Stability of monoatomic nanowires: a first-principles study

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Density functional theory, Nanowires, Tip, Breaking, Equilibrium, Ag, Au, Pd
Pt, LDA, PBE, PW91
Abstract

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Chapter 1

Introduction

With the ongoing miniaturization in microelectronics we are fast approaching scales where the effects of quantum mechanics have an increasing influence on both the mechanical and electrical properties of electrical components. One area which has been shown to be almost ideal for such studies is the study of nanocontacts. The small scales of these nanocontacts provide an almost ideal proving ground, making it possible to directly compare theory and experiments. Understanding the mechanisms in the formation of atomic-size chains may help improving the fabrication process, and also enable the production of chains of different materials with other properties or of longer range.

1.1 Background

1.1.1 Early molecular dynamics simulations

The formation of single-atomic chains of metal atoms was first seen in molecular dynamics (MD) simulations performed by Finbow et al. [1] and Sørensen et al. [2].

Finbow et al. used methods based on classical MD to investigate the mechanisms behind failure under strain in nanosized wires, of Pt and Ag, at low and high temperatures. The wires were prepared using an fcc structure as a basic template. A strain, which was then increased linearly over time, was applied along the length of the wire and the tensile force was calculated as a function of the strain. This was done while observing the structural changes in the wire. It was found that the increasing strain led to the wire gradually getting thinner, which is signalled by a decrease in tensile force, until it breaks when the tensile force reaches zero. At low temperatures the strain was seen to vary with the force in a stepwise fashion. First a period of elastic stretching occurs followed by an abrupt rearrangement, this process keeps repeating until the wire breaks giving rise to a sawtooth-like tensile force curve. Sørensen et al. [2] found that this was not the case for Pt at 273 K. The tensile force gradually decreased until it leveled out at a non-zero value well beyond the point where it was expected to break. The reason for this was that a single chain of atoms up to a length of at least seven atoms was
holding the wire together. This chain grew by pulling out atoms from the body of the still intact wire while keeping the latters crystalline order. The mean length between the atoms in the wire was found to be 4.8 Å, compared to 0.7 Å in an unstretched wire. This effect was only reproducible in a small temperature range and no similar tendencies for Ag were observed.

Sørensen et al. in turn used Molecular Dynamics (MD) and potentials derived from Effective Medium Theory (EMT) to model the evolution of the atomic structure of Au and Ni nanocontacts and the deformation processes that takes place during elongation. Based on these results the electronic conductance during the stretching was then calculated. Calculations were performed at both 12 K and 290 K in different crystal orientations. The nanocontacts in these simulations consisted of a neck with a circular cross section, with a perfect fcc structure, attached to a bottom and top slab whereby periodic boundary conditions were applied. No important differences between the results for 12 K and 290 K were observed. This, as Sørensen et al. points out, should not be seen as a lack of temperature dependence due to the rate of stretching in the simulations being about eight times faster than the ~100 Å/s in a scanning tunnelling microscope (STM) experiment. It was found that for Au[100] a long chain of atoms was produced in some of the simulations, consisting of six atoms before rupture. The atomic chain gives rise to a 10 Å long plateau in the conductance curve at \( G_0 \), where \( G_0 = 2e^2/h \) (~13 kΩ\(^{-1}\)) is the quantum conductance unit. Also calculated was the equilibrium interatomic distance between Au atoms in a one-dimensional chain of atoms, which for Density Functional Theory (DFT) yielded 2.54 Å and EMT 2.47 Å. At this point Sørensen et al. raised questions about the accuracy of the potential used to describe these chains, along with questions whether they would be stable over longer times frames and higher temperatures.

1.1.2 Experiments using transmission electron microscopy

The first publications treating experimental observations of chains of atoms were presented in Nature’s October issue in 1998 by two independent groups [3, 4]. These papers showed how gold nanowires could be made to self-assemble while thinning the contact diameter between nanocontacts. These occurrences were not expected and showed conductance values close to the quantum unit, \( G_0 \), while being stable for long times at low temperatures, and at the same time being able to handle large current densities. A large benefit with these nanowires is that they are readily prepared for measurements of electrical transport properties due to their inherent metallic nature. Them being freely suspended enhances their one-dimensional character making them, as earlier stated, ideal for comparisons directly against theory.

Ohnishi et al. [3] used an ultrahigh-vacuum (UHV) high-resolution transmission electron microscope (HRTEM) in conjunction with two different manipulation techniques to produce, visualize and make measurements on Au nanowires. First a miniature scanning tunnelling microscope (STM), see Fig. 1.1, was placed at the specimen position of a HRTEM to simultaneously observe the relation between structure and electronic properties (conductance). The second technique utilized
1.1 Background

A very thin gold film together with a strong electron beam, instead of the miniature STM, in order to resolve the individual atoms in the produced structures. The electron beam was produced by a field emission gun operating at 200 kV mounted on the HRTEM. All experiments were performed at room temperature to allow the atoms enough mobility to optimize their configuration. The gold tips and samples were prepared in situ at $10^{-8}$ Pa to minimize the effects of contaminants on the structure and the conductance. In the first experimental setup the STM was used to indent a substrate surface with the scanning tip, whereby it was retracted. During retraction the connecting bridge between tip and sample gradually got thinner, accompanied with a step-like decrease in conductance, until a single linear chain of atoms was left after which the connection broke. The step-like decrease was of the amount of a conductance unit, $G_0$, and provided strong evidence for quantization of conductance in linear chains along with a single-atomic chain having a conductance of $G_0$. Ohnishi et al. next used the second technique to further study these linear chains. An electron beam at a current density $100 \text{ A/cm}^2$ was used to produce two adjacent holes in a thin gold film resulting in a nanowire bridge between them. The current density was then lowered to $30 \text{ A/cm}^2$. Often this bridge, in the (110) oriented films, was seen to evolve into a single chain of atoms in the [001] direction which lasted for about two minutes before rupture. An Au-Au spacing of 0.35-0.40 nm was observed, which is remarkable considering that the nearest-neighbor distance for gold in bulk is 0.288 nm. This large Au-Au distance was much larger than what had been predicted by any models and more recent calculations show the most likely reason to be minute amounts of contaminants [5].

Later Rodrigues and Ugarte [6] using the same HRTEM and thin-film technique, at $10^4$ times higher gas pressure, confirmed these long interatomic Au-Au distances (3.4-3.6 Å). Takai et al. [7] used a new generation defocus-imaging modulation processing electron microscope to take extremely high resolution images using the same gas pressure and experiment as Rodrigues and Ugarte. One of the major differences is that Takai et al. kept the current density of the electron beam at $\sim 100 \text{ A/cm}^2$ also during the observation phase. The result was that a bulklike Au-Au spacing of 2.9 Å between the atoms in the atomic chain was observed. A reason for this has been speculated to be that the experiment was most likely free of contaminants due to the intense electron irradiation [5]. Also noted was that the atomic chain was rather stable for several seconds, before breaking when the interatomic distances exceeded the nearest-neighbor distance.

1.1.3 Low-temperature experiments

In the second paper published in Nature’s October issue Yanson et al. [4] used a very stable STM and a mechanically controllable break-junction (MCBJ), at the low temperature of 4.2 K, to study the elongation and breaking of gold nanowires. The MCBJ used consisted of a notched gold nanowire on a metal bridge placed on a flexible substrate. The nanowire is then broken and contact between the two ends is re-established by means of piezoelectric control, thus forming a metallic contact. The low temperature allows for a long term stability of the gold chains produced and the vacuum conditions at these temperatures helps to avoid con-
tamination of the nanowires. The experiment was then performed by repeatedly stretching the contact until breaking and then bringing the contact surfaces back together. While the surface structures that make out the metallic contact was not explicitly observed the formation of atomic chains was deduced by measuring the conductance as a function of the stretching. Yanson et al. found that for most curves the conductance dropped in a step-like fashion until encountering a remarkably long conductance plateau before rupture occurs. This step-like behavior was known to be caused by atomic structural rearrangements [8, 9]. The conductance plateau having a conductance value just below $G_0$ (once below this value the conductance will not rise above it), and with a range of $\sim 20 \text{Å}$ made them speculate that a chain of atoms had been formed. This was based on knowing that the electrical transport properties of a point contact are predominantly determined by its narrowest cross section [10], together with a single-atom Au contact having a conductance value near $G_0$. By producing a histogram over the obtained lengths of the last plateau, before breaking, several peaks were observed at lengths corresponding to integer multiples of 3.6 Å. Even though the nearest-neighbor distance for gold being 2.88 Å this supported their speculation of a chain of atoms being formed. Later Kolesnichenko et al. [11] showed that this large Au-Au distance was due to the presence of He gas which influences the work function of metal surfaces introducing an error in the calibration of the MCBJ and STM. Untiedt et al. [12] later corrected these calibration errors and obtained values of $0.25 \pm 0.02 \text{nm}$ which closely agree with theoretical calculations of Au-Au distances for
atomic chains performed by Sørensen et al. in the above mentioned article along with various other publications. Another observation made by Yanson et al. in the Nature paper was that the return distance to re-establish contact was close to a 1:1 correspondence to the length of the last conductance plateau. This indicated that a fragile structure had been formed that upon breaking collapses down and rejoins the banks at each side. They concluded that freely suspended chains of atoms were produced by atoms being pulled out one by one from the banks. Furthermore these chains were remarkably stable, for as long as one hour until the experiment was ended, and capable of sustaining extremely large current densities of up to $8 \times 10^{14}$ Am$^{-2}$, thus proving the electron transport to be ballistic. The chain formation at this low temperature was even more surprising than the results yielded at room temperature by Ohnishi et al. This is because at room temperature the atoms are given enough mobility to produce stable chains due to thermal diffusion peeling off row after row of atoms until a single chain remains. Though, at 4.2 K the atoms are frozen in their initial configuration which is only changed by atomic rearrangements due to stretching of the contact. When a single atom remains as the contact atom another atom has to be pulled out from the banks in order to produce a linear chain of atoms. This without the contact breaking at its weakest spot that is the single atom.

Rubio-Bollinger et al. [13] used an STM mounted on a cantilever, having a substrate mounted on it, to simultaneously measure the conductance and force evolution while a chain of atoms is pulled from the substrate (at 4.2 K). The force curve shows a saw-tooth-like pattern which corresponds to elastic deformations followed by sudden force relaxations indicating discrete bond breaking events. While the conduction is at the last conduction plateau each jump in force is accompanied by a conduction jump a fraction of $G_0$, indicating that an atom has been pulled out from the substrate to be incorporated into the chain. One important thing to note was that the break force was found to be independent of the chain length. This break force was found to be larger than the break force for individual bonds in bulk gold, indicating that the individual chain bonds for Au are stronger than the corresponding bulk bonds.

1.1.4 Chain formation mechanisms

Bahn and Jacobsen [14] studied the possible formation of atomic chains using MD simulations and DFT on Ni, Pd, Pt, Cu, Ag and Au. Using MD a small contact was stretched until a single-atom contact remained. Upon further stretching the contacts either break or begin pulling out atom after atom to form an atomic chain until this chain in turn also breaks. It was seen that the possibility of chain formation was strong for Au and Pt, while no chain formation was seen for the other metals. The contact is deformed in stages of elastic relaxation followed by discrete bond breaks. For the atoms to be incorporated into the chain it has to be easier to break the highly coordinated bonds in the regions close to the chain relative to the low coordinated chain bonds. One of the properties of metals is that the bond strength increases with decreasing coordination number, as seen in DFT simulations. Using DFT calculations Bahn and Jacobsen found the break
force for the chains to be in general 2-3 times larger than the break force for the respective bulk bonds, with Au and Pt clearly sticking out with a value of about 3 for Au and 3.2 for Pt. Au and Pt also had a particularly high chain/bulk ratio for binding energy per bond. These things correlated well with the simulations showing chain formation only for Au and Pt. A consequence of the large differences in binding energies for high- compared to low-coordinated atoms of Pt and Au is the occurrence of surface defects which is absent in the other metals (Cu, Ag, Ni, Pd). One being the missing row reconstruction of (110) surfaces, where every second row in the [100] direction is absent. The reconstruction effects in turn is considered to be caused by relativistic effects on the electronic band structure. Smit et al. [15] used MCBJ to investigate the mechanism behind chain formation by experiments on the 5d metals Ir, Pt and Au, which have shown similar surface reconstructions. These results were then compared with experiments performed on the related 4d elements Rh, Ag and Pd. It was found that while Ir, Pt and Au formed chains; Rh, Ag and Pd did not. This showed a perfect correspondence between surface reconstructions in metals, caused by specific relativistic effects, and chain formation.

1.1.5 Project description

This thesis is mainly aimed at trying to expand on the work done by Zarechnaya et al. [16], which consisted of studies of monoatomic chains, dimers and bulk structures. This will be done by study of the energies and forces acting on a more realistic system consisting of a tip shaped contact. The hope is that this will contribute to the general understanding of the basics behind nanowire formation. The simulations are restricted to Ag, Au, Pd and Pt. DFT has been used in conjunction with LDA, PBE and PW91 potentials. Both spin polarized and non-spin polarized calculations have been performed.

1.1.6 Thesis outline

Chapter 2 will take up theory on which the simulations are based upon, while Chapter 3 will handle some of the aspects of the computational details, mainly the foundation on which the chosen simulation package is based on. Chapter 4 in turn will address results and discussion, finally Chapter 5 deals with conclusions and future work.
Chapter 2

Theory

One way to calculate the quantum mechanical properties of materials is to use computational methods called first principles or \textit{ab initio} methods. These methods solve the Schrödinger equation, to some good approximation, using only fundamental properties of the materials as input. In this chapter the \textit{ab initio} method put forward by Hohenberg, Kohn and Sham, called Density Functional Theory (DFT), will be reviewed. We will begin by first considering the Schrödinger equation which led to the problem that DFT is used to solve.

2.1 Schrödinger equation

The quantum mechanical properties of a system can be found by solving the time-independent Schrödinger equation. A quantum mechanical system is defined by the Schrödinger equation:

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

where

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$$ (2.2)

and

$$\Psi = \Psi(r_1, r_2, ..., r_N, R_1, R_2, ..., R_M)$$ (2.3)

is a wave function depending on the position of the electrons, \(r_i\), and the nuclei, \(R_k\). The Hamiltonian, \(\hat{H}\), is dependent on the electron-electron, nuclei-electron and nuclei-nuclei interactions, and can therefore be rewritten as

$$\hat{H} = -\sum_i^N \frac{\hbar^2}{2m_i}\nabla_i^2 - \sum_k^M \frac{\hbar^2}{2M_k}\nabla_k^2 + E_{ee} + E_{en} + E_{ne}$$ (2.4)
where $E_{ee}$ denotes the electron-electron Coulomb-interaction, $E_{nn}$ the nuclei-nuclei coulomb-interaction, $E_{ne}$ the nuclei-electron interaction, $Z_k$ and $Z_l$ are the atomic numbers of nuclei $k$ and $l$.

\[
E_{ee} = \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{|r_i - r_j|} \quad (2.5)
\]

\[
E_{nn} = \frac{1}{2} \sum_{k \neq l}^{M} \frac{Z_k Z_l e^2}{|R_k - R_l|} \quad (2.6)
\]

\[
E_{ne} = -\sum_{i,k}^{N,M} \frac{Z_k e^2}{|r_i - R_k|} \quad (2.7)
\]

This system is impossible to solve exactly for more than two particles. Because of the large amount of particles included in realistic systems, approximations need to be introduced.

### 2.2 Born-Oppenheimer approximation

One approximation used to simplify the Schrödinger equation is the Born-Oppenheimer approximation \[17\]. This approximation stems from the large mass difference between the electron and the nuclei, thereby making it possible to separate the movements of the electron from that of the nuclei. In effect, the electrons are seen as moving around stationary nuclei. This approximation eliminates the nuclei kinetic energy in the Hamiltonian while transforming the nuclei-nuclei interaction into a constant factor. The previous Schrödinger equation (2.1) has now been transformed into an equation in which the wave function is only dependent on the positions of all the electrons.

\[
\hat{H} \Psi(r_1, r_2, ..., r_N) = \hat{E} \Psi(r_1, r_2, ..., r_N) \quad (2.8)
\]

where

\[
\hat{H} = \sum_i^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{|r_i - r_j|} - \sum_{i,k}^{N,M} \frac{Z_k e^2}{|r_i - R_k|}. \quad (2.9)
\]

Despite this simplified equation the problem is still impossible to solve. Other ways to deal with this problem need to be used.

### 2.3 Density functional theory

Hohenberg and Kohn showed a way to circumvent this problem when they put forth their Density Functional Theory \[18\]. By applying DFT our initial $3N$-variable problem, where $N$ is the number of electrons, is transformed into a problem containing only three variables. DFT can be used to calculate the electron
2.4 Kohn-Sham equations

structure and the properties of a materials ground state. This is done by calculating the ground state total energy. DFT is based on two fundamental theorems:

**Theorem 1** The external potential $V_{\text{ext}}$, is uniquely determined by the ground state electron density $n_{\text{GS}}(r)$. Therefore all ground state properties are determined by $n_{\text{GS}}(r)$.

**Theorem 2** The electron density $n(r)$ that minimizes the total energy, $E[n(r)]$, is the ground state electron density $n_{\text{GS}}(r)$. This energy minimum can be determined using the variational method.

Now consider a system of $N$ electrons moving in an external potential and we get the Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \sum_{i} V_{\text{ext}}(r_i)$$  \hspace{1cm} (2.10)

where $\hat{T}$ is the kinetic operator, $\hat{V}_{\text{ee}}$ the electron-electron interaction operator and $V_{\text{ext}}(r_i)$ the external potential. The two theorems (Theorem 1, 2) can now mathematically be expressed as

$$E[n] = \int V_{\text{ext}}(r)n(r)dr + F[n] \geq E[n_{\text{GS}}]$$  \hspace{1cm} (2.11)

where $F[n]$ is a universal functional, and

$$F[n] = \lim_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle$$  \hspace{1cm} (2.12)

with the minimum taken over all $\Psi$ gives the density $n$. Now, the problem is that these theorems do not show how to calculate this ground state density. While the energy from the external potential is known the nature of the kinetic energy, $\hat{T}$, and the electron-electron interaction, $\hat{V}_{\text{ee}}$, is still unknown.

### 2.4 Kohn-Sham equations

Kohn and Sham [19] solved the above stated problem by looking at the system as a system of non-interacting electrons moving in an effective potential. By doing so they managed to differentiate the contributions to the total energy functional, $E[n(r)]$, and find a way to calculate it. First they showed that the total energy functional could be written as

$$E[n(r)] = T_s[n(r)] + E_{\text{ext}}[n(r)] + E_H[n(r)] + E_{\text{xc}}[n(r)]$$  \hspace{1cm} (2.13)

where $T_s$ is the kinetic energy of the non-interacting electrons, $E_{\text{ext}}$ the potential energy from the nuclei interacting with electrons and $E_H$ the energy from the electron-electron coulomb interaction. The exchange-correlation energy $E_{\text{xc}}$ comes from the many-body effects and is the only term that will need to be approximated.
By using the variational principle (Theorem 2) and the definition for the exchange-correlation potential,

\[ V_{xc} = \frac{\partial E_{xc}[n(r)]}{\partial n(r)} \]  

(2.14)

a set of equation can be derived

\[ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}[n(r)] \right\} \psi_i(r) = \epsilon_i \psi_i(r) \]  

(2.15)

where \( \psi_i \) is the Kohn-Sham orbitals, and

\[ V_{eff}[n(r)] = V_{ext} + \int \frac{e^2 n(r')}{|r-r'|} dr' + V_{xc} \]  

(2.16)

is the potential felt by an electron and the electron density, \( n(r) \), is given by

\[ n(r) = \sum_i |\psi_i(r)|^2 \]  

(2.17)

where

\[ \int n(r) dr = N, \]

where \( N \) is the total number of electrons in the system. These expressions are called the Kohn-Sham equations (2.15-2.17) and are solved self-consistently. This is done by using an initial electron density and then calculating a new electron density until the solutions converge. As stated previously, the Kohn-Sham equations gives an exact description of the system and it is only when calculating the exchange-correlation energy functional that approximations are being introduced.

### 2.5 Exchange-correlation energy functional

One thing that needs to be taken care of in DFT is the exchange-correlation energy functional, \( E_{xc}[n(r)] \). As no explicit form for \( E[n(r)] \) is known it has to be approximated. One such approximation is the widely used Local Density Approximation (LDA) first proposed by Kohn and Sham \([19]\) and holds for slowly varying densities. The local electron density is approximated to be that of a uniform electron gas, with the same exchange-correlation energy in each point. The exchange-correlation energy function is then written as

\[ E_{LDA}^{xc}[n(r)] = \int \epsilon_{xc}[n(r)] n(r) dr \]  

(2.18)

\( \epsilon_{xc} \) being the exchange-correlation energy/particle in a uniform electron gas of density \( n(r) \). \( \epsilon_{xc} \) is often, for practical purposes, split into two parts

\[ \epsilon_{xc}[n(r)] = \epsilon_x[n(r)] + \epsilon_c[n(r)] \]  

(2.19)
2.5 Exchange-correlation energy functional

where $\epsilon_x[n(r)]$ is the contribution from the exchange effects and $\epsilon_c[n(r)]$ from the correlation effects. An analytical expression for $\epsilon_c[n(r)]$ has been interpolated [20] from quantum Monte Carlo data [21]. Other widely used approximations are the Generalized Gradient Approximations (GGA) [22, 23, 24, 25] which differ from LDA in that they also take into account the gradient of the electron density and therefore may better handle inhomogeneous systems. The exchange-correlation energy functional for these approximations is given by

$$E^{GGA}_{xc}[n(r)] = \int \epsilon_{xc}[n(r)]n(r)F_{xc}[n(r), \nabla n(r)]d\mathbf{r} \quad (2.20)$$

where $\epsilon_{xc}[n(r)]$ is the same as used in LDA and $F_{xc}$ is the so-called enhancement factor.
Chapter 3

Computational methods

3.1 VASP

The work in this thesis was performed using VASP (Vienna Ab-initio Simulation Package) [26, 27] which performs *ab initio* quantum-mechanical calculations. The calculations are made within the framework of the DFT by using the Projector Augmented Wave (PAW) [28] method in conjunction with LDA, PW91 and PBE.

3.2 PAW

While the Kohn-Sham equations (2.15)-(2.17) have simplified our initial problem we still need to take care of the wave function, one way to do this is by utilizing PAW. The wave function is split into a core region (muffin-tin sphere) and a valence region. The core region with its rapidly oscillating wave function is expanded into atomic orbitals, solutions to the Schrödinger equation for the isolated atom. The valence region with its smoother behavior is in turn expanded in terms of plane waves. While the frozen core approximation is used PAW is still as accurate as an all-electron method.

PAW joins and extends all-electron methods with the pseudopotential approach, where pseudopotential methods can be seen as approximations [28]. We first start by defining a mapping of a set of smooth auxiliary wave functions $|\tilde{\Psi}_i\rangle$ onto the true all-electron wave functions $|\Psi_i\rangle$,

$$|\Psi_i\rangle = \mathcal{T}|\tilde{\Psi}_i\rangle. \quad (3.1)$$

Where $\mathcal{T}$ is a projector operator. The auxiliary wave functions and the all-electron wave functions are then expanded into partial waves,

$$|\Psi_i\rangle = \sum_m c_m |\psi_m\rangle \quad (3.2)$$

and
The operator $\hat{T}$ is chosen as

$$\hat{T} = 1 + \sum_{R} \tilde{S}_R,$$  \hspace{1cm} (3.4)

where $\tilde{S}_R$ denotes the difference between the all-electron and the auxiliary partial waves inside the muffin-tin sphere of atom $R$. Using equations (3.2) and (3.3) we can define the operator $\tilde{S}_R$ as

$$\tilde{S}_R = |\psi_m\rangle - |\tilde{\psi}_m\rangle.$$  \hspace{1cm} (3.5)

As the contributions from the muffin-tin spheres are supposed to disappear outside the core region we also get the condition

$$\psi_m = \tilde{\psi}_m, \text{ for } |\mathbf{r} - \mathbf{R}| > r_c.$$  \hspace{1cm} (3.6)

Furthermore, the requirement that $\hat{T}$ is to be linear gives

$$c_m = \left\langle \tilde{p}_m | \tilde{\Psi}_i \right\rangle \text{ for } |\mathbf{r} - \mathbf{R}| < r_c,$$  \hspace{1cm} (3.7)

where $\tilde{p}_m$ is some set of projection functions satisfying the condition

$$\left\langle \tilde{p}_m | \tilde{\psi}_n \right\rangle = \delta_{mn}.$$  \hspace{1cm} (3.8)

This, so that the one-center expansion of the smooth auxiliary function $\tilde{\Psi}_i$,

$$|\tilde{\Psi}_i\rangle = \sum_{m} |\psi_m\rangle \left\langle \tilde{p}_m | \tilde{\Psi}_i \right\rangle,$$  \hspace{1cm} (3.9)

equals $\tilde{\Psi}_i$ itself. In conclusion there is now both an expression for the true all-electron functions

$$|\Psi_i\rangle = |\tilde{\Psi}_i\rangle + \sum_{m} \left( |\psi_m\rangle - |\tilde{\psi}_m\rangle \right) \left\langle \tilde{p}_m | \tilde{\Psi}_i \right\rangle,$$  \hspace{1cm} (3.10)

and the transformation operator $\hat{T}$

$$\hat{T} = 1 + \sum_{m} \left( |\psi_m\rangle - |\tilde{\psi}_m\rangle \right) \langle \tilde{p}_m |.$$  \hspace{1cm} (3.11)

An illustration of equation (3.10) can be seen in Fig. 3.2. The transformation operator $\hat{T}$ still involves the true all-electron wave functions and the expressions can be used to derive all-electron results as they can be applied to both core and valence states.
3.2 PAW

Figure 3.1. Illustration of equation (3.10) with its wave function $|\Psi_i\rangle$, plane wave part $|\Phi_i\rangle$, pseudized spherical part $|\tilde{\psi}_m\rangle$ and "true" spherical part $|\psi_m\rangle$. 
Computational methods
Chapter 4

Results and discussions

4.1 Simulation settings

Following the results for bulk, chains and dimers by Zarechnaya et al. [16], as seen in Fig. 4.1 along with Table 4.1, simulations with more realistic settings were desired. This chapter will begin showing results from bulk simulations for Ag, Au, Pd and Pt. The resulting equilibrium lattice parameters, total energies and break forces will in turn be used as input for, and comparison with, simulations on a tip structure. From this, conclusions will be drawn concerning possible nanowire formation together with comparisons to results produced by Zarechnaya et al. [16]. Cutoff energies used for all simulations in this thesis were for LDA, Ag 249.8 eV, Au 229.9 eV, Pd 250.8 eV and Pt 230.2 eV. PBE and PW91 had the same cutoff energies for Ag and Au, but for Pd and Pt it increased by 0.1 eV.

4.2 Computational resources

This research was conducted using the resources of National Supercomputer Center (NSC) in Linköping as well as that of High Performance Computing Center North (HPC2N).
Figure 4.1. Binding energy vs. Lattice parameter calculations for Ag, Au, Cu, Pd, Pt and Ni.
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<tr>
<th>Approximation</th>
<th>Element</th>
<th>Cu (eV/Å)</th>
<th>Ag (eV/Å)</th>
<th>Au (eV/Å)</th>
<th>Ni (eV/Å)</th>
<th>Pd (eV/Å)</th>
<th>Pt (eV/Å)</th>
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<td>1.93</td>
<td>1.38</td>
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<td>2.96</td>
<td>2.47</td>
<td>2.89</td>
<td>2.84</td>
</tr>
</tbody>
</table>

Table 4.1. Simulation results from Zarechnaya et al. [16].
4.3 Bulk simulations

To deduce the atom-atom equilibrium distances to be used in later simulations a face-centered-cubic (fcc) unit cell (Fig. 4.2) was set up containing 20x20x20 k-points, resulting in 770 irreducible k-points generated using the Monkhorst-Pack enclosed in VASP. The atomic properties of the different species were then used as input and simulations were performed at varying lattice parameter values. Spin polarized calculations were performed using the LDA, PBE and PW91 approximations, except for Ag due to calculational reasons. For the spin polarized calculations magnetic moments (in units of $\mu_B$, Bohr magnetons) were introduced, deviations in these numbers are also due to calculational reasons. The resulting data points for total energy were then plotted against the lattice parameter. Curves were then produced by fitting 2nd-degree equations to the data points, together with the use of splines. From the resulting figures, Fig. 4.3-4.5, it was then possible to deduce the energy minima for each simulation set, giving us the corresponding equilibrium lattice parameters. Also seen in the figures are the values of the initial magnetic moments used (MAG). With the calculations being self-consistent no resulting magnetic moments for Ag and Au were observed around the equilibrium. Pd and Pt showed very small resulting magnetic moments at the equilibrium positions but when stretched it increased to $\sim 1/3 \mu_B$ for Pd and $\sim 1/2 \mu_B$ for Pt. From here on we will also, for simplicities sake, be using the term nearest-neighbor (NN) distance to label atom-atom distances in figures and tables. But what the term is to describe will be, if not explicitly expressed, quite
Figure 4.3. Total energy vs. Lattice parameter calculations for Ag, Au, Pd and Pt using LDA.

self-evident.

Another item of interest is the relation between force and lattice parameter, which roughly can be found by measuring the slope (gradient) of the produced total energy curves. These new curves (Fig. 4.6-4.8) in turn yield the break force for the atomic bonds, defined as the maximum slope of the total energy curve, together with the corresponding lattice parameter value. The resulting minimum energies and maximum forces, together with their corresponding lattice parameters, are presented in Table 4.2.

Comparing the values from Table 4.2 with those of Table 4.1 the lattice equilibrium parameters are very much in agreement. The force calculations deviate somewhat, possibly due to differences in magnetic moment values.
Results and discussions

**Figure 4.4.** Total energy vs. Lattice parameter calculations for Ag, Au, Pd and Pt using PBE.

**Figure 4.5.** Total energy vs. Lattice parameter calculations for Ag, Au, Pd and Pt using PW91.
Figure 4.6. Force vs. Lattice parameter calculations for Ag, Au, Pd and Pt using PW91.

Figure 4.7. Force vs. Lattice parameter calculations for Ag, Au, Pd and Pt using PBE.
Results and discussions

Figure 4.8. Force vs. Lattice parameter calculations for Ag, Au, Pd and Pt using PW91.

Table 4.2. Nearest-Neighbor distances $a_{NN}$ for energy minima $E_{\text{min}}$ and force maxima $F_{\text{max}}$. 

<table>
<thead>
<tr>
<th>Approximation</th>
<th>Species</th>
<th>$E_{\text{min}}$ (eV)</th>
<th>$a_{NN}$ (Å)</th>
<th>$F_{\text{max}}$ (eV/Å)</th>
<th>$a_{NN}$ (Å)</th>
</tr>
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<td>2.3611</td>
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</table>
4.4 Tip simulations

The next phase was to construct a tip for further simulations in order to investigate possible chain formation. The resulting tip was built up by three planes containing a total of ten atoms, another atom was then placed on top of this tip, as seen in Fig. 4.9.

4.4.1 Break forces for the nanowire

In the first set of simulations the top most atom is pulled away from the rest of the tip structure in incremental steps, see Fig. 4.10. Total energy and forces are then calculated to find equilibrium distances and break forces. Also this set of simulations was performed using LDA, PW91 and PBE while allowing for spin polarization, except Ag for calculational reasons. For the spin polarized calculations an initial magnetic moment of 0.2-0.3 $\mu_n$ was introduced to the two upper atoms of the tip structure. In all the tip simulations 1x1x15 k-points were used, enough due to the focus on the z-direction. As mentioned earlier the calculated nearest-neighbor distances from the bulk simulations are used in the tip structures.

The resulting total energy results are shown in Fig. 4.11-4.13, where the total energy is plotted against the distance between the two top most atoms. It can be seen that the inherently non-magnetic Ag and Au exhibit the predicted plot curves for energies, while the magnetic Pd and Pt exhibit small kinks in their plots which need to be explained. These kinks may not be overtly visible in the
energy plots but give a pronounced response in the force calculations, as seen in Fig. 4.14-4.16. By performing non-spin polarized calculations for Pd and Pt using LDA, and producing force plots without kinks, the problem was narrowed down to the spin polarization parts of the calculations (see Fig. 4.17). Values for energy minima and force maxima together with their corresponding distances between the two upper atoms can be seen in Table 4.3. To better see why some of the species do not form chains while others do the density of states (DOS) for Au and Pd was calculated using LDA. The calculations allowed for spin polarization. Two different tip configurations were used for each species. The results can be seen in Fig. 4.18-4.21. One of the reasons why Au form chains, while Pd does not, can clearly be seen in these pictures. Pd has high energy states occupied at the Fermi level making the tip energetically unstable when pulling the top most atom. Au lacks these high energy states and is therefore in turn energetically stable during the pull. Even though spin polarized calculations were used no resulting magnetic moment was observed for these two species.
4.4 Tip simulations

Figure 4.11. Total energy vs. distance between the two topmost atoms, $\Delta z$, calculations for Ag, Au, Pd and Pt using LDA.

Figure 4.12. Total energy vs. distance between the two topmost atoms, $\Delta z$, calculations for Ag, Au, Pd and Pt using PW91.
2.000 2.500 3.000 3.500
$\Delta z$ (Å)
−45.0
−35.0
−25.0
−15.0
$E_0$ (eV)
Tip simulation: Total Energy
PBE: Ag Au Pd Pt
Ag MAG=0.2
Au MAG=0.2
Pd MAG=0.2
Pt MAG=0.3

Figure 4.13. Total energy vs. distance between the two top most atoms, $\Delta z$, calculations for Ag, Au, Pd and Pt using PBE.

2.000 2.500 3.000 3.500
$\Delta z$ (Å)
−20.0
−15.0
−10.0
−5.0
0.0
5.0
$F$ (eV/Å)
Tip simulation: Force
LDA: Ag Au Pd Pt
Ag
Au MAG=0.2
Pd MAG=0.2
Pt MAG=0.2

Figure 4.14. Force vs. distance between the two top most atoms, $\Delta z$, calculations for Ag, Au, Pd and Pt using LDA.
Figure 4.15. Force vs. distance between the two top most atoms, $\Delta z$, calculations for Ag, Au, Pd and Pt using PW91.

Figure 4.16. Force vs. distance between the two top most atoms, $\Delta z$, calculations for Ag, Au, Pd and Pt using PBE.
Figure 4.17. Force vs. distance between the two top most atoms, $\Delta z$, non-spin polarized calculation for Pd and Pt using LDA.

Figure 4.18. Spin polarized DOS calculations for Au using LDA. The top most atom is located 2.50 Å above the atom below it. The Fermi level $E_F$ is marked.
4.4 Tip simulations

Figure 4.19. Spin polarized DOS calculations for Au using LDA. The top most atom is located \(2.83\) Å above the atom below it. The Fermi level \(E_F\) is marked.

Figure 4.20. Spin polarized DOS calculations for Pd using LDA. The top most atom is located \(2.33\) Å above the atom below it. The Fermi level \(E_F\) is marked.
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Density of States

$E_F$ (eV)

DOS (#states/unit cell)

Figure 4.21. Spin polarized DOS calculations for Pd using LDA. The top most atom is located 2.67 Å above the atom below it. The Fermi level $E_F$ is marked.

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<th>$E_{\text{min}}$ (eV)</th>
<th>$\Delta z^{F_{\text{max}}}$ (eN)</th>
<th>$F_{\text{max}}$ (eV/Å)</th>
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<td>2.74(3.09)</td>
<td>2.7747(2.6557)</td>
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Table 4.3. Distance $\Delta z$ between the two top most atoms of the tip at each energy minima $E_{\text{min}}$ and force maxima $F_{\text{max}}$, when moving the top atom. Numbers in parenthesis denotes additional force maximas.
4.4 Tip simulations

Another issue to investigate is the possibility of chain formation. A new set of calculations was performed using the same tip structure as previously used. These simulations were non-spin polarized and performed using LDA with the same number of 1x1x15 k-points. The top atom is pulled away in incremental steps as in our previous calculations (chapter 4.4.1) while making sure to capture the earlier calculated energy minima and break points. At each incremental step the atom below it, see Fig. 4.22, is moved around its initial position in the z-direction (9-11 sample points). The reason for not only moving the lower atom in a positive z-direction is the observation that the atoms true equilibrium position is a bit closer to the rest of the tip structure, compared to nearest-neighbor distances used when building the tip structure. For each of the top atoms incremental steps a total energy curve is produced.

By observing how the energy minima evolve as the top atom is pulled out we in effect see how the lower atom moves in response to this (Fig. 4.23, 4.25, 4.27, 4.29). If the energy minimum increasingly moves in a positive z-direction while pulling it means that the lower atom follows the top atom, showing a tendency for chain formation, and if it increasingly moves in the negative direction chain formation is not occurring. Numerical values for energy minima can be found in Table 4.4.

Clear evidence of chain formation were seen for Au where the energy minima is shown to keep moving during the pulling of the top atom (Fig. 4.23). The relative movements of the top two atoms, as the top atom is incrementally pulled away,
can more easily be viewed in Fig. 4.24 where the zero value denotes the un-relaxed nearest-neighbor distance for the lower atom. Also included in this figure is the energy gain (black squares) as a result of the relaxation.

A bit more surprising was the results that showed chain formation also for Ag (Fig. 4.25, 4.26), though Ag has actually been shown in low temperature experiments [15, 29] to form very short chains of two atoms, and at rare times three.

Pd in turn shows a tendency for the lower atom to actually retract closer to the tip structure during the pull (Fig. 4.27, 4.28), indicating that no chain formation is occurring.

Surprisingly Pt showed only small, if any, tendencies for chain formation as seen in Fig. 4.29. A possible reason for this might be the exclusion of spin polarized calculations together with the effects of not taking into account spin-orbit coupling which has a profound effect on both the existence and magnitude of magnetic moments for Pt(5d metals) [30]. Spin polarization might be a delicate issue to work with using our tip geometry. Delin et al. [31] have found magnetism for Pt to be mainly a one-dimensional phenomenon present in one-dimensional atomic chains, 0.7 $\mu_B$ per atom, while significantly smaller, 0.30$\mu_B$ per atom, in short chains between bulk leads. The bulk leads being nonmagnetic, the same being the case with coaxial nanowire geometries. The role of magnetism and spin-orbit coupling have in nanowire formation is in need of further investigation.
Figure 4.24. The two top atoms relative positions in relation to the lower atoms ideal NN distance each time the top atom is pulled further away. The lower atom is shown at its energy minima. Also shown is the energy gain (black squares) in this relaxed state compared to the lower atom being at the NN distance.

Figure 4.25. Total energy vs. translation, dz, from nearest-neighbor distance. Calculated for Ag using LDA at different positions for the topmost atom. The dashed line indicates movement of energy minima.
Results and discussions

**Figure 4.26.** The two top atoms relative positions in relation to the lower atoms ideal NN distance each time the top atom is pulled further away. The lower atom is shown at its energy minima. Also shown is the energy gain (black squares) in this relaxed state compared to the lower atom being at the NN distance.

**Figure 4.27.** Total energy vs. translation, dz, from nearest-neighbor distance. Calculated for Pd using LDA at different positions for the topmost atom. The dashed line indicates movement of energy minima.
4.4 Tip simulations

Figure 4.28. The two top atoms relative positions in relation to the lower atoms ideal NN distance each time the top atom is pulled further away. The lower atom is shown at its energy minima. Also shown is the energy gain (black squares) in this relaxed state compared to the lower atom being at the NN distance.

Figure 4.29. Total energy vs. translation, dz, from nearest-neighbor distance. Calculated for Pt using LDA at different positions for the topmost atom. The dashed line indicates movement of energy minima.
### Table 4.4.

Given a Nearest-Neighbor distance NN, a fixed distance $d_{\text{Top-atom}}$ between the top atom and the default NN-position of the lower atom is set. Given each top atom position the change in the lower atoms position $dz_{E_{\min}}$, compared to its initial nearest-neighbor distance position, is shown. A positive shift means it has been pulled towards the top most atom, while a negative shift corresponds to a lowering towards the rest of the tip structure.
Figure 4.30. The two top atoms relative positions in relation to the lower atoms ideal NN distance each time the top atom is pulled further away. The lower atom is shown at its energy minima. Also shown is the energy gain (black squares) in this relaxed state compared to the lower atom being at the NN distance.
Results and discussions
Chapter 5

Conclusions and future work

5.1 Conclusions

We have calculated lattice parameters for bulk which we later used as basis to construct a tip structure. We saw that pulling the top atom resulted in chain formation for Au and Pt. While spin-polarization was allowed no resulting magnetic moment was seen in the species investigated. The density of states for Au and Pd showed that Au, as seen, should produce chains more easily than Pd due to low energy states at the Fermi level compared to the high energy states for Pd. Further indications of chain formation for Au, as well as Ag, was seen when investigating the energy minima for the lower atom while the tip atom is pulled away. This was not readily observed for Pt, indicating that further studies are needed in this area.

5.2 Future work

As a thesis work this work is prone to being limited in certain aspects. Certain stringent issues about not having a relaxed structure and concerning values of magnetic moments were not addressed. Also simulations with larger structures (along the lines of Zhang et al. [32]) are of interest when it comes to chain formation, together with chains consisting of different species. Further work is also needed in the experimental area to try and if possible produce different kinds of nanowires. The role effects like magnetism and spin-orbit coupling have in chain formation needs further study. Finally an interesting aspect to investigate is the temperature dependence on chain formation.
Bibliography


