitted to large databases which also include van der Waals systems. For a comparison of the accuracies of different methods, see \[106, 107\].

The vdW-DF functional, which belongs to the first group, is fully ab-initio. No empirical parameters are used, and the term containing the van der Waals interaction $E_{c}^{nl}$ is non local, and is derived from the plasmon-pole approximation for the dielectric function. The exchange and correlation energy is given by

$$E_{xc}^{vdw-DF} = E_{x}^{GGA} + E_{c}^{LDA} + E_{c}^{nl}. \quad (A.1)$$
The first (2004) version of the functional used the revPBE exchange for the $E_{\text{GGA}}^x$ term. This particular flavour was chosen because it best reproduced the exact exchange results for noble gas dimers and purely van der Waals systems. The overall performance of this functional is good, significantly improving the results over standard functionals. However, it has shown a consistent tendency to overestimate the binding distances[51]. The new (2010) version[108] uses the PW86 exchange and a slightly different form for the non-local correction $E_{\text{nl}}^{\text{nl}}$. This significantly improves the binding distance and the shape of the binding curve for the S22 set of molecules. Several variations have been proposed, which mostly differ in the exchange term.

The first and still widely used method of the second group has been proposed by Grimme[109]. The energy $E_{\text{disp}}$ to be added to the total energy (obtained from other functionals) is

$$E_{\text{disp}} = -\sum_{j>i} f_{\text{damp}}(R_{ij}, R_{ij}^0) C_{6ij} R_{ij}^{-6}$$

where $C_{6ij}$ is the dispersion coefficient for the $ij$ pair of atoms, $R_{ij}$ is the interatomic distance, $R_{ij}^0$ is the sum of van der Waals radii and $f_{\text{damp}}$ is a damping function. In the original formulation both $C_{6ij}$ and $R_{ij}^0$ were empirical parameters. This approach has been modified and developed extensively, and several flavours exist. In the recent Tkatchenko-Scheffler method[110] (TS-vdW), both parameters $C_{6ij}$ and $R_{ij}^0$ are functionals of the density (they account for the atomic volumes using the Hirshfeld partitioning scheme). Only the range of the damping, which enters in $f_{\text{damp}}$ is left to be empirical.

The third group consists of a variety of empirical functional fitted to different databases. A recent and prominent example is the M06 suite of four meta-GGA functionals[111] (“the Minnesota functionals”) which are trained on a very broad set of benchmarks, including thermochemistry, kinetics, non-covalent interactions, excited states and more. Even though they perform remarkably well on a number of systems, these functional are still missing the long-range part of the van der Waals interaction. Their results can be in fact improved by adding the TS-vdW correction[107].
Bibliography


[42] L.A. Curtiss, Krishnan Raghavachari, P.C. Redfern, and J.A. Pople. Assessment of gaussian-2 and density functional theories for the com-


[111] Y. Zhao and D. G. Truhlar. The m06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four m06-class functionals and 12 other functionals. Theor. Chem. Acc., 120:215, 2008.
Included Papers
Paper I

Localized atomic basis set in the projector augmented wave method
Localized atomic basis set in the projector augmented wave method

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(Received 4 September 2009; revised manuscript received 9 October 2009; published 18 November 2009)

We present an implementation of localized atomic-orbital basis sets in the projector augmented wave (PAW) formalism within the density-functional theory. The implementation in the real-space GPAW code provides a complementary basis set to the accurate but computationally more demanding grid representation. The possibility to switch seamlessly between the two representations implies that simulations employing the local basis can be fine tuned at the end of the calculation by switching to the grid, thereby combining the strength of the two representations for optimal performance. The implementation is tested by calculating atomization energies and equilibrium bulk properties of a variety of molecules and solids, comparing to the grid results. Finally, it is demonstrated how a grid-quality structure optimization can be performed with significantly reduced computational effort by switching between the grid and basis representations.

DOI: 10.1103/PhysRevB.80.195112 PACS number(s): 71.15.Ap, 71.15.Dx, 71.15.Nc

I. INTRODUCTION

Density-functional theory (DFT) with the single-particle Kohn-Sham scheme is presently the most widely used method for electronic-structure calculations in both solid-state physics and quantum chemistry.1–3 Its success is mainly due to a unique balance between accuracy and efficiency which makes it possible to handle systems containing hundreds of atoms on a single CPU with almost chemical accuracy.

At the fundamental level the only approximation of DFT is the exchange-correlation functional which contains the nontrivial parts of the kinetic and electron-electron interaction energies. However, given an exchange-correlation functional one is still left with the nontrivial numerical task of solving the Kohn-Sham equations. The main challenge comes from the very rapid oscillations of the valence electrons in the vicinity of the atom cores that makes it very costly to represent this part of the wave functions numerically. In most modern DFT codes the problem is circumvented by the use of pseudopotentials.4–6 The pseudopotential approximation is, in principle, uncontrolled and is, in general, subject to transferability errors. An alternative method is the projector augmented wave (PAW) method invented by Blöchl.7 An appealing feature of the PAW method is that it becomes exact if sufficiently many projector functions are used. In another limit the PAW method becomes equivalent to the ultrasoft pseudopotentials introduced by Vanderbilt.5

The representation of the Kohn-Sham wave functions is a central aspect of the numerics of DFT. High accuracy is achieved by using system-independent basis sets such as plane waves,7–9 wavelets,10,11 or real-space grids,12,13 which can be systematically expanded to achieve convergence. Less accurate but computationally more manageable methods expand the wave function in terms of a system-dependent localized basis consisting of, e.g., Gaussians14 or numerical atomic orbitals.15,16 Such basis sets cannot be systematically enlarged in a simple way and consequently any calculated quantity will be subject to basis-set errors. For this reason the former methods are often used to obtain binding energies where accuracy is crucial while the latter are useful for structural properties which are typically less sensitive to the quality of the wave functions.

In this paper we discuss the implementation of a localized atomic basis set in the PAW formalism and present results for molecular atomization energies, bulk properties, and structural relaxations. The localized basis set, which we shall refer to as the linear combination of atomic orbitals (LCAO) basis, is similar to that of the well-known SIESTA pseudopotential code18 but here it is implemented in our recently developed multigrid PAW code GPAW.19 A unique feature of the resulting scheme is the possibility of using two different but complementary basis sets. On the one hand wave functions can be represented on a real-space grid which, in principle, facilitates an exact representation and on the other hand the wave functions can be represented in the efficient LCAO basis. This allows the user to switch seamlessly between the two representations at any point of a calculation. As a particularly powerful application of this “double-basis” feature, we demonstrate how accurate structural relaxations can be performed by first relaxing with the atomic basis set and then switching to the grid for the last part. Also adsorption energies, which are typically not very good in LCAO, can be obtained on the grid at the end of a relaxation.

While LCAO pseudopotential codes as well as plane-wave/grid PAW codes already exist and have been discussed extensively in the literature,7,15,16 the combination of LCAO and PAW is different. Compared to the popular SIESTA method, which is based on norm-conserving pseudopotentials, the advantage of the present scheme (apart from the double-basis feature) is that PAW works with coarser grids to represent the density and effective potentials. As an example, Fig. 1 shows the atomic orbitals of iron calculated with the norm-conserving Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials as well as with PAW. Clearly the d wave function is much smoother in PAW. This is essential for larger systems where operations on the grid, i.e., solving the Poisson equation, evaluating the density, and calculating the potential matrix elements become computationally demanding.

II. PROJECTOR AUGMENTED WAVE METHOD

In this section we give a brief review of the PAW formalism. For simplicity we restrict the equations to the case of
The pseudovalence states of iron calculated with PAW and the norm-conserving HGH pseudopotentials. Both methods produce smooth wave functions for the delocalized 4s state but the lack of norm conservation allows the short-ranged 3d state in PAW to be accurately sampled on a much coarser grid.

A. PAW transformation operator

The PAW method is based on a linear transformation $T$ which maps some computationally convenient "pseudo" or "smooth" wave functions $\tilde{\psi}_a$ to the physically relevant "all-electron" wave functions $\psi_a$,

$$|\psi_a\rangle = T |\tilde{\psi}_a\rangle,$$

where $n$ is a quantum state label, consisting of a band index and possibly a spin and $k$-vector index.

The transformation is chosen as $T = 1 + \sum_a T_a$, i.e., the identity operator plus an additive contribution centered around each atom, which differs based on the species of atom. The atomic contribution for atom $a$ is determined by choosing a set of smooth functions $\tilde{\delta}_a^g(r)$, called pseudopartial waves and requiring the transformation to map those onto the atomic valence orbitals $\delta_a^g(r)$ of that atom, called all-electron partial waves. This effectively allows the all-electron behavior to be incorporated by the smooth pseudowave functions. Since the all-electron wave functions are smooth sufficiently far from the atoms, we may require the pseudopartial waves to match the all-electron ones outside a certain cutoff radius, such that $\tilde{\delta}_a^g(r) = \delta_a^g(r)$ for $r > r_c$. This localizes the atomic contribution $T_a$ to the augmentation sphere $r < r_c$. Finally a set of localized projectors $\tilde{p}_a^g(r)$ is chosen as a dual basis to the pseudopartial waves. We further want the partial-wave-projector basis to be complete within the augmentation sphere, in the sense that any pseudowave function should be expressible in terms of pseudopartial waves and therefore require

$$\sum_i |\tilde{\delta}_a^g\rangle \langle \tilde{p}_a^g| = 1, \quad \langle \tilde{\delta}_a^g | \tilde{p}_a^g\rangle = \delta_{ij}.$$

The transformation $T$ is then defined by

$$T = 1 + \sum_a \sum_i (|\delta_a^g\rangle - |\tilde{\delta}_a^g\rangle) \langle \tilde{p}_a^g|,$$

which allows the all-electron Kohn-Sham wave function $\psi_a(r) = (r|\psi_a)$ to be recovered from a pseudowave function through

$$\psi_a(r) = \tilde{\psi}_a(r) + \sum_a \sum_i [\delta_a^g(r) - \tilde{\delta}_a^g(r)] \langle \tilde{p}_a^g| \tilde{\psi}_a\rangle.$$

We emphasize that the all-electron wave functions are never evaluated explicitly but all-electron values of observables are calculated through manipulations which rely only on coarse grids or one-dimensional radial grids. Using Eqs. (1) and (3), the all-electron expectation value for any semilocal operator $O$ due to the valence states can be written as

$$\langle O \rangle = \sum_n f_n (\tilde{\psi}_n|O|\tilde{\psi}_n) + \sum_{n\alpha j} f_n (\tilde{\psi}_n|\tilde{p}_j^\alpha) \langle \delta_a^g|O|\tilde{p}_j^\alpha \tilde{\psi}_n\rangle$$

$$- \sum_{n\alpha j} f_n (\tilde{\psi}_n|\tilde{p}_j^\alpha) \langle \delta_a^g|O|\tilde{p}_j^\alpha |\tilde{\psi}_n\rangle.$$

Inside the augmentation spheres the partial-wave expansion is ideally complete, so the first and third terms will cancel and leave only the all-electron contribution. Outside the augmentation spheres the pseudopartial waves are identical to the all-electron ones and leave only the all-electron contribution. The frozen-core approximation as-
\[ n(r) = \tilde{n}(r) + \sum_a [n^*(r - R^a) - \tilde{n}^*(r - R^a)], \quad (8) \]

where
\[ \tilde{n}(r) = \sum_a f_a |\psi_a(r)|^2 + \sum_a \tilde{\rho}_a(|r - R^a|), \quad (9) \]
\[ n^*(r) = \sum_{ij} D_{ij}^a \rho^*_i(r) \rho^*_j(r) + n^*_a(r), \quad (10) \]
\[ \tilde{n}^*(r) = \sum_{ij} D_{ij}^a \tilde{\rho}^*_i(r) \tilde{\rho}^*_j(r) + \tilde{n}^*_a(r). \quad (11) \]

Here we have separated out the all-electron core density \( n^*_a(r) \) and the pseudocore density \( \tilde{n}^*_a(r) \), where the latter can be chosen as any smooth continuation of \( n^*_a(r) \) inside the augmentation spheres since it will cancel out in Eq. (8). We omit conjugation of the partial waves since these can be chosen as real functions without loss of generality.

C. Compensation charges

In order to avoid dealing with the cumbersome nuclear point charges and to compensate for the lack of norm conservation, we introduce smooth localized compensation charges \( \tilde{Z}(r) \) on each atom, which are added to \( \tilde{n}(r) \) and \( \tilde{n}^*(r) \), thus keeping the total charge neutral. This yields a total charge density that can be expressed as
\[ \rho(r) = \tilde{\rho}(r) + \sum_a [\rho^*(r - R^a) - \tilde{\rho}^*(r - R^a)] \]
\[ \tilde{\rho}(r) = \tilde{n}(r) + \tilde{Z}(r) = \tilde{n}(r) + \sum_a \tilde{Z}^a(r - R^a), \quad (12) \]
in terms of the neutral charge densities
\[ \rho^*(r) = n^*(r) + \tilde{Z}^a \delta^a(r), \quad (13) \]
\[ \tilde{\rho}^*(r) = \tilde{n}^*(r) + \tilde{Z}^a \delta^a(r), \quad (14) \]
where \( \tilde{Z}^a \delta^a(r) \) is the central nuclear point charge. The compensation charges are chosen to be localized functions around each atom of the form
\[ \tilde{Z}^a(r) = \sum_L Q_L^a g^a_L(r) = \sum_{lm} Q_{lm}^a \tilde{g}_L^a(r) Y_{lm}(\hat{r}), \quad (16) \]

where \( g^a_L(r) \) are fixed Gaussians and \( Y_{lm}(\hat{r}) \) are spherical harmonics. We use \( L = l, m \) as a composite index for angular and magnetic quantum numbers. The expansion coefficients \( Q_{lm}^a \) are determined in terms of \( D_{ij}^a \) by requiring the compensation charges to cancel all the multipole moments of each augmentation region up to some order, generally \( l_{\text{max}} = 2 \). The charges will therefore dynamically adapt to the surroundings of the atom. For more details we refer to the original work by Blöchl.\(^3\)

D. Total energy

The total energy can also be separated into smooth and atom-centered contributions
\[ E = \tilde{E} + \sum_a (E^a - \tilde{E}^a), \quad (17) \]

where
\[ \tilde{E} = \sum_n f_n \left( \tilde{\rho}_n - \frac{1}{2} \nabla^2 \tilde{\rho}_n \right) + \sum_a \int \tilde{n}(r) \tilde{\rho}(r - R^a) dr \]
\[ + \frac{1}{2} \int \left( \frac{\tilde{\rho}(r) \tilde{\rho}(r')}{|r - r'|} \right) d^3r + E_{\text{xc}}[\tilde{\rho}], \quad (18) \]
\[ E^a = \sum_{ij} D_{ij}^a \left( \frac{1}{2} \nabla^2 |\psi_i^a|^2 + T_{\text{core}} + \int \left( \frac{\rho^*(r) \rho^*(r')}{|r - r'|} \right) d^3r' \right) + E_{\text{xc}}[n^a], \quad (19) \]
\[ \tilde{E}^a = \sum_{ij} D_{ij}^a \left( \frac{1}{2} \nabla^2 |\tilde{\rho}_j^a|^2 + \tilde{T}_{\text{core}} + \int \tilde{n}(r) \tilde{\rho}(r) dr \right) \]
\[ + \frac{1}{2} \int \left( \tilde{\rho}(r) \tilde{\rho}(r') \right) _{|r - r'|} d^3r' + E_{\text{xc}}[\tilde{n}^a]. \quad (20) \]

The terms \( T_{\text{core}} \) and \( \tilde{T}_{\text{core}} \) are the kinetic-energy contributions from the frozen-core states while \( \tilde{\rho}(r) \) is an arbitrary potential, vanishing for \( r > r^c \). This potential is generally chosen to make the atomic potential smooth while its contribution to the total energy vanishes if the partial-wave expansion is complete.\(^{13}\)

\( E_{\text{xc}} \) is the exchange-correlation functional, which must be local or semilocal as per Eq. (7) for the above expressions to be correct. While the functional is nonlinear, it remains true that
\[ E_{\text{xc}}[n] = E_{\text{xc}}[\tilde{n}] + \sum_a (E_{\text{xc}}[n^a] - E_{\text{xc}}[\tilde{n}^a]) \]
\[ (21) \]

because of the functional’s semilocality: the energy contribution from \( \tilde{n}(r) \) around every point inside the augmentation sphere is exactly canceled by that of \( \tilde{n}^*(r) \) since \( \tilde{n}(r) \) and \( \tilde{n}^*(r) \) are exactly identical here, leaving only the contribution \( E_{\text{xc}}[n^a] \). Outside the augmentation region, a similar argument applies to \( n^a(r) \) and \( \tilde{n}(r) \), leaving only the energy contribution from \( \tilde{n}(r) \) which is here equal to the all-electron density.

E. Hamiltonian and orthogonality

In generic operator form, the Hamiltonian corresponding to the total energy from Eq. (17) is
\[ \tilde{H} = -\frac{1}{2} \nabla^2 + \tilde{\rho} + \sum_{ij} |\tilde{\rho}^a_i| \Delta H_{ij}^a |\tilde{\rho}^a_j|, \quad (22) \]
where
\[ \tilde{\rho} = \tilde{\rho}_n[\tilde{\rho}] + \tilde{\rho} + u_{\text{xc}}[\tilde{n}] \]

is the local effective potential, containing the Hartree, the arbitrary localized and the xc potentials, and where
\[ \Delta H_{ij}^a = \frac{\partial E}{\partial D_{ij}^a} \]
\[ (23) \]

are the atomic Hamiltonians containing the atom-centered contributions from the augmentation spheres. Since the all-
electron wave functions $\psi_n$ must be orthonormal, the pseudo-wave functions $\tilde{\psi}_n$ must obey
\begin{equation}
\delta_{nm} = \langle \psi_n | \psi_m \rangle = \langle \tilde{\psi}_n | T^T T \tilde{\psi}_m \rangle = \langle \tilde{\psi}_n | S \tilde{\psi}_m \rangle,
\end{equation}
where we have defined the overlap operator
\begin{equation}
S = T^T T = 1 + \sum_{aij} |p_i^a|^2 \Delta S_{ij}^a |p_j^a|.
\end{equation}
The atomic contributions
\begin{equation}
\Delta S_{ij}^a = \langle \phi_i^a | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \tilde{\phi}_j^a \rangle
\end{equation}
are constant for a given element.

Given the Hamiltonian and orthogonality condition, a variational problem can be derived for the pseudowave functions. This problem is equivalent to the generalized Kohn-Sham eigenvalue problem
\begin{equation}
\tilde{H}(\tilde{\psi}_n) = S(\tilde{\psi}_n) \epsilon_n,
\end{equation}
which can then be solved self-consistently with available techniques.

### III. LOCALIZED BASIS SETS IN PAW

We now introduce a set of basis functions $|\Phi_r\rangle$ which are fixed, strictly localized atomic-orbital-like functions represented numerically, following the approach by Sankey and Niklewski. We furthermore consider the pseudowave functions $|\tilde{\psi}_n\rangle$ to be linear combinations of the basis functions
\begin{equation}
|\tilde{\psi}_n\rangle = \sum \chi_{\mu n} |\Phi_\mu\rangle,
\end{equation}
where the coefficients $\chi_{\mu n}$ are variational parameters. It proves useful to define the density matrix
\begin{equation}
\rho_{\mu \nu} = \sum_n \chi_{\mu n}^{\ast} \chi_{\nu n}.
\end{equation}
The pseudodensity can be evaluated from the density matrix through
\begin{equation}
\tilde{n}(r) = \sum_{\mu \nu} \Phi_{\mu \ast}(r) \Phi_{\nu \ast}(r) \rho_{\mu \nu} + \sum_a \tilde{n}_a^a(r).
\end{equation}

Ahead of a calculation, we evaluate the matrices
\begin{equation}
T_{\mu \nu} = \langle \Phi_\mu \rangle - \frac{1}{2} \nabla^2 \langle \Phi_\mu \rangle,
\end{equation}
\begin{equation}
P_{\mu \nu} = \langle \tilde{\psi}_\mu | \tilde{\psi}_\nu \rangle,
\end{equation}
\begin{equation}
\Theta_{\mu \nu} = \langle \Phi_\mu | \Phi_\nu \rangle,
\end{equation}
which are used to evaluate most of the quantities of the previous sections in matrix form. The atomic density matrices from Eq. (6) become
\begin{equation}
D_{ij}^a = \sum_{\mu \nu} P_{ij}^{\mu \nu} \rho_{\mu \nu} P_{ij}^{\nu \mu},
\end{equation}
and the kinetic-energy contribution in the first term of Eq. (18) is
\begin{equation}
\sum_n f_n \langle \tilde{\psi}_n | -\frac{1}{2} \nabla^2 | \tilde{\psi}_n \rangle = \sum_{\mu \nu} T_{\mu \nu} \rho_{\nu \mu}.
\end{equation}
We can then define the Hamiltonian matrix elements by taking the derivative of the total energy $E$ with respect to the density-matrix elements, which eventually results in the discretized Hamiltonian
\begin{equation}
H_{\mu \nu} = \frac{\partial E}{\partial \rho_{\mu \nu}} = T_{\mu \nu} + V_{\mu \nu} + \sum_{aij} P_{ij}^{\mu \nu} \Delta S_{ij}^a P_{ij}^{\nu \mu},
\end{equation}
where
\begin{equation}
V_{\mu \nu} = \int \Phi_{\mu \ast}(r) \tilde{V}(r) \Phi_{\nu}(r) d\mathbf{r}.
\end{equation}
The overlap operator of Eq. (25) has the matrix representation
\begin{equation}
S_{\mu \nu} = \langle \Phi_\mu | S | \Phi_\nu \rangle = \Theta_{\mu \nu} + \sum_{aij} P_{ij}^{\mu \nu} \Delta S_{ij}^a P_{ij}^{\nu \mu},
\end{equation}
so orthogonality of the wave functions is now expressed by
\begin{equation}
\sum_{\mu \nu} c_{\mu \nu}^{\ast} S_{\mu \nu} = \delta_{nn}.
\end{equation}
This is incorporated by defining a quantity $\Omega$ to be variationally minimized with respect to the coefficients, specifically
\begin{equation}
\Omega = E - \sum_{\mu \nu} \lambda_{\mu \nu} (c_{\mu \nu}^{\ast} S_{\mu \nu} c_{\mu \nu} - \delta_{\mu \nu}).
\end{equation}
Setting the derivative of $\Omega$ with respect to $c_{\mu \nu}$ equal to 0, one obtains the generalized eigenvalue equation
\begin{equation}
\sum_{\nu} H_{\mu \nu} c_{\nu \mu} = \sum_{\nu} S_{\mu \nu} c_{\nu \mu} \epsilon_n = \delta_{\mu \mu},
\end{equation}
which can be solved for the coefficients $c_{\mu \nu}$ and energies $\epsilon_n$ when the Hamiltonian $H_{\mu \nu}$ and the overlap matrix $S_{\mu \nu}$ are known.

### A. Basis functions generation

The basis functions $|\Phi_r\rangle$ in Eq. (28) are atom-centered orbitals written as products of numerical radial functions and spherical harmonics,
\begin{equation}
\Phi_{\alpha \lambda \mu}(r) = \varphi_{\alpha \lambda}(r) Y_{\lambda \mu}(\hat{\mathbf{r}}).
\end{equation}
In order to make the Hamiltonian and overlap matrices sparse in the basis-set representation, we use strictly localized radial functions, i.e., orbitals that are identically zero beyond a given radius, as proposed by Sankey and Niklewski and successfully implemented in the SIESTA method.

The first (single-zeta) basis orbitals $\varphi_{\alpha \lambda}^{AE}(r)$ are obtained for each valence state by solving the radial all-electron Kohn-Sham equations for the isolated atom in the presence of a confining potential with a certain cutoff. If the confining potential is chosen to be smooth, the basis functions similarly become smooth. We use the same confining potential as proposed in Ref. 17. The smooth basis functions are then
obtained using $\varphi_{nl}(r) = T^{-1} \varphi_{nl}^{AE}(r)$. The result of the procedure is illustrated in Fig. 2.

The cutoff radius is selected in a systematic way by specifying the energy shift $AE$ of the confined orbital compared to the free-atom orbital. In this approach small values of $AE$ will correspond to long-ranged basis orbitals.

To improve the radial flexibility, extra basis functions with the same angular momentum $l$ (multiple zetas) are constructed for each valence state using the split-valence technique. The extra function is constructed by matching a polynomial to the tail of the atomic orbital, where the matching radius is determined by requiring the norm of the part of the atomic orbital outside that radius to have a certain value.

Finally, polarization functions (basis functions with $l$ quantum number corresponding to the lowest unoccupied angular momentum) can be added in order to improve the angular flexibility of the basis. There are several approaches to generate these orbitals, such as perturbing the occupied eigenstate with the highest $l$ quantum number with an electric field using first-order perturbation theory (like in Ref. 16) or using the appropriate unoccupied orbitals. As a first implementation we use a Gaussian-type function of the form $r^l \exp(-ar^2)$ for the radial part, where $l$ corresponds to the lowest unoccupied angular momentum. This produces reasonable polarization functions as demonstrated by the results presented in a following section.

A generator program is included in the GPAW code and it can produce basis sets for virtually any elements in the periodic table. Through our experiences with generating and using different basis sets, we have reached the following set of default parameters: we usually work with a double zeta polarization (DZP) basis. The energy shift for the atomic orbital is taken as 0.1 eV and the tail norm is 0.16 (in agreement with SIESTA (Ref. 16). The width of the Gaussian used for the polarization function is 1/4 of the cutoff radius of the first zeta basis function. Further information can be found in the documentation for the basis-set generator. At this point we have not yet systematically optimized the basis-set parameters, although we expect to do so by means of an automatic procedure.

B. Atomic forces

The force on some atom $a$ is defined as the negative derivative of the total energy of the system with respect to the position of that atom,

$$F_a = -\frac{\partial E}{\partial \mathbf{R}_a}. \quad (43)$$

The derivative is to be taken with the constraints that self-consistency and orthonormality according to Eq. (39) must be obeyed. This implies that the calculated force will correspond to the small-displacement limit of the finite-difference energy gradient one would obtain by performing two separate energy calculations, where atom $a$ is slightly displaced in one of them.

The expression for the force is obtained by using the chain rule on the total energy of Eq. (17). The primary complication compared to the grid-based PAW force formula, Eq. (50) from Ref. 13, is that the basis functions move with the atoms, introducing extra terms in the derivative.

The complete formula for the force on atom $a$ is

$$F_a = -2N \sum_{\mu \in \mathrm{c}, \nu \in \mathrm{v}} \frac{d\Phi_{\nu}(r)}{dR^{\mathrm{c}}_a} \rho_{\mu \nu} + 2N \sum_{\mu \in \mathrm{c}, \nu \in \mathrm{v}} \frac{d\Theta_{\mu}(r)}{dR^{\mathrm{c}}_a} E_{\sigma \nu}$$

$$- 2N \sum_{b \in \mathrm{c}, \nu \in \mathrm{v}} Z^b_{\mu \nu} E_{\gamma \nu} + 2N \sum_{\mu \in \mathrm{c}, \nu \in \mathrm{v}} Z^\sigma_{\mu \nu} E_{\gamma \nu}$$

$$+ 2N \sum_{b \in \mathrm{c}, \nu \in \mathrm{v}} A^b_{\mu \nu} \rho_{\mu \nu} - 2N \sum_{\mu \in \mathrm{c}, \nu \in \mathrm{v}} A^\sigma_{\mu \nu} \rho_{\mu \nu}$$

$$- 2N \sum_{\mu \in \mathrm{c}, \nu \in \mathrm{v}} \left[ \int \frac{d\Phi_{\nu}(r)}{dR^{\mathrm{c}}_a} \varphi(r) \Phi_{\nu}(r) d\mathbf{r} \right] \rho_{\mu \nu}$$

$$- \int \tilde{v}(r) \frac{d\tilde{n}^\sigma_a(|r - R^\mathrm{c}_a|)}{dR^{\mathrm{c}}_a} d\mathbf{r} - \int \tilde{n}(r) \frac{d\tilde{n}^\sigma_a(|r - R^\mathrm{c}_a|)}{dR^{\mathrm{c}}_a} d\mathbf{r}$$

$$- \int \tilde{v}_f(r) \sum L \frac{d\tilde{n}^\sigma_a(|r - R^\mathrm{c}|)}{dR^{\mathrm{c}}_a} d\mathbf{r}.$$ \quad (44)

where

$$A^\mu_{\mu \nu} = \sum_{ij} \frac{d\Phi^\mu_{ij}}{dR^\mu} \Delta H^\mu_{ij} p^\nu_{ij}, \quad (45)$$

$$Z^b_{\mu \nu} = \sum_{ij} \frac{d\Phi^b_{ij}}{dR^b} \Delta S^b_{ij} p^\nu_{ij}, \quad (46)$$

$$E_{\mu \nu} = \sum_{k} S^\mu_k H_k \rho_{\mu \nu}. \quad (47)$$

The notation $\mu \in \mathrm{c}$ denotes that summation should be performed only over those basis functions that reside on atom $a$.

Equation (44) is derived in Appendix. The last three terms are basis set independent and inherited from the grid-based implementation.

IV. IMPLEMENTATION

The LCAO code is implemented in GPAW, a real-space PAW code. For the details of the real-space implementation
we refer to the original paper. In this code the density, effective potential, and wave functions are evaluated on real-space grids.

In LCAO the matrix elements of the kinetic and overlap operators $T_{\mu\nu}$, $\Theta_{\mu\nu}$, and $P_{\mu\nu}$ in Eqs. (31)–(33) are efficiently calculated in Fourier space based on analytical expressions. For each pair of different basis orbitals (i.e., independently of the atomic positions), the overlap can be represented in the form of radial functions and spherical harmonics. These functions are stored as splines which can in turn be evaluated for a multitude of different atomic separations.

The two-center integrals are thus calculated once for a given atomic configuration ahead of the self-consistency loop. This is equivalent to the SIESTA approach. The matrix elements of the effective potential $V_{\mu\nu}$ are still calculated numerically on the three-dimensional (3D) real-space grid since the density is also evaluated on this grid.

Because of the reduced degrees of freedom of a basis calculation compared to a grid-based calculation, the Hamiltonian from Eq. (36) is directly diagonalized in the space of the basis functions according to Eq. (41). This considerably lowers the number of required iterations to reach self-consistency, compared to the iterative minimization schemes used in grid-based calculations.

For each step in the self-consistency loop, the Hartree potential $\tilde{V}_{\text{Hartree}}(r)$ is calculated by solving the Poisson equation $\nabla^2 \tilde{V}_{\text{Hartree}}(r) = -4\pi \tilde{\rho}(r)$ in real space using existing multigrid methods, such as the Gauss-Seidel and Jacobi methods. A solver based on the fast Fourier transform is also available in the GPAW code. The calculations are parallelized over $k$ points, spins, and real-space domains such as in the grid-based case. We further distribute the orbital-by-orbital matrices such as $H_{\mu\nu}$ and $S_{\mu\nu}$, and use SCALAPACK for operations on these, notably the diagonalization of Eq. (41).

**Localized functions on the grid**

Quantities such as the density $\tilde{\rho}(r)$ and effective potential $\tilde{V}(r)$ are still stored on 3D grids. Matrix elements such as $V_{\mu\nu}$ in Eq. (37) and the pseudodensity given by Eq. (30) can therefore be calculated by loops over grid points.

Since each basis function is nonzero only in a small part of space, we only store the values of a given function within its bounding sphere. Each function value inside the bounding sphere is calculated as the product of radial and angular parts, viz., Eq. (42), where the radial part is represented by a spline and the spherical harmonic evaluated in Cartesian form, i.e., as a polynomial. The same method is used to evaluate derivatives in force calculations, although this involves the derivatives of these quantities aside from just their function values.

We initially compile a data structure to keep track of which functions are nonzero for each grid point. When looping over the grid, we maintain a list of indices $\mu$ for the currently nonzero basis functions by adding or removing, as appropriate, those functions whose bounding spheres we intersect. The locations of these bounding spheres are likewise precompiled into lists for efficient processing. The memory overhead due to this method is still much smaller than the storage requirements for the actual function values.

**V. RESULTS**

In this section we calculate common quantities using the localized basis set on different systems. The results are compared to the complete basis-set limit, i.e., a well-converged grid calculation. Note that this comparison can be done in a very systematic way since the calculations on the grid share the same approximations and mostly the same implementation as the calculations performed with the localized basis. All the results presented in this section have been obtained using PAW setups from the extensive GPAW library, freely available online.

**A. Molecules**

In order to assess the accuracy of the LCAO implementation for small molecules, the Perdew-Burke-Ernzerhof (PBE) (Ref. 19) atomization energies for the G2-1 data set are considered. The atomic coordinates are taken from MP2(full)/6-31G(d) optimized geometries. The error with respect to the grid results is shown in Fig. 3 for different basis sets. This error is defined as

$$\Delta E_{\text{LCAO}} - \Delta E_{\text{grid}} = E_{\text{LCAO}}^{\text{grid}} - \sum_{\text{atoms}} \sum_{\text{grid}} \frac{E_{\text{LCAO}}^{\text{grid}}}{\text{atoms}}.$$ (48)

The reference grid results are well-converged calculations in very good agreement with the VASP (Ref. 8) and Gaussian codes. The figure shows that enlarging the basis set, i.e., including more orbitals per valence electron, systematically improves the results toward the grid energies.

It must be noted that some differences with respect to the grid atomization energies still remain, even in the case of large basis sets. This is mainly due to the two following reasons. First, the basis functions are generated from spin-paired calculations and hence they do not explicitly account for possible spin-polarized orbitals. This is in practice accounted for by using larger basis sets in order to include more degrees of freedom in the shape of the wave functions. Second, isolated atoms are difficult to treat because of their long-ranged orbitals. Actual basis functions are, in fact, obtained from atomic calculations with an artificial confining potential thus resulting in more confined orbitals.

**B. Solids**

The equilibrium bulk properties have been calculated for several crystals featuring different electronic structures: simple metals (Li, Na, and Al), semiconductors (AlP, Si, and SiC), ionic solids (NaCl, LiF, and MgO) transition metals (Fe, Cu, and Pt) as well as one insulator (C). The results are shown in Fig. 4. For comparison with grid-based calculations, the bar plots show the deviations from grid-based results for each basis set while the precise numbers are shown in each of the corresponding tables. All the calculations were
performed with the solids in their lowest energy crystal structure, using the PBE functional for exchange and correlation. The quantities were computed using the relaxed structures obtained with the default, unoptimized basis sets. The calculations were generally spin paired, i.e., non-magnetic, with the exception of Fe and the atomic calculations used to get cohesive energies.

The overall agreement with the real-space grid is excellent: about 0.5% mean absolute error in the computation of lattice constants, 4% in cohesive energies, and 5–8% for bulk moduli using double zeta polarized (DZP) basis sets. The calculations were generally spin paired, i.e., non-magnetic, with the exception of Fe and the atomic calculations used to get cohesive energies.

Notice that in many cases remarkably good results can be obtained even with a small single zeta polarized (SZP) basis, particularly for lattice constants. This shows that structure optimizations with the LCAO code are likely to yield very accurate geometries. This is probably due to the fact that calculations of equilibrium structures only involve energy differences between very similar structures, i.e., not with respect to isolated atoms, thus leading to larger error cancellations.

With DZP the primary source of error in cohesive energy comes from the free-atom calculation, where the confinement of each orbital raises the energy levels by around 0.1 eV. Thus, atomic energies are systematically overestimated, leading to stronger binding. This error can be controlled by using larger basis-set cutoffs, i.e., choosing smaller orbital energy shifts during basis generation.

C. Structure optimizations

LCAO calculations tend to reproduce geometries of grid-based calculations very accurately. In structure optimizations, the LCAO code can therefore be used to provide a high-quality initial guess for a grid-based structure optimization.

While it is trivial to reuse a geometry obtained in one code for a more accurate optimization in another, our approach is practical because the two representations share the exact same framework. Thus the procedure is seamless as well as numerically consistent, in the sense that most of the operations are carried out using the same approximations, finite-difference stencils, and so on. With quasi-Newton methods, the estimate of the Hessian matrix generated during the LCAO optimization can be reused as well. For most non-trivial systems, an LCAO calculation is between 25 and 30
times faster than a grid calculation, making the cost of the LCAO optimization negligible.

Figure 5 shows a performance comparison when reusing the positions and Hessian from a LCAO-based structure optimization for a grid-based one, using the default basis set. The system is a 38-atom truncated octahedral gold cluster with CO adsorbed, with the initial and final geometries shown in the inset.

A purely grid-based optimization takes 223 CPU hours while a purely LCAO-based one, requiring roughly the same number of steps, takes 8.4 CPU hours. A further grid-based optimization takes 45 CPU hours, for a total speedup factor

![Figure 4](image)

**FIG. 4.** (Color online) Deviations in lattice parameter (a), cohesive energy (b), and relative bulk modulus (c) from the converged results. The largest bars have been truncated and are shown with dotted edges. See Table I for the precise values.

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**Table I.** Lattice parameter (top), cohesive energy (middle), and bulk modulus (bottom) calculated using different basis sets.

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<td>32</td>
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</table>
of 4. The value of an initial LCAO optimization is of course higher if the initial guess is worse. For systems where a large fraction of the time is spent close to the converged geometry, the speedup may not be as significant.

The energy reference corresponds to the separate cluster and molecule at optimized geometries—the total-energy difference between an LCAO and a grid calculation is otherwise around 30 eV. It is therefore important to choose an optimization algorithm which will handle such a shift well. The present plots use the L-BFGS algorithm\(^{22,23}\) (limited memory Broyden-Fletcher-Goldfarb-Shanno) from the Atomic Simulation Environment.\(^{31}\)

VI. CONCLUSIONS

We have described the implementation of a localized basis in the grid-based PAW code GPAW and tested the method on a variety of molecules and solids. The results for atomicization energies, cohesive energies, lattice parameters, and bulk moduli were shown to converge toward the grid results as the size of the LCAO basis was increased. Structural properties were found to be particularly accurate with the LCAO basis. It has been demonstrated how the LCAO basis can be used to produce accurate initial guesses (both for the electron wave functions, atomic structure, and Hessian matrix) for subsequent grid-based calculations to increase efficiency of high-accuracy grid calculations.

The combination of the grid-based and LCAO methods in one code provides a flexible, simple, and smooth way to switch between the two representations. Furthermore the PAW formalism itself presents significant advantages: it is an all-electron method, which eliminates pseudopotential errors and it allows the use of coarser grids than norm-conserving pseudopotentials, which increases efficiency.

Finally, the LCAO method enables GPAW to perform calculations involving Green’s function, which intrinsically need a basis set with finite support. Current developments along these lines include electron-transport calculations, electron-phonon coupling, and scanning tunnel microscope simulations.

ACKNOWLEDGMENTS

The authors acknowledge support from the Danish Center for Scientific Computing through Grant No. HDW-1103-06. The Center for Atomic-scale Materials Design is sponsored by the Lundbeck Foundation.

APPENDIX: FORCE FORMULA

The force on atom \(a\) is found by taking the derivative of the total energy with respect to the atomic position \(\mathbf{R}^a\). We shall use the chain rule on Eq. (17), taking \(\rho_{\mu\nu}, D_{ij}^\mu, \bar{n}(r), \bar{p}(r), T_{\mu\nu},\) and \(\bar{\mu}(r)\) to be separate variables for the purposes of partial derivatives,

\[
\frac{\partial E}{\partial \mathbf{R}^a} = \sum_{\mu\nu} \frac{\partial E}{\partial \rho_{\mu\nu}} \frac{\partial \rho_{\mu\nu}}{\partial \mathbf{R}^a} + \sum_{ij} \frac{\partial E}{\partial D_{ij}^\mu} \frac{\partial D_{ij}^\mu}{\partial \mathbf{R}^a} + \int \frac{\partial E}{\partial \bar{n}(r)} \frac{\partial \bar{n}(r)}{\partial \mathbf{R}^a} dr + \int \frac{\partial E}{\partial \bar{p}(r)} \frac{\partial \bar{p}(r)}{\partial \mathbf{R}^a} dr + \sum_{\mu\nu} \frac{\partial E}{\partial T_{\mu\nu}} \frac{\partial T_{\mu\nu}}{\partial \mathbf{R}^a}
\]

where \(\bar{\mu}(r) = \sum_{n} \bar{\mu}_n |r - \mathbf{R}^n|\). The remaining quantities in the energy expression pertain to isolated atoms and thus do not depend on atomic positions. The first term of Eq. (A1) is

\[
\sum_{\mu\nu} \frac{\partial E}{\partial \rho_{\mu\nu}} \frac{\partial \rho_{\mu\nu}}{\partial \mathbf{R}^a} = 2\pi \sum_{\mu\nu} H_{\mu\nu} \rho_{\mu\nu} \frac{\partial \rho_{\mu\nu}}{\partial \mathbf{R}^a} = 2\pi \sum_{\mu\nu} \frac{\partial \rho_{\mu\nu}}{\partial \mathbf{R}^a} S \rho_{\mu\nu} \epsilon_{\mu\nu} \epsilon_{\mu\nu},
\]

where we have used Eqs. (29) and (36) in the first step and Eq. (41) in the second. When the atoms are displaced (infinitesimally), the coefficients must change to accommodate the
orthogonality criterion. This can be incorporated by requiring the derivatives of each side of Eq. (39) to be equal, implying the relationship

$$- \sum_{\mu} \epsilon_{\mu}^{*} \frac{\partial S_{\mu \nu}}{\partial R_{\nu}} e_{\nu} = 2 \Re \sum_{\mu} \frac{\partial c_{\mu}^{*}}{\partial R_{\mu}} S_{\mu \nu} e_{\nu}. \quad (A3)$$

Inserting this into Eq. (A2) yields

$$\sum_{\mu \nu} \frac{\partial E}{\partial P_{\mu \nu}} \frac{\partial P_{\mu \nu}}{\partial R_{\nu}} = - \sum_{\mu \nu} \frac{\partial S_{\mu \nu}}{\partial R_{\nu}} e_{\nu} c_{\mu}^{*} - \sum_{\mu \nu} \frac{\partial S_{\mu \nu}}{\partial R_{\nu}} E_{\nu \mu}, \quad (A4)$$

where we have introduced the matrix

$$E_{\nu \mu} = \sum_{\alpha} e_{\nu} c_{\mu \alpha} c_{\nu \alpha} = \sum_{\lambda} S_{\mu \nu}^{0} H_{\lambda \mu} \rho_{\nu \lambda}. \quad (A5)$$

The equivalence of these forms follows from Eq. (41). The overlap matrix elements $S_{\mu \nu}$ depend on $R^{a}$ through the two-center integrals $\Theta_{\mu \nu}$ and $D_{\mu \nu}^{0}$. The derivative of a two-center integral can be nonzero only if exactly one of the two involved atoms is $a$ and for nonzero derivatives, the sign changes if the indices are swapped. Taking these into account, Eq. (A4) is split into those three terms in Eq. (44) which contain $E_{\nu \mu}$.

In the second term in Eq. (A1), we take the $D_{j}^{b}$-dependent derivative for fixed $\rho_{\mu \nu}$, which by Eq. (23) evaluates to

$$\sum_{b \nu} \frac{\partial E}{\partial D_{j}^{b}} \frac{\partial D_{j}^{b}}{\partial R_{\nu}} = 2 \Re \sum_{b \nu \mu} \rho_{b}^{\mu} \Delta H_{b}^{0} \frac{\partial D_{j}^{b}}{\partial R_{\nu}} \rho_{\nu \mu}. \quad (A6)$$

Again most of the two-center integral derivatives are zero. A complete reduction yields the two terms in Eq. (44) which depend on the $A_{\mu \nu}^{b}$ vectors.

Using Eq. (30), the third term of Eq. (A1) is

$$\int \frac{\partial E}{\partial \tilde{n}_{\nu \mu}} \frac{\partial \tilde{n}_{\nu \mu}}{\partial R_{\nu}} d\nu = \int \tilde{v}(r) \frac{\partial \tilde{n}_{\nu \mu}(r)}{\partial R_{\nu}} d\nu = 2 \Re \left[ \sum_{\mu \nu} \int \frac{\partial D_{j}^{0}(r)}{\partial R_{\nu}} \tilde{v}(r) D_{j}^{0}(r) \rho_{\nu \mu} \right] + \int \tilde{v}(r) \frac{\partial \tilde{n}_{\nu \mu}(r - R^{a})}{\partial R_{\nu}} d\nu. \quad (A7)$$

The sum over $\mu$ can be restricted to $\mu \in a$. Consider the fourth term of Eq. (A1). Aside from $\tilde{n}(r)$ and $D_{j}^{b}$, which are considered fixed as per the chain rule, the pseudocharge density $\tilde{\rho}(r)$ depends only on the locations of the compensation charge expansion functions $\tilde{g}_{\nu \mu}^{\gamma}(r)$ which move rigidly with the atom, so

$$\int \frac{\partial E}{\partial \tilde{\rho}(r)} \frac{\partial \tilde{\rho}(r)}{\partial R^{a}} d\nu = \int \tilde{v}_{\mu \nu}(r) \frac{\partial \tilde{\rho}(r)}{\partial R^{a}} d\nu \left[ \sum_{\nu \mu} \frac{\partial \tilde{g}_{\nu \mu}^{\gamma}(r)}{\partial R^{a}} \right] d\nu. \quad (A8)$$

The kinetic term from Eq. (A1) is

$$\sum_{\nu \mu} \frac{\partial E}{\partial T_{\mu \nu}} \frac{\partial T_{\mu \nu}}{\partial R^{a}} = \sum_{\nu \mu} \frac{\partial T_{\nu \mu}}{\partial R^{a}} \rho_{\nu \mu} \quad (A9)$$

and can also be restricted to $\mu \in a$. Finally, the contribution from the local potential $\tilde{v}(r)$ is simply

$$\int \frac{\partial E}{\partial \tilde{v}(r)} \frac{\partial \tilde{v}(r)}{\partial R^{a}} d\nu = \int \tilde{v}(r) \frac{\partial \tilde{v}(r - R^{a})}{\partial R^{a}} d\nu. \quad (A10)$$

By now we have considered all position-dependent variables in the energy expression and have obtained expressions for all terms present in Eq. (44).

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14Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, (2004).
18http://wiki.fysik.dtu.dk/gpaw/setups/setups.html
Paper II

Graphene on metals: A van der Waals density functional study
Graphene on metals: A van der Waals density functional study


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(Received 15 December 2009; revised manuscript received 1 February 2010; published 23 February 2010)

We use density functional theory (DFT) with a recently developed van der Waals density functional (vdW-DF) to study the adsorption of graphene on Co, Ni, Pd, Ag, Au, Cu, Pt, and Al(111) surfaces. In contrast to the local-density approximation (LDA) which predicts relatively strong binding for Ni, Co, and Pd, the vdw-DF predicts weak binding for all metals and metal-graphene distances in the range 3.40–3.72 Å. At these distances the graphene band structure as calculated with DFT and the many-body $G_0W_0$ method is basically unaffected by the substrate, in particular there is no opening of a band gap at the K point.

DOI: 10.1103/PhysRevB.81.081408

PACS number(s): 73.20.Hb, 71.15.Mb, 71.15.Nc

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We focus on the adsorption of graphene on single-crystal surfaces of the 111 metal Co, Ni, Pd, Ag, Au, Cu, Pt, and Al metal (111) surfaces. We fix the atoms in the metal slabs at their experimental lattice constants the graphene lattice constant is mainly due to its very peculiar band structure, with the $\pi$ and $\pi^*$ bands showing linear dispersion around the Fermi level where they touch in a single point. The great variety of physics and chemistry which derives from this electronic structure makes graphene very attractive for a range of applications. In particular, its high stability and good conductivity under ambient conditions makes it an interesting candidate for future nanoscale electronics. In this perspective, the interaction of graphene with metallic contacts plays a fundamental role. Moreover, catalytic growth of graphene on transition metal surfaces from carbon containing gases has become a standard way to obtain high quality graphene samples. Nevertheless the nature of the metal-graphene chemical bond is still not well understood.

The widely used density functional theory (DFT) with local and semilocal functionals for exchange and correlation usually provides an accurate description of covalent and ionic chemical bonds. On the other hand it fails to reproduce nonlocal dispersive forces, in particular van der Waals ionic chemical bonds. On the other hand it fails to reproduce nonlocal dispersion interactions and has proved successful in several cases where standard functionals fail, such as rare gases, benzene dimers, graphite, polymers, DNA, and organic molecules on surfaces. Within the vDW-DF approximation, the exchange-correlation energy is

$$E_{xc}^{vdw-DF} = E_{xc}^{revPBE} + E_{xc}^{LDA} + E_{xc}^{nl},$$

where $E_{xc}^{revPBE}$ is the revPBE (Ref. 23) exchange energy, $E_{xc}^{LDA}$ is the LDA correlation energy, and $E_{xc}^{nl}$ is the nonlocal correction given by

$$E_{xc}^{nl} = \frac{1}{2} \int n(r_1) n(r_2) \phi(q_1, q_2, r_{12}) dV_1 dV_2,$$

where $r_{12} = |r_1 - r_2|$ and $q_1$ and $q_2$ are values of a universal function $\phi(q_1, q_2, r_{12})$. Equation (2) is efficiently evaluated by factorizing the integration kernel $\phi$ and by using fast Fourier transform to compute the self-consistent potential as proposed in Ref. 24 and implemented in the real-space projector augmented wave GPAW code.

In this Rapid Communication we consider graphene on Co, Ni, Pd, Ag, Au, Cu, Pt, and Al metal (111) surfaces. We fix the atoms in the metal slabs at their experimental lattice parameters and relax the graphene sheet using the vdw-DF Hellmann-Feynman forces. We observe that the vdw-DF results do not change significantly if we fix the graphene lattice parameter to its optimized value and adjust the metals correspondingly. We use a (6,6,1) and (4,4,1) Monkhorst Pack k-point sampling, respectively, for the smaller (Co, Ni, and Cu) and the larger (Pd, Ag, Au, Pt, and Al) orthorhombic unit cells. The two different unit cells are needed in order to obtain commensurate structures without significant strain, as discussed in Ref. 10. The metal slabs are modeled with four atomic layers and a vacuum of 14 Å in the direction normal to the surface; the grid spacing is 0.16 Å. The calculations...
for Ni and Co surfaces are spin polarized; notice however that the nonlocal correlation [last term in Eq. (1)] is independent of spin. The calculated binding energies and distances for the relaxed structures are listed in Table I. The vdW-DF results show that the metal-graphene interaction is relatively similar across the different metals. This is in contrast with the LDA prediction of two separate classes of metal-graphene interfaces, as found in very good agreement with Ref. 10. Note that in the LDA calculations the graphene lattice parameter was fixed to its optimized LDA value. We also repeated the same calculations using the revPBE functional, and we obtained no binding for all the metals. Interestingly, for the systems that LDA finds to be weakly bonded (Ag, Au, Cu, Pt, and Al), the binding energies obtained with the vdW-DF are very similar to the LDA ones. Nevertheless the binding distances are systematically slightly larger in the vdW-DF case. In fact it has been reported that the vdW-DF functional usually produces equilibrium distances somewhat larger than experiments.20 In the case of Co, Ni, and Pd, on the other hand, the relatively strong binding predicted by LDA is not found by the vdW-DF functional.

In order to analyze these results, we now focus on the interaction between graphene and Ni(111). Figure 1 shows the binding curves for graphene on the Ni(111) surface calculated with the LDA, revPBE, and vdW-DF functionals. The revPBE curve is positive at all distances, while the LDA curve shows a relatively deep minimum at ~2 Å consistent with previous LDA calculations. The vdW-DF result lies in between, following the revPBE curve at small separations and the LDA curve at larger separations, and it predicts a shallow minimum at 3.5 Å. Note that a metastable plateau is found by the revPBE functional around 2.5 Å.

In Fig. 2 we show the calculated band structure of graphene on Ni(111). The size of the dots indicate the weight of the corresponding Bloch eigenstate on the carbon $p_z$ orbitals with darker meaning larger weight. In free graphene, the carbon $p_z$ orbitals placed at A sites $(p_z^A)$ are decoupled from the $p_z$ orbitals at B sites $(p_z^B)$ at the Dirac point, thus producing two degenerate states (see inset in Fig. 1 for the structure). Since the A sites are located directly on top of Ni atoms at a close distance in the LDA calculation (2.08 Å), a strong hybridization between $p_z^A$ orbitals and Ni$_{1s}$ is observed, which gives rise to an unoccupied antibonding state $\sigma^*$ and two occupied bonding states $\sigma_1$ and $\sigma_2$. The LDA gaps for $\sigma^*-\sigma_1$ and $\sigma^*-\sigma_2$ are 2 and 4 eV, respectively. On the other hand, the $p_z^B$ orbitals (occupied in the spin-up channel and unoccupied in the spin-down one) hardly interact with Ni $d$ states and therefore remain unmodified. The vdW-DF band structures (evaluated at the vdW-DF relaxed distance of 3.50 Å), on the other hand, resemble the free graphene, preserving the Dirac point and only shifting it up by 0.13 eV. A very similar behavior is found for Co and Pd. For the remaining interfaces both the LDA and vdW-DF band structures resemble that of free-standing graphene with the Dirac point shifted with respect to the metal Fermi level. The Fermi level shifts and calculated charge transfer between the metal and graphene are summarized in Table I.

### Table I. Binding energies ($E_b$) per carbon atom and binding distances ($d$) of graphene on metal (111) surfaces.

<table>
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<tr>
<th></th>
<th>Co</th>
<th>Ni</th>
<th>Pd</th>
<th>Ag</th>
<th>Au</th>
<th>Cu</th>
<th>Pt</th>
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<tr>
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<tr>
<td>$d$ (Å)</td>
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<td>3.50</td>
<td>3.50</td>
<td>3.55</td>
<td>3.57</td>
<td>3.58</td>
<td>3.67</td>
<td>3.72</td>
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<tr>
<td>$E_b$ (meV)</td>
<td>30</td>
<td>37</td>
<td>39</td>
<td>33</td>
<td>38</td>
<td>38</td>
<td>43</td>
<td>35</td>
</tr>
<tr>
<td>$\Delta E_b$ (eV)</td>
<td>-0.20</td>
<td>0.13</td>
<td>0.65</td>
<td>-0.40</td>
<td>0.21</td>
<td>-0.43</td>
<td>0.66</td>
<td>-0.51</td>
</tr>
<tr>
<td>$\delta Q (10^{-3} e)$</td>
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<td>-3.0</td>
<td>5.0</td>
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<td>4.0</td>
<td>-4.0</td>
<td>5.0</td>
<td>-8.0</td>
</tr>
<tr>
<td>LDA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>2.08</td>
<td>2.08</td>
<td>2.33</td>
<td>3.32</td>
<td>3.35</td>
<td>3.21</td>
<td>3.25</td>
<td>3.46</td>
</tr>
<tr>
<td>$E_b$ (meV)</td>
<td>175</td>
<td>123</td>
<td>79</td>
<td>45</td>
<td>31</td>
<td>35</td>
<td>33</td>
<td>25</td>
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<tr>
<td>Expt.</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>$d$ (Å)</td>
<td>1.5–2.2$^a$</td>
<td>2.1$^b$</td>
<td>5$^c$</td>
<td>weak $^d$</td>
<td>weak $^e$</td>
<td>weak $^f$</td>
<td>weak $^d$</td>
<td></td>
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<tr>
<td>Hybridization</td>
<td>strong $^a$</td>
<td>strong $^e$</td>
<td>strong $^f$</td>
<td></td>
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</table>
Since LDA is known to underestimate band gaps significantly we have also performed $G_0W_0$ calculations for the graphene-Ni structures corresponding to the LDA and graphene bond distance of 2.1 Å. Earlier low-energy electron diffraction (LEED) measurements found a Ni-graphene bond distance of 2.1 Å. We note that both of these results are in line with the LDA calculations. On the other hand LDA is not expected to work well for highly inhomogeneous systems such as the interface structures investigated here. Similar experimental conclusions are found for the Co/graphene interface, using scanning tunneling microscopy (STMS) techniques. These results might indicate a difficulty for the present $vdW$-DF in describing systems with mixed bonding character, in line with the conclusions of Ref. 22. Moreover, results involving the application of the $vdW$-DF functional to metallic systems should be taken with care due to the choice of the response function employed in the construction of the $vdW$-DF. It should also be noted that the present calculations are restricted to two specific interface configurations and hence do not take into account the variety of Moiré superstructures observed in experiments. Recent ARPES and LEED data is also available for the Pt/graphene interface which provides clear evidence of weak interaction between graphene and the substrate, with an estimated separation of 3.3 Å, in fair agreement with both LDA and our $vdW$-DF results. STS measurements for graphene on Pd (Ref. 32) show a band-gap opening of ~0.3 eV, in contrast with both LDA and $vdW$-DF predictions. STS experiments on the Au/graphene interface, particularly relevant since most electronic contacts employ gold, demonstrate a weak interaction between Au and graphene, and a p-type doping in good agreement with both LDA and our $vdW$-DF results. We have summarized the available recent experimental data in the last two rows of Table I.

Figure 3 shows the total (full lines) and the exchange-only (dashed lines) binding energy curves for revPBE, PBE, and LDA in the case of graphene on Cu(111) (left panel) and on Ni(111) (right panel). The exchange-only energies are calculated without including the correlation energy term in the exchange-correlation functional and have been evaluated non-self-consistently. Clearly, the bonding for the physisorbed graphene on Ag, Au, Cu, Pt, and Al originates partially from the exchange term in the LDA xc-functional, as

![Diagram](https://example.com/diagram1.png)

FIG. 2. LDA (top) and $vdW$-DF (bottom) band structures for graphene on Ni(111) in the top-fcc configuration. Larger dots represent larger weight of the carbon $p_z$ orbitals. Only one spin channel is shown, the other being almost identical.

![Diagram](https://example.com/diagram2.png)

FIG. 3. (Color online) Decomposition of the binding energy $E_b$ into exchange-only contributions (dashed lines—only the correlation term is removed) and total binding energy (full lines) for different functionals.
shown for Cu as an example in the left panel of Fig. 3. This is in principle incorrect since the van der Waals interaction is a purely nonlocal correlation effect. The weak bonding predicted by the vdW-DF functional, similar in magnitude to the LDA results, is produced by the correlation term instead, which is physically correct. Interestingly, this applies to the Ni/graphene system as well, as shown in the right panel of Fig. 3. The LDA exchange-only curve shows a broad and weak attractive contribution between 2 and 5 Å with two local minima. We note that in a genuine covalent bond the exchange contribution to the binding energy is generally significantly larger than in this case. The revPBE and PBE exchange-only curves are repulsive at all separations for both systems. This is the typical behavior which is observed in van der Waals bonded dimers or organic molecules on surfaces.13,21

In conclusion we have performed DFT calculations of graphene adsorbed on different metal surfaces using the recently developed vdW-DF functional which explicitly includes nonlocal correlations. For Ag, Au, Cu, Pt, and Al both LDA and vdW-DF consistently predicts a weak binding. Similar weak binding is found for Ni, Co and Pd with the vdW-DF where LDA on the other hand predicts stronger binding and significant hybridization between graphene and metal d states. At the vdW-DF binding distances graphene’s band structure was shown to be essentially unaffected by the substrate. This appears to be in conflict with LEED and ARPES measurements for graphene on Ni, Co, and Pd indicating that more work is needed in order to reconcile experiments and theory for the graphene-metal interface.

We thank Jens Nørskov and Bengt Lundqvist for useful discussions. The authors acknowledge support from the Danish Center for Scientific Computing through Grant No. HDW-1103-06. The Center for Atomic-scale Materials Design is sponsored by the Lundbeck Foundation.

34 The G0W0 calculations were performed with the "yambo" code.37 We included 100 empty bands (corresponding to 40 eV above the Fermi level), a 12 × 12 k point for the simple rhombohedral unit cell, and a plasmon frequency of 1 Hartree.
Paper III

First-principles calculations of graphene nanoribbons in gaseous environments: Structural and electronic properties
M. Vanin, J. Gath, K. S. Thygesen, and K. W. Jacobsen
First-principles calculations of graphene nanoribbons in gaseous environments: Structural and electronic properties

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(Received 27 August 2010; published 5 November 2010)

The stability of graphene nanoribbons in the presence of typical atmospheric molecules is systematically investigated by means of density-functional theory. We calculate the edge formation free energy of five different edge configurations passivated by H, H₂, O, O₂, N₂, CO, CO₂, and H₂O, respectively. In addition to the well known hydrogen passivated armchair and zigzag edges, we find the edges saturated by oxygen atoms to be particularly stable under atmospheric conditions. Saturation of the zigzag edge by oxygen leads to the formation of metallic states strictly localized on the oxygen atoms. Finally, the vibrational spectrum of the hydrogen- and oxygen-passivated ribbons are calculated and compared.

DOI: 10.1103/PhysRevB.82.195411
PACS number(s): 73.20.At, 73.22.Pr, 71.15.Mb

I. INTRODUCTION

Graphene, a single atomic carbon layer, has attracted extensive research interests in the last few years. Recent advances in experimental techniques have lead to the fabrication of several graphene-based structures for both fundamental physics investigations and promising applications. Graphene nanoribbons (GNRs), in particular, have received considerable attention due to their possible role in future carbon-based nanoelectronics. GNRs are graphene strips of finite width, in which lateral confinement opens an electronic gap as opposed to the vanishing gap in infinite graphene sheets.

Theoretical calculations and experiments have shown that the electronic and transport properties of GNRs are strongly influenced by the actual atomic configuration of the edges, which, contrary to bulk graphene, are very reactive. A detailed knowledge of the stability and electronic properties of the different types of edges is therefore required in order to understand and ultimately design GNRs with specific properties.

Most theoretical calculations on GNRs have considered the armchair and zigzag edges with or without hydrogen passivation. However, recent calculations have shown that other edge configurations can also show high stability. Since molecular hydrogen is one of the most common contaminants even in ultrahigh vacuum experiments, it is certainly relevant to consider its influence at the edges. On the other hand, especially at room temperature and under ambient conditions, the effect of other gas molecules on the edge stability should also be considered. This is also relevant from the perspective of chemical functionalization.

In this paper, we study the stability of five different edge geometries in the presence of H₂, O₂, N₂, CO, CO₂, and H₂O using first-principles calculations. The different edge geometries for the pristine ribbons with the corresponding abbreviations are shown in Fig. 1. We find that the edges passivated by atomic oxygen are the most stable under atmospheric conditions closely followed by the zigzag and armchair edges with hydrogen adsorbed. The oxygen passivated zigzag GNR is found to be metallic with the states at the Fermi level strictly localized on the oxygen $p$ orbitals. The vibrational spectrum of the hydrogen- and oxygen-passivated GNRs are calculated and discussed. Throughout the paper we focus on free-standing graphene and thus neglect any effect related to the substrate. Whether this is a reasonable assumption clearly depends on the strength of the substrate-graphene interaction. This is likely to make the edges less reactive toward gas species since the edges would be already stabilized by the chemical bond to the substrate. For metallic substrates the nature of the substrate-graphene interaction is still unclear but DFT calculations indicate that it can vary considerably depending on the metal.

II. COMPUTATIONAL DETAILS

Density-functional-theory (DFT) calculations are performed with the GPAW code, which is a real-space implementation of the projector augmented wave method. The widths of the nanoribbons are in the range 20 – 23 Å, corresponding to 10 – 12 carbon dimers, which is needed in order to get fully converged results with respect to the width. Note that this size is also relevant to modern experiments, where sub-10-nm-wide GNRs are now achieved. The GNRs are separated by 10 Å in all directions. All calculations are spin polarized and use the revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional. A grid spacing of 0.18 Å is used, and a $(1 \times 1 \times 10)$ Monkhorst-Pack $k$-point grid is employed to sample the Brillouin zone along the periodic direction of the nanoribbons. We relax all the structures until the maximum force is lower than 0.05 eV/Å.

III. STABILITY

A. Adsorption energies

For each of the five edge configurations we calculate the adsorption energy of the different molecules according to

$$E_{\text{ads}} = E^{\text{rib+mol}} - N_{\text{mol}}E^{\text{mol}} - E^{\text{rib}},$$

where $E^{\text{rib+mol}}$ is the total energy of the ribbon with the adsorbed gas molecule, $N_{\text{mol}}$ is the number of adsorbed mol-
ecules, $E^{\text{mol}}$ is the total energy of the molecule in the gas phase, and $E^{\text{ribb}}$ is the total energy of the pristine ribbon. In order to avoid the erroneous DFT description of the O$_2$ gas-phase triplet ground state, we use H$_2$O and H$_2$ as suggested in Ref. 18. The adsorption energies are summarized in Fig. 2 and shown in Table I.

It can be seen that saturation by oxygen is the most favorable for all edge configurations. We note that this is in agreement to Ref. 19 in which the authors conclude that zigzag nanoribbons are more likely to be oxidized than hydrogenated.

While the high reactivity of the zigzag edge is well established,20 we also find the ac(56) to be very reactive; in fact for several species this is the most reactive edge configuration. As for the zigzag edge, the origin of the high reactivity of the ac(56) edge is a (spin-polarized) peak in the density of states close to the Fermi energy. Consistent with their high reactivities, the pristine zz and ac(56) edges also have the highest edge formation energies (see Table II), i.e., they are the least stable edges in the absence of molecular gas species.

Finally, we note that all the reported results are for adsorption at the edge carbon atoms since these are by far the most reactive sites. For example, we find that H adsorption on a carbon atom located next to the edge is already unfavorable compared to H$_2$ in the gas phase.

**TABLE I.** Numerical values of the adsorption energies, $E_{\text{ads}}$, corresponding to Fig. 2. All values are in eV.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>O$_2^{\text{ads}}$</th>
<th>O$_2$</th>
<th>N$_2^{\text{ads}}$</th>
<th>N$_2$</th>
<th>CO</th>
<th>H$_2$O</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ac(677)</td>
<td>−2.59</td>
<td>−4.33</td>
<td>−0.45</td>
<td>0.86</td>
<td>−0.22</td>
<td>−0.97</td>
<td>−1.46</td>
<td>0.66</td>
</tr>
<tr>
<td>ac(56)</td>
<td>−5.36</td>
<td>−9.88</td>
<td>−3.22</td>
<td>−1.95</td>
<td>−1.25</td>
<td>−3.03</td>
<td>−2.49</td>
<td>−0.20</td>
</tr>
<tr>
<td>zz(57)</td>
<td>−2.99</td>
<td>−5.13</td>
<td>−3.09</td>
<td>0.14</td>
<td>0.96</td>
<td>−1.05</td>
<td>−2.24</td>
<td>−0.82</td>
</tr>
<tr>
<td>ac</td>
<td>−3.99</td>
<td>−4.90</td>
<td>−1.29</td>
<td>1.73</td>
<td>0.44</td>
<td>−2.31</td>
<td>−2.56</td>
<td>−0.86</td>
</tr>
<tr>
<td>zz</td>
<td>−5.19</td>
<td>−7.44</td>
<td>−0.96</td>
<td>0.05</td>
<td>0.20</td>
<td>−1.42</td>
<td>−0.85</td>
<td>0.65</td>
</tr>
</tbody>
</table>

**B. Edge-formation energies**

The adsorption energies discussed in the previous section are relevant once a given edge configuration has been formed. More generally, to thermodynamic stability of an edge in the presence of gas molecules should also take the energetic cost of forming the edge into account. To calculate the edge-formation free energy we first calculate the formation energy of the pristine edges

$$E_f = \frac{1}{2L} (E^{\text{ribb}} - N_c E^{\text{bulk}}),$$

where $E^{\text{ribb}}$ is the total energy of a ribbon with $N_c$ carbon atoms in the supercell and $E^{\text{bulk}}$ is the total energy per atom in bulk graphene. Our calculated energies shown in Table II are in very good agreement with Ref. 8. We remark, that for pristine GNRs the zz(57) reconstruction has the lowest edge energy.

The adsorption energy $E_{\text{ads}}$ is used to obtain a free energy by taking into account the chemical potential, $\mu_{\text{gas}}$, of the gas at a given temperature and pressure

$$G_{\text{ads}} = \frac{1}{L} E_{\text{ads}} - \rho_{\text{gas}} \mu_{\text{gas}},$$

where $\rho_{\text{gas}} = N_{\text{mol}}/L$ is the density of adsorbed species. The chemical potential at temperature $T$ and partial pressure $P$ is given by

$$\mu = H^0(T) - H^0(0) - TS^0(T) + k_B T \ln \left( \frac{P}{P^0} \right),$$

where $H^0$ and $S^0$ are enthalpies and entropies of the gas phase molecules at $P^0 = 1$ bar.

Finally, the edge formation free energy in the presence of adsorbates is obtained as

$$G_{f,\text{ads}} = E_f + G_{\text{ads}}.$$
The most stable configurations are the standard zigzag and armchair, followed by the reconstructed zz. The reconstructed edges are generally less stable. This agrees with Ref. 9 where hydrogen passivation was considered. The armchair and zigzag edges saturated by hydrogen are also quite stable. In the hydrogen-passivated case, the zigzag GNR is the most stable one, in the rest of the paper. Note that the negative formation free energies for some of the oxygen saturated edges mean that a graphene sheet will spontaneously break in order to generate edges and lower its energy. However, one needs to be careful in analyzing these results since significant energy barriers may be involved in the process and they are not included in our study. Furthermore, once the oxygen molecule has dissociated, atomic oxygen potentially very complicated.

In addition to H and O, the adsorption of H2O and CO is favored compared to the molecular adsorption. In particular, CO2 bind rather weakly or not at all on all edge configurations. These calculated data can furthermore be used in order to construct phase diagrams as a function of the chemical potential of a given gas species. This might be relevant for guiding experimental investigations in which GNRs are studied in the presence of a given gas species. An example is shown in Fig. 4 for the case of dissociated oxygen at the edges. This shows that for any experimentally accessible pressure of O2, the most stable dissociated oxygen at the edges. This shows that for any experimentally accessible pressure of O2, the most stable dissociated oxygen is the standard zigzag, saturated by oxygen.

IV. OXYGEN-SATURATED ZIGZAG EDGE

In the previous section we found that the zigzag GNR saturated by atomic oxygen is the most stable thermodynamically. For this reason, we investigate in this section the ground state and vibrational properties of the oxygen-passivated zigzag GNR and compare it to the well studied hydrogen-passivated case.

A. Band structure

Figure 5 shows the Kohn-Sham band structure for the oxygen-passivated GNR calculated with the RPBE functional. Contrary to the hydrogen-passivated case, its ground state is spin paired and metallic. The states at the Fermi level are localized at the edges and they have weight on the p orbitals of the oxygen atom. One state has p_z symmetry and it decays into the GNR away from the edge with weight on only one carbon sublattice (left inset of Fig. 5). The other state is almost completely localized on the out of plane p oxygen orbital (right inset of Fig. 5). This is also in contrast to the hydrogen saturated case, where the edge states are entirely localized on the edge carbon atoms.

<table>
<thead>
<tr>
<th>TABLE II. Edge formation free energy at 0 and 300 K for the different nanoribbons and adsorbed species. All energies are in eV/Å.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZZ(57)</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>N2</td>
</tr>
<tr>
<td>O2</td>
</tr>
<tr>
<td>H2O</td>
</tr>
<tr>
<td>CO2</td>
</tr>
</tbody>
</table>

195411-3
B. Vibrational properties

Low-energy spectroscopies probing the vibrational excitations have traditionally been a powerful tool for structure determination in molecules. It has recently become possible to study differences in the vibrational spectrum of GNRs using Raman spectroscopy. In view of this, we have calculated the vibrational spectrum of the zigzag GNRs passivated by hydrogen and oxygen in order to identify features specific to these types of edges.

1. Computational details

To obtain the phonon frequencies we first compute the dynamical matrix in real space. The latter is obtained by numerical differentiation of the forces. A careful procedure to obtain the equilibrium configuration is found essential in order to obtain an accurate description of the phonon frequencies. Thus, for a single unit of the zzGNR, we used a grid spacing of 0.1 Å and a k-point sampling of (1×1×10). The relaxation of the equilibrium structure is continued until the maximal residual forces are less than 0.02 eV/Å.

The dynamical matrix is evaluated in a supercell containing seven primitive cells of the GNR. All atoms in one of the primitive cells are displaced by ±0.02 Å in the x, y, and z directions (a total of 6×N calculations) and the forces on all remaining atoms within a truncation radius of 7 Å of the displaced atom are stored. This requires a total of 6×N calculations, where N is the number of atoms in a primitive cell. For these calculations we use a grid spacing of 0.18 Å and a 1×1×3 k-point sampling. We have verified that our results have converged with respect to these parameters and the truncation radius. The real-space dynamical matrix is obtained from a finite difference of the forces, and the eigenvectors and frequencies are obtained after Fourier transformation.

2. Results

The GNRs are finite in their width direction and thus they are subject to boundary conditions similar to that of a string with free ends. The edges therefore only allow standing waves perpendicular to the ribbon axis and the phonon wave vector for a GNR consisting of N carbon dimers will be quantized as $q_{L,N} = \frac{n\pi}{w}$, where $w$ is the width of the dimers and $n=0,\ldots,N-1$ each corresponding to a normal mode. The dispersion relations therefore consist of six fundamental modes each with $(N-1)$ overtones. A study of the Γ-point spectrum according to this classification has been done in a previous study for hydrogen-saturated nanoribbons with purely zigzag and armchair edges. The modes can be separated into the three categories according to their longitudinal, transverse, and mixed character.

![Figure 3](image-url) FIG. 3. (Color online) Edge-formation free energy of graphene nanoribbons with different edge structures (different symbols) and different adsorbed molecules at the edge. The free energy is evaluated at 300 K. The pressure for each structure with a given adsorbate is taken to be the partial pressure of the gas-phase adsorbate at atmospheric conditions.

![Figure 4](image-url) FIG. 4. (Color online) Edge-formation free-energy for the different edge configurations of a graphene nanoribbon in a background of O2 gas.

![Figure 5](image-url) FIG. 5. (Color online) Band structure of a 22 Å wide zigzag GNR saturated with O. The two insets show the states corresponding to the bands crossing the Fermi level, marked with black circles.
transverse, and out-of-plane nature. It is straightforward to identify which category a particular mode belongs to by weighting each of the three different spatial entries in the polarization vector relative to its total norm. Each of the spatial categories can be separated into acoustical and optical parts giving rise to six series. The Γ-point spectrum is found to be similar to hydrogen-saturated ribbons where a splitting into optical (160–200) meV and acoustical modes (0–160) meV is observed, as shown in Fig. 6. The transverse acoustical modes are seen to follow a near perfect 1/√ω behavior which is understood in terms of the ribbon acting as a spring perpendicular to its axis with fixed spring constant.

A separation of modes associated with the saturation atoms is not as simple in the case of oxygen as it is for hydrogen. Contrary to the hydrogen passivated ribbons where three degenerate pairs of edge localized modes are found at 380, 150, and 125 meV, only one localized degenerate pair of carbon-oxygen modes shows up, namely, the degenerated stretching modes (transverse direction). Similarly to the hydrogen-passivated case, this pair is found to be independent of the ribbon width and is located around 182 meV, except for the very narrow ribbons (N < 4) where it is slightly higher. The last four modes are not separated from the remaining modes as for the case of hydrogen. In fact, the oxygen atoms participate as a continuation of the carbon system and enter in the bulk vibrational modes giving rise to two additional acoustical modes in the longitudinal series and the out-of-plane series. This coupling to the acoustical modes is understood in terms of the comparable masses of the two species. Also, for the transverse series one finds that an optical mode has been converted into an additional acoustical one. The optical modes of the longitudinal and out-of-plane series on the contrary remains similar to what is found for the hydrogen-saturated ribbons, that is, the series are constituted of normal modes only coming from the carbon atoms.

The total vibrational density of states of the 16 dimer wide zigzag ribbon is obtained by integration in the ΓKM direction and is shown in Fig. 7. Note that it represents the whole spectrum of states and not just the Γ points. Except for some distinct peaks the total density of states for the hydrogen- and oxygen-saturated ribbons represents that of graphene fairly well. In order to compare the deviations in the density of states associated with the edge, the states localized on the edges have been separated out for each of the saturating species. The peaks present in the edge contribution are to a large degree recognizable in the corresponding total density of states spectrum. For the hydrogen-saturated ribbon, the two peaks observed are the vibrational mode perpendicular to the carbon-hydrogen bond and out-of-plane mode. For the oxygen-saturated ribbon only the transverse carbon-oxygen has a truly edge-localized vibrational pattern while the peaks observed in the acoustical part of the spectrum originates from individual normal modes in the longitudinal and out-of-plane series.

V. CONCLUSION

As a general reminder, it should be noted that the results in this study do not consider the effects of the substrates. In most experiments, GNRs are grown or deposited on a substrate, which might affect the energetics at the edges. The interaction of the substrate with graphene edges is likely to be much stronger than the interaction with the bulk graphene.12,13

In conclusion we have studied the adsorption of common gas molecules at the edge of several types of GNRs using density-functional theory. We have calculated the edge-
formation free energy in the presence of the adsorbates at the different edges and shown that passivation by atomic oxygen is the most stable closely followed by the hydrogen-passivated GNRs. In contrast to the hydrogen-saturated zigzag edge, passivation by oxygen leads to a nonmagnetic and metallic ground state.

For the vibrational properties, the comparable masses of oxygen and carbon lead to a larger degree of mixing between localized edge and bulk modes. In particular, it is found that the oxygen atoms act as a continuation of the carbon system and participates actively in the longitudinal and out-of-plane series. Only the stretching (transverse) mode of the carbon-oxygen bond is found to be completely localized at the edge and separated from the normal-mode series.

Since O\textsubscript{2} and H\textsubscript{2} are almost always present under realistic conditions, our results suggest that it might be very difficult to functionalize the edge atoms with different species. We suggest that the substitutional route, for example, via electrothermal reactions as demonstrated in (Ref. 27), might turn out to be an easier approach for doping GNRs.

ACKNOWLEDGMENTS

The authors acknowledge support from the Danish Center for Scientific Computing. The Center for Atomic-scale Materials Design is sponsored by the Lundbeck Foundation.

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Paper IV

Mechanism of channelling behaviour of silver nanoparticles on suspended graphene

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Submitted to Nano Letters
Mechanism of channelling behaviour of silver nanoparticles on suspended graphene

Filippo Pizzocchero, Marco Vanin, Tim Booth, Karsten W. Jacobsen, Peter Bøggild

The increasing availability of wafer-scale quantities of high quality graphene layers has highlighted a pressing need for a patterning technique which preserves the crystal quality and orientation of the edges of graphene. The structure and smoothness of the edges are determinant factors for the device behaviour and performance of a wide range of devices [1], along with substrate-induced effects and surface contaminants [2]. Catalytic oxidation or reduction is currently the only technique which produces crystallographically-oriented graphene edges with roughness of less than 1 nm on a large scale, but for control of the phenomenon it is critical that the atomistic processes are better understood. In this work, we compare density functional theory calculations to in-situ transmission electron microscopy experiments of silver nanoparticles channelling on single and bilayer graphene; successfully obtaining a model for the mechanism of zigzag edge formation, an explanation of the rate-limiting step and excellent agreement between the DFT-predicted and experimentally obtained activation energies.

The current toolbox for graphene patterning is in large part adapted from silicon microfabrication, typically involving the use of optical and electron beam lithographies, in combination with physical/chemical etching to define device geometry [3]. While these processes are versatile and based on mature technology, issues arise with (1) precise orientation of lithography with graphene symmetry directions, (2) imperfect edges from mask-based physical/chemical etching, (3) fundamental limits on the resolution achievable with lithographic techniques, and (4) impurities introduced by resist spinning, development, stripping and so on, which can have a serious effect on a system where every atom is directly exposed to the environment.

A possible solution is presented by the catalytic hydrogenation or oxidation of graphene via metal nanoparticles at elevated temperature [4-11]. This process has been studied in graphite for over 60 years [12-21]. When applied to graphene the hydrogenation or oxidation results in channels of microscale length in the topmost graphene layers. These channels present two unique features: a strong tendency to follow the crystal orientations of graphene and a width determined by the
diameter of the nanoparticle [11], which has been demonstrated from the nanometer to the submicrometer scale.

Here we combine in-situ observation of the channelling behaviour of silver nanoparticles on suspended mono- to few layer graphene (Figure 1) in the controlled atmosphere inside an environmental transmission electron microscope (ETEM) with density functional theory (DFT) simulations with the ultimate aim to understand and gain a degree of control over the channeling process. We are able to explain the alignment of the channels and our work supports the hypothesis that the reaction occurs at the interface of the graphene/silver as opposed to carbon atoms from the graphene edge being first dissolved in the silver and later removed from the surface of the silver particle, as has been proposed in literature [17].

A previous report [11] describes the catalytic oxidation of graphene by silver nanoparticles over the temperature range of 600-850 K and with oxygen pressures up to 13 Pa, with all channels aligned parallel to the <100> (zigzag) direction in graphene. The reaction proceeds as:

\[ \alpha C_{graphene} + \beta O_2 \rightarrow \gamma CO + \delta CO_2 \]

where the production of CO is favoured over CO\(_2\) (γ≈δ) [22-24].

In addition to the discrete dynamics of the particles and the calculation of the activation energy reported previously, we show here a number of other observations and calculations which elucidate the atomistic processes involved. In a small number of cases (< 5%) we are able to observe the structure of the graphene interface when nanoparticles channelling in bilayer graphene change from simultaneously removing two layers to just a single layer (Figure 2), or vice versa. We find that the leading edge of a particle which is channelling always presents two 120°-separated facets to the graphene, leaving graphene edges consisting of <100> edges except for rounding at corners (Figure 2).

Moreover, we observe Bragg reflections from channelling particles (Figure 1), which shows that the particles maintain their crystallinity whilst channeling at temperatures exceeding 850 K. This is
expected from the liquid drop model for the thermodynamic behaviour of silver nanoparticles \[25\],
which predicts a maximum suppression of the bulk melting point from 1234 K to 1000 K for spherical
5 nm nanoparticles, the degree of suppression decreasing with increasing particle diameter. We
observe that particles which are stationary at these temperatures have a markedly more spherical
shape. This suggests that the edge of the graphene lattice has a strong influence on the morphology
of the particles which are channelling, since comparably sized and situated particles on the surface
lack facets and Bragg reflections.

We model the graphene/silver interface via Density Functional Theory simulation based on GPAW
\[26\] as a graphene nanoribbon of width equal to 19.8 Å with periodic boundary conditions along its
length, placed edge-on to a step in the (211) surface of silver with the graphene interacting with the
bottom of the step, as shown in Figure 3. Full details on the calculations can be found in the
Supporting Information. We find a DFT-calculated carbon/silver equilibrium distance of 2.3 Å and
2.25 Å respectively for the armchair and zigzag edge. In order to maintain periodic boundary
conditions we vary the lattice parameter of the graphene or the silver so as to have an integer
number of both lattice unit cells in our simulation unit cell. For both zigzag and armchair
nanoribbons the lowest energy interface occurs when the graphene lattice has negligible stress or
strain (Supporting Information). We see this as evidence that the strong C-C bond is likely to alter
the lattice parameter of the first few layers of atoms in the silver particle closest to the graphene
edge.

In our simulations we consider the complete cyclic oxidation of rows of interface atoms for both
zigzag and armchair edges, returning to an equivalent situation except for the gasified carbon atoms
(Figure 4). The zigzag and armchair interfaces differ fundamentally in this respect, since the removal
of a row of interface atoms in an armchair ribbon immediately results in another exposed row of
armchair-like atoms, but the removal of a row of zigzag interface atoms exposes a row of doubly
under-coordinated carbon atoms which must also be removed for the initial zigzag graphene/silver interface to be recovered (Figure 4). At each stage we allow the structure to fully relax.

Plotting the energy change per carbon monoxide molecule produced at the interface for each cycle we note that the removal of zigzag atoms presents an energy barrier of 0.34 eV for the first two steps of the reaction, whereas the removal of armchair interface atoms is downhill in energy (Figure 4). The same $\Delta E_{\text{tot}}$ between initial and final states is found irrespective of whether the edge is zigzag or armchair. It corresponds to the energy balance of the reaction

$$C_{\text{graphene}} + \frac{1}{2}O_2 \rightarrow Ag \rightarrow CO$$

and energetically [27]

$$\Delta E_{\text{tot}} \equiv \Delta G_{CO} - \Delta G_{\text{graphene}} - \frac{1}{2}\Delta G_{O_2} = 1.1 \text{ eV}$$

The removal of atoms along the armchair edge is therefore more favourable with respect to the zigzag edge. In this picture, the channelling proceeds by removing armchair-like edge atoms more readily than zigzag edge atoms. The removal of zigzag atoms is then the limiting step for the reaction and results in purely zigzag edged channels, which is in agreement with our experimental findings.

We note that the calculated barrier for the removal of zigzag atoms, 0.34 eV, compares favourably with the experimentally obtained activation energy of 0.557 eV in literature [11], despite the fact that transition-state barriers between metastable intermediates are not considered in our calculations.

Two incompatible theories suggested in literature describe the mechanism of carbon removal by catalytic oxidation and hydrogenation of graphite. Goethel et al. [17] propose that the carbon atoms at the graphene/catalyst interface diffuse into the nanoparticle, and combine with oxygen on the surface, desorbing as molecular CO. This we will refer to as the surface model. The second theory, first introduced by McKee [13], proposes that oxygen is adsorbed onto the catalyst surface and
diffuses to the interface, here combining with carbon before desorption, which we term the 
interface model.

Strong evidence for the interface model and a lack of adsorbed carbon is provided by the DFT 
calculated binding energies of 7.7 eV and 5.9 eV for carbon atoms on the zigzag and armchair edges 
respectively. These values are much higher than both $k_B T$ and the binding energy of a carbon atom 
on the Ag (111) surface, which is 3.3 eV. This makes the presence of carbon adatoms on the catalyst 
surface unlikely. Additionally, the surface model would result in a correlation between the particle 
surface area and channelling velocity [17]; an effect we are unable to detect in our measurements 
over a range of temperatures and pressures [11].

Particles which move from the graphene surface to the amorphous carbon support film show a 
marked change in morphology and behaviour (Figure 5). While in contact with graphene, the 
particle shows Bragg reflections and a consistent morphology, but when the amorphous carbon is 
reached the particle rapidly melts and flows over the surface in a quasi-liquid state. Our 
interpretation is that the weaker and disorganised bonding in the amorphous carbon leads to a 
much faster dissociation of carbon atoms and a lack of imposed structure. The solubility of graphitic 
carbon in silver is known to be less than $10^{-7}$ at. % at these temperatures [28], so the formation of 
some kind of eutectic or carbide is most likely excluded. Recent observations of cobalt nanoparticles 
on amorphous carbon film which catalytically produce graphene layers have shown strong evidence 
of crystallinity despite an apparently fluid leading edge [29-30]. Our interpretation is that the 
substrate/nanoparticle surface interaction has a dominant role in determining the morphology and 
structure of the nanoparticle – when touching graphite or graphene the metal nanoparticles exhibit 
crystal structure, with liquid-like characteristics when in contact with amorphous carbon.

In this work, silver was deposited on the graphene flake by sputtering, which is well known to induce 
defects [31] which are highly likely to affect the dynamics of the channeling. There are several 
gentler ways of depositing particles that do not lead to damage of the $sp^2$ carbon bonds, such as
metal solution evaporation or size selected deposition [32], as well as methods to deposit the particles in selected areas, for instance through nanostencil lithography [33], which would limit both the particle and defect initiation site to a small and well defined area. As microcleaved graphene and more recently CVD graphene can have a very low defect level [34], the possibility of making well localised, crystallographically oriented and long nanochannels seems realistic.

In summary, we have combined DFT and experimental observations to explain the orientation of the channels in suspended graphene made by catalytic silver nanoparticles. DFT calculations reproduce the experimentally obtained activation energy for the rate limiting step, which is the removal of zigzag edge atoms. The silver-oxygen system is working at a relatively low temperature, several hundred of degrees lower than other investigated systems [4-5,7-10], which may simplify both characterization and development of such novel lithographic techniques. We believe that investigations of the energetics of the system are crucial for any future attempt of achieving low- or zero-disorder edges, of gaining full control of the particle motion including suppression of unwanted changes in particle velocity. Our simulations and observed lack of particle size dependence on channeling rate support the interface model for the removal of carbon atoms from graphene.
References:


Fig. 1  a) Optical image of the holey carbon film of the TEM grid. Scale bar 3 μm. (will be changed) b) TEM image of a suspended bi-layer graphene with silver nanoparticles (black spots) that are etching channels. Scale bar 300 nm. c) TEM image of a single particle from (b). The particle is etching one of the two layers of the suspended bilayer graphene flake. Scale bar 20 nm. d) TEM image of several silver particles etching a multi-layer graphene flake. Bragg reflections are indicated by arrows. Scale bar 35 nm. e) TEM image of silver particles etching various numbers of layers of a few-layer graphene flake. Channelling particles are indicated by arrows, and display a more elliptical cross-section than the static particles. Scale bar 50 nm.
Fig. 2 a-b) TEM images of the transition between monolayer and bilayer etching (and vice versa) within a single channel. These footprints of the interface of the silver particles in the graphene are triangular in shape with $<100>$ orientated edges, parallel to the zigzag direction of the graphene lattice. Scale bars 5nm. c) A schematic representation of the catalytic etching process. (i) The oxygen molecules interact with the silver nanoparticles. (ii) After being adsorbed, the oxygen may dissociate. The atomic oxygen formed diffuses on the surface of the particle, possibly reaching the silver-graphene interface where it interacts with the carbon edge atoms. (iii) Carbon at the edge reacts with the oxygen at the interface and is gasified in the molecular form CO, leaving a void which the catalyst particle moves to fill. d-e) The triangular front of etching particles is clearly visible in these images. Scale bars 25 nm and 20 nm respectively.
Fig. 3 – a) A three dimensional representation of the structure used in the DFT calculation. b-c) Schematic 2D projections of the structure shown in (a). In particular, in (b) the shape of the step is clear, while in (c) the position of the graphene flake with respect to the silver edge is exemplified. d-e) Scale representations in the ZY plane of the actual DFT relaxed graphene-silver interfaces for the armchair and zigzag edges respectively. In (d) two unit cells are shown, with one in (e).
Fig. 4. Energetic path for the modelled etching process for both armchair and zigzag edge. 

(a) In case of the zigzag edge the carbon atoms at the interface are fully oxidized by (b) adding one oxygen atom per undercoordinated carbon atom. (c) The newly formed C-O couples are then removed. To obtain the initial situation another line of carbon atoms has to be removed. (d) Once these doubly under-coordinated atoms are fully oxidized in a similar manner to (b) and removed (e), the initial state (a) has been recovered except for the gasification of two rows of atoms in graphene. (g) For the armchair edge, only one oxidation step is necessary to obtain a complete cycle. (h) The interface at the equilibrium is oxidized and then the C-O species are removed. (i). In our calculations the structure is allowed to fully relax at each step, and the total energy is evaluated. (f) A plot of the energy of each of the states (a-e) and (g-i) per CO molecule gasified, i.e. per carbon atom removed at the interface. The reaction in the zigzag case goes uphill with a calculated energy barrier of 0.34 eV, while it goes downhill in the armchair case. Both paths end up at the same energy level, which corresponds to the gasification of a “bulk” carbon atom, independent of that atoms position in the lattice.
Fig. 5  a-f) Sequential TEM images of a particle that changes from channelling graphene to the amorphous carbon of the grid, taken at elevated temperature in oxygen atmosphere (600-800 K, 4-13 Pa). When the particle is etching graphene a Bragg reflection spot is distinguishable (black arrow). Scale bar 25nm. b) As soon as the particle lands in the amorphous carbon layer, the spot is not visible anymore. At this point the shape of the particle becomes increasingly irregular. g-h) Two further examples of deformed particles etching in the amorphous carbon layer. The yellow lines are a guide for the eye to help distinguish the border of the particles. Scale bars 25 nm and 50 nm respectively.
Paper V

Functionalized graphene as catalyst for CO2 electrochemical reduction
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In preparation
I. INTRODUCTION

The electrochemical reduction of CO$_2$ to chemical fuels has re-gained huge interest in recent years in connection with renewable energy$^{1,2}$. The intermittency of renewable energy sources calls for an efficient energy storage solution$^3$. The iiistorage of energy in the form of chemical bonds represents an attractive approach, in particular if combined with CO$_2$ capture. This makes the electrochemical reduction of CO$_2$ a very attractive candidate for the production of chemical fuels.

However, in order to have any major impact the process must be cost-efficient and a key step in realizing that is finding efficient catalysts. Unfortunately, so far no material is known to catalyze this reaction efficiently and with high selectivity. Copper is the only metal that has been experimentally shown to produce significant quantities of hydrocarbons (CH$_4$ and C$_2$H$_4$) from CO$_2$, albeit at a huge voltage cost$^3$. The origin of the overpotential has remained elusive until recently, when a complete reaction mechanism was elucidated by employing DFT calculations in conjunction with the computational hydrogen electrode (CHE) method$^4$. This ambitious endeavour made it possible, for the first time, to construct a free energy diagram for the entire reaction, including potential side reactions, and identify the potential limiting step. Importantly, the obtained results were in qualitative agreement with experimental data reported by Hori et al.$^5$, and furthermore they explained why hydrocarbons and not methanol, which is commonly produced on copper in gas phase catalysis, are dominant products.

The lack of efficient metallic catalysts for the electrochemical reduction of CO$_2$ to chemical fuels calls for the investigation of other types of materials. Some molecular catalyst, in particular porphyrin-based catalysts, are known to be active for the electoreduction of CO$_2$$^7$-9. This fact, combined with the versatility of graphene-based systems, has prompted us to investigate metal-porphyrine-like functionalized graphene (a schematic picture of its structure is shown in Fig. 1) as potential catalysts for CO$_2$ reduction. With respect to CO$_2$ reduction this graphene-based material has several potential advantages over most metal catalysts. First, the nature of the active site is totally different. In our material there is only one, isolated, active site, which is in stark contrast to traditional metal-based catalysts where usually several binding sites are available for the intermediate. This feature can be seen as a bridge between a metal-based catalyst and a molecular catalyst and opens up possibilities in terms of controlling and manipulating the active site (this prospect becomes especially appealing when considering that the carbon-based chemistry is well defined compared to that of metallic surfaces). Second, a carbon-based material has significant advantages in terms of price. Third, the limitations imposed by scaling relationships$^{5,6}$ (we will return to this issue later) in transition-metal-based catalysis might be less severe in this new type of material.

In the present study, taking the same approach as in
ref. 4, we have calculated free energy levels of all possible intermediates involved in the electroreduction of CO2 over metal-porphyrine-like functionalized graphene. By analyzing the energy differences of the intermediates we have extracted the overpotentials required for either reduce CO2 partially to CO/HCOOH or completely to CH4. Additionally, the hydrogen evolution reaction (HER) has also been considered due to the fact that H* competes with *COOH for the active metal site. In that regard, special attention has been devoted to address selectivity towards the different reaction products. Finally, we have looked at scaling relations between different adsorption intermediates. This information can be used to predict the potential or fundamental limitations of porphyrine-like functionalized graphene in catalyzing various complex reactions.

II. ELECTROCHEMICAL REDUCTION OF CO2

The free energy diagrams for complete and partial CO2 reduction on Ga-porphyrin-like functionalized graphene are presented in Figure 2, along with the free energy diagram for the HER. This system has been chosen since it is the best candidate, among the systems considered, for both the partial and complete CO2 reduction. In the case of the HER, there are much better catalysts, however, we chose to show the data for the same system to stress the selectivity issue that will be addressed later on. The free energy values of each step and the reaction overpotentials for all the other systems are compiled in the supplementary information.

Commonly, whenever applying the CHE method, the free energy diagram is illustrated at U = 0 with respect to the reversible hydrogen electrode (RHE) and at the lowest potential at which all steps are downhill in free energy, i.e. at the overpotential at which all reaction steps become exergonic. Fortuitously, in the case of Ga, there are two such steps that occur at the same potential, U = -0.74 V, which, by chance, is equal to the onset potential for CH4 production on Cu(211)4. The first potential limiting step is the addition of a proton-electron pair to adsorbed CHO to form formaldehyde (H2CO), whereas the second one is protonation of OH to water in the last electrochemical step. For comparison, on Cu(211) protonation of the *CO intermediate was found to be the potential determining step.

In the case of CO evolution (cf. Fig 2 c), which is another reaction of interest, Ga-porphyrine-like graphene was also found to be the best catalyst, featuring somewhat lower overpotential, -0.68 V, than for the CO2 reduction. Note that in this case, in general one also has to take into account the thermodynamical barrier for CO desorption. There is little use of a catalyst if products cannot be removed from the surface12. To make things worse, CO desorption is a potential independent step and thus little can be done to promote it. This is not a problem for the Ga-porphyrine-like system, since the desorption from the site is energetically favorable. As far as the HER is concerned, the Ga-porphyrine-like structure is a very bad catalyst for the reaction, since almost -0.8 V voltage is needed to evolve hydrogen. The best catalyst should have H* binding energy around 0, and the Co-porphyrin-like has been found to be a very good candidate, having $\Delta H^\neq = -0.07$ eV.

Here, we will turn back to the CO2 reduction path, since we have previously omitted to address one more important issue. The lowest possible overpotential is a necessary but not a sufficient condition to have a good CO2 reduction catalyst. This class of material has just one catalytically active site per unit cell. This somewhat simplifies the situation because no coverage effects need to be taken into account. On the other hand, the competition for the active sites, i.e. selectivity, enters as a key parameter that determines the overall performance of the catalyst. In other words, if some of the intermediates that are not directly involved in the CH4 production path bind stronger to the surface, they will poison the active site and the reaction will instantly cease. From Fig. 2 it is clear that all the reaction paths considered proceed through formation of *COOH intermediate except for the HER where H* formation is the key (only) intermediate step. Consequently, the competition between H* and *COOH binding will determine the final product of the reaction. Moreover, since both H* and *COOH formation steps involve transfer of one electron and proton pair, the ratio between the two will not be affected by the change of voltage. This finding is contrary to the results obtained on metal surfaces, or more specifically on Cu(211), where the products' yield was strongly influenced by the potential. Particularly, the H2 yield changed drastically in favour of hydrocarbons as the potential was lowered, which was a clear indication of opening up of *CO formation path, the intermediate that would subsequently repel hydrogen from the surface and enable CO2 reduction. A similar behaviour would never be observed for the catalysts investigated in this work, since the site blocking by adsorbed hydrogen would never leave a space for CO formation. Hence the CO2 reduction would be essentially dead. Unfortunately, the unfavourable ratio between COOH and H is not solely restricted to Ga-porphyrine-like graphene, but as seen in Fig. 3, a rather general rule that extends to all of the systems studied herein. Seemingly, these materials are not good catalysts for CO2 reduction because regardless of the metal atom in the active site, the HER will always prevail against the carbon containing gas molecule's evolution. However, the reaction diagram in Fig. 2 suggests a way to overcome this problem. Namely, if one would reduce CO instead of CO2 then the weak *COOH binding would no longer present an obstacle for the reduction. The path for CO reduction is the same as for CO2 except for the missing first two steps. A trade-off between CO and H would thus become a selectivity criterion. The scaling between the CO and H adsorption energy is plotted in Fig. 3 (bottom). Unfortunately, Ga
which was found to be the best candidate for CO$_2$ reduction is, apart from Al, the only material that does not fulfill the selectivity criterion for CH$_4$ evolution. With the new condition, Co, Rh and Cu also become promising candidates with overpotentials around -0.8 V. Here, it is important to note, that the methane is the only hydrocarbon that can be produced. Making larger hydrocarbon chains would require a Langmuir-Hinshelwood type of reaction, in which two adsorbed carbon containing intermediates join together to form a C-C bond. Since, by design of the catalyst, there is only one active site, this type of reaction can be automatically ruled out.

## III. SCALING RELATIONS

For multi-electron-transfer reactions it is usually difficult to find a good catalyst that can perform the overall reaction at a small overpotential. One of the main reasons for this is that, at least on transition metals, the binding energies of the various reaction intermediates scale, i.e. it is virtually impossible to change the binding energy of one intermediate (without using a different catalyst) without also affecting the binding of the other intermediates in a similar, proportional, manner. Scaling relations are readily observed on transition metals and alloys for the same class of adsorbates i.e. for the adsorbates that bind to the surface through a same type of atom. The linearity in binding energies on transition metals is usually rationalized through the d-band model and the position of the d-band centre.

The structures studied in this work differ from transition metal surfaces in this respect, as the energy levels will be more of atomic character. The difference between the two cases is best seen in Fig. 4, where the densities of states have been projected onto the d orbitals of porphyrin-like graphene. The systems have more sharp peaks compared to the broad features of the d-band for metal surfaces.

The scaling relations are not only confined to metal surfaces, but as it has been recently shown also hold on porphyrine functionalized graphene. The linearity observed in Fig. 3 (top) is striking with Au being the only outlier which is explained by the fact that COOH does not bind on Au. On the other hand, there is a much larger scatter in Fig. 3 (bottom). At first glance, the scatter in the two scaling relations seems a bit peculiar. COOH and CO bind through the same atom and therefore one would expect that their scale much better than COOH and H, whereas opposite is observed. A possible explanation may be found in terms of the orbitals through which COOH, CO and H bind to the metal atom.

In Fig. 5, the HOMO and LUMO orbitals of gas-phase CO and COOH are illustrated. With respect to the vacuum level, the HOMO and LUMO eigenvalues for CO are at -9.1 eV and -2.1 eV, while the HOMO and LUMO for
COOH are at -5 eV and -1.4 eV. The Fermi level of the porphyrin-like structures ranges from -0.5 eV to -1.8 eV, depending on which active atom is considered. Being the HOMO level of COOH unpaired and closer to the Fermi level of the surface site, it may contribute more to the binding compared to the HOMO of CO which is much lower in energy. Since the HOMO orbital of COOH is of s-character locally around the carbon atom, the coupling to the active site is similar to the H case, which is of pure s-character. This is only given as a possible explanation, since a more in-depth investigation is needed for a full understanding of the scaling relations in these systems.

IV. CONCLUSIONS

In summary, we have assessed the catalytic activity of the metal functionalized porphyrine-like structures for the electrochemical reduction of CO₂. This study has been prompted by recent findings on Cu(211). We have carefully compared the results of our study to theirs, especially in terms of the differences in the active site and its significance for selectivity among reaction products. Ga functionalized porphyrine-like graphene was found to be the best candidate for CO₂ reduction, although the major obstacle was established to be hydrogen poisoning of the active site. Moreover, this turned out to be a general problem regardless of which metal comprised the active site. The only way to avoid it is to reduce CO rather than CO₂ because the first intermediate in the CO reduction path has higher binding energy than hydrogen, whereas in the case of CO₂ reduction, COOH binds ca 1 eV more weakly than hydrogen.

V. ACKNOWLEDGMENTS

CAMD is funded by the Lundbeck foundation. The Catalysis for Sustainable Energy initiative is funded by the Danish Ministry of Science, Technology and Innovation. Support from the Danish Center for Scientific Computing, the Danish Council for Technology and Innovation’s FTP program and the Strategic Electrochemistry Research Center is gratefully acknowledged.