TECHNISCHE UNIVERSITÄT
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Studienarbeit

Available Atomic Scale Simulation Software Packages

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Contents

1   Introduction

Physical characteristics of macroscopic materials are determined by thermodynamical parameters of temperature, pressure, spacial sizes (volume) as well as by microscopic parameters of disorder, vacancies. By varying the length scale of a sample over many orders of magnitude from meter to Angstrom, self–averaging over microscopic parameters is violated at mesoscopic scales, and "fingerprint" of disorder has essential influence on the macroscopic parameters of the system. That is way usual classical and thermodynamical descriptions of continuum systems become not valid and the mesoscopic range requires completely different physical approach. Quantum mechanical methods calculate as well the atomic structures of materials, revealing the microscopic properties such as spacial distribution of atoms, chemical bonding, creation energy of different defects etc., as well as the electronic structures, including the band structure,defect levels in the band gap, density of electronic states. For understanding and improving the properties of mesoscopic materials, it is thus crucial to learn atomistic aspects of these materials.

In this respect we note that present day experimental methods to develop new materials are still mainly done by trial and error. Typically the macroscopic equations (e.g. rate equations or hydrodynamic theories) have a very limited physical meaning and can not be used to understand the microscopic behavior of materials. Nowadays the strongest quantum mechanical tool to study the ground state properties of solid states with correlated atoms and electrons on atomic scale is the Density Functional Theory (DFT). Development of ab initio Molecular Dynamics (MD) allows one to investigate a time evolution of atomic positions under assumption of definite interatomic forces. At the same time, inclusion of dynamical frictions in the MD method due to linking a thermal bath to the system makes a physical ground to study the amorphous structures. A central objective should be the combination of detailed "ab-initio" calculations (e.g. DFT) and the molecular dynamics/kinetic Monte Carlo approach for evolution of morphologies and structures. This enables one to study the properties of these materials at finite temperature, and under non-equilibrium conditions. It is only by the use of such simulation techniques that we will be able to assess e.g. the importance of the various individual processes for the film growth, such as diffusion, adsorption and desorption

of different species, attachment of atoms at steps, etc.

1.1 Computational methods

This section give a brief introduction to the physical background and methods of modern material simulations.

1.1.1 Ab-initio simulation methods

DFT The ab–initio DFT method is based to two Hohenberg–Kohn theorems, formulated as follows:

Every observable quantity of a stationary quantum mechanical system is determined by the ground–state density alone.

The exact ground–state density of a system in a particular external potential can be found by minimization of the energy functional.

The practical scheme of calculations has been given by Kohn and Sham, proving that *"the ground–state density of the interacting particle system can be calculated as the ground–state density of an auxiliary non–interacting system"*. According to the Kohn-Sham (KS) scheme the ground–state energy of the electron-ion system in the DFT is given by the following energy functional:

$$E[\rho] = -\frac{\hbar}{2m_e} 2 \sum_{n=1}^{N_e/2} \int \phi_n(\mathbf{r})^* \nabla^2 \phi_n(\mathbf{r}) \mathrm{d}^3\mathbf{r} + \frac{1}{2} \int \frac{\rho^{tot}(\mathbf{r})\rho^{tot}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, \mathrm{d}^3\mathbf{r}\mathrm{d}^3\mathbf{r}' + E_{xc}[\rho(\mathbf{r})] \tag{1}$$

where

$$\rho(\mathbf{r}) = 2 \sum_{n=1}^{N_e/2} |\phi_n(\mathbf{r})|^2, \qquad \rho^{tot}(\mathbf{r}) = \rho(\mathbf{r}) + \rho^{ion}(\mathbf{r}) \tag{2}$$

The number of electrons is given by N_e. The central assumption in the KS scheme is that, for each interacting electron system with external potential $v_0(\mathbf{r})$, a local potential $v_{s,0}(\mathbf{r})$ (the Kohn- Sham potential) exists such that the density $\rho(\mathbf{r})$ of the non–interacting system equals the density $\rho_0(\mathbf{r})$ of the interacting system. The interaction between the electrons is described by an electrostatic term and the exchange correlation energy $E_{xc}[\rho(\mathbf{r})]$, the latter of which is not known exactly. The most popular and simplest approximation to evaluate the exchange–correlation energy E_{xc} is the local density approximation (LDA). Pseudopotentials are used to evaluate the ion-electron

interaction and a complete plane wave basis with N states is used to expand the wave function of an electron in the extended crystalline srtuctures. Early implementations iteratively diagonalized the set of N until self-consistency was achieved, a procedure which scaled as $O(N^3)$, making it prohibitively expensive to study more than a few tens of atoms. More recent approaches overcome the limitations of direct diagonalization by recasting the problem into an iterative search for the lowest energy configuration. Modern implementations include the Car-Parrinello simulated annealing scheme and the more efficient methods based on conjugate gradient energy minimization. These methods typically scale as $O(N^2)$, since they are dominated by the cost of computing the fast Fourier transform (FFT), which scales as Nlog(N), and by wave function orthonormalization, which scales as $O(N^3)$[14].

Tight-Binding approach, [14] The tight-binding (TB) approach significantly reduces the cost of solving the single-electron Schroedinger equations by making several key approximations. First, a minimal basis set of valence atomic orbitals is used to expand the wave function for each of electrons in the system, so that typically 10 to 20 times fewer basis functions are used in TB compared to DFT. Second, self-consistency in the eigensolution is neglected so that iterative solutions are no longer required. Last, all interactions are parameterized. The conventional approach diagonalizes the set of parameterized. TB generally scales as $O(N^3)$.

1.1.2 Molecular Dynamics method

Classical molecular dynamics (MD) simulations describe the atomic scale dynamics of a system, where atoms and molecules move while simultaneously interacting with many other atoms and molecules in their vicinity according to an assumed interaction potential. The dynamic evolution of the system is governed by Newton's equations of motion.

The atomic and molecular interactions describing the system dynamics are given by classical many body force field functions. The interatomic or intermolecular interaction potential $V(\{R_I\})$ can be written in terms of pair and many-body interactions, depending on the relative distances among different atoms. The simplest classical

molecular dynamic model has been proposed as hard-sphere with pairwise interactions, which can be obtained from more accurate quantum simulations. The Lennard-Jones type soft potential were also applied later to study the structure and dynamics of simple liquids.

Atomic forces are obtained as analytic derivatives of the interaction energy functions, $F_I(\{R_I\}) = -dV/dR_I$, and are used to construct Hamilton's equations of motion, which are 2nd order, ordinary differential equations. These equations are approximated as finite difference equations, with a discrete time step dt, and are solved by standard time integration algorithms. The simulations can be performed under a variety of physical conditions through discrete time evolution, starting from specified initial condition.

To model realistic materials, such as metals and semiconductors with complex many-body interactions, three approaches have emerged[8]:

- development of interatomic potential according to the Born-Openheimer expansion (Pearson, Stillinger-Weber);

- constractin of potentials to modelize the local environment using electron density distributions (Embedded Atom Method);

- potentials that introduce the local electronic environment directly into pair potentials (Tersoff).

1.1.3 Kinetic Monte Carlo Methods, [8]

The Monte Carlo (MC) method refers to any stochastic technique, which investigates problems by sampling from random distributions, and utilize concepts of probability theory. The MC method is simply a statistical method for solving deterministic or probabilistic problems. A computer simulation represents a physical experiment carried out numerically. MC simulations generally require random numbers generated according to specific statistical distributions.

In some applications of the MC method, the number of new configurations available to the system at any MC step is finite and enumerable. The configuration space is discrete, rather than continuous. In other words, at each MC step, we can determine all

the phenomena and the rates at which they occur, i.e. all the changes that the system can possibly experience. Therefore, we need not perform a random change in the system at each MC step and then accept or reject that change on the basis of a specified criterion. Based on the relative rates associated with each change, we can choose and execute a single change to the system from the list of all possible changes at each MC step. This is the general idea of the Kinetic Monte Carlo (KMC) method. They can take into account simultaneously many different microscopic mechanisms, covering very different time scales that are difficult to handle with other atomistic simulation techniques. In order to perform a KMC simulation, the first step is to tabulate the rate r_i of events or phenomenon $i = 1, ..., M$, occuring at arbitrary point of the system. The probability of choosing an event is defined as the rate at which the event occurs relative to the sum of the rates of all possible events.

Once an event is chosen, the system is changed appropriately, and the list of events that can occur at the next KMC step is updated. Therefore, at each KMC step, one event denoted by m is randomly chosen from all of the M events that can possibly occur at that step, as follows:

$$\frac{\sum\limits_{i=0}^{m-1} r_i}{\sum\limits_{i=0}^{M} r_i} < \xi < \frac{\sum\limits_{i=0}^{m} r_i}{\sum\limits_{i=0}^{M} r_i}$$

where r_i is the rate at which event i occurs ($r_0 = 0$) and ξ is a random number uniformly distributed in the range $[\in (0, 1)]$. After an event is selected and carried out, the total number of possible events, M, and the sequence in which the events are labeled, are updated.

Advantages

- relation to experimental procedure;

- no thermodynamic quilibrium is required (in algorithm).

Disadvantages

- mechanisms and associated activation barrier have to be know in advance;

- much effort in an efficient coding, data structures.

Field of application

- surface diffusion;

- molecular beam epitaxy growth (MBE);

- chemical vapor deposition (CVD);

- defects formation, diffusion, dislocation motion;

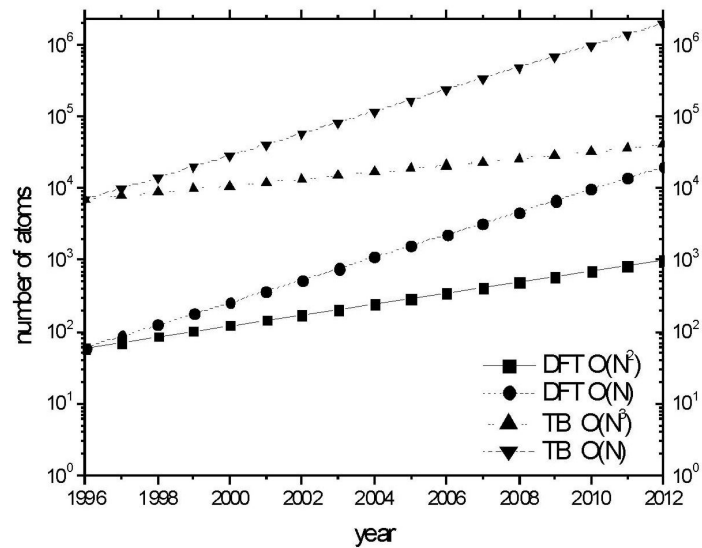- atomic layer deposition, thermal growth.

1.2   Overview

Figure 1: Extrapolated long-term trend of DFT and TB parallel computing capacity for dielectric materials, [14]

method	advantages	disadvantages	best for
ab initio • uses quantum physics • Mathematically rigorous: no empirical parameters	• Useful for a broad range of systems • Does not depend on experimental data • Calculates transition states and excited states	• Computationally expensive	• Small systems (tens of atoms) • Electronic transitions • Systems without experimental data • Systems requiring high accuracy.
Semi-empirical • Uses quantum physics • Uses experimental parameters • Uses extensive approximations	• Less demanding computationally than ab initio methods. • Calculates transition states and excited states	• Requires ab initio or experimental data for parameters. • Less rigorous than ab initio methods.	• medium-sized systems (hundreds of atoms). • Electronic transitions
Molecular-Dynamics • Uses classical physics • Relies on force field with embedded empirical parameters.	• Computationally cheap, fast and useful with limited computer resources. • Can be used for large molecules like enzymes.	• Does not calculate electronic properties • Requires ab initio or experimental data for parameters • Commercial software applicable to a limited range of molecules	• Large systems (thousands of atoms) • Systems or processes that do not involve bond breaking.

Table 1: Sysopsis of modelling techniques[12]

	Empirical interatomic potential	Density Functional Theory	Tight-Binding (TB)
Classical or quantum model?	classical	quantum	quantum
fitted parameters	yes	no	yes
Abilities of electronic structure (bands, gap states) calculations	no	yes	yes
basis set in expansion of wave function	n/a	complete; plane waves	minimal; atomic orbitals
iterate to self-consistency?	n/a	yes	no
computational cost relative to interatomic potential	1	10^5	$10^2 - 10^3$

Table 2: Classification of atomic scale computational models, [14]

2   Related articles

In this section we describe the methods of determination of microscopic properties of a system by "ab-inito methods".

2.1   Film Deposition Simulator, [7]

Film Deposition Simulator has an atomistic simulation tool for thin film deposition in three dimensions named ADEPT. The simulator is designed to ridge the atomic and mesoscopic length scales by using efficient algorithms. It includes an option to speed up surface diffusion using events with multiple diffusion hops. Sputtered particles are inserted and assigned ballistic trajectories with angular distributions appropriate for magnetron sputtering. Atoms on the surface of the film execute surface diffusion hops with rates that depend on the local configuration, and are consistent with microscopic reversibility. The potential energies are chosen to match information obtained from a database of first principles and molecular dynamics (MD) calculations. Efficient computation is accomplished by selecting atoms with probabilities that are proportional to their hop rates. A first implementation of grain boundary effects is accomplished by including an orientation variable with each occupied site. Energies and mobilities are assigned to atoms in grain boundaries using values obtained from MD. In Ref.[7] simulations of the Aliminum deposition on substrate are presented, (see, Fig.2). The film atoms occupy face centered cubic lattice sites of a single crystal. Three-dimensional films deposited on vias and trenches up to 0.05 mm in size have been simulated. We discuss these films in the context of step coverage issues, and scaling to macroscopic sizes. Texture development is discussed in the light of simulations showing anisotropic crystal growth.
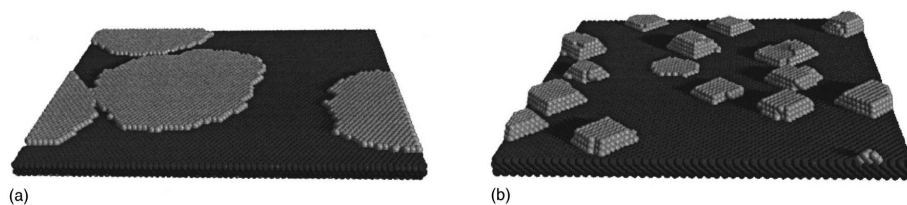

(a)   (b)

Figure 2: Al deposition on different surfaces (a) {111} (b) {100}, [7]

The ADEPT model of deposition includes two basic events in the current level of implementation: the deposition event and surface diffusion. Evaporation of film or substrate atoms could be included if conditions require it. The model can be applied to any materials which form crystalline deposits, provided atomic level information is available on the energies of atoms in representative surface configurations. All atoms are constrained to lie on the sites of a perfect crystal lattice which pervades all of space. Vacancies and clusters of vacancies are the only defects allowed. Interstitials are not included at present, since they have small concentrations in metals under normal conditions. The effect of growth on surfaces with different crystallographic orientations is accomplished by setting the substrate orientation relative to the crystal lattice so that it corresponds to the desired surface.

2.2   Metal Crystal growth, [5]

A method for extending atomistic computer simulations of solids beyond the nanosecond time scale was used to simulate metal crystal growth on the time scale of laboratory experiments. Transitions involving concerted motion of multiple atoms on the crystal surface are found to lead to remarkably smooth growth of pure aluminum. Copper is found to grow with a rougher surface, consistent with experiments. The activation energy of the multi-atom Al processes is surprisingly low, and the vibrational entropy also favors many atom displacement processes.

2.3   Pulsed Laser Deposition, [13]

In this article kinetic Monte Carlo simulations for molecular beam epitaxy (MBE) and pulsed laser depositon (PLD) are compared. It has been shown in [13] that an optimal pattern conservation during MBE is achieved for a specific ratio of diffusion to deposition rate. Furthermore, the pulsed laser deposition is presented as an alternative way to control layer by layer growth. First results concerning the island density in the sub-monolayer regime are shown in the work.
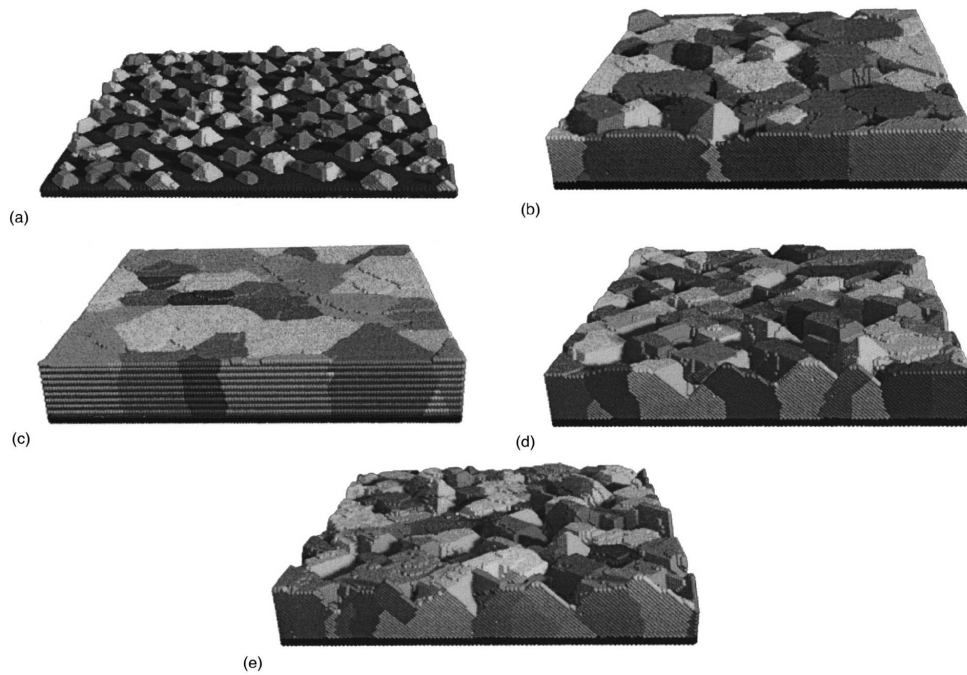
Figure 3: Deposition of Al atoms with the cosine distribution on an amorphous substrate at 300 K. An area of 40×40 nm is displayed. The fcc lattice with a $\langle 100 \rangle$ direction pointing upwards is used and two snapshots are taken at a monolayer coverage (a) and 25 layers coverage (b). A snapshot is also taken when the fcc lattice with a $\langle 111 \rangle$ pointing upward is used (c). The simulation for (b) is repeated with ten times lower grain boundary migration coefficient (d) or ten times higher deposition rate (e). The substrate atoms are shown as dark spheres, and the gray scale indicates orientations of grains, ranging from $0°$ to $180°$, [7]

2.4   MC simulations of epitaxial growth: comparison of PLD and MBE, [16]

The influence of epitaxial growth method on surface morphology was explored for 1×1 Si(001) surface using the solid-on-solid method, rate equation, Monte Carlo simulation. In simulations corresponding to molecular beam epitaxy, films of 10 monolayer thickness were deposited with a steady-state flux of 0.25 monolayers and an adatom energy of 0.3 eV. In simulations corresponding to pulsed laser deposition, films of 10 monolayer thickness were deposited with a pulsed flux of 0.5 monolayers and

0.5 pulsers and adatom energies ranging from 10 to 135 eV. Surface morphology was characterized by surface images, surface height standard deviations, and height-height correlation functions. In comparison to molecular beam epitaxy, pulsed laser deposition was found to result in smaller surface roughness at substrate temperatures below approximately 4008 C and larger surface roughness at higher temperatures. This behavior is attributed to a balance between roughening associated with pulsed deposition and smoothening associated with energetic deposition.
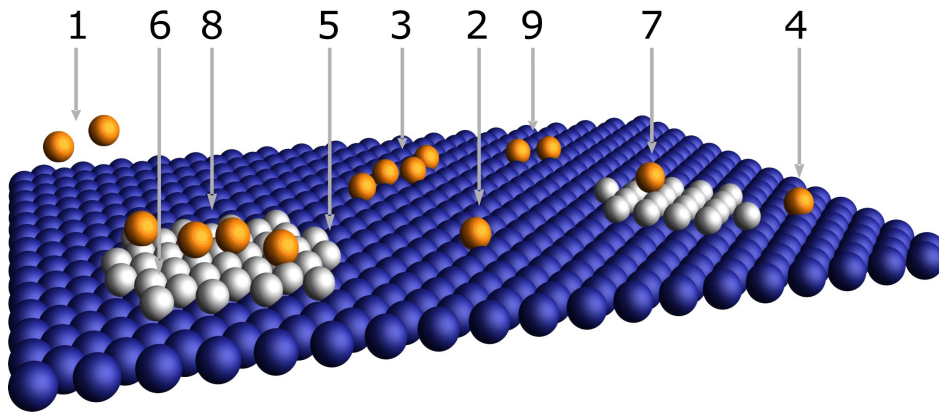

Figure 4: Physical Processes During Epitaxial Growth: (1) deposition, (2) diffusion, (3) nucleation, (4) attachment, (5) detachment, (6) edge diffusion, (7) diffusion down step, (8) nucleation on top of islands, (9) dimer diffusion, parameters obtaint from DFT calculations

2.5   Study of thin film growth in PLD by KMC simulation, [17]

In this study a pulse beam (PB) deposition model based on a square lattice is proposed and is used to simulate the process of thin film growth with the kinetic Monte Carlo method. The influence of frequency and duration of pulse on the nucleation, aggregation, and morphology of thin film growth in the early stage is investigated and discussed. The simulation results show that the morphology, island-size distribution, and dynamics behavior of island growth in PB deposition are different from those in DC deposition when their average deposition rates are the same (Fig.5). With the increase of transient deposition rate during the pulse activation, the island-size distri-

bution and morphology lose the characteristics of the $i = 1$ model. Due to the high transient deposition rate during the pulse activation, PB deposition promotes nucleation, suppresses the growth of islands and increases the island density. The atomistic mechanism of thin film growth in pulse beam deposition is also discussed in the work.
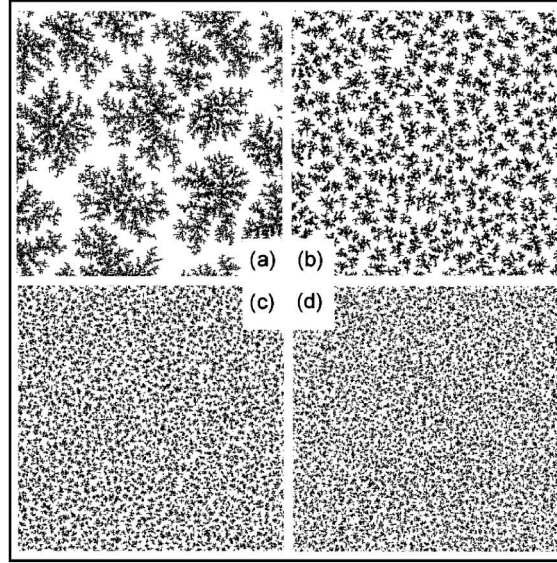

Figure 5: Morphologies of islands at the coverage of $\theta = 0.3$, (a) DC deposition, (b) $T_p = 10^{-6}s$, (c) $T_p = 10^{-9}s$, and (d) $T_p = 10^{-12}s$, when $h = 10^{10}$ Hz and $f = 100$ Hz for pulsed beam deposition.

2.6 Multiple time scale simulations of metal crystal growth, [5]

A method for extending atomistic computer simulations of solids beyond the nanosecond time scale was used to simulate metal crystal growth on the time scale of laboratory experiments. Transitions involving concerted motion of multiple atoms on the crystal surface are found to lead to remarkably smooth growth of pure aluminum. Copper is found to grow with a rougher surface, consistent with experiments, (see, Fig.6). Not only is the activation energy of the multi-atom Al processes surprisingly low, but vibrational entropy also favors processes where many atoms are displaced.
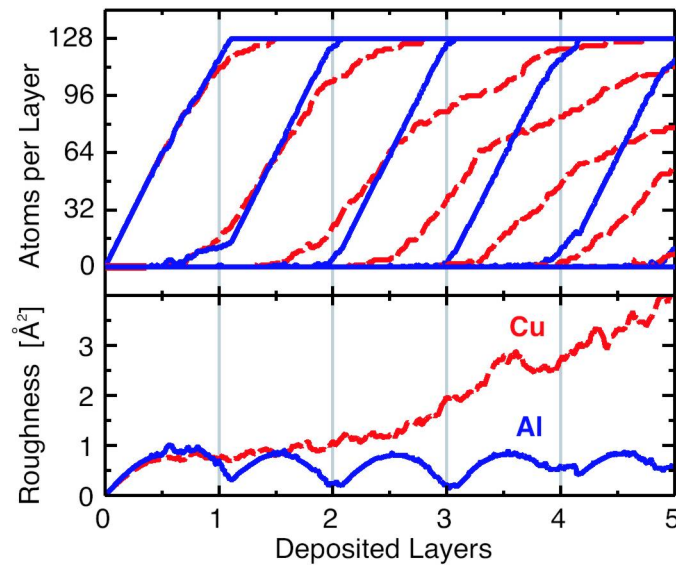
Figure 6: Upper panel shows the number of atoms in each deposited layer; lower panel gives roughness[5]

2.7   Long time scale KMC simulations, [18]

We present a method for carrying out long time scale dynamics simulations within the harmonic transition state theory approximation. For each state of the system, characterized by a local minimum on the potential energy surface, multiple searches for saddle points are carried out using random initial directions. The dimer method is used for the saddle point searches and the rate for each transition mechanism is estimated using harmonic transition state theory. Transitions are selected and the clockis advanced according to the kinetic Monte Carlo algorithm. Unlike traditional applications of kinetic Monte Carlo, the atoms are not assumed to be placed on lattice sites and a list of all possible transitions need not be specified beforehand. Instead, the relevant transitions are found on the fly during the simulation. A multiple time scale simulation of Al(100) crystal growth is presented where the deposition event, occurring on the time scale of picoseconds, is simulated by ordinary classical dynamics, whereas the time interval between deposition events, having the order of milliseconds, is simulated by the long time scale algorithm. The Al(100) surface is found to grow remarkably smooth, even at 30 K because of concerted displacements of multiple atoms with significantly lower

activation energy than adatom diffusion on the flat terrace, (see, Fig.7).

activation energy than adatom diffusion on the flat terrace, (see, Fig.7).

n = 0   n = 88   n = 176   n = 232
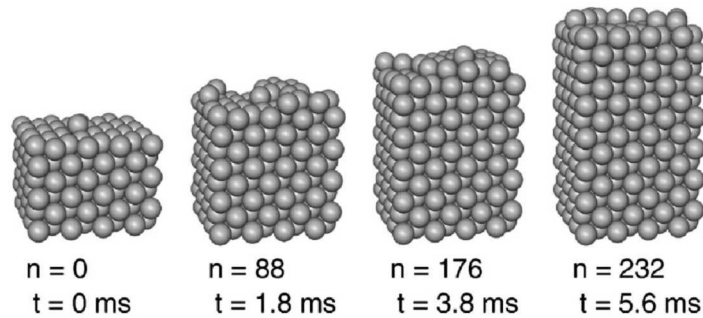t = 0 ms   t = 1.8 ms   t = 3.8 ms   t = 5.6 ms

Figure 7: Seven monolayers of Al were grown at 30 K on the Al(100) substrate. The deposition rate was one monolayer per millisecond. Even at this low temperature, the layers grown are free of defects and the surface is smooth.[18]

It is important to know how a simulation method scales with system size. To determine this, we can consider how the number of force evaluations changes when the system is doubled in size. Force evaluations are considered instead of total computational time, because the evaluation of the force can scale differently depending upon the complexity of the interaction potential. In favorable situations, evaluation of the force scales linearly with system size.

This method for carrying out long time scale dynamics simulations is efficient enough for implementation with first principles calculations, e.g. DFT method, of atomic interactions. We have implemented the method in the VASP code[39]. More information about the implementation can be found on the website http://ikazki01.chem.washington.edu/vasp/.

2.8   DFT of Surface Diffusion and Epitaxial Growth of Metals, [11]

This paper gives a summary of basic concepts of density-functional theory (DFT) and its use in state-of-the-art computations of complex processes in condensed matter physics and materials science. Particularly, the authors discuss the methods of determinations of microscopic growth parameters DFT and the subsequent description of the macroscopic phenomena on the base of obtained growth parameters. To reach the time and length scales of realistic growth conditions, DFT results are complemented
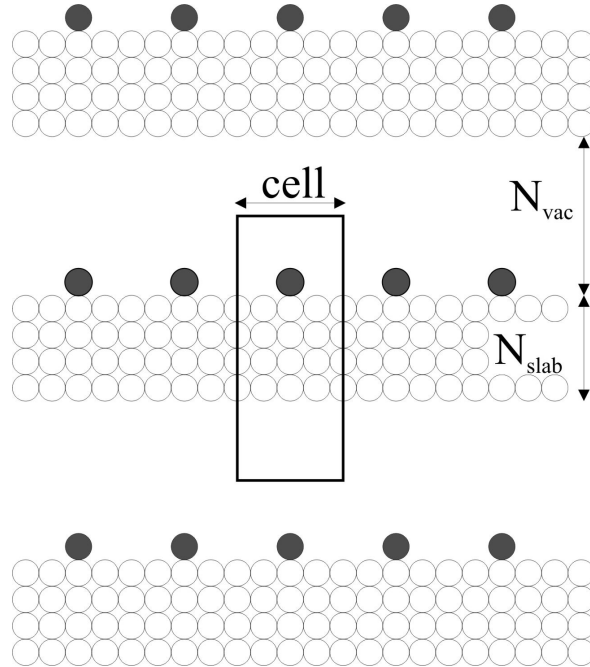
by kinetic Monte Carlo simulations.

Figure 8: Sketch of a supercell describing an "isolated" adatom at a surface (side view).[11]

As illustrated in Fig.8 the geometry repeats periodically in vertical and lateral directions. The lateral periodicity implies that a single adatom placed on a substrate is not at all a single adatom; if the cell size parallel to the surface is chosen, for example, as (2×2) we actually calculate a system with a coverage of 25%. It is therefore important to test that the interaction with the neighboring adatoms can be neglected. On a (111) surface a cell size of (2×2) is usually sufficient, but sometimes larger cells $[(3 \times 3)$ or even $(4 \times 4)]$ are necessary. To model a diffusion event along or across a step one either chooses a small island on top of a substrate or a vicinal surface. The latter has the advantage that only one step exists in the unit cell so a smaller cell size is required to attain a negligible step-step interaction. The system also repeats in the vertical direction separated by a vacuum region. The thickness of the vacuum region must be tested as well, but the computational cost of a thicker vacuum region is relatively small compared to a larger cell size or a higher number of slab layers.
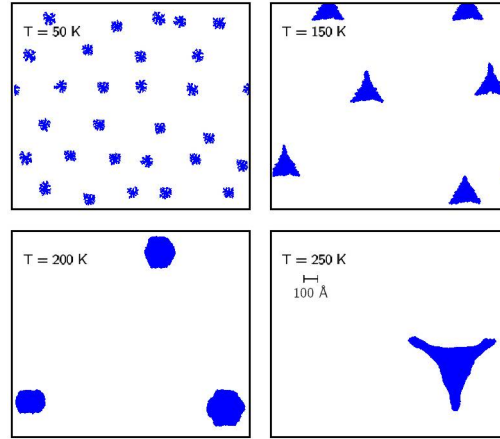
Figure 9: A surface area of (1718×1488)Å at four different substrate temperatures. The deposition rate was 0.08 ML/s and the coverage in each picture is $\theta = 0.04$ ML.

Here, we present first-principles calculations, studying the dependence of the diffusion barrier on the lattice constant for Ag on Ag (111). In the range of $\pm 5\%$ strain the DFT results exhibit an approximately linear dependence with a slope of $\approx 0.7 eV$. The calculated diffusion barrier for the unstrained system, $E_d^{Ag-Ag} = 81 meV$, is in good agreement (within the error margins of the experiment and the calculations) with the scanning tunneling microscopy (STM) results of $E_d^{Ag-Ag} = 97 meV$. The agreement between experiment and theory is achieved for the systems Ag/Pt (111) and Ag/1ML Ag/Pt (111) as well. These results are summarized in Table 3.

System	Experiment	EMT	DFT
Ag/Pt(111)	157	81	150
Ag/1ML Ag/Pt(111)	60	50	65
Ag/Ag(111)	97	67	81

Table 3: Diffusion barriers (in meV) for Ag on Pt (111), Ag on one monolayer (ML) Ag on Pt (111), and Ag on Ag (111).[11]

2.9   Electronic excitations: DFT vs. Green's-function approaches, [15]

Electronic excitations lie at the origin of most of the commonly measured spectra. However, the first-principles computation of excited states requires a larger effort than ground-state calculations, which can be very efficiently carried out within density-functional theory. On the other hand, two theoretical and computational tools can prominently complete each others in the description of electronic excitations. One of them, many-body perturbation theory, is based on a set of Green's-function equations, starting with a one-electron propagator and considering the electron-hole Green's function for the response. An alternative approach to calculating electronic excitations is the time-dependent density-functional theory (TDDFT), which offers the important practical advantage of a dependence on density rather than on multivariable Green's functions. This approach leads to a screening equation similar to the Bethe-Salpeter one, but with a two-point, rather than a four-point, interaction kernel. At present, the simple adiabatic local-density approximation has given promising results for finite systems, but has significant deficiencies in the description of absorption spectra in solids, leading to wrong excitation energies, the absence of bound excitonic states, and appreciable distortions of the spectral line shapes.

2.10   Initial oxidation mechanisms, [20]

Chemisorption of an O_2 molecule from the topmost layer to deeper subsurface layers on the Si(100) surface is studied by employing the spin-polarized generalized-gradient approximation. The calculated results reveal that an O_2 molecule is weakly adsorbed on a clean Si(100) surface with an initial spin-triplet state, but it is adiabatically chemisorbed with a spin-state conversion, when an O_2 molecule arrives at the surface with a low incident energy. Barrierless back-bond oxidation has been found to occur through dissociative chemisorption with a spin-orbit interaction followed by O-atom migration to back-bond centers. According to the depth from the surface, energy barriers are found to be increasingly necessary for chemisorption of an O_2 molecule in subsurface layers, Fig.10.
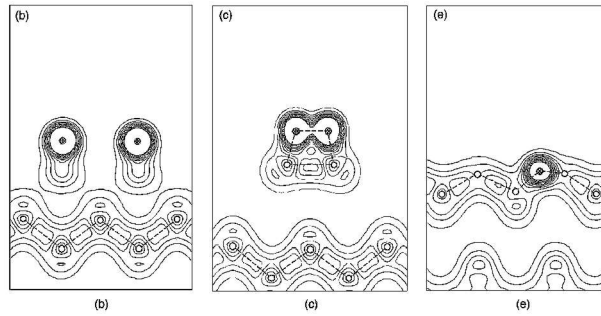
Figure 10: chemisorption of an O_2 molecule in subsurface layers

2.11   Application of TDDFT to calculate the dielectric function, [19]

The dielectric function of nonmetallic crystals of various lattice types is studied by means of a real-space and full-potential time-dependent density-functional method within the adiabatic local-density approximation. Results for the dielectric constant ε_∞ (at optical frequencies) are given for crystals of the sodium chloride, the fluoride, the wurtzite, the diamond, and the zinc-blende lattice structures. The frequency-dependent dielectric function ε_ω for the crystals in the diamond and zinc-blende lattice structures are also presented. We compare our calculation results with experimental data and other theoretical investigations. Our results for the dielectric constants ε_∞ and the dielectric functions ε_ω are in good agreement with the experimental values. The accuracy of the results is comparable to the one which is commonly found for time-dependent density functional theory calculations for molecular systems. On average we find a deviation of $4-5\%$ from experimental results for the group IV and III-V compounds in the wurtzite, zinc-blende and diamond lattice structure, $8-9\%$ for the II-VI and I-VII compounds in the zinc-blende and sodium chloride lattice structure, and up to 14% deviation for the fluoride lattice structure. The spectral features of the dielectric functions ε_ω are revealed in the calculations at relatively low energies compared to experimental data.

A Available DFT/TDDFT packages

A.1 Abinit, [22]

Abinit is a package whose main program allows one to find the total energy, charge density and electronic structure of molcules and periodic solids within Density Functional Theory (DFT) using pseudopotentials and a planewave basis. Abinit also includes options to optimize the geometry according to the DFT forces and stresses, to perform molecular dynamics simulation using these forces, to generate dynamical matrices, Born effective charges and dielectric tensors. Excited states can be computed within the Time-Dependent Density Functional Theory (for molecules), or within many-body Perturbation Theory (GW approximation).

A.2 ADF/Band[23]

ADF is a DFT software package for computational quantum chemistry. It enables first-principles electronic structure calculations and is used by theoretical and computational chemists worldwide, both in industry and in sciences. The ADF software consists of three main modules: the molecular program ADF, the periodic structure program BAND, and a graphical user interface for ADF.

ADF is used virtually in all areas of chemistry, and it is particularly popular in catalysis, inorganic and heavy element chemistries, as well as in spectroscopy. The code can be applied to all systems from proteins, solvents, polymers, surfaces, and solids, to simple molecules in the gas phase.

A.3 ASW, [24]

Properties calculated with the ASW method

- Electronic Properties:

  - electronic dispersions E (k) ("band structure");

  - electronic wave functions;

  - total/partial (site/state projected) densities of states (DOS);

- – Fermi surfaces;

- – charge densities (near future);

- – electric field gradients (near future);

- – charge densities at nuclei $\longrightarrow$ isomer shift;

- – core level spectra.

- Cohesive and Elastic Properties:

  - – cohesive energies;

  - – bulk moduli;

  - – elastic constants (near future);

  - – phonon frequencies (near future).

- Chemical Bonding:

  - – total/partial crystal orbital overlap populations (COOP).

- Magnetic Properties:

  - – total and site/state projected magnetic moments;

  - – magnetic ordering (ferro-, ferri-, antiferromagnetic states);

  - – magnetic energy gains;

  - – spin densities (near future);

  - – spin densities at nuclei $\longrightarrow$ hyperfine fields.

A.4   CAMPOS/Dacapo, [25]

Dacapo is a total energy program based on density functional theory. It uses a plane wave basis for the valence electronic states and describes the core-electron interactions by Vanderbilt ultrasoft pseudo-potentials. The program performs self-consistent calculations for both Local Density Approximation (LDA) and various Generalized Gradient Approximation (GGA) exchange-correlations potentials, using state-of-art iterative algorithms. The code may perform molecular dynamics / structural relaxation

simultaneous with solving the Schrodinger equations within density functional theory. The program may be compiled for serial as well as parallel execution and the code has been ported to many hardware platforms.

A.5 Castep (accelrys version)

CASTEP is an ab initio quantum mechanical program employing the DFT to simulate the properties of solids, interfaces, and surfaces for a wide range of material classes including ceramics, semiconductors, and metals. First principle calculations allow researchers to investigate the nature and origin of the electronic, optical, and structural properties of a system without the need of any experimental input except the atomic number of mass of the constituent atoms. CASTEP is thus well suited to research problems in solid state physics, materials science, chemistry, and chemical engineering where researchers can employ computer simulations to perform virtual experiments which can lead to tremendous savings in costly experiments and shorter developmental cycles.

A.6 Conquest

CONQUEST is an O(N) density functional code, designed to perform accurate, ab initio calculations on large numbers of atoms. Using 512 nodes of a Cray T3E, it was announced at the PsiK2000 conference (August 2000) to be capable of calculations of 16384 atoms.

A.7 CPMD, [28]

The Car-Parrinello Molecular Dynamics (CPMD) code is a plane wave/pseudopotential implementation of Density Functional Theory, particularly designed for ab-initio molecular dynamics. The main characteristics are:

- works with norm conserving or ultrasoft pseudopotentials;

- LDA, LSD and the most popular gradient correction schemes, free energy density functional implementation;

- isolated systems and system with periodic boundary conditions, k-points;

- molecular and crystal symmetry;

- wavefunction optimization: direct minimization and diagonalization;

- geometry optimization: local optimization and simulated annealing;

- molecular dynamics: constant energy, constant temperature and constant pressure;

- path integral MD;

- response functions;

- excited states.

A.8 CP-PAW, [29]

CP-PAW can perform the following calculations:

- Electronic structure (multiple K-points);

- Geometry optimizations (optional: various constraints);

- Transitions states;

- Molecular Dynamics at finite temperature (controlled by a Nose thermostat);

- Vibration frequencies;

- Lattice parameters of periodic substances;

- Hyperfine Parameter;

- Pictures of the density, spin density, wave functions; movies of the trajectory.

A.9 DoD Planewave, [30]

DoD Planewave is a scalable planewave basis density functional code for a general purpose, developed as part of the CHSSI program of the DoD HPCMO. The code treats insulators, semiconductors, metals and magnetic materials, with general symmetry. The zone sampling may be done with the Gamma point only, with special k-points

or with general user specified k-points. The present version (DoD Planewave v3.xx) performs self-consistent electronic structure, total energy and force calculations within the local density approximation. It is also capable of automated structure optimization and molecular dynamics simulations. Starting v3.00 the dynamic memory allocation is fully implemented to DoD Planewave and the dimension files are no longer needed for compilation. DoD Planewave v3.00 can run on SP2 machines or on SGI Orgin 2000 and Power Challenge machines. Future releases will incorporate a much greater range of property calculations and non-local density functionals.

A.10   FHI98, [31]

FHI98md is an efficient code to perform density functional theory total-energy calculations for materials ranging from insulators to transition metals. The package employs first-principles pseudopotentials and a plane-wave basis-set. In order to calculate the exchange and the correlation energies both the local density and generalized gradient approximations are implemented. The code has a low storage demand and performs efficiently on low budget personal computers as well as high performance computers. The main characteristics are:

- Molecular dynamics at finite temperatures;

- Charge states;

- Electric fields;

- LDA, GGA and PBE XC functionals;

- Various output routines : charge density, electrostatic and effective potentials, 3D- and XY-averaged, etc.

A.11   Fleur, [32]

The FLAPW-Method (Full Potential Linearized Augmented Plane Wave Method) is an DFT based all-electron computation method which is universally applicable to all atoms of the periodic table and to systems with compact structures as well as extended structures. It is widely considered to be the most precise electronic structure method

in solid state physics. Due to the all-electron nature of the method, magnetism is included rigorously and nuclear quantities, e.g. isomer shift, hyperfine field, electric field gradient (EFG), and core level shift are calculated routinely. Also simulations of extended systems such as surfaces, clusters or inorganic molecules represent no basic problem. The capability of calculation the forces exerted on the atoms within the LAPW method opens new perspectives in the structure optimization within molecular dynamics, which puts this method up on the same category as the widespread pseudopotential method, but able of treating systems pain-full or unattainable by the pseudopotential method. The main characteristics are:

- Utilization of Local orbitals to supplement the LAPW-basis;

- Computation of forces exerted on the atoms;

- Estimation of Electric fields applied to surfaces;

- Simulations of spin-orbital interactions in combination with magnetism;

- Ability of calculation of non-collinear magnetic structures with and without external constraints, spiral spin density waves;

- Full-relativistic treatment of core electrons (Dirac + Magnetism);

- Application of LDA, GGA XC-functional;

- Use of LDA+U Quasi-Newton-Methods to accelerate charge self-consistency.

A.12   Jaguar, [41]

Possible Calculations:

- Total energy calculations within the Hartree-Fock method, for both restricted and unrestricted (RHF, UHF and ROHF) systems;

- Møller-Plesset second order perturbation corrections theory (MP2) corrections;

- Density Functional Theory (DFT), including hybrid methods, restricted and unrestricted open shell DFT;

- wavefunctions and energies for molecules of up to 5000 basis functions;

- optimization of molecular structures using HF, DFT, LMP2, or GVB wavefunctions (with analytic gradients);

- transition state optimization;

- solution phase geometry or transition state optimization of HF, DFT, LMP2, or GVB wavefunctions;

- coupled perturbed Hartree-Fock (CPHF) polarizability and hyperpolarizability tensors;

- infrared (IR) intensities;

- vibrational spectra for the entire system or selected portions of the system;

- thermochemical properties;

- isotope effects;

- Mulliken populations and Mulliken spin populations;

- orbital, electron density, and potential output on a grid;

- molecular weights and stoichiometry.

A.13   LMTO, [35]

A method is developed for calculations both the valence and high lying conduction band structures of a solid. The basis functions are Linear Muffin-Tin Orbitals (LMTO) with multiple orbitals per angular momentum channel corresponding to different energies. In contrast to the conventional panelling method, the LMTO method treats the valence and conduction bands on equal footing so that the wavefunctions are orthogonal, which avoids the non-orthogonality problem in calculation of transition matrix elements between occupied and unoccupied states, as well as in the calculation of the discontinuity in the bandstructure. An empty lattice test reproduces the free-electron band up to at least 50 eV. The method is applied to Nickel and a comparison with

a different approach based on a modified Linear Augmented Plane Wave method is made.

A.14   LSMS, [36]

The Locally-Self-Consistent Multiple-Scattering (LSMS) Code is a first-principles computer model that simulates the interactions between electrons and atoms in magnetic materials. LSMS can be used to perform the calculations, which involve the interactions between large numbers of atoms (250 to 3000 atoms). LSMS is used to perform fundamental studies of the atomic, electronic, and magnetic microstructure of metals and semiconductors. Such studies include the description of: (i) complex, (ii) disordered states of magnetism, and (iii) microstructural defects in metals and semiconductors.

A.15   PWSCF, [37]

PWscf can currently perform the following kinds of calculation:

- The ground-state energy and one-electron (Kohn-Sham) orbitals;

- atomic forces, stresses, and structural optimization;

- molecular dynamics on the ground-state Born-Oppenheimer surface;

- variable-cell molecular dynamics;

- phonon frequencies and eigenvectors at a generic wave vector;

- effective charges and dielectric tensors;

- electron-phonon interaction coefficients for metals;

- interatomic force constants in real space;

- third-order anharmonic coefficients.

All of the above procedures can be done for both insulators and metals irrespective to crystal structure, for many exchange-correlation functionals (including spin-polarized

cases), for both conventional (Hamann-Schlueter-Chiang) pseudopotentials in separable form, and - in most but not all cases - for ultrasoft (Vanderbilt) pseudopotentials. Some programs for postprocessing are also available.

A.16 Octopus, [42]

A computer package aims to the simulation of the electron-ion dynamics of finite systems, both in one and three dimensions, under the influence of time-dependent electromagnetic fields. The electronic degrees of freedom are treated quantum mechanically within the time-dependent Kohn-Sham formalism, while the ions are handled classically. All quantities are expanded in a regular mesh in real space, and the simulations are performed in real time scale. Although not optimized for that purpose, the program is also able to obtain static properties like ground-state geometries, or static polarizabilities. The employed method is proved to be quite reliable and general one. It has been successfully used to calculate linear and non-linear absorption spectra, harmonic spectra, laser induced fragmentation, etc. of a variety of systems, from small clusters to medium sized quantum dots.

A.17 Siesta, [38]

Siesta (Spanish Initiative for Electronic Simulations with Thousands of Atoms) is a simulation method and its computer program implementation, which is arranged to perform electronic structure calculations and ab initio molecular dynamics simulations of molecules and solids. Its main characteristics are:

- It uses the standard Kohn-Sham self-consistent density functional method in the local density (LDA-LSD) or generalized gradient (GGA) approximations.

- The code uses norm-conserving pseudopotentials in its fully nonlocal (Kleinman-Bylander) form.

- The basis set of the method is a very general and flexible linear combination of numerical atomic orbitals (LCAO). It allows arbitrary angular momenta, multiple-zeta, polarized and off-site orbitals.

- The electron wavefunctions and electron density can be projected onto a real-space grid in order to calculate the Hartree and exchange-correlation potentials and their matrix elements.

- Besides the standard Rayleigh-Ritz eigenstate method, it allows the use of localized linear combinations of the occupied orbitals (valence-bond or Wannier-like functions), making the computer time and memory scale linearly with the number of atoms. Simulations with several hundred atoms are feasible with modest workstations.

It routinely provides:

- Total and partial energies.

- Atomic forces.

- Stress tensor.

- Electric dipole moment.

- Atomic, orbital and bond populations (Mulliken).

- Electron density.

- Geometry relaxations of fixed or variable cell.

- Simulations within the constant-temperature molecular dynamics (Nose thermostat) method.

- Variable cell dynamics (Parrinello-Rahman).

- Spin polarized calculations (collinear or not).

- k-sampling of the Brillouin zone.

- Local and orbital-projected density of states.

- Band structure calculations.

A.18   VASP, [39]

VAMP/VASP is a package for performing ab-initio quantum-mechanical molecular dynamics (MD) using pseudopotentials and a plane wave basis set. The approach implemented in VAMP/VASP is based on a finite-temperature local-density approximation (with the free energy as variational quantity) and an exact evaluation of the instantaneous electronic ground state at each MD-step using efficient matrix diagonalization schemes and an efficient Pulay mixing. These techniques avoid all problems occurring in the original Car-Parrinello method which is based on the simultaneous integration of electronic and ionic equations of motion. The interaction between ions and electrons is described by ultrasoft Vanderbilt pseudopotentials (US-PP) or the projector augmented wave method (PAW). Both techniques allow a considerable reduction of the necessary number of plane-waves per atom for transition metals and first row elements. Forces and stresses are easily calculated within VAMP/VASP, allowing an instantaneous relaxation of atoms into their ground state positions.

A.19   Wien2k, [40]

The program package WIEN2k allows to perform electronic structure calculations of solids within the DFT. It is based on the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (LO) method, being one of the most accurate schemes for band structure calculations. In order to calculate the exchange- correlation energy the local (spin) density approximation (LDA) or the improved version of the generalized gradient approximation (GGA) can be used. WIEN2k is an all-electron scheme, which has many features including computations of

- Relativistic effects;

- Energy bands and density of states;

- electron densities and spin densities, x-ray structure factors;

- total energy, forces, equilibrium geometries, structure optimization within molecular dynamics;

- Phonon spectra;

- electric field gradients, isomer shifts, hyperfine fields;

- spin-polarization (ferro- or antiferromagnetic structures), spin-orbit coupling;

- x-ray emission and absorption spectra, electron energy loss spectra;

- optical properties;

- Fermi surfaces;

- orbital polarization;

- structures of centro- or non-centrosymmetric cells, all 230 spacegroups built in.

B   List of Abbreviations

CDFT	Current Density Functional Theory
CPHF	coupled perturbed Hartree-Fock
DFT	Density Functional Theory
DOF	Degree of Freedom
EAM	Embedded Atoms
EMT	Effective Medium Theory
KMC	Kinetic Monte Carlo
LDA	Local Density Approximation
LGPL	Lesser GNU Public License
LSA	Local Spin Approximation
MD	Molecular Dynamics
ML	Monolayer
PES	Potential Energy Surface
PBC	Periodic Boundary Conditions
QM	Quantum Mechanics
TDDFT	Time-dependent DFT
XC	Exchange- correlation Functional

Acknowledgements

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