Electronic and structural properties of nanoclusters

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The cover image is polyhedra: icosahedron, truncated octahedron and truncated decahedron

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Nanoclusters have gained a huge interest due to their unique properties. They represent an intermediate state between an atom and a solid, which manifests itself in their atomic configurations and electronic structure. The applications of nanoclusters require detailed understanding of their properties and strongly depend on the ability to control their synthesis process. Significant effort has been invested in modelling of nanoclusters properties. However, the complexity of these systems is such that many aspects of their growth process and properties are yet to be understood.

My thesis focuses on describing structural and electronic properties of nanoclusters. In particular, the model for nanoparticles growth in plasma condition is developed and applied, allowing to describe the influence of the plasma conditions on the evaporation, growth and morphological transformation processes. The mechanism driving the morphology transition from icosahedral to decahedral phase is suggested based on force-fields models. Spectroscopic methods allow for precise characterization of nanoclusters and constitute an important tool for analysis of their electronic structure of valence band as well as core-states. The special attention in the thesis is paid to the core-states of nanoclusters and influences that affect them. In particular, the effects of local coordination, interatomic distances and confinement effects are investigated in metal nanoclusters by density functional theory methods. These effects and their contribution to spectroscopic features of nanoclusters in X-ray photoemission are modelled. The relation between the reactivity of nanoclusters and their spectroscopic features calculated in different approximations are revealed and explained. Ceria is a very important system for many applications due to the ability of cerium atoms to change their oxidation state depending on the environment. The shift of the oxidation state and its effects on the core-states is examined with X-ray absorption measurements and modelling allowing to build a rigid foundation for interpretation of the measured spectra and characterization of electronic structure of ceria nanoparticles.

Populärvetenskaplig sammanfattning

Nanokluster har fått mycket uppmärksamhet på grund av deras unika egenskaper och möjliga framtida tillämpningar. De utgör ett tillstånd som ligger mellan en atom och ett fast ämne, vilket påverkar deras atomkonfiguration och elektroniska struktur. Framställning och användning av nanokluster kräver djup förståelse av deras egenskaper och beror starkt på förmågan att styra syntesprocessen. Stora ansträngningar har gjorts för att modellera nanoklusteregenskaper. Emellertid är komplexiteten hos dessa system så stor att många aspekter av deras tillväxtprocess och egenskaper ännu inte är förstådda.

Denna avhandling fokuserar på beskrivningen av strukturella och elektroniska egenskaper hos nanokluster. I synnerhet utvecklades och applicerades modellen för nanopartiklar i plasma. Modellen möjliggjorde beskrivningen av plasmatillståndets påverkan på förångnings-, tillväxt- och morfologiska omvandlingsprocesser.

Spektroskopiska metoder gör det möjligt att noggrannt karakterisera nanokluster och utgör ett viktigt verktyg för analys av deras elektroniska struktur i valensband samt kärnnivåer. Särskild uppmärksamhet i avhandlingen riktades mot kärnelektronerna i nanokluster och det som påverkar dem. Speciellt undersöktes effekterna av lokal koordinering, interatomiska avstånd och inneslutningseffekter i metallnanokluster med hjälp av täthetsfunktionalteori. Dessa effekter och deras bidrag till spektroskopiska egenskaper hos nanokluster i röntgenfotoemission modellerades. Förhållandet mellan katalytiska egenskaper hos nanokluster och deras spektroskopiska egenskaper modellerat i olika approximationer undersöktes och förklarades.

Preface

This thesis is a result of my Ph.D. studies in the Theoretical Physics Division at Linköping University from 2013 to 2018.

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Contents

1	Introduction	1
1.1	Applications of nanoclusters	2
1.2	Synthesis	2
1.3	Structure	4
1.4	Electronic structure	5
2	Classical Molecular Dynamics	7
2.1	Integration scheme	8
2.2	Potentials	8
2.2.1	Pair-potential methods	9
2.2.2	Embedded Atom Method	9
2.2.3	Charge-Optimized Many-Body	10
2.2.4	Charge equilibration	10
2.3	Thermostats	10
3	<i>Ab initio</i> methods	13
3.1	Density functional theory	14
3.2	Exchange-correlation functionals	15
3.3	Basis sets	17
3.3.1	Augmented Plane Waves	18
3.3.2	Projector Augmented Waves	19
3.3.3	Gaussian-type orbital	20
3.3.4	Basis sets for nanosystems	20
4	Spectroscopy	21
4.1	X-ray photoelectron spectroscopy	21
4.1.1	Complete screening picture	23
4.1.2	Model for surface core-level shifts in clusters	24
4.2	X-ray absorption spectroscopy	26

5	Structural properties of nanoclusters	29
5.1	Hollow cathode synthesis	29
5.2	Nanoparticle growth by collection of ions	30
5.3	Evaporation of nanoclusters	31
5.4	Growth of nanoclusters in a plasma	33
5.4.1	Model	33
5.4.2	Analysis of individual events	36
5.5	Structure of charged nanoparticles	39
5.6	Morphological transformation	40
5.6.1	Simulation of the growth process	41
5.6.2	Mechanism of morphology transition	43
6	Electronic properties of nanoclusters	47
6.1	Core-level binding energy shifts in nanoclusters	47
6.2	Adsorption on Pd nanoclusters and core-level shifts	53
6.3	Cerium oxide nanoparticles	56
7	Conclusions	63
	Bibliography	65
	List of included Publications	75
	Related, not included publications	77
	Paper I	79
	Paper II	87
	Paper III	95
	Paper IV	109
	Paper V	117
	Paper VI	125

CHAPTER 1

Introduction

In the last decade, we have been witnessing the explosive growth of nanoscience. This field has relevance for physics, chemistry, biology and engineering. Problems associated with it are ranging from applied technological issues to fundamental understanding of basic principles. The focus of nanoscience is objects which size does not exceed hundreds of nanometers. This size range makes nano-objects an intermediate state between individual atoms or molecules and bulk matter. The properties of these objects may differ drastically from their atomic and bulk counterparts and change dramatically with the size. The control over their size and structure opens possibility of a precise tuning of their properties. Nanoparticles is one example of such system. Their sizes typically range from a few atoms to hundreds of millions of atoms and the dimensions do not exceed *nano* scale. There are two different terms used in the community: *nanoparticle* and *nanocluster*. The term *nanocluster* is commonly applied to the systems with a certain number of atoms and a certain structure and such systems are often referred by these two parameters. The term *nanoparticles* is used more broadly for all systems of the relevant size and identified by their radius or diameter. There is no strict definition and in this thesis sometimes these terms are used interchangeably.

A straightforward consequence of the nanoparticles size is their surface to bulk ratio, which is very high and small nanoparticles properties are mostly determined by their surface. As a result, in small particles translational symmetry breaks and the structure becomes noncrystalline. Small nanoparticles with 1-3 nm diameter often demonstrate strong size dependency of the properties, such as melting temperature, cohesive energy and electronic structure, while properties of 10 nm particles tend to bulk values with increase of the size.

1.1 Applications of nanoclusters

The first documented application of nanoparticles can be attributed to the 4th century AD, ancient Rome. It is the Lycurgus Cup (Fig. 1.1) – a cup made of dichroic glass, which shows different colors (bright red or pale green) depending of the lighting. When the cup was thoroughly studied in 1950s, it was found that the phenomenon of the changing color is explained by the presence of silver and gold nanoparticles in the glass matrix[1, 2]. Later, it was shown that this technology has been used for ceramics and glass all over the world from stained-glass windows in Chartres Cathedral to the Kremlin stars.

With development of the technologies it became evident that nanoparticles have potential for much more applications in different fields. Today nanoparticles are used in catalysis[3], photovoltaics[4, 5], quantum dots[6], plasmonics[7], medicine[8], biology[9], manufacturing[10], and more. As many other advanced technologies nanoparticles may have serious implications on the environment and the discussion of whether nanoparticles is a threat is still ongoing[11, 12].

Figure 1.1. The Lycurgus Cup: A dichroic glass cup from the 4th Century AD[13]

1.2 Synthesis

Applications of nanoparticles require a precise control over their size, structure and composition. A number of synthesis methods have been developed for nanoparticles synthesis[14]. Each method has its advantages for different applications.

Below I would like to give a brief overview of the most common synthesis methods.

Wet-chemistry synthesis

Several methods based on chemical reactions have been developed to obtain clusters with 1-50 nm size[14]. These methods are determined by the concentration and speed of addition of the reactants, the control of the pH, the temperature and the atmosphere. For instance, gold nanoclusters are grown by condensation from unstable $AuSR$ stoichiometric molecules, where SR stands for an alkyl thiolate, $R = C_nH_{2n+1}$ and S is a sulfur atom bound to a gold atom.

During the synthesis process gold atoms combine into larger and larger clusters, while the coalescence of the clusters is prevented by the $RSSR$ groups bound to the surface. Such methods typically do not require high temperatures or pressures and the speed and the amount of the produced particles are relatively small.

Inert gas aggregation synthesis

In gas-aggregation process (IGA)[14], the cluster material is vaporized and released into a flow of cold inert gas. This causes the supersaturation of the vapor and the pressure required for the initial nucleation is high. It is important to notice that the initial nucleation does not occur in binary collisions and requires three-body collision or more. After the nucleation, the growth continues mostly by single-atom addition. This type of growth process has a number of adjustable parameters that affect the outcome: sputtering rate, pressure in the chamber, gas temperature and length of the drift region. The tuning of the parameters allows to grow large clusters (up to 50000 atoms) of wide range of materials with high production rates.

Plasma synthesis methods

Another class of methods is utilizing plasma discharge for evaporation and ionization of the material. There exists a number of various implementations of this approach, but the one that has a particular interest for me is a recently developed method by I. Pilch *et al.*[15]. This method improves the growth rates, expands the materials choice and optimizes the size distribution. It is based on the pulsed plasma ignited in a hollow cathode, which allows to increase the degree of the gas ionization. The details of the method are discussed in Chapter 5.

These three approaches are the pillars of the nanoparticles synthesis and a large number of derivative methods has been developed over the years and their exhaustive description can be found in [16].

1.3 Structure

The arrangement of atoms in nanoclusters can significantly differ from the bulk crystalline structure. The experimental study performed by O. Echt *et al.*[17] showed that some sizes of synthesized Xenon clusters are more frequent than others. The most frequent sizes were found to have $N=13$, 55 and 147 atoms. These numbers turned out to be terms of a series:

$$N = 1 + \sum_{p=1}^n 10p^2 + 2, \quad p \in \mathbb{N}, \quad (1.2)$$

and are called (*structural*) *magic numbers*. This series describes packing of spheres into the shape of icosahedron (Ih), as shown in Fig. 1.2. These structures were named after Mackay[18], who first described their shape. Later, Farges[19] performed the diffraction measurements and showed that the structures match the shapes described by Mackay. From that he concluded that the clusters with the number of atoms corresponding to complete layers arranged in icosahedral structure show higher stability than intermediate sizes.

Figure 1.2. Morphologies of small nanoclusters

The general trend shows that the binding energy E_b in a given structure can be estimated[20]:

$$E_b = aN + bN^{\frac{2}{3}} + cN^{\frac{1}{3}} + d, \quad (1.3)$$

where N is number of atoms, the first term corresponds to the volume contribution, the second term is the surface contribution and the third and the fourth ones are edges and vertices, respectively. The surface and the volume contributions act oppositely. For example, in order to minimize the surface contribution, the structure should be as close as possible to a spherical shape, which is an icosahedron. But icosahedral structure inevitably attains stresses and increases volume contribution, which grows linearly with the size. The volume contribution is growing faster than the surface energy as a function of the size. Thus, at certain size

Table 1.1. Analysis of thermodynamic stability for Cu, Au, Pd[22]

Metal	$N_{Ih \rightarrow Dh}$	$N_{Dh \rightarrow fcc}$
Cu	1000	53000
Pd	< 100	6500
Au	< 100	500

Marks decahedron structure (Dh) becomes more stable, which geometry is shown in Fig. 1.2[21]. Growing further the decahedral configuration eventually becomes less stable than fcc arrangement of atoms. The configuration that corresponds to fcc arrangement is octahedron (Oh) or truncated octahedron (TOh) (Fig. 1.2). For instance, F. Baletto *et al.*[22] conducted an investigation of the structural stability for Cu, Au and Pd (Table 1.1).

The results in Table 1.1 suggest that the transition from Ih to Dh phase in Cu nanoparticles is expected at around 1000 atoms, while crystalline structure stabilizes for particles with more than 53000 atoms. This structure stability investigation was performed for zero temperature. However, the entropic contribution increases with the increase of the temperature. J. Doye *et al.*[23] investigated the influence of the entropic contribution on the structure stability. It was shown that the temperature increases the stability range for Ih and Dh structures.

1.4 Electronic structure

The electronic structure of nanoclusters goes through dramatic changes with increase of the size. The peculiarities of the electronic structure were discovered in sodium clusters. Sodium vapor can be supersonically expanded from an oven with a fine nozzle. As a result of this expansion, clusters are formed and due to the fact that the condensation is an exothermic reaction, the temperature of the cluster increases. During the expansion the clusters cool by evaporating and losing mass and energy. Clusters with low evaporation rates or strong binding energies tend to become abundant. In 1984 Knight *et al.*[24, 25] discovered that clusters with $N=8, 20, 40, 58$ and 92 are more abundant than clusters of other sizes. The measurement of the ionization potential or IP (energy required to remove an electron from the cluster) for clusters of different sizes found that between N and $N+1$ IP drops abruptly. Since sodium is monovalent, the number of electrons in these clusters was $8, 20, 40, 58$ and 92 and the experiments showed that electrons for such clusters are bound more tightly. These numbers are called *electronic magic numbers*. It is important to underline that the numbers are different from *structural magic numbers*. In a sodium cluster valence electrons are strongly delocalized from their atoms and the potential for these electrons is very weak. For such a case, *jellium* model can be applied. Jellium model treats a cluster as a "giant" atom, where a positive nuclear charge of each atom is uniformly distributed over a sphere, which has the size of the clusters. Then a spherically symmetric poten-

tial well can be used to describe the interaction between electron and a positive spherical charge. This problem is similar to a hydrogen atom problem and can be solved analytically[26, 27].

Figure 1.3. Comparison of energy levels in (a) an atom and in (b) a "giant" atom (Na_{40} cluster).

The energy levels for Na atom and a "giant" atom containing 40 Na atoms are shown in Fig. 1.3. The order of the levels is different due to the difference in the potential, as in the case of a "giant" atom, the positive potential is formed by 440 protons.

As was discussed earlier, a nanocluster is an intermediate state between a solid and an atom. Thus, its electronic structure has to go from atomic discrete level to continuous solid bands. The phenomenon of level separation in small metallic particles was first highlighted by Frölich in 1937[28]. But the widespread interest rose after Kubo's description of anomalies in thermodynamics associated with discreteness of the energy levels[29]. According to Frölich-Kubo approach, the electron energy levels in solids are quasi-continuous and the electronic structure is well described by band theory. As the size of the metallic particles is reduced the energy levels become discrete and the number of levels becomes finite with spacing between the adjacent levels of order E_F/N . According to DiCenzo and Wertheim[30], the metallic behavior appears in a partially filled band with the energy levels spacing small enough that a small perturbation is sufficient to create electron-hole pairs and conduct electric current. Kubo suggested a criterion for nanoparticles to exhibit metallic conduction

$$\delta \approx \frac{E_F}{N} \leq kT, \quad (1.4)$$

where δ is the band gap at the Fermi level E_F , also known as Kubo gap, N is the number of atoms and kT is the temperature. When δ is greater than the temperature, metallic behavior is suppressed.

CHAPTER 2

Classical Molecular Dynamics

Molecular Dynamics (MD) is a method for modelling interactions between atoms in gas, liquid or solid phase. MD allows to study processes such as growth, diffusion, phase transition and many more by combining thermodynamic and kinetic phenomena. Unlike approaches based of quantum mechanics (QM), Classical Molecular Dynamics does not treat electrons explicitly and the speed of such calculations is orders of magnitude higher than approaches based on solving QM equations. For instance, a simulation of a few million atoms is absolutely feasible, while QM based methods struggle to cover more than 1000 atoms.

In Classical Molecular Dynamics approach, trajectories of the moving atoms are calculated from the integration of Newton's equations of motion. The integration time-step has to be much smaller then the lattice vibrations time-scale to accurately describe atomic trajectories. The total energy in MD simulations consists of kinetic energy of the system, which is computed from velocities of the atoms and potential energy, obtained from the interaction potentials.

MD allows to use different constraints for different ensembles. Micro-canonical ensemble (NVE) is the most accurate one and for that ensemble number of particles N , volume V and total energy E are preserved. This ensemble is the best for describing natural evolution of the system, however, if the system is coupled to a thermostat and the total energy is not conserved, canonical ensemble (NVT) can be used. In this case, the time evolution of the system may be significantly affected by the way the energy is changed. This is usually done by means of thermostats that will be discussed later.

2.1 Integration scheme

The trajectories of the atoms are calculated from the integration of the Newton's equation of motion

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i V(\{\mathbf{r}_i(t)\}), \quad (2.1)$$

where m_i and $\mathbf{r}_i$ are the mass and the position of atom i , V is the potential energy, t is time. In order to integrate the equations, we need to follow an algorithm or an integration scheme. The usual way to approach the integration of a set of first-order differential equation is to advance the system variables through a discrete time-step Δt and approximate derivatives by finite differences. The propagation of the system requires calculations of forces for all atoms. These calculations consume enormous amounts of CPU time. Thus, it should be calculated as few times as possible. Another important requirement for the integration scheme is stability. Stability implies that small deviation from the correct trajectories does not lead to even greater deviations or that over long-time integration the deviation should be as little as possible. It is also highly important to satisfy conservation laws, so that the energy and momentum drift will be zero.

The integration scheme should be an odd symmetric function of time. This means that if all velocities of a system were reversed at a certain point in time, the system would backtrack over its prior trajectory. Velocity Verlet algorithm[31] has a number of advantages over other integration algorithms, such as Leap Frog, Euler, which are well described in [32]. Velocity Verlet algorithm is fast, accurate and time-reversible and does not have energy drift on long time simulations. Positions and velocities in Velocity Verlet scheme are calculated with the following equations

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\Delta t + \frac{1}{2}\ddot{\mathbf{r}}_i(t)(\Delta t)^2 \\ \dot{\mathbf{r}}_i(t + \Delta t) &= \dot{\mathbf{r}}_i(t) + [\ddot{\mathbf{r}}_i(t + \Delta t) + \ddot{\mathbf{r}}_i(t)] \frac{\Delta t}{2}, \end{aligned} \quad (2.2)$$

where Δt is the integration step.

2.2 Potentials

In MD simulations, the interactions between atoms is described by classical inter-atomic potentials V . The choice of the potential is a crucial component of classical MD. Usually the potentials are obtained from a higher-level theory (for example density functional theory), or experiment by fitting to reproduce certain properties. Hence we use a purely classical model to describe a quantum system. This of course has implications. The models that are used for describing the interaction can be based on a physically motivated model or could be just constructed to better reproduce the desired properties. Another important aspect of empirical potentials is that they are not well transferable, meaning that potentials fitted to describe one system should not be expected to work well for other systems. For

example, potentials that work well for one crystal structure may fail for the same element in another structure. There are different approaches to developing force-fields. Some models are designed in such a way that the terms do not have a direct physical meaning and only serve to reproduce desired properties[33]. They typically have many terms and parameters that need to be fitted. Another approach is based on designing a model that is supposed to capture the physical phenomena.

2.2.1 Pair-potential methods

One of the most simple approximations is Lennard-Jones pair-potential (LJ). In a pair potential model the energy is treated pairwise, i.e. for each pair of atoms (i, j) the potential only depends on their relative distance $V = \sum_{i \neq j}^N v(|\mathbf{r}_i - \mathbf{r}_j|)$. Lennard-Jones potential has two empirical parameters: ϵ the depth of the potential and σ the finite distance where potential becomes zero. These parameter can be fitted to experimental data or *ab initio* calculations.

$$V^{LJ} = \sum_{i \neq j}^N 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (2.3)$$

The physical meaning of each term in (2.3) is transparent. The first term is responsible for repulsion at short distances due to Pauli exclusion principle, which should be an exponential law, but due to computational efficiency, the twelfth-power law was found sufficiently steep and more convenient. The second term is the dipole-dipole interaction.

LJ potential is computationally cheap and often used for describing interactions in noble gases, however the simplicity comes with the price of limitations. The most crucial limitation for metals is that such potentials consider bond strength to be independent of the local coordination of the atoms.

2.2.2 Embedded Atom Method

Embedded atom method (EAM) was developed by Daw and Baskes[34] for metallic systems. Despite the fact that this method does not work well for directional bonding and can not describe covalency or charge transfer, it shows great performance for purely metallic systems and accounts for coordination. It is achieved by introducing a term that mimics the energy of embedding an atom into a medium created by all other atoms (akin to electron density) and a term which treats pair-wise interactions

$$V^{EAM} = \sum_i \left[F_\alpha \left(\sum_{i \neq j} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{\alpha\beta}(r_{ij}) \right], \quad (2.4)$$

where $\phi_{\alpha,\beta}$ is a pair-wise potential, ρ_β is the contribution to the charge density from atom j of type β at r_i and F_α is an embedding function of an atom of type α into the charge cloud, which represents the energy required to place atom i into the charge cloud.

2.2.3 Charge-Optimized Many-Body

EAM misses many interactions that are crucial for nonmetallic systems and therefore mostly used for pure metals. For systems with ionic and covalent bonding, other potentials should be used. Charge-Optimized Many-Body (COMB) potential was developed by T.Z. Shan *et al.*[35, 36] for oxide systems and was based on Tersoff potential[37]. COMB potential has a complex structure and contains seven terms

$$V^{COMB} = \sum_i [E_i^{self}(q_i) + \sum_{j>i} [E_{ij}^{short}(r_{ij}, q_i, q_j) + E_{ij}^{Coul}(r_{ij}, q_i, q_j)] + E^{polar}(q_i, r_{ij}) + E^{VDW}(r_{ij}) + E^{barr}(q_i) + E^{corr}(r_{ij}, \theta_{jik})], \quad (2.5)$$

E_i^{self} is the self-energy of atom i , E_{ij}^{short} is the bond-order potential between i and j , E_{ij}^{Coul} is Coulomb interaction, E^{polar} is polarization, E^{VDW} is the van der Waals energy, E^{barr} is a charge barrier function, E^{corr} is the angular correction term. Thus, COMB potential is capable of describing much wider class of systems, which comes with high computational price and also requires fitting of a very complex set of parameters. An important feature of COMB potential is that all element-specific parameters are kept the same for all bond types in metallic, ionic or organic materials.

2.2.4 Charge equilibration

COMB potential explicitly includes interatomic distances and charges, which makes it possible to apply this potential to charged systems, but the charge needs to be dynamically equilibrated. One of the possible ways for doing redistribution of the charge was suggested by S.W. Rick *et al.*[38], who developed an approach based on electronegativity equalization – QEq. The idea of the methods comes from the fact that in many-atom systems electronegativity χ_i takes the same value at every nuclear site and it is defined as the first derivative of the electrostatic energy E_{es} with respect to the atomic charge q_i

$$\chi_i = \frac{\partial E_{es}}{\partial q_i} = \chi_i^0 + \frac{\partial^2 E_{es}}{\partial q^2} q_i + \frac{1}{2} \left(\frac{\partial^3 E_{es}}{\partial q^3} \right)_0 q_i^2 + \frac{1}{6} \left(\frac{\partial^4 E_{es}}{\partial q^4} \right)_0 q_i^3 + \sum_{j \neq i}^N J_{ij}, \quad (2.6)$$

where J_{ij} is an empirical screened Coulomb potential. Besides, a condition $\sum_u^N q_i = q_{net}$ must be fulfilled. The resulting set of nonlinear equations can be iteratively solved to obtain equilibrium charge distribution. In calculations the charges are equilibrated before every iteration of the Verlet integration.

2.3 Thermostats

In NVT ensemble, the kinetic energy of the system is controlled and the total energy is not conserved. It represents a case where the system is coupled to a

heat bath. There are different ways to control the temperature. In some cases it is acceptable to apply a thermostat, which allows to mimic the coupling to a heat bath accurately. But sometimes an explicit treatment of the medium (e.g. gas or solvent) that regulates the temperature is required. In such cases, a thermostat can be applied to the medium instead of the system itself. This approach allows to avoid influence of the thermostat on the trajectories of the atoms. The most straightforward way to control the temperature of the system is to rescale the velocities every n steps. This method allows to quickly readjust the temperature but it also crucially affects the trajectories of the atoms. If such effects need to be avoided more "gentle" thermostats can be used.

Andersen thermostat[39] couples the system to a heat bath with the desired temperature. This approach introduces a stochastic element to the temperature by having random collisions of atoms with an imaginary heat bath. With certain frequency random atoms are chosen and their velocities are reassigned randomly by a Maxwell-Boltzmann distribution at the desired temperature. However, these collisions cause decorrelation of the velocities much faster than the NVE dynamics. Thus, Andersen thermostat does not preserve the kinetics of the system. For example, diffusion coefficient calculated with this thermostat would give erroneous values.

Nosé-Hoover thermostat[40] introduces a fictitious dynamical variable in Eq. (2.7), whose physical meaning is friction. This friction slows down or accelerates atoms until the desired temperature is reached

$$H = \frac{1}{2} \sum_i \frac{\mathbf{p}_i^2}{m_i} + V(\{\mathbf{r}_i\}) + \frac{\xi^2 Q}{2} + 3Nk_B T \ln s \quad (2.7)$$

where s is the "position" of the heat bath, Q an effective "mass" associated with s and ξ is the friction coefficient. The implication of this approach is that a microcanonical simulation of the extended system (including heat bath) returns a canonical ensemble for the original system. It is important to notice that this thermostat rigorously reproduces thermodynamics of a canonical ensemble and true dynamics of the system, because the time evolution of the atoms is deterministic and does not involve stochastic perturbations.

CHAPTER 3

Ab initio methods

The Schrödinger equation fully describes the state of a solid in the non-relativistic case. However, the exact solution of this equation can only be found for very simple systems, such as a hydrogen atom. The complexity grows exponentially with increase of the number of interacting particles. Thus, for any reasonable system the exact solution is practically impossible to find. For that reason some approximations are absolutely necessary. In solids the Schrödinger equation has the following form

$$\hat{H}\Psi(\{\mathbf{r}_i, \sigma_i\}, \{\mathbf{R}_i, Z_i\}) = E\Psi(\{\mathbf{r}_i, \sigma_i\}, \{\mathbf{R}_i, Z_i\}), \quad (3.1)$$

where $\hat{H}$ is a Hamiltonian of the system, Ψ is the wavefunction of both the electrons at $\mathbf{r}_i$ with spin σ_i and the nuclei at $\mathbf{R}_i$ with charge Z_i . During the years a number of approximations and models has been developed to tackle that problem.

One of the first approximations that has to be made is the Born-Oppenheimer approximation[41]. It assumes that the many-body problem of Eq. (3.1) can be divided into electron and nucleus subsystems. Since the electron subsystem quickly adapts to slowly changing nuclei potential, the electron Schrödinger equation can be solved for fixed atomic positions.

$$\hat{H}_e(\{\mathbf{R}_i, Z_i\})\Phi(\{\mathbf{r}_i, \sigma_i\}) = E(\{\mathbf{R}_i, Z_i\})\Phi(\{\mathbf{r}_i, \sigma_i\}), \quad (3.2)$$

where Φ is the electron wavefunction and the electron Hamiltonian:

$$\hat{H}_e(\{\mathbf{R}_i, Z_i\}) = \hat{T} + \hat{U} + \hat{V}_{ext}(\{\mathbf{R}_i, Z_i\}), \quad (3.3)$$

$\hat{T}$ is kinetic energy, $\hat{U}$ is electron-electron interaction and $\hat{V}_{ext}$ is external nuclei potential.

The periodicity of a solid allows for yet another simplification. The Bloch theorem[42] claims that due to translational symmetry, a single electron wavefunction $\phi(\mathbf{r})$ can be written as

$$\phi_k(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_k(\mathbf{r}), \quad (3.4)$$

where $u_k(\mathbf{r})$ is a periodic function and $\mathbf{k}$ is a crystal wave vector. Thus, according to Bloch's theorem an infinitely large periodic system can be reduced to one primitive cell. Even though this approach substantially simplifies the problem, the exact solution of the electron Schrödinger equation remains an exponential function of the number of particles.

3.1 Density functional theory

The development of density functional theory (DFT) started with Thomas and Fermi[43, 44]. Hohenberg and Kohn[45] have developed a rigorous mathematical justification and later Kohn and Sham[46] developed a practical approach for this theory.

The Hohenberg-Kohn theorems

The conceptual foundations for DFT were developed by Hohenberg and Kohn[45]:

Theorem 3.1 *For any system of interacting electrons in an external potential $V_{ext}(\mathbf{r})$, that potential $V_{ext}(\mathbf{r})$ can be defined, up to a numeric constant, from the ground state electron density $n_0(\mathbf{r})$.*

$V_{ext}(\mathbf{r})$ is a functional of the ground state density $n_0(\mathbf{r})$. Thus, this lemma allows a variable transformation from a complicated wavefunction to electron density, which is a function of a coordinate in three dimensional space.

Theorem 3.2 *For any external potential a valid energy functional $E[n]$ can be defined through electron density $n(\mathbf{r})$. The ground state energy of the system corresponds to the global minimum of the functional, and the density that minimizes the functional is the exact ground state $n_0(\mathbf{r})$.*

The energy functional for a given external potential $V_{ext}(\mathbf{r})$ can be expressed in the following form:

$$E[n] = F[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r, \quad (3.5)$$

where $F[n]$ is the Hohenberg-Kohn functional containing kinetic energy $\hat{T}$ and electron-electron interaction $\hat{U}$ and the last term is interaction with potential $V_{ext}(\mathbf{r})$.

Kohn-Sham equations

Kohn and Sham suggested approach where the many-body problem is replaced with an auxiliary system of non-interacting with each other particles. These particles can only interact with an effective potential, such that the ground state electron density of this auxiliary systems is the same as the many-body problem ground state density[46]. For this system the kinetic energy is:

$$\hat{T}_0 = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2, \quad (3.6)$$

and the Hohenberg-Kohn functional is

$$F[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \frac{e^2}{8\pi\epsilon_0} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{xc}[n(\mathbf{r})], \quad (3.7)$$

where $T_0[n(\mathbf{r})]$ is the kinetic energy functional of the non-interacting particles, $E_{xc}[n(\mathbf{r})]$ is exchange-correlation energy functional, describing all the many-body effects. This transformation leaves the density functional theory exact if we know E_{xc} . The effective potential of the auxiliary systems is

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + V_{xc}(\mathbf{r}) \quad (3.8)$$

The second term of the sum in Eq. (3.8) is the mean-field electrostatic interaction and the third term accounts for exchange and correlation effects appearing due to the fact the original system is an interacting many-body system. This potential can be obtained from the exchange-correlation energy functional:

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (3.9)$$

Constrained Lagrange minimization of the energy functional with respect to the electron density defines the single-particles Kohn-Sham equations:

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{eff}(\mathbf{r}) - \epsilon_i \right) \phi_i(\mathbf{r}) = 0, \quad (3.10)$$

$$n(\mathbf{r}) = \sum_i^N |\phi_i^2(\mathbf{r})|. \quad (3.11)$$

Thus, the Kohn-Sham method allows to obtain the exact density, however, the success of this method depends on how well the xc -functional can be approximated.

3.2 Exchange-correlation functionals

As was shown before, Kohn and Sham suggested a transformation that allows to reduce a very complex many-body problem by a much simpler system of non-interacting particles. The most crucial element of this approximation is the choice of exchange-correlation functional. There are hundreds of functionals with different advantages and weaknesses but there is no "exact" universal functional.

Local and semi-local functionals

A very simple approximation for the exchange-correlation energy functional is the local density approximation (LDA)

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \epsilon_{xc}^{heg}(n(\mathbf{r}))n(\mathbf{r}) d^3r \quad (3.12)$$

here, ϵ_{xc}^{heg} is the xc-energy per particle of a homogeneous electron gas of density $n(\mathbf{r})$. Its exchange part can be derived analytically and the correlation part is known from the parametrisation of quantum Monte Carlo simulations [47, 48]. LDA is exact for homogeneous electron gas and may be a good approximation for cases of nearly free electrons, where electron density varies slowly, such as metal.

In most cases, the density does not vary slowly. Functionals that consider the spatial variation of the density belong to the class of generalized gradient approximations (GGA)

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int f(n(\mathbf{r}), \nabla n(\mathbf{r}))n(\mathbf{r}) d^3r, \quad (3.13)$$

where f is any function of the density and its derivative. GGA functionals are known to perform better. One particular functional proposed by Perdew, Burke and Ernzerhof (PBE)[49] has gained high popularity for its reliability and accuracy[50]. PBE functional is one of the most popular functionals in solid-state community. Despite the accuracy and predictive power local and semi-local functionals have a number of shortcomings, the most important ones are the lack of the derivative discontinuity and presence of self-interaction, which manifests itself in delocalization of the localized states and underestimation of band gaps in semiconductors[50].

DFT+U approach

While there are many factors affecting accuracy of DFT, there is a class of systems where DFT is known to be notoriously bad – correlated systems. Due to over-delocalization of valence electrons and severe underestimation of Mott insulator's band gaps by local and semi-local exchange-correlation functionals, DFT fails at describing systems with strong correlations. It may even give a wrong metallic ground state in some cases.

In order to improve the description of these systems, Anisimov *et al.*[51] suggested to apply a correction to the specific states f or d in LDA functional. This correction has a form of Hubbard-like on-site interaction. Later, this approach was expanded onto other semi-local and local functionals. These methods are often called DFT+U. Within DFT+U the total energy of a system can be written as follows:

$$E_{DFT+U}[n(\mathbf{r})] = E_{DFT}[n(\mathbf{r})] + E_{Hub}[\{n_{mm'}^{I\sigma}\}] - E_{dc}[\{n^{I\sigma}\}], \quad (3.14)$$

here E_{Hub} is the term containing electron-electron interaction from Hubbard Hamiltonian. This correction is additive, hence it is necessary to eliminate from DFT energy functional (E_{DFT}) the part of the interaction contained in E_{Hub} to avoid double-counting E_{dc} , which is modeled as a mean-field approximation to E_{Hub} .

$$n_{mm'}^{I\sigma} = \sum_{k,v} f_{kv}^{\sigma} \langle \psi_{kv}^{\sigma} | \phi_{m'}^I \rangle \langle \phi_m^I | \psi_{kv}^{\sigma} \rangle, \quad (3.15)$$

where ψ_{kv}^{σ} occupied Kohn-Sham orbitals, ϕ_m^I localized basis set, f_{kv}^{σ} are the Fermi-Dirac occupations of the Kohn-Sham states. A. Liechtenstein *et al.*[52] formulated a basis set independent LDA+U

$$E_{Hub}[\{n_{mm'}^I\}] = \frac{1}{2} \sum_{\{m\}, \sigma, I} \langle mm'' | V_{ee} | m'm''' \rangle n_{mm'}^{I\sigma} n_{m''m'''}^{I-\sigma} + (\langle mm'' | V_{ee} | m'm''' \rangle - \langle mm'' | V_{ee} | m'''m' \rangle) n_{mm'}^{I\sigma} n_{m''m'''}^{I\sigma} \quad (3.16)$$

In the fully localized limit[53, 54] E_{dc} has the following form:

$$E_{dc}[\{n_{mm'}^I\}] = \sum_I \frac{U^I}{2} n^I (n^I - 1) - \sum_{\sigma} \frac{J^I}{2} n^{I\sigma} (n^{I\sigma} - 1) \quad (3.17)$$

where $n^{I\sigma} = Tr[n_{mm'}^{I\sigma}]$ and $n^I = \sum_{\sigma} n^{I\sigma}$. Dudarev *et al.*[55] suggested a simplified scheme, where $U \approx \langle mm'' | V_{ee} | m'm''' \rangle$ and $J \approx \langle mm'' | V_{ee} | m'''m' \rangle$ and $U_{eff} = U - J$. Thus, Dudarev's energy functional is

$$E_{DFT+U}[\{n_{mm'}^I\}] = E_{DFT}[n(\mathbf{r})] + \sum_{Im\sigma} \frac{U_{eff}^I}{2} (n_m^{I\sigma} - (n_m^{I\sigma})^2) \quad (3.18)$$

The potential can be obtained by calculating derivative of the energy functional:

$$V_{DFT+U}[n(\mathbf{r})] = V_{eff}[n(\mathbf{r})] + U_{eff} \left(\frac{1}{2} - n_m^{\sigma} \right) \quad (3.19)$$

3.3 Basis sets

In order to solve Kohn-Sham equations (3.10), the wave functions need to be constructed from a basis set:

$$\psi = \sum_i c_i \phi_i \quad (3.20)$$

In practice the sum in equation (3.20) cannot be infinite and it must be truncated, which makes the set incomplete. Thus, the convergence of the total energy with the number plain waves is necessary for obtaining correct results.

3.3.1 Augmented Plane Waves

As was shown by Slater[56], wave functions at the atomic sites are very similar to the atomic wave functions, while in the region between the sites wave functions are smooth and slowly varying. This strongly different behavior of the wave function led to a partitioning of the space into two different regions, the muffin-tin (MT) spheres of R_{MT} centered on the atomic sites and the interstitial region between the MT spheres. In this case, different kinds of basis sets can be used for different regions and then matched to each other on the MT sphere into a smoothly behaving function in all space.

In the interstitial region, the Kohn-Sham wave function can be expanded into plane waves. However, near to the nuclei the wave functions rapidly oscillate and would require too many plane waves for the expansion. Slater proposed a scheme, where plane waves are used for the interstitial region, and inside R_{MT} the basis set is augmented by localized radial orbitals. This method is called Augmented Plane Waves (APW)[57, 58]:

$$\phi_{\mathbf{K}}^{\mathbf{k}}(\mathbf{r}, \varepsilon) = \begin{cases} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} & \mathbf{r} \notin R_{MT} \\ \sum_L f_L^{\mathbf{k}+\mathbf{K}}(r, \varepsilon) Y_L(\hat{\mathbf{r}}) & \mathbf{r} \in R_{MT} \end{cases} \quad (3.21)$$

where $L = (\ell, m)$ and Y_L are spherical harmonics and $f_L^{\mathbf{k}+\mathbf{K}}$ is a radial function:

$$f_L^{\mathbf{k}+\mathbf{K}}(r, \varepsilon) = A_L^{\mathbf{k}+\mathbf{K}} \chi_\ell(r, \varepsilon), \quad (3.22)$$

χ_ℓ is the solution to the radial Schrödinger equation with the coefficients A . The dependence of ϕ on ε significantly increases the computational cost. In order to reduce the complexity, Andersen[59] suggested a Linearised Augmented Plane Wave (LAPW) method to linearise the energy dependence of the localized orbitals. Thus, the radial functions are approximated by an expansion:

$$f_L^{\mathbf{k}+\mathbf{K}} = A_L^{\mathbf{k}+\mathbf{K}} \chi_\ell(r, E_\ell) + B_L^{\mathbf{k}+\mathbf{K}} \dot{\chi}_\ell(r, E_\ell), \quad (3.23)$$

here E_ℓ are linearisation energies and the coefficients A and B are determined by matching solutions at the MT sphere.

Another approach was suggested by Sjöstedt, Nordström and Singh[60] where the general form of APW Eq. (3.21) is not changed but now evaluated at fixed energies E_ℓ in order to keep the linear eigenvalue problem and then local orbitals (lo) are added into MT sphere to have enough variational flexibility in the radial basis functions:

$$g_L(r) = C_L \chi_\ell(r, E_\ell) + D_L \dot{\chi}_\ell(r, E_\ell), \quad (3.24)$$

here coefficients C_L and D_L do not depend on k , which drastically reduces the computational time. A conventional way to specify the size of the basis set is by the product $R_{MT} \cdot K_{max} = 6 - 9$. Often, these methods are used in combinations

and they do not make any assumptions on the shape of the potential and are referred as *all-electron full-potential* methods. This method is implemented in WIEN2k code[61] and was used in this thesis for calculations in Chapter 6.

3.3.2 Projector Augmented Waves

Projector Augmented Waves (PAW) method suggested by Blöchl[62] is another common way to reduce the complexity and avoid large numbers of plane waves. The idea of the method is based on mapping the wavefunction $|\psi\rangle$ onto a smooth auxiliary wavefunction $|\tilde{\psi}\rangle$:

$$|\psi\rangle = \hat{\mathcal{T}} |\tilde{\psi}\rangle, \quad (3.25)$$

here $\mathcal{T}$ is a linear transformation. This smooth auxiliary wavefunction can be efficiently expanded in plane waves and $|\psi\rangle$. Thus, $|\tilde{\psi}\rangle$ differ only near the nuclei

$$\hat{\mathcal{T}} = 1 + \sum_{a=1}^N \hat{\mathcal{T}}^a, \quad (3.26)$$

where $\hat{\mathcal{T}}^a$ has no effect outside a spherical augmentation region near the nucleus. Pseudo wavefunction can be expanded in pseudo partial waves around each atom:

$$|\tilde{\psi}\rangle = \sum_i |\tilde{\phi}_i\rangle c_i, \quad (3.27)$$

since $\hat{\mathcal{T}}$ is linear, coefficients can be written as $c_i = \langle p_i | \tilde{\psi} \rangle$. p_i are called projector functions, such that $\langle p_i | \tilde{\phi}_j \rangle = \delta_{ij}$. All-electron partial waves ϕ are typically chosen to be solutions to the Kohn-Sham equation for an isolated atom. Thus, the transformation $\hat{\mathcal{T}}$ can be expressed as

$$\hat{\mathcal{T}} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i |, \quad (3.28)$$

The full wavefunction can be then written as

$$|\psi\rangle = |\tilde{\phi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\psi} \rangle \quad (3.29)$$

In this equation, only the first term on the right-hand side is calculated for the system of interest, the second term is pre-calculated for each element, which allows for substantial increase of efficiency. For PAW methods the size of the basis set is usually given in terms of the amount of plane waves, which is expressed in energy units and called cut-off energy. The results of Chapter 6 have been obtained in the Vienna Ab-initio Simulation Package, VASP[63], which is one of the realizations of the described method.

3.3.3 Gaussian-type orbital

In molecular systems, where wave functions are strongly localized and more atomic-like, Gaussian-type orbitals (GTO) are more common to use. From physical perspective Slater-type functions, $e^{-\alpha r}$, have the same radial distribution as hydrogen orbitals, but they require numerical integration, whereas GTO, $e^{-\alpha r^2}$, allow for analytical integration. The computational gain is so significant, that the loss of accuracy is justified in most practical cases. However, such a basis set is non-orthogonal, and thus more computationally demanding compared to plain wave basis sets. Thus, GTO are typically used for atomic and molecular systems. One particular implementation of that approach `Gaussian09`[64] was used in this thesis.

3.3.4 Basis sets for nanosystems

In solids, the states with atomic-like wave functions and large binding energies are called *core states* and electrons in partially occupied shells with lower binding energies are called *valence states*. Since valence states are strongly delocalized, plain waves is the most convenient basis set. However, as was discussed in Chapter 1, nanoparticles of different size may possess drastically different electronic structures going from molecule-like discrete configuration to solid-like bands. Both cases can be treated with plain wave basis set, but localized wave functions require more plain waves.

The approaches based on plain wave basis sets are typically developed for solids and incorporate their translational symmetry to minimize the size of the system. In small nanoparticles, translational symmetry is broken and periodic boundary conditions do not apply. These nanoparticles can be treated within a supercell approach, where a nanocluster is separated from the boundaries of the supercell by vacuum to avoid interaction with its repeated image. A big disadvantage of this approach is that vacuum increases computational demand for the calculation. Plain waves are evenly distributed within the supercell even in vacuum, which only serves to avoid interaction with periodic images.

The electromagnetic radiation interacts with matter differently depending on the wavelength. The analysis of this interaction is called spectroscopy and it is an extremely powerful method for characterization of solids, molecules and nanoclusters. In this thesis, a particular range of the radiation is considered for analysis of the electronic structure. The X-ray photon energy corresponds to the binding energy of the core states and hence can be used for their characterization. This kind of spectroscopies have gained a serious boost with the development of advanced synchrotron facilities in the last few decades. Furthermore, the advent of free-electron lasers opened up new horizons in terms of intensity, energy and time-resolution[65–67].

Some of the available X-ray spectroscopies are shown in Fig. 4.1. Binding energies of the core electrons are very sensitive to the local environment and often used for its characterization. Due to the time-scale of the electronic relaxations these processes are much faster than any atomic relaxation.

The interpretation of the measured spectra is not always an easy task. For that reason theoretical methods have been applied to model the processes occurring under the electromagnetic radiation. The general issue of the theoretical spectroscopy for solids arises from the fact that DFT methods are not expected to work well for excited systems and that the energies of the Kohn-Sham particles are not supposed to match the binding energies of electrons. In this chapter, different approximations for modelling XPS and XAS spectra based on DFT are discussed.

4.1 X-ray photoelectron spectroscopy

The phenomenon of electron photoemission was first observed by Hertz in 1887 and later explained as the photoelectric effect by Einstein in 1905. In 1921 he was

Figure 4.1. Core spectroscopy processes. X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS)

awarded a Nobel Prize for that discovery.

X-ray photoelectron spectroscopy as shown in Fig. 4.1 measures the kinetic energy of the electron emitted from the system. The emission of the electron occurs due to the interaction of a core-electron with an X-ray photon. In the experiments the photons are monochromatic and radiated onto the sample. The results are then collected as the intensity (number of particles) for the corresponding photon energy

$$E_B = \hbar\omega - E_{kin} - \phi \quad (4.1)$$

where E_B is the binding energy of an electron, $\hbar\omega$ is the photon energy, E_{kin} is the measured kinetic energy and ϕ is the work function. The presence of a core-hole after the excitation of an electron affects all other electrons. The system before the emission of an electron is often referred as *initial* state and the system after the emission of the core-electron is *final* state. The missing electron is usually called *core-hole* and it may have a prominent effect on the other electrons, which is reflected in the measured spectra. The final state concept can be used to describe the appearance of the *satellite* lines near the main spectral core-line.

The changes of the binding energies are often analyzed as a Core-Level Shift (CLS) or a shift relative to some reference energy: $E_{CLS}^{exp} = E_B - E_B^{ref}$. For solids, this reference energy is usually the corresponding binding energy in bulk system of the pure element. There are many different effects that may affect the binding energies of electrons, which make them very sensitive to the changes in the local environment. These effects include[68]:

- Interatomic charge transfer
- Intra-atomic charge transfer
- Changes in the screening of the core-hole in final state
- Size of the system
- Geometry and structure
- Local coordination

It is important to notice that if the shift is very small or zero, it does not automatically imply that the system of interest does not differ from the reference system, because different contributions may cancel each other.

As was discussed earlier, DFT is not supposed to work for excited systems and can only be expected to give reliable results for systems in the ground state. However, due to error cancellation the changes of the binding energies of Kohn-Sham particles were found to agree well with experimental values[68, 69]. Thus, DFT approach was shown to work for XPS calculations and in this thesis only the methods based on independent particles approaches are discussed.

4.1.1 Complete screening picture

The shifts of the core-electron binding energies can be obtained directly from the difference between binding energies of Kohn-Sham particles. The effects of the core-hole can also be incorporated by introducing a hole to the state of interest (removing an electron). However, as we discussed in Chapter 3, the treatment of core-electrons in the system makes calculations more demanding, while pseudopotential approach can significantly decrease computational time. Hence approaches without explicit treatment of the core-electrons, such as *complete screening approximation*, can be used in order to decrease computational demand. In the complete screening approximation the binding energy shifts can be calculated from total energies. Thus, the calculations require total energy of the unperturbed initial state and relaxed final state with the core-hole. The main assumption of this approximation is that in metallic systems a core-hole of the final state is fully screened by the valence electrons, as shown in Fig. 4.2.

Figure 4.2. Initial and final state

The initial and final states can be connected through Born-Haber cycle in a thermodynamics model approach[69]. The core-ionized atom Z^* (atomic number Z) is replaced

by an atom of the next element in the periodic table $Z+1$. The core-hole is assumed to act similarly to an extra proton in the atoms, such that the screening by the valence electron is essentially the same as in $(Z+1)$ atom. The Born-Haber cycle can give a more intuitive justification for this approximation and also provides a scheme how CLS can be calculated using experimentally measured thermodynamic properties.

In Fig. 4.2, initial and final states are schematically depicted. After the ejection of the core-electron, the core-hole is screened by electrons in the valence band. The screening results in the appearance of an extra electron in the valence states of the atom.

The complete screening picture was successfully used by Johansson and Mårtensson[69] to calculate CLS between free atoms and atoms in solids. Olovsson[70] and Marten[71] performed a comprehensive study of CLS in alloys. Core-level shift for surface atoms were studied by Alden *et al.*[72, 73]. This approach is also used in molecular systems where the shifts are typically larger than in solids. Thus, it was shown that $Z+1$ calculations produce accurate results. However, nanoclusters is a complex case since it is an intermediate system between individual atom and bulk solid. Grönbeck[74] have applied complete screening picture to investigate the CLS in thiolate coated gold nanoclusters and shown that this approximation holds even from small nanoclusters and can reproduce the experimental results with reasonable accuracy. Tchapyguine *et al.*[75] adapted the Born-Haber cycle for the case of nanoclusters.

In Chapter 6, the results of the comprehensive study of the CLS in metal nanoclusters using complete screening picture are provided and the origins of the shifts are explained and discussed in great detail.

4.1.2 Model for surface core-level shifts in clusters

Because surface atoms in clusters have different chemical environment from core atoms, their binding energies are shifted. These shifts can be explained in a simplified model showed in Fig. 4.3. This model was adapted from solids for the case of nanoclusters large enough to form electronic bands. Surface atoms have smaller coordination numbers and thus narrower valence bands. Fig. 4.3 is a schematic representation of how density of states (DOS) of core and valence differ for core and surface atoms of a nanocluster. Fig. 4.3a represents the case of transition metals with less than half-filled d^x bands with $x \lesssim 5$. Bands in red color corresponds to core DOS and blue ones correspond to the shell. In the left panel, we see a hypothetical state, where we allow the narrowing of the band on the surface, but have not allowed the charge transfer between core and surface atoms. In this state the binding energies of the core states E_B^b and E_B^s , for core and surface correspondingly, essentially do not change because the effect of only valence band narrowing does not have any strong impact on the core states. The major effect is due to the fact that the Fermi level on the surface moves above that of core. To bring the Fermi level $E_F^{s,b}$ of core and shell back to equilibrium a small amount of charge must flow from the surface bands into core, as shown in the right panel. This charge transfer leads to the shift of the electrostatic potential and thus

Figure 4.3. Model for the surface-atom core level shifts for a) transition metals with less than half-filled d -band, b) transition metals with more than half-filled d -band and c) noble metals. See text for more discussion.

moves both surface-atoms bands and core-state by a comparable amounts. The scheme shows how centers of gravity of bands $\langle \epsilon \rangle_{b,s}$ shift together with the core states $E_B^{s,b}$

For the case of more than half-filled band d^x , where $x \gtrsim 5$, the states move in the opposite direction. Fig. 4.3b shows how narrowing of the d -band lowers the Fermi level E_F^s of the surface atoms. The charge transfer from core of a cluster to its surface aligns the bands and causes the shift of the binding energies toward smaller values.

This simple model can also be applied to noble metal clusters with $d^{10}s^1$, as shown in Fig. 4.3c. The left panel shows a hypothetical state where undercoordination of surface atoms causes the narrowing of the valence band. Which in turn lowers the Fermi level of surface atoms. The charge transfer from core to surface atoms defines the shift of the core states.

4.2 X-ray absorption spectroscopy

X-ray absorption spectroscopy measures the absorption of the electromagnetic irradiation by the sample in the X-ray region. As shown in Fig. 4.1, X-ray photon promotes an electron from a core state into the valence band. The transition from different states is denoted by K , L or M for principal quantum numbers $n = 1, 2, 3$, respectively. A typical absorption spectrum is shown in Fig. 4.4. The work presented in this thesis concerns only the edge of the spectrum, depicted XANES in Fig. 4.4, since it reflects the state of the electrons. The extended part of the spectra is related to the processes of scattering of the promoted electron in interaction with the neighboring atoms and can be used to characterize local structure.

Figure 4.4. Typical absorption spectrum. X-ray absorption fine structure (XAFS), X-ray absorption near edge structure (XANES), Extended X-ray absorption fine structure (EXAFS).

The X-ray absorption coefficient is proportional to the transition rate as given by Fermi's golden rule. A straightforward approach for calculations of X-ray absorption are based on the one-electron approximation of the golden rule:

$$\mu \propto \sum_f |\langle \psi_f | \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (4.2)$$

The wave functions ψ_i and ψ_f are the initial and final states of the effective one-electron Hamiltonians H for the initial state and H' for the final state, with energies E_i and E_f , respectively. $\mathbf{p}$ is the momentum operator and $\mathbf{A}(\mathbf{r})$ is the vector potential of the incident electromagnetic field, which may be approximated $\mathbf{A}(\mathbf{r}, t) \cong \hat{\epsilon} A_0 e^{i\mathbf{k} \cdot \mathbf{r}}$. For core-states $\mathbf{k} \cdot \mathbf{r} \ll 1$ then $e^{i\mathbf{k} \cdot \mathbf{r}} \cong 1$, this is called dipole approximation

$$\mu \propto \sum_f |\langle \psi_f | \hat{\epsilon} \cdot \mathbf{r} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (4.3)$$

The X-ray absorption selection rules determine that the transition matrix $|\langle \psi_f | \hat{\epsilon} \cdot \mathbf{r} | \psi_i \rangle|$ is nonzero if the orbital quantum number of the final state differs by 1 from the initial state ($\Delta L = \pm 1$, i.e. $s \rightarrow p$, $p \rightarrow s$ and so on) and the spin is conserved ($\Delta S = 0$). The quadrupole terms can also be included into the transition matrix: $|\langle \psi_f | \mathbf{p} \cdot \hat{\epsilon} + i(\mathbf{p} \cdot \hat{\epsilon})(\mathbf{k} \cdot \mathbf{r}) | \psi_i \rangle|$. The quadrupole contribution is of order $(Z\alpha)^2$, where Z is the nuclear charge and $\alpha \cong 1/137$ is the fine structure constant. In quadrupole approximation, the transitions imply that the orbital quantum number differs by 2 from the initial state ($\Delta L = \pm 2$, i.e. $s \rightarrow d$, $p \rightarrow f$ or $\Delta L = 0$, i.e. $s \rightarrow s$ and so on). They are typically 100 times smaller and can be neglected for most cases. In the dipole approximation, the shape of the absorption spectrum should appear as the partial density of empty states projected on the absorbing site, convoluted with a Lorentzian. The Lorentzian broadening is due to the finite lifetime of the core-hole. The effect of the core-hole can be included explicitly by removing an electron from one of the core states. In calculations, after the removal of the core electron, the charge density has to be relaxed in a self-consistent manner. This approximation gives an adequate accuracy for the cases, where the interaction between the electrons in the final state is relatively weak, but such calculations require explicit treatment of core-electrons.

Structural properties of nanoclusters

The structure of nanoclusters may significantly differ from the structure of the bulk material. For most applications the structure is crucial and needs to be controlled with high precision. As was discussed in Chapter 1, the thermodynamically favorable structure is determined by the competing contributions from strains and the surface energies. However, the growth conditions of the synthesis process may affect the structure in a major way. Thus, the kinetics of the growth is an important phenomenon that needs to be considered. During the growth process, the morphology may change and this transition can play a determining role for the resulting structure.

5.1 Hollow cathode synthesis

The synthesis of nanoclusters is a very complex issue and the requirements for the resulting nanoclusters are very strict. In order to fulfill these requirements, the synthesis should allow for a very fine tuning of the parameters and have a high growth rates in a wide range of sizes. A very promising method was developed by I. Pilch *et al.*[76]. The method is based on a high power pulsed hollow cathode (HC) discharge. The authors of the method showed that this technique allows to achieve a high degree of ionization of the sputtered species compared to other plasma based synthesis techniques.

In Fig. 5.1, the sketch of the experimental setup is shown. The cathode is made of material of growth and plays the role of a target. The anode ring is placed below the cathode and forces the discharge through the region where the nanoparticles grow. The growth process starts with the nucleation in three-body collisions of the sputtered vapor[77]. After the dimers are formed the growth continues by attaching atoms to the growth nuclei. When the density becomes high enough

Figure 5.1. Experimental setup. [76]

the particles coagulate and form larger clusters. Small clusters can be neutral or get charged positively or negatively in stochastic processes. However, when the cluster attains a certain size (around a few nanometers), the charge stabilizes by the balance between ion and electron currents to the cluster[78]. Nanoparticles that attained the balanced charge repel each other and cannot coagulate. Thus, the growth can only continue by attaching atoms or ions. The estimates show that the collection cross section of singly-charged ions is two orders of magnitude larger than cross section of atoms. Finally, the particles are collected on the substrate. It was shown that by varying the pulse parameters such as frequency, pulse width, or peak current, it is possible to change the size and structure of the nanoparticles.

One of the main drawbacks of the plasma-based synthesis methods is their low productivity due to a poor utilization of the material. The results show that the growth rates in the HC method can achieve 470 nm/s, while the growth from neutral atoms is estimated to be around 3 nm/s[15]. The authors suggest that the increased trapping can be explained by orbital motion limited (OML) collection of ions.

5.2 Nanoparticle growth by collection of ions

The growth of the nanoparticles in plasma conditions can be treated within OML[79, 80] approximation, as was shown in [15]. The OML theory was initially proposed for the conditions when the shielding length is much larger than the nanoparticles radius, and the collisions are rare and can be neglected. However, it was shown that even rare collisions can result in an increase of the ion current[81–84]. Several of the suggested theories are based on OML theory and also include collision-enhanced collection (CEC) (see Fig. 5.2) of ions[81, 82, 85]. There, the

ion current includes both the OML contribution and has a term corresponding to the collection of ions after collision within a capture radius. Despite the fact that the mean free path is much larger than the capture radius, the volume of the sphere with a capture radius is so large that the contribution from CEC is noticeable.

Figure 5.2. Sketch of the collection processes for orbit motion limited (OML) collection and collision enhanced collection (CEC)

Thus, a model that includes both OML and CEC was adapted to the parameters of the HC method. It was shown that the estimated growth rates are in a good agreement with experiment. The contribution of CEC in the ion current turned out to be 10% despite the fact that the ion mean free path is four orders of magnitude larger than the nanoparticle radius and two orders of magnitude larger than the capture radius of the CEC model.

The applicability of the developed model has been thoroughly explored. In particular, in the case of temperatures where the evaporation of the particles becomes faster than the growth rates such a model cannot be applied. See details in Paper III. In fact the rates of the evaporation depend on the size and temperature of the nanoparticles in a complex manner.

5.3 Evaporation of nanoclusters

It is known that the temperature of nanoparticles in plasma growth process can significantly differ from the gas temperature. Thus, the evaporation rates may have a crucial effect on the process if the temperature is high enough. In order

to estimate the rates of evaporation as a function of the size of a copper nanocluster and its temperature, Classical Molecular Dynamics simulations have been performed. The simulations were carried out with embedded atom-method potentials[86]. The evaporation process was simulated in a long runs of 400 ns for each size and temperature to collect sufficient statistics. The evaporated atoms were removed from the simulation to avoid condensation. Temperature control was carried out by rescaling of the velocities, such that when an atom leaves the cluster the temperature is quickly readjusted back to the initial value.

Figure 5.3. The evaporation rate as a function of the temperature, calculated by Molecular Dynamics simulations, for nanoparticles with cluster sizes from 108-2048 atoms.

The simulations for each temperature value were performed in series of five in order to facilitate the error estimations. In Fig. 5.3, the error bars for low temperatures are noticeably larger, this is due to poor statistics of evaporation events at these temperatures. The evaporation rates exponentially drop with the decrease of the temperature. Thus, the evaporation events become rare and in order to obtain a value with small error, the length of the simulation needs to be increased, which is very computationally expensive. The deviation from the linear dependence in an Arrhenius plot should also be attributed to statistical effects. The calculated evaporation rates are compared to the rates for the bulk material of copper using Ohring2002

$$\Gamma_{ev,bulk} = \frac{\beta}{\sqrt{2\pi m_{Cu} k_B}} \cdot \frac{p_v}{\sqrt{T}} \approx 4.38 \cdot 10^{25} \cdot \frac{p_v}{\sqrt{T}} \quad (5.1)$$

where β is a constant between 0 and 1, p_v the vapor pressure in Torr and T the temperature of the material in K. The units of the evaporation rates are $m^{-2}s^{-1}$ with a maximum rate of evaporation when $\beta = 1$. For estimates of the bulk evaporation rates, the data for the vapor pressure and temperatures were taken from [87]. The trend shows that the evaporation rate for bulk copper is

one order of magnitude higher compared to small nanoparticles and quickly tends to the bulk value with increase of the size. The largest size considered in our simulations is 2048 and even for such small clusters the evaporation rates are very similar to the bulk values. The estimated deposition rate of ions is $10^{25} m^{-2} s^{-1}$, which is too low for Molecular Dynamics simulations. However, a comparison with bulk evaporation rate can be made: for $T = 1205\text{ K}$ and $p_v = 10^{-5}\text{ Torr}$ $\Gamma_{ev,bulk} = 1.27 \cdot 10^{19} m^{-2} s^{-1}$. Thus, the evaporation will be compensated by deposition at temperatures below $T = 1200\text{ K}$

5.4 Growth of nanoclusters in a plasma

In the previous section, the growth of nanoclusters in plasma has been analyzed on a macro-scale. This section is devoted to analysis of this process on a scale of an individual nanocluster and the processes of growth in plasma is compared to inert gas aggregation (IGA) growth. The results of this section are presented in Paper I.

The balance of ion and electron fluxes determine the charge on a cluster. Once a nanocluster attains a certain size, the charge stabilizes and the growth continues by collection of ions and neutral atoms and no coagulation between clusters is possible thanks to the repulsion forces. Thus, it would be interesting to consider this stage by means of Molecular Dynamics. One way to approach it is to add metal atoms into the simulation and model the growth process from the initial nucleation as was done by G. Grochola *et al.*[88]. Another approach suggests to consider growth from a certain stage where the seed of the growth has been formed[89].

5.4.1 Model

MD does not treat electrons explicitly and can not include a number of processes occurring in plasma. Therefore we have to neglect thermal radiation, luminescence, thermionic emission, electron detachment, and field emission of electrons. In Fig. 5.4, a simplified scheme of the plasma environment is depicted. Due to Coulomb attraction, ions will be accelerated towards the surface of a nanocluster, but since they have random initial thermal velocities, the angle of incidence will depend on the initial conditions. If the initial velocity is small, the ion will be trapped by the NC. In the case of high energy, ions may be scattered on NC and not be trapped. The estimations show that a potential for a NC of 1 nm should be within a range from -1 to -4 eV.

Simulation of charged particles in MD is a very difficult task, since charge transfer requires explicit treatment of the electrons. However, it is possible to compute trajectories of ions up to a certain *release* radius, where they can be released with known velocity and no charge.

In order to compute the trajectories of the ions and their angular distribution within the field of NC, we need to solve a two-body problem as shown schematically in Fig. 5.5. The ion velocities far from NC can be considered isotropic. Therefore,

Figure 5.4. Model of a cluster in plasma. Velocities and angular distribution of ions moving in the Coulomb potential are calculated analytically up to the release radius. Within the release sphere, the calculation of the ion trajectory is computed in MD simulations.

the probability distribution for the angle α_0 between the radius to the ion and the ion velocity is

$$\int 2\pi A \sin \alpha_0 d\alpha_0 = 1 \quad (5.2)$$

From the conservation of angular momentum

$$\mathbf{r}_0 \times m\mathbf{v}_0 = \mathbf{R} \times m\mathbf{v} \quad (5.3)$$

Figure 5.5. Scheme of interaction between an incoming ion and a cluster with opposite charges.

where $\mathbf{r}_0$ is the distance from the center of the cluster to the initial position of the ion and $\mathbf{v}_0$ is the corresponding velocity, $\mathbf{R}$ and $\mathbf{v}$ are the distance and velocity of the ion near the cluster surface, m is the ion mass and α is an angle between $\mathbf{R}$ and $\mathbf{v}$. Then

$$r_0 v_0 \sin \alpha_0 = R v \sin \alpha \quad (5.4)$$

α_0 can be derived from (5.4)

$$\alpha_0 = \arcsin \left(\frac{Rv}{r_0 v_0} \sin \alpha \right) \quad (5.5)$$

Transformation of the coordinates can be written as

$$\frac{d\alpha_0}{d\alpha} = \frac{\frac{Rv}{r_0 v_0} \cos \alpha}{\sqrt{1 - \left(\frac{Rv}{r_0 v_0} \right)^2 \sin^2 \alpha}} \quad (5.6)$$

Finally, the angular distribution near the cluster surface is derived

$$\int \frac{2\pi B^{1/2} \left(\frac{Rv}{r_0 v_0} \right)^2 \sin 2\alpha}{\sqrt{1 - \left(\frac{Rv}{r_0 v_0} \right)^2 \sin^2 \alpha}} d\alpha = 1 \quad (5.7)$$

Figure 5.6. Angular distribution for particles obtained from expression (5.7) for four energies IGA (0.03), 1, 5, and 10 eV. The distributions are calculated with parameters: $R = 10 \text{ nm}$, $r_0 = 100 \text{ nm}$, $v_0 = 300 \text{ m/s}$, $m = 10^{-25} \text{ kg}$.

In Fig. 5.6, the angular distributions are calculated for four different energies: 0.03 (corresponding to IGA), 1, 5, and 10 eV, each of them corresponds to a different potentials on the cluster. The distributions for IGA and 1 eV look similar. However, for high energy ions with 5 and 10 eV the distribution is more narrow and most of the particles bombard the surface with acute angles. The trajectories can bend around the cluster, but if the energy is too high, the particles escapes from the cluster. The maximum of the distribution IGA and 1 eV particles is at 45° , which means that very few atoms approach the surface with normal or grazing incident. It is important to notice that despite the fact that IGA particles have

a maximum of the distribution at 45° , they will have normal incidence, due to the fact the short-range interaction with the atoms of the cluster is much stronger than the kinetic energy of a particle. For this reason, the incidence angle changes from α to 0. Thus, we conclude that the angular distribution can be neglected for IGA simulations. In the considered model, only Coulomb interaction between ions and a cluster are included, however, when an ion approaches the surface the interaction with the atoms will accelerate the particles and make the distribution ever narrower. This effect was not included in the model but will be captured in MD simulations.

5.4.2 Analysis of individual events

For the simulation of the growth, we chose a seed consisting of 147 copper atoms. It is a magic number and the cluster has three complete layers. The simulations were performed with EAM potentials with Foiles parametrization[90]. The incoming particles in the simulations were randomly generated outside the cutoff radius of the potential with velocities corresponding to 1 eV and angle α with the distribution derived in (5.7). Previous work has shown that an inert gas environment has little or no significant effect on kinetics of the growth process[88] in IGA. Therefore, the simulations were performed in NVT-ensemble and the temperature was controlled by Nosé-Hoover thermostat. In the synthesis process, the temperature of the clusters is determined by the balance between cooling and heating. For the case study, we assume the temperature to be 300 K

Figure 5.7. Snapshots from a single event simulation. The color of an atom represents its kinetic energy.

Fig. 5.7 shows a typical simulation, where the color represents kinetic energy of the atom. Initially, the incoming atom has a pink color, indicating that its kinetic energy is higher than that of cluster atoms. Then, upon collision with the surface the atom becomes red due to acceleration by the potential. In the following collisions, the atoms consequently thermalize by transferring its kinetic energy to the heat and this heat transfer has a crucial impact on the growth process. To understand the difference in kinetics of the growth in IGA and plasma, we can analyze the heat transfer. In Fig. 5.8, the kinetic energy is shown as a function of time for particles incoming with different incidence angles. The curves are the result of the averaging over 160 independent simulations. The heat transfer for atoms with normal incidence is very fast and the atom loses most of the energy in the first collision. For the case of grazing incidence particles, the heat transfer is significantly slower and grazing atoms lose their kinetic energy in multiple

collisions. In the IGA process atoms approaching the surface slower and that results in a slower heat transfer.

Figure 5.8. Kinetic energy of incoming particles with incidence angle α as a function of time. Six curves correspond to high energy, 1 eV, particles for six different angles. The IGA curve corresponds to particles with thermal energy, 0.03 eV

To describe the difference between the processes, we analyze the thermalization time for incoming particles in IGA and the plasma growth. Fig. 5.9 shows how fast a particle thermalizes depending of the incidence. We can consider a particle to be thermalized when its initial kinetic energy decreases by a factor of 3. Thus, for the IGA process the incidence does not play any role, while for 1 eV particles the incidence significantly affects the thermalization. Each point in this figure is the result of averaging over 160 independent simulations.

Figure 5.9. Rate of thermalization as a function of incidence angle for particles in the plasma growth with energy 1 eV and particles in the IGA process with thermal energy 0.03 eV

The longer thermalization times mean longer diffusion on the surface. Fig. 5.10 provides the analysis of the diffusion of the incoming atoms on the cluster surface. Grazing incidence of the collision favors the longer diffusion paths as the particle loses its kinetic energy in a multiple iterations. On the contrary, in IGA process the collisions are always normal and the diffusion is highly restricted.

Figure 5.10. Diffusion of the incoming particles with different incidence angle on the surface of the cluster.

Fig. 5.11 shows the dependence of the diffusion on the angle of incidence. The diffusion in IGA process is clearly independent of the angular distribution, while for the 1 eV particles the diffusion length doubles going from normal incidence to the maximum of the distribution at $\approx 45^\circ$

Figure 5.11. Dependence of the surface-diffusion length on the incidence angle for the incoming particles.

Thus, IGA and plasma growth processes can significantly differ at the early

stage of the growth. The developed approach can be successfully applied for simulations and these simulations show that the angular distribution plays an important role for the growth from high-energy particles. It is especially important for the early stages of growth when the particles are small and the structure of the cluster is set, because geometrical factor with the increase of the size leads to a gradual decrease of the difference between the effects of grazing and normal incidence particles. Within the suggested approach it becomes evident that depending on the Coulomb interaction potential three possible regimes can be distinguished. The first one corresponds to the case when the Coulomb interaction is weak. Due to the low energy of this interaction the incoming particles will be accelerated within the potential field and fall with normal incidence on the surface. In the second regime, the Coulomb interaction is significant, such as 1 eV, and the trajectories of the incoming particles bend around the cluster and the angular distribution of their velocity looks similar to (5.7). The third regime corresponds to the case where the interaction is strong (10 eV). The incoming ions bombard the cluster almost perpendicularly to the surface. The analysis of the kinetics suggests that the growth accompanied by the fast heat transfer and small incidences can accelerate healing of defects in the cluster, whereas the growth from grazing incidence particles would tend to a layer-by-layer growth with nearly perfect structure.

5.5 Structure of charged nanoparticles

The approach described in the previous section does not account for the effects of a charge on the nanoparticle structure. Depending on the distribution of the charge, the relative stability of different morphologies can be affected. In Chapter 2 the combination of classical force-fields COMB with charge equilibration QEq is described. This combination can be utilized to investigate relative stabilities of Ih and Dh nanoclusters, but the relevance of the used approximations has to be assessed critically. In order to verify the reliability of classical force-fields for charge nanoparticles, *ab initio* calculations have been performed. The calculations of charged clusters were done with the PBE functional[49] and 6-31G basis set[91] using the quantum-chemical software Gaussian09[64].

As shown in Fig. 5.12, the expansion of 13 atom copper cluster under influence of a charge is accurately reproduced by COMB+QEq. It is important to notice that attaining a second electron for a nanoparticles in plasma is unlikely and even more unrealistic would be charges of 4,6 and 8 e. From Fig. 5.12 it is evident that even for a very small particle and high charges, the effects of the charge on the interatomic distances do not exceed 0.06 Å.

To assess the influence of a charge on the relative stability of Ih and Dh copper nanoclusters the COMB+QEq calculations were performed. Fig. 5.13 shows a comparison of the cohesive energies of neutral and charged nanoparticles with charge $q = -2$. For clusters below 50 atoms, the charge noticeably decreases stability or cohesive energy of the structure. For instance, in Ih clusters with 13 atoms that difference was found to be 0.4 eV, which suggests that the for small particles such effects may play an important role. However, the contribution of

Figure 5.12. Difference in the interatomic distances in 13 atom copper cluster with different charges as calculated in Gaussian09 and COMB+QEq

the charge in the cohesive energy quickly decays with increase of the particles size and we see that for nanoparticles larger than 100 atoms the effect is negligibly small.

A charged nanoparticle in a very crude approximation can be modeled by a uniformly charged sphere. For that approximation the potential can be easily found: $U = \frac{3}{5} \frac{1}{4\pi\epsilon_0} \frac{q^2}{R}$.

Another simple approximation is a charged shell, which potential can also be found: $U = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{q^2}{R}$. Here, R is particle's radius and ϵ_0 is the vacuum permittivity. Fig. 5.14 shows the difference in calculated cohesive energies of charge and neutral particles. It also becomes evident from Fig. 5.14, that the effect of the charge depends of the radius of a particle. It appears that in all cases energies quickly drop with increase of the particles radius and for particles larger than 1 nm the charging effects can be safely neglected.

5.6 Morphological transformation

In the previous section, we have provided comprehensive analysis of the kinetics of the growth process in different environments. Now we would like to study how these processes affect the structure of the nanoclusters. All the details can be found in Paper II.

The analysis of the thermodynamics showed that for copper the most stable structure for $N < 1000$ atoms is icosahedron, followed by decahedron with $1000 < N < 30000$. The most favorable structure for large clusters is fcc[22].

Figure 5.13. Cohesive energy as a function of number of atoms for charged ($q=-2$) and neutral nanoparticles. Dh1 and Dh2 correspond to decahedral particles with different number of intermediate layers: 2 and 4, correspondingly.

Figure 5.14. The difference between cohesive energy of charged and neutral Ih nanoparticles as a function of particle's radius. Potentials of a charged sphere and a charged shell as a function of radius.

However, many experimental work report high percentage of energetically unfavorable morphologies for different synthesis methods[92, 93]. It is known to be related to the kinetics of the growth process.

By means of MD F.Baletto *et al.*[89] have shown the possibility of the morphological transition in silver nanoclusters and gave an explanation of the mechanism[94]. They claimed that the transition from Ih to Dh phase goes through an intermediate amorphous state or melting. The possibility of a solid-solid transition mechanism has also been discussed[95].

5.6.1 Simulation of the growth process

In order to investigate the kinetics of the morphological transition from Ih to Dh phase in copper nanoclusters, MD simulations of the growth starting from the Ih seed consisting of 147 atoms have been performed. This size covers the most relevant range of sizes, because the barrier of the transition for larger clusters is too high and the probability of the transition is very low. It is also important to notice that morphological transition for smaller clusters are less crucial for the final structure.

In the simulations, new atoms were generated near the surface of the seed, slightly above the cutoff of the potential. A new atoms was introduced every 100 ps with velocity corresponding to one of the three: (IGA) thermal growth with

kinetic energy of 0.03 eV and incidence within $\pi/2$ range, (NI) normal incidence particles with energy of 1 eV, and (FD) particles with "full" distribution derived in 5.7 and energy 1 eV.

The rates of the deposition in the simulation are significantly higher than in real growth, thereby a Nosé-Hoover thermostat is used to cool the clusters down before the next particles is introduced.

Figure 5.15. Classification of the morphology based on BAA analysis.

For each temperature and growth regime, 50 independent simulations have been performed. During each simulation, 300 new atoms were introduced. The result of each simulation has to be assessed and in each simulation the final morphology needs to be recognized. The amount of work required for the analysis can be reduced by deriving criteria for distinguishing simulations with morphology transition.

The final structures were analyzed by means of bond-angle analysis(BAA). This method was suggested by Ackland and Jones[96] for distinguishing local structure for fcc, hcp and bcc lattice. Thus, each atomic configuration was assign two parameters: number of hcp and fcc atoms as determined by BAA. Based on these parameters, the morphology can be recognized. This is a classification problem that can be efficiently solved by machine learning. In particular, support vector machine (SVM)[97] was used as a model for linear binary classification as implemented in `scikit-learn` library[98]. The structures for the training were extracted from two simulations with morphology transition and without one. Fig. 5.15 shows the result of classification from the described model.

This model can be used to recognize simulations with morphology transition, but cases where the model predicted borderline probabilities have to be analyzed

manually. The results are assembled in Table 5.1. From the results it is evident, that despite the fact that Ih structure is the most stable for these sizes, up to 30% of the simulations ended up in a non-icosahedral phase.

Temp, K	NI, %	FD, %	IGA, %
400	28	16	26
450	20	16	22
500	10	10	18
600	8	8	12
700	4	2	2

Table 5.1. The fraction of the clusters that went through morphology transition for different temperatures.

5.6.2 Mechanism of morphology transition

In order to understand what drives the morphology transition, we can analyze one typical simulation, where the transition to decahedral phase has occurred.

Fig. 5.16 shows coordination of atoms computed with (BAA)[99].

Figure 5.16. Bond-angle analysis of the cluster structure. Squares and triangles correspond to decahedrons and icosahedrons with magic number of atoms. Sizes: Ih (147, 309) and Dh (146, 192, 318, 389).

Initially, a perfect 147 icosahedral cluster is recognized by BAA as ≈ 50 atoms in hcp and the rest ≈ 100 surface atoms identified as disorder, i.e. neither hcp nor fcc. As the cluster attains the size of ≈ 250 atoms, the structure transforms to decahedral phase. The transformation can be identified by the drop in the amount hcp atoms and rise of the amount of fcc atoms. Since the number of disordered atoms does not change, it must be atoms with hcp structure that transformed into fcc coordination. After the transition, the number of fcc atoms dominates over

hcp ones, which means that no other morphological transition has occurred during the simulation. In Fig. 5.16, squares and triangles correspond to perfect clusters with magic number of atoms. In the beginning of the simulation, the coordination is very similar to a perfect Ih(147) cluster and significantly differs from Dh(146) structure. After the transition, the comparison shows that Ih(309) and the cluster in the simulation have a very different number of fcc and hcp atoms. At the same time, it closely matches with Dh(318) and later with Dh(390), which can be considered a solid proof of the morphology transition.

Figure 5.17. Analysis of the potential energy and the surface area of the simulation.

The analysis of the potential energy of the cluster with time and its surface area are shown in Fig. 5.17. The transition occurs between addition of 101st and 102nd atoms. The potential energy strongly fluctuates after 101th atom has been introduced from 20 ps to 35 ps. It is the result of the diffusion of the new atoms on the surface. Then the potential energy drops and the structure falls into a potential well and we see no more fluctuation of the energy. The transition takes approximately 2 ps. On the contrary, the surface area of the cluster significantly increases upon transition, which is expected knowing that Dh phase has larger volume.

The structure of the cluster before and after transition is shown in Fig. 5.18. It is important to notice, that before the transition all the facets are (111) and after the transition (100) facets appear. The height of the barrier was found to be 0.8 eV and the energy difference between two phases is 1.9 eV. For comparison barriers for other sizes were calculated and it was found that for 185-atom cluster the height is 0.6 eV and for the cluster with 376 atoms it approaches 2 eV.

The Ih phase is the most favorable structure for many noble metals[22] due

Figure 5.18. The structures and the potential energy surface in the vicinity of the transition.

to small surface area, despite that fact that it has strong internal strains. Dh structure has smaller internal strains whereas the surface area is larger. In the growth process, when the incoming atoms are not able to diffuse on the surface and form a new layer they get stuck in islands of disordered atoms on the surface. These islands increase both strains and surface area and Ih phase becomes no longer favorable. In such a case, the structure transforms into decahedron, which has lower potential energy than icosahedron with the disorder on the surface.

Figure 5.19. Mechanism of the morphology transitions from Ih to Dh phase

The results in Table 5.1 demonstrate that when the temperature is high, the diffusion becomes faster and the growth continues more uniformly preventing formation of the islands. In the cases, where the atoms have normal incidences, as in IGA and NI case, the number of transition is higher due to restricted surface diffusion.

The analysis of the large number of transitions allows to recognize a common pattern for these transitions. Generally the mechanism looks as follows, the impinging atoms form islands on the surface and increase the surface area. These islands of disturbed atoms arrange into a "belt" around ordered (111) facets, as shown in Fig. 5.19b. Above and under this belt two pyramids can be distinguished. These pyramids do not require major rearrangements for the transition to Dh, because their structure does not change and it is only necessary to twist them to align their edges and form the rectangular facets, as shown in Fig. 5.19c. Upon

this alignment, the "belt" undergoes major rearrangements from hcp to fcc.

A similar mechanism was described by Mackay[18] for the direct geometrical transformation from cuboctahedron into icosahedron. This mechanism later was shown in other systems[100]. However, these mechanisms were only shown in perfect structures and the effect of the disorder was not included and did not include the kinetics of the growth, which is crucial for the real growth process. Thus, the suggested mechanism is an extension of the diamond-square mechanism for a wider class of transitions. This mechanism includes disorder and as was demonstrated, the restricted surface diffusion promotes morphology transition. It is also important to notice, based on our previous results, that the growth in plasma environment boosts surface diffusion.

Electronic properties of nanoclusters

As we discussed in Chapter 1, the electronic structure of nanoclusters has a number of remarkable features and spectroscopic studies can be used to investigate them. Interpretation of the spectra and analysis of the electronic structure of nanoclusters can be facilitated by applying theoretical modeling. Thus, *ab initio* modeling allows to study different effects influencing the structure independently.

6.1 Core-level binding energy shifts in nanoclusters

One of the most important applications of nanoclusters today is catalysis and the electronic structure of the clusters is of high importance for such applications. XPS measurements have been actively used for the characterization of the electronic structure of nanoclusters[101]. Moreover, in the work of Kaden *et al.*[102], it was shown that shifts of the binding energies of core electrons strongly correlate with the reactivity of Pd nanoclusters. Thus, understanding of the origin of the core-level shifts is important for their characterization and designing clusters with desired properties.

In order to investigate CLS in nanoclusters, I have performed calculations within Z+1 approximation for magic number clusters of different morphologies. The goal of this work is to distinguish trends in behavior of CLS for different sizes and structures of nanoclusters. However, this approach has certain limitations that have to be mentioned. The charge transfer from the substrate is known to affect the CLS[103], but these effects are not included, as all calculations are performed for unsupported nanoclusters. Moreover, the clusters considered in this work are neutral and the charging effects are not included. As it was shown before, the nanoclusters may be charged, which strongly affects the shifts[104–

106]. However, the charging effects can be described reasonably well by classical models and depend on the size of a particle. The model system of choice is gold for its relevance for catalysis[107–110], moreover gold has the largest SCLS of all noble metals, which simplifies the task of distinguishing trends[111].

A number of experimental works have shown that with the decrease of the size the $4f$ states shift toward higher binding energies[112, 113]. Wertheim[114] suggested that this is due to final state relaxation induced by charging. The broadening of $4f$ peak in small particles has been observed in a number of experiments[104, 115, 116] and was attributed to the initial state shift due to the change in the electrostatic potential. However, the structural effects have not been comprehensively investigated. Thus, we study shifts of binding energies from an individual atom to a solid through atomic clusters.

The calculation of CLS with final state effects have been performed in $Z+1$ approximation with PAW method, as discussed in Chapter 3. For the initial-state approximation CLS calculations, the Kohn-Sham equation is solved inside the PAW sphere for core electrons, after self-consistency with frozen core electrons has been attained[117]. For reasons of simplification and relevance for experimental spectra, further we discuss $4f$ -states, but the same arguments concern other core states.

Contributions affecting shifts of the core states

Coordination effects Fig. 6.1a shows how the position of the $4f$ state changes for different local coordination. Different facets can have different coordination of the surface atoms. CLS calculated for atoms of different facets in a big slab with the bulk lattice parameter allow to avoid contributions from size effects and lattice relaxation on the surface and thus only the coordination effect is expected to contribute to the shift. The shift calculated for surfaces (124), (112), (100), (111) correspond to coordination of 6, 7, 8, 9. In bulk fcc the coordination is 12 and the shift is zero. The matching of the shift in initial state and complete screening approaches suggests that the effect is to a high extent described by the shift of the electrostatic potential. Only for coordination of 6 discrepancy becomes noticeable.

Strain effect Core states are very sensitive to strains. As shown in Fig. 6.1b, under uniform compression the states move toward higher binding energies and in the opposite direction under stretching of the lattice. The change of the lattice parameter by 2% leads to the shift for 0.25 eV and the dependency is linear for small distortions.

Size effect Another parameter that affects the shifts is the size of a cluster or confinement effect. In Fig. 6.2, the core-level shifts are calculated for central atoms in cubic clusters in fcc structure and bulk lattice parameters. The sizes of the clusters are in the range from 13 to 256 atoms. This approach allows to avoid contributions from strain and coordination, because the lattice parameter corresponds to bulk and coordination is 12 for all central atoms. The behavior of

Figure 6.1. a) Au 4f CLS of atoms with different coordinations b) Au 4f CLS of atoms in bulk structure with distorted lattice parameter. Distortion is denoted in percent of the perfect bulk lattice parameter.

the shifts is clearly nonlinear and for large clusters the shifts approach zero. The electronic structure of a nanocluster is an intermediate state between individual atom and bulk solid, which is clearly manifested in CLS. It is also important to emphasize that the shift changes the sign at around 100 atoms.

In Fig. 6.3, the change of the valence bandwidth is shown. The red dots denote the center of the valence band. DOS in 13-atom cluster does not show a full band for the valence states and has the structure similar to a molecular one. With increase of the number of atoms the band appears and the width of the band does not show significant change for sizes above 13 atoms. The mechanism of the surface core-level shift in solids has been thoroughly discussed in Chapter 4. In clusters the correlation between the valence band center and the shift in complete screening approximation suggests that the shifts are determined by the electrostatic potential.

Thus, we conclude that there are three main contributions to the shifts of 4f state in nanoclusters: coordination, strains and confinement.

Core-level shifts in nanoclusters

In order to investigate how these contributions affect the spectral features, calculation for fully relaxed nanoclusters with magic number of atoms or closed geometric shells can be performed.

Icosahedral nanocrystals At small sizes icosahedral structure is the most favorable, as was discussed in Chapter 1. The calculations were performed for clusters of 55, 147 and 309 atoms. In Fig. 6.4a, the shifts for 55-atom cluster are shown. All atoms are colored corresponding to their CLS. Black bars denote calculated

Figure 6.2. Core-level shift as a function of the size of the cluster. The structures are fcc unrelaxed clusters, where the position of the 4f states is calculated for the central atom.

CLS. To facilitate comparisons with experimental data, a convolution of the CLS with a 0.05 eV Gaussian is shown. Undercoordinated atoms on the surface have a strong negative surface core-level shift of -0.5 eV. The central atom has 13 atoms in the coordination shell, which is even more than coordination in bulk solid. Besides, the central atom is compressed by all other atoms. These effects combine into a shift of 0.5 eV. The second layer shows the shift of -0.1 eV. The features in Fig. 6.4a are well separated and each one corresponds to a specific layer. For the cluster with 147 atoms the shifts follow similar trends: surface undercoordinated atoms have negative shift and compressed core atoms have positive shifts. The largest negative shift is observed for vertex atoms -0.3 eV. The distance between the central atom and its neighbors increases by 0.1 Å for the larger cluster. In 309-atom cluster similar trends are observed and the surface atoms approach SCLS of 0.3 eV, suggesting that the confinement effect is rather small for clusters with over 300 atoms. The widths of the features increase for large clusters and only two peaks can be distinguished: surface and core.

Figure 6.3. Density of states in the valence band of the central atom in nanoclusters with different number of atoms, where red dots denote the center of the valence band

Decahedral nanocrystals For decahedral phase, three sizes should be considered: 49, 146, 318 atoms, as shown in Fig. 6.5. The choice of the sizes is motivated by the proximity to the closest magic numbers in icosahedral clusters to simplify comparison. In a cluster with 49 atoms, all atoms are surface atoms and have negative CLS, with exception of two core atoms along 5-fold symmetry axes. These two atoms have small but positive CLS due to long interatomic distances. In larger decahedral cluster, more atoms are in the core, hence the spectral weight of positive shift feature increases. The symmetry of decahedron is lower than icosahedron, which explains broader features compared to Ih structures. In 318-atom cluster the surface peak consists of two main contributions from $\langle 100 \rangle$ and $\langle 111 \rangle$ surfaces, which closely approaches bulk values. It is also important to notice that for sizes around 300 atom, the contributions of core atoms catches up with the surface ones. Icosahedral morphology can be described by an index - number of layers. Decahedral structure has more independent parameters. As shown in Fig. 6.6, it is possible to change the number of layers between the pyramids without changing the pyramids. In Fig. 6.6, we see how the number of these layers affects the spectral features for decahedral clusters. The contribution of $\langle 100 \rangle$ surface atoms is small in 247-atom cluster and the positive shifts are small, which indicates small internal stress. However, with the increase of the number of layers the contribution of $\langle 100 \rangle$ surface shifts increases and the contribution from $\langle 111 \rangle$ surface does

Figure 6.4. CLS in icosahedral nanoclusters: 55, 147, and 309 atoms.

Figure 6.5. CLS in decahedral nanoclusters: 49, 146, and 318 atoms.

not change.

Octahedral nanocrystals Truncated octahedron structure is the least favorable out of all considered morphologies. TOh structure is the closest to fcc lattice and the clusters should have the least internal stresses and the largest surface area. In Fig. 6.7, TOh clusters are shown with the corresponding CLS. The smallest cluster with 38 atoms has surface atoms shift of -0.2 eV. For larger clusters, the surface shifts increases, while the core-atom contributions is rather small. Similarly to Ih and Dh clusters, TOh nanocrystal with increase of the size exhibits two main features originating from surface and core. The surface peak is formed by the two main surfaces: $\langle 111 \rangle$ and $\langle 100 \rangle$. The shifts for these surfaces are close to the shifts of extended surfaces.

Thus, we have found that clusters of all morphologies have the largest surface shifts for vertex atoms, while central atoms show positive shifts due to internal stresses. For clusters with typically more than 200 atoms, the features form two distinct peaks: one for core atoms and one for surface atoms. The CLS are determined by combination of three factors, where the confinement size effect is negligibly small for large clusters. Understanding of the origin of the CLS is of high importance for catalysis and potentially for structure characterization.

Figure 6.6. CLS in large decahedral nanoclusters: 247, 318, 389 atoms.

Figure 6.7. CLS in octahedral nanoclusters: 38, 116, and 201 atoms

6.2 Adsorption on Pd nanoclusters and core-level shifts

The most common application of nanoclusters today is catalysis. In order to characterize catalytic properties of different systems many descriptors have been developed.

Calle-Vallejo *et al.*[118] suggested a generalized coordination number (GCN) as a descriptor for the reactivity that accounts for the number of nearest neighbors and their coordinations. Mpourmpakis also suggested a descriptor based on geometry of nanoclusters[119]. Another approach developed by Xianfeng Ma *et al.*[120] is based on an orbital-wise coordination number CN_{α} , which can be calculated from hopping integrals. Detailed discussion on different descriptors can be found in[121].

J. Nørskov suggested a model that explains the adsorption energies for transition metals by the position of their d -band relative to the Fermi level[122, 123]. As was discussed earlier, the position of the core states is determined by the shift of the electrostatic potential to a high extent and also strongly correlates with the position of the valence band. Thus, it would be important to see how well adsorption energies correlate with the core-state binding energies, as measured in

Figure 6.8. π -mode adsorption of an ethylene molecule on icosahedral Pd nanocluster with 55 atoms.

XPS. W.E. Kaden in his work [102] presented results indicating that reactivity correlates with the position of the core-states in Pd nanoparticles. Nevertheless, the comprehensive investigation of this phenomenon has not been reported and the effects of the core-hole on this correlation have not been discussed.

In order to investigate these effects in detail, calculations for ethylene adsorption on Pd nanoclusters and their CLS have been performed. The calculations were performed with GGA exchange-correlation functional in PBE form as implemented in VASP. The choice of the system was motivated by the importance of this reaction for upgrading of biofuels. In particular, it has been suggested that ethylene hydrogenation start with π -mode adsorption[124–126]. The π -mode configuration is shown in Fig. 6.8 and the σ -mode was not considered in our study.

Figure 6.9. Structures of Pd nanoclusters. Octahedral clusters: 13, 38, 79 and 116 atoms. Icosahedral clusters: 13 and 55 atoms. Red letters mark sites where E_{ads} and CLS were calculated

Two morphologies of Pd clusters were considered in this study: icosahedral and octahedral. The adsorption energies were calculated as a difference between total energy of a cluster with unbound molecule and cluster with a molecule bound to its surface. The calculations of CLS and adsorption energies were performed for clusters of different size, as shown in Fig. 6.9. The results of the calculations are presented in Table. 6.1 and described in greater detail in Paper V.

Table 6.1. Calculated core-level shifts in initial state and complete screening approximations CLS_{init} and $CLS_{complete}$, correspondingly. E_{ads} is adsorption energy of ethylene and GCN is a generalized coordination number for clusters and surfaces

Cluster	Site	GCN	Eads	$CLS_{complete}$	CLS_{init}
Pd13TOh		2.67	-1.58	-0.88	-1.31
Pd38TOh	A	6.00	-0.67	-0.24	-0.41
Pd38TOh	B	4.00	-1.18	-0.47	-0.80
Pd79TOh	A	4.08	-1.13	-0.37	-0.75
Pd79TOh	B	5.00	-1.12	-0.48	-0.67
Pd79TOh	C	6.67	-0.78	-0.25	-0.35
Pd116TOh	A	4.00	-1.16	-0.45	-0.80
Pd116TOh	C	5.17	-1.15	-0.32	-0.55
Pd116TOh	B	6.33	-0.89	-0.20	-0.40
Pd116TOh	D	6.67	-0.91	-0.30	-0.38
Pd13Ih		3.50	-1.52	-0.81	-1.07
Pd55Ih	B	4.33	-1.36	-0.50	-0.85
Pd55Ih	A	5.67	-1.15	-0.47	-0.78
Pd(100)		6.67	-0.89	-0.35*	
Pd(111)		7.50	-0.78	-0.29*	

*Reference[127]

In Fig. 6.9, red letters mark atoms where E_{ads} and CLS were calculated. Due to high symmetry of the structures only a few atoms are inequivalent and need to be considered. The correlation of the CLS in the initial state approach with E_{ads} is shown in Fig. 6.10. The correlation coefficient is consistently strong in all range of sizes and R^2 is 0.88. This result again confirms validity of the d -band model.

The effect of the core-hole on the correlation is shown in Fig. 6.11. The comparison of the initial and final state CLS shows that the correlation for the final state case is lower, $R^2 = 0.82$. The screening process typically lowers the shift relative to the initial state which leads to deviation from the corresponding adsorption energies.

However, it is important to notice that despite the discrepancies caused by the core-hole, the correlation is fairly strong for all sizes. Therefore, the relaxation energy due to core-hole should be relatively small. In Fig. 6.12 the core-level shifts calculated in complete screening approximation and initial state approximation are presented. The results suggest the relaxation energies are consistently small and do not exceed ≈ 0.1 eV.

Catalytic descriptors based of the geometry of the clusters are often used for estimations of their properties. One of the most commonly used is GCN. However, as it was shown, behavior of the electronic structure of the nanoclusters with the sizes is strongly nonlinear and thus descriptors that do not account for these effects have a limited accuracy. In Fig. 6.13, the accuracy of this descriptor is shown. However, despite the limitations, the correlation is fairly strong and $R^2 = 0.79$.

Thus, we just saw that CLS with final-state effects can be used as a descriptor for the adsorption energy in nanoclusters and that the core-hole relaxation energy

Figure 6.10. Adsorption energy of an ethylene molecule on the surface of Pd nanoclusters with CLS calculated within initial state approximation

Figure 6.11. Adsorption energy of an ethylene molecule on the surface of Pd nanoclusters with CLS calculated within complete screening approximation

Figure 6.12. Core-level shifts calculated in initial state approximation and complete screening approximation in Pd nanoclusters.

Figure 6.13. Adsorption energy of an ethylene molecule on the surface of Pd nanoclusters with generalized coordination number.

is relatively modest even for small nanoclusters. Another argument in favor of CLS descriptors is that CLS can be measured with high accuracy. Moreover, the calculations of CLS do not require relaxation of the atomic positions, which significantly decreases the computational time.

6.3 Cerium oxide nanoparticles

Cerium oxide nanoparticles due to their ability to shift the oxidation state depending on the environment have found many applications in medicine[8, 128, 129], environmental technologies[130] and catalysis[131]. The mechanism of the oxidation state transition the oxidation state was explained by Skorodumova *et al.*[132].

In the biomedical field, particular interest for ceria nanoparticles have attracted

their regenerative scavenging of Reactive Oxygen Species (ROS). Cerium dioxide in bulk systems has mostly Ce^{+4} oxidation state, while reduction of the size significantly increases the relative fraction of Ce^{+3} ions[133], which prominently improves their scavenging properties.

The amount of Ce^{+3} can be further increased by implementation of Gd doping. Gd trivalent atom has seven unpaired electron in 4f band, which gives it a large magnetic moment. This property is utilized for Magnetic Resonance Imaging (MRI) contrast enhancement[134]. Today, gadolinium is the most commonly used material for MRI in clinic[135]. Gd ionic radius is 1.053 Å which is less than Ce^{+3} (1.143 Å) and more than Ce^{+4} (0.970 Å). Thus, Gd doping promotes formation of vacancies[136]. Babu *et al.*[137] showed experimentally that the concentration of gadolinium can reach 40% or even higher, according to theoretical modeling.

Figure 6.14. HR-TEM images of individual nanoparticles in (column a), distribution Feret Diameter of (column b), minimum Feret diameter (column c) and Aspect Ratio (column d) based on measurements from a minimum of 100 nanoparticles of respectively CeO_x , $\text{CeO}_x:\text{Gd}9\%$, $\text{CeO}_x:\text{Gd}19\%$ and $\text{CeO}_x:\text{Gd}46\%$

For this study, gadolinium doped CeNPs have been synthesized. The particles were characterized using Dynamic Light Scattering (DLS), Zetapotential, X-ray Diffraction (XRD), High-Resolution Transmission Electron Microscopy (HR-TEM), Relaxameter, Near Edge X-ray Absorption of Fine Structures (NEXAFS). The synthesized NPs have been studied in cell ROS production. The result in this study shows that gadolinium-implemented CeNPs are a highly promising material for theranostic applications. The details of the research can be found in Paper VI.

The results of HRTEM analysis are shown in Fig. 6.14. The increase of Gd contribution is accompanied by reduction of the size. The shape of the particles also changes and becomes more elongated for smaller particles. The crystalline structure of the particles is clearly observed and suggests that particles consist of a single crystal domain. The size distribution increases with implementation of Gd.

XANES measurements have been suggested as a promising method for quantitative evaluation of the oxidation state of Cerium compounds[138]. Therefore, the combination of experimental measurements of XANES M-edge and theoretical calculation can allow to interpret the spectra for characterization of Gd doped CeNP's oxidation state. In Fig. 6.15, the measured spectra are shown. The multiplet structure of the $M_{4,5}$ absorption edge reflects transition from core $3d$ to unoccupied $4f$ states. The prominent features of M-edge has been described by Magnuson *et al.*[139]. Both edges M_4 and M_5 differ in shape and intensity depending on the oxidation state. A number of approaches has been applied for the theoretical description of the $M_{4,5}$ XANES. Gunnarsson and Schönhammer used the Anderson impurity model to show how the partial occupation of $4f$ states is responsible for the satellite peak in CeO_2 [140]. Kucheyev *et al.*[141] have used atomic multiplet approach to calculate the spectra. Here, the results for *ab initio* DFT calculations of XANES $M_{4,5}$ edge in CeO_2 and Ce_2O_3 are presented.

DFT calculations allow to perform calculations in dipole approximation as described in Chapter 4, where Kohn-Sham orbitals are used for the initial and final states. In order to account for effects of the core-hole, all-electron calculations have been done. This approach allows to account the core-hole explicitly by removing an electron from $3d$ states. The calculations were performed in WIEN2k code with the local density approximation (LDA) for exchange-correlation functional. Hubbard correction U of 6 eV has been applied to f -states. CeO_2 in fluorite structure with 96 atoms in a supercell and Ce_2O_3 in hexagonal structure with 60 atoms in a supercell have been calculated. The calculations were converged self-consistently for a $2 \times 2 \times 2$ k-mesh, including spin-orbit coupling and spin polarization.

The results of the calculations are presented in Fig. 6.16. The absolute energies have been shifted for comparison with experimental spectra. It is evident that upon transition from Ce^{+3} to Ce^{+4} the peak shifts by 2 eV toward lower energies, this shift matches the experimental values. In the case of Ce_2O_3 the main peak has a doublet structure, which are reproduced in experiment (A and B). The origin of this doublet can be determined from the DOS analysis. In Fig. 6.17 the calculated spectra are shown next to the densities of states. Due to strong on-site interaction in Ce_2O_3 partially occupied $4f$ band splits into occupied and unoccupied states. This results in a relative shift of the $4f$ state for different spin

Figure 6.15. XANES spectrum of a) CeO_2 nanopowder, b) Ce(III)acetate , c) CeO_x , d) $\text{CeO}_x:\text{Gd}46\%$ and e) $\text{CeO}_x:\text{Gd}46\%$ treated with 10 mM hydrogen peroxide.

Figure 6.16. Calculated XANES spectra for CeO_2 and Ce_2O_3 . Both spectra are shifted to experimental values.

components. Besides, Ce_2O_3 has a prominent feature C, which lays within the band gap and can be attributed to excitonic effects. However, excitonic effects can not be reproduced in a single-particle approach and are not reproduced in our calculations. In the case of CeO_2 , the $4f$ band is empty and the doublet structure does not appear. The calculated CeO_2 spectrum consists of one main peak, whereas in experiment a satellite C is observed. The origin of this satellite is related to the charge transfer from oxygen $2p$ states. Such complex excitations cannot be captured by a single-particle approach, hence they are missing in our calculated spectra. The relative intensities of M_4 and M_5 edge were fitted to experiment. The analysis of the DOS in Fig. 6.17 suggests that the presence of the core-hole causes significant shift of the $4f$ states in the excited atom.

Thus, provided analysis allows us to identify all prominent features in the $M_{4,5}$ edge corresponding to different oxidation states. Understanding of the origin of the feature allows us to claim that no features specific for nanoparticles is observed in the spectra. The measurement of XANES spectra clearly show how implementation of Gd with different concentration systematically increases the amount of Ce^{+3} ions and allows to design NP with improved properties.

Figure 6.17. Calculated electronic density of states of $4f$ and $5d$ states and XANES $M_{4,5}$ for CeO_2 and Ce_2O_3

CHAPTER 7

Conclusions

In this thesis, a number of different problems of nanoclusters science have been addressed. The main attention was paid to understanding their properties and finding possible ways for improvement and characterization. Special interest was focused on understanding the growth process and developing models capable of describing it in plasma conditions. The approach developed for Molecular Dynamics simulation allows to account for Coulomb interaction between ions and a charged nanoparticle without explicit treatment of the charge. According to the results obtained in this work, the growth regime is highly affected by the cluster charge. In particular, the kinetics of the growth and surface diffusion during the process is determined by the angular distribution of ion velocities. As was discussed in detail in the thesis, the structure of nanoclusters is of high importance for applications and requires precise control and understanding of the mechanisms affecting it. Thus, the mechanism of the morphology transition in copper clusters, that was identified within the developed model allows to describe growth condition that favor icosahedral or decahedral structure.

The analysis of the core-level shifts in nanoclusters gives a comprehensive understanding of the effects determining the shifts of the core states binding energies. As we have seen in the core-level shift investigation, there are three effects influencing the binding energies, but the confinement effect is the most difficult to determine and predict due to nonlinear dependency on the size. All three contributions to the shift of the binding energy of the core states are determined by the shifts of the electrostatic potential, which makes it possible to accurately describe them within initial state approximation. Based on the provided consideration, core-level shifts can be utilized as a descriptor of the reactivity of nanoparticles. Moreover, it was shown that fundamentally similar process determine the adsorption energy and the shift of the core state and their values are highly correlated. The screening of the core-hole may decrease the correlation, but this effect is con-

sistently small for all sizes of clusters. Besides, XPS provides a way to determine the core-level shifts with high accuracy, which makes it possible to measure such a descriptor experimentally.

The investigation of ceria nanoparticles presented in this thesis reveals perspectives of the Gd doped CeNP for medical applications. *Ab initio* modeling of the XANES $M_{4,5}$ edge allowed to explain the origin of all prominent features that are present in the spectra and understanding of their origin provides means to characterize the oxidation state of ceria particles or compounds.

Bibliography

- [1] Ian Freestone et al. “The Lycurgus Cup – A Roman nanotechnology”. In: *Gold Bull.* 40 (2007), pp. 270–277.
- [2] Renwen Yu et al. “Structural Coloring of Glass Using Dewetted Nanoparticles and Ultrathin Films of Metals”. In: *ACS Photonics* 3 (2016), pp. 1194–1201.
- [3] Eric C. Tyo and Stefan Vajda. “Catalysis by clusters with precise numbers of atoms”. In: *Nat. Nanotechnol.* 10 (2015), pp. 577–588.
- [4] Maksym V. Kovalenko et al. “Prospects of Nanoscience with Nanocrystals”. In: *ACS Nano* 9 (2015), pp. 1012–1057.
- [5] Suljo Linic, Phillip Christopher, and David B. Ingram. “Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy”. In: *Nat. Mater.* 10 (2011), pp. 911–921.
- [6] Young-Shin Park et al. “Effect of the Core/Shell Interface on Auger Recombination Evaluated by Single-Quantum-Dot Spectroscopy”. In: *Nano Lett.* 14 (2014), pp. 396–402.
- [7] Vincenzo Amendola et al. “Surface plasmon resonance in gold nanoparticles: a review”. In: *J. Phys. Condens. Matter* 29 (2017), p. 203002.
- [8] Ankur Gupta et al. “Controlling the surface chemistry of cerium oxide nanoparticles for biological applications”. In: *J. Mater. Chem. B* 4 (2016), pp. 3195–3202.
- [9] Darren Yohan and B. Devika Chithrani. “Applications of Nanoparticles in Nanomedicine”. In: *J. Biomed. Nanotechnol.* 10 (2014), pp. 2371–2392.
- [10] Kwang Joo Kim et al. “Structural and optical characteristics of crystalline silicon carbide nanoparticles synthesized by carbothermal reduction”. In: *J. Am. Ceram. Soc.* 92 (2009), pp. 424–428.

- [11] T.M. Scown, R. van Aerle, and C.R. Tyler. “Review: Do engineered nanoparticles pose a significant threat to the aquatic environment?” In: *Crit. Rev. Toxicol.* 40 (2010), pp. 653–670.
- [12] Muhammad Sajid et al. “Impact of nanoparticles on human and environment: review of toxicity factors, exposures, control strategies, and future prospects”. In: *Environ. Sci. Pollut. Res.* 22 (2015), pp. 4122–4143.
- [13] Wikipedia contributors. *Lycurgus Cup*. 2018. URL: https://en.wikipedia.org/wiki/Lycurgus_Cup.
- [14] J.A. Alonso. “Experimental Production of Clusters”. In: *Struct. Prop. At. Nanoclusters*. Imperial College Press, 2011, pp. 7–19.
- [15] I. Pilch et al. “Fast growth of nanoparticles in a hollow cathode plasma through orbit motion limited ion collection”. In: *Appl. Phys. Lett.* 103 (2013), p. 193108.
- [16] “Gas-Phase Synthesis of Nanoparticles”. In: *Gas-Phase Synth. Nanoparticles*. Ed. by Yves Huttel. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2017, pp. 59–78.
- [17] O. Echt, K. Sattler, and E. Recknagel. “Magic numbers for sphere packings: Experimental verification in free xenon clusters”. In: *Phys. Rev. Lett.* 47 (1981), pp. 1121–1124.
- [18] A.L. Mackay. “A dense non-crystallographic packing of equal spheres”. In: *Acta Crystallogr.* 15 (1962), pp. 916–918.
- [19] J. Farges et al. “Noncrystalline structure of argon clusters. II. Multilayer icosahedral structure of Ar N clusters $50 < N < 750$ ”. In: *J. Chem. Phys.* 84 (1986), pp. 3491–3501.
- [20] T.L. Hill. *Thermodynamics of Small Systems*. Dover Books on Chemistry Series. Dover Publications, 1963.
- [21] L. D. Marks and L. D. Marks. “Surface structure and energetics of multiply twinned particles”. In: *Philos. Mag. A Phys. Condens. Matter, Struct. Defects Mech. Prop.* 49 (1984), pp. 81–93.
- [22] F. Baletto et al. “Crossover among structural motifs in transition and noble metal clusters”. In: *J. Chem. Phys.* 116 (2002), pp. 3856–3863.
- [23] J.P.K. Doye and F. Calvo. “Entropic effects on the size dependence of cluster structure”. In: *Phys. Rev. Lett.* 86 (2001), pp. 3570–3573.
- [24] W.D. Knight et al. “Electronic Shell Structure and Abundances of Sodium Clusters”. In: *Phys. Rev. Lett.* 52 (1984), pp. 2141–2143.
- [25] Walt A. de Heer et al. “Electronic Shell Structure and Metal Clusters”. In: 1987, pp. 93–181.
- [26] B.K. Rao, S.N. Khanna, and P. Jena. “Designing New Materials Using Atomic Clusters”. In: *J. Clust. Sci.* 10 (1999), pp. 477–491.
- [27] M. Koskinen, P.O. Lipas, and M. Manninen. “Electron-gas clusters: the ultimate jellium model”. In: *Zeitschrift für Phys. D Atoms, Mol. Clust.* 35 (1995), pp. 285–297.

- [28] H. Fröhlich. “Die spezifische wärme der elektronen kleiner metallteilchen bei tiefen temperaturen”. In: *Physica* 4 (1937), pp. 406–412.
- [29] Ryogo Kubo. “Electronic Properties of Metallic Fine Particles. I.” In: *J. Phys. Soc. Japan* 17 (1962), pp. 975–986.
- [30] G.K. Wertheim, S.B. DiCenzo, and D.N.E Buchanan. “Noble- and transition-metal clusters: The d bands of silver and palladium”. In: *Phys. Rev. B* 33 (1986), pp. 5384–5390.
- [31] William C. Swope et al. “A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters”. In: *J. Chem. Phys.* 76 (1982), pp. 637–649.
- [32] Daan Frenkel et al. “Chapter 4 – Molecular Dynamics Simulations”. In: *Underst. Mol. Simul.* 2002, pp. 63–107.
- [33] Evgeny V. Podryabinkin and Alexander V. Shapeev. “Active learning of linearly parametrized interatomic potentials”. In: *Comput. Mater. Sci.* 140 (2017), pp. 171–180.
- [34] Murray S. Daw and M.I. Baskes. “Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals”. In: *Phys. Rev. B* 29 (1984), pp. 6443–6453.
- [35] Tzu-Ray Shan et al. “Charge-optimized many-body potential for the Hf/HfO system”. In: *Phys. Rev. B* 81 (2010), p. 125328.
- [36] Tao Liang et al. “Classical atomistic simulations of surfaces and heterogeneous interfaces with the charge-optimized many body (COMB) potentials”. In: *Mater. Sci. Eng. R* 74 (2013), pp. 255–279.
- [37] J. Tersoff. “Empirical interatomic potential for silicon with improved elastic properties”. In: *Phys. Rev. B* 38 (1988), pp. 9902–9905.
- [38] Steven W. Rick, Steven J. Stuart, and B.J. Berne. “Dynamical fluctuating charge force fields: Application to liquid water”. In: *J. Chem. Phys.* 101 (1994), pp. 6141–6156.
- [39] Hans C. Andersen. “Molecular dynamics simulations at constant pressure and/or temperature”. In: *J. Chem. Phys.* 72 (1980), pp. 2384–2393.
- [40] Denis J. Evans and Brad Lee Holian. “The Nose-Hoover thermostat”. In: *J. Chem. Phys.* 83 (1985), pp. 4069–4074.
- [41] M. Born and R. Oppenheimer. “Zur Quantentheorie der Molekeln”. In: *Ann. Phys.* 389 (1927), pp. 457–484.
- [42] Felix Bloch. “Über die Quantenmechanik der Elektronen in Kristallgittern”. In: *Zeitschrift für Phys.* 52 (1929), pp. 555–600.
- [43] L.H. Thomas. “The calculation of atomic fields”. In: *Math. Proc. Cambridge Philos. Soc.* 23 (1927), p. 542.
- [44] E. Fermi. “Un Metodo Statistico per la Determinazione di alcune Proprieta dell’Atomo”. In: *Rend. Accad. Naz. Lincei* 136 (1927), pp. 602–607.

- [45] P. Hohenberg and W. Kohn. “Inhomogeneous Electron Gas”. In: *Phys. Rev.* 136 (1964), B864–B871.
- [46] W. Kohn and L.J. Sham. “Self-consistent equations including exchange and correlation effects”. In: *Phys. Rev.* 140 (1965), A1133–A1138.
- [47] D. Ceperley. “Ground state of the fermion one-component plasma: A Monte Carlo study in two and three dimensions”. In: *Phys. Rev. B* 18 (1978), pp. 3126–3138.
- [48] D.M. Ceperley and B.J. Alder. “Ground state of the electron gas by a stochastic method”. In: *Phys. Rev. Lett.* 45 (1980), pp. 566–569.
- [49] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. “Generalized Gradient Approximation Made Simple”. In: *Phys. Rev. Lett.* 77 (1996), pp. 3865–3868.
- [50] R.O. Jones. “Density functional theory: Its origins, rise to prominence, and future”. In: *Rev. Mod. Phys.* 87 (2015).
- [51] Vladimir I. Anisimov, F. Aryasetiawan, and A.I. Lichtenstein. “First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA + U method”. In: *J. Phys. Condens. Matter* 9 (1997), pp. 767–808.
- [52] A.I. Liechtenstein, V.I. Anisimov, and J. Zaanen. “Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators”. In: *Phys. Rev. B* 52 (1995).
- [53] M. T. Czyżyk and G.A. Sawatzky. “Local-density functional and on-site correlations: The electronic structure of La_2CuO_4 and LaCuO_3 ”. In: *Phys. Rev. B* 49 (1994), pp. 14211–14228.
- [54] Vladimir I. Anisimov, Jan Zaanen, and Ole K. Andersen. “Band theory and Mott insulators: Hubbard U instead of Stoner I”. In: *Phys. Rev. B* 44 (1991), pp. 943–954.
- [55] S.L. Dudarev et al. “Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study”. In: *Phys. Rev. B* 57 (1998), pp. 1505–1509.
- [56] J. C. Slater. “Wave Functions in a Periodic Potential”. In: *Phys. Rev.* 51 (1937), pp. 846–851.
- [57] J.C. Slater. “An Augmented Plane Wave Method for the Periodic Potential Problem”. In: *Phys. Rev.* 92 (1953), pp. 603–608.
- [58] M.M. Saffren and J.C. Slater. “An Augmented Plane-Wave Method for the Periodic Potential Problem. II”. In: *Phys. Rev.* 92 (1953), pp. 1126–1128.
- [59] O.K. Andersen. “Linear methods in band theory”. In: *Phys. Rev. B* 12 (1975), pp. 3060–3083.
- [60] E. Sjöstedt, L. Nordström, and D.J. Singh. “Alternative way of linearizing the augmented plane-wave method”. In: *Solid State Commun.* 114 (2000), pp. 15–20.

- [61] P. Blaha et al. *WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*. Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001.
- [62] P. E. Blöchl. “Projector augmented-wave method”. In: *Phys. Rev. B* 50 (1994), pp. 17953–17979.
- [63] G. Kresse. “From ultrasoft pseudopotentials to the projector augmented-wave method”. In: *Phys. Rev. B* 59 (1999), pp. 1758–1775.
- [64] M. J. Frisch et al. *Gaussian 09, Revision B.01*. Wallingford CT, 2009.
- [65] Jon Marangos. “Laser science: Even harder X-rays”. In: *Nature* 481 (2012), pp. 452–453.
- [66] Joachim Ullrich, Artem Rudenko, and Robert Moshhammer. “Free-Electron Lasers: New Avenues in Molecular Physics and Photochemistry”. In: *Annu. Rev. Phys. Chem.* 63 (2012), pp. 635–660.
- [67] L.X. Chen, X. Zhang, and M.L. Shelby. “Recent advances on ultrafast X-ray spectroscopy in the chemical sciences”. In: *Chem. Sci.* 5 (2014), pp. 4136–4152.
- [68] P Citrin and G Wertheim. “Photoemission from surface-atom core levels, surface densities of states, and metal-atom clusters: A unified picture”. In: *Phys. Rev. B* 27 (1983), pp. 3176–3200.
- [69] Börje Johansson and Nils Mårtensson. “Core-level binding-energy shifts for the metallic elements”. In: *Phys. Rev. B* 21 (1980), pp. 4427–4457.
- [70] Weine Olovsson et al. “First principle calculations of core-level binding energy and Auger kinetic energy shifts in metallic solids”. In: *J. Electron Spectros. Relat. Phenomena* 178179 (2010), pp. 88–99.
- [71] T. Marten et al. “Ab initio study of disorder broadening of core photoemission spectra in random Cu-Pd and Ag-Pd alloys”. In: *Phys. Rev. B - Condens. Matter Mater. Phys.* 72 (2005).
- [72] Magnus Aldén, H.L. Skriver, and Börje Johansson. “Ab initio surface core-level shifts and surface segregation energies”. In: *Phys. Rev. Lett.* 71 (1993), pp. 2449–2452.
- [73] Magnus Aldén, Hans L. Skriver, and Börje Johansson. “Surface core-level shifts for simple metals”. In: *Phys. Rev. B* 50 (1994), pp. 12118–12130.
- [74] Henrik Grönbeck. “The bonding in thiolate protected gold nanoparticles from Au4f photoemission core level shifts”. In: *Nanoscale* 4 (2012), p. 4178.
- [75] M. Tchapyguine et al. “Absolute core-level binding energy shifts between atom and solid: The Born-Haber cycle revisited for free nanoscale metal clusters”. In: *J. Electron Spectros. Relat. Phenomena* 166-167 (2008), pp. 38–44.
- [76] I. Pilch et al. “Size-controlled growth of nanoparticles in a highly ionized pulsed plasma”. In: *Appl. Phys. Lett.* 102 (2013), p. 033108.

- [77] M.A. Lieberman and A.J. Lichtenberg. *Principles of Plasma Discharges and Materials Processing*. Wiley, 2005.
- [78] Chunshi Cui and J. Goree. “Fluctuations of the charge on a dust grain in a plasma”. In: *IEEE Trans. Plasma Sci.* 22 (1994), pp. 151–158.
- [79] H.M. Mott-Smith and Irving Langmuir. “The theory of collectors in gaseous discharges”. In: *Phys. Rev.* 28 (1926), pp. 727–763.
- [80] J.E. Allen. “Probe theory - the orbital motion approach”. In: *Phys. Scr.* 45 (1992), pp. 497–503.
- [81] Márton Lampe et al. “Trapped ion effect on shielding, current flow, and charging of a small object in a plasma”. In: *Phys. Plasmas* 10 (2003), pp. 1500–1513.
- [82] S. A. Khrapak and G. E. Morfill. “An interpolation formula for the ion flux to a small particle in collisional plasmas”. In: *Phys. Plasmas* 15 (2008), p. 114503.
- [83] I.H. Hutchinson and L. Patacchini. “Computation of the effect of neutral collisions on ion current to a floating sphere in a stationary plasma”. In: *Phys. Plasmas* 14 (2007), p. 013505.
- [84] Marco Gatti and Uwe Kortshagen. “Analytical model of particle charging in plasmas over a wide range of collisionality”. In: *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* 78 (2008), p. 046402.
- [85] Z. Zakrzewski and T. Kopiczynski. “Effect of collisions on positive ion collection by a cylindrical Langmuir probe”. In: *Plasma Phys.* 16 (1974), pp. 1195–1198.
- [86] S.M. Foiles, M.I. Baskes, and M.S. Daw. “Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys”. In: *Phys. Rev. B* 33 (1986), pp. 7983–7991.
- [87] R.E. Honig and D.A. Kramer. *Vapor Pressure Data for the Solid and Liquid Elements*. RCA Laboratories, David Sarnoff Research Center, 1969.
- [88] Gregory Grochola, Salvy P. Russo, and Ian K. Snook. “On morphologies of gold nanoparticles grown from molecular dynamics simulation”. In: *J. Chem. Phys.* 126 (2007), p. 164707.
- [89] F. Baletto, C. Mottet, and R. Ferrando. “Reentrant Morphology Transition in the Growth of Free Silver Nanoclusters”. In: *Phys. Rev. Lett.* 84 (2000), pp. 5544–5547.
- [90] S.M. Foiles, M.I. Baskes, and M.S. Daw. “Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys”. In: *Phys. Rev. B* 33 (1986), pp. 7983–7991.
- [91] W.J. Hehre, R. Ditchfield, and J.A. Pople. “Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules”. In: *J. Chem. Phys.* 56 (1972).

- [92] Karine Gouriet, Marc Sentis, and Tatiana E. Itina. “Molecular Dynamics Study of Nanoparticle Evaporation and Condensation in a Gas”. In: *J. Phys. Chem. C* 113 (2009), pp. 18462–18467.
- [93] Francesca Baletto and Riccardo Ferrando. “Structural properties of nanoclusters: Energetic, thermodynamic, and kinetic effects”. In: *Rev. Mod. Phys.* 77 (2005), pp. 371–423.
- [94] F. Baletto, C. Mottet, and R. Ferrando. “Microscopic mechanisms of the growth of metastable silver icosahedra”. In: *Phys. Rev. B* 63 (2001), p. 155408.
- [95] Y.K. Lan et al. “Nucleation of decahedral Ag nanocrystals”. In: *RSC Adv.* 4 (2014), p. 13768.
- [96] G.J. Ackland and A.P. Jones. “Applications of local crystal structure measures in experiment and simulation”. In: *Phys. Rev. B - Condens. Matter Mater. Phys.* 73 (2006).
- [97] Chih-Chung Chang and Chih-Jen Lin. “LIBSVM: A Library for Support Vector Machines”. In: *ACM Trans. Intell. Syst. Technol. Artic.* 2 (2011).
- [98] F. Pedregosa et al. “Scikit-learn: Machine Learning in Python”. In: *Journal of Machine Learning Research* 12 (2011), pp. 2825–2830.
- [99] Alexander Stukowski. “Structure identification methods for atomistic simulations of crystalline materials”. In: *Model. Simul. Mater. Sci. Eng* 20 (2012), pp. 45021–15.
- [100] Georg Rollmann et al. “Shellwise Mackay transformation in iron nanoclusters”. In: *Phys. Rev. Lett.* 99 (2007), pp. 61–46.
- [101] Riccardo Ferrando, Julius Jellinek, and Roy L. Johnston. “Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles”. In: *Chem. Rev.* 108 (2008), pp. 845–910.
- [102] W.E. Kaden et al. “Electronic Structure Controls Reactivity of Size-Selected Pd Clusters Adsorbed on TiO₂ Surfaces”. In: *Science* 326 (2009), pp. 826–829.
- [103] Yaroslava Lykhach et al. “Counting electrons on supported nanoparticles”. In: *Nat. Mater.* 15 (2016), pp. 1–6.
- [104] S. Peters et al. “Size-dependent XPS spectra of small supported Au-clusters”. In: *Surf. Sci.* 608 (2013), pp. 129–134.
- [105] S. Peredkov et al. “Size determination of free metal clusters by core-level photoemission from different initial charge states”. In: *Phys. Rev. B - Condens. Matter Mater. Phys.* 76 (2007), pp. 1–4.
- [106] S. Peredkov et al. “Free nanoscale sodium clusters studied by core-level photoelectron spectroscopy”. In: *Phys. Rev. B* 75 (2007), p. 235407.
- [107] Rudy Coquet, Kara L. Howard, and David J. Willock. “Theory and simulation in heterogeneous gold catalysis”. In: *Chem. Soc. Rev.* 37 (2008), p. 2046.

- [108] Eric C. Tyo and Stefan Vajda. “Catalysis by clusters with precise numbers of atoms”. In: *Nat. Nanotechnol.* 10 (2015), pp. 577–588.
- [109] R. Meyer et al. “Surface chemistry of catalysis by gold”. In: *Gold Bull.* 37 (2004), pp. 72–124.
- [110] Liang Zhang and Graeme Henkelman. “Computational Design of Alloy-Core@Shell Metal Nanoparticle Catalysts”. In: *ACS Catal.* 5 (2015), pp. 655–660.
- [111] P.H. Citrin, G.K. Wertheim, and Y. Baer. “Core-level binding energy and density of states from the surface atoms of gold”. In: *Phys. Rev. Lett.* 41 (1978), pp. 1425–1428.
- [112] Dan Dalacu, Jolanta E. Klemberg-Sapieha, and Ludvik Martinu. “Substrate and morphology effects on photoemission from core-levels in gold clusters”. In: *Surf. Sci.* 472 (2001), pp. 33–40.
- [113] A. Howard et al. “Initial and final state effects in photoemission from Au nanoclusters on TiO₂”. In: *Surf. Sci.* 518 (2002), pp. 210–224.
- [114] G.K. Wertheim, S.B. DiCenzo, and S.E. Youngquist. “Unit Charge on Supported Gold Clusters in Photoemission Final State”. In: *Phys. Rev. Lett.* 51 (1983), pp. 2310–2313.
- [115] Wei Ping Zhou et al. “Size effects in electronic and catalytic properties of unsupported palladium nanoparticles in electrooxidation of formic acid”. In: *J. Phys. Chem. B* 110 (2006), pp. 13393–13398.
- [116] M.C. Patterson et al. “Formation and stability of dense arrays of Au nanoclusters on hexagonal boron nitride/Rh(111)”. In: *Phys. Rev. B* 89 (2014), p. 10.
- [117] Lukas Köhler and Georg Kresse. “Density functional study of CO on Rh(111)”. In: *Phys. Rev. B* 70 (2004), p. 165405.
- [118] Federico Calle-Vallejo et al. “Introducing structural sensitivity into adsorption-energy scaling relations by means of coordination numbers”. In: *Nat. Chem.* 7 (2015), pp. 403–410.
- [119] Giannis Mpourmpakis, Antonis N. Andriotis, and Dionisios G. Vlachos. “Identification of Descriptors for the CO Interaction with Metal Nanoparticles”. In: *Nano Lett.* 10 (2010), pp. 1041–1045.
- [120] Xianfeng Ma and Hongliang Xin. “Orbitalwise Coordination Number for Predicting Adsorption Properties of Metal Nanocatalysts”. In: *Phys. Rev. Lett.* 118 (2017), p. 036101.
- [121] Marçal Capdevila-Cortada et al. “Reactivity descriptors for ceria in catalysis”. In: *Appl. Catal. B Environ.* 197 (2016), pp. 299–312.
- [122] J.K. Norskov and S. Holloway. “On the electronic factor in catalysis”. In: *Vacuum* 33 (1983), p. 876.
- [123] B. Hammer and J.K. Norskov. *Why gold is the noblest of all the metals*. 1995.

- [124] Matthew Neurock and Rutger A. van Santen. “A First Principles Analysis of C-H Bond Formation in Ethylene Hydrogenation”. In: *J. Phys. Chem. B* 104 (2000), pp. 11127–11145.
- [125] Christopher J. Heard, Samira Siahrostami, and Henrik Grönbeck. “Structural and Energetic Trends of Ethylene Hydrogenation over Transition Metal Surfaces”. In: *J. Phys. Chem. C* 120 (2016), pp. 995–1003.
- [126] Toshiaki Ohtani et al. “Suppression of formation of ethylidyne on Pt(111) by reversibly adsorbed di- σ -bonded ethylene studied by in situ IRAS”. In: *Surf. Sci.* 415 (1998), pp. L983–L987.
- [127] Viktor Nilsson et al. “Trends in adsorbate induced core level shifts”. In: *Surf. Sci.* 640 (2015), pp. 59–64.
- [128] Can Xu and Xiaogang Qu. “Cerium oxide nanoparticle: a remarkably versatile rare earth nanomaterial for biological applications”. In: *NPG Asia Mater.* 6 (2014), e90–e90.
- [129] Soumen Das et al. “Cerium oxide nanoparticles: applications and prospects in nanomedicine”. In: *Nanomedicine* 8 (2013), pp. 1483–1508.
- [130] Geert Cornelis et al. “Solubility and Batch Retention of CeO₂ Nanoparticles in Soils”. In: *Environ. Sci. Technol.* 45 (2011), pp. 2777–2782.
- [131] Tiziano Montini et al. “Fundamentals and Catalytic Applications of CeO₂-Based Materials”. In: *Chem. Rev.* 116 (2016), pp. 5987–6041.
- [132] N.V. Skorodumova et al. “Quantum Origin of the Oxygen Storage Capability of Ceria”. In: *Phys. Rev. Lett.* 89 (2002), p. 166601.
- [133] Sameer Deshpande et al. “Size dependency variation in lattice parameter and valency states in nanocrystalline cerium oxide”. In: *Appl. Phys. Lett.* 87 (2005), p. 133113.
- [134] Peter Caravan et al. “Gadolinium(III) Chelates as MRI Contrast Agents: Structure, Dynamics, and Applications”. In: *Chem. Rev.* 99 (1999), pp. 2293–2352.
- [135] Peter Caravan. “Strategies for increasing the sensitivity of gadolinium based MRI contrast agents”. In: *Chem. Soc. Rev.* 35 (2006), p. 512.
- [136] Johan O. Nilsson et al. “Ionic conductivity in Gd-doped CeO₂: Ab initio color-diffusion nonequilibrium molecular dynamics study”. In: *Phys. Rev. B* 93 (2016).
- [137] Suresh Babu et al. “Dopant-mediated oxygen vacancy tuning in ceria nanoparticles”. In: *Nanotechnology* 20 (2009).
- [138] Duane J. Smythe et al. “Quantitative determination of cerium oxidation states in alkali-aluminosilicate glasses using M4,5-edge XANES”. In: *J. Non. Cryst. Solids* 378 (2013), pp. 258–264.
- [139] M. Magnuson et al. “Electronic-structure investigation of CeB₆ by means of soft-x-ray scattering”. In: *Phys. Rev. B* 63 (2001), p. 075101.

- [140] O. Gunnarsson and K. Schönhammer. “Electron spectroscopies for Ce compounds in the impurity model”. In: *Phys. Rev. B* 28 (1983), pp. 4315–4341.
- [141] S.O. Kucheyev et al. “Electronic structure of nanoporous ceria from x-ray absorption spectroscopy and atomic multiplet calculations”. In: *Phys. Rev. B* 76 (2007), p. 235420.

List of included publications and contrubtions

- [I] **Molecular dynamics simulation of the growth of Cu nanoclusters from Cu ions in a plasma**

A. Tal, P. Munger, I. Abrikosov, N. Brenning, I. Pilch, U. Helmersson
Physical Review B **90**, 165421 (2014).

I took part in planning the project. I carried out theoretical calculations and data analysis. I wrote most of the manuscript.

- [II] **Morphology transition mechanism from icosahedral to decahedral phase during growth of Cu nanoclusters**

A. Tal, P. Munger, I. Abrikosov
Physical Review B **92**, 020102 (2015).

I planned the study, carried out calculations and data analysis. The majority of the manuscript was written by me.

- [III] **Nanoparticle growth by collection of ions: orbital motion limited theory and collision-enhanced collection**

I. Pilch, L. Caillault, T. Minea, U. Helmersson, A. Tal, I. Abrikosov, P. Munger and N. Brenning
Journal of Physics D: Applied Physics **49**, 395208 (2016).

I took part in planning the study. I performed numerical simulations for the evaporation of nanoparticles and contributed to the manuscript.

- [IV] **Origin of the core-level binding energy shifts in Au nanoclusters**

A. Tal, W. Olovsson, I. Abrikosov
Physical Review B **95**, 245402 (2017).

I took part in planning the study. I performed numerical simulations and

wrote majority of the manuscript.

[V] **Correlation of core-level shifts and ethylene absorption in Pd nanoclusters**

A. Tal, A. P. Borbon, H. Grönbeck, I. Abrikosov

To be submitted

I planned the study, carried out calculations and data analysis. The majority of the manuscript was written by me.

[VI] **Cerium oxide nanoparticles with antioxidant capabilities and gadolinium integration for MRI contrast enhancement**

P. Eriksson, A. Tal, A. Skallberg, C. Brommesson, Z. Hu, R. D. Boyd, W. Olovsson, N. Fairley, I. A. Abrikosov, X. Zhang and K. Uvdal

Submitted to Scientific Reports

I participated in planning the study. I performed numerical calculation of the spectra and participated in data analysis and contributed to the manuscript.

Related, not included publications

- [1] **Pressure-induced crossing of the core levels in 5d metals**
A. Tal, M. I. Katsnelson, M. Ekholm, J. Jönsson, L. Dubrovinsky, N. Dubrovinskaia and I. Abrikosov
Physical Review B, **93**, 205150 (2016).

- [2] **Effects of rhenium on graphene grown on SiC(0001)**
C. Xia, A. Tal, L. I. Johansson, W. Olovsson, I. A. Abrikosov, C. Jacobia
Journal of Electron Spectroscopy and Related Phenomena, **222**, 117-121 (2018).

- [3] **Damage accumulation in diamond during ion implantation**
R. Khmel'nitsky, V. Dravin, A. Tal, E. Zavedeev, A. Khomich, A. Khomich, A. Alekseev and S. Terentiev
Journal of Materials Research, **30**, 1583-1592 (2015).

Papers

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