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# DFT calculations of solids with LAPW and WIEN2k

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## Abstract

In solids one often starts with an ideal crystal that is studied on the atomic scale at zero temperature. The unit cell may contain several atoms (at certain 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. One among the most precise schemes to solve the KS equations is the linearized-augmented-plane-wave (LAPW) method that is employed for example in the computer code WIEN2k to study crystal properties on the atomic scale (see [www.wien2k.at](http://www.wien2k.at)). Nowadays such calculations can be done—on sufficiently powerful computers—for systems containing about 100 atoms per unit cell. A selection of representative examples and the references to the original literature is given.

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## 1. Introduction

Solid materials are of great technological interest. Different materials are governed by very different length and time scales. They may differ by many orders of magnitude depending on their applications. Let us focus on the length scale, where from meters (m) to micrometers ( $\mu\text{m}$ ) classical mechanics and continuum models are the dominating concepts to investigate the properties of the corresponding materials. However, when one comes to the nanometer (nm) scale or atomic dimensions measured in  $\text{\AA}$ , the properties are determined by the electronic structure of the solid. In the development of modern materials an understanding of the atomic scale is frequently essential in order to replace trial and error procedures by a systematic materials design. Modern devices in the electronic industry provide such an example, where the increased miniaturization is one of the key advances. Other applications are found in the area of magnetic recording or optical storage media. A typical example in chemistry is heterogeneous catalysis, in which one likes to understand the details of catalytic

processes between molecules interacting with a solid surface, e.g., in zeolites.

One way of studying complex systems is to perform computer simulations. Calculation of solids in general (metals, insulators, semiconductors, minerals, etc.) can be performed with a variety of methods from classical to quantum mechanical (QM) approaches. The former are mainly force field schemes, in which the forces that determine the interactions between the atoms are parameterized in order to reproduce a series of experimental data such as equilibrium geometries, bulk moduli or special vibrational frequencies (phonons). Such schemes have reached a high level of sophistication and are useful in their range of applicability, namely within a given class of materials provided good parameters are already known from closely related systems. If, however, such parameters are not available, or if a system shows unusual phenomena that are not yet understood, one often must rely on *ab initio* calculations. They are more demanding in terms of computer resources and thus allow only the treatment of cell units smaller than force-field calculations. The advantage of first-principle (*ab initio*) methods lies in the fact that they can be carried out without knowing any experimental data of the system. The following presentation

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will be restricted to ab initio methods whose main characteristics shall be briefly sketched.

The fact that electrons are indistinguishable and are fermions requires that their wave functions be anti-symmetric when two electrons are interchanged. This situation leads to the phenomenon of exchange. Starting with molecules there are mainly two types of approaches for a full quantum mechanical treatment, HF and DFT. The traditional scheme is (or was) the Hartree–Fock (HF) method which is based on a wave function description (with one Slater determinant). Exchange is treated exactly but correlation effects are ignored by definition. The latter can be included by more sophisticated approaches (e.g., a linear combination of Slater determinants) such as the configuration interaction (CI) scheme that progressively requires more computer time with a scaling as bad as  $N^7$  when the system size ( $N$ ) grows. As a consequence it is only feasible to study small systems, which contain a few atoms.

An alternative scheme is the DFT that is commonly used to calculate the electronic structure of complex systems containing many atoms such as large molecules or solids [1,2]. It is based on the electron density rather than on the wave functions and treats exchange and correlation, but both approximately. Since it became the method of choice for solids it will be described in more detail below.

The ideal crystal is defined by the unit cell, which may contain many atoms and is repeated indefinitely according to translational symmetry. Periodic boundary conditions are used to describe the infinite crystal by knowing the properties in one unit cell. The additional symmetry operations (inversion, rotation, mirror planes, etc.) that leave the ideal crystal invariant allow both providing symmetry labels and simplifying the calculations. Each ideal structure belongs to one of the 230 space groups that are characterized in the International Tables [3]. Only the electronic ground state is studied. When thermal vibrations are considered in the form of phonon calculations [4] an adiabatic (Born Oppenheimer) approximation in which the electronic degrees of freedom are decoupled from the nuclear motions is used.

## 2. Density functional theory (DFT)

### 2.1. The Kohn–Sham equations

The well-established scheme to calculate electronic properties of solids is based on the DFT, for which Walter Kohn has received the Nobel Prize in chemistry in 1998. DFT is a universal approach to the quantum mechanical many-body problem, where the system of interacting electrons is mapped in a unique manner onto an effective non-interacting system that has the same total density. Hohenberg and Kohn [1] have shown that

the ground state electron density  $\rho$  (in atoms, molecules or solids) uniquely defines the total energy  $E$ , i.e.,  $E[\rho]$  must be a functional of the density. Thus one does not need to know the many-body wave function. The non-interacting particles of this auxiliary system move in an effective local one-particle potential, which consists of a classical mean-field (Hartree) part and an exchange-correlation part  $V_{xc}$  (due to quantum mechanics) that, in principle, incorporates all correlation effects exactly. According to the variational principle a set of effective one-particle Schrödinger equations, the so-called Kohn–Sham (KS) equations [2], must be solved. Its form is

$$[-\nabla^2 + V_{\text{ext}}(\vec{r}) + V_C[\rho(\vec{r})] + V_{xc}[\rho(\vec{r})]]\Phi_i(\vec{r}) = \varepsilon_i\Phi_i(\vec{r}) \quad (1)$$

when written in Rydberg atomic units for an atom with the obvious generalization to molecules and solids. The four terms represent the kinetic energy operator, the external potential from the nucleus, the Coulomb-, and exchange-correlation potential,  $V_C$  and  $V_{xc}$ . The KS equations must be solved iteratively till self-consistency is reached. The iteration cycles are needed because of the interdependence between orbitals and potential. In the KS scheme the electron density is obtained by summing over all occupied states, i.e., by filling the KS orbitals (with increasing energy) according to the aufbau principle.

$$\rho(\vec{r}) = \sum_i^{\text{occ}} [\phi_i(\vec{r})]^2. \quad (2)$$

From the electron density the  $V_C$  and  $V_{xc}$  potentials for the next iteration can be calculated, which define the KS orbitals. This closes the SCF loop. The exact functional form of the potential  $V_{xc}$  is not known and thus one needs to make approximations. Early applications were done by using results from quantum Monte Carlo calculations for the homogeneous electron gas, for which the problem of exchange and correlation can be solved exactly, leading to the original local density approximation (LDA). LDA works reasonably well but has some shortcomings mostly due to the tendency of overbinding, which cause e.g., too small lattice constants. Modern versions of DFT, especially those using the generalized gradient approximation (GGA), improved the LDA by adding gradient terms of the electron density and reached (almost) chemical accuracy, as for example the version by Perdew, Burke, Ernzerhof (PBE) [5].

In the study of large systems the strategy differs for schemes based on HF or DFT. In HF based methods the Hamiltonian is well defined but can be solved only approximately (e.g., due to limited basis sets). In DFT, however, one must first choose the functional that is used to represent the exchange and correlation effects (or approximations to them) but then one can solve this

effective Hamiltonian almost exactly, i.e., with very high precision. Thus in both cases an approximation enters (either in the first or second step) but the sequence is reversed. This perspective illustrates the importance in DFT calculations of improving the functional, since this defines the quality of the calculation.

## 2.2. Solving the DFT equation, the choice of basis sets and wave functions

Many computer programs that can solve the DFT equations are available but they differ in the basis sets. Many use an LCAO (linear combination of atomic orbitals) scheme in one form or another. Some use Gaussian or Slater type orbitals (GTOs or STOs), others use plane wave (PW) basis sets with or without augmentations, and some others make use of muffin tin orbitals (MTOs) as in linear combination of MTOs (LMTO) or augmented spherical wave (ASW). In the former schemes the basis functions are given in analytic form, but in the latter the radial wave functions are obtained by numerically integrating the radial Schrödinger equation, whereas the angular dependence is given analytically.

Closely related to the basis set used is the explicit form of the wave functions, which can be well represented by them. These can be nodeless pseudo-wave functions or all-electron wave functions including the complete radial nodal structure and a proper description close to the nucleus.

## 2.3. The form of the potential

In the muffin tin or the atomic sphere approximation (MTA or ASA) an atomic sphere, in which the potential (and charge density) is assumed to be spherically symmetric, surrounds each atom in the crystal. While these schemes work reasonably well in highly coordinated, closely packed systems (as for example face centered cubic metals) they become very approximate in all non-isotropic cases (e.g., layered compounds, semiconductors, or open structures). Schemes that make no shape approximation in the form of the potential are termed full-potential schemes (see Section 3.2).

With a proper choice of pseudo-potential one can focus on the valence electrons, which are relevant for chemical bonding, and replace the inner part of their wave functions by a nodeless pseudo-function that can be expanded in PWs with good convergence.

## 2.4. Relativistic effects

If a solid contains only light elements, non-relativistic calculations are well justified, but as soon as a system of interest contains heavier elements, relativistic effects can no longer be neglected. In the medium range of atomic

numbers (up to about 54) the so-called scalar relativistic schemes [6] are often used, which describe the main contraction or expansion of various orbitals (due to the Darwin  $s$ -shift or the mass-velocity term) but omit spin-orbit splitting. This version is computationally easy and thus is highly recommended for all systems. The spin-orbit part can be included in a second-variational treatment [7]. For very heavy elements it may be necessary to add  $p_{1/2}$  orbitals [41] or to solve Dirac's equation, which has all these terms included.

## 2.5. Method of choice and properties

As a consequence of the aspects described above, different methods have their advantages or disadvantages when it comes to computing various quantities. For example, properties, which rely on the knowledge of the density close to the nucleus (hyperfine fields, electric field gradients, etc.), require an all-electron description rather than a pseudo-potential approach with unphysical wave functions near the nucleus. On the other hand for an efficient optimization of a structure, in which the shape (and symmetry) of the unit cell changes, it is very helpful to know the corresponding stress tensor. These tensors are much easier to obtain in pseudo-potential schemes and thus are available there. In augmentation schemes, however, such algorithms become more tedious and consequently are often not implemented. On the other hand all-electron methods do not depend on choices of pseudo-potentials and contain the full wave function information. Thus, the choice of method for a particular application depends on the properties of interest and may affect the accuracy, ease or difficulty to calculate them.

## 3. The full-potential linearized augmented plane wave (LAPW) method

One among the most precise schemes for solving the Kohn–Sham equations is the full-potential linearized augmented plane wave (FP-LAPW) method (see e.g., [8]). There are several programs employing this method such as FLAPW (Freeman's group), FLEUR (Blügel's group), D. Singh's code and others. Here we focus on the WIEN code that has been developed in our group during the last two decades and is used worldwide by more than 500 groups coming from universities and industrial laboratories. The original version (WIEN) was the first LAPW code that was published [9] and thus was made available for other users.

### 3.1. The LAPW method

In the LAPW method [8] the unit cell is partitioned into (non-overlapping) atomic spheres centered on the

atomic sites (I) and an *interstitial* region (II). For the construction of basis functions—and only for that—the *muffin tin* approximation (MTA) is used according to which the potential is assumed to be spherically symmetric within the atomic spheres but constant outside. Atomic-like functions are used in region I but plane waves (PW) in region II. Each PW is augmented by a corresponding atomic solution inside every atomic sphere.

Three schemes of augmentation (APW, LAPW, APW+lo) have been suggested over the years and illustrate the progress in this development of APW-type calculations that was discussed in a recent paper [10]. Here only a brief summary will be given. The energy dependence of the atomic radial functions  $u_\ell(r, E)$  can be treated in different ways. In Slater's APW [11] this was done by choosing a fixed energy  $E$ , which leads to a non-linear eigenvalue problem, since the basis functions become energy dependent. In LAPW, suggested by Andersen [12], a linearization of this energy dependence is used by solving the radial Schrödinger equation for a fixed linearization energy  $E_\ell$  but adding an energy derivative of this function to increase the variational flexibility. Inside sphere  $\alpha$  the atomic function is given by a sum of partial waves (radial functions times spherical harmonics), where  $L$  labels the quantum numbers ( $\ell, m$ ).

$$\sum_L [a_L^{\alpha K} u_\ell^\alpha(r') + b_L^{\alpha K} \dot{u}_\ell^\alpha(r')] Y_L(\vec{r}). \quad (3)$$

The corresponding two coefficients  $a$  and  $b$  (weight for function and derivative) can be chosen such as to match each plane wave (characterized by  $K$ ) to the atomic solution in value and slope at the sphere boundary (for details see e.g., [8,10]). In the APW plus local orbitals (APW+lo) method by Sjöstedt et al. [13] the matching is again (as in APW) only done in value.

The crystalline wave functions (of Bloch type) are expanded in these APWs leading (in the latter two cases of LAPW or APW+lo) to a general eigenvalue problem. The size of the matrix is mainly given by the number of plane waves (PWs) but is increased slightly by the additional local orbitals that are used. As a rule one needs about 50–100 PWs for every atom in the unit cell in order to achieve good convergence.

APW+lo leads—on the one hand—to a significant speedup (by an order of magnitude) and—on the other hand—to a comparable high accuracy with respect to LAPW [14]. The historical development and the details of this latest development, which is the basis for the new WIEN2k program [15], is given in Refs. [10,14]. The new version combines the best features of all APW-based methods. It was known that LAPW converges somewhat slower than APW due to the constraint of having differential basis functions and thus it was advantageous to go back to APW. However, the energy-independent basis introduced in LAPW is crucial, since it avoids the

non-linear eigenvalue problem of APW, and thus is kept. The local orbitals provide the necessary variational flexibility that make the new scheme efficient [10,13,14].

### 3.2. The muffin tin approximation and the full potential

The MTA was frequently used in the 1970s and works reasonably well in highly coordinated (closed packed) systems. However, for covalently bonded solids, open or layered structures, MTA is a poor approximation and leads to serious discrepancies with experiment. In all these cases a full-potential treatment is essential. In the full-potential schemes both, the potential and charge density, are expanded into lattice harmonics inside each atomic sphere:

$$\sum_{LM} V_{LM}(r) Y_{LM}(r) \quad (4)$$

and as a Fourier series in the interstitial region:

$$\sum_K V_K e^{i\vec{K}\cdot\vec{r}}. \quad (5)$$

Thus, their form (shown for the potential in Eqs. (4) and (5)) is completely general so that such a scheme is termed full-potential calculation. The foundation was laid by the pioneering work of the Freeman group leading to the FLAPW [16,17]. In order to have the smallest number of LM values in the lattice harmonics expansion (Eq. (4)) a local coordinate system for each atomic sphere is defined according to the point group symmetry of the corresponding atom. A rotation matrix relates the local to the global coordinate system of the unit cell. In addition to reducing the number of LM terms in Eq. (4) the local coordinate system also provides orbitals that are properly oriented with respect to the ligands, which may help the interpretation.

The choice of sphere radii is not very critical in full-potential calculations in contrast to MTA, in which one would, e.g., obtain different radii as optimum choice depending on whether one looks at the potential (maximum between two adjacent atoms) or the charge density (minimum between two adjacent atoms). Therefore in MTA one must make a compromise between these two criteria which are both reasonable. In full-potential calculations one can efficiently handle this problem and is rather insensitive to the choice of atomic sphere radii.

### 3.3. Computational considerations

In the newest version WIEN2k [15] the alternative basis set (APW+lo) is used inside the atomic spheres for the chemically important orbitals, whereas LAPW is used for the others [10,14]. In addition new algorithms for the computer intensive general eigensolver were implemented. The combination of algorithmic

developments and increased computer power has led to a significant improvement in the possibilities of simulating relatively large systems on moderate computer hardware. Now, PCs or a cluster of PCs can be used efficiently instead of the powerful workstations or supercomputers that were needed about a decade ago. Several considerations are essential for a modern computer code and were made in the development of the new WIEN2k package [15]:

**Accuracy:** extremely important in the present case. It is achieved by the well-balanced basis set, which contains numerical radial functions that are recalculated in each iteration cycle. Thus these functions adapt to effects due to charge transfer or hybridization, are accurate near the nucleus (important for EFG) and satisfy the cusp condition. The PW convergence can be essentially controlled by one parameter, namely the cutoff energy corresponding to the highest PW component. There is no dependence on selecting atomic orbitals or pseudo-potentials. It is a full-potential and all electron method. Relativistic effects (including spin orbit coupling) can be treated with a quality comparable to solving Dirac's equation. All atoms in the periodic table can be handled.

**Efficiency and good performance:** should be as high as possible. The new mixed basis APW+lo/LAPW optimally satisfies this criterion. The smaller matrix size helps to save computer time and thus larger systems can be studied. The scaling is less than  $N^3$ .

**Parallelization:** the program can run in parallel, either in a coarse grain version where each  $\mathbf{k}$ -point is computed on a single processor, or—if the memory requirement is larger than that available on a single CPU—in a fine grain scheme that requires special attention for the eigensolver, the most time consuming part. Both options, full and iterative diagonalization, are implemented to (automatically) select the most efficient routines.

**Architecture:** the hardware in terms of processor speed, memory access and communication is crucial. Depending on the given architecture, optimized algorithms and libraries are used during installation of the program package.

**Portability:** requires the use of standards as far as possible, such as FORTRAN90, MPI, BLAS (level 3), SCALAPACK, etc.

**User friendliness:** is achieved by a web based graphical user interface (GUI), called w2web. The program package provides an automatic choice of default options and is complemented by an extensive User's Guide. As one example for the GUI the structure generator is illustrated in Fig. 1 and is discussed in the case of titanium carbide (TiC).

It should be mentioned that TiC is a refractory metal compound that crystallizes in the rock-salt structure and has the unusual combination of properties, namely a

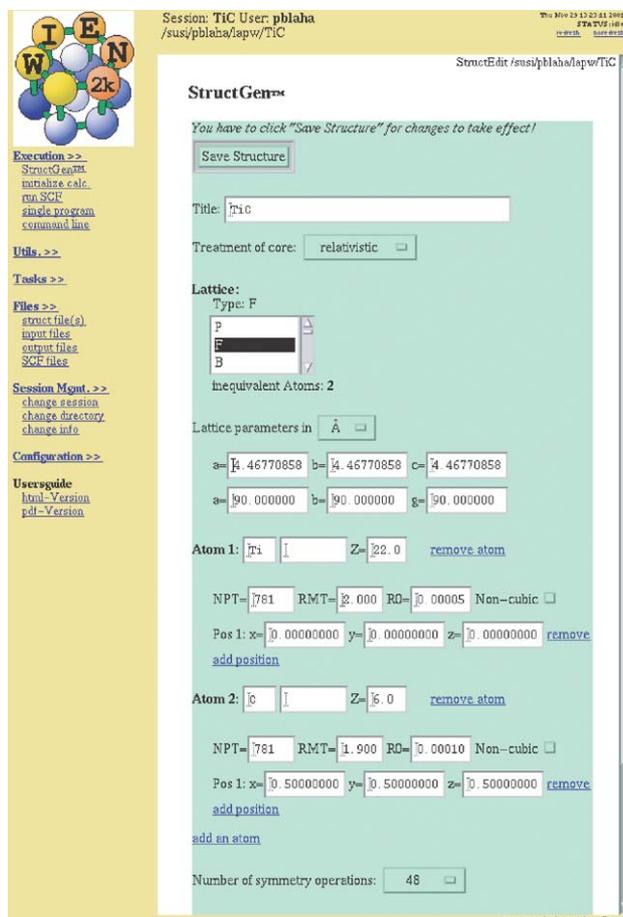


Fig. 1. The graphical user interface w2web in WIEN2k: Structure generator for titanium carbide.

melting point of about 3100°C, metallic conductivity and the hardness of diamond. It is used, e.g., for cutting tools in the steel industry. Fig. 1 illustrates how a calculation for a crystal structure is set up. One chooses a title for the compound, selects the treatment of core electrons (relativistic), defines the lattice type (face centered cubic) and lattice parameters ( $a, b, c, \alpha, \beta, \gamma$ ). In a cubic system as in TiC there is only one independent lattice constant and all angles are 90°. Then the atoms, Ti and C, need to be specified, with the atomic number  $Z$ , the muffin tin radius (RMT) of the sphere and the corresponding position in the unit cell.

This illustrates the first principle nature of such calculations. If the lattice constant is not known from the experiment, it can be optimized by minimizing the energy. In more complicated cases one can also use the space group symmetry and enter only the position of one of the symmetry-related atoms, where others are generated automatically.

### 3.4. Alternative DFT methods

Other schemes of comparable quality to solve the KS equation are available too, e.g., modern

pseudo-potentials or other full-potential methods. There are also simplified versions of electronic structure calculations such as the linear muffin tin orbital (LMTO) or augmented spherical wave (ASW) method, in which often the atomic sphere approximation (ASA) is made, where within the self-consistency cycle a spherically averaged potential and charge density is assumed around each atomic site. Although these schemes (with the ASA) are computationally faster, they often do not provide high enough accuracy to study details of the electronic structure, especially for mechanical properties. Note that full-potential LMTO and ASW exist as well.

## 4. Applications of WIEN2k

### 4.1. Systems

The problems considered so far in QM calculations using the LAPW method (employed in various versions of the WIEN code) have covered a wide spectrum, including in particular insulators, semiconductors, (transition) metals up to *f*-electron systems or intermetallic compounds. The band structure can directly be compared to experiment in weakly correlated cases. However, the electronic structure of highly correlated systems such as the high *T<sub>c</sub>* superconductors or the often-discussed late transition metal oxides would require treatments beyond LDA or GGA. In some solids magnetism plays an important role and as long as the magnetic moments are ordered in a collinear arrangement (e.g., ferro-, ferri- or antiferromagnets) a proper description is relatively easy. Recently an extension to non-collinear magnetic systems (e.g., canted spins or spin spirals) has been provided. Below several examples, which illustrates a variety of problems that can be studied are briefly sketched.

### 4.2. Results of band structure calculations using LAPW and the WIEN code

The results of LAPW calculations provide the basis for the interpretation of chemical bonding and the comparison with several experimental data. It should be mentioned again that there are other LAPW implementations besides the WIEN code but the latter is probably the most widely used LAPW code (with more than 500 groups worldwide). Many research results were obtained by means of WIEN calculations, most of which can be found on the web ([www.wien2k.at](http://www.wien2k.at)). Although this list of references is not complete, it contains only about 200 references from the last 3 years. In order to select representative references, we first summarize some properties (Sections 4.2.1–4.2.8) but restrict the examples to work made in our group. The second part (see

Section 4.2.9) is devoted to exciting research topics based on WIEN calculations that were done by other groups. Most of the corresponding references can be found on the web and the related topics are sketched at the end of this section (see Section 4.2.9) showing the broad variety of possible applications.

#### 4.2.1. Band structure and density of states (DOS)

The energy band structure and the corresponding density of states are the dominant quantities that determine the electronic structure of a system. Their inspection provides information about the electric property (metal, insulator or semiconductor) and gives insight into the chemical bonding. By looking at site-decomposed partial densities of states one can find a hint for the strength of interactions between the orbitals of the constituting atoms. As one example the bonding in the mineral andalusite,  $\text{Al}_2\text{SiO}_5$ , was discussed using these DOS [18].

The band structure is useful e.g., in connection with photoelectron spectra. A three-dimensional band mapping is possible by angle-dependent very-low-energy diffraction and photoemission. A representative example is given for Cu [19], for which the calculated band structure agrees very well with the experimental data.

#### 4.2.2. Electron densities

The electron density is the key quantity in DFT. By taking its Fourier transform the static structure factors can easily be obtained, which can be compared with the X-ray diffraction measurements. The comparison, however, is delicate, since the experiments are taken at finite temperature and must be corrected for thermal smearing, absorption and extinction. Determining the static structure factors from the experimental data requires a model in order to allow a comparison with theory. Therefore a *Multipole Refinement Project* [20] has been proposed by the International Union of Crystallography (IUCr) with the focus on corundum,  $\text{Al}_2\text{O}_3$ , for which a detailed analysis from experimental data, via a model to theory is given. Another example is stishovite,  $\text{SiO}_2$ , which recently was investigated using high-energy synchrotron radiation [21]. The earlier work on silicon, for which almost perfect crystals are available, should be mentioned in this context [22]. In this case the accuracy of the experimental data was so high that the quality of different exchange correlation potentials could be evaluated.

In most cases the total electron density has maxima only at nuclear positions, but there are examples of non-nuclear maxima (NNM) in metals [23] or sodium electro sodalite (SES) [24]. In SES a NNM appears in the center of the cage at the color center (see Section 4.2.5 and Fig. 2). A controversial issue was the chemical bonding in cuprite,  $\text{Cu}_2\text{O}$ , that was revisited recently [25]. In this case limitations of DFT and schemes beyond LDA are

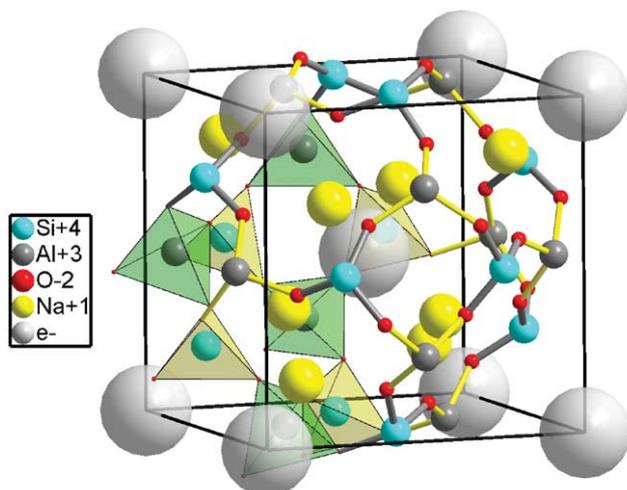


Fig. 2. Structure of sodium electro sodalite (SES)  $\text{Na}_8(\text{AlSiO}_4)_6$ . The cage consists of alternating  $\text{SiO}_4$  and  $\text{AlO}_4$  corner-shared tetrahedra. Inside each cage the charge is compensated by 4  $\text{Na}^+$  ions and an electron  $e^-$  (color center) at the center of the cage, where no nucleus is positioned. For details see Ref. [24].

discussed in order to derive a picture that is consistent with experimental observations.

In the discussion of chemical bonding various schemes which rely on the electron density are used. These are for example partial charges, which always depend on the underlying model. In our case partial charges can easily be computed by taking the fractions that reside inside the atomic spheres but these values obviously depend on the sphere radii chosen. Inside each sphere a partitioning into  $\ell$ -like charges ( $s, p, d, f$ ) can be done according to our atomic basis functions. These charges can be further decomposed with respect to the corresponding point group symmetry of each atomic site according to the  $m$ -components (e.g.,  $p_x, p_y, p_z$ ) or their symmetry adapted combinations. This latter decomposition corresponds to the local coordinate system, which may coincide with the symmetry axes of coordination polyhedra. In such a case the interpretation of bonding is helped by having a proper orbital basis.

An alternative scheme [26] is based on a topological analysis following Bader's quantum theory of atoms in molecules (AIM). Space partitioning into atomic basins is uniquely defined, where an atomic basin is limited by a surface that is not crossed by gradient vectors, i.e., the 'zero flux' criterion holds for each surface point

$$\nabla\rho(r)\cdot n(r) = 0, \quad (6)$$

where  $n(r)$  is the surface normal vector [26]. Further analysis looks at the bond critical points (b.c.p.), at which the gradient of the density vanishes, and so too are the density at these points and the Laplacian. Such an analysis was made for example for stishovite [21], and the topological analysis compared theory and experiment.

Difference electron densities taken between the crystalline density and an artificial reference state (defined by a superposition of atomic densities) enhance the changes that occur in the formation of a solid with respect to neutral atoms. Such a characterization of chemical bonding is illustrated for anadulsite [18]. A similar scheme is used in crystallography but in reciprocal space.

In the case of magnetic systems, spin densities are available. In collinear systems, the difference between spin-up and spin-down densities and the magnetization density, shows where the related spin magnetic moment resides, although the electrons are delocalized, e.g., in itinerant magnets.

#### 4.2.3. Electric field gradients (EFG)

Nuclei with a nuclear quantum number  $I > \frac{1}{2}$  have an electrical quadrupole moment  $Q$ . The nuclear quadrupole interaction (NQI) can aid in determining the distribution of the electronic charge surrounding such a nuclear site, which is characterized by the EFG tensor. This interaction can be measured by nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), Mössbauer or by perturbed angular correlation (PAC) measurements and is determined by the product

$$v \approx eQ\Phi/h, \quad (7)$$

where  $\Phi$  is a traceless tensor characterizing the EFG

$$\Phi_{ij} = \frac{\partial^2 V(0)}{\partial x_i \partial x_j} - \frac{1}{3} \delta_{ij} \nabla^2 V \quad (8)$$

which is the second derivative of the electrostatic potential with respect to two coordinates.

The EFG is sensitive to the anisotropy of the charge density distribution close to the nucleus. In 1985 we have shown for  $\text{Li}_3\text{N}$  that the EFG can be calculated from first principles [27], since the EFG is uniquely defined by the charge distribution and thus the electron density. Since this first application to  $\text{Li}_3\text{N}$  the EFGs of many compounds have been studied e.g., the high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [28], for which the origin of the EFG was interpreted for all oxygen positions. In this work it was shown that the anisotropy in the charge density around the oxygen atoms (characterized by the difference in the  $p_x, p_y$  and  $p_z$  occupation numbers inside the oxygen spheres) is directly proportional to the corresponding EFG. At this point it should also be mentioned that the EFG at one of the copper positions (Cu(2) in the Cu–O layer that leads to superconductivity) deviates by more than a factor of two from experiments. This indicates that the present versions of DFT are not yet suited to treat such highly correlated systems in all details, whereas certain aspects (like the EFGs around oxygen) are properly described.

Other systems (from minerals, sodium-nitroprusside to rare-earth borocarbides) have been studied as well [18,29,30]. One noteworthy was the calculation of EFGs for a series of iron compounds in relation to the experimental NQI data, that made it possible to even determine a new value for the nuclear quadrupole moment  $Q$  of  $^{57}\text{Fe}$ , the most important Mössbauer isotope that was twice as big as the old value in Ref. [31].

#### 4.2.4. Total energy and phase transitions

With the total energy the relative stability of different phases can be computed. In such a case it is advisable to keep as many parameters constant as possible in order to have a cancellation of systematic errors. These parameters can be, for example, the size of the atomic spheres, the plane-wave cutoff, the  $\mathbf{k}$ -mesh, the DFT functional, the treatment of relativity, etc. Energy differences are often rather small and thus a consistent treatment of the systems to be compared will help to minimize these computational effects. A few examples can be found in applications to metals [32], an insulator  $\text{CaCl}_2$  [33] or a defect structure [34]. In each of these cases a new interpretation for the interplay between the structure of a solid and the electronic structure is given.

#### 4.2.5. Forces and structure optimization

Closely related to the total energy is the structure optimization that is often needed in this context. In cases where the atoms occupy general positions that are not fixed by the crystal symmetry, the knowledge of the forces acting on the atoms helps to optimize the structure parameters. Forces can be computed in WIEN2k and are crucial for such optimizations.

An example that was used to test the new APW+lo scheme is discussed below. The structure is sodium electro sodalite (SES), a rather unusual system that contains 44 atoms per unit cell (Fig. 2). The main building block is an ordered aluminum silicate, in which corner-shared units form the cage with alternating  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra. Aluminum has one charge less than silicon and thus the three charges missing per cage can be compensated for example by sodium ions. Three  $\text{Na}^+$  ions are needed for charge neutrality but (according to cubic symmetry) a fourth ion can enter the cage and thus one electron is too much and forms a color center placed at the center of the cage. Note that there is no nucleus at this position. There is an antiferromagnetic coupling between these color centers in neighboring cages. The properties of SES are discussed in Ref. [24] and the use of forces is analyzed in Ref. [14], where it is shown that about half the matrix size is needed in APW+lo to obtain an accuracy comparable to LAPW reducing the computational effort by about an order of magnitude (due to the  $N^3$  scaling). This example illustrates the complexity of a system that nowadays can efficiently be treated already on a PC. Increased

computer power will let us study larger systems containing up to a few hundred atoms per unit cell.

#### 4.2.6. Materials with unusual properties

The magnetic interactions in a spinel ( $\text{LiV}_2\text{O}_4$ ) has recently attracted much attention due to the presence of a heavy fermion behavior in a  $3d$  metallic system [35]. The electronic structure of a mixed valence system has been studied as well [36]. The pyrochlore metal  $\text{Cd}_2\text{Os}_2\text{O}_7$  has unusual properties [37] which require a proper treatment of spin-orbit coupling of the transition element that dominates the energy bands near the Fermi energy. Metastable states e.g., of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  can be used for an optical storage medium using holography [38]. In this case the NO group can form linkage isomers, which are metastable states, between which one can switch with proper laser light.

#### 4.2.7. Spectra

The photoelectron spectra have been mentioned (see Section 4.2.1) in connection with the energy bands [19]. Some spectra can be interpreted using EFG results as discussed above (see Section 4.2.3). X-ray emission and absorption spectra can be calculated using the partial densities of states and the transition probabilities between a valence and a core state. Such spectra provide useful information on the local binding situation of the atom, whose core state is involved. Sometimes the core-hole screening should be taken into account, at least approximately [39]. Optical spectra and related quantities are available too.

#### 4.2.8. Other properties and extensions of the program

Many applications in connection with magnetism have been done, and they fall beyond what can be presented in a short presentation like here. Sometime the present versions of DFT, LDA or GGA are not sufficient to treat a given solid, for example a highly correlated system as the high temperature superconductor mentioned above [28]. There are several attempts to go beyond LDA, for example, by including a Hartree-Fock-like treatment of the electron repulsion between electrons, as defined by a Hubbard  $U$ . Such schemes can be and have been implemented and are applied, e.g., to  $\text{FeAl}$  [40], where correlation effects induce a paramagnetic ground state that can be obtained using LDA+ $U$ , whereas GGA leads to a ferromagnet in contrast to experiment.

#### 4.2.9. Variety of applications with LAPW or the WIEN code

At the beginning of Section 4.2 it was mentioned that many research problems were studied through WIEN calculations and most of these references can be found on the web ([www.wien2k.at](http://www.wien2k.at)), although this list is by no means complete. Above, several examples (mainly work

from my group) were mentioned to demonstrate some possibilities to use LAPW results. In order to illustrate the broad range of applicability and how the WIEN results can be used, several topics are summarized below but without details that can be found in the original literature.

For a large variety of structures the following topics were investigated, such as chemical bonding, structural stability, high-pressure phases, Jahn–Teller distortions, charge disproportionation, phase transitions, ferroelastic, ferroelectric or elastic properties. Intrinsic semiconductors were studied looking at band gaps, effective (electron or hole) masses, alloying or heavy doping. Magnetic solids (including intermetallic compounds) were investigated and the investigation concerned the role of spin and orbital magnetic moments, magnetic ordering (ferro-, ferri-, antiferro-magnetic) or metamagnetism. Such research work included magnetic circular dichroism, the Farady effect or spin-density waves. LAPW calculations can help to understand various spectroscopies (optical, core-level, photoelectron, Mössbauer, NMR) and can provide information on hyperfine or crystal fields, the magneto-optical Kerr effect or electric field gradients. Other interesting topics are surfaces, multilayers, superlattices, or intercalation compounds. Here the work at the Fritz Haber Institute (Scheffler's group) should be mentioned as a representative case. In this group WIEN based calculations were much used to investigate the interaction of molecules with a solid surface. A recent paper [42] is a nice example of how DFT results (at  $T = 0$  and ambient pressure) can be extended to realistic conditions that are used in catalysis by using additional thermodynamic models. Many related references can be found at the corresponding web page ([www.fhi-berlin.mpg.de/th/th.html](http://www.fhi-berlin.mpg.de/th/th.html)).

## 5. Summary and Conclusion

DFT calculations—for example by the LAPW method and the WIEN code—can provide useful information concerning the electronic structure of ordered crystal structures. The results depend on the exchange and correlation potential that is chosen for the calculations. In comparison with real systems it should be stressed that all kinds of imperfections are ignored. Some of them can be simulated. For example, it is possible to represent defects, e.g., an impurity, by studying (in a simple case) a  $2 \times 2 \times 2$  super-cell, doubling the original unit cell in all the three dimensions. Sometimes a large super-cell may be needed to simulate the physical situation. When one atom in this large unit cell is replaced by an impurity atom, the neighboring atoms can relax to new equilibrium positions. Such a super-cell is repeated periodically and approximately represents

an isolated impurity. Super-cells can also be used to simulate surfaces and their interaction with atoms or molecules. These examples illustrate how theory can carry out computer experiments. Hypothetical or artificial structures can be considered and their properties can be calculated, irrespective of whether they can be made or not. Such calculations can predict the property of a system (e.g., insulator or metal) or find its magnetic structure. In addition to the properties that were discussed here, other data concerning the electronic, optic or magnetic properties are available. Simulations can be carried out to predict how the system may change with deformations, under pressure or substitutions. Pressure is an easy parameter for DFT calculations in contrast to experiments. The opposite is true for estimating temperature effects which are easier in experiments rather than in theory. Finite temperature effects can be included using lattice vibrations, which may be obtained from calculations (e.g., using frozen phonons or by direct methods displacing atoms) or approximated from known phonon data. Recently the latter procedure was illustrated for titanium under high pressure [4]. DFT results may provide crucial parameters for other models which are needed to study effects on larger length scales. The examples given here are just a small selection to illustrate some possibilities the WIEN2k code can provide. Additional references can be found on the web ([www.wien2k.at](http://www.wien2k.at)) referring to the papers of the many WIEN users.

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## References

- [1] P. Hohenberg, W. Kohn, *Phys. Rev.* 136B (1964) 864–871.
- [2] W. Kohn, L.S. Sham, *Phys. Rev.* 140 (1965) A1133–A1138.
- [3] Th. Hahn, in: *International Table of Crystallography*, Vol. A, Kluwer Academic Publ, Dordrecht, Boston London, 1995.
- [4] P.T. Jochym, K. Parlinski, M. Sternik, *Eur. Phys. J. B* 10 (1999) 9–13.
- [5] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865–3868.

- [6] D.D. Koelling, B.N. Harmon, *J. Phys. C: Solid State Phys.* 10 (1977) 3107–3114.
- [7] A.H. MacDonald, W.E. Pickett, D.D. Koelling, *J. Phys. C: Solid State Phys.* 13 (1980) 2675–2683.
- [8] D.J. Singh, *Plane Waves, Pseudopotential and the LAPW Method*, Kluwer Academic Publisher, Boston, Dordrecht, London, 1994.
- [9] P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, *Comput. Phys. Commun.* 59 (1990) 399–415.
- [10] K. Schwarz, P. Blaha, G.K.H. Madsen, *Comput. Phys. Commun.* 147 (2002) 71–76.
- [11] J.C. Slater, *Phys. Rev.* 51 (1937) 151–156.
- [12] O.K. Andersen, *Phys. Rev. B* 12 (1975) 3060–3083.
- [13] E. Sjöstedt, L. Nordström, D.J. Singh, *Solid State Comm.* 114 (2000) 15–20.
- [14] G. H. K. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, L. Nordström, *Phys. Rev. B* 64 (2001) 195134-1-9.
- [15] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, *An augmented plane wave plus local orbitals program for calculating crystal properties*, Vienna University of Technology, Austria (2001) ISBN 3-9501031-1-2.
- [16] E. Wimmer, H. Krakauer, M. Weinert, A.J. Freeman, *Phys. Rev. B* 24 (1981) 864–875.
- [17] M. Weinert, E. Wimmer, A.J. Freeman, *Phys. Rev. B* 26 (1982) 4571–4578.
- [18] M. Iglesias, K. Schwarz, P. Blaha, D. Baldomir, *Phys. Chem. Minerals* 28 (2001) 67–75.
- [19] V. N. Strocov, R. Claessen, G. Nicolay, S. Hüfner, A. Kimura, A. Harasawa, S. Shin, A. Kakizaki, H.I. Starnberg, P.O. Nilsson, P. Blaha, *Phys. Rev. B* 63 (2001) 205108-1-16.
- [20] S. Pillet, M. Souhassou, C. Lecomte, K. Schwarz, P. Blaha, M. Rérat, A. Lichanot, P. Roversi, *Acta Cryst. A* 290 (2001) 290–303.
- [21] A. Kirfel, H.-G. Krane, P. Blaha, K. Schwarz, T. Lippmann, *Acta Cryst. A* 57 (2001) 663–677.
- [22] J.M. Zuo, P. Blaha, K. Schwarz, *J. Phys.: Condens. Matter* 9 (1997) 7541–7561.
- [23] G.H.K. Madsen, P. Blaha, K. Schwarz, *J. Chem. Phys.* 117 (2002) 8030–8035.
- [24] G. H. K. Madsen, Bo. B. Iversen, P. Blaha, K. Schwarz, *Phys. Rev. B* 64 (2001) 195102-1-6.
- [25] R. Laskowski, P. Blaha, K. Schwarz, *Phys. Rev. B* 67 (2003) 075102-1-8.
- [26] R.F.W. Bader, *Atoms in Molecules*, Oxford Science, Oxford, 1990.
- [27] P. Blaha, K. Schwarz, P. Herzig, *Phys. Rev. Lett.* 54 (1985) 1192–1195.
- [28] K. Schwarz, C. Ambrosch-Draxl, P. Blaha, *Phys. Rev. B* 42 (1990) 2051–2061.
- [29] P. Blaha, K. Schwarz, W. Faber, J. Luitz, *Hyperfine Interactions* 126 (2000) 389–395.
- [30] M. Diviš, K. Schwarz, P. Blaha, G. Hilscher, H. Michor, S. Khmelevskiy, *Phys. Rev. B* 62 (2000) 6774–6785.
- [31] Ph. Dufek, P. Blaha, K. Schwarz, *Phys. Rev. Lett.* 75 (1995) 3545–3548.
- [32] G.B. Grad, P. Blaha, J. Luitz, K. Schwarz, A. Fernández Guilmeret, S.J. Sferco, *Phys. Rev. B* 62 (2000) 12743–12753.
- [33] J.A. Válgoma, J. Perez-Mato, A. García, K. Schwarz, P. Blaha, *Phys. Rev. B* 65 (2002) 134104–1341-8.
- [34] M. Chall, B. Winkler, P. Blaha, K. Schwarz, *J. Phys. Chem. B* 104 (2000) 1191–1197.
- [35] D.J. Singh, P. Blaha, K. Schwarz, I.I. Mazin, *Phys. Rev. B* 60 (1999) 16359–16363.
- [36] P. Novák, F. Boucher, P. Gressier, P. Blaha, K. Schwarz, *Phys. Rev. B* 65 (2001) 235114-1-8.
- [37] D. J. Singh, P. Blaha, K. Schwarz, J. Sofo, *Phys. Rev. B* 65 (2001) 155109-1-8.
- [38] M. Imlau, S. Haussühl, Th. Woike, R. Schieder, V. Angelov, R.A. Rupp, K. Schwarz, *Appl. Phys.* 68 (1999) 877–885.
- [39] J. Luitz, M. Maier, C. Hébert, P. Schattschneider, P. Blaha, K. Schwarz, B. Jouffrey, *Eur. Phys. J. B* 21 (2001) 363–367.
- [40] P. Mohn, C. Persson, P. Blaha, K. Schwarz, P. Novák, H. Eschrig, *Phys. Rev. Lett.* 87 (2001) 196401-1-4.
- [41] J. Kuneš, P. Novák, R. Schmid, P. Blaha, K. Schwarz, *Phys. Rev. B* 64 (2001) 153102-1-3.
- [42] K. Reuter, M. Scheffler, *Phys. Rev. Lett.* 90 (2003) 046103-1-4.