



UNIVERSITÉ CATHOLIQUE DE LOUVAIN

Faculté des Sciences Appliquées

CERMIN

Unité PCPM

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electronic, and superconducting
properties of nanotubes and nanowires**

Dissertation présentée en vue de l'obtention du grade de
Docteur en Sciences Appliquées

par

Matthieu Verstraete

Promoteurs:

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Membres du jury:

Prof. Xavier Gonze, promoteur

Prof. Jean-Christophe Charlier, promoteur

Prof. Jean-Didier Legat, président

Prof. Jean-Paul Issi

Prof. Philippe Lambin

Prof. Angel Rubio

Prof. Gian-Marco Rignanese

Juin 2005

To whom it may concern

Acknowledgements

Countless people contribute to a PhD thesis, and mine is no exception. Mentors, friends, family, even complete strangers at conferences can set off trains of thought and spark ideas or understanding. This means I'll be forgetting someone, but with a little luck he or she will never read this introduction, so I'm safe. Now, in what order should one thank this multitude? Chronological? By order of "importance"? Here we will opt for geographical criteria: UCL, Belgium, then Europe, and the rest of the world...

En tout premier lieu, je dois profusément et chaleureusement remercier Xavier et Jean-Christophe. Ils ont formé un parfait petit couple de promoteurs, complémentaires en tout. Xavier a démontré une grande patience pédagogique. Même quand je prenais plusieurs semaines pour découvrir de mon côté que la voie qu'il me recommandait depuis le début était bien celle à suivre. Même quand il expliquait en rentrant au labo qu'il "n'est pas là". Jean-Christophe conserve intact son flair légendaire en matière scientifique, pouvant estimer à la pente, à l'exposition, et à la qualité du terroir les bons crus carbonés dans lesquels il faut investir et chercher. On a bien publié et on a bien ri. Que vouloir de plus?

Une affectueuse révérence aux paters du labo, Jean-Paul et Jean-Pierre, qui ont su avec une attention humaine et une exigence scientifique créer un biotope unique pour faire fleurir les chercheurs. Après bien des conférences et des discussions avec des amis et collègues dégoutés par leur environnement de travail, j'en suis arrivé à la conclusion qu'il n'existe pas d'autre exemplaire de laboratoire aussi diversifié et calé professionnellement, qui démontre en même temps un esprit de famille soudée et solidaire. Il reste aux descendants actuels de faire fructifier héritage, envers les intempéries financières et politiques qui menacent.

Un grand merci à Jean-Michel, Bernard, et Jean-Paul, sans qui nous n'en serions nulle part et tout le monde ne tournerait plus que des jobs sequentiels sur son propre PC. Nous sous-estimerons toujours leur travail et leur importance jusqu'au jour où (en Octobre pour moi) nous nous retrouverons sans eux, face à un daemon récalcitrant ou à un point de

montage introuvable. En vrac mentionnons Tux, Pux, Deepflow, Boop, Cox, Turing, Decci, Fock, et surtout Max, qui m'est resté bien dévoué pendant toute la fin de la thèse. Enfin je n'oublierai pas les tutoriels et les explications cabalistiques de Yann Pouillon, qui prosélytise pour Tom Lord et le bon code.

Gian Marco é sempre stato d'un grande aiuto teorico e pratico, con in piu le sue passione per la comprensione rigorosa delle equazione, e per la politica sincera. Merci à Yann Michel d'avoir partagé son intuition des méandres de la théorie many-body, et à Sylvain celles des structures électroniques et du transport. La palme des cobureauteurs revient à Cédric, hackeur devant l'éternel. Let's do the time warp again. Merci à Sébastien Michotte pour ses explications et bibliographies précieuses sur la supraconductivité nanoscopique. Hanako-sensei, tanso-kei-ni kanshite iro-iro-to giron shite kudasari, doumo arigato goza-imashita. Sorera-no giron-wo kono ronbun deha zannen nagara inn-yo dekimasendesita-ga, atsuku kansha site orimasu. Au Gang des poulettes, qui se reconnaîtront, où qu'elles soient allé picorer (picoler?). Une grande reconnaissance est due au travail de Brigitte, sans qui le labo ne tournerait pas du tout, qui brave le vrai monde de la comptabilité et de l'administration avec une constance infailible.

Un paragraphe pour Manu, qui m'a soutenu et supporté (dans tous les sens du verbe) en cette fin d'époque, et qui maintient sa curiosité scientifique. Et maintenant, mon amour, en Albion!

Merci à Luc Henrard et surtout à Philippe Lambin pour leurs discussions et explications nanotubiennes et électroniques, toujours caractérisées par une grande sympathie namuroise. Merci a Jacques Dumont et toute l'équipe du LISE *et al.* pour nos collaborations fructueuses, qui ne figurent hélas pas dans ces pages. Ainsi qu'à Philippe Ghosez et Marek Veithen, maîtres perturbateurs diélectriques.

Un grande omaggio a tutti gli simulatori italiani all'estero: Alfredo Pasquarello, Roberto Car, e Alfonso Baldereschi. Sono stati loro a trascinarci nel'ab-inizio, questa selva oscura della quale non c'é diritta via di scampo.

Merci a mes parents, qui n'ont pas fait exprès, mais n'ont pas pu faire autrement que de me transmettre le virus de la physique. On verra si c'est récessif.

Reconnaissons les courageux expérimentateurs, Jean-Paul Salvetat, Mathieu Kociak, qui ont pu supporter les commentaires naïfs des théoriciens "Mais il suffit de faire du EELS en même temps!". Et le courageux simulateur Xavier Blase pour avoir partagé ses tentatives de comprendre le monde absurde de la supraconductivité 1D. Merci à Chris Ewels, qu'il gardé toujours son flegme britannique, et à Florent Tournus pour sa

quête improbable et illimitée de la compréhension du spin en DFT.

Gracias a Angel Rubio por su ayuda y ospitalidad, siempre con tanta clase. Agradecimentos a Miguel Marques pela sua fé e por compartilhar seu conhecimento largo de la DFT comigo, und Ludger Wirtz für seine Aufmerksamkeit zum Detail und Härte im Graphit. A Javier Junquera tambien, por nuestra lunga lucha debajo la bandera XML.

Vielen dank, Hardy, für die Verwicklungen von SCDFE geduldig erklären, und auch Martin Fuchs für viel Erklärungen über Pseudopotenzialen usw. Danke Mathias Schreck, für die Hilfe und das Gefühl der experimentalists.

No waffling about in thanking Kay Dewhurst and Sangeeta Sharma for huge help in electron-phonon interactions and code integration.

Thanks to Dragan Mihailovic for his enthusiasm and help in understanding what we do and don't know about molybdenum disulfide.

Further abroad, many thanks to Don Hamann and Doug Allan for precious insights and productive suggestions.

A final global thanks to the ABINIT team, too diverse and numerous to be listed exhaustively, and too spread out over the globe to fit in one category here. It's been good, let's keep abinit rolling. And a bit faster if possible.

Abstract

The structural, electronic, and superconducting properties of one dimensional materials are calculated from first principles, using the density functional theory. Nanotubes and nanowires are important building blocks in nanotechnology, in particular for nanoelectronics. In this manuscript, the growth of carbon nanotubes is studied through the interaction between carbon and the transition metal atoms used as growth catalysts. The accepted model for a new phase of nanotube-like molybdenum disulfide is critically examined using comparisons of energetic stability and types of chemical bonding in different candidate structures which have similar compositions. The epitaxial growth of diamond carbon on (100) iridium is exceptionally favorable. The differences between various substrates used experimentally are studied, and the specificity of Ir is shown. Finally, the characteristics of the electron-phonon interaction in aluminium nanowires are determined. The structural instabilities and the differences in the electron-phonon coupling are calculated for straight monoatomic wires, zigzag wires, and thicker straight wires. The constrained geometry of the wires generates a coupling which can be very strong or almost vanish, depending on the structural details, but which is concentrated in the longitudinal high-frequency phonons.

Preface

No science misleads as a science; the error is in that we know it not.

Miguel de Cervantès,
in *Persiles y Sigismunda*

The word is out: physics is dead. In the 1990s someone stated that the twentieth century had been the century of physics, and that the twentyfirst would be the century of biology. After the revolutions of quantum mechanics and relativity, lasers, semiconductors and black holes, society's attention is turning now to genomics, protein structure and expression, and genetically modified organisms. Physics and chemistry will stay on in the scientific toolbox, but the money is elsewhere. We'll see. Nevertheless: what is the role of physics in society today? Are we (we the physicists) a high tech luxury? Is a commercial or industrial product the only final justification for research, even if this product is 50 years down the line in an entirely different domain? Is science there only to make a better refrigerator? Maybe. In a way the refrigerator reflects society's state of well being and a form of usefulness, material comfort or even happiness. What more can we expect from cold hard science? Bettering society itself and making it more just through science has not been popular since the seventies. Primitive utilitarian thinking now shows up glaringly in the political justifications for scientific research, and in grant applications: over the past 30 years industrial applications and even putative "job creation" have become central to obtaining money to do science. This is, of course, absurd. Science must be justified on some level, and prove its usefulness as a whole, but imposing short term accountability on string theorists borders on the insane. It remains that there can be a certain amount of satisfaction in believing that one's work has a form of direct utility, or an impact on life outside the university's ivory bunker. These are some of the questions which will not be addressed in this manuscript.

Well, so much for the preface. I entirely agree that it is superfluous, but as it has now been written, there let it stay.

And now, to business.

Fyodor Dostoyevsky,
in the preface to *The brothers Karamazov*

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Symbols and Abbreviations

Follow the main symbols and acronyms used in this thesis. Consistency with traditional usage has been maintained as far as possible. Vectors are printed in bold-faced fonts.

$\bar{G}$	Matrix of reciprocal space lattice vectors
$\bar{R}$	Matrix of real space lattice vectors
β	Inverse temperature $1/T$
χ	Electron affinity
ϵ	Static dielectric constant
ϵ_i	Band energy of the i^{th} electronic state
ϵ_0	Static dielectric constant in vacuum
ϵ_∞	Electronic dielectric constant
$\gamma, \bar{\gamma}$	Phonon linewidth matrix
$\hat{S}$	Symmetry operation
$\hbar$	Reduced Planck constant
$\mathcal{H}, \hat{H}$	Hamiltonian operator
$\mathcal{H}_{\text{ep}}$	Electron-phonon coupling Hamiltonian
$\mathcal{V}$	Volume
μ_0	Magnetic constant
μ_B	Bohr magneton
∇	Gradient operator
ω	Frequency
ω_D	Debye frequency
ω_n	Matsubara fermion frequency $\pi T(2n + 1)$
ω_ν	Matsubara boson frequency $2\pi T\nu$
$\omega_{\mathbf{q}j}$	Phonon frequency
Φ	Metal work function
Ψ	Many-body wavefunction
ψ	One electron wavefunction
ψ_c	Wavefunction of a core state

ψ_i	Wavefunction of the i^{th} state
Σ_{ep}	Electron-phonon part of the electron self-energy
Σ_{F}	Fock part of the electron self-energy
Σ_{SC}	Screened Coulomb part of the electron self-energy
$\tilde{D}_{\kappa\alpha;\kappa'\beta}(\mathbf{q})$	Dynamical matrix
$\mathbf{A}$	Magnetic vector potential
$\mathbf{a}$	First vector of the primitive unit cell
$\mathbf{B}$	Magnetic flux density
$\mathbf{b}$	Second vector of the primitive unit cell
$\mathbf{c}$	Third vector of the primitive unit cell
$\mathbf{d}_{\mathbf{q}j}$	Phonon displacement vector
$\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$	Unit vector along the x , y , or z -direction resp.
$\mathbf{G}$	Reciprocal space lattice vector
$\mathbf{k}$	Wave vector, usually in the BZ
$\mathbf{k}_F$	Wave vector at the Fermi surface
$\mathbf{q}$	Phonon wavevector in reciprocal space
$\mathbf{r}$	Vector in real space
$\mathbf{R}_{\kappa}^a$	Position vector of atom κ in unit cell a
$\mathbf{u}_{\mathbf{q}j}$	Phonon polarization vector
ξ	Magnetization density
A	Magnetic potential
a	Lattice constant
$a_{\mathbf{q}j}^{\dagger}$	Phonon creation operator
$a_{\mathbf{q}j}$	Phonon annihilation operator
B	Magnetic field
c	Electron annihilation operator
c	Speed of light in vacuum
$c^{\dagger}$	Electron creation operator
$C_{\kappa\alpha;\kappa'\beta}(a, b)$	Interatomic force constant
$c_{\mathbf{k}}(\mathbf{G})$	Component of a wavefunction for one plane wave
e	Elementary charge
$E, \mathcal{E}$	Energy
E_0	Ground state energy
E_c	Correlation energy
E_F	Fermi energy
E_i	Energy of the i^{th} one-electron state
E_{xc}	Exchange-correlation energy
E_x	Exchange energy
$g_{\mathbf{k}i, \mathbf{k}'i'}^{\mathbf{q}j}$	Electron-phonon coupling matrix element
h	Planck constant
I	Electric current
K	Degree Kelvin

k_B	Boltzmann constant
l	Angular quantum number
m	Angular quantum number along $\mathbf{e}_z$
m^*	Electron effective mass
M_κ	Mass of nucleus κ
m_e	Electron mass at rest in vacuum
n	Electron density
N_F	DOS at the Fermi level
$n_\downarrow$	Spin-down electron density
N_{atom}	Number of atoms in the primitive unit cell
N_{band}	Number of electronic bands included in the calculation
$n_\uparrow$	Spin-up electron density
s	Spin quantum number
$s^{\alpha\beta}$	Symmetry operation matrix in cartesian coordinates
T	Temperature
t	Time variable
$u_{\mathbf{k}}(\mathbf{r})$	Periodic part of a Bloch wavefunction
V_{local}	Local component of a pseudopotential
V_{ps}	Pseudopotential
Y_{lm}	Spherical harmonic function
Z, Z_κ	Nuclear or ionic charge of atom κ
Z_{ion}	Ionic charge
ACFD	Adiabatic connection fluctuation dissipation theorem
BCS	Bardeen Cooper Schrieffer
BEN	Bias enhanced nucleation
BO	Born Oppenheimer
BS	Band structure
BZ	Brillouin zone
C	Degree Celsius
CCVD	Catalyzed chemical vapor deposition
CNT	Carbon nanotube
CVD	Chemical vapor deposition
DDB	Derivative database
DFPT	Density functional perturbation theory
DFT	Density functional theory
DNA	Desoxyribonucleic acid
DOS	Density of states
DWNT	Double wall nanotube
EDX	Energy dispersive X-Ray
EELS	Electron energy loss spectroscopy
EPI	Electron phonon interaction
ESR	Electron spin resonance (spectroscopy)

EXX	Exact exchange
FCC	Face centered cubic
FFT	Fast Fourier transform
FS	Fermi surface
GGA	Generalized gradient approximation
GKK	Matrix elements for electron-phonon coupling
GPL	General public license
GS	Ground state
GW	The GW approximation of Hedin
HEG	Homogeneous electron gas
HF	Hartree-Fock
HGH	Hartwigsen Goedecker Hutter
HK	Hohenberg-Kohn
HOPG	Highly oriented pyrolytic graphite
IBZ	Irreducible Brillouin zone
IFC	Interatomic force constant
KB	Kleinman Bylander
KLI	Krieger Li Iafrate
KS	Kohn-Sham
LAPW	Linearized augmented plane waves
LDA	Local density approximation
LMTO	Linear muffin tin orbital
LWD	(Phonon) linewidth
LYP	Lee Yang Parr
MFM	Magnetic force microscopy
MP	Monkhorst-Pack
MPa	Mega-Pascal
MWNT	Multi-wall nanotube
NLCC	Non-linear core correction
NT	Nanotube
OEP	optimized effective potential
PAW	Projector augmented wave
PBC	Periodic boundary conditions
PBE	Perdew Burke Ernzerhof
PECVD	Plasma enhanced CVD
PSC	Phase slip center
PW	Plane wave
PZ	Perdew Zunger
QMC	Quantum Monte Carlo
SC	Self consistent
SEM	Scanning electron microscope
SIC	Self-interaction corrected

STM	Scanning tunneling microscope
STS	Scanning tunneling spectroscopy
SWNT	Single-wall nanotube
TB	Tight binding
TDDFT	Time dependent DFT
TEM	Transmission electron microscope
TM	Troullier Martins
TPa	Tera-Pascal
USPP	Ultra-soft pseudopotential
VdW	Van der Waals
WF, WFK	Wavefunction
XC	Exchange correlation

Chapter 1

Introduction

Order and simplification are the first steps toward mastery of a subject – the actual enemy is the unknown.

Thomas Mann

The present manuscript deals with applied numerical physics. Applied because the link to industry and applications is visible, if not always strong. Numerical because we use computer simulations to calculate the properties of materials, molecules, and atomic-scale systems. Numerical physics is a fairly young field with a special relationship to both experiment and “pure” theory. It is not “pure” theory in that the essential equations and interactions are known and well established. It is not experiment because, though many hypothetical structures can be experimented with, there is no guarantee of their pertinence to reality. Understanding basic processes can involve either the development of new theories or the application of old theories in new complex situations, to understand mechanisms. The niche of numerical physics is the modeling of systems and the use of computer power to carry out calculations beyond the simple models which are accessible analytically. In this way one can hope to explain experiments, by proving that certain structural or compositional models would give the behavior observed in the system, and that other plausible models would not.

In order to explain experiments we need a direct relationship with experimentalists. It is essential to understand what they really do and what they really understand, before forging ahead to calculate fictitious systems which have little to do with reality (this is a very real threat). Most of the projects carried out in this thesis have involved close collaboration with experimentalists, fleshing out the limitations of both

theory and characterization methods. Numerical tools can also be used to explore mechanisms, to get a “feel” for them and to propose new applications and experiments. The ideal situation (which very rarely happens) is to think up a new system and to be able to predict its properties before it is ever produced in the lab.

Different approximations and levels of theory are routinely used to model the properties of physical systems. At the upper size limit, finite element methods and fluid dynamics simulations can provide very detailed accounts of the macroscopic behavior of liquids, solids, and gases. These techniques cover phenomena from global weather and climate modeling down to the plasticity and breaking of machine parts. At some point, a greater degree of granularity must be introduced, when the atomic structure of the system becomes apparent and determines the properties of interest. Using classical potentials one can treat systems of many millions of atoms, but the physics involved remains rudimentary. A further step of complexification uses tight-binding or other semi-classical approaches to gain further precision in the modeling of atomic interactions. The added complexity increases the computational difficulties and system sizes are limited to hundreds of thousands of atoms. The fully quantum simulation of atomic systems, involving the most precise theories which are presently tractable, is limited to from a few hundreds to a few thousands of atoms. Our work concerns this lower end of the scale: the nanoscale. Progressively better approximations have been developed in this field, from Thomas-Fermi and nearly-free electrons to Hartree-Fock, to density functional theory and then many-body theories which treat ever more detail in the infinitely complex interactions between electrons, nuclei, and electromagnetic fields.

Specific applications of numerical simulations can (and indeed do) enter into almost any domain of science. The most popular for the moment are new technologies: nanotechnology and electronics, chemical processes and catalysis, or biology and biochemical reactions. The latter remain the most challenging because of the daunting size (up to several microns!) and complexity of the systems involved. We will be applying density functional theory methods to the calculation of structural, electronic, and vibrational properties of low dimensional systems which are of interest in nanotechnology.

The applications presented in this thesis concern nanotubes and nanowires. The first chapters (Chap. 2 and 3) present the wide palette of concepts and theories needed for our different calculations: density functional theory, superconductivity, and the physics of nanotubes. Chap. 4 covers three different aspects of the growth and characterization of carbon nanotubes and related structures: first the presence of stray atoms

of metal catalyst in carbon nanotubes, then the structure of a new dichalcogenide phase made from bundled tubes of molybdenum, sulfur, and iodine, and finally the interaction between carbon and different metals used as substrates for the growth of thin films of diamond. Chap. 5 describes different properties of nanoscale wires made from aluminum. Their ground state geometrical and electronic structure, their vibrational instabilities, and finally electron-phonon interactions, which determine their superconducting properties.

Chapter 2

Theory

A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it.

Albert Einstein

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2.1 Elements of solid state physics

We will start our presentation of numerical quantum mechanics from the point of view of solid-state physicists. This will allow us to introduce important and non-intuitive concepts such as reciprocal space and lattice symmetries, which will be needed later on. Kittel[134] and Ashcroft and Mermin[7] have written the most widely used reference books on condensed matter theory. Elements of symmetries and group theory in molecules and solids can be found in Ref. [184] and [8].

Unless otherwise specified, we will be using Hartree atomic units throughout, i.e. $m_e = \hbar = e = 1$. The unit of energy is the Hartree (Ha = 27.211 eV or $4.359 \cdot 10^{-18}$ Joule), length is in bohr radii ($a_0 = 0.0529177$ nm), time is expressed in a.t.u. (or $2.41888 \cdot 10^{-17}$ s), mass in electron masses ($19.109381 \cdot 10^{-31}$ kg), forces in Ha/bohr ($8.238 \cdot 10^{-8}$ N or 51.422 eV/Å), and pressure in Ha/bohr³ ($2.942 \cdot 10^{13}$ Pa or 183.63 eV/Å³).

2.1.1 Crystal structures and lattices

The physics we will be describing is that of electrons in electromagnetic interaction with atomic nuclei. These interactions govern most of the observable properties of matter, such as hardness, electrical conductivity, and optical properties. The three other forces in physics are either too short ranged or too weak to have a perceptible influence. In this context, for the time-independent case, the appropriate physics is described by the following Schrödinger equation[245, 247, 246]

$$\hat{\mathcal{H}}\Psi = E\Psi \quad (2.1)$$

where $\hat{\mathcal{H}}$ is the system's Hamiltonian, Ψ the full, or “many-body”, wavefunction for all the particles in interaction (electrons, nuclei, and in principle also the electromagnetic field), and E the energy corresponding to Ψ . In most standard cases, $\hat{\mathcal{H}}$ can be expressed as a sum of a kinetic and a potential energy, the latter being a multiplicative local operator: $\hat{\mathcal{H}} = \hat{\mathcal{T}} + \hat{\mathcal{V}}$. The only potential which will enter into the equation's Hamiltonian in our case is the Coulomb interaction. This is exceedingly simple, but the long range of the Coulomb interaction makes its treatment very complex, and requires the approximations and analysis we will present in later sections. In most of this work we will be in a regime where only scalar-relativistic effects need be taken into account.

2.1.2 Symmetries

All of the physical properties of crystals reflect the symmetries they possess. The symmetries will determine which directions and atoms are equivalent, and impose constraints on the possible states the system can be in. The solutions of the Schrödinger equation will present a spectrum of eigenvalues whose degeneracies depend on the symmetries of the Hamiltonian, and the spatial dependencies of the eigenstates will reflect their character and the irreducible representation they belong to.

Symmetry operations in normal 3-D space are composed of a 3x3 matrix of rotation or reflection, and a translation vector. The operations form a group. We will use reduced coordinates wherein the matrices only contain 1s, 0s, and -1s.

2.1.3 Bloch functions and plane waves

Given that our problem is periodic by construction, the natural basis for representing all functions is a set of plane waves. Bloch[24] showed that the total wavefunction (we will consider a lone electron in the crystal for the moment) can be decomposed into a strictly periodic part $u_{\mathbf{k}}(\mathbf{r})$ and a plane wave $\exp(-2\pi i \mathbf{k} \cdot \mathbf{r})$ characterized by a wave vector $\mathbf{k}$. By Fourier transforming $u_{\mathbf{k}}(\mathbf{r})$, we can obtain its discretized representation

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}}(\mathbf{G}) \exp(-2\pi i \mathbf{G} \cdot \mathbf{r}) \quad (2.2)$$

The coefficients $c_{\mathbf{k}}(\mathbf{G})$ are complex, and in the more general relativistic case become spinors. The sum is performed over a set of vectors $\mathbf{G}$ which belong to the reciprocal lattice, the dual of the real-space lattice. The basis vectors of the reciprocal lattice are defined as being orthogonal to two unit cell vectors, and normalized so that the scalar product with the third is unity. The vectors are another basis for three dimensional space, called reciprocal because of its dual relationship with “real” space. The corresponding unit cell in reciprocal space is known as the Brillouin Zone (BZ). The solutions of the Schrödinger equation now become $\mathbf{k}$ dependent.

2.1.4 K-points and bands

A point in reciprocal space is usually denoted $\mathbf{k}$ or $\mathbf{q}$. In general $\mathbf{k}$ is arbitrary but from the definitions above one can see that adding a $\mathbf{G}$ vector to $\mathbf{k}$ simply shuffles the sum over $\mathbf{G}$. As a result, the wavefunction can always be represented as $u_{\mathbf{k}}(\mathbf{r})$ times a plane wave with a $\mathbf{k}'$ in the Brillouin Zone. As a result, by restricting $\mathbf{k}'$ to the BZ we will recuperate

the other solutions (for $\mathbf{k}$ outside the BZ) as additional, higher-energy solutions at $\mathbf{k}'$ (initially only the lowest energy solution at $\mathbf{k}$ was needed). The wavefunctions acquire an additional index i which runs over all the additional solutions, or bands. The total number of electrons present in the system determines up to which energy the bands are filled. This energy is called the Fermi energy E_F , and the surface of points in reciprocal space where an eigenenergy is equal to E_F is called the Fermi surface (FS).

2.2 The Density Functional Theory

Calling the subject nonlinear dynamics is like calling zoology ‘nonelephant studies’

Stanislaw Ulam

cited in “Chaos” by J. Gleick

2.2.1 An introduction to DFT

Density Functional Theory (DFT) is presently the most widely used framework for the simulation of the electronic structure of materials and molecules. Its scope is very large and in principle can cover the prediction of properties of the ground state of any system of electrons. Relativistic extensions exist and the coupling to classical electromagnetic fields is becoming commonplace. DFT is a delicate balance between precision and numerical tractability. As we shall see in the following sections there are a number of approximations which are usually made in order to render the computations accessible to present-day computers, and we shall mention a few standard extensions (more precision for a higher computational cost). In brief the final limitation is computer power. The more operations per second can be executed, the larger the systems we can calculate and the greater the precision, and our appetite for new systems is infinite.

DFT has gained momentum over the past 40 years since its inception, and even more so in the past 10 years: workstation power has risen and at the same time the size of objects accessible to experiment has shrunk, such that now there is a growing overlap between what can be simulated and what can be characterized in the lab. DFT is not the final theory of atomic and solid-state systems, but its failures and limitations are beginning to be well mapped out. Good reviews of DFT and its methods abound. A few can be found in Ref. [210, 102] and the very complete and recent book by Martin[176].

2.2.2 Fundamentals of DFT

2.2.2.1 The Hohenberg-Kohn theorem

In 1964, Hohenberg and Kohn set out a simple theorem which relates the potential and the electronic density in a quantum system[121]. The theorem states that there is a one to one relationship between the potential v and the density n , in such a way that the infinitely complex many-body

problem of solving the Schrödinger equation for N particles (i.e. for the full wavefunction $\Psi(\mathbf{r}_1, s_1 \dots \mathbf{r}_N, s_N)$) can be replaced by an equation for the density $n(\mathbf{r})$. In the straight resolution of the Schrödinger equation it is obvious that giving the external potential fixes the Hamiltonian, and solving the equations determines the wavefunctions and hence the density. However, Hohenberg and Kohn showed that the converse is true, and that the external potential can be expressed as a functional of the density, up to a constant.

The proof follows by supposing that another potential v' , which differs from v by more than a constant, generates the same density. If the total energy has a (unique) minimum for each potential, then we arrive at a contradiction. A reformulation of the proof as a constrained search was given by Levy[162, 164].

The density is presumed to be n -representable, i.e. it integrates to N electrons and is regular enough. This is usually ensured by deriving n from a set of wavefunctions.

The potential is presumed to be local and multiplicative. There are issues of existence of solutions, known as v -representability, which means there does not always exist an acceptable potential for a given density n [163, 166].

2.2.2.2 The Kohn-Sham scheme

The potential v and the total energy E are universal but unknown functionals of the density. Kohn and Sham (KS)[137] showed that there exists a mapping between the full interacting problem and a one-particle problem, in which the one-particle wavefunctions give the exact density. Most of the terms in the energy can be estimated from a single-particle picture. E is the minimum of a functional which we write as the sum of the energies coming from the external potential, the Hartree repulsion between electrons, the independent-particle kinetic energy, and an unknown term E_{xc} which must be approximated. The total energy (which we recall is a functional of the density alone) is then re-written as a functional of the auxiliary (orthonormal) one-particle wavefunctions ψ_i which were introduced:

$$E[n] = - \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle - \sum_I \frac{Z_I n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} + \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \quad (2.3)$$

where

$$n(\mathbf{r}) = \sum_i \psi_i^\dagger(\mathbf{r}) \psi_i(\mathbf{r}) \quad (2.4)$$

The index I runs over the atomic nuclei in the system (placed at $\mathbf{R}_I$ and bearing a charge Z_I) and i runs over the occupied electronic states (bands and kpoints in the BZ). E_{xc} is called the exchange-correlation energy because it contains contributions from the Hartree-Fock (HF)-like exchange of electrons of same spin, and the correlation of the individual electrons, due to Pauli repulsion in particular.

Minimizing E gives a Schrödinger-like equation for the ψ_i :

$$\left[-\nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n] \right] \psi_i = \varepsilon_i \psi_i \quad (2.5)$$

where $v_{xc}[n] = \frac{\delta E_{xc}}{\delta n}$.

Kohn and Sham consider the limit of a slowly varying density and approximate the full functional $E_{xc}[n]$ by a mean-field expression:

$$E_{xc}^{\text{LDA}}[n] = \int d\mathbf{r} \epsilon_{xc}^{\text{HEG}}(n(\mathbf{r}))n(\mathbf{r}) \quad (2.6)$$

where $\epsilon_{xc}^{\text{HEG}}$ is the exchange-correlation energy density for the homogeneous electron gas (HEG). This is known as the local density approximation or LDA, and is the most widely used approximation to date for DFT. The LDA works exceptionally well for fortuitous but known reasons (see for example Ref. [106] [105] [155] and [156]), related to respecting sum rules and spherical averaging of the interaction with all the other electrons.

The function $\epsilon_{xc}^{\text{HEG}}$ is analytical in the simplest cases but must in general be obtained from another theory. The most common practice is to use Quantum-Monte-Carlo (QMC) calculations where full variational wavefunctions are calculated for the full interacting problem, in order to extract numerical and fitted data for ϵ_{xc} . Ref. [38] is the most widely used for the QMC data for the HEG, and a common LDA parametrization is that of Perdew and Wang (1992)[216].

2.2.2.3 The gradient corrected approximations

The next step beyond the local-density approximation is to include the gradients of the density at the point where we want to calculate ϵ_{xc} . This still results in a local expression for ϵ_{xc} , and gives the various gradient-corrected functionals. Simplistically extending the expressions for the LDA to higher order gives disastrous results, because a number of sum rules are violated. This was resolved with the appearance of the generalized gradient approximations (GGA)[155, 212]. A great number of them have appeared, but the most popular are those of Perdew, Burke, and Ernzerhof (PBE)[213] and Perdew and Wang(PW91)[215].

2.2.2.4 Beyond GGA: exact exchange and better correlation

Several directions have emerged over the past 20 years to obtain better approximations to E_{xc} . Continuing in the spirit of the LDA and GGA, and adding additional exact constraints to functionals of n , ∇n , and Δn or the kinetic energy density, one arrives at the so-called meta-GGA[77, 214, 264] approximations. Their complexity is great, and some do not have an explicit expression for v_{xc} so it is not clear meta-GGA will provide the way forward.

Other functionals[104, 217] have appeared since the early 1980s which have attempted to correct for the self-interaction problem: in the standard Hartree energy term, the density of a given electron interacts with itself. This interaction is spurious, and is taken out exactly in HF by the exchange term, but not in LDA or GGA. The improvement is limited and not systematic, but clearly indicates a large part of the problem with simple local DFT approximations.

Another alternative is to mix a term of Hartree-Fock exchange with a correlation functional from DFT. This gives the so-called hybrid approaches, which are very popular in quantum chemistry. In particular the empirically parametrized model of Becke[20] with correlation from PBE (B3PBE), PW91 (B3PW) or from the functional of Lee, Yang, and Parr[159] (B3LYP). These functionals usually give better results, but the inclusion of the full HF exchange term overcorrects, and the fitting procedures used to fix this introduce empirical parameters. The theory does not provide systematic ways to improve accuracy.

There exists an implicit way to calculate E_x through an integral equation. This leads to the exact exchange (EXX) or optimized effective potential (OEP)[259] method, effectively approximated by Krieger, Li, and Iafrate[145, 146]. At convergence the exchange term is in principle reproduced exactly, and the method corrects an important defect in Hartree-Fock theory: the potential becomes a one-body potential again. The treatment of correlation can also be carried out with other techniques such as the adiabatic-connection integral on the coupling constant in the electron interaction, and using the fluctuation-dissipation theorem (ACFD)[157, 158]. Both of these theories have the one-particle orbitals intervene directly in the functional, instead of only the density. This may be where the next good approximations for functionals will come from, once proper and efficient simplifications are made to the full integral formalism for the OEP and/or ACFD.

2.2.3 The ground state

2.2.3.1 Total energy

The total energy and the ground state density are calculated by minimizing equation 2.3 with respect to the one-particle wavefunctions. Initially the only physical information which can be extracted is the total energy and the total charge density, but we shall see below that a number of other quantities can also be calculated or estimated.

2.2.3.2 The Born-Oppenheimer approximation

Up to now we have given no consideration to the atomic nuclei (or ions) with which our electrons are interacting. In the vast majority of DFT implementations, calculations are performed within the Born-Oppenheimer (BO) approximation[31, 30]. This means that the ions are presumed to move much more slowly than the electrons. As such, the electrons are in their instantaneous ground state at all times for the given positions of the atoms: the atomic positions are simply classical (not quantum) parameters in the electronic total energy.

The BO approximation is a hypothesis on the time scales which are important for the ionic and electronic dynamics, viz. that the electronic time scale is much shorter. There is a corresponding interpretation in terms of energy: the energy hyper-surface for the ground state must be well separated from that of the first electronically excited state, such that the energetically low-lying ionic motions (phonons) will never mix the ground and excited states. There are however cases when this approximation breaks down, if the ions move very fast or if the Fermi velocity is particularly low. In some cases the energy manifolds can touch or cross[290], and the BO approximation breaks down altogether. Formally, in metals, there are electronic excitations infinitesimally close to the Fermi level. These can then always couple to acoustic phonon excitations. The treatment of metals with a finite temperature formalism does away with this difficulty (see Sec. 2.2.4.2) by dealing with a canonical ensemble average of systems, for which the BO approximation holds. There is still a coupling between electrons and phonons, but the electrons will now stay in their instantaneous ensemble-averaged ground state.

In most of the following we will presume the approximation to hold, but a few comments will be in order, concerning the electron-phonon coupling and superconductivity.

2.2.3.3 Self-consistency and energy minimization algorithms

Given the nature of DFT, expressing a one to one correspondence between v and n , the KS equations must be resolved iteratively until they are self-consistent, i.e. until n and v match. A trial set of ψ_i are entered, give n , and the v is calculated. Solving Eq. 2.5 gives new wavefunctions, and so on until a given convergence criterion is reached. Many different algorithms have been proposed to minimize the total energy. In the simplest cases, if there are very few degrees of freedom, the Hamiltonian matrix can be diagonalized explicitly. In most cases, however, there are many electrons present and many degrees of freedom per electron, and iterative methods are needed for the diagonalization as well. The gradient of the energy with respect to the wavefunction coefficients (see Sec. 2.2.5 below) are calculated analytically, and this gradient is used as a search direction for a better set of wavefunctions. The most common algorithms are reviewed and compared in Ref. [144]. The most popular are the conjugate gradient and those of Pulay[228] and Broyden[33].

The search directions can often be advantageously pre-conditioned, eliminating spurious or exaggerated reactions of the system to the convergence steps. Most of these schemes are based on the estimation of the dielectric response of the system (or a model)[144, 287, 271, 265].

2.2.3.4 Structural relaxation

The total energy of an atomic structure can be of interest in and of itself, but often one is looking for specific equilibrium configurations, minima of the total energy with respect to atomic positions and/or the shape and size of the unit cell. In order to find these minima, one has to calculate the derivative of the total energy with respect to the different (classical) parameters ($\mathbf{R}_I, \mathbf{a}, \mathbf{b}, \mathbf{c}$). Thanks to the now standard theorem of Hellman and Feynman[117, 76],

$$\frac{d}{dR} \langle \psi | \hat{O} | \psi \rangle = \langle \psi | \frac{d\hat{O}}{dR} | \psi \rangle \quad (2.7)$$

($\hat{O}$ is any operator) the derivatives are simplified, and give us access to the forces on atoms in a given configuration, and the total (tensorial) stress on the system. These can then be used to evolve the shape of the cell and the positions of the atoms in order to find minima, phase equilibria and transitions, metastable states, or pathways for chemical reactions.

The same algorithms presented in Sec. 2.2.3.3 can usually be used to optimize the geometrical parameters described above. In particular, we

have used the Broyden algorithm[33] for structural relaxations. Finding reaction pathways and saddle points on the BO potential energy surface is even more complex than finding just a single minimum. To this end many different techniques have been invented, and several of the more important ones are reviewed in Ref. [119].

2.2.3.5 Car Parrinello

In 1985, a very influential paper appeared in Physical Review Letters by Car and Parrinello[36]. They proposed a unified scheme which simultaneously evolved the electronic and ionic degrees of freedom. They also furnished a number of other improvements in algorithms, and proposed using fast Fourier transforms (FFT). The basis of their method is the decoupling of the two types of degrees of freedom in a common Lagrangian. From this decoupling follow equations which keep the electrons close to their instantaneous ground state as the atomic positions evolve, without having to calculate the ground state explicitly. This has applications in particular for calculating molecular dynamics trajectories, but the basic method has several drawbacks. In its simplest form it can not be applied to metallic systems, and several integration parameters must be fixed with care to ensure the electrons stay sufficiently “cold”.

2.2.4 K-space considerations

This section contains details pertaining to band structures and k-space integration.

2.2.4.1 Band structures

Formally, as was mentioned above, conventional DFT only gives access to the total energy of the system, not to the spectral functions of the electron, and in particular to the single-particle excitations. The one-particle wavefunctions which are introduced in the Kohn-Sham scheme are purely auxiliary variables. It is however tempting to observe the system from an independent-particle viewpoint and to consider that individual electrons occupy the eigenstates and eigenenergies which come out of Eq. 2.5. In the case of Hartree-Fock theory there exists a theorem by Koopmans[140] which states that to zeroth order the one-particle eigenvalues are the eigenenergies of an additional particle that could be added to the system, and that the difference in eigenenergies is the energy absorbed in vertical transitions. The approximation is gross, because no relaxation of the other electrons due to the perturbation (addition of an electron or promotion to an excited state) is accounted for, but it gives

a certain legitimacy to interpreting eigenstates as “one-particle” excitations. An extension of Koopmans’ theorem to spin-dependent DFT was recently given by Gritsenko and Baerends[101].

Many papers using HF or DFT present band structures, plots of the eigenenergies of valence and conduction electrons near the Fermi level (in the approximation described in the preceding paragraph), along various directions in reciprocal space. These directions are chosen to be highly symmetrical, because degeneracies and level splittings happen most frequently along rotation axes or mirror planes, and because these directions give a picture of the full behavior of the bands in the BZ. The example of aluminum is shown in Fig. 2.1 Several nomenclatures exist

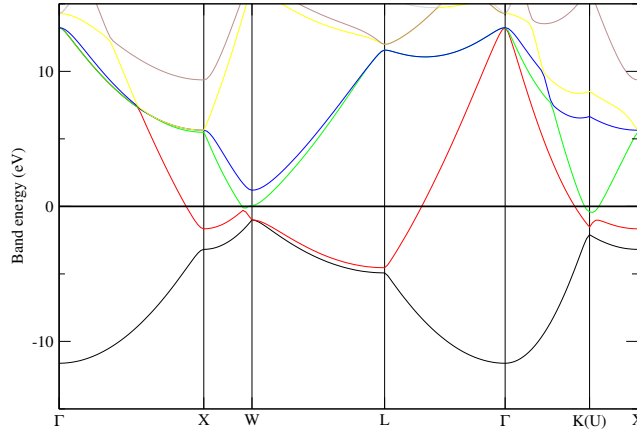


Figure 2.1: Band structure (in eV) for face-centered-cubic aluminum, along high-symmetry directions in the BZ. The thick black line is the Fermi level.

for the points of highest symmetry in reciprocal space, but the most common one is due to Bouckaert, Smoluchowski, and Wigner[32].

Band structures are usually related to experiments in optics, or (inverse) photo-electron spectroscopy, where an electron can be added or removed from the system[205]. As such, the states which are probed are collective excitations of the full system, reacting to the presence of an electron, a hole, or one of each. In many cases the energy spectrum of these excitations is very peaked (a structure known as a quasi-particle), the width of the peak being linked to the inverse of the lifetime of the excited state. In this light, the DFT band structure is simplistic in that the peaks are Dirac δ functions placed on the bands: the lifetimes are infinite.

Nevertheless, in many cases the DFT band structure is a very good

approximation, the largest error being a rigid shift in the energy bands for semiconducting systems (see Sec. 2.2.4.4 below).

2.2.4.2 Finite temperature formalism

The HK theory was quickly generalized to finite temperatures by Mermin [187]. The appropriate statistics for fermions is the Fermi-Dirac distribution. Mermin added fractional occupation numbers f_i and an entropy term to get a free-energy functional which is variational. In this way the calculation samples the canonical ensemble: the result is an ensemble average of the real system, and no longer a pure state. This gives a statistical interpretation to the fractional occupation of states near the Fermi level. A good introduction to and review of the finite-temperature and ensemble density functional formalisms is given in Ref. [177].

2.2.4.3 K-space integration

Several terms in the total energy we are calculating can be expressed as integrals over the BZ. On a computer, the integral will be approximated by a weighted sum. The grid of k-points used for this sum must be converged and sufficiently dense to well represent the variations of the integrand, which is typically determined by the fine structure of the Fermi surface. Baldereschi[12], Chadi and Cohen[39], and then Monkhorst and Pack (MP)[197] showed that certain sets of points in the BZ minimize the error in the calculation of the integrals. These sets of points depend on the symmetry of the system, and must be systematically converged in each case study.

In 1983, Fu and Ho[84] presented a scheme to accelerate the convergence with respect to the number of k-point, which adds a Gaussian smearing function of width σ on each state in the density of states. In this way, states near the Fermi level are populated according to their distance from the FS. Without this smearing, states near to but above the Fermi level are not counted at all, and convergence is slower. In fact, the smearing scheme can be shown to be equivalent to the finite-temperature scheme, with a modified entropy function depending on the smearing function (see Ref. [177] and references therein). Several other smearing schemes have been invented over the past 20 years[188, 58, 178]. The most widely used is still the Gaussian version of Fu and Ho, but the most precise one should be the “cold-smearing” scheme of Marzari and coworkers[177, 178]. In the latter case the smearing function is designed to leave the total (free) energy invariant with respect to the smearing width, up to third order in σ .

An alternative to smearing schemes is to interpolate the electronic bands and integrate the interpolated values. Interpolating linearly and dividing space into tetrahedra gives the tetrahedron method[161], which has the advantages of simplicity and robustness. An improved and corrected scheme, adapted to MP grids, was devised by Blöchl et al.[27]. Higher order interpolations and extrapolations are possible, but often unstable. The fundamental problem with band interpolation schemes is the complex behavior of electronic bands. Bands can often have very variable dispersion behaviors throughout the BZ, and can either cross or avoid each other (which is known as an avoided- or anti-crossing) depending on whether they belong to different irreducible representations or not. Interpolating bands usually excludes the possibility of band crossings, and band shapes in most real materials necessitate fine integration meshes to be well reproduced. The simple case of aluminum is represented in Fig. 2.1. Band crossings can be observed between Γ and X, and anticrossing for the fourth and fifth bands at L.

2.2.4.4 Quasiparticles, GW, and things I will not get into

To go beyond the simplistic band structure calculated in DFT, one must employ more general theories. In principle the excited states of the system are functionals of the ground state density, but these functionals are completely unknown and probably very complex. A time-dependent density-functional theory (TDDFT) was developed by Runge and Gross[238] in the 1980s and has had many successes, in particular for optical excitations. However, the only theory in regular use today which allows one to access excitations systematically is Hedin's GW approximation[115, 6, 205]. The first order diagrams in perturbation theory are calculated explicitly based on the one-particle eigenvalues and eigenstates from the DFT calculation. This corrects the band gap energy and band widths in most systems, and generates more realistic spectra for quasiparticles.

2.2.5 Basis functions

The wavefunction ψ_i has up to now been used as a block concept. Different choices exist for the representation of the ψ_i . One common set of basis functions is plane waves (which we will be using in our calculations), but other implementations of DFT use Gaussian[275] or atomic-like basis sets centered on atoms[129], or even finite elements[73], or wavelets[42, 56]. Plane wave basis sets present several advantages. Convergence is straightforward, since increasing the number of plane

waves always increases accuracy, usually in an exponential way. The independent-particle kinetic energy has a very simple expression, and FFT are very easy to use. Finally there are few issues of basis-dependent Pulay type forces[227]. In all other cases the mathematics becomes more involved, but localized bases present different advantages: the basis size is usually much smaller (and hence the calculation lighter), and, at a certain distance, pieces of the system become decoupled and the numerical effort required in calculations increases linearly with the size N of the system (these are known as order- N or $O(N)$ methods[88]). In most standard implementations the effort scales as the cube of the system size.

Finite systems in periodic boundary conditions

The methods of present-day computational chemistry and physics can be divided into two types: the chemists tend to start from a molecular point of view, and localized orbitals around the atoms in a system which is isolated in vacuum. The physicists tend to start from the “opposite” point of view of an infinite periodic solid crystal, described by a unit cell and with orbitals which are more delocalized, and of infinite extent throughout the crystal. The two points of view can be reconciled: quantum chemistry codes build in periodic boundary conditions, and adapt their basis sets to describe more diffuse wavefunctions, and physicists make artificial “crystals” built up from molecules in very large unit cells, such that the periodic images of the original molecule do not interact perceptibly with the molecule being considered. It is in this way that one may examine the properties of a finite system (surface, interface, molecule) using a formalism which is inherently made for infinite, periodic systems.

In a plane wave basis set, the size of the basis set gives the finest detail which can be calculated in real space. Plane waves are added with longer $\mathbf{G}$ vectors, which describe higher spatial frequency variations, i.e. finer details, until a convergence is reached. The density of electrons near the nucleus is strongly peaked, and to be described properly requires a huge number of plane waves. However, in most routine systems describing bulk crystals, chemical reactions, and so on, the electrons in the core of the atom are basically unchanged with respect to an isolated atom. Only the valence electrons (in the outermost atomic shells) participate and can change their wave functions perceptibly compared to the isolated atom. These two factors, the difficulty in describing core electrons with plane waves, and the fact that we do not need to since they are essentially frozen, brings us to the next section on pseudopotentials.

2.2.6 Pseudopotentials

2.2.6.1 An introduction to pseudopotentials

The idea behind pseudopotentials is to replace the generic Coulomb potential $-Z/|\mathbf{r} - \mathbf{R}|$ felt by all the electrons by a more complicated operator which takes into account not only the potential of the nucleus, but also the screening and repulsion by the core electrons. In this way, the core electrons are eliminated from the problem (the frozen core approximation), and we are left with an effective potential for the valence electrons. A reference calculation is carried out for the isolated atom with all of its electrons, and then an analytical pseudopotential is fitted in order to reproduce the same spectrum and wavefunctions as in the all-electron calculation. The valence electrons must be constrained to be orthogonal to the core electrons. In the all-electron case this means the valence wavefunctions have a large number of nodes near the nucleus. One of the reasons we are pseudizing is to make the wavefunction variations smoother, so these must be eliminated. A cut-off radius is chosen, and the pseudopotential's bound states will reproduce the valence wavefunctions outside this radius, and be smooth inside.

Local

The simplest pseudopotential is a local multiplicative function[112]. Far from the nucleus the potential must behave like $Z_{ion}/|\mathbf{r}|$ where Z_{ion} is Z minus the number of core electrons. However, this functional form leaves few degrees of freedom to fit the valence states with. Even for first and second row elements this form was found to be sometimes insufficient.

Non-local

A natural generalization is to add projector functions to the local potential. These projectors are chosen to make the valence states orthogonal to the core states[219]. We obtain

$$V_{ps} = V_{local} + \sum_c \alpha_c |\psi_c\rangle\langle\psi_c| \quad (2.8)$$

where c runs over core states. The exact ψ_c which are used and the values of α_c can be chosen to fit the valence eigenstates. An alternative is to write the projectors as a sum over angular momenta, with one projector per l value:

$$V_{ps} = V_{local} - \sum_{lm} \alpha_l |Y_{lm}\rangle\langle Y_{lm}| \quad (2.9)$$

Bachelet, Hamann, and Schlüter published an exhaustive list of pseudopotentials of this form[10].

Separability, the Kleinman-Bylander construction, and ghost states
 Kleinman and Bylander[135] showed that pseudopotentials could advantageously be put in a so-called “separable” form like $\sum_{lm} |p_{lm}\rangle\langle p_{lm}|$, such that matrix elements with basis functions could be calculated quickly, as the products $\langle\psi|p_{lm}\rangle$ factorize. However, this can produce spurious, or ghost, states lower in energy than the physical states. Gonze et al.[93, 95] analyzed the appearance of ghost states and gave criteria for their elimination.

Non-linear core corrections

In some cases, if the overlap between core and valence electrons is important, the standard frozen-core pseudopotential approximation may be too harsh. Louie, Froyen, and Cohen[171] showed that introducing a model core charge into the pseudopotential could correct for this. The fitted core charge is added to the valence charge to give a better estimate of the density in the calculation of the exchange correlation energy (which is a complex, non-linear functional of the density).

2.2.6.2 Types of pseudopotentials

Troullier-Martins

The most popular type of pseudopotential for the moment is that invented by Troullier and Martins[276]. They generalize ideas from Kerker[132] to propose a smooth analytical form for the projector functions.

Hartwigsen-Goedecker-Hutter

Hartwigsen, Goedecker, and Hutter[113] presented a generalized form of pseudopotential, in separable form by construction, which was numerically fitted for elements up to Rn. Their method (along with that of Teter[270]) presents the advantage of being able to use several projector functions per angular momentum channel, e.g. for both 2s and 3s electrons in Na with 9 valence electrons.

2.2.6.3 PAW and Ultrasoft pseudopotentials

All of the pseudopotentials mentioned up to now, and all those we will use in the following chapters, are constructed subject to a constraint which is intuitive and natural (due to Hamann, Schlüter, and Chiang[111]): the charge contained inside the cut-off radius for the pseudo and all-electron wavefunctions must be the same (beyond the cut-off the wavefunctions should be identical). This is known as norm-conservation, but is not inherent to the pseudopotential technique. In 1990 Vanderbilt[280] and Blöchl[25, 26] introduced similar formalisms (respectively ultrasoft pseudopotentials (USPP) and the projector aug-

mented wave (PAW) method) which relax this condition. The PAW method is more general, and encompasses both pseudopotential theory and its main rival, the linearized augmented plane waves (LAPW)[4, 141] method. The additional degrees of freedom gained from relaxing the norm-conserving condition can be used to make much smoother pseudopotentials, requiring a smaller plane-wave basis set.

2.2.7 Density Functional Perturbation Theory

2.2.7.1 Introduction to DFPT

Up to now, we have described essentially ground state properties, the total energy, and forces and stresses which are the first derivatives of E . One can go further and examine higher derivatives of E with respect to ionic positions and lattice parameters, or with respect to macroscopic applied external (typically electric) fields. The formalism which calculates the response functions of a DFT system is known as density functional perturbation theory or DFPT[18, 85, 92, 94, 17].

If the perturbation strength is characterized by a parameter λ , then the energy, potentials, and wavefunctions have an expansion as a function of λ :

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \quad (2.10)$$

The forces and stresses are in $E^{(1)}$, and many experiments probe $E^{(2)}$, such as Raman and infra-red spectroscopy, linear optics, and elastic constants. It was shown that the “ $2n + 1$ ” theorem can be applied in DFPT, giving $E^{(2n+1)}$ from $\psi^{(n)}$. There is also a variational principle for $E^{(2n)}$ which allows the determination of the wavefunctions using a technique similar to that for the ground state. In order to calculate $\psi^{(1)}$, we must solve what is known as a Sternheimer equation[255]:

$$P_c(H^{(0)} - \epsilon_\alpha^{(0)}) | \psi_\alpha^{(1)} \rangle = -P_c H^{(1)} | \psi_\alpha^{(0)} \rangle \quad (2.11)$$

where P_c is the projector on the conduction bands, $\epsilon_\alpha^{(0)} \psi_\alpha^{(0)}$ the ground state eigenenergies and functions, and $H^{(1)}$ the first-order perturbed Hamiltonian.

There are also non-stationary expressions of derivatives of the energy, which allow one, for example, to calculate several second derivatives once one first-order wavefunction is known.

In practice the perturbation often has a directional dependence, described by a vector $\mathbf{q}$ in reciprocal space. This could be the direction of propagation of an electric field or a phonon (see below). The traditional approach to calculating a perturbation (i.e. without perturbation theory) is to freeze a finite perturbation into the system, and to calculate

the energies for different values of λ in order to numerically extract the derivatives. This method is known as the frozen-phonon technique for atomic perturbations. Calculating a frozen phonon for $\mathbf{q} \neq 0$ requires a supercell to describe the full fluctuation of the perturbation (which is modulated by $\exp(-i\mathbf{q}\mathbf{r})$). As a result calculations can get unwieldy for small or unsymmetrical $\mathbf{q}$ vectors, and are impossible if $\mathbf{q}$ is not commensurate with the lattice. DFPT does not suffer from this drawback and can be used with arbitrary $\mathbf{q}$.

2.2.7.2 Phonons

In the case of phonons, one wants to calculate all the second derivatives of E with respect to the displacements of two atoms. This derivative gives the inter-atomic force constants (IFC)[220], which can be understood as the change in the force on an atom if another atom is displaced from its original position. The IFC can be defined as:

$$C_{\kappa\alpha;\kappa'\beta}(a,b) = \frac{\partial^2 E}{\partial R_{\kappa\alpha}^a \partial R_{\kappa'\beta}^b} \quad (2.12)$$

where a and b label unit cells, κ, κ' label atoms in the unit cells, and α, β label reduced directions in which the atoms are displaced. The atomic positions are $\mathbf{R}_{\kappa}^a$ and $\mathbf{R}_{\kappa'}^b$. In many systems, the IFC die off slowly with the distance between the atoms. The movement of an atom can influence the force on an atom many cells away.

The Fourier transform of $C_{\kappa\alpha;\kappa'\beta}(a,b)$ with respect to the unit cell lattice gives the dynamical matrix $\tilde{D}_{\kappa\alpha;\kappa'\beta}(\mathbf{q})$ (with an additional factor of $1/\sqrt{M_{\kappa}M_{\kappa'}}$). Diagonalizing $\tilde{D}$ gives the phonon frequencies squared $\omega_{m\mathbf{q}}^2$ and the phonon polarization vectors. The former can be directly compared to experiment: if $\mathbf{q} = 0$ to Raman and infra-red frequencies, and the full phonon band structure can be obtained from different techniques, such as inelastic X-Ray scattering. It can occur that an eigenvalue of $\tilde{D}$ is negative. If the structure is in equilibrium, this corresponds to an atomic displacement which lowers the total energy, and hence characterizes an unstable phonon mode. Unstable, or soft, phonons appear in phase transitions and when symmetry is broken, for example in Peierls transitions. By convention the soft phonon frequencies are plotted in phonon band structures, with a negative frequency $-\sqrt{|\omega_{m\mathbf{q}}^2|}$.

For the specific case of $\mathbf{q} = 0$ in an insulator, an additional non analytical term intervenes if the crystal is polar (i.e. composed of more than one type of atom). In this case, the displacement due to a phonon

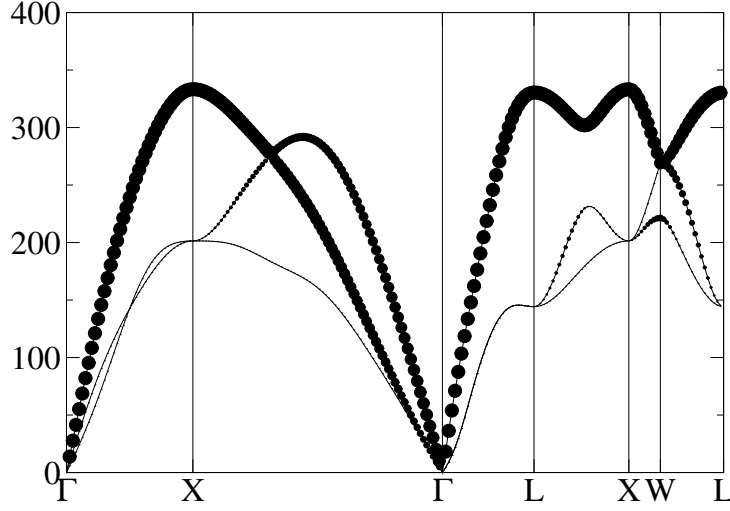


Figure 2.2: Phonon band structure of bulk FCC Al (in cm^{-1}). The symbol thickness indicates the longitudinal character of the mode.

can create a finite electrical polarization, and this field can then create forces on the atoms. We must then also calculate the perturbation of the system by an electric field.

In calculating $\partial^2 E / \partial R_{\kappa\alpha}^a \partial R_{\kappa'\beta}^b$, one can use a number of equivalent expressions[94] but in so doing one always needs to apply the first order Hamiltonian $H^{(1)}$ to the ground state wavefunctions $\psi_{\mathbf{k}n}^{(0)}$. Taking a matrix element with the wavefunctions $\psi_{\mathbf{k}+\mathbf{q}n'}^{(0)}$ gives a very important quantity related to the electron phonon interaction, which will be used in Sec. 2.3.

An example of a phonon band structure for aluminum is shown in Fig. 2.2

2.2.8 The ABINIT code

All of the work contained in this thesis was performed using the ABINIT package. ABINIT is a suite of DFT programs and utilities which calculates ground state properties, response functions (through DFPT), and even excited states (through the GW approximation or TDDFT) of systems. It employs plane wave basis sets and pseudopotentials from most of the popular families.

ABINIT is not the fastest code around, but it is one of the best featured and best maintained. The number of different features im-

plemented is greater than any other free code, and greater than many commercial or semi-commercial ones. This is achieved through the cooperative work of dozens of programmers, each one contributing as a function of his or her interests and research priorities. Since its inception, the project has grown substantially and added much in the way of documentation (the routines and other help is available on-line) and a set of coding rules are enforced on each contribution to the package.

One of the code's specificities is that it is free software. ABINIT was one of the first DFT implementations to be made available under the GNU general public license (GPL <http://www.gnu.org/copyleft/gpl.txt>), whereby the sources are and must remain freely accessible to anyone (open source). This is a revolution in the way science is carried out. Previously, either a program was commercialized and bought, and calculations carried out trusting to the good faith and competence of the programmers, or, more commonly, everyone implemented their own code and extensions had to be carried out on each code individually. Results and techniques were published, but the details of implementation and the dirty tricks used were often invisible. Over the duration of my thesis, many of the most widely used codes in electronic structure have become GPL or otherwise freely available. Researchers have much greater opportunities to use the most cutting edge developments in theory immediately for their own applications and problems, and can implement relatively simply any new design which they invent or read about.

2.3 Superconductivity

2.3.1 Introduction

Who says there's no free lunch? We are intuitively used to associate all actions with dissipative forces, friction and thermal effects. These consume energy, and many processes need a driving force to attain a “stable state”. But the basic equations for free particles never include these effects, and the theoretical physicist can live in a world where movement is eternal and momentum is conserved. Even for electrons in a crystal, the solutions of the independent-particle Schrödinger equations give rise to perfect quasiparticles with infinite lifetimes and infinitely precise energy levels. As such, once an electron is sent into a perfect crystal, it should continue in the same state $\Psi_{\mathbf{k}}$ forever. Being in materials science, we have developed some intuition, and we know that dissipative processes do exist; the most important are scattering with impurities and phonons. For some crystals the former can be almost entirely eliminated and/or neglected, but, for phonons, no physical system will ever be without them (at finite temperature). As a result, even ideal monocrystals have a finite electrical resistance, as the phonons interfere with the ideal electronic states, and “slow them down”. It comes about, however, that conflict is not the only solution, and that cooperative effects between phonons and electrons can also appear, in certain materials and in certain circumstances. In this case, the ideal zero resistivity reappears, no longer for perfect electrons, but for perfect pairs of electrons. This effect was called *supraconductivity* by H.K. Onnes, who discovered it in mercury[206], below a critical temperature of $T_c = 4.154$ Kelvin.

Since then many other materials have been discovered to possess the same property: aluminum, lead, niobium, and other elemental and alloyed metals. The infinite conductance of these systems has important consequences. In particular, the perfect superconductor can not support a magnetic field inside itself. This is known as the Meissner effect[185]. The magnetic field is expelled to a thin layer at the surface of the material, as first explained by London and London[170]. Bardeen showed that this is consistent with the existence of a gap in the energy spectrum[14]. In some cases, the magnetic field is expelled progressively from the material (type II superconductors), and subsists in flux channels through a fraction of the bulk. This difference was explained by the phenomenological Ginzburg-Landau model[86, 1]. The external magnetic field can be kept out up to a critical field H_c , which then destroys the superconducting order and restores normal conductance. With decreasing temperature H_c increases, following a law close

to $\sqrt{1 - (T/T_c)^2}$. The influence of phonons in superconductivity was proved by the isotope effect: changing only the isotopic mass of one species (and therefore the phonon frequencies) changes the critical temperature accordingly[180, 230] (decreasing the mass increases the phonon frequencies and T_c).

In 1987, a new revolution occurred with the appearance of high critical temperature superconductors[21]. These are ceramics composed of layers of copper oxide (cuprates), mixed with Ba, Y, Bi, Sr, Ca, or other elements (with the basic structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$). By varying the species, and especially the oxygen content away from stoichiometry (doping), T_c can be increased further. As T_c went above the temperature of liquid nitrogen (and up to 138 Kelvin at the time of writing), it became economically feasible to use the cuprates for applications, but they are difficult to shape, very brittle, and have limited current densities, which has impeded their widespread use. The mechanism behind superconductivity in cuprates is still not clear. The pairing of electrons may happen due to a large-scale phonon effect, electron-electron interactions (correlation), or yet other mechanisms. There appears to be a kind of isotope effect in some systems[237, 107], but not in others[286].

Several exceptional systems with intermediate values of T_c have been discovered in the past decade. The most prominent are MgB_2 , a fairly standard material which becomes superconducting at 39 K[198], and alkali-doped fullerene solids (see Sec. 3.7). Both appear to use the normal mechanism of pairing through phonons. The anisotropic but phonon-based nature of the superconductivity was very nicely demonstrated in the theoretical calculations of Ref. [43], which even required anharmonic phonon terms to justify the full T_c .

In the following we outline the different microscopic theories which were developed to account for standard (phonon-based) superconductivity. The sections are summaries of the references cited and the standard review for Eliashberg theory, which is the book chapter by Allen and Mitrović in Solid State Physics[3]. Another complete reference is the book by Grimvall[100].

2.3.2 Pairing interaction models

The importance of phonons in the mechanism of superconductivity had been sniffed out by Frölich[82]. He estimated the effect of the emission and re-absorption of virtual phonons on the energy of a system of free electrons, and concluded that there can be a net interaction between electrons, which is attractive and gives a new type of statistics, slightly perturbed from the normal state Fermi statistics. In the first Frölich

model, electrons tend to leave the Fermi surface and concentrate in the same direction in k -space (which would give rise to a current without the presence of an electric field), or, if spherical symmetry is preserved, to concentrate in shells around the Fermi sphere. A gap appears inside the spectrum of excitations of electrons (which is not the case for a normal metal near the FS). The isotope effect was predicted from the dependency of the interaction energy on the atomic mass.

2.3.3 Bardeen-Cooper-Schrieffer theory

A much more complete theory of superconducting phenomena was put forward by Bardeen, Cooper, and Schrieffer in 1958[15]. They include both the virtual phonon processes and Coulomb interactions in their model. The two effects compete to respectively bind and separate a pair of electrons. Two years earlier Cooper had postulated the importance of paired electrons (Cooper pairs) in superconductivity[50], the electrons having opposite spin and momentum. Pairing electrons leads to a lower total energy, and the excitation spectrum of the resulting system possesses a gap, whether to excite a single electron or a pair. All the features of a superconductor are reproduced by the BCS theory, but it remains a qualitative theory giving universal behaviors. In particular, the variation of H_c and of the gap with temperature are well reproduced for all the superconductors which were known at the time. After the modification of the energy levels, the statistics remain those of fermions. The ratio of specific heat to T_c is also predicted in agreement with experiment.

2.3.4 Nambu and Gor'kov

The BCS theory was cast in a more general Green's function form by Nambu[199] and Gor'kov[96]. Nambu corrected the gauge invariance of the theory, and used a two component notation (one each for creation and annihilation of an electron) and the Pauli matrices to simplify notations. The standard results are arrived at through a Hartree-Fock like mean field approximation. The expectation values of creators and annihilators of Cooper pairs are zero in the normal state, but become finite once we go below T_c . The corresponding "anomalous" Green's functions $\langle T_\tau c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow} \rangle$ and $\langle T_\tau c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger \rangle$ were introduced by Gor'kov to describe the evolution of the pairs, in a finite-temperature Green's function formalism (c and $c^\dagger$ annihilate and create individual electrons). In this framework, the free-particle Green's functions are defined for times τ in the interval $-\beta < \tau < \beta$ ($\beta = 1/T$), and have a form of periodicity,

such that their Fourier transforms are discrete, with components for the uneven Matsubara frequencies $i\omega_n$ where $\omega_n = \pi T(2n+1)$. The electron-phonon interaction, however, was still modeled in a very simplistic way, as a time-independent scalar multiplied by the creation/annihilation of a Cooper pair $c_{-\mathbf{k}'\downarrow}^\dagger c_{\mathbf{k}'\uparrow}^\dagger c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow}$.

2.3.5 Migdal theory for the normal state

The electron-phonon interaction was treated more cleanly by Migdal[193] for the normal state of conduction. The electrons are presumed to have known band structures and eigenstates, and the phonons are presumed known and “realistic”. This is a fudge, in the sense that we should be using bare unscreened phonons, but these are very bad and far from experiment[3]. All practical calculations of phonons include preliminary electronic screening, and it is at this condition that the electron-phonon coupling can be considered a small perturbation. The form of the coupling is taken from Frölich:

$$\mathcal{H}_{\text{ep}} = \sum_{\mathbf{k}\mathbf{q}} \langle \mathbf{k} + \mathbf{q} | \nabla V | \mathbf{k} \rangle \cdot \mathbf{d}_{\mathbf{q}} c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}}, \quad (2.13)$$

where $\mathbf{d}_{\mathbf{q}}$ is the displacement vector operator for the phonons

$$\mathbf{d}_{\mathbf{q}} = \sum_j \left(\frac{\hbar}{2NM\omega_{\mathbf{q}j}} \right) \mathbf{u}_{\mathbf{q}j} (a_{\mathbf{q}j} + a_{-\mathbf{q}j}^\dagger), \quad (2.14)$$

$a_{\mathbf{q}j}$ and $a_{\mathbf{q}j}^\dagger$ are the annihilation and creation operators and $\mathbf{u}_{\mathbf{q}j}$ the polarization vector, for a phonon of frequency $\omega_{\mathbf{q}j}$, wavevector $\mathbf{q}$ and mode j . ∇V is a perturbed potential which scatters the electrons, and $\mathbf{d}_{\mathbf{q}} \cdot \nabla V$ is known as the deformation potential. The relation between the perturbation and the electronic screening is complex (see the comments on the Coulomb interaction and on Ref. [279] below). As the phonons already contain screening, $\mathcal{H}_{\text{ep}}$ is only destined to calculate the electronic Σ .

Migdal showed that very good results are obtained by including only the lowest order term in the expansion of the electron self-energy Σ , viz. the emission and re-absorption of a phonon by a single electron. The approximation is justified by the fact that higher-order terms (those which are not included in the self-consistent solution of the first order Σ) are smaller by a factor $N_F\omega_D$, where ω_D is the Debye frequency. This is known as the Migdal approximation or theorem, and carries over into superconductivity. The approximation omits “crossed” processes, where a second phonon is emitted, and is re-absorbed after the first.

These can become important for small $\mathbf{q}$ or if there is nesting in the FS, i.e. portions of the surface which are planar and parallel (see also Ref. [98, 223, 99, 35]).

Here we define the electron-phonon spectral function $\alpha^2 F$, related to the phonon spectral function (and hence to the phonon DOS traditionally called F):

$$\alpha^2 F(\mathbf{k}, \mathbf{k}', \Omega) = N_F \sum_j |g_{\mathbf{k}, \mathbf{k}'}^{\mathbf{q}j}|^2 \delta(\Omega - \omega_{\mathbf{k}-\mathbf{k}'j}), \quad (2.15)$$

in which

$$g_{\mathbf{k}, \mathbf{k}'}^{\mathbf{q}j} = \frac{\hbar}{\sqrt{2M\omega_{\mathbf{q}j}}} \mathbf{u}_{\mathbf{q}j} \cdot \langle \mathbf{k} | \nabla V | \mathbf{k}' \rangle, \quad (2.16)$$

where $\mathbf{k} = \mathbf{k}' + \mathbf{q}$. The sums over $\mathbf{k}$ are integrals over the Fermi surface, and there is presumed to be only one atom per unit cell, of mass M . The term with $\mathbf{u}_{\mathbf{q}j}$ gives phonon mode-specific contributions, which are then summed. Two partial averages of $\alpha^2 F(\mathbf{k}, \mathbf{k}', \Omega)$ are

$$\alpha^2 F(\mathbf{k}, \Omega) = N_F \sum_{j, \mathbf{k}'} |g_{\mathbf{k}, \mathbf{k}'}^{\mathbf{q}j}|^2 \delta(\Omega - \omega_{\mathbf{k}-\mathbf{k}'j}) \delta(\epsilon_{\mathbf{k}'}), \quad (2.17)$$

and

$$\alpha^2 F(\Omega) = N_F \sum_{j, \mathbf{k}, \mathbf{k}'} |g_{\mathbf{k}, \mathbf{k}'}^{\mathbf{q}j}|^2 \delta(\Omega - \omega_{\mathbf{k}-\mathbf{k}'j}) \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}'}), \quad (2.18)$$

where the $\delta(\epsilon_{\mathbf{k}})$ functions select states on the Fermi surface. These quantities describe scattering from $\mathbf{k}$ to any point on the FS, or from and to any point on the FS. The strength of the scattering of electrons on the FS is quantified by $\alpha^2 F(\mathbf{k}, \mathbf{k}', \Omega)$.

Examining the low frequency behavior of the full Green's function gives a renormalization of the quasi-particle energies by a factor $1/(1 + \lambda)$, or of the effective mass by a factor $(1 + \lambda)$. The term $\lambda = -\partial \Sigma / \partial \omega$ is known as the mass enhancement factor, and for low temperatures:

$$\lambda_{\mathbf{k}\mathbf{k}'} = 2 \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2 F(\mathbf{k}, \mathbf{k}', \Omega), \quad (2.19)$$

i.e. λ is simply the first inverse moment of the electron-phonon spectral function. It too has useful FS averages

$$\lambda_{\mathbf{k}} = 2 \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2 F(\mathbf{k}, \Omega), \quad (2.20)$$

and

$$\lambda = 2 \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2 F(\Omega). \quad (2.21)$$

Anticipating Sec. 2.3.6.2 we add another form of λ which incorporates the free phonon propagator

$$\lambda_\nu(T) = \int_0^\infty d\Omega \alpha^2 F(\Omega) \frac{2\Omega}{(2\pi T\nu)^2 + \Omega^2}. \quad (2.22)$$

Note that the last definition uses the boson Matsubara frequencies, because we will be considering λ at differences of the fermion frequencies.

All of these functions, and the self-energy and Green's functions, are calculated on the Fermi surface. Analytical calculations decompose them on a complete basis of functions over the Fermi surface[2], then revert to the $\mathbf{k}, \mathbf{k}'$ basis for numerical implementations. For the simplest case (a sphere) the basis functions are spherical harmonics.

2.3.6 Eliashberg theory

Eliashberg[71] extended Migdal's theory to the superconducting state, including anomalous propagators for pair creation and annihilation. The theory includes the realistic phonon coupling of Eq. 2.13, the Coulomb interaction is formally included exactly, as is the diagram which is first order in the phonon propagator. Using the Nambu notation, the Green's function and the different components of the self-energy become 2-matrices, and are decomposed on the Pauli matrices $\hat{\tau}_i$, $i = 0, 1, 2, 3$. Notations and details can be found in Ref. [3].

$$\hat{\Sigma}_{\mathbf{k}, i\omega_n} = i\omega_n(1 - Z_{\mathbf{k}, i\omega_n})\hat{\tau}_0 + \chi_{\mathbf{k}, i\omega_n}\hat{\tau}_3 + \phi_{\mathbf{k}, i\omega_n}\hat{\tau}_1 + \bar{\phi}_{\mathbf{k}, i\omega_n}\hat{\tau}_2, \quad (2.23)$$

where Z , χ and the ϕ are unknown functions, which formally gives the Green's function

$$\begin{aligned} \hat{G}_{\mathbf{k}, i\omega_n} &= [i\omega_n Z_{\mathbf{k}, i\omega_n} \hat{\tau}_0 + (\epsilon_{\mathbf{k}} + \chi_{\mathbf{k}, i\omega_n}) \hat{\tau}_3 + \phi_{\mathbf{k}, i\omega_n} \hat{\tau}_1 + \bar{\phi}_{\mathbf{k}, i\omega_n} \hat{\tau}_2] / \det(\hat{G}^{-1}) \\ \det(\hat{G}^{-1}) &= (i\omega_n Z)^2 - (\epsilon_{\mathbf{k}} + \chi)^2 - \phi^2 - \bar{\phi}^2. \end{aligned} \quad (2.24)$$

The components of the self-energy in Eliashberg theory are the electron-phonon part Σ_{ep} , the Fock part Σ_{F} , and the screened Coulomb part Σ_{SC} . As it is presumed that the calculations start with band energies from Hartree-Fock or other band theories, Σ_{F} and Σ_{SC} should already be accounted for the normal state. The terms included here are therefore the differences in Σ_{F} and Σ_{SC} between the normal and the superconducting states.

Using these diagrams for the expansion of the self-energy, we obtain formulations for the components of Σ as functions of $\hat{G}$ and the spectral functions. Equating the terms for each $\hat{\tau}_i$ gives a set of equations for determining Σ self-consistently. The off-diagonal (anomalous) parts of $\hat{G}$ come from the terms in $\hat{\tau}_{1,2}$, ϕ and $\bar{\phi}$. If a solution exists with $\phi \neq 0$ then the system becomes superconducting. This condition defines T_c as the maximum T for which $\phi \neq 0$ can be found.

2.3.6.1 Approximation of Coulomb effects

The standard dirty treatment of the Coulomb terms in Σ for the Eliashberg theory is described in Ref. [3] with great detail and criticism. The important diagonal parts of $\Sigma_F + \Sigma_{SC}$ are considered to be incorporated in the band structure (for the normal state), and a very simple model is used for the energy dependence of the electronic DOS and the deformation potential matrix elements. This precludes the determination of Coulomb enhancement of T_c with this theory (which is in particular a possibility in the cuprates). The full Coulomb correction to Σ reduces to a single scalar μ^* (which must be fitted).

2.3.6.2 Anisotropic Eliashberg equations

If most of the energy dependencies are neglected (being very close to the FS and supposing the quantities involved do not vary too quickly with energy), only two unknown functions are left to be determined: $Z_{\mathbf{k},i\omega_n}$, which is the coefficient of $\hat{\tau}_0$ in $\hat{G}$ (Eq. 2.24), and $\Delta_{\mathbf{k},n} = \phi_{\mathbf{k},i\omega_n}/Z_{\mathbf{k},i\omega_n}$, which turns out to be the gap in the quasi-particle energy spectrum on the real axis. The final anisotropic equations in $\mathbf{k}$ -space and imaginary frequency are

$$Z_{\mathbf{k},i\omega_n} = 1 + \frac{\pi T}{|\omega_n|} \sum_{\mathbf{k}'n'}^{|\omega_{n'}| < \omega_c} \frac{\delta(\epsilon_{\mathbf{k}'})}{N_F} \lambda_{\mathbf{k},\mathbf{k}';n-n'} s_n s_{n'} \quad (2.25)$$

$$Z_{\mathbf{k},i\omega_n} \Delta_{\mathbf{k},n} = \pi T \sum_{\mathbf{k}'n'}^{|\omega_{n'}| < \omega_c} \frac{\delta(\epsilon_{\mathbf{k}'})}{N_F |\omega_{n'}|} (\lambda_{\mathbf{k},\mathbf{k}';n-n'} - \mu^*) \Delta_{\mathbf{k}',n'}. \quad (2.26)$$

$\epsilon_{\mathbf{k}}$ are the band energies with respect to the Fermi level, the $\delta(\epsilon_{\mathbf{k}})$ select states on the FS, s_n is the sign of ω_n , n runs over the Matsubara frequencies ω_n , and ω_c is a cutoff, on the order of $5\omega_D$.

As mentioned at the end of Sec. 2.3.5, all quantities have angular dependencies, and in particular $\Delta_{\mathbf{k}',n'}$, which gives, in the simplest cases, s-type, then p-type and d-type superconductivity, for which the spin part of the wavefunctions also adoption singlet, triplet, etc... characters.

2.3.6.3 Isotropic Eliashberg theory

Averaging all quantities over the Fermi surface gives equations which depend only on energy

$$Z_{i\omega_n} = 1 + \frac{1}{|2n+1|} \sum_{n'}^{| \omega_{n'} | < \omega_c} \lambda_{n-n'} s_n s_{n'} \quad (2.27)$$

$$Z_{i\omega_n} \Delta_n = \sum_{n'}^{| \omega_{n'} | < \omega_c} \frac{1}{|2n'+1|} (\lambda_{n-n'} - \mu^*) \Delta_{n'}. \quad (2.28)$$

This procedure is valid for simple metals (which are usually cubic and free-electron like anyways), but fails miserably for anisotropic cases like MgB₂[43]. Staying at first order, the isotropic equations give a linear matrix equation for Δ_n

$$\Delta_n = \sum_{n'}^{| \omega_{n'} | < \omega_c} \frac{1}{|2n'+1|} S_{n,n'} \Delta_{n'}, \quad (2.29)$$

with

$$S_{n,n'} = \lambda_{n-n'} - \mu^* - \delta_{nn'} \sum_{n''}^{| \omega_{n''} | < \omega_c} \lambda_{n-n''} s_n s_{n''}. \quad (2.30)$$

These equations are solved for T_c , but do not give the interesting value of the gap for real frequencies (only for imaginary $i\omega_n$). The self-energies can be analytically continued to the real axis[175], but the equations are much more complex. The most famous solution of the gap equations in real space is that of McMillan[183]. He also gave an approximate formula for T_c , which was later generalized to:

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right), \quad (2.31)$$

where

$$\omega_{\log} = \exp \left(\frac{2}{\lambda} \int_0^\infty d\Omega \alpha^2 F(\Omega) \frac{\ln(\Omega)}{\Omega} \right). \quad (2.32)$$

2.3.7 Superconductivity in lower dimensions

There has been a large quantity of theoretical work on superconductivity in lower (1 or 2) dimensional solids, using, for example, the renormalization group method[208], and/or model interactions[37, 13]. General

consensus is that the smaller screening effects of the Coulomb potential in these systems will increase the repulsion between electrons and limit superconductivity (see Ref. [70] for example). There are however other issues, related to the finite size of the system. The phonons will change frequency, although this can enhance or suppress T_c , depending. The granular and defectuous nature of films and wires becomes very important. Defects scatter electrons and will limit the coherence of Cooper pairs. Paramagnetic impurities are even worse, as they immediately suppress spin coherence, and kill superconductivity. One must distinguish several regimes as a function of size. In the superconducting phase the coherence length of Cooper pairs can be formally larger than the sample dimensions, but the electrical conductance is usually still 3D. Therefore experiments are often in crossover regimes between 3D or 2D and 1D. The validity of the Migdal approximation in 1D is not obvious - in fact it is probably false, and some work has been done to go beyond the first-order perturbational expansion in the Debye frequency e.g. Ref. [98, 223, 99]. The presence of peaks in the DOS (in particular due to Van Hove singularities in 1D) restricts the states which will participate in superconductivity and can also invalidate Migdal's approximation[35]. Finally, quantum confinement makes the band energies discrete in nanoscopic systems. Anderson[5] showed that once the number of electrons is too small (≤ 1000), and the level spacing becomes comparable to the superconducting gap, the system no longer supports a superconducting state.

Experiments on films have shown a number of finite size effects. Strongin, in Ref. [257], compared Al, Sn, Pb, and Nb thin films. He showed that for weak coupling T_c goes up then down with decreasing size (and increasing disorder), whereas for strong coupling superconductors T_c only decreases. At a limiting thickness parts of the film become insulating, and electrons must tunnel between the superconducting islands, which increases resistance when T is lowered. For the thinnest films disorder becomes important and destroys superconductivity. The most important factors in granular systems are laid out theoretically in Ref. [126], and a generic critical size (film thickness) of 30 Å is established. There is competition between grain size, inter-grain coupling, and Coulomb charging effects as to which will destroy superconductivity first.

Experimental work on true 1D systems is still very rare. Most nanowires have cross-sections containing thousands of atoms (and hence conduction channels). Two exceptions are carbon nanotubes, whose structure can be remarkably pristine, and mono-atomic wires. Small diameter carbon nanotubes were recently found to be superconduct-

ing when grown in zeolite pores[260]. The most popular theories predict the existence of a Luttinger liquid in carbon nanotubes at low temperatures[69, 131] (as should happen for 1D systems), and some experimental results support this hypothesis[28, 289]. Other studies have considered Hubbard[13] or tight-binding and renormalization group models[150]. CNT also become superconducting when they are synthesized in bundles[136]. This was explained as arising from the superior screening of the Coulomb forces in this (nearly) 3D environment[90, 91].

The limiting case of monoatomic nanowires of metal has only been realized with gold[202, 288]. Larger wires or tubes of Au[138] and Pt[209] have also been purportedly seen under TEM, but are not expected to have superconducting properties, as the bulk noble metals have no perceptible superconductivity.

Superconductivity in nanowires has been studied for a number of elements such as Pb[191, 284], Sn[274, 190], and Ru[282]. In all of these examples, superconductivity occurs, with the bulk T_c , until sizes around 3 nm are reached. Effects are similar to those in films. Here again, once systems are sufficiently small to be interesting and truly 1D, the amount of disorder is usually overwhelming and superconductivity disappears. Recent work has concentrated on the fluctuation of the superconducting order parameter when strong currents are passed through the wire. Starting from the Ginzburg-Landau model, different properties of the order parameter amplitude and phase are considered. In particular, phase slip centers (PSC)[167] can appear, where the amplitude goes to zero and the phase can change by a multiple of 2π . In this way a resistive quasi-stationary state is maintained, the current building up a phase difference, which then slips (dissipation) back to a lower value. The phase slips are either thermally activated[153, 182] or result from the tunneling through a finite barrier between states with different values of the phase[87]. Phase slips are dynamical phenomena under transport conditions, and are far beyond what can presently be calculated in DFT.

We will be considering 1D systems in a very coarse manner: the same formalism will be used as in the 3D case. This has two main implications, the first good and the second not so good. Firstly, since our basic calculation of the electrons and phonons comes from self-consistent DFT, the screening should be realistic, whatever the geometry we choose (1D or bulk). However, the simplistic treatment of the Coulomb interaction used in Eliashberg theory remains, and its development should in principle be re-evaluated and re-derived explicitly for 1D systems. Using the μ^* parameter for the bulk (as we shall) is a further approximation, but if μ^* were fitted in each case no comparative conclusions could be drawn.

2.3.8 Discussion of diabatic and Coulomb effects

The diagrammatic processes of superconductivity involve energy differences for electrons ($\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}$) and phonons ($\omega_{\mathbf{q}j}$) which are of the same order. As such, the processes are necessarily beyond the Born-Oppenheimer approximation. Most calculations of the electron-phonon coupling, and in particular most in DFT and ours as well (see below) nevertheless calculate the “non-interacting” phonons and electrons in a BO framework, then consider their coupling using an additional “perturbing” Hamiltonian. Two recent advances in the ab initio study of superconductivity, due to Van Leeuwen[279] and the Gross group[79] go beyond BO, and start from a very general formalism where the nuclear positions stay quantum parameters, and are expanded perturbatively around the phonon modes.

The subsequent approximations and the derivation of density functionals are very complicated, in particular because the theories also aim to fix a second problem with standard implementations: the Coulomb interaction. The treatment of the Coulomb effects (that is, the difference between the normal and superconducting state Coulomb effects) is primitive in Eliashberg theory, and is unjustifiable in any system beyond simple free electron metals. It supposes that good quasiparticle energies for the bare electrons are present, that the superconducting correction to these is negligible, and that the energy dependence of the DOS and Coulomb matrix elements is (almost) trivial. The general problem of dealing with electronic responses is very difficult, and their treatment in standard DFT may not actually be sufficiently good for our purposes. Electronic screening, exchange, and correlation should be present, and retardation effects can become very important, which implies using frequency-dependent kernels and time-dependent theories. Van Leeuwen[279] pointed out that electronic screening has already been carried out in the calculation of the phonon frequencies, and therefore the standard theory somehow double counts the screening in the full Hamiltonian. Finally, let us note that the fact that only the *differences* in Σ_F and Σ_{SC} appear in the theory suggests that good approximations could come from calculations that are inherently not very good at including exact self-energy effects for bare electrons.

The explicit treatment of individual bands in recent theories will also allow for much greater precision in complex systems, where bands will not have the same character, localization, or behavior.

2.3.9 Superconductivity in DFT

Applications of density functional theory to superconductivity are of essentially two types: those that consider the electron-phonon coupling as a perturbation, and treat it as a post-processing step after a calculation of normal phonons by normal DFT, and those that explicitly model the superconducting electrons, using an analog of the two component fluid introduced qualitatively by Gorter and Casimir[97] at the beginning of superconductivity theory.

2.3.9.1 The electron-phonon coupling

The first calculations of the electron-phonon coupling using DFT methods were carried out almost 20 years ago by the Cohen/Louie group in Berkeley[55, 151] using frozen phonon methods. The extension to DFPT linear response calculations was done by Savrasov[242] for LMTO methods and Liu[168]. Our implementation is fundamentally similar to the latter two, and we describe some technical details in the following. The coding implementation, with names of subroutines and a flowchart through them, is presented in Sec. 5.2.

The simplest way to treat the coupling between electrons and phonons “in DFT” is to take the Eliashberg equations and ask which elements we can calculate ab initio. The answer is simple: almost all the individual components. The electronic states ($\psi_{\mathbf{k}i}$ and $\epsilon_{\mathbf{k}i}$), the phonons ($\omega_{\mathbf{q}j}$ and $\mathbf{u}_{\mathbf{q}j}$), and the matrix elements of the perturbed potential ($g_{\mathbf{k},\mathbf{k}'}^j$). What we actually calculate for the latter (see Sec. 2.2.7.2) are the derivatives of the total energy with respect to displacements of one atom in one reduced direction, for a given $\mathbf{q}$ vector

$$\langle \psi_{\mathbf{k}i} | \frac{\partial \mathcal{H}}{\partial R_\alpha} | \psi_{\mathbf{k}'i'} \rangle, \quad (2.33)$$

where α runs over the $3N_{\text{atom}}$ reduced directions for all atoms.

The generalization of Eq. 2.16 for several atoms I in the unit cell and several electronic bands i is:

$$g_{\mathbf{k}i,\mathbf{k}'i'}^{\mathbf{q}j} = \frac{\hbar}{\sqrt{2\omega_{\mathbf{q}j}}} \sum_{\alpha} d_{\mathbf{q}j,\alpha} \bar{g}_{\mathbf{k}i,\mathbf{k}'i'}^{\mathbf{q}\alpha}, \quad (2.34)$$

where

$$\bar{g}_{\mathbf{k}i,\mathbf{k}'i'}^{\mathbf{q}\alpha} = \langle \psi_{\mathbf{k}i} | \frac{\partial \mathcal{H}}{\partial R_\alpha} | \psi_{\mathbf{k}'i'} \rangle, \quad (2.35)$$

and

$$d_{\mathbf{q}j,\alpha} = \frac{1}{\sqrt{M_{I(\alpha)}}} u_{\mathbf{q}j,\alpha}. \quad (2.36)$$

The sum over α runs to $3N_{\text{atom}}$, $I(\cdot) = 1, 1, 1, 2, 2, 2, \dots, N_{\text{atom}}, N_{\text{atom}}, N_{\text{atom}}$ runs over the atoms, and $M_{I(\alpha)}$ is the mass of the atom $I(\alpha)$.

The dependency in the electronic bands is still present at this stage (a full $n_{\text{band}} \times n_{\text{band}}$ matrix is calculated). Weights $w_{\mathbf{k}i}$ can be given to the different states based on their distance from the Fermi surface. The simplest scheme replaces the Dirac function in Eq. 2.17 by gaussians $\delta(\epsilon_{\mathbf{k}i} - E_F)$ of fixed width. Another possibility is to interpolate the $g_{\mathbf{k}i, \mathbf{k}'i'}$ linearly, by attributing weights from the tetrahedron method[27]. Both methods have been tried, and are compared in Sec. 5.3.2.1.

The expression of $\bar{g}_{\mathbf{k}i, \mathbf{k}'i'}^{\mathbf{q}\alpha}$ contains a gauge freedom, due to the phase in the wavefunctions. This phase is eliminated in $\alpha^2 F$ by taking the norm squared of the matrix element. However, if symmetry operations are used to complete the $\bar{g}_{\mathbf{k}i, \mathbf{k}'i'}^{\mathbf{q}\alpha}$, we will end up with sums like $\bar{g}_{\mathbf{k}i, \mathbf{k}'i'}^{\mathbf{q}\alpha} + \bar{g}_{S^{-1}\mathbf{k}''i, S^{-1}\mathbf{k}'''i'}^{S^{-1}\mathbf{q}\beta}$. In this case, fixing the gauge is important, as the relative phase of $\psi_{\mathbf{k}}$ and $\psi_{S^{-1}\mathbf{k}''}$ affects the result. In order to avoid this, we will treat the gauge-invariant matrix quantity

$$\bar{\gamma}_{\mathbf{k}i, \mathbf{k}'i'}^{\alpha\beta} = \left[\bar{g}_{\mathbf{k}i, \mathbf{k}'i'}^{\mathbf{q}\alpha} \right]^\dagger \bar{g}_{\mathbf{k}i, \mathbf{k}'i'}^{\mathbf{q}\beta}, \quad (2.37)$$

where α, β run over the $3N_{\text{atom}}$ reduced directions for all atoms. This technique is used in the PWSCF code as well. The $\bar{\gamma}_{\mathbf{k}i, \mathbf{k}'i'}$ matrix has the same symmetries as the dynamical matrix, so it can be symmetrized using the small group which preserves the $\mathbf{q}$ vector.

Writing the phonon displacement vector $\mathbf{d}_{\mathbf{q}j}$ in the reduced basis gives

$$\gamma_{\mathbf{k}i, \mathbf{k}'i'}^j = \frac{1}{2\omega_{\mathbf{q}j}} \sum_{\alpha\beta} d_{\mathbf{q}j, \alpha}^\dagger \bar{\gamma}_{\mathbf{k}i, \mathbf{k}'i'}^{\alpha\beta} d_{\mathbf{q}j, \beta}, \quad (2.38)$$

which only depends on the phonon mode j . In later steps we will need to interpolate the γ matrices in reciprocal space. The phonon polarization vectors are an inappropriate basis to do this, as they are not aligned with each other for different $\mathbf{q}$ points. The natural basis for interpolation is that of Cartesian directions and unit cell atoms:

$$\gamma_{\mathbf{k}i, \mathbf{k}'i'}^{ab} = \sum_j u_{\mathbf{q}j, a} \gamma_{\mathbf{k}i, \mathbf{k}'i'}^j u_{\mathbf{q}j, b}^\dagger, \quad (2.39)$$

where a, b now run over the $3N_{\text{atom}}$ Cartesian directions for all atoms. These steps are pedantically expounded to make clear the different bases used for the representation of the γ . The two quantities written $\bar{\gamma}_{\mathbf{k}i, \mathbf{k}'i'}^{\alpha\beta}$ and $\gamma_{\mathbf{k}i, \mathbf{k}'i'}^{ab}$ are related by a rotation matrix from reduced to Cartesian coordinates, $1/M$ factors, and the $1/\sqrt{2\omega_{\mathbf{q}j}}$.

The γ matrix at an equivalent qpoint $\mathbf{q}' = \hat{S}\mathbf{q}$ can be deduced from:

$$\gamma_{\mathbf{k}i, \mathbf{k}+\hat{S}\mathbf{q}i'}^{ab} = \sum_{ml} (s^{am})^\dagger \gamma_{\hat{S}^{-1}\mathbf{k}i, \hat{S}^{-1}\mathbf{k}+\mathbf{q}i'}^{ml} s^{lb}, \quad (2.40)$$

where

$$s^{lb} = \sum_{\alpha\beta} R^{l\alpha} \hat{S}^{\alpha\beta} G^{\beta b} \quad (2.41)$$

and $\hat{S}$ is the matrix (in reduced coordinates) for a symop which brings $\mathbf{q}$ onto $\mathbf{q}'$, and R and G are the matrices of unit cell vectors for real and reciprocal space respectively.

Summing over bands gives

$$\gamma_{\mathbf{k}, \mathbf{k}'}^{ab} = \sum_{ii'} \gamma_{\mathbf{k}i, \mathbf{k}'i'}^{ab} w_{\mathbf{k}i} w_{\mathbf{k}'i'}, \quad (2.42)$$

and summing $\gamma_{\mathbf{k}, \mathbf{k}'}^{ab}$ once over the FS (remembering $\mathbf{k}' = \mathbf{k} + \mathbf{q}$) and diagonalizing the (a, b) matrix gives the phonon linewidths $\gamma_{\mathbf{q}j}$.

To calculate the electron-phonon spectral function Eq. 2.18 we need to perform a full sum over the BZ for $\mathbf{q}$. Most phonon calculations use a dense $\mathbf{k}$ mesh, but a fairly sparse $\mathbf{q}$ mesh. The $\mathbf{q}$ dependence of the phonons is usually very simple to model, and a Fourier interpolation gives very precise results throughout the BZ starting from a small number of $\mathbf{q}$. This turns out to be true for electron-phonon quantities as well, and we use this interpolation to calculate $\gamma_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{ab}$ for a finer mesh of $\mathbf{q}$ points, identical to that of the $\mathbf{k}$ points (though necessarily centered on Γ since the $\mathbf{q}$ points are differences of $\mathbf{k}$ points). The $\gamma_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{ab}$ are inverse Fourier transformed to real space with respect to $\mathbf{q}$, then Fourier transformed back to $\mathbf{q}$ points on the $\mathbf{k}$ point grid. The values at any $\mathbf{q}$ points could be calculated, but would be more complicated to use, since we do not have the band energies for $\mathbf{k}' = \mathbf{k} + \mathbf{q}$.

From the spectral function, one can calculate the coupling strength λ (Eq. 2.21), then ω_{log} (Eq. 2.32) and the McMillan T_c Eq. 2.31.

Better, we can calculate the matrix $S_{n, n'}$ (Eq. 2.30) for the 1D energy-only Eliashberg equation:

$$S_{n, n'} = \lambda_{n-n'} - \mu^* - \delta_{nn'} \sum_{n''} \lambda_{n-n''} S_{n, n''}. \quad (2.43)$$

The matrix $S_{n, n'}$ is Hermitian when written in this form, and it enters Eq. 2.29 for the gap Δ_n :

$$\Delta_n = \sum_{n'}^{|w_{n'}| < w_c} \frac{1}{|2n' + 1|} S_{n, n'} \Delta_{n'}, \quad (2.44)$$

where we must define the inner product as $\sum_{n'} 1/|2n' + 1|$ (which is a valid inner product since the fraction is positive). The existence of superconductivity translates to $S_{n,n'}$ having a maximum eigenvalue of 1. Therefore, we will vary T , which enters into the $\lambda_{n-n'}$ and the sum limit $|\omega_{n'}| < \omega_c$, until the eigenvalue condition is satisfied.

Two methods can be employed. Either straightforward diagonalization, but this can become heavy for large matrices (typically for weak coupling superconductors), or iteratively applying $S_{n,n'}$ to a trial vector in Matsubara-frequency space. The latter procedure rapidly filters out the eigenvector we want, and we can then deduce eigenvalue from the evolution of the norm of the trial vector (this is also described in, for example, Ref. [3] and [174]).

2.3.9.2 Multi-component SC-DFT

Another way of considering the problem of superconductivity in DFT is to model two densities[204], one each for the normal and superconducting electrons. This has the advantage of treating the superconducting electrons explicitly, but still requires a hypothesis about the form of the pairing interaction (see also Ref. [174]), and treats the phonons quite simplistically. Very recently, a further extension of the multi-component DFT formalism was developed to include formally the density matrix Γ for the nuclei as well. Kreibich and Gross showed the importance of choosing a good coordinate frame for the later expansion of the Hamiltonian, which in its primitive form has full rotational and translational invariance, and does not reflect the structure of the system (molecule or solid)[143]. The development of accurate exchange-correlation functionals for the three density system has been ongoing and appears to be coming to fruition[78, 79]. This fully ab initio method will render obsolete calculations based on Eliashberg-like models with approximate electron interactions, but is still very experimental and heavy, and contains many approximations of its own.

Van Leeuwen's formalism[279] is even more general, extending the work of Hedin and Lundqvist[116] from the many-body perturbation theory side, to obtain diagrammatic expansions of the self energies. He arrives at a full set of coupled equations for the electrons and nuclei, including diagrams and vertex functions for the electronic and ionic screening of the electrons. This framework is used to evaluate and improve on various models for the electron-phonon coupling, but has not yet produced applications to real systems.

Chapter 3

An introduction to nanotubes

Organic chemistry is the chemistry of carbon compounds. Biochemistry is the study of carbon compounds that crawl

Mike Adams

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3.1 Carbon forms and definitions

Carbon is a, if not the, primary element in human life. It is hard to choose between carbon and oxygen, hydrogen, or nitrogen, but it is safe to say carbon is a central building block of organic chemistry, chemistry, but also physics and engineering. The introduction of carbon into iron to make steel was one of the pivotal points in human technological evolution. Probably the main reason for carbon's omnipresence is its polymorphism: like no other element the carbon atom's electronic structure is perfectly balanced in such a way that it can bond in sp^1 to make chains, in sp^2 to make planar structures, and in sp^3 to make three dimensional networks. Silicon is similarly placed in the table of the elements, but it does not form planes or chains, and tends to become metallic more easily than carbon. This topological diversity is what gives plastics, lubricants, and cutting tools made out of the same basic backbone: covalently bonded carbon. Many reviews on the science of carbon have been published, and we refer the reader to Ref. [63, 62, 221] in particular.

The most stable form of pure carbon is hexagonal graphite, made from sheets of hexagons of sp^2 carbon, stacked with an offset between neighboring sheets of $1/2$ of a lattice constant in an A-B-A-B layering. The sheets are separated by a larger distance (3.35 Å) and interact weakly with a mixture of covalent and van der Waals bonding. This is what gives graphite strong lubricating properties, as pieces of graphite planes can glide along each other almost frictionlessly[179, 61]. The weak bonding of graphite in the direction perpendicular to the planes (the elastic constant c_{33} is only 36.5 GPa and the shear constant c_{44} is only 4.5 GPa[221]) makes the synthesis of monocrystalline graphite almost impossible: the planes can shift with respect to each other, and they can also rotate. This gives so-called turbostratic graphite, which has very crystalline planes of graphene, but with orientational disorder between them. The best commercial graphite is highly-oriented pyrolytic graphite (HOPG) which has reduced disorder, but still remains polycrystalline. The theoretical interest in being able to play with true monocrystals of graphite is immense[201, 34].

Diamond is only slightly higher in energy than graphite, and metastable. In contrast to the weak bonding between graphite planes, diamond is the hardest material yet synthesized, with a Young's modulus of up to 1250 GPa[221], due to the very strong covalent bonding between all atoms. Theory predicts that the in-plane modulus of one sheet of graphite (known as graphene) is even higher than that of diamond, but this is at the price of its dimensionality, since the sp^2 bonding is not

extended out of plane. Some speculation has appeared as to how to make a 3-D bonded sp^2 solid[52], but these will probably be built at the expense of the effective modulus, since the carbon will no longer be 100% sp^2 . Diamond has many attractive properties, besides being a girl's best friend. The thermal conductivity of diamond is very large, as is its carrier mobility[221]. The doping of diamond was a problem for a long time, but recent advances have been made in p-type doping. Because of its large band gap diamond is resistant to radiation damage as well, and it could prove to be an important alternative medium for semiconductor applications. Section 4.3 presents our work to further the understanding of the most promising method yet for the synthesis of films of diamond.

The physico-chemical study of carbon naturally dates back a long way. Nevertheless, regularly, revolutions in the understanding or production of carbon-based materials have upset the picture and widened the perspective. In the 1950s and 1960s carbon fibers were developed[67], with unsurpassed strength for weight. Then came novel types of graphite, in which the leaves of carbon were intercalated with different species[293].

3.1.1 Buckminsterfullerenes

In 1986 a new form of carbon was synthesized by Kroto et al.[149]. This phase was no longer 3D, 2D, or even 1D, it was 0D: a super-molecule of 60 regularly arranged carbon atoms resembling what 95% of the world calls a football. Due to its similarity to the domed houses dreamed up by the architect Buckminster-Fuller, the molecules were dubbed Buckminsterfullerenes, or fullerenes for short. New and larger shapes were discovered, with 70, 76, 82, 84 atoms[147, 60, 294], and even more. It was also discovered that fullerenes mimic the 2D behavior of graphite, and can stack on each other either in a solid[142], or concentrically in onions[148, 277]. Now here we must pause to ask ourselves: where do fullerenes fit into the florilège of carbon phases? Their dimensionality is 0, even lower than sp^1 alkane chains, but their bonding is mixed. It resembles the sp^2 of graphite, but as their surface is curved, a sp^3 component is also present (on the order of 10% for C_{60}). The bigger the fullerene, the greater its radius of curvature, and the more it resembles planar graphene.

C_{60} is made of 20 hexagons and 12 pentagons. Each carbon atom is at the intersection of two hexagons and one pentagon. When compared to planar graphene, the introduction of a pentagon gives a positive curvature to the surface. Euler's rules dictate that to create a closed

surface we need a total “curvature charge” of 12. As a result all the simple fullerenes will have the same number of pentagons, 12, and differ only by the number of hexagons inserted between them. The extreme fullerene C_{20} , made of only pentagons, is too curved to be stable, as are the other intermediate fullerenes before C_{60} , which defines the “isolated pentagon” rule: all pentagons in a stable fullerene must be surrounded by hexagons.

Fullerenes can be doped endohedrally with different atoms[108], in particular with alkali metals. Some theoretical work has been done on substitutional doping[103], but experimental interest is tapering off.

Many prospective applications were imagined for fullerenes, exploiting their cage-like structures and their relative chemical inertness to deliver pharmaceutical molecules in the human body, or using their shape to optimize lubricants. However, nearly 20 years later, few industrial successes have developed.

3.1.2 Graphene and nanotubes

In 1991, Sumio Iijima discovered[124] yet another strange form of carbon: nanotubes. In the soot recovered from the discharge of an electrical arc between graphite electrodes he found ultra-thin tubules of carbon. Based on high-resolution transmission electron microscope (TEM) images, and topological considerations, he proposed an atomic model based on a rolled-up sheet of graphene. The resulting tube would have different shapes and sizes depending on the way the sheet was rolled up. Whiskers had been observed before in some of the innumerable works on carbon blacks[67], in particular those of Endo and Oberlin, but Iijima was the first to recognize and model the extremely simple geometry of carbon nanotubes (CNT). Followed a second avalanche of publications and experimental results, which still continues today. Countless papers on nanotubes, their properties, and applications have appeared in every journal of physics, chemistry and materials science.

3.1.3 The geometry of nanotubes

Nanotubes have one of the highest aspect ratios of any objects in nature. Their length can exceed several millimeters for diameters down to less than a nanometer. The geometrical characteristics of a nanotube, and the position of every atom in it, can be determined by just two integers. The nanotube can be described as an infinite strip cut out of a graphene sheet and rolled up along the direction perpendicular to the strip. All we need is to define the circumference of the tube, which joins the two

equivalent atoms along the circumference. These will be superposed once the strip is rolled up. The vector between the two graphene atoms $\mathbf{C}_h$ (called the chiral vector) is part of the 2-D crystalline lattice, and denoted by two integer indices, n and m . Many people call the different helicities of carbon nanotubes, and the (n, m) indices, “chiralities”. This is technically wrong, as a chirality is simply left or right, and denotes the behavior of a molecule under the operation of a symmetry plane. However, as the denomination “nanotube chirality” has become common we may employ it occasionally.

If $\mathbf{a}$ and $\mathbf{b}$ are the lattice vectors of a 2-D graphene plane, $\mathbf{C}_h = n\mathbf{a} + m\mathbf{b}$. The circumference of the tube is the length of $\mathbf{C}_h$, or $L = a\sqrt{n^2 + m^2 + nm}$. Here a is the in-plane lattice constant, equal to about $2.49\text{\AA}$ experimentally, for an inter-atomic distance of $d_{\text{C-C}} = 1.44\text{\AA}$. The diameter of the tube is $d_t = L/\pi$.

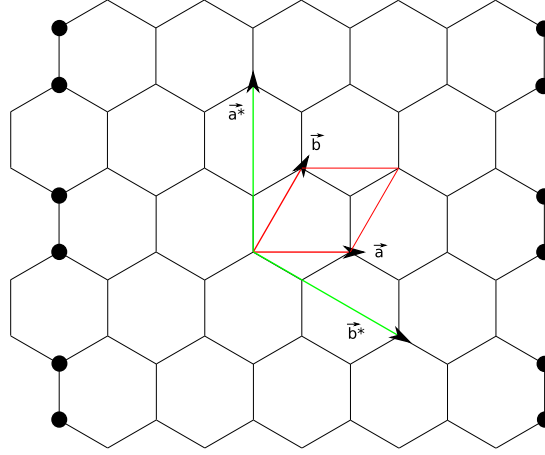


Figure 3.1: Strip of graphene for a $(5,0)$ zigzag nanotube. The graphene unit cell vectors and reciprocal space lattice vectors are shown. Large dots are equivalent atoms, which are superimposed when the strip is rolled into a tube.

3.1.4 Symmetry and topological properties

A nanotube with indices (n, m) can be constructed, using symmetry operations, from only one or two irreducible atoms. The basic operation is a screw (rotation + translation) along the axis of the tube. In certain cases, additional symmetry operations can be present. In particular, the two extreme configurations are the armchair case where $n = m$ and the zigzag case where $m = 0$. Both are represented in Fig. 3.2, and have

additional planes of symmetry, and a true n -fold rotation axis. In these cases, the two primitive atoms in the original graphene unit cell remain equivalent, and all atoms in the the nanotube are images of each other.

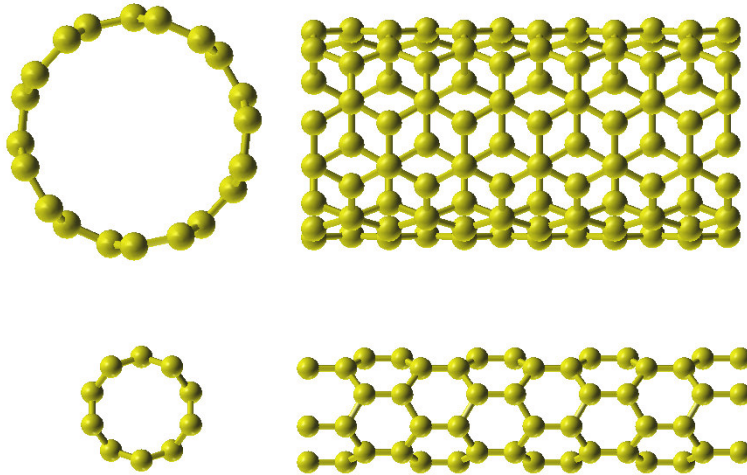


Figure 3.2: Axis-on and side views of a $(5,0)$ zigzag (bottom) and a $(5,5)$ armchair (top) nanotubes. Scale between the two nanotubes is only roughly respected.

Several methods can be used to determine experimentally what the indices of a nanotube are: STM and electron diffraction[152, 47] can give actual indices, and Raman spectroscopy gives access to the tube radius and defines a small number of possible tube structure (see also Sec. 3.4.3). These are still very difficult experiments, require theoretical input in the form of simulated STM images or diffraction patterns, and are far from routine. The simultaneous determination of (n, m) and other physical properties, in order to establish correlations and use theoretical models, is a hot topic of research.

One can wonder how a nanotube ends. The simplest termination is a hemispherical cap, in fact half a fullerene. General rules have been determined to describe the topology of the termination as a function of the indices n and m [65, 66] (essentially, one must place 6 pentagons in the cap, and the larger the tube the greater the number of possible end-caps). The prototypical example is shown in Fig. 3.3. In the general case, there is not always a hemispherical fullerene to cap any given tube,

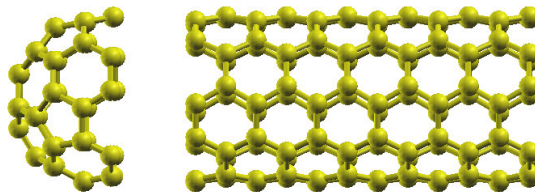


Figure 3.3: A $(5,5)$ nanotube capped with half of a C_{60} fullerene molecule

but a graphene-like lattice can always be constructed. Experimentally, tubes can also be either open or terminated by faceted surfaces.

Topologically, heptagons have the opposite effect of pentagons, and give negative curvature. Using the positive and negative curvatures of pentagons and heptagons, one can create an infinite variety of graphene-like surfaces. They can be globally flat, or can join tubes with different structures or orientations[186, 289, 268].

3.1.5 Single-wall and multi-wall nanotubes

The type of nanotube described above has only one sheet of graphene. This was not, however, what Iijima originally found under his microscope. In the absence of catalysts, one produces nanotubes with several walls; concentric tubes of carbon which are separated by a distance similar to that between sheets in graphite. These multi-wall nanotubes (MWNT) can have different properties from the single-wall (SWNT) variety, synthesized later[125, 22]. SWNT and MWNT are visible in the TEM micrographs in Fig. 3.4.

The sheets in a MWNT can glide along each other, and can have different electrical properties (see section 3.2). There is some theoretical evidence that the interaction between sheets in a MWNT can have an effect on its global electronic properties, despite the weakness of the interaction[203]. Particular interest has emerged recently in double-wall nanotubes (DWNT), since a route has been found which produces a large fraction of DWNT (see Ref. [54] for example). The DWNT system is sufficiently simple to be analyzed theoretically and by electron diffraction, which allows the spectacular determination of the (n, m) indices for a specific DWNT[48].

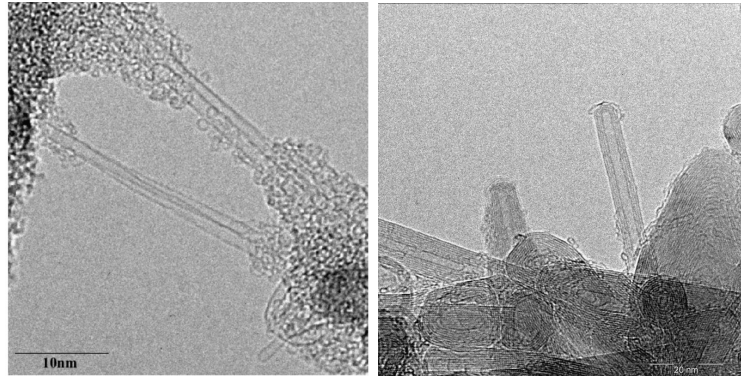


Figure 3.4: TEM images of nanotubes grown by a combustion flame method. Left: SWNT with stray fullerenes. Right: MWNT with carbon onions. Photos courtesy of H. Okuno.

3.1.6 Bundling

In many methods, the SWNT which are synthesized appear in bundles. A few to a few hundred tubes are stuck together, and often have similar or identical diameters and (n, m) indices. Bundling is usually a problem rather than an advantage: in order to exploit the properties of the individual CNT they must be isolated physically. Contacting a CNT electrically implies having the room around it to deposit electrodes, or setting the nanotube down onto existing contacts. The mechanical properties of a bundle are much worse than those of isolated tubes: the tensile strength is limited because tubes slip with respect to one another inside the bundle. The elasticity of the bundle under flexion is similarly limited for the same reasons: tube slipping makes the deformation of the bundle plastic.

3.2 The electronic structure of nanotubes

A graphene sheet is a very particular semi-metal. The Fermi surface is reduced to a single point at K in the BZ. As a result the DOS at the Fermi level is zero. In graphite, the weak interaction between layers very slightly increases the band overlap, but the DOS is still very small. This particular band structure will carry over into nanotubes. Given our construction of nanotubes as rolled-up strips of graphene, the band structure can be obtained in first approximation by folding the band structure of graphene along the correct lines (for this section see

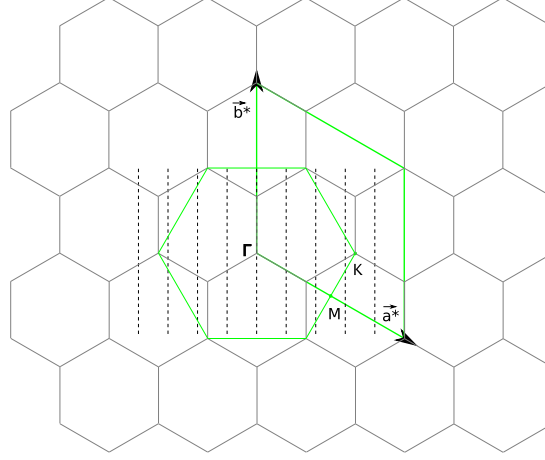


Figure 3.5: The reciprocal unit cell of graphene, with the K and M special points. The dashed lines correspond to k -points sampled in the band structure of a $(5,0)$ zigzag nanotube. As no line passes through K, the tube should be semiconducting based on the zone-folding construction.

pp. 113- of Ref. [62]). The finite size of the tube along the circumferential direction shows up as a discretization of the band structure. The sub-sampling of the BZ due to the rolling-up of the tube is shown in Fig. 3.5 for a $(5,0)$ tube.

One sees, as a result, that the final tube can be either metallic, if the sub-sampling passes through K, or semiconducting otherwise, with a gap which depends on how close the sampling comes to K. As the sampling becomes denser, when we consider larger tubes, we regain the band structure of graphene. The zone folding calculation shows that if $n - m$ is a multiple of 3 then the tube is metallic. Hence, zigzag tubes with n a multiple of 3 are metallic. These rules were first expounded by Hamada and coworkers[110]. Armchair tubes (with $n - m = 0$) are always metallic, but with an important difference: the K point is folded back onto Γ . As Γ is always sampled, whatever the continuous deformation the tube or the band structure undergo, the armchair tubes will remain intrinsically metallic. The zigzag tubes will not.

The effect of curvature on the band structure is relatively small, except for the very thinnest tubes[23]. These will be affected by $\sigma - \pi$ hybridization, which makes semiconducting tubes metallic. This happens in particular for the $(5,0)$ tube shown above. Further, it has recently come to light that Peierls instabilities can then appear, which distort the tube's cylindrical structure and revert it to an semiconducting state[49].

With successively increasing levels of accuracy, the calculated $(5,0)$ band structure thus goes from insulating, to metallic, and back again.

3.3 Present-day applications of nanotubes

Contrary to fullerenes, a few applications have emerged for nanotubes which are already being produced industrially. The huge aspect ratio of CNT gives a correspondingly huge enhancement factor when they are used as tips for field emission of electrons[57, 232, 200]. This feature has been extended to make thin-film displays in which nanotubes grown on a surface emit electrons onto the phosphors in the screen.

The Young's modulus of single wall nanotubes is very high along the tube axis (up to a TPa or more), and the nanotubes are very elastic under flexion[239, 226, 278]. This suggests using them to reinforce materials, in particular plastics. The problem remains, however, that the matrix must adhere to the nanotube to benefit from its mechanical properties. As the walls of CNT are chemically inert, this is difficult. Efforts are underway to graft other species and molecules onto the walls of CNT in order to improve their interaction with a matrix[192]. The use of MWNT is further complicated by the fact that the individual tubes do not adhere well, and can slide out of larger tubes like a sheath[243]. It is not yet clear that CNT will surpass traditional additives (in particular carbon fibers) to polymer matrices for mechanical properties.

They can be added also for their conducting properties, to make the plastic conduct electricity thanks to the percolation of electrons through the channels formed by the CNT.

Another promising avenue for CNT applications is lithium-ion batteries. The very high specific area of CNT provides a matrix for the battery ions, in the cathode, and results[45] show that CNT are superior to graphite for this purpose. The tubes must however first be ground, apparently in order to break open end caps and make more of the surface (or surfaces for MWNT) available.

Prospectives have opened up following discoveries of the interaction between CNT and polymer chains[172], in particular DNA[295]. The polymers interact by a type of VdW interaction, and some have a tendency to wrap CNT. DNA adopts its well known helical shape around a CNT of the correct diameter, which could be exploited to make sensors or bio-chips.

It has been shown that by depositing metal contacts on a semiconducting CNT one can create a field effect transistor[154, 127, 263, 262]. Extending this idea, one can use a continuous tube joining semicon-

ducting and metallic segments to make diodes or transistors purely out of carbon[289]. This allows many people to dream of making full integrated circuits out of nanotubes, alternating the nature of the conductivity through the local tube indices, and building junctions by welding nanotubes together[165, 189].

Hopes for encapsulating and delivering pharmaceutical drugs in CNT remain chimeric for the moment.

3.4 Experimental methods and details

In this section we give relevant details as to the methods of synthesis for CNT, and a few methods of characterization, which will be considered in the following chapters. This will certainly not exhaust the subject or the different techniques which are used, and is solely included for the self-consistency of the manuscript.

3.4.1 Methods of synthesis

Arc-discharge

Historically, the first method used to produce CNT, both MWNT and SWNT, was arc-discharge. Two graphite electrodes are put in a vacuum chamber under a small pressure of helium or other inert gases, and a large current is passed through them. The electrodes are consumed and the remaining soot which is deposited in the cavity and on the electrodes contains multi-wall nanotubes. Adding a transition metal catalyst (see Sec. 3.4.2) to the electrodes produces single-wall CNT. This is a general feature: a catalyst is needed to produce SWNT. The CNT produced in this way are of excellent quality, long, and quite defect-free. However the method is too expensive to produce large quantities. The temperatures reached in this method are very high, up to 3000 or 4000 K, which explains the high degree of graphitization and the quality of the resulting tubes.

Chemical vapor deposition

Chemical vapor deposition (CVD) can produce larger quantities of CNT [139, 109]. A reactant gas containing carbon (often methane) is inserted into a chamber at a given temperature (between 600 and 1000 K). In the presence of an appropriate catalyst (catalytic CVD or CCVD) the gas is decomposed and, in the right conditions of temperature and pressure, the carbon can feed the growth of CNT. In some cases the gas is ionized into a plasma before contacting the catalyst. This is known as plasma-enhanced CVD (PECVD). Tubes grown by CVD are usually not straight and contain large quantities of defects.

Torch method

A variant on the CVD synthesis uses an acetylene torch in air. Applying the torch plume to a cooled substrate (with a catalyst) for a short time can produce carbon nanotubes, as shown in Fig. 3.4. This is also a medium-temperature-range technique.

Laser vaporization

Another technique for the production of nanotubes is simply to vaporize graphite using a laser[272]. Carbon is thrown out and heated to very high temperatures, and can form CNT. If the target contains a catalyst, SWNT are formed. This produces tubes of almost as high quality as arc discharge. The temperatures attained are lower (1200 to 2000 K), which explains the residual difference in graphitization.

3.4.2 Catalysts

As mentioned above, the synthesis of SWNT, but also MWNT by CVD, requires the presence of a catalyst. The efficient catalysts are all transition metals: Ni, Co, Fe, Y and others. To our knowledge no systematic comparisons have been performed using the same setup with many different catalysts, although partial comparisons exist, as in Ref. [41], and a review of carbon fibers from CVD can be found in Ref. [234]. The most efficient catalyst in terms of productivity of CNT is presently a mixture of Ni and Y[128] for the arc-discharge method, and Ni-Fe for the laser vaporization method. The role of the catalyst in the growth is still a subject of great debate, as we shall elaborate in Sec. 3.5, and study in Sec. 4.1 and 4.3, but it is believed to be a buffer of some kind, absorbing and expelling carbon. In CVD, the catalyst is also required to decompose the reactant gas, usually a hydrocarbon, freeing the carbon to be used in growing the nanotube. The presence of a catalyst determines whether SWNT will be synthesized, although in some cases (as for Pd in section 4.1) MWNT grow anyway.

The morphology of the catalyst has also been shown to be very important[267, 234]. The diameter of the resulting tubes appears to be linked to the initial size of the catalyst particles. A uniform film of catalyst can give a uniform forest of CNT after the film re-disperses into small clusters.

3.4.3 Characterization techniques

All of the methods of characterization used in mainstream physics can be applied to nanotubes. The minimal amount of matter for techniques such as Raman spectroscopy can now be synthesized, although purity

and uniformity of the sample are still issues.

Transmission Electron Microscopy

Transmission electron microscopy is routinely used to determine nanotube morphology, once they have been dispersed. Electron diffraction can be added to determine the crystallinity of a bundle, or even to determine tube indices (see Sec. 3.1.4). The chemical composition of tubes and their contents can also be determined using Electron Energy Loss Spectroscopy (EELS).

Scanning Electron Microscopy

SEM is a standard fast characterization method which gives surface morphology and characteristics.

Raman spectroscopy

Raman spectroscopy probes the low-lying excitations of the system with a laser beam. The energy lost by the incoming photons is transferred to zone-center phonons, if they have the correct symmetry. For metallic systems, there are also low-lying electronic excitations. In this case the spectrum of excitations is continuous and no information can come from normal Raman spectroscopy. Resonant Raman employs a laser energy tuned to an inter-band electronic transition, and continues to work for metallic systems. Access to phonons gives in particular the radial-breathing-mode frequency of a tube, which is proportional to the inverse of its diameter (see Ref. [64] for a review). Additional resonances at higher energies give the D, G, and G' bands. The G band is a normal graphitic mode. The D and G' bands are correlated to the amount of defects in the structure, because they become active only when the symmetry is broken. Recent results on graphite show that they may come from the electron-phonon coupling of modes at K, which gives linear dispersion to an optical mode at K and Γ [225].

Electron Spin Resonance

Electron Spin Resonance (ESR) is a technique similar to nuclear magnetic resonance: a large (several Tesla) magnetic field splits electronic spin levels, and a small source of electromagnetic radiation is used to probe these levels. The frequency of the source is varied to find the resonances at which the sample absorbs energy (for photon energies close to inter-level transitions). The presence of an ESR signal depends on several factors: there must be free spins present, in order to have something to excite into resonance. The spin can either be a localized unpaired spin or an itinerant spin in a metallic system [72, 74, 68, 224].

With CNT we are in the second case, but ferromagnetic atoms introduce unpaired localized spins which drown out the carbon signal. The electron spin must also be able to propagate for a sufficient time without being perturbed, in order to have a chance to absorb the incoming

radiation. The electron can still be diffused provided that the spin is not affected. The average time between scatterings is called the spin-lattice relaxation time. It must be sufficiently long to increase the cross-section of absorption, but if it is too long the electron is almost certain to encounter an impurity which will scatter its spin. The main scattering process is through spin-orbit interaction. The energy is then relaxed to the lattice through phonons and thermal effects. Pure graphitic materials show a sharp intense line, owing to the weak spin-orbit coupling with carbon atoms. Arc-grown MWNT of sufficient purity can exhibit a signal similar to that of graphite[252]. In contrast, all measurements performed to date on single wall nanotubes have shown no conduction electron signal at all[218, 252]. The only (small) resonance present is due to localized spins in dangling bonds.

3.5 Growth models

The growth mechanism for carbon nanotubes is still far from clear, and several models and flavors of models exist. We will describe the most common model, and comment on some other proposals which have been made. Different mechanisms can be envisaged for single wall and multi wall nanotubes; we will concentrate on single wall tubes.

The growth of single wall carbon nanotubes is usually described following the Baker model[11], initially created for carbon filaments and fibers grown by CVD. The synthesis happens in a plasma of carbon (created by a discharge or a laser) or in a carbon containing gas (where atoms or clusters are created by decomposition of the gas at the surface of the catalytic particle in CVD). Carbon atoms are dissolved as interstitials in the metal lattice of the particle. After reaching a critical concentration, the carbon is expelled, and a graphene layer forms at the particle surface, initiating filament growth. In this model, the term catalytic is often used to evoke the role of metallic particles, which are presumed to be unaffected by the filament growth and to serve only as a buffer for the diffusing carbon atoms (beyond their catalytic role for gas decomposition). Growth can continue as long as carbon atoms are provided to the catalytic particle. In such a model, metal atoms are implicitly supposed to diffuse very slowly compared to carbon atoms, so that pure carbon filaments are formed out of the metallic germs. Nanotube growth modeling recently received an unprecedented push, from the experimental filming of the growth of a filament under a TEM[118]. The catalytic nickel particle clearly stays at the end of the filament, and the authors propose a growth mechanism where the interaction of carbon

atoms and graphene sheets with steps in the metallic surface explains the movement of the particle and the growth direction of graphitic planes. The study also contains *ab initio* calculations which indicate that Ni atoms diffuse faster than carbon along the surface. The migration of step edges and the change in particle shape are governed by processes at the Ni/graphene interface. Whether incorporation of carbon into the lattice occurs is still open, but the particle appears to remain crystalline in Ref. [118]. This new information calls into question the Baker model in some respects: the carbon no longer needs to diffuse into the full bulk, and specific mechanisms based on local crystallography explain growth, instead of thermodynamic considerations like solubility (although they are not mutually exclusive). Much more modeling work will be necessary to ascertain that the new model is correct or if it is the only mechanism, independent of catalyst nature and growth conditions. In any event, both models remain somewhat simplistic in their treatment of the catalyst particle, as we shall show in Sec. 4.1.

Besides the Baker model and numerous works supporting it, a number of reports state that metallic germs go through a solid-liquid transition before growth starts, which would explain why metal particles are often found inside the nanofilament core [40]. This transition would occur at a temperature much lower than the bulk melting point, suggesting nano-size effects. However, no direct experimental proof of this transition has been reported. Surface melting above 600°C, leading to coalescence, has been reported by Wang et al. for Pt nanoclusters [285].

3.6 Flavors of nanotubes

Since the discovery of carbon nanotubes, a plethora of other flavors of tubes have been synthesized.

3.6.1 Boron nitride

Nanotubes based on boron nitride were predicted to be stable by Rubio et al. [236] in 1994. Only a year or two later, a number of different experimental groups [44, 89, 169, 269] managed to synthesize nanotubes based on boron nitride. The similar geometric properties in BN and graphite (BN is also a graphitic, hexagonal structure with weak inter-layer binding) leads to similar tubes. However, BN is an insulator with a large gap, which carries over to the tubes.

3.6.2 MoS₂

About the same time, Tenne and coworkers synthesized large diameter fullerenes, then nanotubes of molybdenum disulfide[173, 75]. As a graphitic structure, MoS₂ is more complex, as it is composed of bonded molybdenum and sulfur. The resulting layers are stiffer, the fullerenes are often faceted, and the tubes have much larger diameters (100 to 300 Å). The tubes have been studied using group theory[194] and tight-binding methods[250]. There is continued interest in these systems for tribological and other applications similar to those of carbon tubes. In 2001, Remskar and coworkers[229] synthesized a kind of “fur” made from filaments of MoS₂. They interpreted them as bundled (3, 3) nanotubes of MoS₂ with very small diameters. In Sec. 4.2, we present the work we carried out to test their hypothesis, using density functional calculations of bundle structures and energies.

3.6.3 And the rest (BC₃, NbS₂ ...)

A large number of other flavors of nanotubes have been synthesized, but their technological interest remains questionable. Few have found applications, and their increased complexity compared to carbon tubes has steered research and development to the latter. Different di-chalcogenide systems like WS₂[266] have given nanotubes. Mixing boron, carbon, and nitrogen has yielded a variety of B_xC_yN_z tubes (e.g. Ref. [254]). On the theoretical side, tight binding results appeared for the dichalcogenides [248, 249], and ab initio results for BC₂N[196] (once again before their synthesis), and even CN[195].

3.7 Superconductivity in carbon phases

The face-centered-cubic phase of solid C₆₀ is superconducting when doped with alkali metals[122, 114], and hole doping can significantly raise the critical temperature[261]. This has been explained by the fine-tuning of the electronic states at the Fermi surface and their relation to the dominant phonons of the C₆₀ molecules[281, 181].

Recently several works have extended the analysis to the electron-phonon interaction in nanotubes[90, 29]. In 2001, Kociak et al.[136] showed that pure nanotubes in ropes could become superconducting. Globally, results are less spectacular: in order to have a consequential coupling the nanotubes must be of very small diameter. Given the present lack of control on the diameter and helicity during synthesis, this is an important problem. Small diameter tubes are also much less sta-

ble, and have been synthesized most successfully in zeolite matrices[283]. Superconducting measurements[260] in this configuration are promising but remain very delicate and difficult to interpret, due to the lack of data on the exact structure of the tubes, and how defect-ridden they are.

Here we come to one of the cruxes of this thesis: superconductivity in low dimensional systems appears to be strongly dependent on the size and structure of the system. It should be possible to tailor the Fermi surface and the nature of the relevant phonons in order to enhance the electron-phonon coupling and produce useful devices employing minimal power. Our ambition is to both develop the study of nanotubes and nano-systems (wires, films, etc...) and be able to calculate electron-phonon coupling strengths in order to predict the inter-relationships between structure, electronic structure, phonons, and superconductivity.

3.8 Onward

In the following chapter we will develop on different aspects of the growth and catalysis of nanotubes and related systems. Each endeavor is motivated by the recent work of a group of experimentalists, and attempts to aid and develop their work by proposing or testing structural models for the nanostructures they have synthesized. Section 4.1 presents a study of the interaction between carbon nanotubes and palladium atoms, following the group of Jean-Paul Salvetat. It pertains to the use of catalysts for tube growth and their importance in growth models and in post-synthesis characterization, which has been by and large underestimated. Section 4.2 contains an exploration of a series of systems resembling bundles of nanotubes of molybdenum disulfide. The experimental group of Dragan Mihailovic presented a structural model for the fibers they created, and we compare their suggestion with a number of other possibilities. This section is a foray into the complex and still quite uncharted world of exotic nanotubes made from different chemical species, which can behave completely differently from carbon tubes. Section 4.3 departs a little from nanotubes per se and discusses the growth of diamond films on different metal surfaces. Many experimental groups have worked on diamond films over the past ten years, but the discovery of Mathias Schreck and coworkers that iridium produces films of exceptional crystallinity has spurred the field anew. The interactions between diamond and transition metals are very similar to those which occur during the growth of graphene sheets. The chemical vapor deposition processes are very close, and this study should give insights into the

behavior of carbon during the growth of nanotubes as well.

Chapter 4

Nanotubes: applications

The ordinary novel would trace the history of the diamond - but I say, 'Diamond, what! This is carbon.' And my diamond may be coal or soot and my theme is carbon

D.H. Lawrence

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4.1 The interaction of Pd atoms with nanotubes

4.1.1 Introduction

Understanding the growth mechanism of carbon nanostructures is of primary importance for a number of applications. Catalytic growth from metallic nanoparticles is used in many processes to produce different kinds of nanotubes or filaments [234]. In this section we present work performed in collaboration with the experimental group of Jean-Paul Salvetat in Orleans. The framework and the specific problem we tackled are presented, and some explanations are added regarding the techniques used for synthesis and characterization. Then we detail our contribution to understanding and explaining the experimental results, and describe the extension of growth models.

The most popular theory of CCVD growth relies on the archetypal model of Baker and Harris [11] (see Sec. 3.5). We recall that in this model the metallic particles are supposed to act as simple catalysts. The particles should decompose the reactant gas but remain more or less intact. Atoms of metal should not remain mixed in with the carbon, aside from the nanofilament tip where the particle comes to rest. We shall see in the following that this is not at all trivial or certain, and that accretion of the particle probably happens during growth, mixing metal into the growing nanotube.

The next section briefly outlines the important details of the experimental setup and results. Then we go on to describe the calculational details and the two types of models used: planar and curved sheets of graphene. In both cases palladium atoms are substituted in the matrix and adsorbed on the surface, and the energies and relaxed structures are examined. Modifications to present growth models are considered in a last section before conclusions are drawn.

4.1.2 Experimental results

In the experimental setup of Salvetat and coworkers, isolated, nm diameter palladium clusters are deposited by plasma sputtering on Si substrates covered with SiO₂ native oxide (see details in [273]). They use such substrates to grow small-diameter nanofilaments at low temperatures ($\leq 600^\circ\text{C}$) by catalytic decomposition of acetylene.

In a series of experiments, a small amount of Pd ($\approx 10^{14}\text{at./cm}^2$) is deposited at the surface, in order to produce Pd nanoparticles with an average diameter less than 10 nm, once coarsening is taken into account. After growth on these substrates, filament length remains limited to a few hundreds of nanometers, whatever the deposition time. This

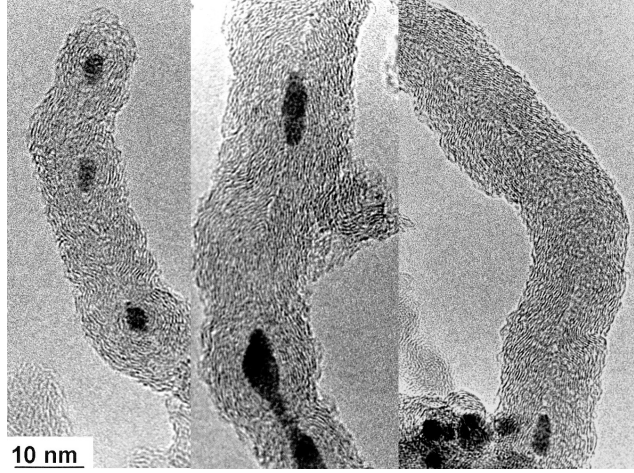


Figure 4.1: TEM pictures of short filaments. Catalyst nanoparticles are observed encapsulated in graphene layers

is observed by SEM on substrates, and TEM after scratching the deposit (Fig. 4.1). It is to be noted that the average diameter of the Pd nanoparticles observed by TEM after growth is much smaller than the diameter of the nanofilaments.

Contrarily to Co, Ni or Fe, which are ferromagnetic, Pd is a paramagnetic metal. This allows one in principle to perform Electron Spin Resonance (ESR) measurements on the as-grown samples, without the perturbation of a ferromagnetic signal. The samples, which have *herringbone* or *stacked-cup* morphologies, do not show any resonance at all, which indicates (see Sec. 3.4.3) that the spin-lattice relaxation time is drastically decreased.

4.1.3 Computational details

We used a maximal plane wave energy cutoff of 50 Ha. The atomic positions were relaxed until the atomic displacements were inferior to 0.0005 nm, and a distance of 0.7 nm was maintained between image sheets of graphene. Finally, the exchange correlation energy was approximated by the GGA of PBE[213], and we used pseudopotentials of the Troullier-Martins type[276]. In the following sections we present the different microscopic models used to analyze the interaction between Pd atoms and carbon nanotubes and nanofilaments. The tubes are essentially composed of stacked sheets of graphene, and we will consider different geometries and configurations.

4.1.4 Planar graphene

The first model considered is a planar sheet of graphene (60 atoms), with a palladium atom either adsorbed at the center of a hexagon, or substituted in the carbon lattice (see Fig. 4.2). The substituted atom buckles out of the plane by 0.15 nm, whereas the adsorbed Pd sits 0.19 nm above the plane. In the first case the C-Pd bond length is 0.20 nm, and in the second 0.24 nm, indicating a weaker bond. The positions of third and further neighbors of the Pd atom were perturbed very little with respect to the pristine sheet.

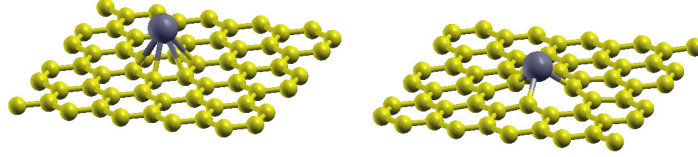


Figure 4.2: Relaxed geometries of adsorbed (left) and substitutional (right) Pd atoms on graphene.

Both structures were tested in spin-polarized initial configurations, but neither displays a magnetic moment. The substitutional graphene is unstable by -2.5 eV, whereas adsorbed Pd is stabilized by 1.1 eV with respect to separated graphene and metallic Pd. This suggests a strong affinity of the carbon lattice for Pd atoms, which can stay wedged between graphene sheets in order to maximize their adsorption energy.

4.1.5 The effect of curvature

The curvature-induced hybridization of the π and σ orbitals of graphene can change both electronic structure and reactivity. In order to check this effect, we impose a wave-like geometry to the sheet, where the curvature at the crest of the wave corresponds to the radius of a (10,10) nanotube (1.4 nm). The distance between periodic images is increased to 1 nm, in order to render their interaction negligible. Only the Pd and its 1st and 2nd nearest neighbors are allowed to relax. Binding is enhanced, the positions under and over the wave being stabilized by 2.3 and 2.4 eV respectively, and the substituted atom being unstable by -1.8 eV (these energies refer to a wave of carbon, to account for the strain energy). The charge on the adsorbed Pd atom is calculated with the Hirshfeld method[120]. The Pd atom has a net charge of +0.13, and

its electrons are transferred to the 1^{st} and 2^{nd} neighbors on the graphene sheet.

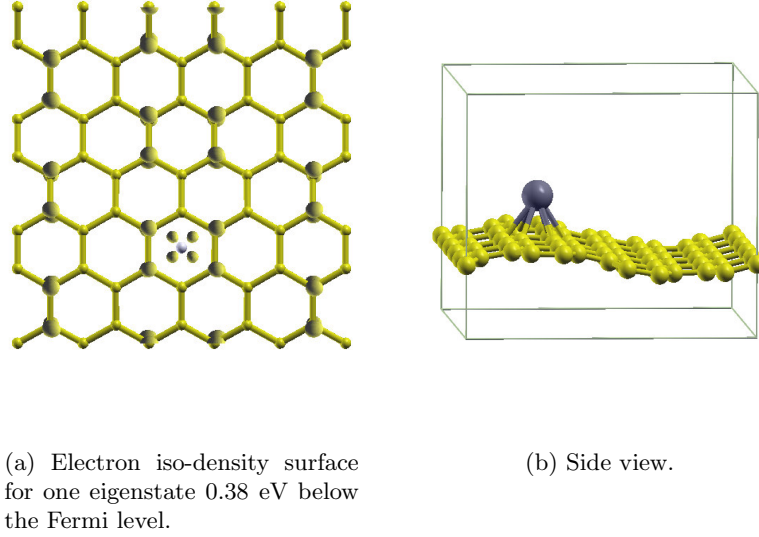


Figure 4.3: Pd atom adsorbed on top of a wave of graphene.

4.1.6 Electronic structure

Finally, we consider the effect of adsorbed palladium on the electronic states of the graphene wave. The states near the Fermi energy are composed of atomic d states on the Pd, hybridized with carbon π states. As can be seen in Fig. 4.3(a), certain electronic states contain concentrations of electrons both on Pd and on the whole carbon network. The overlap between these orbitals and the π conduction electrons will be very strong. Even though Pd is not ferromagnetic, electron spins will scatter easily on the heavy atom, as it presents a strong spin-orbit interaction, which is the usual relaxation mechanism for conduction electron spins [81]. These results confirm that the absence of ESR line can be explained by the presence of Pd atoms, incorporated in the atomic structure of the nanofilament during growth.

4.1.7 Discussion of the growth model

The fact that tubule length is limited can be explained by the rapid poisoning of the catalyst. We suggest here that in fact the Pd nanoparticle is partly consumed during growth, so that the catalytic activity of the particles is reduced, as their active surface decreases during root growth. This is illustrated in Fig. 4.4. As mentioned in Sec. 4.1.2 the particle

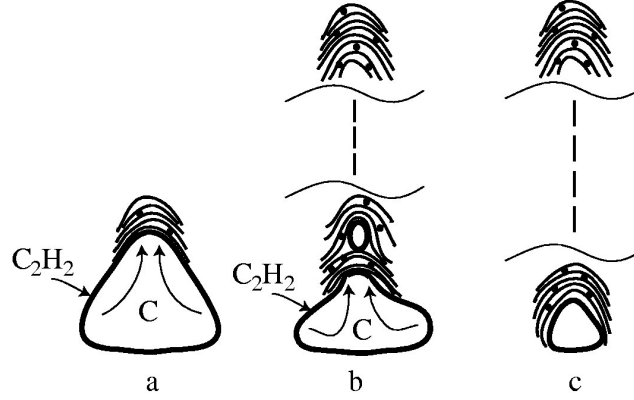


Figure 4.4: Sketch of nanofilament growth. Dots represent Pd atoms adsorbed on graphene. Germ size decreases during growth due to incorporation of Pd in the carbon network

size decreases during growth, which is also coherent with the attrition of the catalyst. The presence of Fe impurities in nanofilaments has been observed recently by Kiselev et al. using EELS [133].

Two mechanisms can contribute to the catalyst consumption: first, the adsorption of Pd atoms at the graphene surface, second, the trapping of small Pd clusters escaping from the germ surface during growth (see Fig. 4.4 and 4.1).

The adsorption of a Pd atom on graphene is exothermic, as shown above, by up to 2.4 eV/atom. This is a lot of energy by any standard, and indicates Pd atoms will stay wedged between graphitic planes. Our growth model supposes either a quasi-liquid state of the particle during growth, or very fast diffusion at the surface - see Sec. 3.5 and in particular Ref. [118], where the authors also suggest very fast diffusion of metallic atoms. This is contrary to some previous wisdom, which held that the metallic particle moves slowly, and that carbon diffused quickly into and around it. Although the role of the metal catalyst is still not definitively established (as a reservoir for carbon or atomic-scale template or both or something else altogether), it seems clear here that it will not remain

intact.

The behavior of small Pd clusters is probably similar to that of atoms, and in any event the adsorption energy should be comparable. Studying these shape effects will require much larger systems, and are further from present-day computational capabilities.

The presence of Pd impurities is also supported by the absence of signal in the Electron Spin Resonance experiments. A disordered heringbone structure precludes the ballistic transmission of charge and spin, which occurs in single-shell nanotubes: transport must proceed by hopping from one cup to another. This implies that spin diffusion on remote impurities should be limited by the structure. Nevertheless the constriction is not so strong as to kill the ESR signal; the size of one heringbone should be sufficient for free spins to absorb the probe radiation. The absence of ESR signal must therefore be the result of relaxation on Pd impurities incorporated in the filaments. As shown above, this assumption is supported by calculations of the electronic states of model graphene-Pd systems. There are states at the Fermi level (i.e. involved in conduction) which hybridize the atomic states of Pd with those of the graphene sheet. The overlap between the wavefunctions of incoming conduction electrons and the defect will be very large, since they share planar graphene π -like states, and scattering will be very efficient.

4.1.8 Conclusions

In the preceding section, we have presented evidence that, in the synthesis of carbon nanofilaments using a Pd catalyst, atoms of the catalytic particle are detached and adsorbed in the graphitic structure. This reduces the activity of the particle and provides large quantities of scattering centers for the conduction electrons. If this feature is general to all types of catalyst and methods of synthesis, it poses serious questions as to the purification of CNT. The effect could be stronger in CVD grown nanotubes than for arc-grown varieties, but CVD is the most cost-efficient technique, and the easiest to scale industrially. If these tubes can not be produced with purities such that their ballistic transmission properties are insured, their technological usefulness will be severely impaired.

The various models proposed so far in the literature for filament growth do not include modification and consumption of the metallic germs by atomic diffusion and trapping. Although it is certainly a second-order effect, we suggest that a realistic model should take this effect into account. The modification of the particle structure may have important consequences on the growth (see again Ref. [118]) and struc-

tural defects in the tube can occur due to this effect, particularly for nm-size germs.

4.2 The synthesis of bundles of MoS₂ nanotubes

4.2.1 Introduction

Following the synthesis of carbon nanotubes, experimental groups attempted to produce nanotubes from other layered materials. The first successful compounds were from the dichalcogenide family (i.e. WS₂, MoS₂ see Sec. 3.6) which consists of alternating layers of metal and sulfur [266, 173, 75]. These “multi-wall” nanotubes were produced by passing reactive gases such as H₂S over films of W or Mo in reducing atmospheres. During the reaction, cylindrical structures a few dozen nanometers in diameter and of micron length are formed. Metal dichalcogenide nano-structures have been used as very high aspect-ratio scanning microscope tips [235], and also exhibit interesting lubricating properties [46].

In 2001, the synthesis of MoS₂ nanotube *bundles* with *very small diameter* tubes was reported [229] by Remskar, Mihailovic and coworkers. The nanotubes are homogeneous in size and the bundles contain iodine, which is used as a transport agent, in proportions 1 Mo for 2 S for 1/3 I. Transmission electron microscope images reveal hexagonally packed tubes with 9.6Å between adjacent tube axes. The space group P6₃ (C₆⁶) is compatible with electron-diffraction images of the bundles. A potential structural model in which the iodine is placed in high-symmetry interstitial positions between the tubes, was also suggested, and is illustrated in Fig. 4.5

We set out in 2001 to try to validate this structural model. TEM images alone rarely give atomic resolution, and different structures can correspond to similar high-resolution images. Further, the different scattering power of different types of atoms (S is very light compared to the other nuclei) leaves a great deal of uncertainty in the structure and the stoichiometry when there is more than one species present (this is not a problem with carbon nanotubes). In this context, ab initio simulations can be of great use in determining possible candidate structures and eliminating others. The number of possibilities to be explored must be whittled down using the available experimental information on space group, unit cell size, or stoichiometry. Synthesis is often a non-equilibrium process. As such, the reaction pathway is at least as important as the global stability of the final compound. Pathways are unfortunately very complex to calculate, as they involve large sets of atomic configurations. Although innovative methods have been invented to calculate saddle points and reaction pathways more efficiently (see Sec. 2.2.3.4), we will have to be content with the “first order” estimation offered by the relative stability of the different systems (at equilibrium).

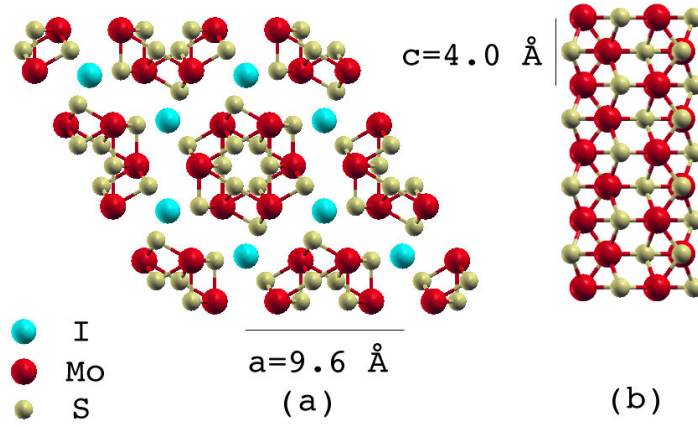


Figure 4.5: (a) Axis-on view of a periodic array of MoS_2 (3,3) armchair nanotubes, proposed by Remskar et al. An entire MoS_2 tube (Mo: large red, S: small yellow spheres) is present at the center, surrounded by 6 iodine atoms (I: blue spheres) and the edges of neighboring tubes within a 2×2 unit cell. An isolated MoS_2 armchair nanotube is extracted from this structure and depicted along its axis in (b).

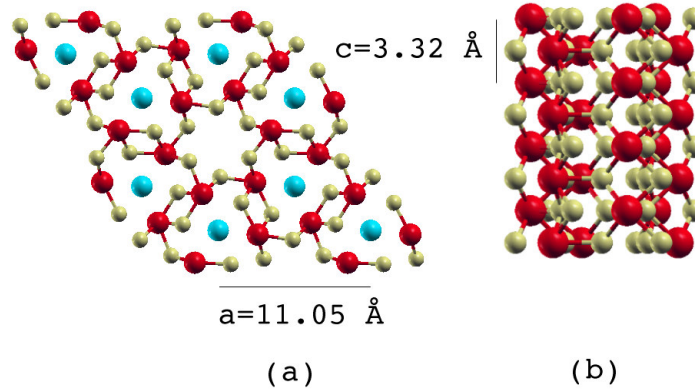


Figure 4.6: (a) View of a cross-section of a periodic array of MoS_2 (3,3) armchair tubes with interstitial I (relaxed ab initio). (b) Side-view of an isolated MoS_2 (3,3) armchair nanotubes extracted from the structure in (a).

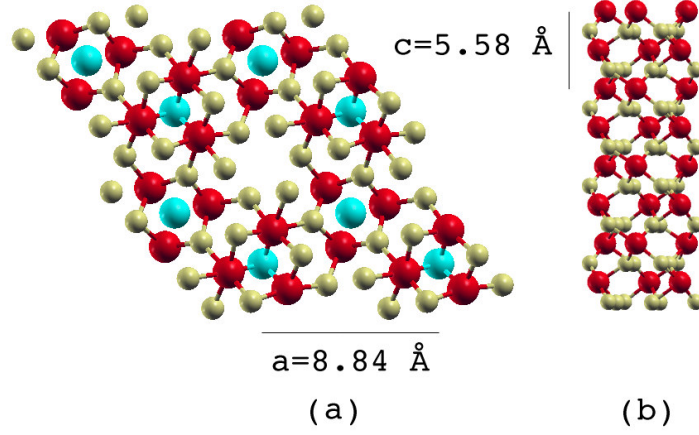


Figure 4.7: (a) View of a cross-section of a periodic array of MoS₂ (3,0) zigzag nanotubes with interstitial I. (b) Side-view of an isolated MoS₂ (3,0) zigzag nanotube extracted from the structure in (a).

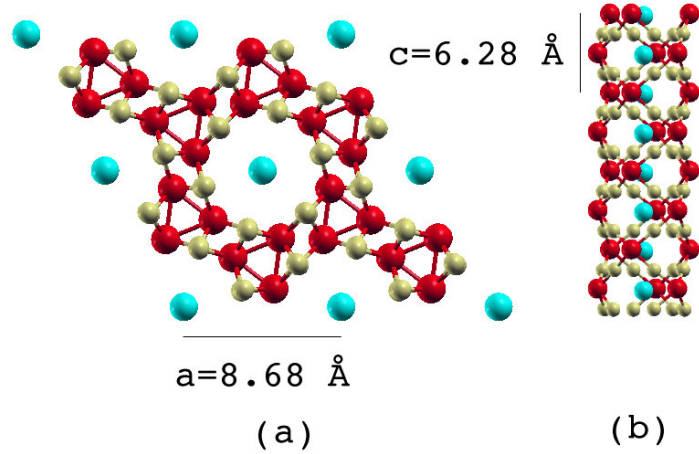


Figure 4.8: (a) View of a cross-section of a periodic array of MoS₂ (3,0) zigzag tubes with iodine centered in the tube channels. (b) Side view.

4.2.2 Model systems

We first consider the model as a hexagonal assembly of nanotubes of MoS₂. As shown in Ref. [250], a realistic topology of free-standing MoS₂ nanotubes is obtained similarly to that of carbon tubes, with half the

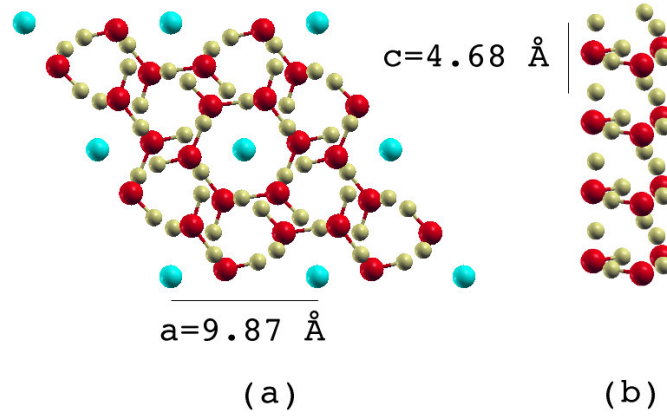


Figure 4.9: (a) View of a cross-section of a periodic array of MoS_2 (3,3) armchair tubes with iodine centered in the tube channels. Spin-unpolarized calculation. (b) Side view.

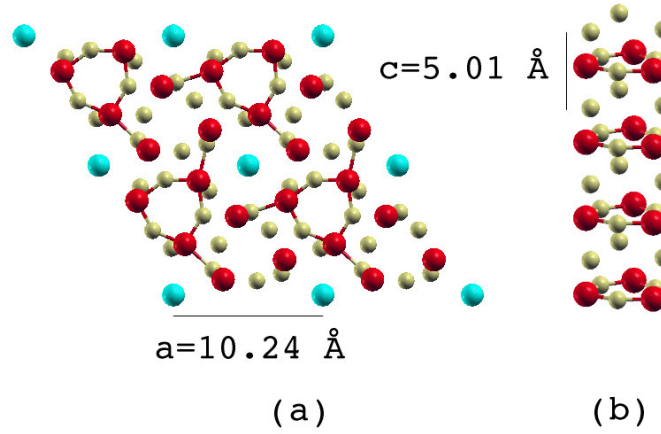


Figure 4.10: (a) View of a cross-section of a periodic array of MoS_2 (3,3) armchair tubes with iodine centered in the tube channels, from a spin-polarized calculation. A permanent magnetic moment of $12 \mu_B$ appears, and the structure relaxes to a significantly different minimum. (b) Side view.

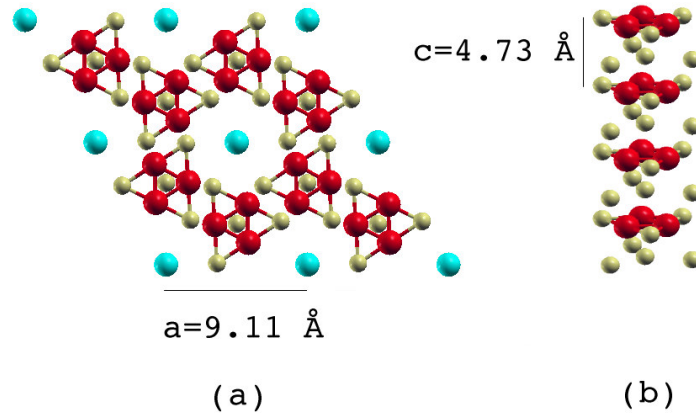


Figure 4.11: (a) View of a cross-section of a system of Mo₃S₄ with iodine centered in the channels of the Nb₃S₄ type structure. (b) Side view.

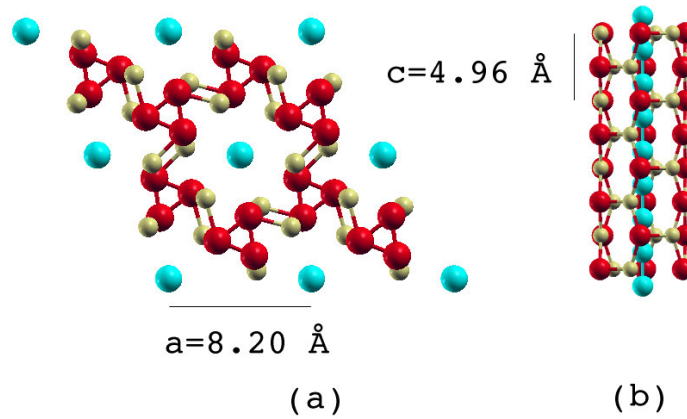


Figure 4.12: (a) View of a cross-section of a system of Mo₆S₆ with iodine centered in the channels. The structure resembles a carbon nanotube, with half the atoms replaced by Mo and the other half by S. (b) Side view.

carbons replaced by Mo, and the other half by two sulfur atoms: one inside and the other outside the average tube radius. The construction of fullerene-type systems by the same method produces endcaps which respect the stoichiometry and topological conditions. Only large diameter tubes are predicted to be stable, and indeed are observed experi-

mentally. Making a bundle out of very small diameter tubes introduces very different constraints, as we will show in section 4.2.5.

The bundles we consider to begin with are assemblies of both zigzag (3,0) and armchair (3,3) configurations, with iodine first in interstitial then in “in-tube” positions along the tube axis. Sulfur being a lighter element than iodine or molybdenum, there is more uncertainty in its stoichiometry from the EDX experiments of Ref. [229]. Two systems with less sulfur content are therefore also modeled, with stoichiometries Mo_3S_4 and Mo_6S_6 . The unit cell contains 6 Mo, 2 I atoms, and from 6 to 12 S atoms.

For all configurations, the unit cell was kept hexagonal, and the space group of the system was always P6_3 (C_6^6), as suggested in Ref. [229]. This is one constraint which could be loosened to search for other MoS_2 phases.

Based on the experimental stoichiometry of one iodine for three molybdenum, we suppose that the I atoms sit in high symmetry positions for P6_3 . There are two possibilities. Either in $(1/3, 2/3, 0)$ and $(2/3, 1/3, 1/2)$, which we will call the interstitial positions, in reference to the initial structure proposed by Remskar et al. (Fig. 4.5). Or, the iodines can lie in $(0, 0, 0)$ and $(0, 0, 1/2)$, which we will call the “in-tube” or centered positions, as the iodine then lies in the channels of the tubes for the initial nanotube model. We emphasize that these are naming conventions, labeled with respect to the initial structure; the relaxation of these systems to their equilibrium positions in several cases completely changes the structure (though not the position of the I, which are fixed by symmetry).

Six model systems are thus investigated: armchair tubes with interstitial I (the model proposed in Ref. [229] Fig. 4.5 and Fig. 4.6), or with centered I (Fig. 4.9 and 4.10). Then zigzag tubes with interstitial (Fig. 4.7) or centered I (Fig. 4.8). Finally the two phases with less sulfur, Mo_3S_4 (Fig. 4.11) and Mo_6S_6 (Fig. 4.12), with centered iodine atoms.

4.2.3 Calculation details

We performed calculations using the generalized-gradient approximation (GGA) of Perdew-Burke-Ernzerhoff [213]. A kinetic-energy cutoff of 40 Ha is used for the plane-waves, and the pseudopotentials are of the Trouiller-Martins type [276].

The atomic positions and lattice constants are allowed to relax completely using the Broyden algorithm [33], until the forces were less than $5 \cdot 10^{-4}$ eV/Å and the stresses less than $3 \cdot 10^{-3}$ GPa. The one exception was the armchair centered system with spin polarization, whose forces

Remskar	zz in	ar in	zz ch	ar ch	ar ch sp
1.58	0.39	0.57	0.50	0.98	0.67

Table 4.1: Binding energies for different MoS₂ based systems in eV/atom. The first column gives the value for the model from Remskar et al. **zz in**: zigzag nanotubes with interstitial iodine. **ar in**: armchair nanotubes with interstitial iodine. **zz ch**: zigzag tubes with iodine in the tube channels (centered). **ar ch**: armchair tubes with iodine in the tube channels (centered). **ar ch sp**: as **ar ch**, from a spin-polarized calculation.

and stresses saturated at a value less than $5 \cdot 10^{-2}$ eV/Å and $5 \cdot 10^{-2}$ GPa. The resulting displacements of atoms are smaller than 0.05 Å from step to step, and show no drift, so the positions are considered converged.

The relaxation can be very lengthy due to soft modes of vibration, in which the tubes rotate around their axis. The total energies are converged to less than 2 meV per atom with 8 k-points sampling the irreducible wedge of the Brillouin zone. A cold-smearing broadening of 0.01 (Ha) was used to accelerate the convergence with respect to the number of kpoints [177, 178].

4.2.4 Energetic stability

In this section we consider the relative stability of the different MoS_x systems. The four nanotube systems we consider have the same number of atoms of each atomic species, so the comparison of their relative stability is simple. In the case of the Mo₃S₄ and Mo₆S₆ systems, we have to choose reference systems in which the energy of one Mo, S, or I atom is well defined, in order to determine the relative binding energies. This choice will influence the final result: for example, choosing isolated atomic iodine as a reference will favor all systems where the iodine is bound. Choosing diatomic iodine will reduce this dependency, as I in I₂ has a lower energy.

The reference system of greatest interest in our case is planar hexagonal MoS₂. This is the bulk substance that is used in experimental synthesis, and is the most stable phase of MoS₂. The choice of h-MoS₂ gives the additional advantage of providing an external reference: instead of just considering the relative stabilities of the compounds, we can evaluate their “absolute” stability. Crystalline MoS₂ is a layered structure where the sheets are bound together by Van der Waals interactions. The difference with h-MoS₂’s binding energy represents the

strain needed to roll up the S-Mo-S layer, the interaction between tubes, and the binding energy of Mo and S with the iodine. For reference, a (10,0) carbon nanotube (with a diameter of around 8 Å) is estimated to have a strain energy of 0.1 eV/atom based on an LDA calculations [51].

We begin by comparing the stabilities of the phases with MoS_2 stoichiometry. The energy of an equivalent amount of bulk MoS_2 and gaseous I_2 is subtracted from the total energy of the phases, and then divided by the number of atoms in the system (20). Our results are summarized in Table 4.1. The results refer to spin-unpolarized calculations except column **ar ch sp**. Adding spin-polarization showed no magnetic moment in any system except the armchair tubes with centered iodine. In this case, quite surprisingly, a huge magnetic moment of 12 μ_B is found to be stable, and further relaxation of the geometric structure occurs (see below for the details of the geometrical and electronic effects, and a discussion of the calculation). As far as the energy is concerned (Table 4.1 column **ar ch sp**) it is lowered with respect to the spin-unpolarized case for armchair tubes with I in the channels.

The most stable phase is found to be zigzag tubes and interstitial iodine. The other nanotube-based structures come next, including the spin-polarized armchair case with centered I, within less than 0.3 eV/atom from the zz interstitial value (apart from the non spin polarized armchair case). We thus have a set of phases with different atomic arrangements and similar binding energies.

The binding energies for systems with differing stoichiometries are calculated as follows. First a simple calculation is carried out for the systems of metallic (BCC) Mo, and isolated molecules of I_2 and S_2 . The energies of these systems give us the reference chemical potential μ of each species, and we can calculate the free energy H of the different phases as a function of μ_{S_2} and μ_{I_2} :

$$H = E_{\text{tot}} - N_{\text{Mo}} * (\mu_{\text{Mo}} - \mu_{\text{Mo}^{\text{ref}}}) - N_{\text{S}} * (\mu_{\text{S}_2} - \mu_{\text{S}_2^{\text{ref}}}) - N_{\text{I}} * (\mu_{\text{I}_2} - \mu_{\text{I}_2^{\text{ref}}}) \quad (4.1)$$

The variation of H with respect to the chemical potentials of S and I is shown in Fig. 4.13. The reference energy on the vertical axis (horizontal lines) is h- MoS_2 for μ_{I_2} and metallic Mo with I_2 for μ_{S_2} . The different $\text{Mo}_6\text{S}_{12}\text{I}_2$ phases are parallel lines, the most stable being the zigzag interstitial case. The Mo_3S_4 , Mo_6S_6 , MoS_2 , and reference phases are noted in Fig. 4.13. In Fig. 4.13(a) bulk h- MoS_2 remains substantially more stable than even the best bundle phase. This is due to the strain energy which is added because of the strong curvature present in all these structures when compared to the planar sheet. The model from Ref. [229] is the least stable: it was proposed based on symmetry and

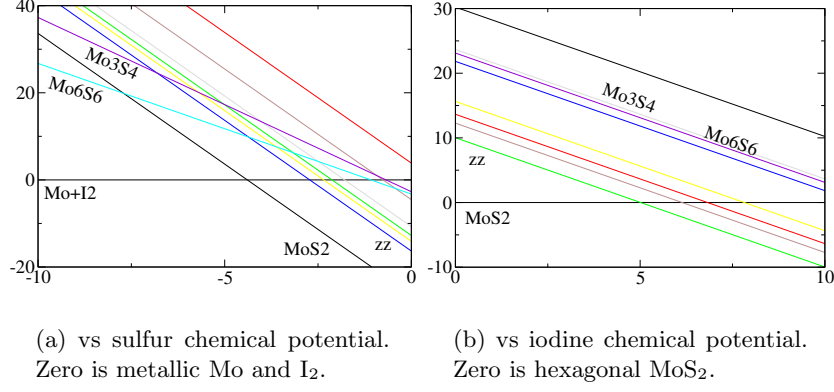


Figure 4.13: Free energies H (in eV) for the different bundle systems, as a function of the chemical potentials of S and I (in eV with respect to the references $\mu_{S_2}^{ref}$ and $\mu_{I_2}^{ref}$). The different lines are described in the text.

volume considerations only, and had not been refined with energetic or steric considerations. As μ_{S_2} is lowered, separated metallic Mo with I_2 becomes stable before any of the bundles, even the two sulfur-poor phases. For $\mu_{I_2} > \mu_{I_2}^{ref} + 5$ eV, the bundle phases become more stable than isolated MoS_2 and I_2 . This may explain the conditions of synthesis which are employed, supersaturating the phase with I_2 could lead to conditions where the bundles are preferred energetically.

The two main characteristics of our system, compared in particular to h- MoS_2 or to the large diameter free-standing tubes, are the bundle structures and the presence of iodine. The iodine can bind with both molybdenum and sulfur, lowering the total energy. Binding of a tube with its neighbors expands the tube diameters, reduces curvature, and thus decreases internal strain. To separate the contributions of iodine binding and inter-tube binding, we first calculate the energy of a bundle without iodine. Then, a further calculation is carried out in which the tubes are separated by several Å. In this way the two different contributions can be estimated.

This procedure is carried out for the most promising systems presented thus far (best binding energy and best geometry resp.), viz. the zigzag interstitial and armchair centered spin-polarized systems. The zigzag interstitial system without iodine is found to be 3.53 eV higher in energy (Mo binding to the two I atoms). When we further separate the tubes by about 7 Å, the system is then 11.7 eV (i.e. 0.65 eV/atom)

higher in energy than the bundle with iodine. We emphasize that the tube was not allowed to relax to its equilibrium diameter, so the energy difference is only due to the binding between neighboring tubes. Since the tubes have precise Mo_1S_2 stoichiometry, we expect no dangling bonds, and negligible Van Der Waals interaction between tubes at this distance.

In the armchair centered case, extracting the iodine actually gives a slightly less bound system, by 1.48 eV. This corresponds to the picture of Fig. 4.10 (b) where the iodine appear bound to each other but to nothing else. Separating the two tubes in each unit cell by 6 Å raises the energy by 11.8 eV. This value is similar to that obtained for the manifestly bound zigzag interstitial case, which implies that the tubes are still strongly bound together in the armchair case: although the distance between atoms in separate tubes of the relaxed structure is larger, the clusters of Mo_3S_6 are interleaved, and still interact with neighboring tubes.

4.2.5 Geometry and relaxed structures

The relaxed atomic structure of the solid state phases is a very important criterion to extract interesting models from the chaff. In the GGA, most lattice parameters can be calculated to within a few percent of experiment. Exceptions are systems with long-range or Van der Waals forces, which are not accounted for in standard density functionals, or highly ionic systems, in which the pseudopotential approximation could become apparent. Our system could fall into the first of these categories, as h- MoS_2 displays VdW interactions between its layers. Nevertheless, we expect at least reasonable agreement with the experimental values of $a \simeq 9.6\text{Å}$ and $c \simeq 4.0\text{Å}$

	Remskar	zz in	ar in	zz ch	ar ch	ar ch sp	Mo_3S_4	Mo_6S_6
a	9.6	8.84	11.05	8.68	9.87	10.24	9.11	8.20
c	4.0	5.58	3.32	6.28	4.68	5.01	4.73	4.96
vol	214.04	235.81	253.41	274.4	264.8	304.9	228.2	193.9

Table 4.2: a and c hexagonal lattice parameters (Å) and unit cell volumes (Å^3) for MoS_2 based compounds in zigzag and armchair configurations, with I in interstitial and centered positions, and in Mo_3S_4 and Mo_6S_6 configurations as explained in Table 4.1. The first column gives the corresponding values used in the model of Remskar et al., estimated from experiment using TEM and X-Ray diffraction data.

4.2.5.1 Lattice parameters

In this section we present the relaxed lattice parameters and atomic positions for the six phases described above. The lattice constants and unit cell volumes are summarized in Table 4.2.

The two zigzag configurations and Mo_6S_6 have lattice parameters a smaller than the experimental value; armchair tubes and Mo_3S_4 give a larger a . The c lattice parameter is systematically too large, except for the armchair interstitial case. The specific case of the armchair configuration with spin-polarization presents the largest volume. This is probably the effect of same-spin electron repulsion: the total magnetic moment is large, and the majority spin state is very populated. Mo_6S_6 is the only system with a small unit cell volume. This is natural, as the number of sulfur atoms is much smaller than in the other models (6 instead of 12). Similarly, the volume of Mo_3S_4 is lower than that of the other systems. Globally, the overestimation of the volume is an effect of the GGA approximation which usually overestimates distances (whereas LDA underestimates them).

4.2.5.2 Bond lengths and angles

The types of bonding vary widely between the different models. The bond lengths and the angles between bonds in the relaxed structures are summarized in Tables 4.3 and 4.4. Values are also given for the initial model in Ref. [229], along with the VdW and covalent radii, and the bonds in h-MoS_2 . The fact that GGA usually overestimates distances must be kept in mind when analyzing the bond lengths.

Covalent bonding appears between Mo and S in all cases, but the initial nanotube structures are completely distorted. Bonding appears between tubes and forms a 3-D lattice in the zigzag cases, the armchair interstitial, and in Mo_6S_6 . In the armchair interstitial structure, the inter-tube Mo-S bond is $2.60\text{\AA}$ (somewhat longer than the $2.39\text{\AA}$ intra-tube distance), but in the zigzag case there are Mo-S inter-tube bonds of only $2.32\text{\AA}$, and the intra-tube bonds are either 2.27 , 2.33 , or $2.44\text{\AA}$. The systems are thus very strongly bound and the structures are not so much a bundle of loosely held tubes as a kind of zeolite structure with nano-channels at the center of the “tubes”. Iodine in the centered position binds to other I, whereas there are many I-Mo bonds in the interstitial structures, and the whole structure is tightly bound. The Mo_3S_4 structure consists of small clusters of 3 Mo and 3 S atoms, capped with an S atom above and below. The clusters are separated from each other by roughly $2.9\text{\AA}$, and are stacked in alternating planes at the

$(1/3, 2/3, 0)$ and $(2/3, 1/3, 1/2)$ positions of the hexagonal unit cell.

The armchair centered structure also shows an interesting evolution: from the initial nanotube structure, the spin-unpolarized relaxation gives an exploded structure with S–Mo–S units. The further spin-polarized calculation re-constitutes clusters, as in Mo_3S_4 , which are hexagons of Mo_3S_6 , in alternating layers once again, and separated by 2.7 Å. The hexagons overlap each other with sulfur atoms, but can be seen as interlaced tube-like structures. With respect to these new tubes, whose axes are now at $(2/3, 1/3)$ or $(1/3, 2/3)$, the iodine is once again interstitial. The tube packing is no longer simply hexagonal: the two tube positions alternate on a hexagon around the channels of iodine. The configuration is shown in part (b) of Fig. 4.10.

species-pair	zz in	ar in	zz ch	ar ch
Mo – Mo	3.06	3.32	2.83	3.59
Mo – S	2.32, 2.37, 2.40, 2.46, 2.53	2.44, 2.45, 2.55, 2.60, 2.91	2.33, 2.36, 2.41, 2.46, 2.51, 2.55	2.24, 2.61, 2.65, 2.79
Mo – I	2.64	3.33	3.85	3.70
S – S	3.26, 3.35, 3.37, 3.40	2.93, 3.01, 3.29, 3.32	2.86, 3.11, 3.17, 3.34, 3.38, 3.45	2.71, 2.78
S – I	2.96, 3.33, 3.42	3.09, 3.87	3.61, 3.69	3.27
I – I	5.58	3.32	3.14	2.34
α_{S-Mo-S}	87, 91, 6, 93, 174	69, 72, 86, 84, 133, 136, 146	85, 93, 73, 123, 147	90, 94, 101, 124

Table 4.3: Bond lengths (Å) in $(\text{MoS}_2)_6\text{I}_2$ compounds for nanotube-based configurations (armchair and zigzag tubes), with iodine in interstitial and centered positions. The last line shows S-Mo-S angles in degrees.

species-pair	ar ch sp	Mo_3S_4	Mo_6S_6	Renskar	VdW	cov	h-MoS ₂
Mo – Mo	4.15, 4.36	2.46	2.30	3.51		2.60	3.15
Mo – S	2.35, 2.49, 2.62, 2.98	2.43, 2.50, 2.76, 2.86	2.51, 2.63, 2.68	2.46, 2.49, 3.36		2.32	2.35
Mo – I	3.61	4.23	3.75	3.37		2.63	
S – S	2.84, 2.92	3.00, 3.49	3.26	2.49	3.6	2.04	2.98, 3.66
S – I	3.31	3.49	3.42	2.79	3.78	2.35	
I – I	2.44	2.37	2.48	4.00	3.96	2.66	
α_{S-Mo-S}	79, 101, 103, 111	82, 91, 180	79, 172, 127	60, 90, 108, 122, 146			101

Table 4.4: Bond lengths (Å) in the spin polarized armchair channel case, the $(\text{MoS}_x)_6\text{I}_2$ compounds, and the model from Renskar et al. Column 5 shows the Van der Waals radii, column 6 the covalent radii, and column 7 the bond lengths in crystalline MoS_2 . The last line shows S-Mo-S angles in degrees.

The coordination of Mo can vary strongly in its different oxidation states, so the wide variety of S-Mo-S angles should not come as a surprise. Only the armchair centered case (with or without spin polarization) presents angles similar to those in h- MoS_2 , but the trimers of S-Mo-S involved are not strictly perpendicular to the tube axis.

Our findings can be compared with the isolated MoS_2 nanotube calculations of Seifert et al. [250] who used a DFT-based tight-binding method: they find the tubes are stable for large diameters ($> 20 \text{ \AA}$), and their strain energy follows a $1/D^2$ law where D is the diameter of the tube. Extrapolating their calculations of strain energies, stand-alone (3,3) and (3,0) tubes should be highly unstable. Furthermore, according to the trend in Ref. [250], these isolated (3,m) tubes should have very small diameters $\sim 5 \text{ \AA}$.

The atoms which should correspond to individual nanotubes, cut out of the bundles, are shown in parts (b) of Figures 4.7 to 4.12. The effective diameter of the “tubes” is found to be much larger: $8 \text{ \AA}$ for the zigzag and $8.5 \text{ \AA}$ for the armchair tubes. In the armchair centered structure, the effective diameter is $8.3 \text{ \AA}$. Once the structure is allowed to spin polarize, the new tubes which form have a very small $\sim 5 \text{ \AA}$ diameter, but a topology which is different from the original armchair.

4.2.6 Electronic structure and magnetism

4.2.6.1 Band Structures

In Ref. [229] it is suggested that the tubes should be metallic. In order to check this, we calculate the band structures of the various bundle systems. All of the systems are metallic (contrarily to h- MoS_2 which is an insulator).

Fig. 4.14 and Fig. 4.15 show the electronic band structure for the armchair and zigzag bundles, respectively, with iodine in the interstitial position. Both systems are also metallic along the tube axis (Γ -A line). This is consistent with calculations for isolated nanotubes [250], where the band gap increases with the tube diameter, and is close to 0 for diameters around $9\text{--}10\text{ \AA}$. But both bundles are also metallic in the direction perpendicular to the tube axis. This is a further consequence of the strong bundle structure.

In Fig. 4.16 the band structure for the armchair centered case is shown.

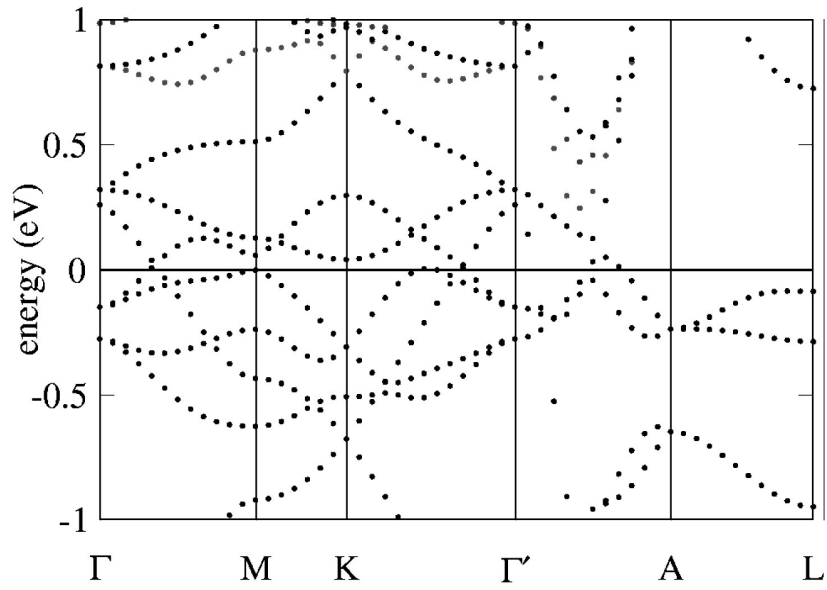


Figure 4.14: Band structure of a bundle of armchair MoS₂ nanotubes with interstitial I.

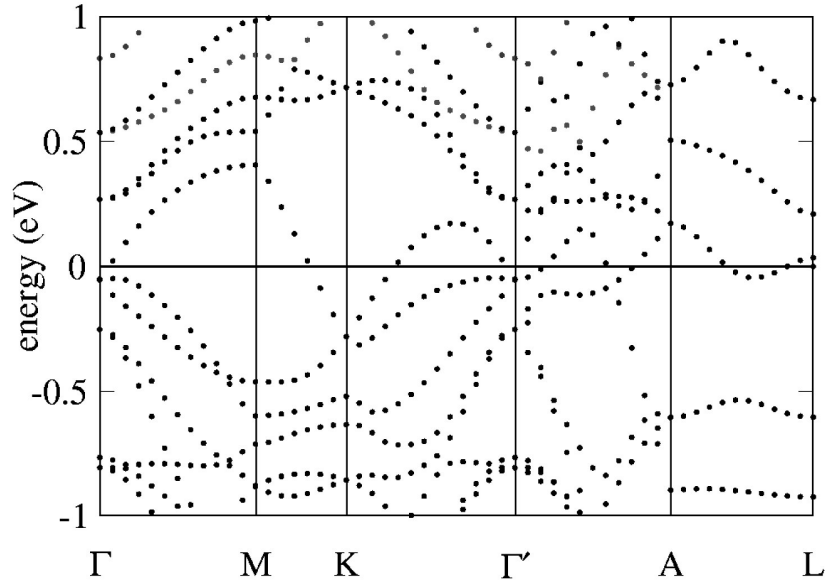


Figure 4.15: Band structure of a bundle of zigzag MoS₂ nanotubes with interstitial I.

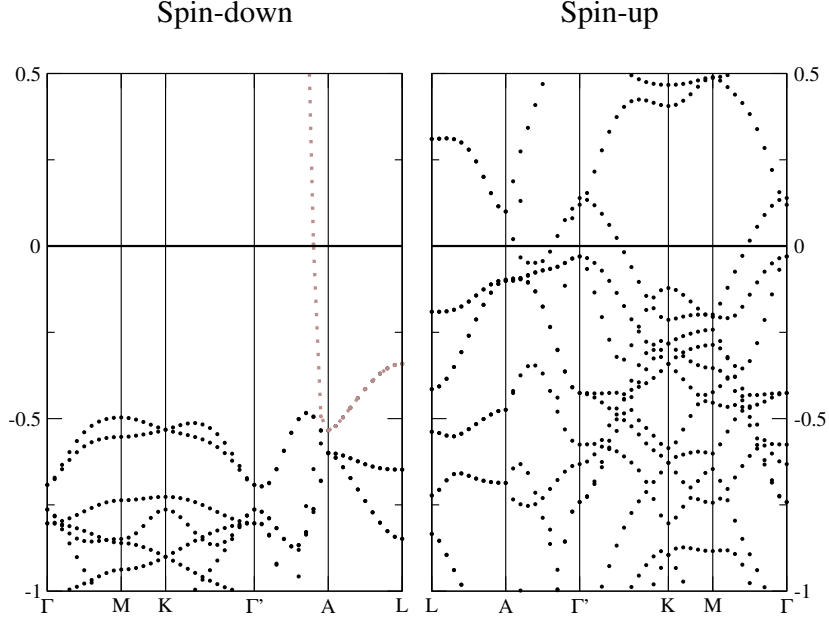


Figure 4.16: Band structure of a bundle of armchair MoS_2 nanotubes with centered I.

4.2.6.2 Magnetism

The entire set of systems was re-calculated in spin-polarized DFT where two spin orientations are allowed. The exchange-correlation energy then depends on both spin-up and spin-down densities, or equivalently on the total electron density and on the magnetization density (cf. Ref. [213])

$$\xi(x) = \frac{n_{\uparrow}(x) - n_{\downarrow}(x)}{n(x)}$$

Among the six systems, only the armchair centered case displays a net magnetic moment. This is very intriguing, as the different configurations can be very similar in stoichiometry and/or geometry.

The zigzag tubes with centered I have a very similar structure in the x-y plane, and the molybdenum atoms are roughly in the same place. However, in the armchair case the sulfur are in the same plane as the Mo, whereas for the zigzag case they are in alternating planes halfway between the Mo. As a result, the zigzag structure has a smaller a lattice constant, and a larger c ; the armchair configuration has to accommodate all the Mo and S atoms in the same plane, and thus becomes larger. In

both cases there are sulfurs which bridge from one Mo atom to another, but in the armchair configuration there are also S atoms with only one molybdenum neighbor.

A cross-section of the difference between spin-up and spin-down densities is shown in Fig. 4.17. The residual spin-up density is localized in d-orbital-like regions around the molybdenum atoms. An analysis of the angular momentum character of the bands near the Fermi surface reveals that the spin-up states (which are metallic) are of mixed Sulfur-p and Molybdenum-d character. The spin-down states have Sulfur-p character below the gap and Molybdenum-d character above it. From the spin-difference we see that the p-character spin-down density on the sulfur is perfectly compensated by the p component of the hybridized spin-up states. The Mo-d component is not compensated and accounts for the observed magnetic moment. The p character for spin-up states below E_F is located predominantly on the isolated S atoms. For spin-down states the p character is distributed on both S atoms, but the states closest to E_F are also located on the isolated sulfur.

The initial spin-up spin-down symmetry must be broken in order for the system to converge to its physical minimum. This is done by starting from initial densities $n_\uparrow$ and $n_\downarrow$ which favor the up or down density on certain atoms. We also tested that the aligned configuration is the minimum of the energy when the starting density has anti-parallel spins on the two inequivalent sulfur atoms. A simulation of the system without the Iodine atoms also reveals a similar magnetic moment.

4.2.7 Discussion

The binding energies of all the phases are within an interval of 0.5 eV/at. In these conditions, one can envisage their coexistence, and the phase which will actually be synthesized will depend very strongly on the experimental conditions, on the catalysts used, and on the kinetics of the reaction. We now consider the experimental data and other criteria which can help us evaluate the different models, and propose new directions for research on these materials.

4.2.7.1 Formal valence and coordination

The natural valence states for S is -2, and therefore a Mo which is +4 (as in MoS_2) satisfies the valence. Mo can adopt a number of different oxidation states, from +2 to +5 or even +6 with fluorine (in MoF_6). The presence of iodine in the lattice complicates the balance: the iodine can be in a -1 or a neutral (0) state. In all the centered cases, the proximity

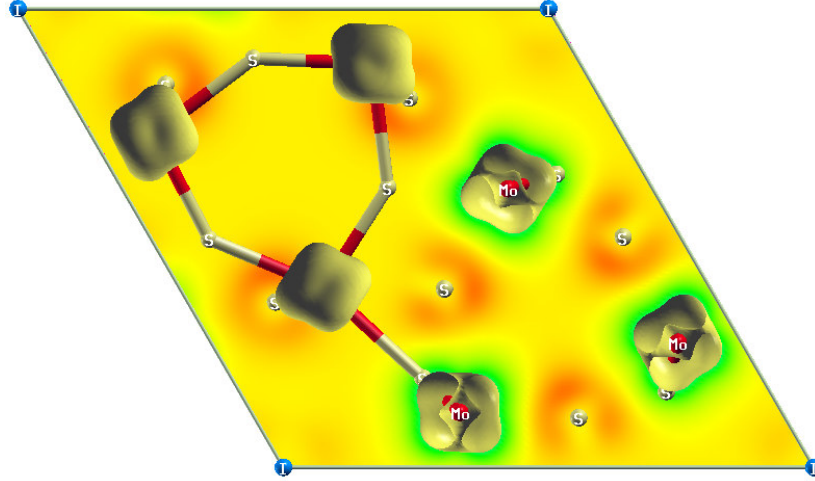


Figure 4.17: Spin-up - spin-down electron density difference: cross-section of the unit cell of a bundle of armchair MoS_2 nanotubes with centered I. Red = zero density Green = highest density. Spin-up density is dominant in d-like orbitals around the Mo atoms, shown by an iso-density at 0.05 eV/bohr^3 .

of other iodine atoms and the greater distance from Mo and S make the 0 valence more realistic. This is also coherent with the binding energy of iodine in the armchair centered case (see below). In the interstitial cases, the iodine is much more closely bound to Mo or S, and is more probably I^- . Some of the Mo should become +5, but by symmetry all of the atoms are equivalent, so the formal valence state is a partial +4.333. In the case of $\text{Mo}_3\text{S}_4\text{I}$, the formal valence is satisfied for I^- , if the Mo are +3.

The +3 state should correspond to an octahedral coordination of the Mo, as explained in Ref. [233]. In Mo_3S_4 and Mo_6S_6 , the Mo are in clusters with 3 Mo, bridging S atoms, and additional capping S for Mo_3S_4 . This follows remarkably well the distortion of the lattice observed in Ref. [233], where 3 atom Mo clusters are also formed. The presence of Li, or iodine in our case, can change the average valence by adding or subtracting an electron, and favors metallic Mo-Mo bond formation.

Mo +4, as in MoS_2 should lead to Mo atoms at the center of trigonal

prisms. Mo +3 or +5 is roughly octahedral once again, as in MoCl_5 and MoCl_6 [53]. The only difference between the trigonal and octahedral shapes is the elongation of one axis. In the armchair interstitial system the environment is trigonal prismatic although severely distorted. A 7th sulfur atom is present at 2.9 Å. For the armchair centered model, the Mo is in a distorted octahedral site, but two of the sulfurs are at 2.7 Å, and one apex is an iodine which is far away at 3.6 Å. This difference in coordination is suggested to play a key role in the magnetization which appears. The coordination of the sulfur is also particular in this system: there are S atoms with only one close Mo neighbor. The other systems always present S which is at least 2-fold coordinated.

The zigzag interstitial system presents almost perfectly octahedral coordination for Mo, with one iodine neighbor: each S and each I is shared by 3 Mo atoms. The structure is strikingly similar to that of MoCl_4 , which also creates hexagons of Mo linked by (divalent) Cl atoms. In the zigzag centered model, the Mo is 8-fold coordinated: 3-atom Mo clusters form (as in Mo_3S_4 and Mo_6S_6), and the surrounding octahedron of sulfur is still present.

To sum up, the coordination of Mo is always octahedral-like, but in the armchair cases it is more severely distorted. Octahedral is the preferred coordination for Mo in clusters and solids; the trigonal coordination only appearing for exactly +4 valence, as in h-MoS_2 . Perfect trigonal coordination is not observed in our systems, either because of a fractional valence, or for steric reasons.

4.2.7.2 Inter-tube binding

In the Mo_3S_4 and the armchair centered systems, there are loosely bound clusters of atoms. This is important, as Remskar et al. [229] report that by sonication they can separate ropes of very small numbers of tubes from the bulk bundles. It would be interesting to analyze the chemical composition of the rope (for example by Electron Energy Loss Spectroscopy) to see if it still contains iodine or if the dispersion succeeded in isolating just MoS_2 tubes. The tight covalent bonding between all atoms in the other models studied would seem to preclude this possibility. In carbon nanotube bundles, the intra-tube binding is very strong (similar to the in-plane graphite sp^2 bond), and the interaction between tubes is much weaker (Van der Waals). The dispersion of individual carbon tubes is thus fairly simple.

4.2.7.3 Iodine desorption

Experimentally, pumping over the MoS_2 bundles releases almost all of the iodine ¹. In the interstitial cases, the extraction of the iodine will be difficult, as the binding energy for the zigzag tubes is positive. However, the system is more stable in energy per atom in the final state. This is probably due to the “frustrated” valence of Mo described above. In the armchair centered configuration, the expulsion of iodine is almost certain: no binding occurs, and the iodine is probably already in a 0 valence state, so no charge transfer to the lattice is needed before I_2 can escape. The iodine only takes up space in the crystal, which explains why the system relaxes even further when the I is extracted. The binding energy per atom in the lattice is then more advantageous without iodine. As experiment demonstrates the presence of I in the lattice, it is probable that kinetic factors dominate, and I is incorporated into the lattice during its formation.

4.2.7.4 Iodine as an insertion component

Since the iodine in our systems is an insertion component, a natural way to change the lattice parameter is by adding or removing iodine. The quantity of iodine actually incorporated in the lattice will determine how bloated it is, and once the iodine is extracted a will return to its equilibrium value. Another possibility is the substitution of I for one of the S atoms. Iodine has a larger ionic radius, but only one valence electron to take from the system, instead of two for sulfur.

Iodine often substitutes for Sulfur atoms in inorganic compounds. This effect could contribute to the residual iodine which is not desorbed. However, we have not studied the energy of substitution here, because of the stoichiometric amount of the Iodine in the compound, and the manifest long range periodicity of the system. There is too much Iodine for the atoms to be randomly substituted. It is more probable that they occupy a given optimal place in the lattice. Nevertheless, adding iodine substitution opens many additional routes to model building, which should also be considered.

4.2.7.5 Stoichiometry

Accurate measurements of the stoichiometry of the bundles would bring precious evidence for further simulation work. As shown by Mo_3S_4 , a

¹D. Mihailovic, private communication.

similar lattice parameter and binding energy can be obtained with a sulfur-poor phase.

4.2.7.6 The effects of helicity

Hsu and coworkers reported the synthesis of MoS_2 nanotubes with a new method using MoS_2 powder instead of the MoO_3 [123] used previously. This is similar to the process used by Remskar and coworkers [229], and in both cases tubes grow perpendicular to the substrate. Hsu et al. argue that this type of perpendicular growth favors zigzag tubes, and they observe zigzag structures in the tubes they synthesize. The energetics suggest this is could be true: the zigzag tubes are more stable, with I centered or interstitial. However, the difference in binding energy is small, and the lattice geometries suggest the experimental phase is not one of the zigzag ones, as they both underestimate a (which should be overestimated, based on the considerations in section 4.2.5).

As the experimental tube spacing is intermediary between those we find for zigzag and armchair tubes, it is natural to think of intermediate-diameter tubes, with $(n,m) = (3,1)$, or $(3,2)$ as possible candidates for models. The resulting structure will probably be distorted, as it is observed for $(3,0)$ and $(3,3)$ tubes, but the relative dimensions of the systems could be conserved. As the size of the repeated periodic cell increases dramatically for chiral tubes (i.e. 260 atoms for $(3,1)$ and 380 atoms for $(3,2)$ instead of 20, due to the tube chirality and the added iodine), these *ab-initio* calculations would be lengthy, given the difficult relaxation and soft modes present. Further, we do not believe that this is a very promising path, for several reasons. For one, the high degree of crystallinity of the system would be blurred. With chiral nanotubes, diffraction spots are doubled according to the chiral angle of the tubes [152, 47], and the spots are rotated with respect to the tube axis. Also, the relative stacking of the tubes would have to be fixed, or even more disorder would be present in the system: in a bundle of tubes with intermediate helicities, there can be an offset, along the tube axis, between equivalent atoms of any two neighboring tubes, which adds additional (internal) degrees of freedom to the system.

The apparent uniformity of the bundles throughout the “fur” described in Ref. [229] is actually very different from carbon nanotube bundles, which are never mono-helical once they pass a certain size, and the individual tubes also have a spread of diameters. This can be explained by a crystal structure like those we present in this chapter: 3-D growth would create only one type of “tube” or crystal. All previous synthesis of MoS_2 nanotubes and fullerenes had yielded multi-layer

structures[75, 123].

4.2.7.7 Electronic structure

The metallicity of the bundles is something which should be easy to measure by scanning tunneling microscopy (STM). Further, scanning tunneling spectroscopy (STS) could differentiate between the proposed structural models based on their local densities of states. STM would also be an interesting complementary technique to study the atomic structure of the bundles. This will probably necessitate low-temperature STM experiments, for atomic resolution and for accurate STS measurements.

The unexpected magnetic results could be verified locally with magnetic force microscopy. One could presume the magnetic structure is erroneous, in particular the error could be due to the pseudopotential approach and the absence of dynamic interactions with the core electrons. However, in this case the error should be present in all of our very similar structural models. The fact that only one of the systems presents a magnetic moment, and that this moment is very stable with respect to geometric relaxation, magnetic perturbation, and the extraction of the iodine leads us to believe that the moment is a true physical characteristic of the atomic configuration. Nevertheless, we hope that this result in particular will be checked in the future using all-electron methods.

4.2.8 Conclusions

We have presented first-principles simulations of MoS_2 nanotube bundle systems. Starting from the model proposed in Ref. [229], based on experimental data, we explore a set of physically reasonable models with different stoichiometries and geometries, looking for the most probable candidate to explain the experimental data. Based on our present calculations, there is not enough experimental evidence to discern which of the phases has been truly synthesized. Several conclusions can nevertheless be reached.

Firstly, the experimental model based on the armchair configuration with interstitial I can probably be infirmed, as such a structure gives too large lattice parameters, is less stable than the zigzag configuration, and gives a tightly bound 3-D crystal. However the closely related armchair centered model could be a realistic candidate.

Six different $\text{MoS}_x + \text{I}$ phases have been studied, with relatively similar binding energies. Further experimental work will be needed to

determine whether the phase in Ref. [229] is among them, and if some or all of the systems we have reviewed can be synthesized by changing the experimental conditions. Other MoS_2 phases can be generated by changing the symmetry or the stoichiometry even further. We believe the most representative examples have been covered here, ie. those with the space group proposed from experiment, and which conserve the experimental stoichiometry for the heavier elements Mo and I, and S when possible. In each system, there is only one irreducible Mo atom, and two S atoms: all the other positions are deduced from the symmetry.

In the interstitial systems, the iodine is more tightly bound to the lattice. This is a first important test for experiment: can all of the iodine present in the bundles be extracted, or only a fraction, or none at all? Only the armchair centered and Mo_3S_4 systems present Van der Waals interactions in the plane perpendicular to the bundle axis. As such, the second important experimental criterion is the dispersion of small strands of the phase, which excludes the possibility of strong binding between the strands in the bundle.

We hope that the present study will stimulate more experimental work on these small-dimensional dichalcogenide systems, in order to provide evidence of their structure at the atomic level. This could be done using STM or MFM imaging, or EELS studies of the bundle stoichiometry. The catalytic mechanism, which uses C_{60} , still has to be clarified, and could also shed light on the charge state of the different elements in the system.

4.3 Epitaxial diamond growth on Ir (100)

4.3.1 Introduction

The growth of large single crystals of diamond has been an experimental goal for several decades now. Diamond has many interesting features, firstly its unsurpassed hardness, used in many applications for cutting tools, coatings, and tribology. In electronics, the growth of diamond films has attracted experimental attention due to other properties. Diamond conducts heat more than 10 times better than silicon (which would allow microchips to be cooled more efficiently), has higher carrier mobilities, and is very resistant to radiation damage, thanks to its large band gap.

Recently, synthesis techniques based on chemical vapor deposition (CVD) techniques have become popular because they use low temperatures and pressures. In this way diamond crystallites of up to a few hundred μm can be synthesized[160]. For applications in electronics, diamond is used as the semiconducting medium. In order to benefit from the optimal mechanical, thermal, and electronic properties of diamond, the films must be as monocrystalline as possible.

The choice of the substrate is primordial in determining the properties of the film: the lattice mismatch with the substrate, its chemical reactivity with the CVD precursor (namely its tendency to form stable carbides), and the solubility of carbon in the substrate will all influence the way diamond is nucleated and grown. Typical substrates for diamond CVD are silicon, $\beta\text{-SiC}$, and transition metals. Over the past five years, several studies have shown that iridium (100) is an exceptional substrate for diamond growth[244]. The crystallinity of the films, determined by X-ray diffraction, is an order of magnitude better than for other substrates (Si[80], Pt[130], Pd[130], Ni[253], or Re[19]).

The fact that iridium stands out so strongly calls for an explanation. In the following, we present calculations of the interactions between diamond and different substrates used experimentally. We differentiate the systems based on their interface energies and especially the dissolution energies of carbon atoms in the bulk metal lattices. We further characterize the carbon-iridium interaction by studying the migration energies of carbon in bulk Ir. Based on these results we explain the uniqueness of Ir, and propose a growth model for diamond on Ir(100).

4.3.2 Model systems and calculational details

Iridium, platinum, silicon, and rhenium are compared as substrates for diamond growth. Silicon is a popular and economical choice, platinum

is very close to iridium in crystal structure and chemical nature, and finally rhenium shows interesting features experimentally[19], as it can absorb much more carbon than Ir can.

Several different models are also considered. Firstly supercells containing alternating layers of metal and diamond, in order to calculate their interface energy. For Ir, Pt and Si, the (100) orientation of diamond and the metal are matched (for Si the cubic diamond cell is doubled and the Ir (100) direction is aligned with the Si (110)). In the case of hexagonal rhenium, the orientations are (111) for diamond and (0001) for Re. These are the growth configurations which have been studied experimentally. The lattice parameter mismatch produces lattice strain, so we calculate the interface energy with respect to strained diamond (all atomic positions, and lattice parameters perpendicular to the surface, are relaxed). The values of the strain are 7.8%(Ir), 9.7%(Re), 10.2%(Pt), and 7.9%(Si). The Brillouin zone was sampled with a $6 \times 6 \times 3$ mesh of k-points, using the cold-smearing scheme[177] and a smearing width of 0.01 Ha.

Secondly, single atoms of carbon are placed in supercells of bulk metal. The full system is allowed to relax (cell and atomic positions), for several sizes of supercell. For the cubic cases, k-point meshes of $8 \times 8 \times 8$ (1 unit cell) and $4 \times 4 \times 4$ (2 or 8 unit cells) points were used. For Re $6 \times 6 \times 4$, $3 \times 3 \times 4$, and $3 \times 3 \times 2$ meshes were chosen, for 1, 4, and 8 unit cells resp.

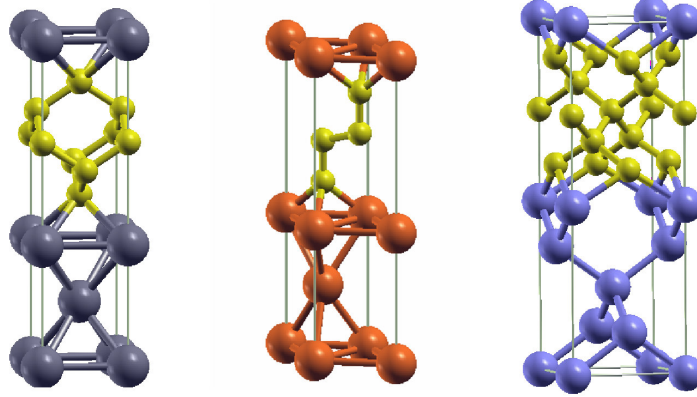


Figure 4.18: Supercell structures for diamond interfaces with Ir,Pt (left) Re (middle), and Si (right). Small spheres represent carbon atoms.

The Generalized Gradient Approximation [213] of Perdew, Burke,

and Ernzerhof is used to approximate the exchange-correlation energy. A planewave kinetic-energy cutoff of 40 Ha is used throughout this section. Structural relaxations are performed with a tolerance on forces of $5 \cdot 10^{-5}$ Ha/bohr and on stresses of $5 \cdot 10^{-7}$ Ha/bohr³.

4.3.3 Interface energies

We calculate the interface energy of diamond with the various metal substrates using a supercell containing three to five layers of metal and four or five of diamond, as in Fig. 4.18. In all cases, convergence tests were performed on the number of diamond and metal layers: using unstrained diamond as a reference gives a constant drift of the interface energy as a function of diamond layers, equal to the additional strain energy for each additional layer of carbon. For silicon ten layers of Si were used (thicker than in Fig. 4.18). In these configurations, the interface energy is calculated from the difference in energy between the supercell and the individual bulk materials (metal and strained diamond). The in-plane lattice parameter is fixed to that of the metal, to simulate the presence of a thick substrate.

The interface energies obtained are 0.42, 0.38, 0.04, 0.36 eV/Å² for Ir, Pt, Re, and Si respectively. The energies per unit area are very close, except that of rhenium, which is significantly lower. This behavior of Re is consistent with a general tendency of transition metals to create carbides if the d-shell is less than half filled[258, 222], but may be simply due to the diamond presenting its (111) face instead of (100). Surprisingly, iridium does not present a better interface than platinum or silicon. This leads us to the conclusion that kinetic effects dominate the CVD process. Finally, let us recall that these energies do not contain the contribution of diamond strain, and are idealized. In practice the stability of a macroscopic interface will depend on other factors: the thicker the film, the greater the force which will detach the diamond, as happens with rhenium[19], unless the interface strain can be relaxed with dislocations and defects.

4.3.4 Dissolution of C in the substrates

In CVD diamond growth it is not clear which species are the most important source of carbon. C, C⁺, C⁻, C₂, CH, CH₂, CH₃, C₂H₂, and others may be present[160]. The most successful CVD growth techniques for diamond require that, in a first nucleation phase, a bias voltage be applied to the plasma (Bias-Enhanced Nucleation BEN [291, 244]). Carbon atoms can then implant themselves into the surface. Post-hoc analysis

of the samples shows that a varying amount of carbon finally stays inside the metal lattice, depending on the substrate and on the process details.

In order to understand the dynamics of the implantation and nucleation process, we consider a supercell of metal with an additional carbon atom. The atom is either in an interstitial position or in substitution in the lattice. We calculate the difference in energy ΔH for the lattice with and without a carbon atom:

$$\Delta H = E_{\text{tot}} - N_{\text{C}}E_{\text{dia}} - N_{\text{metal}}E_{\text{metal}}, \quad (4.2)$$

where N_{C} and N_{metal} are the number of carbon and metal atoms, E_{dia} the energy of one atom in diamond, and E_{metal} the energy of one atom in the bulk metal. In this way we can determine the behavior of carbon atoms in the bulk or near the metal surface: if the ΔH is positive and sufficiently high to overcome barriers to diffusion, then the carbon will be expelled to the surface.

For the FCC metals, there is only one natural interstitial site, the octahedral site. For silicon, one tetrahedral site is occupied by a silicon atom, so the only site left is the other tetrahedral one. For rhenium the site at $(1/3, 2/3, 1/4)$ is the most stable.

4.3.4.1 Dissolution energies

Calculations were performed with interstitial and substitutional carbon for various concentrations between 0 and 50%. The resulting interstitial dissolution energies are shown in Fig. 4.19(a), and the substitutional energies in Fig. 4.19(b). We stress here that these numbers should not be directly compared to equilibrium concentrations of carbon in metal. The latter are governed by equilibria between different phases, and carbon can cluster at grain boundaries and defects, which increases the effective local concentration. Our calculation shows a difference in affinities and behaviors as a function of concentration.

The most striking feature in the case of interstitial carbon is the behavior in iridium for low concentrations, where the inclusion of carbon is very favorable. For larger concentrations (15%), however, carbon quickly becomes unstable in the lattice. Rhenium has a very different behavior, as carbon is only slightly unstable in the lattice, and stays so up to a much higher concentration of 20 or even 30%. Substitutional carbon is uniformly less stable than interstitial, except for very high concentrations, close to 50%, where carbide formation is evident for Si, and, to a lesser extent, Re. The differences between Re, Ir, and Pt follow the broad tendency of carbon interacting more strongly with less filled

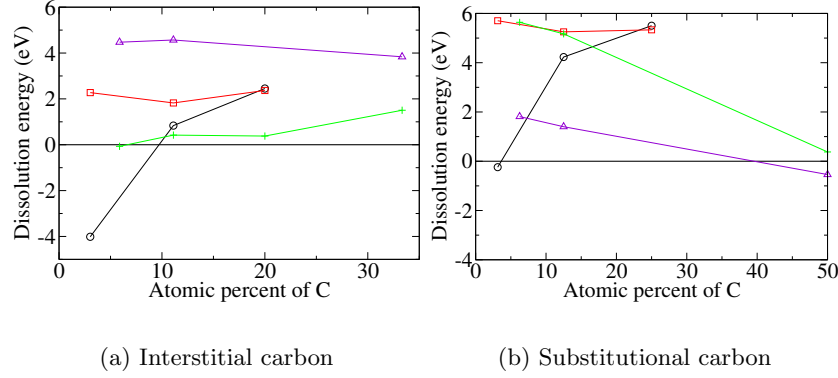


Figure 4.19: Dissolution energies of carbon in different metal substrates. circle = Ir, plus = Re, square = Pt, triangle = Si. Dissolution in Ir is very favorable at low concentrations and remains possible in Re up to much higher concentrations.

d-shell transition metals. Ir is the limiting case of the first non-carbide-forming 5d metal[258].

4.3.4.2 Lattice parameters

The introduction of carbon atoms into the metal lattices can either expand or contract the average lattice parameter, depending on the position of the C and on the concentration. For Ir and Pt the situation is simple: substitution shrinks the lattice, whereas interstitial C inflates it. In the case of Si, the two species are very similar but C is smaller, and substitution decreases the lattice parameter linearly, leading to the β SiC phase. Interstitial C leads to almost no increase in the lattice parameter, as C simply fills the holes in the silicon lattice. Finally, for Re the evolution of a and c with C concentration is much more complex. Broadly speaking, the c parameter is constant or decreases and the a parameter increases with C content, but for 50% C the carbide phase regains a shorter value of a . The point at a carbon concentration of 20% corresponds to a system with much lower symmetry, and should probably not be considered in the convergence of the lattice constants. Its dissolution energies are nevertheless coherent with the other concentrations.

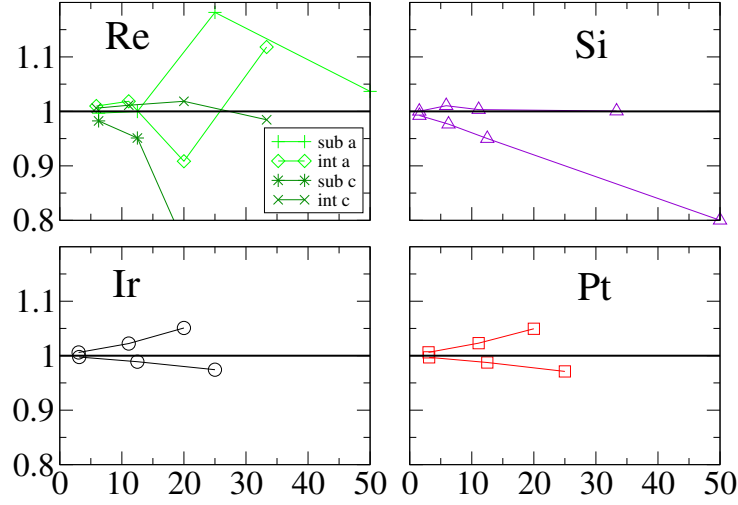


Figure 4.20: Relative variation of the metal lattice parameter with atomic concentration of carbon (atomic %). circle = Ir, plus = Re, square = Pt, triangle = Si. For Re the inset explains the symbols for the a and c lattice parameters with substitutional and interstitial C.

4.3.5 Migration of C in Ir

In order to complete our study of carbon in iridium, we estimate the diffusion barrier of C in bulk iridium in the following way: the energy of a $2 \times 2 \times 2$ FCC supercell of bulk Ir is calculated, with a carbon atom in different positions. First in the octahedral and tetrahedral sites, then in the center of a face of an octahedron. Atomic positions are relaxed. In the last case the Ir is constrained in the octahedron face.

The octahedral site is the most stable, at 0.84 eV, followed by the tetrahedral one at 2.17 eV (energies are calculated, as above, with respect to bulk metal and diamond). The real barrier to migration lies at in the octahedron face the atom must squeeze through to pass into the tetrahedron. The face site is at 3.26 eV (a maximum value). The barrier should be compared to the dissolution energy for a carbon atom in bulk Ir above. From this point of view we see that above a concentration of 15 to 20 at.% in carbon, the migration of the atoms becomes possible, leading to segregation.

4.3.6 Growth model and conclusions

At this stage it has become evident what the difference is between the substrate metals, and we can suggest a scenario for the CVD nucleation and growth of diamond. Iridium happily accepts carbon at the beginning of the CVD process. Employing BEN further increases the quantity of carbon beyond equilibrium, and once the concentration goes above 10% the carbon is expelled to the surface. The large quantity of carbon present allows nucleation and growth to proceed. There is much speculation on the precise effect of using BEN[160], and many results suggest that the induced changes in surface morphology give many nucleation sites, and/or that carbon clusters are needed as seeds, and are created during BEN. Both of these phenomena would be enhanced for Ir, due to the very rapid transition from carbon-absorbing to carbon-expelling regimes. BEN also increases etching but this is not taken into account in our study, and is probably less substrate-specific.

In Re, carbon can also be incorporated, though not spontaneously. However, it is retained inside the lattice up to much greater concentrations. For the other substrates, little carbon is allowed into the lattice, and all nucleation must occur using only the carbon present at the surface.

We note that the carbon concentrations considered here concern only the last few nm of metal. Our calculations remain “equilibrium” estimations, and must be taken with the appropriate grain of salt, but nevertheless demonstrate clearly the uniqueness of Ir.

In conclusion, we have demonstrated the chemical specificity of the interaction between carbon and iridium. Interface and dissolution energies were calculated for a number of representative substrates used in CVD diamond growth. The differing behavior of iridium was suggested: carbon dissolution in bulk Ir is highly favorable for low concentrations, but increasing the concentration beyond 15 at.% makes the system unstable. Si and Pt do not dissolve carbon easily. Rhenium can also dissolve carbon, but does so up to much higher concentrations. Only Ir, therefore, expels sufficient amounts of carbon to its surface sufficiently fast for efficient diamond nucleation and growth. The concentration of carbon must nevertheless be pushed beyond the thermodynamical equilibrium using BEN. The migration of carbon atoms in bulk Ir is shown to be possible once the concentration is higher than 15%.

Exploiting the model proposed here for diamond nucleation will require a finer understanding of the dynamics of the carbon migration processes. In particular in order to determine more precisely the critical conditions which favor carbon segregation at the right moment during

nucleation. The role of temperature in particular is very important in activation processes like migration/segregation and also determines the diffusion rates on the surface. The position of iridium as a borderline case suggests experimenting with ruthenium and copper, the corresponding 4d and 3d elements. Finding a silicon-based, or otherwise less expensive, substrate which presents a dissolution vs. concentration curve similar to Ir would open the way to large scale industrial applications of diamond transistor technology.

Chapter 5

Electron-phonon coupling

There Ain't No Such Thing As A Free Lunch

Robert Heinlein
in “The Moon is a Harsh Mistress”

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5.1 Introduction

A number of different DFT simulation codes incorporate the electron-phonon interaction in their available packages. In particular, DECAFT [59] and PWSCF/ESPRESSO [16] implement schemes very similar to ours, and also use plane wave pseudopotential formalisms. In this chapter we present the implementation details, describing subroutines, inputs, files for data and output, and a systematic study of the convergence with respect to different parameters (kpoints, qpoints and integration techniques). The basic articles in both planewave[168] and LMTO[242] formalisms present very little in the way of implementation. The nitty-gritty details and convergence tests are not interesting research as such, and are never included in published work. It is for this reason that we collect them here, in order to facilitate the use and especially the extension of the present implementation in ABINIT. Re-reading and understanding your own code is hard enough, but digesting someone else's is close to impossible, even if it is correctly documented in-line.

The electron-phonon part of the present version (4.6) of the ABINIT package calculates essentially isotropic quantities, which are averaged over the Fermi surface and the bands near the Fermi level. In particular, the main outputs are the phonon linewidths, which describe the finite lifetime of phonons due to their interaction with electrons, and the electron-phonon coupling through the isotropic Eliashberg spectral function α^2F . The integral weight of α^2F gives the coupling strength λ , which enters into the McMillan formula for T_c . Globally, the code begins by reading in the raw matrix elements, then processes them to obtain the matrices $\gamma_{\mathbf{k}i,\mathbf{k}'i'}^{ab}$ from Eq. 2.39, in cartesian coordinates. These are summed over bands, then once over kpoints, to give isotropic quantities which depend only on the qpoint. The $\mathbf{q}$ dependent quantities are Fourier transformed and then interpolated. This gives the values of the phonon linewidths, which are interpolated along a path in reciprocal space which is input. Then, interpolating on a very fine grid and integrating over $\mathbf{q}$, the $\alpha^2F(\Omega)$ function is calculated. Integrating over Ω gives λ and ω_{log} , which in turn give T_c through McMillan's formula.

5.2 Coding details

This section contains coding details for the implementation of the electron-phonon coupling in ABINIT. The main formulas have been presented in Sec. 2.3.9.1, and this section defines the subroutines of the `anadddb` utility which are responsible for the treatment and output of electron-phonon data. Sec. 5.2.1 contains the flowchart and comments data flow, and Sec. 5.2.2 gives more specifics on the different subroutines.

5.2.1 Subroutine flowchart

The flowchart through the electron-phonon subroutines of the `anadddb` utility in the ABINIT package are shown on the following pages. Subroutine names are contained in boxes. Lines follow command execution, and files which are input or output are shown in shaded boxes (arrow in/out for in/output).

5.2.2 Details of subroutines and data flow

The first step in a calculation of electron phonon properties is a straightforward calculation of all the phonon modes of a system, for the `kpoint` and `qpoint` grids chosen. This is explained in the ABINIT tutorials, but in our case *all perturbations must be carried out explicitly*. No reduction by symmetry is presently accepted, and each perturbation (i.e. the displacement of each atom in all 3 reduced directions) must be present, for reasons explained in Sec. 2.3.9.1. Only the irreducible `qpoints` need be used, however: once the full γ matrices are known for one `qpoint`, the other equivalent `qpoints` can be completed. The output of the phonon run which we are interested in are the `_DDB` file, which contains the second derivatives of the total energy for the different perturbations, and the `_1WF` files, which contain the first-order wavefunctions (which we do not need), and the matrix elements of the first-order Hamiltonian (which we do). The `mrggkk` utility is included in the package, to extract the matrix elements and to put them into a single file, called the `_GKK` file, which will be fed to `anadddb`.

5.2.2.1 mrggkk

The input to `mrggkk` is similar to that of `mrgddb`, and an example for Al is shown below:

```
Al_GKK.bin          # Name of the output file to be produced
0                   # flag for binary (0) or ASCII(1) output
oAl_DS1_WFK         # GS wavefunction file
24 1 3              # number of _1WF _GKK and _1WF files
```

```

oPbGam_DS3_1WF1
oPbGam_DS4_1WF2
oPbGam_DS5_1WF3
oPbL_DS3_1WF1
oPbL_DS4_1WF2
oPbL_DS5_1WF3
...
oPbX_DS5_GKK

```

The fourth line contains three integers: **mr_gg_kk** can merge both raw `_1WF` files, and pre-processed `_GKK` files. In the latter case, the user must specify the number of `_GKK` files listed, and the number of perturbations contained in all the `_GKK` files which will be read. The `_1WF` then the `_GKK` are listed in the order they will be read. It is presumed that all the perturbations for a given qpoint are grouped together in the `_GKK` file, which will be read sequentially.

5.2.2.2 anadddb

With the `_GKK` and `_DDB` files in hand, we can now run **anadddb**. The new input parameters for version 4.6 of the package are the following:

- **elphflag** (integer) : flag to use the electron-phonon capabilities of **anadddb**. Set to 1.
- **elphsmear** (real) : width in Hartree for the Gaussian smearing of the Dirac δ functions in sums over the BZ. Typical value 0.01.
- **kpath** (real, dimension (3,nkpath)): reduced-reciprocal-space coordinates of the special points on the path in q-space, used for the output of phonon linewidths and the associated phonon band structure.
- **kptrlatt** (integer, dimension (3,3)): kpoint grid basis vectors, from abinit. Only the individual kpoints are passed in the header, but **kptrlatt** is needed for tetrahedron integration, and must be re-copied here from the abinit output.
- **mustar** (real) : value of the Coulomb pseudopotential μ^* . Typical value 0.1.
- **nkpath** (integer) : number of special points in the q-space path along which the phonon band structure and the linewidths will be output.

- `telphint` (integer) : flag to use Gaussian (1) or tetrahedron (0) integration weights for FS integrals. Default is 1.
- `tkeepbands` (integer) : flag to sum over bands (including the integration weights) immediately after reading in. For all isotropic calculations (i.e. all those implemented at the time of writing) this does not change anything. Set to 0.

An example of a path in q-space for an FCC lattice and `nkpath=7` is:

```
kpath
0.0 0.0 0.0    # Gamma
1/2 1/2 0.0    # X
1 1 1          # Gamma'
1/2 1/2 1/2    # L
1/2 1/2 0.0    # X
1/2 3/4 1/4    # W
1/2 1/2 1/2    # L
```

In the present state of the code, an auxiliary file, named `fort.101`, is read in, which contains flags for the storage of different binary data. The flags signal whether different arrays should be stored on disk or kept in memory, and whether they already exist (and should be read in). The arrays are those for $\gamma(\mathbf{q})$ on the input (sparse) qpoint grid, the $\gamma(\mathbf{r})$ on the dual real-space grid, the $\gamma(\mathbf{q})$ on the fine grid (identical to the input kpoint grid), and the phonon frequency data for the fine grid. The corresponding file names are `gkqfile`, `gkk_rpt_file`, `gkk2file`, and `phfrqfile` respectively. An example `fort.101` file is:

```
0 0 1 # gkq   write exist and symmetrize?
0 0   # gkrpt write exist
0 0   # gkk2  write exist
0 0   # phfrq write exist
```

which indicates that none of the files are present (second column) and none should be written to disk (first column). The additional flag on the first line indicates that quantities should be symmetrized using the input symops. This should be left as 1, and the whole file will eventually disappear, either favoring default values of the flags or their transfer into the `anaddb` input file.

A module has been created, contained in `Src_defs/defs_elphon.F90`, which contains two data structures. The first is the `elph_type` for electron-phonon data, dimensions, and file unit numbers. This is used to pass “global” parameters among the different routines called in `elphon`. The

other, `phon_type`, is a container for data and dimensions used to interpolate phonon frequencies and eigenvectors at random qpoints. This packages the needed geometrical and dimensional data, along with the real-space interatomic force constants. A simple call to the `inpphon` subroutine with `phon_type` and a qpoint returns the frequencies, eigenvectors, and the mode atomic displacements.

The point of entry into the code is the call of `elphon` from `anaddb`. Basic geometric data is set up and initializations are performed (routine `rchkGSheader`) for the kpoint grid (routines `getkgrid`, `get_fs_kpts`, `order_fs_kpts`, `mkFSkgrid`), and qpoint grid (routines `mkqpotequiv`, and `smpbz`). ABINIT usually employs only an irreducible set of kpoints, and they are not ordered. Here the full grid in the BZ is determined, and sorted such that kpoints are aligned in strings with increasing k_z , then k_y , then k_x (this facilitates analysis and the graphical representation of $\mathbf{k}$ dependent quantities). The kpoint integration weights are calculated, either with the Gaussian smearing method, or with the tetrahedron method (calling `get_tetra` to set up the tetrahedra in the full BZ and `get_tetra_weight` to calculate the weights).

The first major step in the data processing is reading in the `_GKK` file, and calculating the $\gamma_{\mathbf{k}i,\mathbf{k}'i'}^{ab}$. Following Eq. 2.33:

$$\langle \psi_{\mathbf{k}i} | \frac{\partial \mathcal{H}}{\partial R_\alpha} | \psi_{\mathbf{k}'i'} \rangle, \quad (5.1)$$

the matrix elements for the electron-phonon coupling are calculated in ABINIT for perturbations of one atom in one reduced direction $\alpha = 1 \dots 3N_{\text{atom}}$. We are interested in phonon-mode-specific quantities like the linewidths, which are linear combinations of the basic matrix elements. The sums are performed in `get_all_gkq`. First the flags from `fort.101` are tested and the appropriate files are opened, then `read_gkk` is called to read in the `_GKK`. In `read_gkk`, the `_GKK` file is read sequentially, and the $g_{\mathbf{k}i,\mathbf{k}'i'}^{\mathbf{q}\alpha}$ are collected for a given qpoint and $\alpha = 1, 3N_{\text{atom}}$, mapping the kpoints which are actually calculated by `abinit` onto the full grid in the BZ. Once the $3N_{\text{atom}}$ perturbations are in memory, the γ^{ab} are calculated in subroutine `completeperts`. The full γ matrices in cartesian coordinates are

$$\gamma_{\mathbf{k}i,\mathbf{k}'i'}^{ab} = \sum_j u_{\mathbf{q}j,a} u_{\mathbf{q}j,b}^\dagger \frac{1}{2\omega_{\mathbf{q}j}} \sum_{\mu\nu} d_{\mathbf{q}j,\mu}^\dagger d_{\mathbf{q}j,\nu} \tilde{\gamma}_{\mathbf{k}i,\mathbf{k}'i'}^{\mu,\nu}. \quad (5.2)$$

Here $a, b = 1 \dots 3N_{\text{atom}}$. The matrices are then symmetrized according to the subgroup for the present qpoint. The γ matrices possess the same symmetries as the dynamical matrices, so this calls upon routine

d2sym3. The γ are finalized in `normsq_gkq` (Eq. 2.37 and 2.39): several options are available in `normsq_gkq`: either summing over bands (`nmsq_gam_sumFS` this should be the default) or keeping the band dependency of the γ . In the latter case one can either multiply by the integration weights $w_{\mathbf{k}i}$ (`nmsq_gam`) or not (`nmsq_pure_gkk`).

Finally `complete_gkk` is called, to complete the data for unknown qpoints by symmetry, through Eq. 2.40

$$\gamma_{\mathbf{k}i, \mathbf{k}+\hat{S}\mathbf{q}i'}^{ab} = \sum_{mn} (s^{am})^\dagger \gamma_{\hat{S}^{-1}\mathbf{k}i, \hat{S}^{-1}\mathbf{k}+\mathbf{q}i'}^{mn} s^{nb}, \quad (5.3)$$

The output of all the γ matrices for all kpoints and qpoints is in the file `gkqfile`.

After the γ matrices have been calculated and completed, they are integrated (once) over the BZ in `integrate_gamma`

$$\gamma_{\mathbf{q}}^{ab} = \sum_{\mathbf{k}ii'} w_{\mathbf{k}i} w_{\mathbf{k}'i'} \gamma_{\mathbf{k}i, \mathbf{k}+\mathbf{q}i'}^{ab}, \quad (5.4)$$

as in Eq. 2.42. The result is Fourier transformed to real space (in routine `ftgam`). In `mkelph_linwid` the real-space γ are transformed back to reciprocal space, interpolating their values on the qpoints along the path specified in the input file. The interpolated matrices are still in Cartesian coordinates, and must be diagonalized to obtain the phonon linewidths:

$$\gamma_{\mathbf{q}j} = 2\pi\omega_{\mathbf{q}j} \text{diag}(\gamma_{\mathbf{q}}^{ab}) \quad (5.5)$$

where $\text{diag}()$ means the eigenvalues of the $3N_{\text{atom}} \times 3N_{\text{atom}}$ matrix $\gamma_{\mathbf{q}}$. The $\gamma_{\mathbf{q}j}$ are output to the `_LWD` file. The phonon band structure along the same path is output to the `_BST` file.

In `mka2f`, the γ are interpolated on a dense grid, identical to that of the kpoints, and integrated over the full BZ to calculate the $\alpha^2 F$ function (Eq. 2.18), which depends on frequency. The first inverse moment of $\alpha^2 F$ gives the mass enhancement factor λ_ν Eq. 2.22 (which depends on T through the Matsubara frequencies):

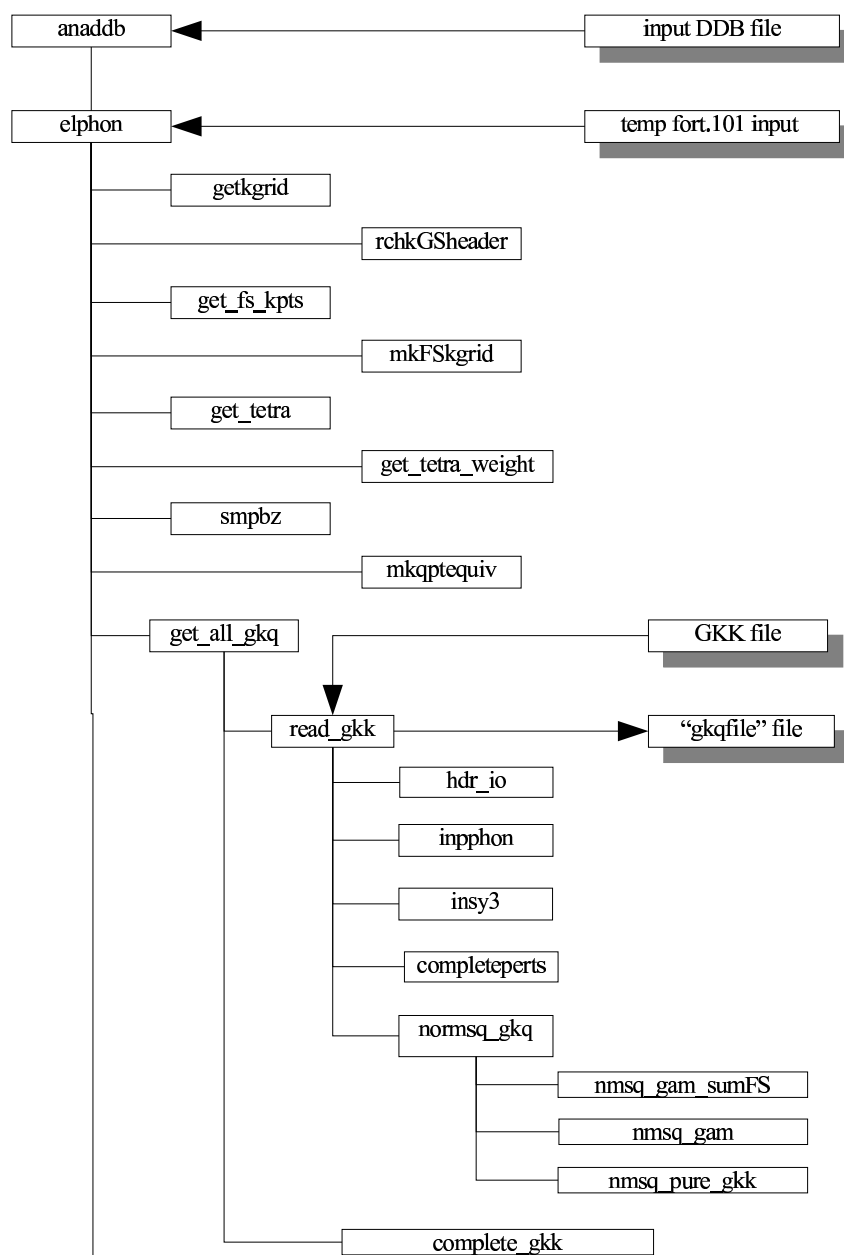
$$\lambda_\nu(T) = \int_0^\infty d\Omega \alpha^2 F(\Omega) \frac{2\Omega}{(2\pi T\nu)^2 + \Omega^2}. \quad (5.6)$$

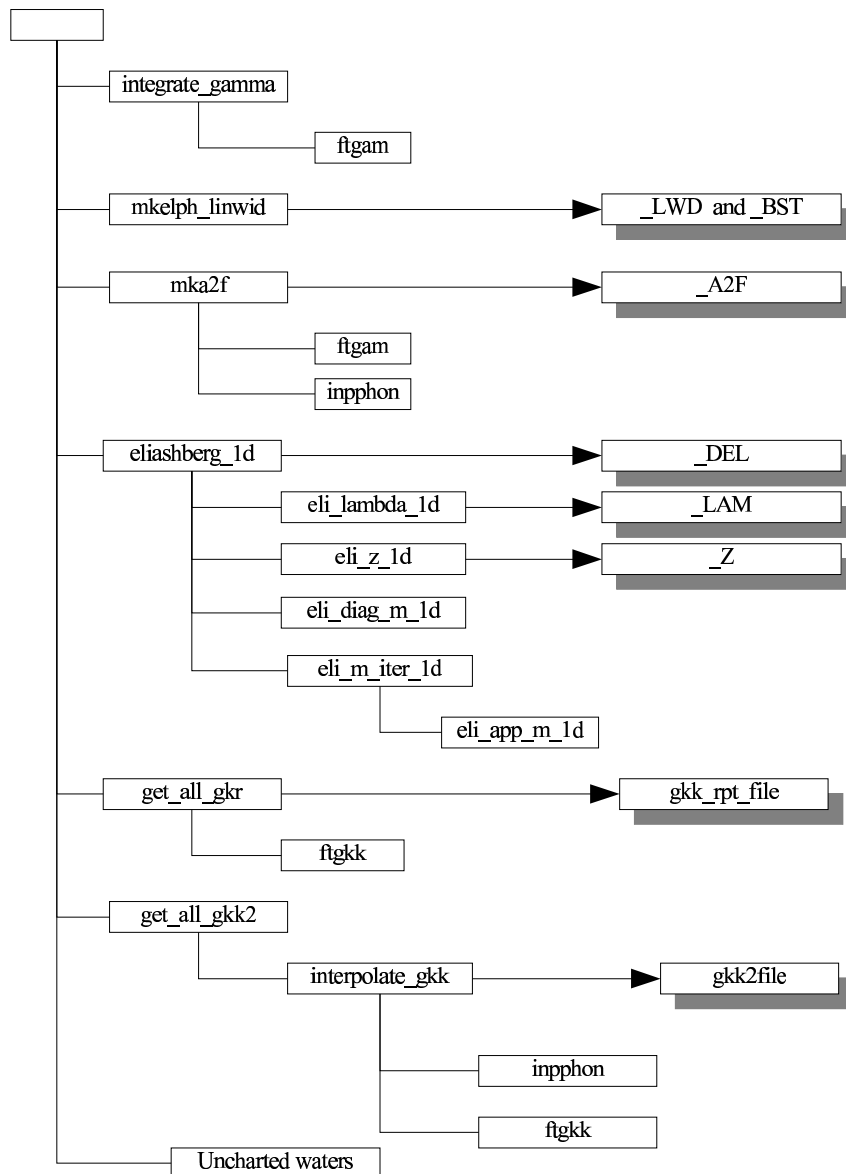
The logarithmic average of $\alpha^2 F$ gives the log-averaged frequency $\omega_{\log}$ Eq. 2.32. From $\lambda_{\nu=0}$ and $\omega_{\log}$ the McMillan formula gives the superconducting T_c .

The `eliashberg_1d` subroutine solves the linearized isotropic Eliashberg equations (Eq. 2.29), to calculate the critical temperature. A trial

temperature is used to calculate the fermionic Matsubara frequencies (their number can vary, as the cutoff frequency is kept fixed), then the values of λ_ν on the boson Matsubara frequencies (`eli_lambda_1d`), and the Z matrix (`eli_z_1d`), which are then assembled to give the matrix $S_{nn'}$ of Eq. 2.30. The matrix is diagonalized (`eli_diag_m_1d`), and T is adjusted to increase or decrease the maximum eigenvalue ζ , until it is equal to 1 within a fixed tolerance: if $\zeta > 1$, superconductivity is present and T must be increased, and if $\zeta < 1$ T must be decreased. This procedure does not always converge well, and little time has been spent optimizing convergence, as this is not within the scope of the present thesis.

Preparing for work on anisotropic quantities, two further routines perform the interpolation, described above for isotropic quantities, for the full $\mathbf{k}\mathbf{k}'$ and eventually band dependent quantities $\gamma_{\mathbf{k}i,\mathbf{k}'i'}^{ab}$. The Fourier transform to real space is carried out in `get_all_gkr`, and the interpolation is done in `get_all_gkk2`, producing the `gkk_rpt_file` and `gkk2file` files.





5.3 Simple electron-phonon applications

5.3.1 Introduction

The methods for calculating the electron-phonon coupling were described in Sec. 2.3.9.1. In this chapter we will apply them to study a test system of FCC aluminum. The tests will concern the integration of different quantities in reciprocal space, convergence in $\mathbf{q}$ and $\mathbf{k}$ points, and the comparison with different codes.

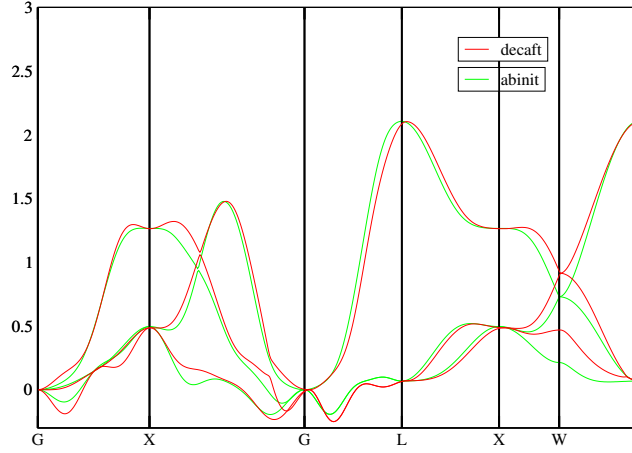


Figure 5.1: Comparison of phonon linewidths calculated with DECAFT and ABINIT using the same pseudopotential.

5.3.2 The testbed: aluminum

Aluminum is a standard test of superconductivity calculations because of its very simple Fermi surface and the low kinetic energy cutoff associated with Al pseudopotentials. Further, the electron-phonon coupling is weak, and all of the approximations made in Sec. 2.3.6 should be legitimate. The first simple test of the code is to reproduce the results of a similar code. DECAFT is such a code, written by Kay Dewhurst[59], and has the advantage of using the same pseudopotentials as ABINIT. This is essential in reproducing results. Any difference in implementation can influence the results, and, in particular, pseudopotentials can change system behaviors drastically. A comparison of the phonon line widths (Eq. 2.42 and following) between DECAFT and ABINIT is shown in Fig. 5.1. The calculations use $16 \times 16 \times 16$ kpoint grids, a $4 \times 4 \times 4$ qpoint grid, a Fermi surface smearing of 0.01 Ha, and a HGH pseudopotential (see Sec. 2.2.6.2). The agreement is quite good, and the residual differences are due to the slightly different schemes used to interpolate the

linewidths and to generate the electron-phonon matrix elements. The negative linewidths near Γ are due to the interpolation.

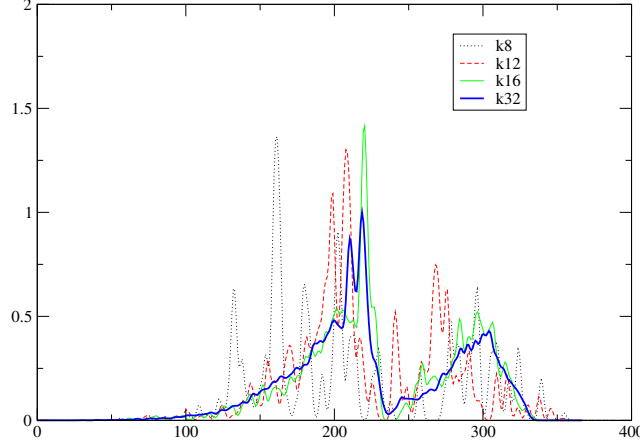


Figure 5.2: Convergence of the Eliashberg spectral function with respect to the number of kpoints, using the tetrahedron method (and a $2 \times 2 \times 2$ qpoint grid).

5.3.2.1 The Gaussian smearing and tetrahedron methods

The integral over the Fermi surface is expressed as a sum over a finite grid of kpoints, to which we must attribute weights. The weights $w_{\mathbf{k}i}$ will be attributed as a function of the KS eigenvalues $\epsilon_{\mathbf{k}i}$, which are known for all the kpoints used in the ground state calculation. The simplest method is to use a Gaussian smearing of width σ

$$w_{\mathbf{k}i} = \frac{1}{\sqrt{\pi}\sigma} \exp \left[-((\epsilon_{\mathbf{k}i} - E_F)/\sigma)^2 \right]. \quad (5.7)$$

Another possibility is to interpolate the value of the function between neighboring kpoints. Linear interpolation is the essence of the tetrahedron method [161, 27], which divides up space into (equal-volume) tetrahedra. With values at 4 points in space, the linear interpolation of any function is fixed, and the integral of the linearized function can be computed analytically. This gives a second type of weights for integration, which converges faster than the Gaussian method, as information about the integrated function on points between the grid points is included.

Summing the integration weights gives the density of states at the Fermi surface.

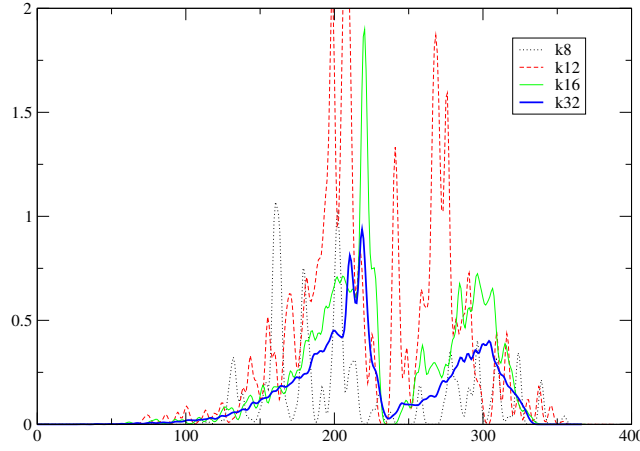


Figure 5.3: Convergence of the Eliashberg spectral function with respect to the number of kpoints, using a Gaussian smearing of 0.01 Ha (and a $2 \times 2 \times 2$ qpoint grid).

The convergence of electron-phonon quantities with the number of kpoints is notoriously slow. This is due to the double δ function in the sum over the BZ, which gives an integrand which is zero almost everywhere. Smearing out the δ function improves convergence, but a too large smearing width will include kpoints far from the FS and produce erroneous results. To estimate the convergence of our calculations and to compare the two integration techniques, we will consider $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $8 \times 8 \times 8$ qpoint grids, and kpoint grids among $8 \times 8 \times 8$, $12 \times 12 \times 12$, $16 \times 16 \times 16$, and $32 \times 32 \times 32$ (also referred to as the k8, k12, k16, and k32 grids in the following). To begin we consider kpoint convergence for the smallest qpoint grid (the results will have little to do with experiment). The convergence of $\alpha^2 F(\Omega)$ calculated using the tetrahedron method as a function of the number of kpoints is shown in Fig. 5.2. The results for $16 \times 16 \times 16$ and $32 \times 32 \times 32$ kpoints are quite close. Peak heights are not completely converged, but all the features are in the right places, and the coupling strength λ , which is an integrated value of $\alpha^2 F$, is converged to within 2% for the $16 \times 16 \times 16$ grid.

The convergence of the spectral function with kpoint grid density is shown in Fig. 5.3, for a Gaussian smearing of width 0.01 Ha. Clearly the $8 \times 8 \times 8$ and even $12 \times 12 \times 12$ grids are completely false, even for a simple metal like Al. The $16 \times 16 \times 16$ grid is better, but the convergence remains slow. As can be seen comparing the scales of Fig. 5.2 and 5.3, only with $32 \times 32 \times 32$ kpoints is the Gaussian method converged.

To sum up, the tetrahedron method appears to be superior, in speed of convergence but also in that it does not use an adjustable parameter, like σ , which would require additional convergence checks. Using the tetrahedron method, even a $16 \times 16 \times 16$ kpoint grid gives reasonable results for $\alpha^2 F$.

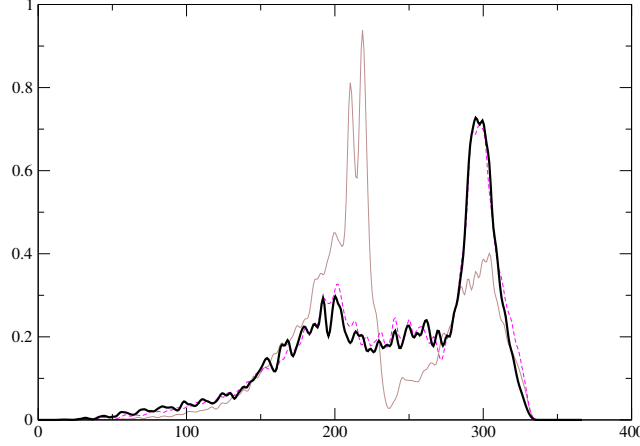


Figure 5.4: Spectral function convergence as a function of qpoint grid. Thin line - $2 \times 2 \times 2$ grid, dashed line - $4 \times 4 \times 4$ grid, thick line $8 \times 8 \times 8$ grid (and a $32 \times 32 \times 32$ kpoint grid with the tetrahedron method).

5.3.2.2 Convergence in the number of qpoints

The full $\mathbf{q}$ dependence of the phonon frequencies and the electron-phonon matrix elements is interpolated using a Fourier transform, from a sparse grid of qpoints in the BZ onto the dense grid which is used for the kpoints. This interpolation is very efficient, as the phonon bands are usually well behaved and suited to the algorithm. Here we establish the number of independent points (in the sparse grid) which are needed to converge the $\mathbf{q}$ dependent quantities. The variation of the Eliashberg spectral function with progressively denser qpoint grids is shown in Fig. 5.4. Clearly the $4 \times 4 \times 4$ grid is completely converged.

5.3.2.3 Phonon linewidths

The phonon linewidths describe the lifetime of a “perfect”, non interacting phonon, due to the electron-phonon interaction. Non-interacting means not with each other: the standard DFT Born Oppenheimer phonons in the harmonic approximation. Once electronic transitions

are allowed (between states on the FS essentially), these perfect quasiparticles acquire a finite lifetime. The phonon-phonon interaction adds a second term to the lifetime of the phonons, but requires the calculation of higher-order derivatives of the energy, and will not be considered here.

The phonon linewidths for FCC Al are shown in Fig. 5.5, for a $4 \times 4 \times 4$ qpoint grid and a $32 \times 32 \times 32$ kpoint grid, using the tetrahedron and Gaussian integration weights. The two types of integration agree fairly

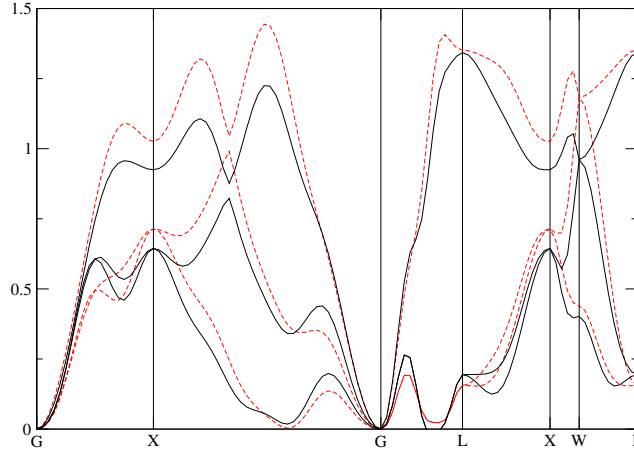


Figure 5.5: Phonon linewidths of FCC aluminum, for a $4 \times 4 \times 4$ qpoint grid and a $32 \times 32 \times 32$ kpoint grid. Dashed line = tetrahedron weights, continuous line = Gaussian weights.

well. The largest difference is at the X point. Empirically, this point is very sensitive to the integration technique, and small variations of the smearing or using the tetrahedron method changes the value of $\gamma(X)$ perceptibly, which then changes the interpolated values. The oscillations in the line width curves, between Γ and X or between Γ and L, are due to the Fourier interpolation, which is not quite as efficient as in the case of the phonon band structure. Other types of interpolation should be considered, to improve the local convergence of the linewidths.

Finally, we turn to the calculation of critical temperatures and the fitting of the μ^* parameter. With a DOS at the Fermi level of 5.27 states/Ha/spin, and a value of $\mu^* = 0.136$ we obtain $T_c = 1.19$ K (experimentally $T_c = 1.18$ K). Our values of $\omega_{\log} = 287$ K and $\lambda = 0.46$ are slightly higher than but in good agreement with published values (0.45[55], 0.44[242], 0.438[168]). The pseudopotential (or the all-electron method) chosen is probably the largest source of discrepancy.

Chapter 6

Superconductivity in metallic nanowires

God hangs the greatest weights upon the smallest
wires

Francis Bacon

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6.1 Introduction

One of the fundamental questions in the applications of modern superconductivity is the lower limit in size for its appearance. A broad outline of superconductivity in films, nanotubes and nanowires was given in Sec. 2.3.7. The main experimental concern is disorder, which impedes the global phase coherence of Cooper pairs. In *ab initio* calculations using periodic boundary conditions, disorder is absent, and defects of any kind require very large supercells. DFT is thus an ideal tool to consider the effects of intrinsic parameters on the superconductivity of nanoscale systems. The regime we can consider is the extreme atomic

limit, whereas the best experiments to date remain at the lower end of the mesoscopic limit. Making nanowires with sufficient crystallinity to maintain superconductivity will be a great challenge for nanoscience in the years to come. Hopefully, by the time they are synthesized, simulation will have progressed to the point of realistic predictions for system sizes at the crossover from mesoscopic to nanoscopic.

As has already been discussed in Sec. 2.3.7, the treatment of Coulomb effects in our approach, using the Eliashberg theory, is very simplistic. Nevertheless, our accurate calculations of phonons and electronic screening will allow us to consider the impact of reduced dimensionality on the different components of superconductivity, viz. the phonon modes and the electronic states at the Fermi surface. In a constrained (e.g. 1D) system, the phonon modes can become harder. If the electron-phonon coupling remains important, this can increase T_c . The density of states at the Fermi level can also vary substantially, due to the presence of Van Hove singularities. This will similarly affect superconductivity.

We consider a series of nanowires of aluminum, testing their stability, phonon modes (and instabilities) and calculating their electron-phonon interaction. A number of works have appeared very recently on the geometry[251], electronic structure[9] and on the Peierls instabilities[207] of mono-atomic Al nanowires. Mono-atomic metallic wires were shown to be unstable against distortion by Fröhlich[83] and Peierls[211] in the 50s.

A feature which has attracted much attention is the spontaneous magnetization of mono-atomic nanowires[292, 9]. As the Fermi energy goes through a Van Hove singularity in the DOS, the Stoner criterion[256] for ferromagnetism is satisfied and the wire acquires a permanent magnetic moment. This occurs in particular when the wire is stretched. We will be considering structures near equilibrium, and have checked that for our wire geometries no magnetic moment subsists.

The atomic forces and unit cell stresses in the following are fully relaxed (less than $5 \cdot 10^{-5}$ Ha/bohr and $1.5 \cdot 10^{-7}$ Ha/bohr³ resp.) in all of the models considered, and the lateral cell size is tightly converged at 30 bohr. A plane-wave kinetic energy cutoff of 8 Ha and a TM type pseudopotential (see Sec. 2.2.6) are employed for Al.

6.2 Al nanowire systems

Most of the candidate structures we tried are unstable against certain distortions (as we shall show in Sec. 6.5), which usually break the symmetry or depart from the close-packed geometry. These effects are charac-

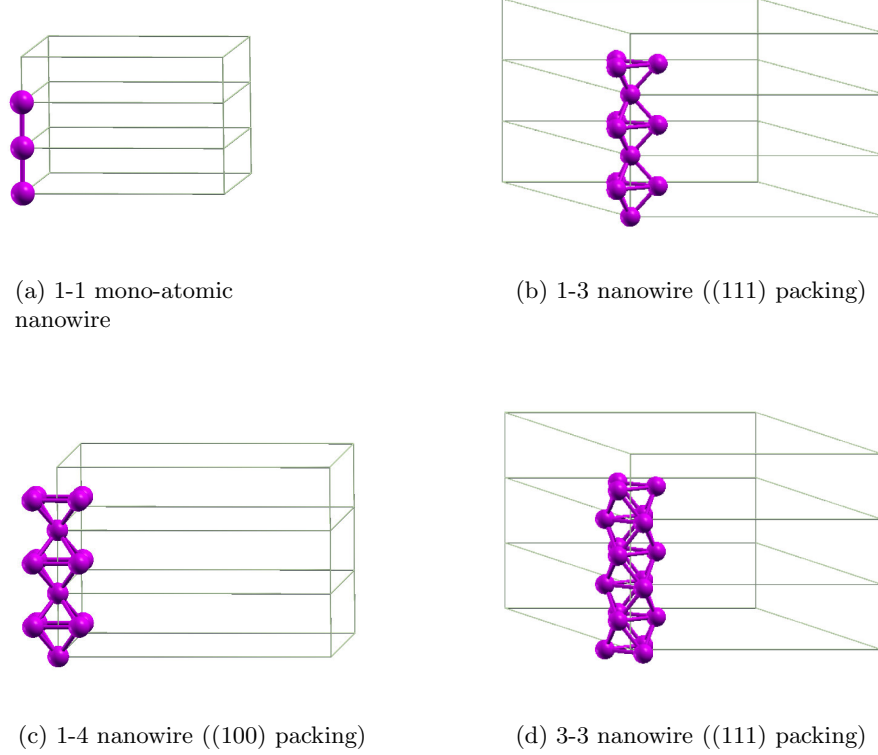


Figure 6.1: Models of Al nanowires with unit cells (hexagonal or square)

teristic of systems with Peierls distortions or severe under-coordination, like our few-atom nanowires. The nomenclature we have adopted for the different systems is the following: 1-1 designates a straight mono-atomic nanowire, 1-3 a wire alternating 1 atom and a triangle of 3 atoms in FCC (111) A-B-A-B packing, 1-4 alternates 1 and 4 atoms in a FCC (100) packing, and 3-3 alternates triangles pointing in opposite directions, in FCC (111) B-C-B-C packing. These structures are depicted in Fig. 6.1(a) to Fig. 6.1(d) respectively. The unit cell is hexagonal for the wires with a 3-axis, and square based otherwise. All of these wires present phonon instabilities (detailed below). In the mono-atomic case the instability is fairly simple, as also found by Ribeiro and Cohen[231] and gives a zigzag nanowire, with an angle of either $\simeq 60^\circ$ or $\simeq 140^\circ$. The two are shown in Fig. 6.2. Similar zigzag structures have been found for gold nanowires, and used to explain very large inter-atomic distances which have been observed experimentally[241]. The same zigzag is ob-

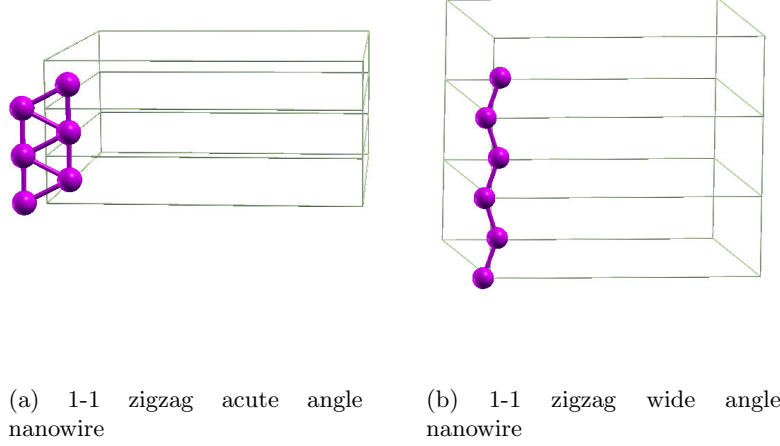


Figure 6.2: Models for zigzag nanowires of Al.

served for nanowires of many different metals[240, 231] for an angle around 60° in all cases, and for an additional angle above 120° as well in some metals (Au, Al, Rh, Ru).

Experiments with mono-atomic nanowires (mainly of gold up to now) often consider break junctions, where a small constriction of metal is pulled apart until only an atomic wire is left standing between two electrodes. To test this configuration, we pull on both zigzag nanowires. For the wide angle case, stretching by 2% has the effect of eliminating the residual instabilities in the phonon spectrum. For the acute angle case, stretching by 2% changes almost nothing. Stretching by 10% eliminates the soft modes at X but leaves others for intermediate qpoints.

6.3 The ground state: energy and geometry

We characterize the wire structures by their total energy and the bond lengths between Al atoms. The total energies per atom E_{tot} (Ha), interlayer distances d ($\text{\AA}$), and Al-Al bond lengths l ($\text{\AA}$) are presented in Tab. 6.1. The energy per atom lowers with increasing coordination, towards the asymptotic limit of FCC Al. The mono-atomic wires present large interlayer distances, as they do not correspond to any natural stacking in FCC Al, whereas the 1-3, 1-4, and 3-3 wires have short interlayer distances compared to the bulk. All of the wires show relatively short

	1-1	1-3	1-4	3-3	FCC Al
E_{tot}	-2.022	-2.044	-2.056	-2.066	-2.100
d	2.38	1.92	1.84	2.10	2.29 1.98
l	2.38	2.56 2.95	2.65 2.69	2.65 2.79	2.80

Table 6.1: Total energies (in Ha) per atom, interlayer distance d , and bond lengths l (in Å) for different nanowire systems (described in the text), and FCC aluminum. The two values of d for FCC Al are along the (111) and (100) directions, respectively. The two values of l for the 1-3, 1-4 and 3-3 wires are for two atoms along the wire axis and two atoms in a plane perpendicular to the axis.

	wide	wide 2%	acute	acute 2%	acute 10%
E_{tot}	-2.023	-2.023	-2.054	-2.053	-2.049
d	2.33	2.38	1.21	1.25	1.32
l	2.46	2.49	2.41 2.64	2.49 2.65	2.65 2.67

Table 6.2: Total energies (in Ha) per atom, interlayer distance d , and bond lengths l (in Å) for zigzag nanowires (described in the text). The two values of l for the acute angle wires are for two atoms along the wire axis and for a bond which is not along the axis, respectively.

bond lengths along the wire axis, which tend to the bulk value of 2.8 Å as the thickness of the wire is increased, as do the bond lengths perpendicular to the axis. The geometry appears to be converging quickly to that of bulk Al, with only a few shells of atoms in the wire. The energy difference, with respect to the bulk, for the thickest 3-3 wire is still almost 1 eV/atom, which precludes being able to isolate free-standing wires.

The energies and bond lengths for the zigzag wires are shown in Tab. 6.2, in columns “wide” for the fully relaxed wide-angle case, “wide 2%” for the wire stretched by 2% along its axis, “acute” for the zigzag with an angle of 60°, and “acute 2%” and “acute 10%” for the acute wire stretched by 2 and 10%. The differences for the wide case with respect to the straight wire are small, the bond length increasing slightly as the coordination of the atoms is higher in the zigzag configuration. The angle between successive Al pairs is 142° in the relaxed case and 145° in the stretched wire, to be compared with 120° in the perfect FCC case

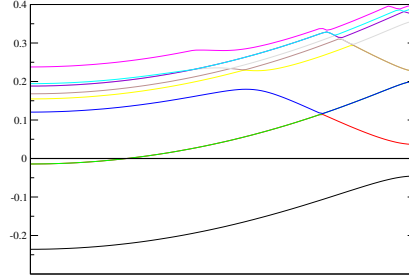


Figure 6.3: Electron band structure of a straight mono-atomic Al nanowire (in Ha) from Γ to X. The thick horizontal line is the Fermi level.

with 12 neighbors, and 139° in GGA from Ref. [251].

The acute angle wires have smaller bond lengths along the wire axis, and longer bonds which are not aligned with the wire (these are closer to the values in bulk and in the thicker wires above). The relaxed angle between successive bonds is 54° , and not 60° as reported in Ref. [251] for GGA. This difference is surprising, but there is no a priori reason to have only one type of bond length. The wires are all significantly more stable than the linear or wide angle cases.

6.4 Electronic structure

The electronic structure of the straight mono-atomic Al wire is shown in Fig. 6.3. The band behavior is free-electron like, with an opening in the bands at the X point. The band structures of the other nanowires are quite analogous to that of the straight wire, folded back into the IBZ since their unit cells are doubled along the wire direction. All of the electronic band structures are shown in Fig. 6.4. For the 1-1 wire the band structure has been folded back into half of the BZ, for comparison with the other wires. For the 1-3, 1-4, and 3-3 wires the band structure of Fig. 6.3 is doubled, with an offset, corresponding to the two different types of layers, but with basically the same dispersion. The acute angle zigzag wires present an anti-crossing of the σ bands near the X point, as was already observed for the mono-atomic case in Ref. [231].

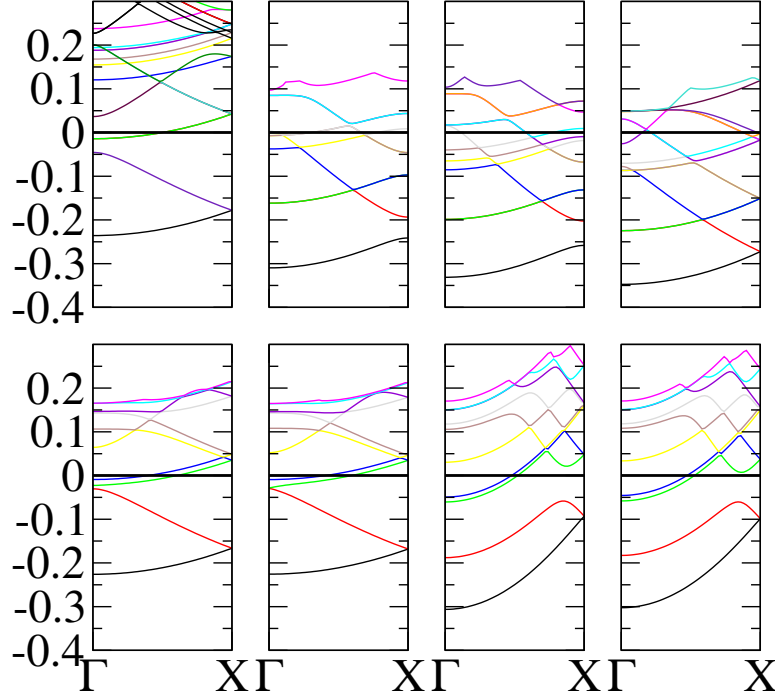


Figure 6.4: Electron band structure of different Al nanowires. Top row from left to right: 1-1, 1-3, 1-4 and 3-3 wires. Bottom row: zigzag wires, with, from left to right: wide, wide stretched 2%, acute, acute stretched 2%. The thick horizontal line is the Fermi level.

6.5 Phonon modes

The phonon spectrum of bulk Al extends up to about 350 cm^{-1} , as shown in its phonon band structure (Fig. 2.2). In this section we present the phonon modes and frequencies calculated for the different Al nanowires described above. The phonon band structures for the 1-1, 1-3, 1-4, and 3-3 wires are shown in Fig. 6.5(a) to 6.5(d), interpolated from 6 qpoints between Γ and X (except for the 1-1 case where the qpoint grid was doubled to 11 points). The phonon band structures of the different zigzag wires (wide and acute angle for different elongations) are shown in Fig. 6.6(a) to 6.6(e). In all the systems with more than one atom in the unit cell, there is a low frequency (usually negative) mode corresponding to the rotation of the wire on its axis. The residual frequency is due to (very small) interactions with neighboring image wires and to the discrete nature of the real-space grid used to calculate

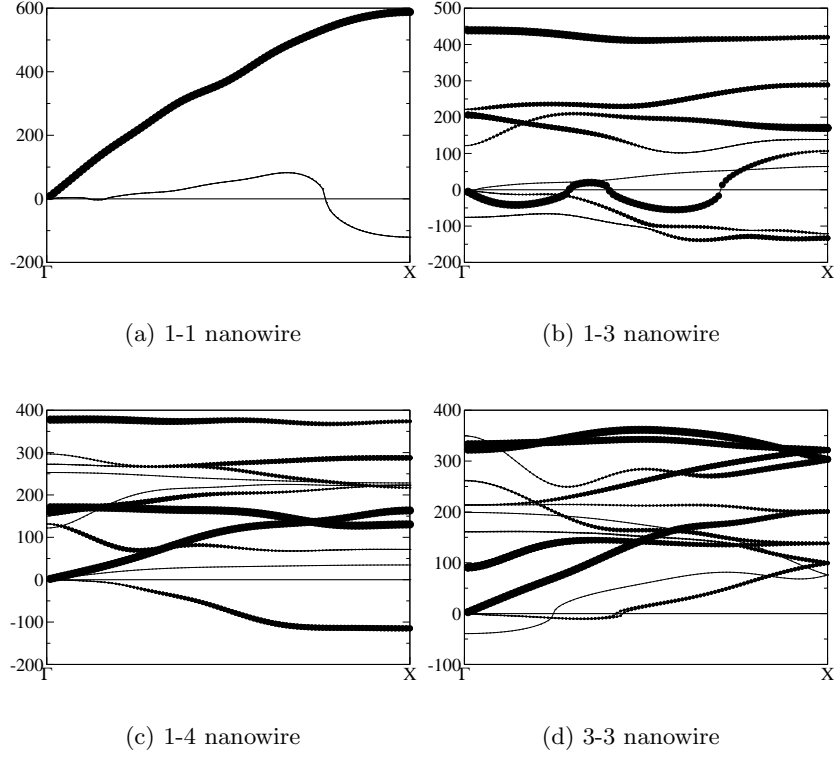


Figure 6.5: Phonon band structures of the different symmetric wires. The thickness of the lines is proportional to the longitudinal character of the phonon mode.

the exchange-correlation energy. This grid effect also gives slightly non-zero acoustic modes in 3D solids, as strict translational symmetry is broken. The amplitude of the error depends on the kinetic energy cutoff (through the spacing of the grid) and on the pseudopotential. In our case the effect on the translational acoustic modes is small, and can be corrected by imposing the acoustic sum rule. The rotational “acoustic” mode remains, but has a frequency below 10 cm^{-1} at Γ . Outside of the Γ point, the rotation becomes a continuous twist of the wire. This can increase the coordination, but in all of the wires examined here the twist mode becomes positive at the X point.

The 1-1 and 1-4 wires present transverse instabilities which double the unit cell. The 1-1 wire leads to the zigzag cases we have already considered, and the 1-4 wire doubles its unit cell, rocking successive

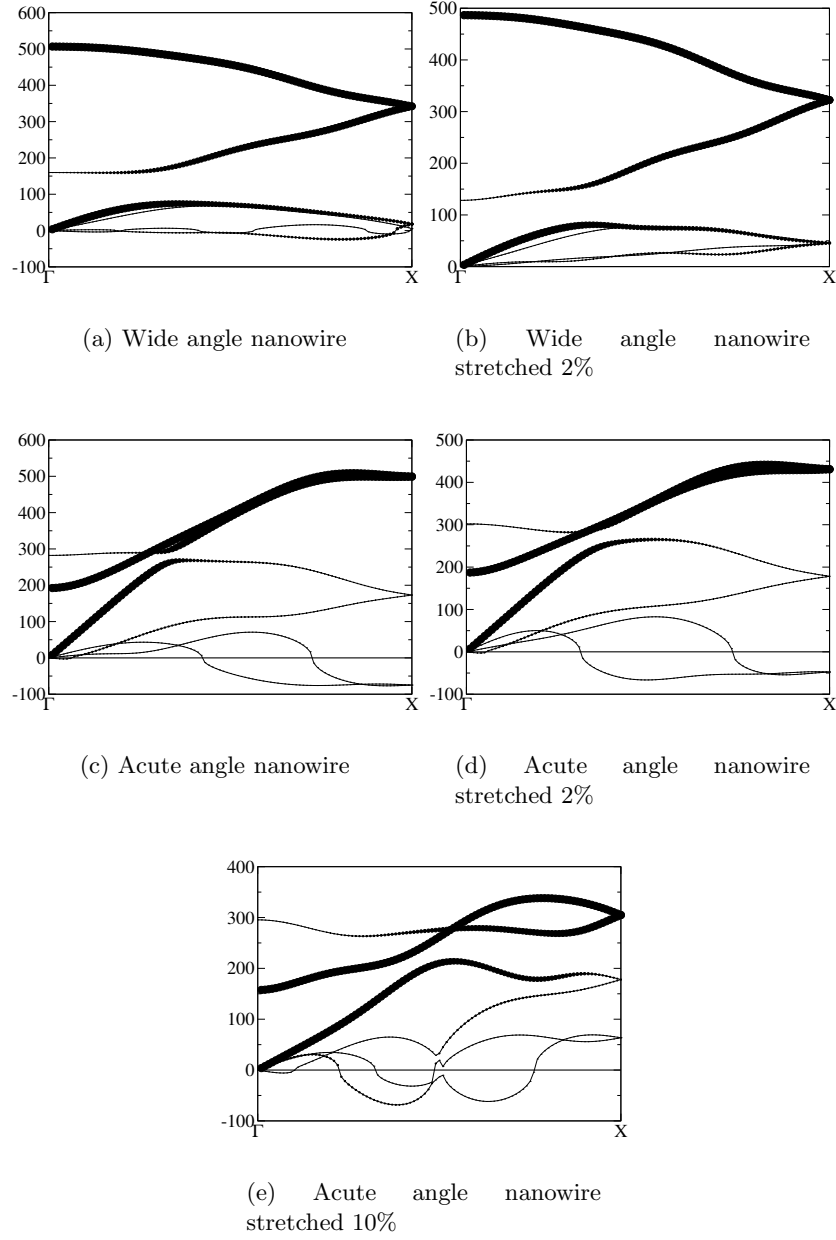


Figure 6.6: Phonon band structures of the different zigzag nanowires. The thickness of the lines is proportional to the longitudinal character of the phonon mode.

pyramids of 5 atoms (Fig. 6.1(c)) in opposite directions. The instabilities in the 1-3 wire (Fig. 6.1(b)) are much more complex. The softest mode (doubly degenerate) breaks the symmetry of the equilateral triangle (shortening one bond and repelling the third atom). The second mode is an in-plane shift of successive layers, which breaks the compact A-B-A-B stacking. The 3-3 wire (Fig. 6.1(d)) is almost stable: the rotation mode gives a slightly soft twisting mode for $\mathbf{q} \neq 0$, which may be entirely due to the XC effects described above. For $q_z < 0.2$ there is a transverse “wave” mode which comes from the transverse acoustic modes and makes the whole wire undulate in the xz or yz planes. This type of mode also appears for the zigzag wires (both the wide and acute angle types).

For the very thinnest wires (the mono-atomic ones), the phonon modes are significantly enhanced, up to 600 cm^{-1} for the straight wire, but the modes of the 3-3 wire are already depressed to less than 350 cm^{-1} (like in bulk Al). The geometry is still apparent in the presence of complex optical modes; they will disappear in the bulk (which only has acoustic modes) with increased (12 fold) coordination.

The zigzag wires also present hard modes up to 500 cm^{-1} , and the maximum frequency appears to decrease systematically as the atoms in the wires acquire higher coordination. Stretching the wide angle nanowire may have relevance to the wires which could be observed experimentally: as the junction is pulled apart, the simpler, high symmetry configurations may become stable. The natural tendency of the FCC metal wires is to maximize their coordination by rolling up, thus minimizing their surface energy. High frequency modes, however, soften as the wires are stretched, in both the wide and acute angle cases. The modes correspond to bond stretches, which are easier when the inter-atomic spacing (especially with second nearest neighbors) is increased.

6.6 Electron-phonon interaction

Strictly speaking, the electron-phonon interaction can only be evaluated for systems with positive phonon spectra. The γ matrices contain a square root of the phonon frequency, and are thus ill defined for $\omega < 0$. Nevertheless, it can be of theoretical interest to examine the coupling of electrons to soft phonons, as these are responsible for structural and phase transitions. We therefore propose a slight generalization of the definition of $g_{\mathbf{k}i,\mathbf{k}'i'}^{\mathbf{q}j}$ (Eq. 2.34), introducing an absolute value for $\omega_{\mathbf{q}j}$:

$$g_{\mathbf{k}i,\mathbf{k}'i'}^{\mathbf{q}j} = \frac{\hbar}{\sqrt{2|\omega_{\mathbf{q}j}|}} \sum_{\alpha} \frac{1}{\sqrt{M_{I(\alpha)}}} u_{\mathbf{q}j,\alpha} \langle \psi_{\mathbf{k}i} | \frac{\partial \mathcal{H}}{\partial R_{\alpha}} | \psi_{\mathbf{k}'i'} \rangle. \quad (6.1)$$

As the ω dependent factor cancels out of the expression for the linewidths, this should allow us to calculate the linewidths for soft modes as well. It turns out that in the case of Al linewidths are negligible: in all of the wires the instabilities are linked to transverse acoustic modes or rotational modes, which must have zero frequency and line width at Γ . The Eliashberg spectral functions for the symmetric wires are shown in Fig. 6.7. As mentioned, the low and negative frequency modes contribute very little to the electron phonon coupling. The coupling is mainly due to longitudinal optical modes. It is interesting to observe the difference in scale in the $\alpha^2 F$ function between the 1-1 wire and the others: for the 1-1 wire the coupling is almost zero everywhere, but as soon as more layers are added, the coupling is up to 10 times larger than in bulk aluminum. Again this shows the importance of the optical phonons, which do not exist for the bulk or the 1-1 wire, in the superconducting strength of the wires. The spectral functions for the different zigzag wires are shown in Fig. 6.8. In the wide angle case there are low frequency modes which couple to the electrons, but the overall coupling is smaller. The importance the low frequency modes appears in the formula for the electron-phonon coupling strength Eq. 2.21: the integral in the expression for λ contains a factor $1/\omega$, which damps the contributions of high-frequency modes. This makes physical sense, as the phonons will be coupling states near the Fermi surface. States further from the FS contribute proportionally less, as do higher energy phonons. The values of the density of states at the FS, the coupling strength λ , and of the McMillan T_c are shown in Tab. 6.3. The density of states at the Fermi level is always significantly higher than in bulk Al (5.27 states/Ha/spin). The 1D geometry leads to Van Hove singularities, and the bands around the Fermi level have edges which enhance the DOS, in particular for the 1-3 wire.

The symmetric nanowires show a jump in λ of three orders of magnitude when going from the linear wire to the thicker ones. The values of $\omega_{\log}$ are high but relatively indifferent to the structure of the wire. Here λ is comparable to bulk Al, but $\omega_{\log}$ is much lower. For the wide angle wire λ decreases on stretching, whereas for the acute angle wire λ increases. For all of the zigzag wires λ and $\omega_{\log}$ have opposite trends, but the net effect on T_c varies. The important difference between the wide and acute wires is the low frequency structure of the phonon bands, which have the most weight in the integrals of λ and $\omega_{\log}$.

The McMillan critical temperatures are given for reference, and should not be taken physically: in particular, the McMillan T_c formula presents a divergency as a function of λ for a value slightly higher than μ^* . Here we have used $\mu^* = 0.136$ as in the bulk, so with a λ of 0.01, the T_c for the

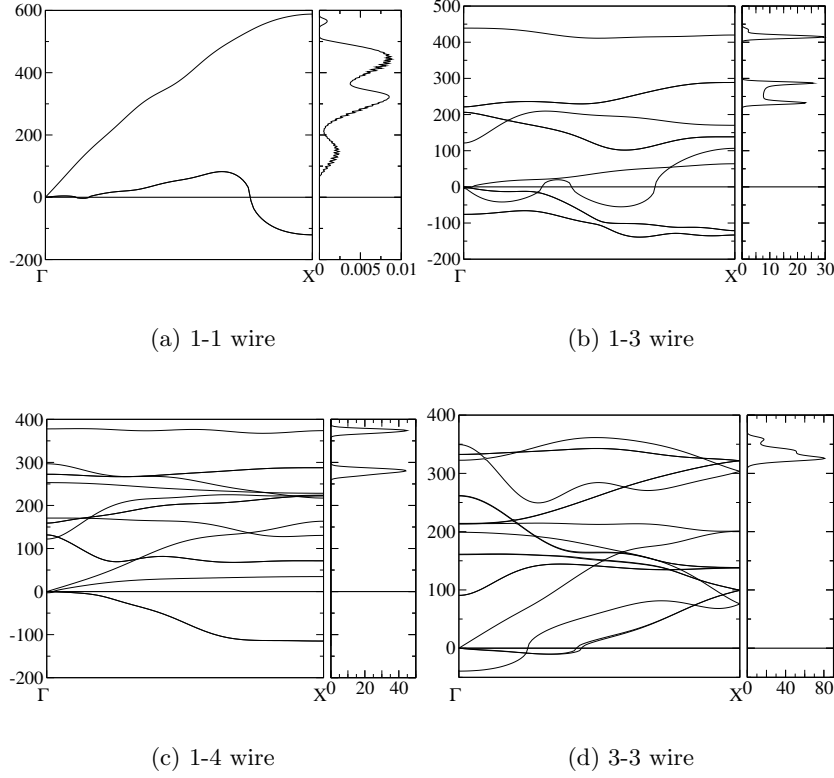


Figure 6.7: Phonon band structures and Eliashberg spectral functions for the different symmetric wires.

1-1 wire explodes. For $\lambda > 2 \cdot \mu^*$ the McMillan formula is mathematically better behaved; the T_c can be compared between the different wires, but are not physical, in that the Coulomb interaction is not cleanly approximated. A high T_c is the result of a combination of a high λ , either from the actual coupling or from the DOS, and a high $\omega_{\log}$. The integration in $\omega_{\log}$ also weights low frequency modes, but less strongly than that in λ .

To sum up, the electron-phonon coupling seems to be enhanced in the thicker wires, due to the optical modes which have a strong coupling. To boost superconductivity, wires should be thicker than 1 atom, but not too thick, or the benefits of the optical modes will be lost: the inner atomic shells will acquire a FCC environment and only the surface atoms will retain optical modes. Stretching the zigzag wires can have positive or negative effects on the values of $\omega_{\log}$ and λ , and on the net T_c ,

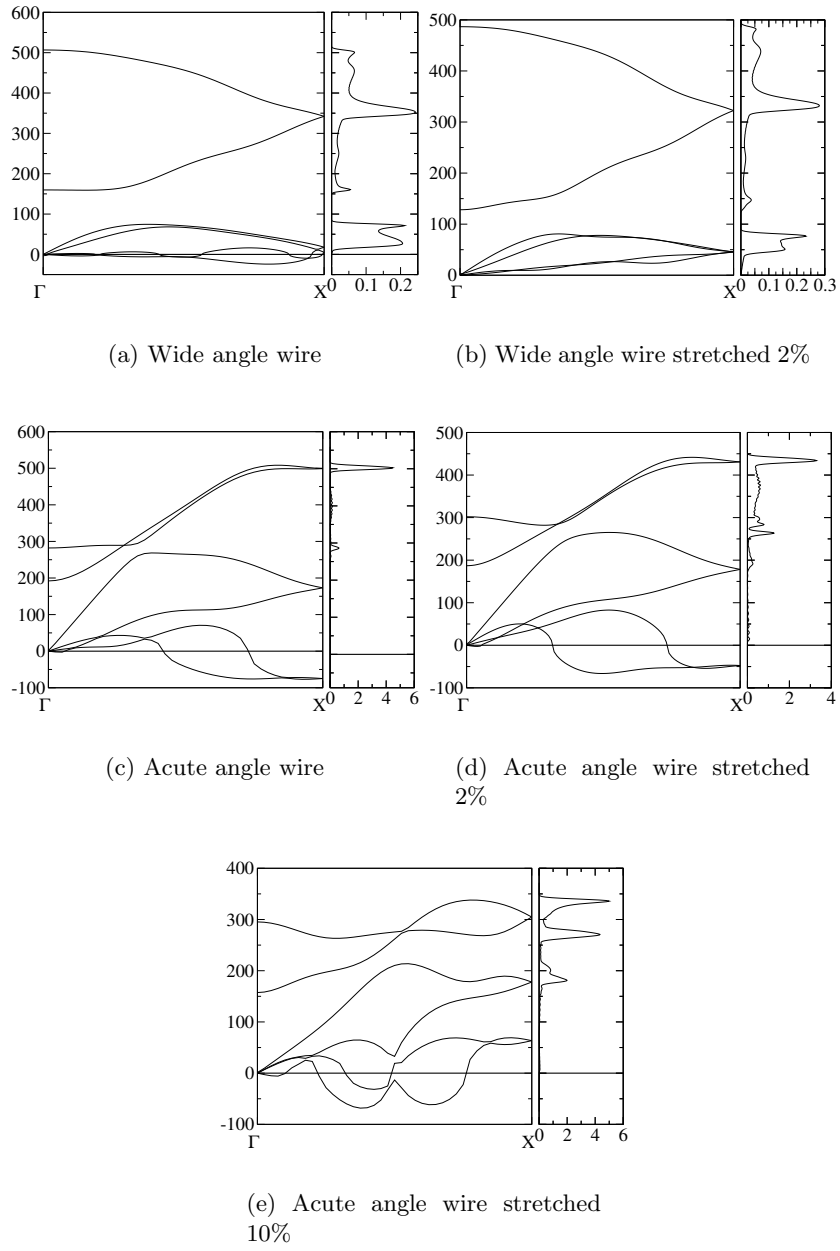


Figure 6.8: Phonon band structures and Eliashberg spectral functions for the different zigzag nanowires.

	DOS	λ	$\omega_{\log}$	T_c^{McM}
1-1	19.78	0.01	405	(1459196)
1-3	76.25	8.15	410	93
1-4	31.93	8.25	444	101
3-3	35.27	10.94	480	114
wide	39.04	0.67	68	1.47
wide stretch 2%	39.83	0.33	136	0.03
acute	9.26	0.34	539	0.16
acute stretch 2%	12.57	1.01	266	16
acute stretch 10%	20.82	1.97	167	22
FCC Al	5.27	0.46	287	1.19

Table 6.3: DOS (states/Ha/spin), coupling strength λ , $\omega_{\log}$ (K), and McMillan T_c (K) for the different Al wires considered.

depending on the structure. This will probably remain true for thicker wires.

Chapter 7

Conclusions and perspectives

In the preceding pages we have presented the result of five years of work simulating the properties of materials at the nanoscale. Many other aspects and projects have been omitted from this manuscript. A thesis is two things: one is a written and bound volume representing a, supposedly monolithic, body of work and contributions; the other is a period of time one sacrifices to research, and this is anything but monolithic. The inherent mechanisms of research, and PhD theses in particular, preclude any ballistic conduction of graduate students through time, by which the student could have ended up somewhere near where his or her supervisors aimed them, in something like the state he or she should have been in.

Density functional theory tools for the calculation of the electronic, structural, and phononic structure of atomic and crystalline systems were described and then applied to the study of different nanotube and nanowire based systems. It was shown that interstitial atoms of catalyst palladium metal could stay adsorbed on the walls of carbon nanotubes. This has important implications for the growth models and purification of carbon nanotubes, whose unique chemical and conducting properties depend strongly on their walls being pristine. The crystal structure of a new phase of stoichiometry $\text{MoS}_2\text{I}_{1/3}$ was critically analyzed, in the light of the calculated geometry and energetics for different atomic models. The preliminary conclusions, based on experimental facts only, were infirmed, and alternative structures were proposed. The rich variety of phases and types of chemical bonding was demonstrated. Interactions between carbon and different metallic crystalline lattices was investigated, to elucidate the particularly favorable behavior of iridium

in the deposition of thin films of diamond. The dissolution of carbon in metal and interface and migration energies together demonstrate iridium's specificity, and suggest a model for the kinetics of diamond nucleation and deposition.

Finally, the limits of low-dimensional superconductivity were probed in nanowires of aluminum. The ground state structure of (few-) atomic wires can be very complex, and the most intuitive packings and structures present phonon instabilities, which were mapped out. The electron-phonon coupling in these constrained 1D systems was also calculated, and some implications for nanoscopic superconductivity were brought to light. Low dimensional and nanoscale superconductivity is a wide open field, in which little theory and almost no experiments have burrowed. Our calculations bring us immediately to the limits of standard theory. Extending the new higher order approximations to the electron-phonon interaction will be essential, and may even bring novel insight into the mechanisms of higher temperature beyond-BCS superconductivity. Further applications abound for other superconducting metals (lead nanowires are in the works). One could even imagine the creation of superconductivity in gold by exploiting nanoscale structures, or other, more exotic, anisotropic and constrained systems.

Appendix A

List of Publications

1. Frédéric Wiame, Jacques Dumont, Robert Sporken, Matthieu Verstraete, and Xavier Gonze, *Atomic structure of the Te/Si(100)-(2×1) surface*, accepted in PRB
2. Matthieu Verstraete and Jean-Christophe Charlier, *Why is Iridium the best substrate for single crystal diamond growth?*, Appl. Phys. Lett. **86**, 191917 (2005)
3. Xavier Gonze, Gian-Marco Rignanese, Matthieu Verstraete, Jean-Michel Beuken, Yann Pouillon, Razvan Caracas, Francois Jollet, Marc Torrent, Gilles Zerah, Masayoshi Mikami, Philippe Ghosez, Marek Veithen, Jean-Yves Raty, Valerio Olevano, Fabien Bruneval, Lucia Reining, Rex Godby, Giovanni Onida, Donald R. Hamann and Douglas C. Allan *A brief introduction to the ABINIT software package*, Z. Kristallogr. **220**, 558-562 (2005)
4. Yannick Breton, Romain Fleurier, Jean-Paul Salvetat, Anne-Lise Thomann, Matthieu Verstraete, and Jean-Christophe Charlier, *Growth of carbon nanofilaments limited by catalyst consumption*, App. Phys. Lett. **85**, 5376-5378 (2004)
5. Matthieu Verstraete, Jacques Dumont, R.L. Johnson, Frdric Wiame, Kristiaan Temst, Johan Swerts, Frdric Mirabella, Jacques Ghijsen, Robert Sporken, and Xavier Gonze, *Structural and electronic properties of Ag-Pd superlattices*, Phys. Rev. B **70**, 205427 (2004)
6. Matthieu Verstraete and Xavier Gonze, *First-principles calculation of the electronic, dielectric, and dynamical properties of CaF₂*, Phys. Rev. B **68**, 195123 (2003)

7. Matthieu Verstraete and Jean-Christophe Charlier, *Ab initio study of MoS₂ nanotube bundles*, Phys. Rev. B **68**, 45423 (2003)
8. X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, and D.C. Allan, *First-principles computation of material properties: the ABINIT software project*, Computational Materials Science **25**, 478-492 (2002)
9. Matthieu Verstraete and Xavier Gonze, *Smearing scheme for finite-temperature electronic-structure calculations*, Phys. Rev. B **46** 035111 (2002)

Proceedings

1. Y. Breton, M. Verstraete, R. Fleurier, T. Cacciaguerra, J.-C. Charlier, A.-L. Thomann, and J.-P. Salvetat *Anomalous ESR behavior of carbon nanofilaments grown from palladium seeds*, Carbon **42**, 1049-1052 (2004)
2. Matthieu Verstraete, Jacques Dumont, Frederic Mirabella, Frederic Wiame, Kristiaan Temst, Johan Swerts, Jacques Ghijsen, Robert Sporken, and Xavier Gonze *Electronic structure of Ag-Pd heterostructures*, Computational Materials Science Volume **30**, Issues 1-2, May 2004, Pages 34-43 Selected papers of the Twelfth International Workshop on Computational Materials Science (CMS2002)
3. Matthieu Verstraete and Xavier Gonze, *Metals at finite temperature: a modified smearing scheme*, Computational Materials Science Volume **30**, Issues 1-2, May 2004, Pages 27-33 Selected papers of the Twelfth International Workshop on Computational Materials Science (CMS2001)

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