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Practical Aspects of Computational Chemistry I

An Overview of the Last Two Decades and Current Trends

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Chapter 7
Electronic Structure of Solids and Surfaces with WIEN2k

Karlheinz Schwarz and Peter Blaha

Abstract Density functional theory (DFT) in various modifications provides the basis for studying the electronic structure of solids and surfaces by means of our WIEN2k code, which is based on the augmented plane wave (APW) method. Several properties, which can be obtained with this code, are summarized and the application of the code is illustrated with four selected examples focusing on very different aspects from electron-structure relations, complex surfaces or disordered layer compounds to the dependence of the equilibrium lattice constants on the DFT functionals.

Keywords Quantum mechanics • Density functional theory • Augmented plane wave method • WIEN2k • Solids • Surfaces

7.1 Introduction

In many cases an understanding of materials on the atomic scale becomes an essential requirement. This is true for modern devices in the electronic industry or magnetic recording as well as for surface science and catalysis. When one comes to atomic dimensions measured in Å, all properties are determined (or critically influenced) by the electronic structure governed by quantum mechanics. This holds for solids, surfaces or molecules. One needs to consider a sequence of topics from chemical composition (including defects or vacancies), atomic structure (with the position of all atoms), the electronic structure (based on quantum mechanics) analyzed in terms of convergence and parameters all the way to properties which can

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be directly compared with experimental data (e.g. spectra). During the last decades a large variety of theoretical methods have been developed, which all have their advantages and disadvantages depending on the system in question.

We focus on the atomic scale, where one often starts with an ideal crystal that is studied at zero temperature. The unit cell contains several atoms (with their nuclei at specified positions) and is repeated with periodic boundary conditions. Quantum mechanics governs the electronic structure that is responsible for properties such as relative stability, chemical bonding, relaxation of the atoms, phase transitions, electrical, mechanical, optical or magnetic behavior, etc. Corresponding first principles calculations are mainly done within Density Functional Theory (DFT), according to which the many-body problem of interacting electrons and nuclei is mapped to a series of one-electron equations, the so-called Kohn-Sham (KS) equations. For the solution of the KS equations several methods have been developed, with the Linearized-Augmented-Plane-Wave (LAPW) method being among the most accurate. During the last 30 years we have developed a computer code – WIEN2k – that is now used worldwide to solve crystal properties on the atomic scale (see www.wien2k.at). The major steps in the development during the last four decades were described in detail in a recent review article [1].

Our presentation is oriented around that code. The paper is organized as follows: Sect. 7.2 describes the quantum mechanical aspect, Sect. 7.3 summarizes the major steps in the development of the augmented plane wave (APW) method and its implementation in WIEN2k, Sect. 7.4 discusses various properties that are derived from the electronic structure of a condensed matter system with illustrations using selected examples of published research; Sect. 7.5 summarizes the role of theory and gives a short conclusion.

7.2 Quantum Mechanics

The quantum mechanical treatment of systems on the atomic scale has been discussed in many papers and thus can be omitted here. However, a few general remarks are appropriate following [1]. Because electrons are indistinguishable Fermions, their wave functions must be antisymmetric when two electrons are interchanged leading to the phenomenon of exchange. In a variational wave-function description (with one Slater determinant) this can be treated exactly with the Hartree Fock (HF) approximation. The HF equations have the computational disadvantage that each electron moves in a different potential. Exchange is treated exactly but correlation effects, which occur because of the Coulomb interaction, are omitted by definition. The latter can be included by more sophisticated approaches such as configuration interaction (CI) or coupled cluster (CC) schemes [2] but such refinements progressively require more computer time with a scaling as bad as N^7, where the system size is proportional to N, the number of electrons. Therefore such highly accurate solutions can only be obtained for relatively small systems (atoms

or small molecules), which are important test cases for finding a proper quantum mechanical treatment. When the system size is significantly bigger (as often in condensed matter applications), approximations are unavoidable.

The predominant scheme for calculating the electronic properties of solids (and often of large molecules) is based on density functional theory (DFT), a universal approach to the quantum mechanical many-body problem. It was shown by Hohenberg and Kohn [3], and Kohn and Sham [4] that the key quantity is the electron density ρ, which uniquely parameterizes the variational principle for the total energy E of the system. In DFT the system of interacting electrons is mapped uniquely onto an effective non-interacting system with the same total density. In practical DFT calculations exchange and correlation effects are included, but both approximately. Due to a compensation of errors DFT is better than HF (due to the inclusion of correlation) but worse since the exchange is only treated approximately (leading to the self interaction error). From a numerical point of view an important idea of Kohn-Sham [4] was to calculate the kinetic energy (a large quantity) of non-interacting electrons (quasi particles) by introducing orbitals, which allows computing this large number very accurately. The quantum mechanics is contained in the exchange-correlation energy E_{xc} and the corresponding potential V_{xc} that is defined as the functional derivative with respect to the density. The exact functional form of the exchange-correlation energy, and hence the potential V_{xc}, is not known, and thus one needs to make approximations. The results from quantum Monte Carlo calculations for the homogeneous electron gas, for which the problem of exchange and correlation can be solved exactly, led to the modern version of the local density approximation (LDA) [5]. LDA works reasonably well but has some shortcomings mostly due to its tendency to overbind, which often causes shortened lattice constants relative to experiment. Modern XC approximations, especially those using the generalized gradient approximation (GGA), often improve upon LDA by introducing an extra term that depends on the gradient of the electron density. For long time the Perdew-Burke-Ernzerhof (PBE) [6] version was believed to be the "best" GGA, but now new types of GGAs have been developed which perform better, at least for certain properties (as will be discussed in Sect. 7.4.4). There is an extensive literature about DFT, which we do not attempt to cover here. After LDA and GGA, meta-GGA functionals were proposed (for example in [7]), which depend not only on the density and its gradient, but also on the kinetic energy density τ. The main advantage of all these DFT schemes lies in the fact that they allow calculating the electronic structure of complex systems containing many atoms such as very large molecules or solids.

Besides wave-function based methods (HF, CI, CC) or DFT there is a third category that became important recently, namely many-body physics, which can handle correlation effects on a different level. Traditionally such schemes were often based on parameters but now they can be combined with DFT results. For example one can start with an LDA calculation and transform the basis set from a Bloch-picture to a Wannier description (see for example [8]). In the latter the correlated electrons can be described by the dynamical mean field theory (DMFT) which can

account for the local correlation effects using a Hubbard U and hopping parameters that were extracted from LDA results. Such combinations are called LDA + DMFT as described in a recent review [9].

In general it can be said that theory has gained a lot by combining the expertise from the three (previously separated) fields, namely wave-function based methods, DFT, and many-body theory. All three have their strength and weaknesses but in a combined effort one can gain new insight.

7.3 The Augmented Plane Wave Based Method and WIEN2k

In the present paper we focus on crystals and surfaces. We choose DFT as the quantum mechanical treatment of exchange and correlation. This means that we must solve the Kohn-Sham (KS) equations by means of a proper basis set. For this purpose we use the augmented plane wave (APW) scheme, which originally was proposed by Slater [10]. The development of APW and its linearized version, which led to the WIEN code [11] and its present version WIEN2k [12], was described in detail in a recent review [1] and previous articles [13–15]. The main concepts are summarized below:

The unit cell is partitioned into (non-overlapping) atomic spheres that are centered at the atomic sites (region I) and an interstitial region (II), for which different basis functions are used. For the construction of these functions the *muffin tin* approximation (MTA) is used, i.e. the potential is assumed to be spherically symmetric within each atomic sphere but constant outside. Plane waves are used in region II. Each plane wave is augmented by corresponding atomic partial waves, i.e. atomic-like solutions inside each atomic sphere (region I) consisting of a radial function u_ℓ times spherical harmonics.

The energy dependence of the atomic-like radial functions can be treated in different ways. In the original APW this was done by choosing a fixed energy for each radial function, which led to a non-linear eigenvalue problem. In LAPW this energy dependence of each radial basis function $u_\ell(r,E)$ is linearized (that is, treated to linear order) according to Andersen's prescription [16] by taking a linear combination of a solution $u_\ell(r,E_\ell)$ at a fixed linearization energy E_ℓ (chosen at the center of the corresponding band) and its energy derivative $\dot{u}_\ell = \partial u_\ell / \partial \varepsilon$ computed at the same energy. Each plane wave is joined continuously (in value and slope) to the one-center solutions inside the atomic sphere, thereby defining the relative weights of the u_ℓ and $\dot{u}_\ell$ contributions. This LAPW basis set allows finding all needed eigenvalues with a single diagonalization, in contrast to APW. The more strict constraint (matching in value and slope) had the disadvantage that more PWs were needed to reach convergence.

The LAPW method made it computationally attractive to go beyond the MTA. It was important to treat the crystal potential (and charge density) without any shape approximation as pioneered by the Freeman group [17]. The potential and charge density are expanded inside each atomic sphere into a radial part times lattice

harmonics (a symmetry-adapted linear combination of spherical harmonics) and as a Fourier series in the interstitial region. This scheme is termed a full-potential calculation.

WIEN2k is an all-electron scheme. Core states are low in energy and the corresponding KS orbitals (or densities) are (practically speaking) completely confined within the atomic spheres and can be obtained using the spherical part of the potential (but using a thawed core instead of a frozen core approximation). Valence states are high in energy with delocalized orbitals which are responsible for chemical bonding and form energy bands. However, between the core and valence states for some atoms there might be so called semi-core states, which reside mostly inside the spheres but have a "core-leakage" of a few per cent. For them Singh [18] proposed adding local orbitals (LO) to the LAPW basis set in order to accurately treat states with different principal quantum numbers (e.g. 3p and 4p states) while retaining orthogonality. For further details see review [1]. The concept of LOs fostered another idea, namely the APW plus local orbitals (APW + lo) method [19]. These local orbitals (lo) are denoted with lower case to distinguish them from the semi-core LOs just discussed. In APW+lo, one goes back to the APW basis but with the crucial difference that the radial wave functions are expanded at fixed energies. This new scheme is significantly faster (up to an order of magnitude) while keeping the convenience of LAPW [20]. The details of the three types of schemes (APW, LAPW, APW+lo) were described in [1, 15]. A combination of the latter two schemes provides the basis for the WIEN2k program [12].

In systems with heavier elements, relativistic effects must be included. In the medium range of atomic numbers (up to about 54) the so called scalar relativistic scheme is often used [21]. It describes the main contraction or expansion of various orbitals (due to the Darwin s-shift or the mass-velocity term), but omits spin-orbit interaction. The latter becomes important for the heavy elements or when orbital magnetism plays a significant role. In the present version of WIEN2k the core states always are treated fully relativistically by numerically solving the radial Dirac equation. For all other states, the scalar relativistic approximation is used by default, but spin-orbit interaction (computed in a second-variational treatment [22]) can be included if needed [23].

The computational aspects like parallelization (k-points or MPI), algorithms, accuracy and efficiency were discussed in the review [1]. WIEN2k can treat all atoms in the periodic table. The high accuracy of WIEN2k comes from a balanced mixed basis set of plane waves and atomic functions, whose radial functions are recalculated numerically in the new potential. This allows them (in each iteration) to expand or contract according to the potential and ionicity (charge state). The main control of basis size convergence is done via a single parameter, RK_{max}, the product of the smallest sphere radius R times the largest plane wave vector K_{max}. Therefore the convergence is easy to test. Integration in reciprocal space requires a proper **k**-point mesh in the irreducible Brillouin zone (BZ) which needs to be checked for convergence.

7.4 Properties and Applications

When the electronic structure of a condensed matter system is calculated with WIEN2k several topics need to be considered. A short summary is given below but the reader is referred to the review [1] for more references and details (especially Sect. 6):

1. In a system with translational symmetry (a perfect infinite crystal) one makes use of periodic boundary conditions and thus can expand the wave functions in a plane wave basis set. The concept of a unit cell is appropriate for (nearly) perfect single crystals, but a real crystal has surfaces and may have imperfections such as impurities or vacancies. Such effects can approximately be treated with slabs or supercells.
2. KS eigenvalues with respect to the reciprocal k-vector can be represented as band structure. The corresponding wave functions contain the information how much various basis sets contribute to each state. In the APW framework this can be done by using the partial charges $q_{t\ell m}$, which define the fraction of the corresponding total charge density (normalized to unity in the unit cell) that resides in the atomic sphere t and comes from the orbital characterized by the quantum numbers ℓm. The fraction from the interstitial regions is contained in q_{out}. These numbers help to interpret each state in terms of chemical bonding. From all energy eigenvalues in the Brillouin zone the density of states (DOS) can be calculated and again decomposed into partial DOS.
3. The key quantity in DFT is the electron density. It contains the essential ingredient for understanding chemical bonding. By computing difference electron densities (with respect to superposed atomic densities) the bonding features become more apparent. Another possibility is to use the topological analysis by Bader [24] for example to define atomic charges within atomic basins, a relevant quantity for charge transfer estimates.
4. The electric field gradient (EFG) is a ground state property that is sensitive to the asymmetry of the charge distribution around a given nucleus. By measuring the nuclear quadrupole interaction (e.g. by NMR) the EFG can be determined experimentally. This local probe is often essential for distinguishing between different atomic arrangements.
5. The total energy of the system is a crucial quantity for any given atomic configuration. Often this can be a rather big number which nowadays can be calculated with high precision. Total energy differences, for example, tell which structure is more stable. The derivative with respect to nuclear coordinates yield the forces acting on an atom. These forces are needed to optimize the atomic positions towards an equilibrium geometry, which corresponds to a minimal total energy and vanishing forces. In addition they can be used to calculate phonons.
6. If a system is magnetic, the calculation must be carried out in a spin-polarized fashion. Often a collinear arrangement of the magnetic moments like in an (anti-) ferromagnet is assumed but there is the possibility to study non-collinear arrangements.

7. In connection with spectroscopy various properties can be calculated like x-ray emission or absorption spectra (XES, XAS), optical spectra or photoelectron spectra (UPS). The data for hyperfine interaction can be obtained from WIEN2k too.

Since the WIEN2k program package is used worldwide by more than 1,850 groups many papers have appeared that make use of this program. Here we illustrate from our own research how results obtained with WIEN2k can help to solve interesting problems in material sciences.

7.4.1 *Verwey Transition in $YBaFe_2O_5$*

A perovskite ABO_3 (like $SrTiO_3$) contains as the main building block the B atom that is octahedrally coordinated by oxygen. An oxygen-deficient double perovskite, however, has B with a pyramidal coordination, in which the sixth oxygen is missing. One member of this group is $YBaFe_2O_5$ whose crystal structure is well established [25]. It is particularly interesting, because it shows a temperature induced phase transition at about 309 K. At low temperatures it forms a charge ordered (CO) state (with Fe^{2+} and Fe^{3+} at the two crystallographic inequivalent sites) but above the transition temperature a valence-mixed (VM) state (sometimes called mixed valence) appears in which Fe has the formal oxidation state of $Fe^{2.5+}$ [26]. Such a change is called Verwey transition [27] as has originally been suggested for magnetite Fe_3O_4, a system that is still often discussed. In $YBaFe_2O_5$ the structure changes from a strongly distorted orthorhombic to a nearly tetragonal symmetry. With this structural change both the magnetic and conducting behaviour change significantly. In the CO phase (with space group Pmma) the Fe^{2+} and Fe^{3+} form chains along the a direction and have an antiferromagnetic (AFM) arrangement (Fig. 7.1 top).

A standard GGA calculation would lead to a metallic behavior and magnetic moments that are much smaller than the experimental values. Therefore one must go beyond GGA and include the local correlation effects (that are important for Fe oxides) by means of a Hubbard U. Although this introduces a parameter that is not strictly given on a first principles basis, a GGA+U calculation (with an effective U of around 7 eV) gives a proper description of the system as discussed in detail in [26]. A structural optimization of the atomic coordinates leads to different bond length around Fe^{2+} and Fe^{3+} (Fig. 7.1 bottom) in the CO phase, whereas they are similar in the VM phase. In addition a gap opens up making it a semiconductor and the magnetic moments obtained with GGA+U are in agreement with experiment. The AIM charges (according to Bader's atoms in molecules [24]) are +1.84 for Fe^{3+} and +1.36 for Fe^{2+} in the CO phase but +1.52 in the VM phase. The origin for this clear difference can be traced down to an orbital ordering which shows up in the partial DOS associated with various Fe-d-orbitals. The hyperfine fields and the electric field gradients are consistent with experimental data, provided a proper U

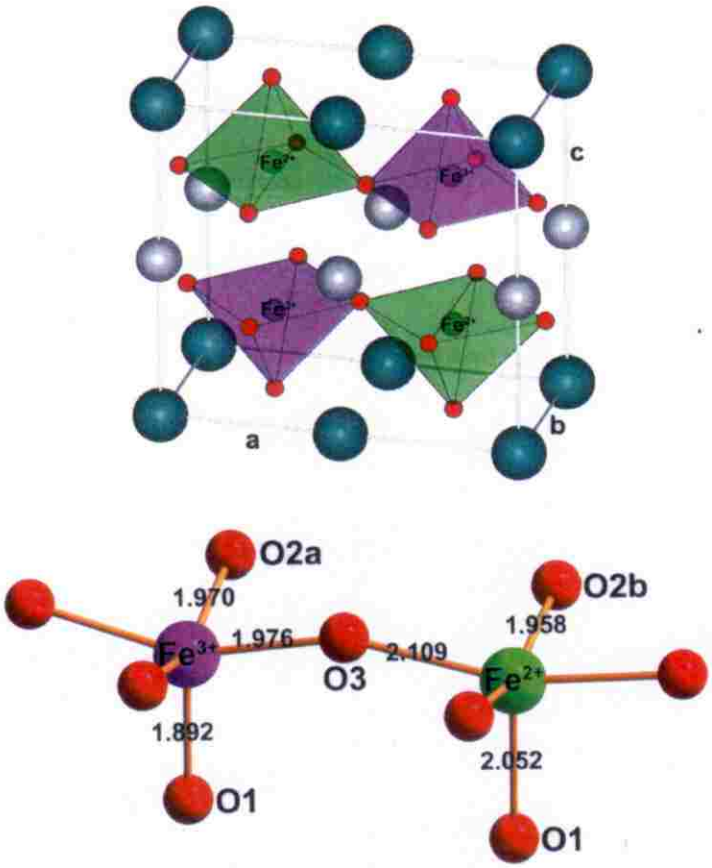

Fig. 7.1 The charged-ordered (CO) phase of the oxygen-deficient double perovskite $YBaFe_2O_5$: (*top*) orthorhombic unit cell with a chain of alternating Fe^{2+} and Fe^{3+} ions along the a direction; (*bottom*) the local coordination of the two iron sites giving the nearest neighbor distances as optimized by a GGA+U calculation

is used. In summary one can say that in the CO phase the Fe^{2+} is in a d^6 high-spin configuration in which a single spin-down electron of d-xz symmetry is occupied which triggers a cooperative Jahn-Teller distortion. The apparent strong electron-lattice coupling cause in the VM phase (with its similar bond lengths) that the Fe $d\text{-}z^2$ spin-down orbital (at the top of the valence band) become partly occupied.

Chemical bonding changes the total electron density only by small amounts and thus the difference between the final SCF density and the superposition of free atomic densities (the start of an SCF cycle) shows the main reorganization due to bonding. In such a difference electron density (see Figs. 8 and 9 of ref. [26]) the two phases, CO and VM, clearly differentiate between Fe^{2+} and Fe^{3+} in the former but not in the latter case.

One numerical detail shall be mentioned, namely the magneto-crystalline anisotropy, which is this difference in total energy when the magnetic moments point in different crystallographic directions [100], [010] or [001], a question for which spin-orbit interaction is essential. The lowest total energy is −115,578.24065 Ry, when the moments point in the y direction, while the other directions are about 0.4 mRy higher in energy; thus the difference is in the tenth decimal. This illustrates which numerical precision is needed for such a quantity. For more details see the original paper [26].

7.4.2 *Nanomesh with h-BN on a Rh(111) Surface*

When borazin is thermally decomposed on a Rh(111) surface a self-assembling structure is formed, which Corso et al. called a nanomesh [28]. It consists of a hexagonal boron nitride (h-BN) that binds to a Rh(111) surface. Originally these authors described the structure with a double layer of BN where the top layer has holes. However, DFT calculations [29] proposed a different atomic structure of this surface, consisting of a single but highly corrugated layer of h-BN. There is a lattice mismatch between h-BN and Rh(111) of about 8%, with the result that 13×13 unit cells of h-BN match 12×12 unit cells of the underlying Rh(111) with a periodicity of about 3.2 nm. Such a system is a real challenge for theory, since it is metallic and already a crude model of the surface contains many atoms. In order to simulate this complex structure, a slab was constructed containing three layers of Rh (corresponding to the three layers A, B, C of an fcc structure) and h-BN layers on both sides (top and bottom) of the metal layers. This is done for computational reasons to keep inversion symmetry, which makes the matrices real instead of complex. This supercell contains 1,108 atoms (and around 25.000 electrons), which makes the calculation rather demanding but feasible nowadays (see Fig. 4 in [1]).

The structure optimization started with a flat h-BN layer but allowed the atoms to relax, which led to a significant surface corrugation (Fig. 7.2). Due to the lattice mismatch and the relative rigidity of h-BN there are regions with different bonding situations. The preferred orientation for boron is a hollow site above three Rh atoms, whereas nitrogen likes to be on top of a Rh atom (Fig. 7.3). This situation is almost satisfied in the so called "low" region (Fig. 7.2 bluish region) where h-BN binds strongly to the metals leading to short distances to the Rh sublattice. Otherwise the more repulsive interaction between N and the surface cannot compensate the weaker B attraction and thus the h-BN is further away from the surface leading to the "high" region (Fig. 7.2 yellow region). An analysis has shown that the B atoms have predominantly attractive forces towards Rh (with bonding orbitals) whereas for N the repulsive forces dominate (due to partial occupation of antibonding orbitals). The lattice mismatch causes locally different lateral orientations of h-BN with respect to the Rh-subsurface. The combination of these two scenarios (with favorable and unfavorable bonding) caused a corrugation that can be seen

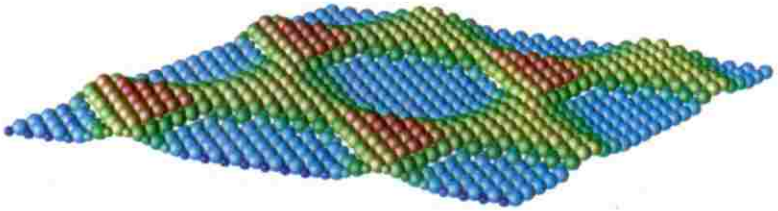

Fig. 7.2 The corrugation of the hexagonal boron nitride layer in the h-BN/Rh(111) nanomesh showing a 2×2 supercell. The "low" region (close to Rh) appears in *blue* but the "high" region (further away from the Rh sublayer) are in *yellow*. The B atoms (visible in the *front*) are shown with *small* but the N with *large spheres* (see also Figs. 4 and 5 in [1])

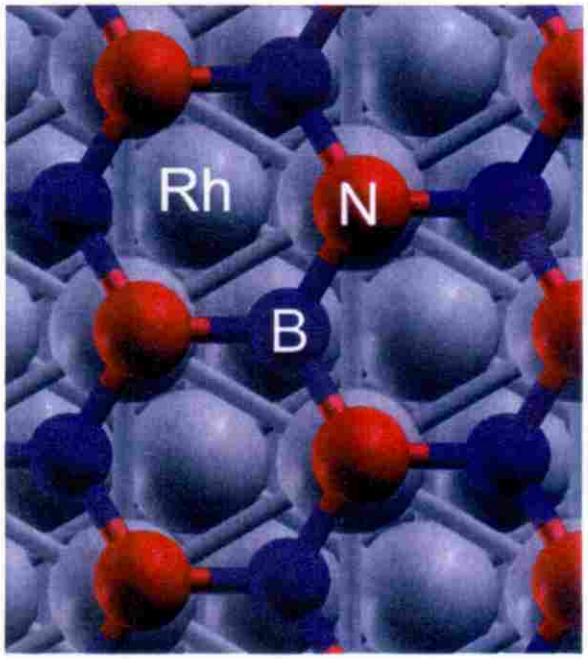

Fig. 7.3 The local atomic arrangement of h-BN on Rh(111) in the "low" region, where N (in *red*) is about on top of Rh (*grey*) and B (*blue*) is in the hollow position optimally binding to the three Rh underneath. Further details can be found in [29]

in experiment, e.g. by scanning tunneling microscopy (STM). Once the structure is unraveled, other experimental data can be explored, for example X-ray absorption spectroscopy, or N-1s core level shifts as discussed in [29, 30]. Some additional discussions can be found in [1].

7.4.3 The Misfit Layer Compounds

Hexagonal transition metal dichalcogenites such as TaS_2 are layered compounds, which easily can be intercalated for example with Li ions. When they are intercalated with a pseudocubic double layer such as PbS, they belong to the so called

misfit layer compounds [31]. Because of the different crystal symmetries of the two subsystems, the lattice constants can match only in one direction forming a periodic structure (e.g. in the b direction). Perpendicular to this commensurate direction there is an incommensurate lattice mismatch due to the ratio between the two lattice constants, in our case between TaS_2 and PbS. This ratio can be approximated with 4/7 leading to periodic boundary conditions. This means that 4 lattice constants of PbS match to a good approximation 7 of TaS_2 corresponding to the misfit layer compound $(PbS)_{1.14}TaS_2$ as discussed in our paper and references therein [32]. These materials have interesting properties and are rather stable. The main question that remained open was to explain what causes the stability. In this context previous experimental studies proposed two possible binding mechanisms, namely non-stoichiometry or metal cross substitution that should be responsible for the stability.

This is an ideal starting point for theory, since one can try both schemes and find out which is more likely to be correct or consistent with experimental details. The idealized system (forced to be commensurate) contains 74 atoms per unit cell and consists of alternating perfect layers of TaS_2 and double layers of PbS. First DFT test calculations showed that the binding energy between the ideal layers of TaS_2 and the PbS-double layer is nearly zero. Therefore one of the proposed mechanisms may provide a clue for the stabilization and thus they need to be explored. Now disorder comes into play, either in form of defects or when one substitutes Pb into TaS_2 or Ta into PbS. With our WIEN2k we must enforce periodic boundary conditions and thus artificially introduce some order. In order to be more realistic and avoid artifacts (like rows of impurity atoms) an even larger supercell with 296 atoms was used in some of the calculations. In such large supercells one cannot explore all possible configurations of disorder. However, one can follow certain strategies. For example if one puts 2 Ta atoms replacing Pb in PbS, then they can be close together (clustering) or far apart (avoiding each other), or in the same PbS layer or in adjacent layers. For each of the explored configurations one optimizes the atomic positions (till the forces acting on all atoms vanish) and determines the corresponding total energy. Different configurations can be compared by their total energy, leading to an insight how the impurities prefer to distribute. For example, it turned out that it is energetically more favorable to have the Ta impurities in the same PbS layer than putting them in the adjacent layer. The computer experiments that were carried out made use of the rules that have been learned from previous results. Configurations which are likely to be unfavorable need not to be studied. This strategy reduces the effort and makes the investigation of such a complicated system (with so many atomic configurations) feasible. A representative configuration is shown in Fig. 7.4, in which one sees (upon substitution) relatively little changes in the TaS_2 layer but significant relaxations in the substituted PbS layer. This difference is caused by the size change (small Ta vs. larger Pb) and the structural details between the TaS_2 layer, in which only a small breathing of sulfur atoms around the large Pb is possible. However, the small Ta atom can move a lot towards the sulfur leading to large distortions of the pseudo-NaCl planes of PbS.

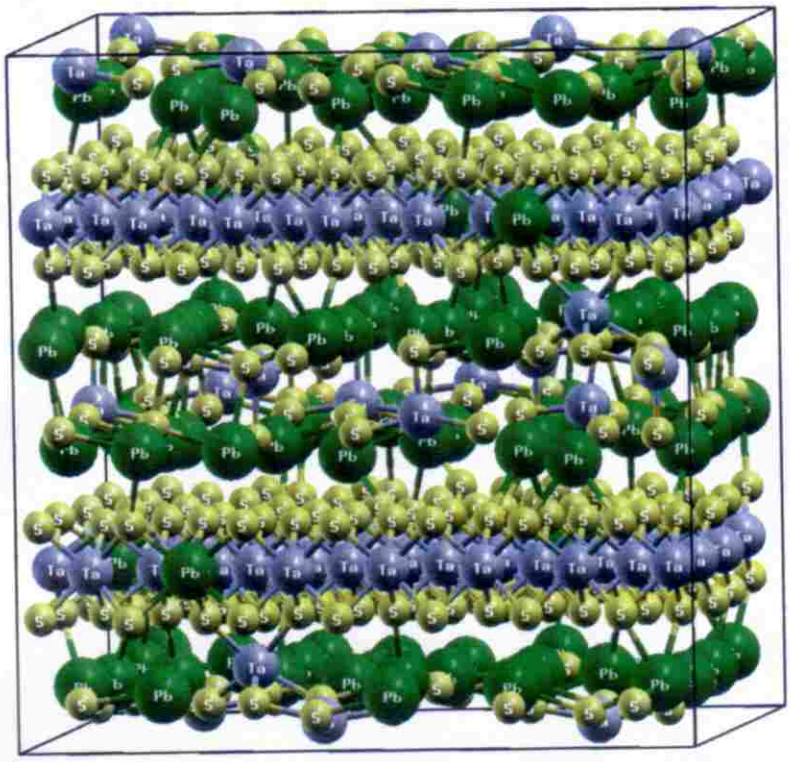

Fig. 7.4 The large supercell representing the $(PbS)_{1.14}TaS_2$ misfit layer compound containing 296 atoms. In the TaS_2 layer 4 Ta atoms are substituted by Pb and in the PbS double layers 12 Ta atoms substitute the corresponding Pb atoms leading to a strong relaxation. For further details see [32]

From the calculated total energies one can conclude [32] that the metal cross substitution alone cannot stabilize this compound whereas the nonstoichiometric model works, when Ta substitutes Pb mainly in one of the PbS double layers. This case shows large lattice relaxations (Fig. 7.4) which stabilize the misfit layer compounds but are accompanied by charge transfer effects. In addition the insulating behavior of PbS is lost in the stoichiometric compound, whereas Ta doping leads to a charge transfer that brings the PbS layer closer to be an insulator. For further details see [32]. A Ta impurity concentration of about $x = 0.13 - 0.19$ is energetically most favorable which is in excellent agreement with experimental findings. In this case DFT calculations could find an explanation for the stability and confirm one of the proposed mechanisms.

7.4.4 *Performance of Various GGA Functionals*

In recent years several attempts were made to improve the performance of various generalized gradient approximations. In this context one usually investigates small systems which can be well characterized as ideal crystals without any structural uncertainties such as defects, impurities or non-stoichiometry. It is well known that LDA gives too small lattice constants while the standard PBE version of GGA [6] always leads to larger values than LDA but often also with respect to experiment. By choosing crystals without structural uncertainties and a computational scheme which is highly accurate (as results with WIEN2k) one can test the quality of functionals when compared with experimental data. Otherwise one would have a combination of effects from structure over DFT to convergence of basis sets. In the latter case one would not be able to come to firm conclusions.

We were involved in one of such investigations of GGA functionals and want to summarize some results (see [33] and references therein). From the newly proposed GGA functionals (in addition to the standard PBE [6]) we mention the functional by Wu and Cohen (WC) [34], AM05 by Armiento and Mattssson [35] and PBEsol [36]. In GGA the exchange correlation energy can be expressed in terms of an enhancement factor F_{xc}

$$E_{xc}^{GGA}[\rho] = \int \varepsilon_x^{LDA}(r_s(r))F_{xc}(r_s(r), s(r))d^3r$$

which depends on the Wigner-Seitz radius r_s , a measure of the electron density $\rho(r)$,

$$r_s = [3/(4\pi\rho)]^{1/3}$$

and the reduced gradient density s

$$s = |\nabla\rho| / [2(3\pi^2)^{1/3}\rho^{4/3}]$$

The variation of the (exchange only) enhancement factor F_{xc} with s is shown in Fig. 7.5 for one example, namely $r_s = 0$, but more cases are depicted in [33]. For the chosen functionals there is a significant difference in the enhancement factors for larger s but they are all smaller than that of PBE. Now one can analyze various systems from metals, to insulators or covalently bonded systems and explore which s-values are relevant. The detailed analysis has shown that it is not only the value of the enhancement factor but also its derivative with respect to s and r_s which determine the equilibrium lattice constant. In addition it was found that in most solids (in contrast to molecules) vales of s larger than 1.5–2.0 or values of r_s larger than 4 bohr hardly occur. Let us illustrate this situation for the covalently bonded system of diamond (see Fig. 7.6) which shows how the s value changes in the unit cell. The surprising result is found that in the region of the covalent bond (between

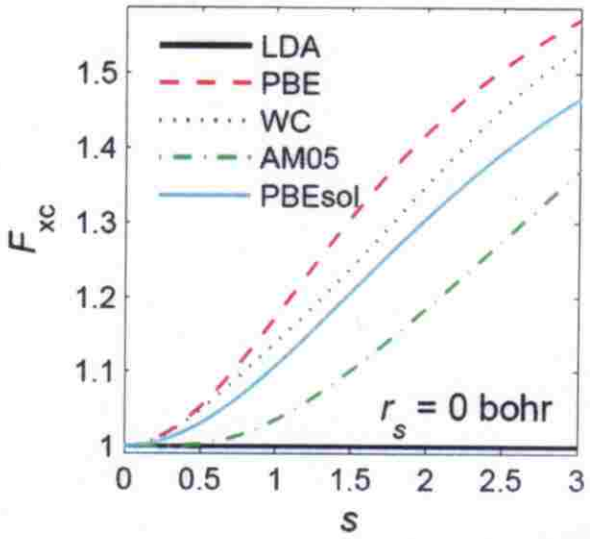

Fig. 7.5 The enhancement factors F_{xc} (for $r_s = 0$ bohr) with respect to the LDA exchange energy as a function of s, the reduced density gradient, is shown for the four functionals PBE, WC, AM05, and PBEsol. Additional plots for other r_s values are given in [33]

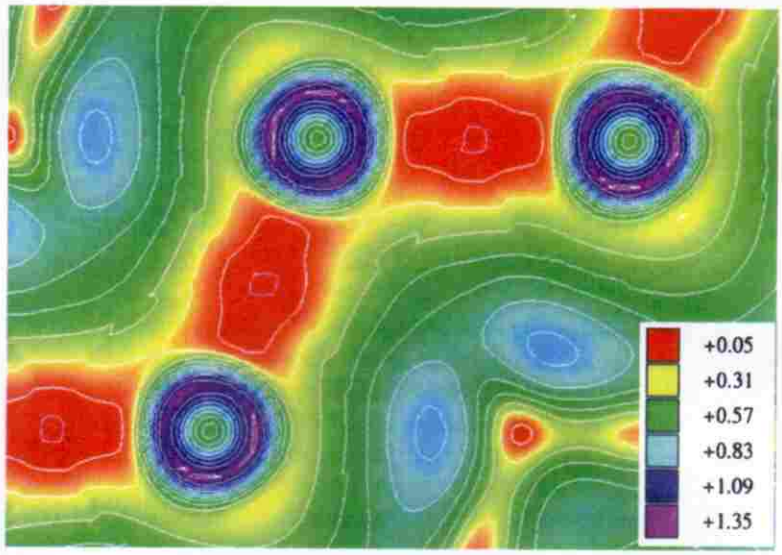

Fig. 7.6 A two-dimensional plot of the reduced density gradient s is shown for *diamond* in the (110) plane. The *color coding* indicating the value of s is specified in the insert

the carbon atoms) s is small and thus all enhancement factors remain small so that we are almost left with LDA. Large values of s appear in the range separating core from valence states around all carbon atoms, but also in the interstitial region. These are the important regions, in which the enhancement factors differ between the functionals and thus these – rather than the bonding regions – are responsible for the equilibrium lattice constant. A functional with a large enhancement factor in the important region usually leads to larger lattice constants.

7.5 Summary and Conclusion

In this paper we discussed the status of quantum mechanical calculations focusing on solids and surfaces. In the quantum mechanics section DFT was presented with respect to the alternative approaches such as wave function based methods or many-body physics. For the solution of the DFT Kohn Sham equations we use an adapted augmented plane wave method implemented in our WIEN2k code, which can be shortly summarized as a full-potential, all electron and relativistic code that is one of the most accurate for solids and is used worldwide by more than 1,850 groups in academia and industry.

In the spirit of Coulson ("Give me insight not numbers") many properties and detailed analyses are needed to solve complex material problems. For that purpose WIEN2k provides many tools to compute a large variety of properties and results, from energy bands, DOS, electron and spin densities, magnetic moments, optical spectra, total energies, forces, EFG, hyperfine interactions, spin-orbit coupling etc. Often several of these results are needed to explain the open questions.

In the four examples presented here different aspects were highlighted. In the first case (Verwey transition) the unit cell is small and well defined but the electron-lattice coupling (with a cooperative Jahn-Teller distortion) requires a high level description (GGA + U) to get the physics right. In the nanomesh example the size of the system (more than 1,100 atoms per unit cell) of a metallic system is a challenge. For the misfit layer compounds we demonstrate another area, namely performing computer experiments on disordered systems, which lead to strategies that allow us to focus on the likely structures that may be present in the real system. With such a scheme it became possible to describe the system and explain the stability between the layers of the misfit compound. In the last example we explore different GGA functionals in order to find out which system dependent parameters are essential for obtaining lattice constants in good agreement with experiment. In the latter case we restrict our efforts to very ideal crystals with small unit cells. The chosen examples are just a small selection to illustrate what can be obtained with the WIEN2k code. The used basis set (containing atomic orbitals) allows interpretations in chemical terms, which can be an important advantage over pseudo-potentials methods. The high accuracy is achieved partly by the numerical basis (for the radial wave functions) but also by the fact that the convergence (with the number of plane waves) can be controlled with one parameter (RK_{max}).

Therefore DFT calculations with approximate functionals can provide extremely useful information concerning the electronic structure of ordered crystal structures and surfaces irrespective whether they can be prepared or not. Nowadays relatively large systems can be simulated due to the increased computer power combined with improved algorithms and efficient parallelization.

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