Simulation of field emission from carbon nanotubes using time-dependent density functional theory and the effect of nitrogen and boron doping

Sherif Tawfik

Follow this and additional works at: https://fount.aucegypt.edu/etds

Recommended Citation

APA Citation

MLA Citation

This Thesis is brought to you for free and open access by AUC Knowledge Fountain. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of AUC Knowledge Fountain. For more information, please contact mark.muehlhaeusler@aucegypt.edu.
SIMULATION OF FIELD EMISSION FROM CARBON NANOTUBES USING
TIME-DEPENDENT DENSITY FUNCTIONAL THEORY AND THE EFFECT OF
NITROGEN AND BORON DOPING

by

Sherif Tawfik

A thesis submitted to the Department of Physics
in partial fulfillment of the requirements for the degree of

Masters of Science

(Department of Physics)
Prof. Salah El Sheikh, Dr. Noha Salem
at the

American University in Cairo

14 September 2010
TABLE OF CONTENTS

ABSTRACT ........................................................................................................ 4

LIST OF TABLES .............................................................................................. 6

LIST OF FIGURES ............................................................................................ 7

1 Introduction .................................................................................................... 9

1.1 Nanotechnology and Nano-emitters ........................................................... 9

1.2 Graphene .................................................................................................... 10

1.2.1 Structure ............................................................................................... 10

1.2.2 Electronic Properties ............................................................................ 11

1.3 From Graphene to Carbon Nanotubes ....................................................... 11

1.3.1 Structure ............................................................................................... 12

1.3.2 Electronic Properties of Carbon Nanotubes ......................................... 14

1.3.3 Applications ......................................................................................... 14

1.4 Electron Field Emission ............................................................................. 14

1.5 Applications of Carbon Nanotube Field Emitters ..................................... 17

1.5.1 Field Emission Display ........................................................................ 17

1.5.2 Atomic Force Microscopy ...................................................................... 17

1.6 Our Approach ............................................................................................. 18

1.7 Outline of the Thesis .................................................................................. 18

2 Field Emission from Nanostructures .............................................................. 19

2.1 Computation of the Field Emission Current ............................................. 19

2.1.1 The Classical Fowler-Nordheim Theory of Field Emission .................. 19

2.1.2 Ab initio Simulation of Field Emission from Carbon Nanotubes ....... 21

2.1.3 Field Emission Calculations for Graphene .......................................... 24

2.2 Enhancing Field Emission .......................................................................... 25

2.2.1 Chemical Treatments ............................................................................ 25

2.2.2 Nanowelding ......................................................................................... 26
Appendix

5 Conclusions ................................................................. 67

LIST OF REFERENCES ...................................................... 69

APPENDICES

Appendix A: Input Files ...................................................... 76
Appendix B: Charge Calculation Code for Octopus ................. 82
Appendix C: Java Codes ..................................................... 84
ABSTRACT

We investigated the mechanism of electron field emission in pristine short carbon nanotubes using ab-initio computation in isolated and periodic simulation cells. We computed the evolution of the wave functions using Time-Dependent Density Functional Theory, where we have utilized the Crank-Nicholson propagator. We found that in pristine carbon nanotubes, emitted charge tends emerge mostly from electrons that are concentrated at the nanotube tip region, unlike metallic tips. The charge beam concentrates into specific channel structures as the wave function approaches the anode. Nitrogen doping of carbon nanotubes improves emission, in line with experimental findings, and the nitrogen dopant closer to the nanotube tip produces optimal emission performance. However, the nitrogen dopant causes dispersion of the charge cloud, which might lead to wasting of the emission current. Boron doping either impedes field emission in nanotubes or produces minimal effect.
ACKNOWLEDGMENTS

Masters of science, to many, is a merely transitory experience towards obtaining the PhD dissertation. However, the amount of learning I have gained along the way from serious, sincere and patient advisors and an educational institution as open to knowledge as the AUC have all been factors that delivered a special 2 years long Masters degree. I admit that I have taken too long in so many aspects of my research. However, Prof. Salah El Sheikh and Dr. Noha Salem have endured great efforts in asserting the value of professionalism and timeliness throughout my research activities. I am deeply indebted to them, and will always remember their keen desire to enable a physics lover to take a project to its successful end. And I would like to acknowledge my great appreciation for the physics department’s decision to grant me the Fellowship status, without which such study might not have been possible.

Dina, my wife, endured the day-to-day hassles of the research. Her encouragement has been extremely inspiring to me. And the extraordinary 15-months-old Zeina gave me the reason to look forward.
DISCARD THIS PAGE
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Comparisons of field emission characteristics in terms of turn-on electric field and emission current density on different CNTs (treated and non-treated) reported by different researchers. CNTs stand for Carbon nanotubes; CNTs:N stand for Nitrogen-treated carbon nanotubes; N-CNTs:Cl stand for Chlorine-treated nitrogen-based carbon nanotubes; N-CNTs stand for nitrogen-based CNTs.</td>
<td>29</td>
</tr>
<tr>
<td>2.2 Nitrogen contents vs. plasma treatment times</td>
<td>29</td>
</tr>
<tr>
<td>4.1 Extracted current (µA) from pristine carbon nanotube against an applied electric field (V/Å). Our results for the isolated simulation box are higher than results reported in [1] and elsewhere.</td>
<td>57</td>
</tr>
<tr>
<td>4.2 Extracted current (µA) from pristine carbon nanotube against an applied electric field (V/Å). Our results are almost close to those reported in [1] when the applied field is in the range 0.2-0.8V/Å. For larger values, reported results for the current differ from the result reported in [1] due to the difference in length of the nanotube used.</td>
<td>58</td>
</tr>
<tr>
<td>4.3 Extracted current (µA) from pristine vs. nitrogen-doped/boron-doped carbon nanotube against an applied electric field of 0.2V/Å. All are H-passivated with no extra electrons</td>
<td>64</td>
</tr>
</tbody>
</table>
DISCARD THIS PAGE
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Graphene unit cell</td>
<td>11</td>
</tr>
<tr>
<td>1.2</td>
<td>Making a nanotube from graphene</td>
<td>13</td>
</tr>
<tr>
<td>2.1</td>
<td>Diagram showing a one-dimensional potential barrier problem</td>
<td>20</td>
</tr>
<tr>
<td>2.2</td>
<td>$I - E$ characteristics, showing the exponential dependence of the emission current on the applied electric field $E$</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>Charge evolution, showing the amount of electric charge remaining in the lower half of the simulation box (where the nanotube is situated) while an electric field is applied</td>
<td>24</td>
</tr>
<tr>
<td>3.1</td>
<td>Change in total energy using retarded Hamiltonian approximation</td>
<td>42</td>
</tr>
<tr>
<td>3.2</td>
<td>Filling factor $f$ (open circles) and energy level of localized states $\epsilon_{loc}$ with respect to the Fermi level (filled circles) as a function of the external field ($E_{appl}$). The solid and dashed lines are guides to the eye.</td>
<td>50</td>
</tr>
<tr>
<td>4.1</td>
<td>Prestine carbon nanotube</td>
<td>55</td>
</tr>
<tr>
<td>4.2</td>
<td>Charge evolution diagrams for the highest energy state under the influence of an external electric field of 1 V. Time units are in 0.1 a.u., while charge units are arbitrary.</td>
<td>56</td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison between the $I - V$ results obtained by our calculations, and those by [1] and [2].</td>
<td>59</td>
</tr>
<tr>
<td>4.4</td>
<td>Evolution of the wave function: highest energy wave function. Units are arbitrary.</td>
<td>60</td>
</tr>
<tr>
<td>4.5</td>
<td>Evolution of the wave function into the vacuum region: highest energy wave function. Units are arbitrary.</td>
<td>61</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.6</td>
<td>Evolution of the wave function into the vacuum region: highest energy wave</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>function, close to the upper surface of the simulation box. The horizontal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>axis is the intersection between the plane crossing the nanotube vertically</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and the upper face of the simulation box. The vertical axis shows the charge</td>
<td></td>
</tr>
<tr>
<td></td>
<td>in arbitrary units.</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>Relative positions of nitrogen (or boron) dopant on the carbon nanotube tip</td>
<td>63</td>
</tr>
<tr>
<td>4.8</td>
<td>Evolution of the wave function into the vacuum region: highest energy wave</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>function. Units are arbitrary.</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>Evolution of the wave function into the vacuum region: highest energy wave</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>function. Units are arbitrary.</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Nanotechnology and Nano-emitters

A biological system can be exceedingly small. Many of the cells are very tiny, but they are very active; they manufacture various substances; they walk around; they wiggle; and they do all kinds of marvelous things; all on a very small scale. Also, they store information. Consider the possibility that we too can make a thing very small which does what we want; that we can manufacture an object that maneuvers at that level. Richard P. Feynman, 1959 [3].

Nanotechnology – the science of “extreme miniaturization” and control of things at the nanometer scale [4] – is a multidisciplinary field of knowledge which pertains to any technology at the level of the nanoscale that can be utilized in the real world [4]. Owing to the very small length scale, which ranges from a couple of nanometers to a few micrometers, scientists have observed novel physical properties in various nanostructures, and several nanostructures have ignited unprecedented research interest as manifest in the huge number of annual peer-reviewed publications concerned with the physics, chemistry biology and engineering of a variety of special nanostructures such as carbon fullerenes, graphene, and metallic nanoclusters, just to mention a few.

Recent advancement in nanotechnology has opened the possibility for the fabrication of a wide variety of nanometer-scale devices using graphitic nanostructures, such as carbon nanotubes and other carbon-based materials [5]. Interesting phenomena in graphitic ribbons were predicted by
theoretical studies. According to theoretical results based on the tight-binding model for the π electrons, zigzag graphitic ribbons are always metallic, while armchair graphitic ribbons are either metallic or insulating depending on the widths of the ribbons. The study also pointed out that zigzag ribbons exhibit specific electronic states, highly localized at the ribbon edges (edge states). This was supported by first-principles calculations based on density-functional theory (DFT).

1.2 Graphene

After a series of unsuccessful attempts, graphene was first isolated experimentally in 2004. A year later, several groups successfully modelled the conduction electrons of graphene by a massless Dirac particle, reproducing electronic properties close to those predicted by the tight-binding approach.

1.2.1 Structure

Graphene is a one-atom-thick planar sheet of $sp^2$-bonded carbon atoms that are densely packed in a honeycomb crystal lattice, where the carbon-carbon bond length is about 0.142 Å. The three valence electrons in each carbon atom in graphene are bonded in the $sp^2$, whereas the fourth valence electron (which is the $p_z$ orbital in each carbon atom) forms the π band of graphene.

Each unit cell of graphene contains two $p_z$ electrons, thus forming two bands: π and π* bands per unit cell. The two lattice vectors (because it is a two dimensional structure) of the unit cell are

$$\vec{a}_1 = a_0 \sqrt{3} \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right), \quad \vec{a}_2 = a_0 \sqrt{3} \left( -\frac{1}{2}, \frac{\sqrt{3}}{2} \right),$$

where $a_0 = 0.142$ Å, the CC bond length. Those vectors are depicted in Fig[1.1] below.
1.2.2 Electronic Properties

In the LCAO (Linear Combination of Atomic Orbitals) formalism, we assume that each electron wave function is well localized around the carbon nucleus. The total Hamiltonian is thus

$$H = \frac{p^2}{2m} + \sum_{\mathbf{r} \in G} \left( V_{at}(\mathbf{x} - \mathbf{x}_1 - \mathbf{r}) + V_{at}(\mathbf{x} - \mathbf{x}_2 - \mathbf{r}) \right),$$

where $V_{at}$ is the atomic potential, $\mathbf{x}_i$, $i = 1, 2$ are the positions of the carbon nuclei within the unit cell.

1.3 From Graphene to Carbon Nanotubes

Ever since the publication of Iijima’s groundbreaking discovery of carbon nanotubes in 1991 [10], research groups around the world have actively participated in one of the most euphoric research areas in the past few decades. Their outstanding physical properties, as well as their
tremendous potential in the commercial world, have all made of carbon nanotubes a fascinating re-
search topic, and a particularly enriching research experience. However, they were slow in driving
serious business investment for utilizing their properties in the commercial world. This is because,
primarily, of the exceptionally high production costs of high quality carbon nanotubes.

Carbon nanotubes are molecular-scale tubes made of rolling graphitic carbon (graphene layers,
which are basically a honeycomb lattice of Carbon atoms) forming a cylinder. Several studies have
reported on their outstanding mechanical properties, being the stiffest and strongest fibers known,
as well as their unique electronic structure characteristics.

1.3.1 Structure

A single-wall carbon nanotube is formed by folding a graphene sheet into a cylinder. To demon-
strate this, let us choose any two carbon atoms on a graphene sheet, atoms \( A \) and \( B \). The two atoms
will subsequently be the same atom in the tubular form. The position of each of these atoms can be
represented in terms of the graphene unit vector \( \vec{a}_i \) presented above. The two vectors intersect at
a point (and there is only one unique point of intersection if we follow the unit vectors), as shown
below, giving us a triangle were the lines perpendicular to the line connecting \( A \) and \( B \) pass by the
carbon atoms to be connected together. The chirality vector, \( \mathbf{C}_h \) is a unique vector representing
how we shall connect the two perpendicular lines together:

\[
\mathbf{C}_h = n\vec{a}_1 + m\vec{a}_2,
\]

and each carbon nanotube can be uniquely represented by the chirality numbers \((n, m)\) \[\mathbb{I}\]. Sev-
eral such chirality vectors are presented in Fig. \[\mathbb{I.2}\] below.
Figure 1.2 Making a nanotube from graphene.

The tube diameter can be obtained as follows:

\[ d = \frac{|C_h|}{\pi} = \frac{a_0}{\pi} \sqrt{n^2 + nm + m^2}. \]

Finally, there are three distinct ways in which a graphene sheet can be rolled into a tube:

1. Armchair: Hexagons are arranged around the circumference in such a way that one can trace out a shape that resembles an armchair.

2. Zigzag: Hexagons make a zigzag shape around the circumference of the tube.

3. Chiral: This is the most common type, in which the tube can exist in two mirror images.
1.3.2 Electronic Properties of Carbon Nanotubes

The nature of the bonding of a nanotube is described by applied quantum chemistry, specifically, orbital hybridization. The chemical bonding of nanotubes is composed entirely of $sp^2$ bonds, similar to those of graphite. This bonding structure, which is stronger than the $sp^3$ bonds found in diamonds, provides the molecules with their unique strength. Nanotubes naturally align themselves into ropes held together by Van der Waals forces.

1.3.3 Applications

Nanotubes are sought for their unique electrical and mechanical properties in a number of applications. Their high tensile strength lends them to clothes manufacturers in waterproof tear-resistant textiles, combat jackets, sports equipment, concrete where they increase the tensile strength, and halt crack propagation [12]. In biology, due to their giant elongations and contractions when a current is run through them, CNTs are ideal for synthetic muscles [13]. In high tensile strength fibers, a large number of research groups have spun fibers of single wall carbon nanotubes embedded into a polymer. For example, fibers produced with polyvinyl alcohol required 600 J/g to break [14]. Therefore, carbon nanotubes may be able to replace steel in suspension bridges. They also lend themselves to fire protection, where covering material with a thin layer of buckypaper significantly improves its fire resistance due to the efficient reflection of heat by the dense, compact layer of carbon nanotubes or carbon fibers [15].

Utilizing their electrical properties, they have been exploited as artificial muscles (fold when subject to an electric voltage) [16], conductive films (developed by Unidym Inc.), solar cells, superconductors [17], as well as being utilized as electric circuit components and interconnects.

1.4 Electron Field Emission

Since the discovery of the field electron emission process, whereby an electron-rich material emits electrons when subjected to an electric field, the scientific community has been interested in understanding the physical mechanism that underpin such a phenomenon, as well as exploring the
potential applications of it. Schittkey was the first to present an approximate theory explaining the phenomenon, followed by Millikan, Eyring and Lauritsen during the beginning of the 20th century. Then, in 1928, Nordheim presented a quantum mechanical explanation of the phenomenon, which has drawn great interest as it was considered the state-of-the-art model at the time. Using elementary quantum mechanics, Nordheim and Fowler derived a formula for the emission current which, in spite of its simplicity, was a benchmark for researchers until today. It was not until recently that researchers started to realize that a better explanation of the phenomenon should be aided by more comprehensive quantum mechanical calculations of the systems at hand. Thus, several researchers started applying \textit{ab-initio} Density Functional Theory calculations to model smaller systems, mainly nano sized field emitters.

Much of the literature covering the theoretical and experimental aspects of FE is scattered in various books and peer-reviewed articles. However, the Wikipedia article on Field electron emission \cite{18} provides an astonishingly comprehensive coverage of the theory. The authors of the article covered the documentation of the phenomenon as early as Winkler’s account \cite{19} in 1744, and provided a rich insight into the quality of today’s literature on the subject. The authors presented the equations following the International System of Quantities \cite{20}, which required the authors to convert much of the equations in the literature into this format (rationalized-meter-kilogram-second (rmks) system of equations), thus ensuring coherence of the theoretical presentation. Thus, we referred to several references that were cited in that article.

Field electron emission (FE) (also known as field emission and - in some contexts - electron field emission) is the emission of electrons from the surface of a condensed material (either solid or liquid), into vacuum or into another material, by subjecting the former material to an electric field. The target may be a gas, a liquid, or a non-metallic solid with low electrical conductivity. FE occurs at surface locations where the local surface electric field is particularly high. To generate significant amounts of emission, fields of 1 volt per nanometre (1 V/nm, or 1 000 000 000 volts per meter) or more are required. The exact field needed depends both upon the nature of the materials involved and on the amount of electron current being generated. When external stimulation (in particular, heating) is applied, we obtain cold field emission (CFE) in contrast to the cathode-ray
tube [1]. CFE is a statistical emission regime, in which the electrons in the emitter are initially in internal thermodynamic equilibrium, and in which most emitted electrons escape by Fowler-Nordheim tunneling from electron states close to the emitter Fermi level.

Quantum mechanically, field emission occurs due to the wave-mechanical tunneling of electrons out of the condensed material. As electrons obey Schrödinger's wave-equation, they exhibit wave-like behaviour and can tunnel through a surface barrier that has been made sufficiently thin by the applied electric field, without gain or loss of energy. The theoretical treatment will be the subject of Chap. 2.

Most metal emitters that are applied in field emission are designed to have a sharp edge (with radius \( \approx 1 \mu m \)) for increasing the magnitude of the local electric field at the emitter's tip, thus achieving a high rate of electron tunneling [1, 21]. Nowadays, researchers can produce nanotips (with radius \( \approx 1 \text{nm} \)) [1], in which the field is greatly enhanced at the tip region [1], and where the low density of states (DOS) at the tip makes the emitted electrons highly coherent and monoenergetic so that they can be used as an efficient source of the low-energy electron point source microscope [1, 21, 22, 23].

Researchers, as was elaborated by Semet et al. [24], usually confront two problems in studies of electron emission from carbon nanotubes. Firstly, purifying the surface is a very expensive process which does not necessarily yield optimal results. Secondly, it is difficult to determine the exact geometry of the actual emitter during the emission unless the emission is from an isolated, individual nanotube. Our study is thus concerned with a single isolated nanotube, and the effect of nitrogen impurities on field emission performance.

Among the various applications for carbon nanostructures, electron field emitters made from carbon allotropes show significant promise for novel electronic devices [25] because they can maintain stable forms under extremely high field-emission (FE) current densities owing to tight covalent-bonds [26]. Chen et al. [27] performed an FE experiment using graphite platelet nanofibers (GPNs) with several thousand graphitic ribbons stacked together like a deck of cards. Wu et al. [28] carried out FE measurements of carbon nanowalls (CNWs), which are nano-graphitized sheets grown perpendicularly on substrates, and pointed out that CNWs are good candidates for nanoscale
field emitters as well as carbon nanotubes. For the development of efficient field emitters, examination of FE properties of graphitic nanostructures is interesting and meaningful both from the viewpoint of fundamental science as well as technological applications of the field emitters.

To improve the performance of the nanotube field emitter by tuning the structural parameters such as the radius, end geometry, and packing density, it is essential to understand the emission mechanism of the nanotube. While the Fowler-Nordheim (F-N) theory has been successful in describing the field emission of micron-sized tips, many experiments reflect that the F-N theory is not sufficient for a full understanding of the field emission of nanotubes, such as the nonlinear I-V characteristics in the F-N plots [29]. In addition, the energy distribution of emitted electrons exhibits a sharp peak which shifts to a lower energy side almost linearly as the applied field increases [30]. All of these observations are incompatible with the picture that the emission current originates purely from the usual metallic (extended) states, suggesting that localized states [31] may contribute to the emission current significantly.

1.5 Applications of Carbon Nanotube Field Emitters

1.5.1 Field Emission Display

Carbon nanotubes have been regarded as a promising material to be used as electron emitters in the field emission display (FED) [32]. The unusually high aspect ratio as well as the mechanical and chemical stability of the nanotube are main advantages over the conventional metallic tips. The viability toward the practical device application is being examined, and the carbon-nanotube-based FED is expected to be commercialized in the near future [33, 34].

1.5.2 Atomic Force Microscopy

Single-walled carbon nanotubes are used as Atomic Force Microscopy probes with radii in the Angstrom scale, which is comparable to molecular-scale dimensions [35, 36]. Individual SWNTs can bundle together, driven by attractive van der Waals forces, to form SWNT ropes containing up to hundreds of nanotubes each [35]. The greatest advantage in using carbon nanotubes as probes is the mechanical robustness, which enables the nanotube tip to resist deformations at high
voltage [37]. The ability to use the same tip, with the radius of curvature remaining constant after many scans, permits analytical assessment of the surface morphology, which is important in the evaluation of deposition processes for thin films in state-of-the-art microelectronics.

1.6 Our Approach

In this work we investigate the mechanism of electron field emission in pristine short carbon nanotubes using \textit{ab-initio} computation. We adopt the Time-Dependent Density Functional Theory, following the scheme of Araidai et al. [22]. We then study the effect of nitrogen and boron doping on the field emission properties of carbon nanotubes.

1.7 Outline of the Thesis

After introducing the subject of our research in Chap. [1] we provide an overview of research efforts towards studying the characteristics of field emission from carbon nanotubes in Chap. [2]. We outline the different applications of carbon nanotube field emitters, as well as the different techniques that aim at enhancing the field emission properties of carbon nanotubes. We cover a number of theories that explain the field emission phenomenon, starting from the classical Fowler-Nordheim theory up to the recent time-dependent \textit{ab-initio} simulations. We give a more detailed exposure on the time-dependent density functional theory simulation in Chap. [3]. In Chap. [4], we provide our setup and results, and explain the various graphs obtained for the different wave functions in each nanotube configuration. We explain those results and arrive at our conclusions in Chapter [5].
Chapter 2

Field Emission from Nanostructures

In this chapter, we present an overview of the classical theory of field emission, the Fowler-Nordheim theory, which is based on the idea of quantum tunneling, and the modern ab-initio techniques based on quantum mechanical simulations. Then, we review the research efforts that were dedicated to improving the performance of field emission from carbon nanotubes. We conclude this chapter with an emphasis on the significance of nitrogen doping in enhancing field emission.

2.1 Computation of the Field Emission Current

2.1.1 The Classical Fowler-Nordheim Theory of Field Emission

An electron just below the surface of a metal can be viewed as being inside a potential well of depth \( W \), the work function of the surface. For a 1D system, the Schrödinger equation is (using the original notation of Fowler-Nordheim [38]:

\[
\frac{d^2 \psi}{dx^2} + \kappa^2 (W - C + Fx) \psi = 0 \quad x > 0, \tag{2.1}
\]

\[
\frac{d^2 \psi}{dx^2} + \kappa^2 W \psi = 0 \quad x < 0. \tag{2.2}
\]

where \( C \) is the height of the barrier depicted in Fig. 2.1 below, \( W \) is the eigen energy, \( F \) is the electric field. The current formula derived by Fowler and Nordheim is [38]

\[
I = 6.2 \times 10^{-6} \frac{\mu^{1/2}}{(\chi + \mu)^{1/2}} F^2 e^{-2 \times 10^8 \chi^{5/2}/F}.
\]
where $\chi$ is the thermionic work function, $\mu$ is the familiar parameter in the electron distribution in the Fermi-Dirac distribution function. Gadzuk et al. [39, 40] derived the following FN formula:

$$I = A \frac{1.5 \times 10^{-6}}{\phi} (\frac{V}{d})^2 \gamma^2 e^{\frac{10.4}{\sqrt{\phi}}} e^{-\frac{6.44 \times 10^9 \gamma^{1.5} d}{\phi}},$$

[2.3]

where $V$ is the applied voltage, $F = \gamma V/d$ is the local field at the emitter surface, $d$ is the inter-electrode distance, $\gamma$ is the field enhancement factor, $A$ represents the emitter area, and $\phi$ is the work function with dimensions of $eV$. The values of $A$ and $\phi$ are usually determined experimentally by tracing the FN plot. Note that the notation used for the local field here ($F$) is different from the $F$ used to represent the electric field in Fowler-Nordheim’s work.

Figure 2.1 Diagram showing a one-dimensional potential barrier problem.

Several authors have also worked on extending the Fowler-Nordheim model. Alexander et al. [41] have generalized the field emission theory to the case of Luttinger liquids as well as carbon nanotubes, while Shi Dong et al. [42] developed a generalized Fowler-Nordheim theory of the carbon nanotube field emission, in which the behavior of the current-voltage (I-V) characteristics depends on the electric field and the diameter of the carbon nanotubes. This formalism reveals the key differences of field emission between conventional bulk metallic emitters and low-dimensional emitters and gives a clear physical understanding of the non-Fowler-Nordheim feature of the I-V characteristics of the carbon nanotube field emission. The work of Bonard et al. [36] yielded by fitting the following formula for $\gamma$:

$$\gamma = 1.2 \left(2.5 + \frac{h}{r}\right)^{0.9} \left[1 + 0.013 \left(\frac{d - h}{d}\right)^{-1} - 0.033 \left(\frac{d - h}{d}\right)\right].$$

[2.4]
for a cylinder of height $h$ which is terminated by a hemisphere of radius $r$.

### 2.1.2 *Ab initio* Simulation of Field Emission from Carbon Nanotubes

Buldum and Lu [43] carried out theoretical investigations that incorporate geometrical effects and the electronic structure of nanotubes, showing that emission is improved as we go closer to the carbon nanotubes tip. They have also demonstrated that field emission current deviates from the exponential Fowler-Nordheim behavior due to the variation of the local field in the electron tunneling region. Han *et al.* [44] performed first principles calculations on various edge geometries of $(n, n)$ carbon nanotubes, showing that the most favorable edge geometry is the zigzag edge exposed by a slant cut due to the existence of unpaired dangling bond states around the Fermi level. The next most favorable edge geometry is the capped nanotube where p-bonding states localized at the cap and pointing in the tube axis direction occur at the Fermi level. Liang *et al.* [45] have examined the intrinsic electron energy spectra in field emission from the single-wall carbon nanotubes based on the quantum tunneling theory with the tight-binding approximation. They determined that for the metallic tubes, as temperature or electric field increases, the main peak of the energy spectrum becomes high and wide, and some sub-peaks occur above or below Fermi energy. For the semiconducting tubes, the energy gap at the Fermi energy may occur leading to a double peak spectrum. Electric field competes with temperature to balance the height of the two peaks. Strong field makes the low-energy peak high, while high temperature enhances the high-energy peak. Adessi and Devel [46], based on methods derived from quantum and electromagnetic theory, found that the energy distributions of the emitted electrons, obtained for various kinds of single walled nanotubes, confirm the implication of localized states in the emission process. However, the (10,0) nanotube seems to give rise to emission only by a very peaked localized state, whereas the Fermi sea also contributes for the (5,5) nanotubes. Moreover, despite a larger field enhancement, the (5,5) capped nanotube does not allow for currents as large as those emitted by the open-ended one.

Open-ended single-walled carbon nanotubes were studied by Zhou *et al.* [47]. They reported that an open-ended single-walled carbon nanotube has much better field-emission properties than a
closed single-walled carbon nanotube; owing to geometrical effects that slightly influence the work
function and the amplification factor, an open-ended single-walled carbon nanotube with relaxation
has higher threshold voltage and higher current density compared to one without relaxation. It is
suggested that adjusting the localized electronic states of the emitting regions, by electronic and
geometrical means, could improve the field-emission properties of carbon nanotubes.

A number of papers have investigated the application of time-dependent density functional
theory (TDDFT) in examining field emission, among which the paper by Han et al. [1] pays
particular attention to the theoretical derivation. Our research followed most of the procedure set
in that paper. Han and Ihm [4] published another paper in the same year about the role of the filling
factor in the calculation of the current in periodic systems. They reported that the emission current
from the states localized at the tip end is more than ten times greater than direct contributions from
extended metallic states.

In Fig. 2.2 and Fig. 2.3 below we show the charge evolution and $I - E$ characteristics from
Han et al. [1].
Figure 2.2 $I - E$ characteristics, showing the exponential dependence of the emission current on the applied electric field $E$. 
2.1.3 Field Emission Calculations for Graphene

Field emission from Graphene has not attracted as much as attention as that of nanotubes because the field emission process itself is very challenging. According to Eda et al. [48], the reason for this is that graphene sheets are produced by deposition methods that lay the graphene sheet on substrate layers, thus making it hard to obtain field emission current from the isolated graphene. Lee et al. [49] reported in their experimental publication the extraction of 0.17 μA upon subjecting graphene to 12.1 V, which is equivalent to V/Å. They also fitted their calculations with the Fowler-Nordheim theory as follows:
\[ I(E) = A \frac{q}{8\pi^2 \hbar \phi} \left( \gamma E \right)^2 e^{-\frac{A^4}{4\pi^2 \hbar^2 \phi^3} \sqrt{2m\phi^2}}, \]

where \( I \) is the emission current, \( E \) is the applied electric field, \( \gamma \) is the field enhancement factor, \( \phi \) is the work function, \( A \) is the area of the graphene sheet, and \( m \) is the electron mass. The study assumed that the work function of graphene is 5 eV.

On the other hand, Araidai et al. \cite{22} performed ab-initio calculations on graphene ribbons using Time-Dependent Density Functional Theory. They studied field emission from a narrow graphene ribbon upon subjecting it to an electric field of 0.1V/Å that is parallel, and perpendicular, to the ribbon’s axis. In the case of applying a parallel field, they reported the extraction of 0.37\( \mu \)A per unit cell in case of a pure graphene ribbon (with dangling bonds), and 0.14\( \mu \)A in the case of a hydrogen-passivated graphene ribbon. They used zigzag graphene in order to examining the effect of H passivation and edge states on field emission behavior. Their work is one of very few papers on ab-initio field emission calculation from graphene.

2.2 Enhancing Field Emission

There is a huge body of literature that is concerned with the different nanotechniques that could enhance the amount of current extracted from nanoemitters, as well as prolonging the emission time.

2.2.1 Chemical Treatments

Pan et al. \cite{50} prepared Carbon nanotube (CNT) cathode with and without interfusing nanometal particles using screen-printing technology, and showed that Fe/CNT film achieves high emission characteristics and emission uniformity. Liua et al. \cite{51} decorated double-walled CNTs’ surface with ruthenium (Ru) metal nanoparticles, showing remarkable improvement in field emission properties. Using traditional Fowler-Norheim calculations, the field enhancement factor calculated from the slope of the FN plot is 1349 and 2231 for the pristine DWCNTs and Ru-DWCNTs, respectively. Srivastava et al. \cite{52} synthesized Nitrogen-doped CNTs using simple microwave
plasma enhanced chemical vapor deposition technique. CNT films produced showed very good field emission characteristics with threshold field in the range of 2.65-3.55 V/µm. CNT film with flower like morphology showed lower threshold field as compared to vertically aligned structures. Open graphite edges on the side surface of the bamboo-shaped CNT are suggested to enhance the field emission characteristics which may act as additional emission sites.

CNTs having strong covalent bonds are very stable against chemical attacks. Breaking these strong covalent bonds and changing surface state would be expected to change the CNTs physical property as well as chemical property [8,9]. As field emission behavior takes place at the tip of the CNT, one could control the field emission property by changing the structure and surface state of the CNT tips.

Lee et al. [53] examined different ways to improve field emission of MWCNTs. CNT tips were opened and defects working as trap sites were generated on the CNT surface by the chemical modification process leading to improvement of field emission property. The CNTs were chemically modified by oxygen plasma, nitric acid (HNO3), and hydrofluoric acid (HF). Zou et al. [54] reported that the application of a novel post-treatment method in NaCl electrolyte can solve the problem of poor field emission characteristics of printed CNT films, observing that the total emission current of the treated film that has the same printing are as the untreated one increased from about 100 to about 1800 µA.

2.2.2 Nanowelding

Zhao et al. [55] used ultrasonic nanowelding to improve the field emission properties of carbon nanotube (CNT) cathodes. The emission current density (J) is 503 and 40 µA/cm² in welded and non-welded CNTs respectively at 8.5 V/µm. The dramatic increase of the emission current density is caused by the low contact resistance between the CNTs and the metal substrate after nanowelding treatment. As for emission stability, the current fluctuates more severely and decreases gradually in the non-welded sample. After the welding of the sample, the current fluctuation is lower and the average current does not decrease during this period. The improved stability can be explained by the strong adhesion between CNTs and metal substrate.
2.2.3 Mechanical Treatment

Chai et al. [56] studied the electron emission from the sidewall of a bent individual multi-wall carbon nanotube. The electron field emission from the sidewall of CNT was measured, and compared with that from the tip of the CNT. The turn-on voltage from the sidewall of CNT is significantly lower than that from the tip. An enhancement factor as large as 400,000 has been obtained for the electron emission from the side wall. Jang et al. [57] studied field emission properties for a wider variety of geometries: base-model well-aligned carbon nanotubes (Base-CNTs), curled carbon nanotubes (Curled-CNTs), and tip model well-aligned CNTs (Tip-CNTs). The nanotubes were fabricated by means of direct current plasma-enhanced chemical vapor deposition using different ammonia (NH$_3$) pre-treatment plasma currents. The field enhancement factor $\gamma$ of Base-CNTs, calculated from a Fowler-Nordheim plot, was higher than that for the Curled-CNTs and Tip-CNTs. The straightening process enhanced the emission properties of the as-grown Curled-CNTs films by decreasing the turn-on field and increasing the total emission current. Thus, morphology parameters of the MWNTs significantly affect the emission properties of CNTs.

2.2.4 Thermal Treatment

Sveningsson et al. [58] showed that the resistivity of CNT’s are influenced by radiative cooling and temperature, and that a consideration of the temperature change due to the electron emission process itself, known as the Nottingham effect, is crucial to obtain good agreement with the experimental data. For CNT-ZnO composite materials, Huang et al. [59] showed that the higher temperature (550°C) the underlying CNTs were grown at, the better the field emission properties the materials have. Results by Jayatissa et al. [60] indicate that MWNTs synthesized at low temperature had low emission threshold voltages and high emission current levels that are favorable properties for field emission-based display device applications. In thin films, Zhu et al. [61] demonstrated that the turn-on field and work function decrease with increasing temperature, where an increase of the carrier concentration with increasing temperature leads to a reduction in the tunnel barrier width, resulting in an enhancement of the emission current.
2.2.5 Nitrogen Doping of Carbon Nanotubes

2.2.5.1 Synthesis

Nitrogen-doped carbon nanotubes (CN$_x$) have been synthesized by acetonitrile vapor decomposition over catalyst nanoparticles produced in the result of thermolysis of solid solutions of Fe and Ni bimaleate [62]. Lai et al. [63] modified their CNT bundles array by post-growth nitrogen plasma treatment.

2.2.5.2 Why Nitrogen Doping?

Experimentalists have reported an enhancement of the field emission properties of CNT’s upon nitrogenation i.e. replacing carbon atoms close to the nanotube tip with nitrogen atoms by chemical processing. Gohel et al. [64] showed that the N$_2$ treated MWCNTs showed significant improvement in field emission properties, compared to the Ar treated MWCNTs that displayed poorer field emission characteristics compared to untreated MWCNTs. Kurt et al. [65] studied field emission in vacuum and revealed that for arrays of nanotubes thinner than 50 nm an onset field below 3 V/µm was observed and a field amplification factor $\beta$ of 1200 was determined in that case. Doytcheva et al. [66] performed measurements on individual nitrogen-doped multi-walled carbon nanotubes mounted on tungsten support tips. Both the current/voltage characteristics and the energy spectrum of the emitted electron beam revealed field emission behavior similar to that shown for the best metallic emitters, but is highly sensitive to small amounts of impurities deposited on the surface of the nanotube. Nitrogen-doped multi-walled CNTs CN$_x$ ($x < 0.1$) were synthesized by pyrolysis of ferrocene/benzilamine mixtures at 1120 K in an Ar atmosphere. Individual N-doped multi-walled carbon nanotubes were mounted on tungsten support tips using a nanomanipulator (Omicron) in a scanning electron microscope (SEM, Philips). The authors obtained experimental data for 5 different CNTs (with different lengths and tungsten support tip radii) shown in Tab. 2.1 below, and obtained field enhancement factors in the range $0.82 \pm 0.01$ to $1.81 \pm 0.02$ by fitting data to Fowler-Nordheim exponential model. Ray et al. [67] observed that the current density of chlorinated Nitrogen-doped CNTs is enhanced from $1.3 \mu A/cm^2$ (N-CNTs) to about $15 \mu A/cm^2$.
(N-CNTs:Cl) at an electric field of 1.9 V/µm. In Tab. ?? below, we the comparison between the turn on field in different CNTs:

Table 2.1 Comparisons of field emission characteristics in terms of turn-on electric field and emission current density on different CNTs (treated and non-treated) reported by different researchers. CNTs stand for Carbon nanotubes; CNTs:N stand for Nitrogen-treated carbon nanotubes; N-CNTs:Cl stand for Chlorine-treated nitrogen-based carbon nanotubes; N-CNTs stand for nitrogen-based CNTs.

<table>
<thead>
<tr>
<th>CNT</th>
<th>Turn on field (V/µm)</th>
<th>Current density (J) (mA/cm²)</th>
<th>Applied Field (V/µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-CNTs</td>
<td>1.0</td>
<td>1.3</td>
<td>1.9</td>
</tr>
<tr>
<td>N-CNTs:Cl</td>
<td>0.875</td>
<td>15</td>
<td>1.9</td>
</tr>
<tr>
<td>CNTs:N [quoted sources]</td>
<td>1.73</td>
<td>0.45</td>
<td>3</td>
</tr>
<tr>
<td>CNTs:N [quoted sources]</td>
<td>4.7</td>
<td>11</td>
<td>8.0</td>
</tr>
<tr>
<td>CNTs</td>
<td>2.5</td>
<td>100</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Ding et al. [68] analyzed aligned CNₓ nanotubes that were fabricated by pyrolyzing ethylenediamine on p-type Si(1 1 1) substrates using iron as the catalyst. They reported the extraction of 20µA/cm² upon applying 1.4V/µm. Lai et al. [63] examined nitrogenated carbon nanotube arrays and found that the lowest threshold electric field of 2.3V/µm was observed when the nitrogen content of CNTs was 4.08 at.%, which was obtained from 70 min. of nitrogen plasma treatment. They reported the following I – V diagrams for different nitrogen doping concentrations (note that the time durations in the legend correspond to Tab. ?? below):  

Table 2.2 Nitrogen contents vs. plasma treatmeant times

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>10</th>
<th>40</th>
<th>70</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>N content (at.%)</td>
<td>0</td>
<td>2.17</td>
<td>3.40</td>
<td>4.08</td>
<td>1.96</td>
</tr>
</tbody>
</table>

The enhanced field emission performance of CNₓ nanotube is due to the presence of lone pairs of electrons on nitrogen atom that supplies more electrons to the conduction band. That is, nitrogen
atoms modify the conductance property of N-doped nanotubes by donating electrons [69]. It has also been predicted that $CN_x$ nanotubes have n-type conductivity, low resistance and good field electron emission property [70]. In addition, it has been reported that it is feasible to control the nitrogen concentration by varying experimental parameters (such as the temperature, flow rate of gas, etc.) and hence the field emission performance [69]. Qin et al. [71] attributed the enhanced field emission characteristics of nitrogenated carbon nanotubes to vacancy defects (that is, dangling bonds) the are caused by plasma treatment.
Chapter 3

Theoretical Background

In this chapter, we present a concise overview of the main features of the Time-Independent Density Functional Theory and the Time-Dependent Density Functional Theory (TDDFT) that were utilized in our calculations. However, we give a short overview of the Hartree-Fock theory which is important in our explanation of the Exchange and Correlation potentials in Sec. 3.3. We have used the Octopus code that was developed by Castro et al. [72, 73] which has been around in the scientific computation community for around a decade. We present more details on the software in the appendix.

3.1 Hartree-Fock Theory

We follow the notation and treatment of Parr and Yang [74]. The Hamiltonian of a system of nuclei each surrounded by electrons can be represented as follows:

\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{r_\alpha} + \sum_{i<j}^{N} \frac{1}{r_{ij}}. \]  

[3.1]

where $Z_{\alpha}$ is the nuclear charge of atom $\alpha$, $r_\alpha$ is the distance between electron $i$ and atom $\alpha$, $r_{ij}$ is the distance between electron $i$ and electron $j$, and $\alpha = 1 \ldots M$. We try to find eigen functions for the above Hamiltonian in the form
\[ \psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_N(x_1) \\ \psi_1(x_2) & \cdots \\ \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \cdots & \psi_N(x_N) \end{vmatrix} \]  

that would minimize the total energy functional:

\[ E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \]

\[ = \sum_i H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \]

where

\[ H_i = \int \psi_i^*(x)\left(-\frac{1}{2} \nabla^2 + v(x)\right)\psi_i(x) dx, \]

and the Coulomb integral

\[ J_{ij} = \int \psi_i(x_1)\psi_j^*(x_2) \frac{1}{r_{12}} \psi_j^*(x_1)\psi_i(x_2) dx_1 dx_2, \]

and the exchange integral

\[ K_{ij} = \int \psi_i(x_1)\psi_j(x_2) \frac{1}{r_{12}} \psi_i(x_2)\psi_j(x_1) dx_1 dx_2. \]

Upon minimization, we obtain the following set of equations:

\[ \hat{F}\psi_i(x) = \sum_{j=1}^N \epsilon_{ij} \psi_j(x) \]

where

\[ \hat{F} = -\frac{1}{2} \nabla^2 + v + \hat{g}, \]

\[ \hat{g} = \hat{j} - \hat{k}, \]
where $v$ is the electron-nuclear potential, and the two operators $\hat{j}$ and $\hat{k}$ are defined as follows for any arbitrary function $\phi(x)$:

$$\hat{j}(x_1)\phi(x_1) = \sum_{k=1}^{N} \int \psi^*_k(x_2)\psi_k(x_2) \frac{1}{r_{12}} \phi(x_1) dx_2,$$

[3.11]

$$\hat{k}(x_1)\phi(x_1) = \sum_{k=1}^{N} \int \psi^*_k(x_2)\phi(x_2) \frac{1}{r_{12}} \psi_k(x_1) dx_2.$$

[3.12]

Now, instead of working with $\psi$ as the dependent variable and hence dealing with $4N$ independent variables (space and time variables for each of the $N$ electrons), we wish to work in terms of another variable, the electron density $\rho$ defined by the formula

$$\rho(r) = \sum_{i}^{\text{occ}} |\phi_i(r)|^2 .$$

[3.13]

where occ is the number of occupied states. The possibility of such a simplification was made possible by the introduction of the Hohenberg-Kohn theorem, which will be the subject of the next section. To arrive at such theorem, we first treat the more cumbersome first-order reduced density matrix

$$\rho_1(r'_1, r_1) = N \int \cdots \int \psi(r'_1s_1x_2 \cdots x_N)\psi^*(r_1s_1x_2 \cdots x_N) ds_1 dx_2 \cdots dx_N$$

[3.14]

and the second-order reduced density matrix

$$\rho_2(r'_1r'_1, r_1r_2) = \frac{N(N - 1)}{2} \int \cdots \int \psi(r'_1s_1r'_2s_2x_2 \cdots x_N)\psi^*(r_1s_1r_2s_2x_2 \cdots x_N) ds_1 ds_2 dx_3 \cdots dx_N.$$

[3.15]

Total energy can then be represented as follows:

$$E = -\frac{1}{2} \int \left[ \nabla_r^2 \rho_1(r'_1, r_1) \right]_{r'_1 = r} dr + \int v(r)\rho(r) dr + \int \int \frac{1}{r_{12}} \rho_2(r_1, r_2) dr_1 dr_2,$$

[3.16]

where the first term is the electronic kinetic energy, the second is the nuclear-electron potential, and the third is the electron-electron Coulomb potential.
3.1.1 Pair-Correlation Hole

In the above Eq. 3.16, the electron-electron Coulomb potential

\[ \int \int \frac{1}{r_{12}} \rho_2(r_1, r_2) dr_1 dr_2 \]  

accounts for all electrostatic repulsive forces between electrons. In classical electrostatic theory, such forces are modelled by Coulomb’s law between every two charge densities, thus a classical form for Eq. 3.17 is

\[ J[\rho] = \frac{1}{2} \int \int \frac{1}{r_{12}} \rho(r_1) \rho(r_2) dr_1 dr_2. \]  

The difference between the actual and classical exchange potentials is accounted for by the pair-correlation function \( h(r_1, r_2) \):

\[ \rho_2(r_1, r_2) = \frac{1}{2} \rho(r_1) \rho(r_2) [1 + h(r_1, r_2)], \]  

from which we define the pair-correlation hole of an electron at point \( r_1 \)

\[ \rho_{XC}(r_1, r_2) = \rho(r_2) h(r_1, r_2). \]  

In terms of \( \rho_{XC} \),

\[ V_{ee} = J[\rho] + \frac{1}{2} \int \int \frac{1}{r_{12}} \rho(r_1) \rho_{XC}(r_1, r_2) dr_1 dr_2 \]  

3.1.2 Exchange Energy for a Uniform Electron Gas

Now, we wish to evaluate the exchange energy in the case of a uniform electron gas (the well-known Thomas-Fermi model), in which – in Fermi’s own words in his 1927 seminal paper – “electrons are distributed uniformly in the six-dimensional phase space for the motion of an electron at the rate of two for each \( h^3 \) of volume, and that there is an effective potential field that is itself determined by the nuclear charge and this distribution of electrons” [74]. Given this assumption, the formula for the total energy of a uniform electron gas
\[ E[\rho] = T[\rho] + \int \rho(r) v(r) dr + V_{ee}[\rho], \]  

where \( T[\rho] \) is the kinetic energy, \( V_{ee}[\rho] \) is the electron-electron interaction energy. The total energy can be evaluated as follows: take \( V_{ee}[\rho] \) to be the classical electron-electron Coulomb repulsion term \( J[\rho] \), and insert \( T[\rho] \) of that of a non-interacting uniform electron gas. Starting from wave functions for a particle in a periodic box, we arrive at the follow form for the kinetic energy:

\[ T[\rho] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho(r)^{5/3} dr, \]

and the exchange energy:

\[ K[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho^{4/3}(r) dr. \]

### 3.2 Density Functional Theory

In recent years, Density Functional Theory (DFT) has been gaining more attention from the computational physics community in contrast to Hartree-Fock (HF) and post-HF methods for studying electronic structure of materials, and it is considered as the preferred method in many applications for molecules and solids \[75\]. The theory starts from the Hohenberg-Kohn Theorem \[76\] that for a system with \( n \) electrons in Coulomb interaction the functional \( E[\rho] \) is only the functional of the electron density. Here, interacting ground state density \( \rho(r) \) is

\[ \rho(r) = \sum_i \langle \phi_i(r) | \phi_i(r) \rangle. \]

The interacting ground state is obtainable through the solution of the Kohn-Sham equations

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

Here, \( v_{KS}[\rho] \), the Kohn-Sham potential, has a functional dependence on \( \rho \), and

\[ v_{KS}[\rho] = v_{ext}[\rho] + v_{Hartree}[\rho] + v_{XC}[\rho]. \]
Due to the functional dependence on the density, these equations form a set of nonlinear coupled equations. The standard procedure to solve it is iterating until self-consistency is achieved.

The total energy of the system can then be obtained as

$$ E_{KS}[\rho] = T_s[\rho] + \int d^3r \, v_{ext}(r) + E_{Hartree}[\rho] + E_{XC}[\rho]. \quad [3.28] $$

where $T_s[\rho]$ is the non-interacting kinetic energy, $v_{ext}$ is the external potential, and $E_{XC}[\rho]$ and $v_{XC}[n]$ are the exchange and correlation energy and potential respectively. We shall treat $E_{XC}[\rho]$ in Sec. 3.3. More explicitly, this formula can also be written as

$$ E[\rho] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{m} \int \psi_i^*(\mathbf{r}_1) \nabla^2 \psi_i(\mathbf{r}_1) d\mathbf{r}_1 - \sum_{i=1}^{N} \int \frac{Z_I e^2}{4\pi\epsilon_0 r_{I1}} \rho(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2) e^2}{4\pi\epsilon_0 r_{I2}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{XC}[\rho], \quad [3.29] $$

where $\psi_i$ are the Kohn-Sham eigen functions [77]. The first term is the kinetic energy, the second is the electron interaction with nuclei, the third term is the Hartree energy that accounts for the classical electrostatic repulsion between the electron clouds at the points $\mathbf{r}_1$ and $\mathbf{r}_2$; the fourth represents the exchange-correlation energy which arises from other interactions (see Sec. 3.3). Minimization of this quantity will yield the following set of coupled partial differential equations, the Kohn Sham equations [78]:

$$ \left\{ -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{I=1}^{N} \int \frac{Z_I e^2}{4\pi\epsilon_0 r_{I1}} + \int \frac{\rho(\mathbf{r}_2) e^2}{4\pi\epsilon_0 r_{I2}} d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) \right\} \psi_i(\mathbf{r}_1) = \epsilon_i \psi_i(\mathbf{r}_1). \quad [3.30] $$

Such cumbersome set of equations are impossible to solve exactly. Therefore, we seek iterative solutions that would maintain the self-consistency of the equations. The algorithm that performs such iteration is the core of any Density Functional Theory code.

### 3.3 Exchange and Correlation Potential

The $V_{XC}$ potential represents effects of the Pauli exclusion principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons. It can be obtained exactly if we solve the
Kohn-Sham equations exactly, which is formidable in typical many-body systems. There is a huge number of proposed approximations for the exchange correlation potential, and we choose the Local Density Approximation (LDA), which is derived in the analytic theory of a uniform electron gas and applied, directly or with empirical modifications, to non-uniform densities. Generally, it has the form

$$E_{\text{XC}}^{\text{LDA}}[\rho] = \int e_{\text{XC}}(\rho) d\mathbf{r},$$

where the exchange-correlation energy density $e_{\text{XC}}$ is a functional of $\rho$ only. In the LDA approximation, the exchange component is given by Eq. 3.24.

Correlation is a much more difficult problem than exchange, so physicists resort to fitting empirical data to certain proposed parametrizations. The one we have used is the parametrization proposed by Perdew and Zunger [79]:

$$\epsilon_c = \begin{cases} 
\frac{\gamma}{1 + \beta_1 r_s^{1/2} + \beta_2 r_s}, & r_s \geq 1 \\
A \ln r_s + B + C r_s \ln r_s + Dr_s, & r_s < 1 
\end{cases}, \tag{3.32}$$

where $\gamma, \beta_1, \beta_2, A, B, C$ and $D$ are all fitting parameters.

### 3.4 Pseudopotentials

The many-electron Schrödinger equation can be greatly simplified if electrons are divided in two groups: valence electrons and inner core electrons. The electrons in the inner shells are strongly bound and do not play a significant role in the chemical binding of atoms, thus forming with the nucleus an inert core. Binding properties are almost completely due to the valence electrons, especially in metals and semiconductors. This separation implies that inner electrons can be ignored, reducing the atom to an inert ionic core that interacts with the valence electrons. This suggests the use of an effective interaction, a pseudopotential, that gives an approximation to the potential felt by the valence electrons due to the nucleus and the core electrons. This can significantly reduce the number of electrons that have to be dealt with. Moreover, the pseudo wave
functions of these valence electrons are much smoother in the core region than the true valence wave functions, thus reducing the computational burden of the calculations.

Modern pseudopotentials are obtained by inverting the free atom Schrödinger equation for a given reference electronic configuration, and forcing the pseudo wave functions to coincide with the true valence wave functions beyond a certain cutoff distance. The pseudo wave functions are also forced to have the same norm as the true valence wave functions, and the energy pseudo eigenvalues are matched to the true valence eigenvalues. Different methods of obtaining a pseudo eigenfunction that satisfies all these requirements lead to different non-local, angular momentum dependent pseudopotentials. Some widely used pseudopotentials are the Troullier and Martins potentials \[80\], the Hamann potentials \[81\] and the Vanderbilt potentials \[82\].

3.4.1 Algorithm for Constructing the Pseudopotential

Pseudopotential construction is an inverse problem, where we invert the Schrödinger equation of the pseudowave function to obtain the potential. The steps are generally as follows. First, we solve the all-electron radial Schrödinger equation for a given distribution of electrons in the different energy levels. Then, we generate the pseudo-wave functions using one of the available methods (we have chosen the famous Troullier-Martins method, see Sec. 3.4.2). Then, we evaluate the inverted radial Schrödinger equation (which is supposed to be the Schrödinger equation for the pseudo-wave functions) to obtain the screened pseudopotential. Finally, we perform an unscreening of the pseudopotential to obtain the final pseudopotential by subtracting the Hartree and exchange-correlation potentials that were computed only for the valence electrons.

3.4.2 The Troullier-Martins Method

The Troullier-Martins wave function has the form \[80\]:

\[
R_{l}^{TM} = r^{l+1} e^{p(r)},
\]

[3.33]

where \(R_{l}\) is the radial function, \(l\) is the quantum number, \(p(r)\) is a polynomial function of the form
\[ p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}, \]  

[3.34]

and the coefficients are determined from the following conditions:

1. Norm-conservation

2. Continuity of the pseudo-wave function and its first 4 derivatives

3. \( \left. \frac{dR_{PS}}{dr} \right|_{r=0} = 0 \), which amounts to the equation: \( c_2^2 + c_4(2l + 5) = 0 \).

### 3.5 The Time-Dependent Kohn-Sham Equations

The solution of the time-dependent Kohn-Sham equations

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \psi_i(r, t) = \left[ -\frac{\nabla^2}{2} + v_{KS}(r, t) \right] \psi_i(r, t)
\]

[3.35]

has the following exact expression:

\[
\psi_j(T) = T \exp \left\{-i \int_0^T H(\tau) \right\} \psi_j(0),
\]

[3.36]

where \( T \exp \) is the time-ordered exponential, which is a short-hand for:

\[
\psi_j(T) = \left\{ \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_0^t d\tau_1 \cdots \int_0^t d\tau_n H(\tau_1) \cdots H(\tau_n) \right\} \psi_j(0)
\]

[3.37]

If the Hamiltonian commutes with itself at different times, we can drop the time-ordering product, and leave a simple exponential. If the Hamiltonian is time-independent, which makes it trivially self commuting, the solution is simply written as:

\[
\psi_j(T) = \exp \left\{-iTH \right\} \psi_j(0).
\]

[3.38]

Unfortunately, this is not the case for TDDFT when the system is exposed to external time-dependent perturbations like electric and magnetic fields or pulsed lasers. But even without an
external time-dependency, there remains the intrinsic time-dependency of the Kohn-Sham Hamiltonian, which is built “self-consistently” from the varying electronic density.

The first step to tackle this problem is to split the propagation of the long interval $[0, T]$ into $N$ smaller steps by utilizing the group-theoretic property

$$U(T, t) = U(T, t')U(t', t)$$

of the time evolution operator. This yields the following time discretization:

$$U(T, 0) = \prod_{i=0}^{N-1} U(t_i + \Delta t, t_i),$$

where $t_0 = 0$, $t_N = T$, $\Delta t = T/N$. So at each time step we are dealing with the problem of performing the short-time propagation:

$$\psi_j(t + \Delta t) = U(t + \Delta t, t)\psi_j(t) = \exp \left\{-i \int_t^{t+\Delta t} d\tau H(\tau) \right\} \psi_j(t). \quad [3.39]$$

### 3.6 Calculating the Propagator

There is a large number of methods for computing the propagator for the time-dependent Kohn-Sham equations. These propagators solve the problem of approximating the orbitals $\psi_j(t + \Delta t)$ by the knowledge of $\psi_j(\tau)$ and $H(\tau)$ for $0 \leq \tau \leq t$. Some methods require the knowledge of the Hamiltonian at some points $\tau$ in time between $t$ and $t + \Delta t$.

#### 3.6.1 The Classical Propagator: Crank-Nicholson Method

Also known as the implicit midpoint rule, the Crank-Nicholson Method is the most famous method used to compute the time-evolution of the Schrödinger equation.

This method is based on the following implicit midpoint rule $[83, 84, 85]$, which is the average of the forward Euler and backward Euler integration methods:

$$i \frac{\psi_{n+1} - \psi_n}{\Delta t} = H(t_{n+1/2}) \frac{1}{2} (\psi_{n+1} + \psi_n);$$

where
\[ t_{n+1/2} \equiv 1/2 (t_{n+1} + t_n), t_n = n \Delta t. \]

Then, by straightforward algebra we obtain the following:

\[ \psi_{n+1} = \frac{1 - i \Delta t \frac{1}{2} H(t_{n+1/2})}{1 + i \Delta t \frac{1}{2} H(t_{n+1/2})} \psi_n. \]

which is also known as the Cayley approximation of the exponential to the second order of \( \Delta t \). To the third order of \( \Delta t \), the Cayley approximation is

\[ \psi_{n+1} = \left[ \frac{1 - i \Delta t \frac{1}{2} H(t_{n+1/2})}{1 + i \Delta t \frac{1}{2} H(t_{n+1/2})} + O(\Delta t^3) \right] \psi_n. \]

The problem of evaluating the evolution operator becomes that of solving the following linear matrix equation:

\[ \left[ \hat{I} + i \Delta t \frac{1}{2} H(t_{n+1/2}) \right] \psi(n + 1) = \left[ \hat{I} - i \Delta t \frac{1}{2} H(t_{n+1/2}) \right] \psi_n. \]

This method has two important properties:

1. Unitarity: the method preserves the norm of the wave function at all times.

2. Time reversibility: exchanging \( n \leftrightarrow n + 1 \) gives the same numerical results.

To demonstrate the preservation of unitarity, we compute the norm of the wave function after one time step:

\[ \langle \psi_1 | \psi_1 \rangle = \int \psi_0^* \frac{1 + i \Delta t \frac{1}{2} H(t_{1/2})}{1 - i \Delta t \frac{1}{2} H(t_{1/2})} \frac{1 - i \Delta t \frac{1}{2} H(t_{1/2})}{1 + i \Delta t \frac{1}{2} H(t_{1/2})} \psi_0 d\mathbf{x} = \int \psi_0^* \psi_0 d\mathbf{x} = 1. \]

However, there is a tendency to prefer the other method, which is the Split-Operator method where the exponential of the Hamiltonian is split into exponentials of its composite terms (the kinetic and potential energies) \[85\]. Nevertheless, good accuracy can then be achieved by the Crank-Nicholson method only for very small time steps (such as the time step used here, which is 0.00242 fs, as the computational error is proportional to the cube of the time step at each step of the algorithm \[86, 83\]).
3.6.2 The Octopus Implementation

In Octopus, there is a deficiency in the computation of the Crank-Nicholson method as the code uses the retarded hamiltonian $H(t_n)$ in place of $H(t_{n+1/2})$ in

$$\left[\hat{I} + i \frac{\Delta t}{2} H(t_{n+1/2})\right] \psi(n+1) = \left[\hat{I} - i \frac{\Delta t}{2} H(t_{n+1/2})\right] \psi_n,$$

which is essentially the predictor step’s equation:

$$\left[\hat{I} + i \frac{\Delta t}{2} H(t_n)\right] \psi(n+1) = \left[\hat{I} - i \frac{\Delta t}{2} H(t_n)\right] \psi_n.$$

The consequence of using the retarded Hamiltonian is the continuous decrease in energy every time-step because we will be using a retarded potential that arises from the retarded Hamiltonian. Our computations show such decrease in total energy as is depicted in the graph below:

![Figure 3.1 Change in total energy using retarded Hamiltonian approximation](image-url)
3.6.3 Determination of the time-step

The time step used in the calculation is sensitive to the mesh size according to the following formula

\[
\frac{1}{\Delta t_{\text{max}}} = \frac{G_{\text{max}}^2}{2} = \frac{2\pi}{h^2},
\]

where \( h \) is the mesh spacing, \( G_{\text{max}} \) is the reciprocal lattice vector [85].

3.7 Practical Considerations in Theoretical Field Emission Calculations in Carbon Nanotubes

According to Lou et al. [87], it would be computationally prohibitive to attempt to determine the emission current from a micron length nanotube. For this reason, different authors have experimented with short nanotubes and tried to extrapolate field emission behavior of actual size nanotubes [2]. Having short nanotubes also requires that we fill the dangling bonds at the bottom of the tube in order to mimic actual nanotubes. However, different authors treat that matter differently [87]. Generally speaking, it is crucial to recognize the theoretical limitations and their impact on the reliability of data, especially when we realize that different authors produce different results as will be discussed below.

3.7.1 Heaviside vs. Constant Electric Field Potential

Different authors reported using either of the two methods in their calculations. We particularly mention the work reported by Han et al. [1] and Masaaki Araidai et al. [22] where the former applied their method on a (5,5) carbon nanotube, while the later applied their method on graphene nanoribbons.

By a Heaviside electric field, we mean an electric field of the form:

\[
E = \begin{cases} 
0 & t = 0 \\
E_z & t > 0.
\end{cases}
\]
Han *et al.* [1] stated that using such potential results in oscillations in the charge evolution, and thus they preferred to use a constant field and then correct the wave functions, as will be shown later in this section.

### 3.7.2 Hydrogen Passivation of Nanotube Ends: The Role of Dangling Bonds

Dangling bonds occur whenever a valence electron is left unpaired. They arise from vacancy defects and act as electron traps. When a bulk material with a vacancy defect is subjected to an electric field, vacancy defects tend to reduce its conductivity by virtue of trapping conduction electrons. However, ab-initio calculations have shown that, in nanostructures, vacancy defects play a different role in field emission; they tend to enhance field emission.

The simulated carbon nanotube is cut out from a longer one, leaving dangling bonds on both sides. At the upper end of the tube (the side facing vacuum), dangling bonds are reported to enhance field emission. Among the four different configurations in the study by Seungwu Han *et al.* [2], (an open nanotube with dangling bonds at the zigzag-type edge, a capped nanotube, an open nanotube with dangling bonds passivated by Hydrogen, and slant cut end), the first produces the highest field emission current. However, dangling bonds at the bottom of the tube should have an opposite effect, as they act as charge traps. Most of the studies cited in this research use Hydrogen passivated nanotubes “for computational convenience”. Ideally, unsatisfied dangling bonds are electron traps, thus should reduce the emission current. However, in an experiment we have conducted on the short isolated (5,5) nanotube, we discovered that the presence of Hydrogen reduces the field emission current.

Araidaie *et al.* [22] studied the impact of hydrogen passivation on the field emission current from narrow graphene ribbons. Using TDDFT, they simulated a graphene ribbon under the effect of an electric fields that is parallel to the ribbon’s axis, as well as perpendicular to it. Their study indicates that the presence of hydrogen reduces the amount of current extracted in both cases, indicating that dangling bonds in graphitic nanostructures cease to act as electron traps when subjected to an electric field. In Masaaki’s paper, σ bond (H-terminated states) and dangling bonds are parallel to the parallel field, and tend to respond to the field. However, dangling bonds (arising from
vacancy defects) tend to enhance the emission current by almost double the current emitted from H-terminated graphene.

### 3.7.3 Screening Effects and the Role of the Spacing between Nanotubes

Screening is the damping of electric fields caused by the presence of mobile charge carriers. The idea is that we consider electrons as particles flowing in some fluid where each electron is a negatively charged particle that is surrounded by an electric field that repels other electrons. Thus, it is surrounded by a region with low electron density. This region can be treated as a positively-charged "screening hole". Viewed from a large distance, this screening hole has the effect of an overlaid positive charge which cancels the electric field produced by the electron. Only at short distances, inside the hole region, can the electron’s field be detected.

Screening effects of field emission from CNTs were studied by Chen et al. \[88\]. They discovered an interplay between the geometry of CNTs and their electronic structure. When the array spacing between neighboring nanotubes is three times the nanotube length, the applied external field is strongly screened. They also arrived at the important conclusion that increasing the thickness of a nanotube array would not significantly improve the field emission. Their calculations have shown that to minimize the screening effect the individual emitters/CNTs should be evenly separated such that their spacing is greater than their height.

### 3.7.4 Adding/Removing Electrons

We investigate the effect of adding and removing electrons to the system, in line with the work of Lou et al. \[87\]. The Octopus code implements the process of adding or removing electrons as follows: the amount of charge is obtained from the input file, which is then added to the total valence charge of the system. Then, the number of states is obtained by dividing the total charge by 2. The code allows to indicate which states should carry the extra charges. However, it does not allow us to locate those extra electrons at specific locations within the structure.
3.7.5 Limitation of Nanotube Length

Han et al. [2] stated that “since the system size is severely limited in the *ab initio* calculation, it is a serious issue whether one can mimic the realistic situation and extract meaningful information on field emission through *ab initio* calculation for small-size tubes”. Luo et al. [87] shared this concern, stating in their 2002 paper:

“Properly speaking, what [the *ab initio* calculation] really describes should be a short single-walled carbon nanotube polarized in the uniform external electric field. The field near the tube tip thus calculated is then a combination of this external field and that generated by the induced charge. However, in real circumstances, when connected to an electron reservoir and with the applied voltage, the single-walled carbon nanotube emitter inevitably carries net negative charge at its tip, and, due to the large aspect ratio of the single-walled carbon nanotube, the electric field near its tip should be, to a great extent, the result of this charge.”

However, Han et al., in the aforementioned paper, calculated values for $E_{loc}$ (local electric field at the tip, which increases linearly with the applied external electric field) versus the nanotube length, indicating that a beyond length of 60 Å, $E_{loc}$ begins to saturate, which enables one to extrapolate values for micron-length nanotubes. In another paper, Han et al. [1] stressed that “a short nanotube under a strong field may well simulate a long nanotube under a weak field as far as the electron emission is concerned”. The linear dependence between $E_{loc}$ and $E_{applied}$ can be modeled with the formula [2]

$$\eta = \alpha l,$$

where $\eta$ is the field enhancement factor, $l$ is the tube length, and $\alpha$ is a proportionality constant. Using the above two relations, it is possible to extrapolate the field emission behavior of carbon nanotubes according to their length. Beyond 70 Å, length ceases to have an effect.
3.7.6 Finite vs. Infinite Systems

Infinite systems that model real world structures such as slabs (2D), polymers (1D) and crystals (3D) are characterized by a band structure, dispersion relations, a Fermi level, and an charge field that is dispersed all over the structure i.e. over an infinite volume. From among the three most famous Time-Dependent Density Functional Theory codes available under the GPL license, Octopus, ABINIT and yamboo, only Octopus supports TDDFT calculations under periodic boundary conditions. Using the Octopus code, calculation of charge evolution in TDDFT under periodic boundary conditions yield lower results from calculations in isolated systems. An explanation will be provided below.

3.7.7 Different Methods, Different Results

For (5,5) carbon nanotubes, different authors have reported different results, using different methods. Adessi et al. [46] reported the extraction of a current of $2.98 \times 10^{-7}$ A under an applied field of $0.25$ V/Å. Values reported by Han et al. [1] are at much lower order. Luo et al. [87] reported extracting $0.16 \mu$A under a field of $0.05$ V/Å [87], which is yet a much higher quantity (which is because the nanotube they simulated is charged with four extra electrons, unlike the previous papers). Many other papers concerned with ab-initio simulation (for example, [2] and [89]) were limited to extracting qualitative features that can be considered precursors for field emission, casting more doubts on the releability of ab-initio field emission calculations in addition to concerns regarding the limited tube length that were considered in the above section. However, Han et al. [2] approach is the closest one to experimental findings, so we rely on it as a benchmark for our calculations.

Here, we list the different methods for calculating the current.

3.7.7.1 Method of Araidai et al. [22]: plain Time-Dependent Density Functional Theory

The field emission current is obtained by integrating the probability density of each eigenstate within the body of the nanostructure, then summing the rate of change of charge with respect to
time for each eigenstate. In their work, calculations were performed on periodic boundary conditions. They refer to “amount of charge” as the “number of electrons remaining in the structure’s region”. The formula used for calculating the current is the same as the one below except that they did not use the filling factor. Their calculations started from a Heaviside potential function for modelling the external electric field, unlike Han et al.’s method in which a constant potential was used. They used a seventh order Taylor expansion for computing the propagator, unlike Han et al.’s Split-Operator approach.

### 3.7.7.2 Method of Han et al. [1]: correcting the wave functions for Time-Dependent Density Functional Theory

After performing ab-initio self-consistent computation of the ground state wave functions, those wave functions could not be directly inserted into the evolution operator; the authors had to introduce a “relaxation step” to adjust the wave functions inside the emitter region to the exact eigenfunctions before computing the evolution operator. On page 3 of their paper, their provide the following method for deriving the exact wave function.

- First, we add a strong repulsive potential for the vacuum region to the total Kohn-Sham Hamiltonian in order to prevent escape of the electron during the relaxation step:

\[
v_{\text{rep}} = v_0 \theta(z - z_0),
\]

where the authors choose \( v_0 = 1 \text{ Ry} \).

- Then we start updating the wave functions iteratively in such a way as to reduce the residual vector defined as follows:

\[
\delta = \langle R | R \rangle, |R\rangle = (H' - \langle \psi | H' | \psi \rangle)|\psi\rangle
\]

and

\[
H' = H_{KS} + v_{\text{rep}}.
\]

The amount of the electron remaining in the emitter region at time \( t \) for a particular wave function is given by
\[ Q_n(t) = \int_0^{z_0} \int |\psi|^2 \, dx, \quad [3.40] \]

and in terms of the lifetime \(\tau_n\) of state \(n\),

\[ Q_n(t) = e^{-\frac{t}{\tau_n}}, \quad [3.41] \]

which implies linear behavior of \(Q_n(t)\) in the short time interval. From this formula, the current generated by a wave function is given by

\[ I_n = e \frac{dQ_n(t)}{dt} \approx -\frac{1}{\tau_n} \quad [3.42] \]

in the short time range. The total current is

\[ I = e \sum f_n \frac{dQ_n(t)}{dt} \]

where \(f_n\) is the filling factor which was plotted in the graph below for a periodic system by Han et al. [44]:
Figure 3.2 Filling factor \( f \) (open circles) and energy level of localized states \( \epsilon_{\text{loc}} \) with respect to the Fermi level (filled circles) as a function of the external field \( (E_{\text{appl}}) \). The solid and dashed lines are guides to the eye.

Note that for fields below 0.2, the method of Han et al. would seem totally useless, as the filling factor is very close to zero.

### 3.7.7.3 Kubo formula

Luo et al. [87] have extracted the emission current using a Kubo current formula applied over the ground state eigen functions, and using an isolated short nanotube. Due to using a short isolated system, they indicated that they had to “substitute the Fermi level of the long single-walled carbon nanotube with the HOMO energy of the short model, because determining the former from the electronic structures of the short model is a real challenge” [87]. They have also added four extra electrons to the system (that is, four extra states) and extracted 0.16\( \mu \text{A} \) upon applying 0.05\( V/\text{Å} \). Current is obtained using the following formula:
\[ I(E) = \frac{4e}{\hbar} \int_0^\infty f(E)T(E)dE, \]

where \( f(E) \) is the Fermi function,

\[ f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}, \]

\( T(E) \) is the transmission coefficient with the electron at energy \( E \), and \( E_F \) is the tube’s Fermi level (that is, the HOMO energy). This formula was also applied in [90] (however, they did not present an \( I - V \) diagrams as they were mainly interested in observing trends in \( T(E) \)).

### 3.8 Implementation: Octopus

Octopus [91] is a GPL licensed Fortran (F90) \textit{ab initio} code that is geared towards time-dependent functional theory computations. Electrons are described quantum-mechanically within the Density-Functional Theory (DFT), in its time-dependent form (TDDFT) when doing simulations in time. Nuclei are described classically as point particles. Electron-nucleus interaction is described within the Pseudopotential approximation.
Chapter 4

Computational Details

We measured the electric field emission from a short carbon nanotube, with and without extra electrons, by performing Time-Dependent Density Functional Theory calculations following the scheme of Araidai et al. [22], and using a Heaviside external electric field. We measured the current extracted from the nanotube, and examined the effect of doping it with boron or nitrogen.

4.1 Time Step

The time units in Octopus is in $\hbar/eV=0.658$ fs. The time step used in the time-dependent run is $0.0037 \hbar/eV$, which corresponds to $0.1$ a.u. = $0.00242$ fs, the same time step used in [11]. We also experimented with a smaller time step ($0.000242$ fs) and we obtained the same results, which shows that this time step is optimal for the Crank-Nicholson algorithm.

4.2 Simulation Box

We perform our simulations once on an isolated system – that is, a system that is non-periodic in all dimensions – and once on a slab periodic simulation box – a simulation box that is periodic in the $xy$ directions. The isolated simulation box imposes the following Dirichlet boundary conditions: $u(x) = 0$, where $x$ lies outside the wall boundary. On the other hand, in the periodic simulation box, periodic boundary conditions apply on the side boundaries (the vertical faces) and the Dirichlet boundary conditions apply at the top and bottom faces. The simulation box size is $30\AA \times 30\AA \times 30\AA$, with a grid cutoff of 710.832 eV. We choose only one $k$ point, the $\Gamma$ point at
Treating only one $k$ point, instead of a more comprehensive selection of $k$ points, is one of the requirements, as well as the shortcomings, of the Octopus time-dependent code.

One of the bottle necks in our calculations has been the choice of the mesh spacing, which determines the size of the volume units. A large spacing is incompatible with low bond lengths, and would hardly converge in the presence of hydrogen. Small spacing imposes extra computational demands that are sometimes unaffordable by our hardware. However, we eased the convergence criteria in such a way that we can obtain convergence with the mesh spacing of $0.9\text{Å}$ with hydrogen. Given this mesh spacing, the carbon nanotube simulation box contains $33 \times 33 \times 33 = 35937$ volume units.

We performed Density Functional Theory computation using the Local Density Approximation for exchange and correlation potential by Pedrew and Zunger \[79\]. The system employs the LCAO wave functions. The density matrix is mixed according to the Broyden mixing scheme \[92\], and we solve the eigen value problem using the Conjugate Gradient algorithm.

### 4.3 Parameters for Ground State Calculations

Convergence usually takes more time for a simulation box in which the molecule is placed assymetrically than otherwise. In our system, where the nanostructure is placed at the lower half of the box, we had to fine tune a number of ground state parameters to achieve convergence of our calculations: mixing parameters, convergence parameters and mesh spacing (which was treated in Sec. 4.2).

As for the convergence parameters, we adopted by the criterion of reducing the difference between the relative density between two subsequent iterations:

$$\epsilon = \frac{1}{N} \int d^3r (\rho_{\text{out}}(r) - \rho_{\text{inp}}(r))^2 = 10^{-7}.$$  

As for mixing parameters, we adopted the Broyden mixing scheme \[92, 93\]. (write the mixing scheme and parameters explicitly)
4.4 Structure

The carbon nanotube studied is the armchair type with chirality (5,5), depicted in Fig. 4.1, which is a metallic conductor. The nanotube lies in the lower half of the simulation box (the anode), whereas the upper half is vacuum. The nanotube is composed of 70 carbon atoms, where the bottom carbon atoms are passivated with hydrogen atoms in order to avoid the presence of unnecessary dangling bonds. In case of doping the nanotube with a nitrogen or boron dopant, we place the dopant atom by substituting a carbon atom at one of the top three carbon layers. The hydrogen-passivated nanotube is 8.6 Å long, with a diameter of 6.75 Å. The tip of the nanotube lies at the center of the simulation box, and we calculate the charge in the lower 63% of the simulation box (which includes the lower 50% plus an extra volume past the nanotube tip).

4.5 Prestine Carbon Nanotube

Our computations on the pristine carbon nanotube with and without extra electrons, as well as a non-hydrogen-passivated nanotube, yielded the results in Tab. 4.1.
4.5.1 **Isolated Simulation Cell**

As time elapses, charge starts migrating from the lower half of the simulation cell into the upper half. Thus, the quantity of charge $Q_n$ of every wave function $n$ diminishes in the lower half and increases in the upper half in a nearly linear fashion as is show in Fig. 4.2 below. This behaviour is more strongly exhibited in upper energy states – that occupy the nanotube tip – than lower energy states. This indicates that the electrons that contribute more to the current are those lying at the tip of the nanotube.
Figure 4.2 Charge evolution diagrams for the highest energy state under the influence of an external electric field of 1VÅ. Time units are in 0.1 a.u., while charge units are arbitrary.

We compared our results for the isolated system with those reported in the literature ([1, 87]) in order to show that, although calculations in isolated systems reproduce an exponential relationship between $I$ and $V$, numbers reported from an isolated system are always higher, as is shown in Tab. 4.1 below. (You did not add a figure for the dangling bonds, and did not add the figure for the CNT in a box)
Table 4.1 Extracted current ($\mu A$) from pristine carbon nanotube against an applied electric field ($V/\AA$). Our results for the isolated simulation box are higher than results reported in [1] and elsewhere.

<table>
<thead>
<tr>
<th></th>
<th>0.05</th>
<th>0.2</th>
<th>0.25</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-H-passivated, no extra electrons</td>
<td>0.36506</td>
<td>1.30414</td>
<td>5.6666</td>
<td>14.48579</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-passivated, 2 extra electrons</td>
<td>0.2895203</td>
<td>3.143824</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-passivated, 4 extra electrons [87]</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-passivated, no extra electrons</td>
<td>0.277237</td>
<td>3.729901</td>
<td>12.687888</td>
<td>61.531997</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-passivated, minus 2 electrons</td>
<td></td>
<td></td>
<td>2.65339</td>
<td>9.8553</td>
<td>24.7036</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-passivated, minus 4 electrons</td>
<td>0.3620623</td>
<td>0.4200016</td>
<td>0.63375</td>
<td>1.91444</td>
<td>6.3989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-passivated, minus 5 electrons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9756889</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Han et al. [11]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.9</td>
<td>5.8</td>
</tr>
</tbody>
</table>

We had to remove 5 electrons (a positively charged nanotube) in order to reproduce the results of Han et al. [1]. Our results are close to those of Luo et al. [87] even without adding any extra electrons. Adding 2 electrons produce a value for the extracted current that is double the value they reported (given that they have added 4 electrons to obtain their number). At any rate, results of Luo et al. [87] are higher than those reported from experimental measurements. Note that
Lou et al. [87] also performed the simulation in an isolated simulation box, but used a different computational scheme (the Kubo formula, see Sec. 3.7.7.3).

### 4.5.2 Periodic Simulation Cell

In Tab. 4.2 below, we show our results in the case of a slab periodic simulation box. The results are also depicted in Fig. 4.3.

Table 4.2 Extracted current ($\mu$A) from pristine carbon nanotube against an applied electric field ($V/\AA$). Our results are almost close to those reported in [1] when the applied field is in the range $0.2-0.8V/\AA$. For larger values, reported results for the current differ from the result reported in [1] due to the difference in length of the nanotube used.

<table>
<thead>
<tr>
<th></th>
<th>0.2</th>
<th>0.25</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our calculations</td>
<td>0.0161</td>
<td>0.02957</td>
<td>0.1148</td>
<td>0.3958</td>
<td>0.9591</td>
<td>1.9608</td>
<td>3.8304</td>
</tr>
<tr>
<td>Han et al. [1]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.9</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Han et al. [44]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.9</td>
<td>4.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Mayer et al. [94]</td>
<td>0.0298</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.3 Comparison between the $I - V$ results obtained by our calculations, and those by [1] and [2].

Our simulation results in a periodic simulation box are close to the results reported by Han et al. [1] for the applied field in the range 0.2 V/Å to 0.6 V/Å, and are very close to the result reported by Mayer et al. [94] at a field of 0.25 V/Å (note that Han et al. have reported different results in two different publications, [1] and [44] as is indicated in the Tab. 4.2 above). At an applied field of 1.0 V/Å, both results reported by Han et al. are slightly higher than ours, which is due to the difference in size between the nanotubes used; that is, shorter nanotubes generally yield lower current than longer nanotubes [2].

Our results for a hydrogen-passivated isolated carbon nanotube are about 4-7 times higher than results from periodic calculations. The reason for the difference is that there is a loss of charge due to escape of electrons horizontally into neighboring copies of the simulation box. We have tested this explanation by calculating the charge evolution into a thin vertical slab attached to one of the vertical faces of the simulation box. We found that in a periodic simulation box, the charge tends to reach the thin slab more slowly than in the case of the isolated simulation box. This is due to the fact that, in the periodic box, charge is spread over a larger (infinite) space, whereas it is
constrained to a limited space in the isolated box. This makes the impact of the field less effective on the nanotube charge in the periodic box.

In the following figures (Fig. 4.4 and Fig. 4.5), we present the evolution of the cross section of the highest energy wave functions in a pristine nanotube under an external field of $0.8\, V/\AA$.

![Figure 4.4](image)

Figure 4.4 Evolution of the wave function: highest energy wave function. Units are arbitrary.
Figure 4.5 Evolution of the wave function into the vacuum region: highest energy wave function. Units are arbitrary.

We notice in Fig. 4.5 the evolution of charge of the wave function as the base of shape (A) extends forward. We also note that by 15 a.u., a branch emerges (B) from the shape, which vanished completely by 30 a.u. as the wave function becomes more concentrated into the shape (A). Also note that the relative height of shape (A) is less at time 30 a.u. than that at time 5 a.u., which is due to the fact that a portion of the charge of that wave function flows into the vacuum region. We can gain a better insight by noticing the evolution of the terminal curves at the end of the simulation box below.
Figure 4.6 Evolution of the wave function into the vacuum region: highest energy wave function, close to the upper surface of the simulation box. The horizontal axis is the intersection between the plane crossing the nanotube vertically and the upper face of the simulation box. The vertical axis shows the charge in arbitrary units.

Fig. 4.6 shows clearly that the wave functions are concentrated into certain “channels” as time elapses, which indicates that the emitted current is concentrated towards the anode, instead of being dispersed into space. Studying such behaviors can be instrumental when the exact shape of the electron beam is concerned (when producing very high precision beams in atomic force microscopes is required). It is also of great importance whether we can influence the shape of the beam by adding certain dopants, or by performing structural modifications. This issue will be treated in a later publication.

In such a short nanotube, dangling bonds at the terminal carbon atoms (opposite to the tip) play a significant role. We observed that field emission in the non-hydrogen-passivated isolated carbon nanotube is almost 50% higher than that of the hydrogen-passivated one. This is in line with the idea established in [22], that dangling bonds (arising from vacancy defects and non-passivation with hydrogen at the terminal bonds) are the prime contributors to the field emission current.
4.5.3 Nitrogen-doped and Boron-doped Carbon Nanotube

Here we consider three different nitrogen and boron doping configurations:

- Configuration N1: Nitrogen dopant replacing a carbon atom at the top ring
- Configuration N2: Nitrogen dopant replacing a carbon atom at the second ring below the tip
- Configuration N3: Nitrogen dopant replacing a carbon atom at the third ring below the tip
- Configuration B1: Boron dopant replacing a carbon atom at the top ring
- Configuration B2: Nitrogen dopant replacing a carbon atom at the second ring below the tip
- Configuration B3: Nitrogen dopant replacing a carbon atom at the third ring below the tip

In Fig. 4.7 below, we show the location of the dopant at the relative position on the nanotube body.

Figure 4.7 Relative positions of nitrogen (or boron) dopant on the carbon nanotube tip
Table 4.3  Extracted current (µA) from pristine vs. nitrogen-doped/boron-doped carbon nanotube against an applied electric field of 0.2V/Å. All are H-passivated with no extra electrons

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Current</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>0.0161</td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>0.53394</td>
<td>33</td>
</tr>
<tr>
<td>N2</td>
<td>0.0796</td>
<td>4.9</td>
</tr>
<tr>
<td>N3</td>
<td>0.0164</td>
<td>1.02</td>
</tr>
<tr>
<td>B1</td>
<td>0.02198</td>
<td>1.37</td>
</tr>
<tr>
<td>B2</td>
<td>0.013469</td>
<td>0.84</td>
</tr>
<tr>
<td>B3</td>
<td>0.0268016</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Our results for boron doping, in agreement with those reported by L. Qiao et al. [90], indicate that boron dopants would impede field emission (however, this is only at certain locations). On the other hand, nitrogen doping enhances field emission. The nitrogen dopant should be located at the first level of carbon atoms at the top (configuration N1) in order to obtain optimal field emission current.

In order to understand the mechanism whereby a dopant enhances or impedes emission, we present in Fig. ?? the charge evolution graphs for both the N1 and B2 configurations.
Figure 4.8 Evolution of the wave function into the vacuum region: highest energy wave function. Units are arbitrary.
Fig. 4.8 indicates the occurrence of a strong propagation of the wave function into the vacuum region. The influence of the nitrogen atom, however, did not concentrate the charge into a specific direction, or directions. Charge dispersed into a region that is almost 5µÅ wide. Fig. 4.9 below shows the impact of the boron dopant: the charge does not seem to change at all, which means that the electron is held back into the nanotube tip.
Chapter 5

Conclusions

Using time-dependent density functional theory, we studied the mechanism of field emission from a short carbon nanotube. We utilized the classical Crank-Nicholson method to compute the wave function propagator, and used a small time step in order to reduce the computational error. Dangling bonds tend to considerably increase the field emission current in nanotubes; $\pi$ bonds do not contribute to field emission as much as $\sigma$ bonds. We found that the higher electronic density at the nanotube tip (which takes place due to the pentagonal structure, and which occupy higher molecular orbitals) are the prime contributors to field emission, unlike the case of metallic tips where emission is produced by the continuum of electrons in the metal [23]. We reproduced the results reported by Han et al. [1] by using periodic boundary conditions. The charge cloud emerging from the tip appears to concentrate into narrower channels as the cloud approaches the cathode surface. We shall study the possibility of controlling the shape of the charge cloud in a subsequent publication. In the case of an isolated carbon nanotube, we had to remove 5 electrons in order to reproduce results close to those reported by Han et al. [1], and removing the electrons accounts for the charge that dissociates into neighboring copies of the simulation box. Our computations yield exponential $I - V$ curves, which is consistent with basic Fowler-Nordheim theory as well as with the experimental results. Doping carbon nanotubes with nitrogen adds an extra electron to the conduction band, while boron removes an electron from the structure. Thus nitrogen generally improves field emission, while boron mildly affects emission (and at certain locations, it impedes emission).

On the course of our research, we were met with a number of theoretical and practical considerations. Structural deformations in nanotubes have been studied in terms of the impact of the
deformation on the electronic structure, and the effect of deformation on field emission [95]. However, we believe that more effort needs to be devoted to this direction as it provides an invaluable parameter that can control field emission, and gives more insight into novel field emission mechanisms. Equally important is the impact of adding larger dopant atoms on the structure, hence the field emission mechanisms, such as adding iron atoms close to the tip. Another important consideration is the choice of the right exchange-correlation potential for this type of time-dependent density functional theory calculation, and whether it is more accurate to simulate a spin-polarized rather than a spin-compensated system (hence, utilizing exchange-correlation potentials such as PBE, etc.). As for simulating an isolated system, a consideration arises regarding the scale of the deviation from experimental results, and the actual reason for that deviation. Although we have provided an explanation for the deviation, we are still interested in finding ways to reach more reliable results using an isolated simulation box, particularly because those results will be closer to cases were we use an isolated nanotube as a field emitter (instead of using a nanotube bundle as is common in field emission microscopy). In such a way, we can better understand the reasons behind the reported structural deformation that occur in isolated nanotube electron emitters [95, 96, 97, 98], and whether it is possible, at least theoretically, to rectify those deformations. One final theoretical consideration is the use of other propagator methods (besides the Crank-Nicholson method) such as the Split-Operator method which is known to be more founded theoretically [1, 85], as well as the Magnus Expansion method [85]. Such attempts will be taking place as soon as they have been developed in the Octopus code (at the time of writing, they are not fully implemented in Octopus).
LIST OF REFERENCES


Appendix A: Input Files

A.1 Ground State, 2 electrons removed

CalculationMode = gs
Units = eV_Angstrom

FromScratch = yes
BoxShape = 4

%Lsize
15 | 15 | 15
%

spacing = 0.9
MaximumIter = 0
MixNumberSteps = 20
Mixing = 0.7

TypeOfMixing = broyden
ConvRelDens = 0
ConvRelEv = 1e-7

ExcessCharge = 2

%Coordinates
"C" | -0.1382 | 1.2132 | 0 | no
"C" | 1.0937 | 0.5303 | 0 | no
"C" | 0.8249 | -0.8523 | 0 | no
"C" | -0.573 | -1.0239 | 0 | no
"C" | -1.168 | 0.2524 | 0.7004 | no
"C" | -1.1224 | -2.0151 | 0.7004 | no
"C" | -2.2803 | 0.4685 | 0.7004 | no
"C" | -0.276 | 2.3378 | 0.7004 | no
"C" | 2.1207 | 1.0093 | 0.7004 | no
| C  | 1.5978 | -1.6811 | 0.7004 | no |
| C  | -0.3053 | -2.8914 | 1.4403 | no |
| C  | 1.017 | -2.729 | 1.4403 | no |
| C  | -2.8611 | -0.5793 | 1.4403 | no |
| C  | -2.2983 | -1.7867 | 1.4403 | no |
| C  | -2.4263 | 1.6577 | 1.4403 | no |
| C  | -1.419 | 2.5663 | 1.4403 | no |
| C  | 0.8095 | 2.8444 | 1.4403 | no |
| C  | 1.9748 | 2.1985 | 1.4403 | no |
| C  | 2.6837 | -1.1748 | 1.4403 | no |
| C  | 2.3978 | 0.133 | 1.4403 | no |
| C  | -2.2084 | -2.5215 | 2.6391 | no |
| C  | -0.9765 | -3.2043 | 2.6391 | no |
| C  | 1.7439 | -2.8703 | 2.6391 | no |
| C  | 2.7739 | -1.9097 | 2.6391 | no |
| C  | 3.2968 | 0.7807 | 2.6391 | no |
| C  | 2.7016 | 2.0572 | 2.6391 | no |
| C  | -1.0929 | 3.1239 | 2.6391 | no |
| C  | 0.3048 | 3.3857 | 2.6391 | no |
| C  | -3.3662 | -0.0378 | 2.6391 | no |
| C  | -3.0971 | 1.3447 | 2.6391 | no |
| C  | -2.6857 | -2.0094 | 3.7725 | no |
| C  | -3.2807 | -0.733 | 3.7725 | no |
| C  | -0.289 | -3.3379 | 3.7725 | no |
| C  | 1.1091 | -3.1663 | 3.7725 | no |
| C  | 3.1134 | -1.2971 | 3.7725 | no |
| C  | 3.3823 | 0.0855 | 3.7725 | no |
| C  | 2.2239 | 2.5694 | 3.7725 | no |
| C  | 0.9921 | 3.2522 | 3.7725 | no |
| C  | -1.7277 | 2.918 | 3.7725 | no |
| C  | -2.7575 | 1.9572 | 3.7725 | no |
| C  | 2.7233 | 1.9786 | 4.9936 | no |
| C  | 3.2926 | 0.6999 | 4.9936 | no |
| C  | 0.3519 | 3.3477 | 4.9936 | no |
| C  | -1.0402 | 3.2014 | 4.9936 | no |
| C  | -3.3661 | 0 | 4.9936 | no |
| C  | -3.0751 | 1.3691 | 4.9936 | no |
| C  | -2.2524 | -2.5015 | 4.9936 | no |
| C  | -1.0402 | -3.2014 | 4.9936 | no |
| C  | 2.7233 | -1.9786 | 4.9936 | no |
| C  | 1.6831 | -2.9152 | 4.9936 | no |
| C  | 3.3661 | 0 | 6.2147 | no |
A.2  Time Dependent, 2 electrons removed
BoxShape = 4

%Lsize
15 | 15 | 15
%

spacing = 0.9

MaximumIter = 0

MixNumberSteps = 20

Mixing = 0.7

TypeOfMixing = broyden

ConvRelDens = 0

ConvRelEv = 1e-7

ExcessCharge = 2

dt = 0.0037

TDEvolutionMethod = crank_nicholson

TDMaximumIter = 5/dt

TDTimeStep = dt

TDOutput = geometry + multipoles + td_occup

%StaticElectricField
0 | 0 | 0.2
%

%Coordinates
"C" | -0.1382 | 1.2132 | 0 | no
"C" | 1.0937 | 0.5303 | 0 | no
"C" | 0.8249 | -0.8523 | 0 | no
"C" | -0.573 | -1.0239 | 0 | no
| C | -1.168 | 0.2524 | 0 | no |
| C | -1.1224 | -2.0151 | 0.7004 | no |
| C | -2.2803 | 0.4685 | 0.7004 | no |
| C | -0.276 | 2.3378 | 0.7004 | no |
| C | 2.1207 | 1.0093 | 0.7004 | no |
| C | 1.5978 | -1.6811 | 0.7004 | no |
| C | -0.3053 | -2.8914 | 1.4403 | no |
| C | 1.017 | -2.729 | 1.4403 | no |
| C | -2.8611 | -0.5793 | 1.4403 | no |
| C | -2.2983 | -1.7867 | 1.4403 | no |
| C | -2.4263 | 1.6577 | 1.4403 | no |
| C | -1.419 | 2.5663 | 1.4403 | no |
| C | 0.8096 | 2.8444 | 1.4403 | no |
| C | 1.9748 | 2.1985 | 1.4403 | no |
| C | 2.6837 | -1.1748 | 1.4403 | no |
| C | 2.9378 | 0.133 | 1.4403 | no |
| C | -2.2084 | -2.5215 | 2.6391 | no |
| C | 0.9765 | -3.2043 | 2.6391 | no |
| C | 1.7439 | -2.8703 | 2.6391 | no |
| C | 2.7739 | -1.9097 | 2.6391 | no |
| C | 3.2968 | 0.7807 | 2.6391 | no |
| C | 2.7016 | 2.0572 | 2.6391 | no |
| C | -1.0929 | 3.1239 | 2.6391 | no |
| C | 0.3048 | 3.3857 | 2.6391 | no |
| C | -3.3662 | -0.0378 | 2.6391 | no |
| C | -3.0971 | 1.3447 | 2.6391 | no |
| C | -2.6857 | -2.0094 | 3.7725 | no |
| C | -3.2807 | -0.733 | 3.7725 | no |
| C | -0.289 | -3.3379 | 3.7725 | no |
| C | 1.1091 | -3.1663 | 3.7725 | no |
| C | 3.1134 | -1.2971 | 3.7725 | no |
| C | 3.3823 | 0.0855 | 3.7725 | no |
| C | 2.2239 | 2.5694 | 3.7725 | no |
| C | 0.9921 | 3.2522 | 3.7725 | no |
| C | -1.7277 | 2.918 | 3.7725 | no |
| C | -2.7575 | 1.9572 | 3.7725 | no |
| C | 2.7233 | 1.9786 | 4.9936 | no |
| C | 3.2926 | 0.6999 | 4.9936 | no |
| C | 0.3519 | 3.3477 | 4.9936 | no |
| C | -1.0402 | 3.2014 | 4.9936 | no |
| C | -3.3661 | 0 | 4.9936 | no |
| C | -3.0751 | 1.3691 | 4.9936 | no |
| "C" |    |    | 4.9936 | no |
| "C" |    |    | 4.9936 | no |
| "C" |    |    | 4.9936 | no |
| "C" |    |    | 4.9936 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 6.2147 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |
| "C" |    |    | 7.4358 | no |

Output = potential + geometry + dos + wfs_sqmod + wfs

OutputHow = axis_x + axis_y + axis_z + plane_x + plane_y + plane_z
Appendix B: Charge Calculation Code for Octopus

The following code snippet was inserted into the Octopus source file src/td/td.F90, version 3.2.0, between the two comments as indicated below:

```fortran
! mask function?
    if(hm%ab == MASK_ABSORBING) call zvmask(gr, hm, st)

! update density
    call states_calc_dens (st, gr)

!Start of added code
!-----------------------------------------------------------------------------
!-----------------------------------------------------------------------------
!-----------------------------------------------------------------------------

ispin=1
if(gr%mesh%idx%sb%box_shape == HYPERCUBE) then
    write(message(1)),'its a hypercube!
    call write_info(1)
end if

do inik=1,st%d%nik
do inst=1,st%nst
    total_Q_per_state = 0
    do ip = 1, gr%mesh%np
        !First, obtain the x-y-z representation for the index
        ix = 0
        if(gr%mesh%idx%sb%box_shape /= HYPERCUBE) then
            forall (idir = 1:gr%mesh%sb%dim)
                ix(idir) = gr%mesh%idx%Lxyz(ip, idir)
            end forall
        else
            call hypercube_i_to_x(gr%mesh%idx%hypercube, &
                gr%mesh%sb%dim, gr%mesh%idx%nr, &
                gr%mesh%idx%enlarge(1), ip, ix)
        end if
        
        !Then, get the charge distribution at each point
        if(st%wfs_type == M_CMPLX) then
            sqr_wf = (real(st%zpsi(ip, 1, inst, inik), REAL_PRECISION)**2 + aimag(st%zpsi(ip, 1, inst, inik))**2)
        else
            sqr_wf = st%dpsi(ip, 1, inst, inik)**2
    end do
end do
```

82
end if

! Now, only consider the Emitter region, below some z
if(ix(3) >= ~4 ) then
if (gr%mesh%use_curvilinear) then
  total_Q_per_state = total_Q_per_state +sqr_wf*gr%mesh%vol_pp(ip)
else
  total_Q_per_state = total_Q_per_state + sqr_wf
end if

!write(message(1),'(i7,i7,i7)'),ix(1),ix(2),ix(3)
!call write_info(1)
end if

end do
if (gr%mesh%use_curvilinear .eqv. .false.) then
if(ix(3) >= ~4 ) then
  total_Q_per_state= total_Q_per_state*gr%mesh%vol_pp(1)
end if
end if

write(file_total_charge,'(i7,i7,3f30.20)'),
inst,inik,total_Q_per_state
end do
end do

!-----------------------------------------------------------------------------
!-----------------------------------------------------------------------------
!-----------------------------------------------------------------------------
!#############################################################################
!#############################################################################

generate = .false.

if(ion_dynamics_ions_move(td%ions)) then
  if(td%dynamics /= EHRENFEST .or. .not. td_rti_ions_are_propagated(td%tr)) then
    call ion_dynamics_propagate(td%ions, sys%gr%sb, sys%geo, iter*td%dt, td%dt)
    generate = .true.
  end if
end if
end if
Appendix C: Java Codes

The following is the Java code used for calculation of the current that is output from the time-dependent runs on Octopus as per the code snippet above.

```java
package postoctopus;

import flanagan.analysis.*;
import java.io.*;
import java.util.*;

/**
 * @author Sherif Tawfik
 */
public class ChargeAndCurrent {

    public ChargeAndCurrent(String[] args) {
        int numWaveFunctions = Integer.valueOf(args[1]);
        int numTimeSteps = Integer.valueOf(args[2]);
        String input = args[0];
        double[][] charge = new double[numWaveFunctions][numTimeSteps];
        BufferedReader in = null;
        try {
            in = new BufferedReader(new FileReader(input));
            String line;
            for (int i = 0; i < numTimeSteps; i++) {
                for (int l = 0; l < numWaveFunctions; l++) {
                    line = in.readLine();
                    StringTokenizer st = new StringTokenizer(line);
                    st.nextToken();
                    st.nextToken();
                    // st.nextToken();
                    charge[l][i] = Double.valueOf(st.nextToken());
                }
            }
            String gnuplotScript = ""
        }
    }
    
    String gnuplotScript = "";
```
FileWriter fstreamGnuplot = new FileWriter("gnuplot" + input);
BufferedWriter outGnuplot = new BufferedWriter(fstreamGnuplot);

for (int l = 0; l < numWaveFunctions; l++) {

    FileWriter fstream = new FileWriter(input + "-" + (l + 1));
    BufferedWriter out = new BufferedWriter(fstream);

    gnuplotScript +=
        "set title " + (l + 1) + "\n"
        + "set xlabel " + (l + 1) + "\n"
        + "set ylabel " + (l + 1) + "\n"
        + "plot " + (l + 1) + "\n"
        + "set size 1.0, 0.6 \n"
        + "set terminal png medium \n"
        + "set output " + (l + 1) + "\n"
        + "replot\n"
        + "set terminal x11\n"
        + "set size 1,1\n"
        + "!mv my-plot.png energy" + digCounter(l + 1) + ".png\n";

    for (int i = 0; i < numTimeSteps; i++) {
        out.flush();
        out.write(String.valueOf(charge[l][i]));
        out.newLine();
    }
    out.close();
}

outGnuplot.write(gnuplotScript);
outGnuplot.close();

double current = 0;
int counted = 0;
int maxTimeStep = 300;
int minTimeStep = 200;
//Perform least squares fitting

for (int i = 0; i < numWaveFunctions; i++) {
    /*
    double []tempY=new double[maxTimeStep];
    */
double [] tempX=new double[maxTimeStep];
for(int j=0;j<maxTimeStep;j++)
{
    tempY[j]=charge[i][j];
    tempX[j]=j;
}
*/

double[] tempY = new double[maxTimeStep-minTimeStep];
double[] tempX = new double[maxTimeStep-minTimeStep];

for (int j = minTimeStep; j < maxTimeStep; j++) {
    tempY[j - minTimeStep] = charge[i][j];
    tempX[j - minTimeStep] = j;
}

Regression r = new Regression(tempX, tempY);
r.polynomial(1);
double regError = r.getSumOfSquares();
r.setTitle("EnergyLevel=" + i);
//r.plotXY();
double coeff[] = r.getCoeff();
//System.out.println("regError["+i+"]= "+regError++, slope = "+coeff[1]);
System.out.println(coeff[1]);

if (coeff[1] < 0 && regError < 0.01) {
    current += coeff[1];
    counted++;
}
}
current *= -1.60217646 * Math.pow(10, -19) / (0.00242 * Math.pow(10, -15));
System.out.println("Current=" + current + ", number of counted wf's=" + counted);
}

```java
} catch (IOException e) {
    e.printStackTrace();
}
```
String digCounter(int i) {
    int l = Integer.toString(i).length();
    if (l == 3) {
        return Integer.toString(i);
    } else if (l == 2) {
        return "0" + Integer.toString(i);
    } else {
        return "00" + Integer.toString(i);
    }
}

} // end if

} // end finally

}