

# Quantum Mechanical Computations at the Atomic Scale for Material Sciences

**Karlheinz Schwarz\* and Peter Blaha**

Institute of Materials Chemistry  
Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria  
e-mail: [kschwarz@theochem.tuwien.ac.at](mailto:kschwarz@theochem.tuwien.ac.at)

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## Abstract

In advanced materials several parameters as temperature, pressure, structure, composition, disorder determine their properties. In addition the length scale can vary over many orders of magnitude from meters, mm,  $\mu\text{m}$ , nm all the way to atomic dimensions given in  $\text{\AA}$ . This wide range requires completely different descriptions and thus other physical laws from continuums to quantum mechanics. Here 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 (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. For the solution of the KS equations several methods have been developed, with the Linearized-Augmented-Plane-Wave (LAPW) method being one among the most accurate. We have developed a computer code - WIEN2k - that is now used worldwide by more than 500 groups to solve crystal properties on the atomic scale (see [www.wien2k.at](http://www.wien2k.at)). The elastic properties of an ideal crystal can be obtained by deforming the unit cell either under hydrostatic pressure (i.e. varying the volume) or by applying strain. In this process the atoms may change their positions but can be brought to equilibrium by monitoring the forces acting on them. From a series of strained lattices the static lattice potential, corresponding to the band structure total energy, is calculated. From such results the equilibrium volume, the elastic constants, the bulk modulus and its pressure derivative can be derived. Nowadays calculations of this type can be done - on sufficiently powerful computers - for systems containing about 100 atoms per unit cell. DFT results may provide crucial parameters for other models which are needed to study effects on larger length scales.

## 1 Introduction

Solid materials and their mechanical properties are of great technological interest. They are governed by very different length and time scales which may differ by many orders of magnitude depending on their applications. Let us focus on the length scale, where from meters (m) down to micrometers ( $\mu$ ) classical mechanics and continuums 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 mechanical properties are determined by the electronic structure of the solid. In the development of modern materials an understanding on an atomic scale is frequently essential in order to replace trial and error procedures by a systematic materials design. In this context the electronic properties of solids need to be described by a quantum mechanical treatment. 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 other storage media.

One possibility to study complex systems that contain many atoms is to perform computer simulations. Calculation of solids in general (metals, insulators, minerals, etc.) can be performed with a variety of methods from classical to quantum mechanical (QM) approaches. The former are force field or semi-empirical schemes, in which the forces that determine the interactions between the atoms are parameterized in such a way to reproduce a series of experimental data such as equilibrium geometries, bulk moduli or special vibrational frequencies (phonons). These schemes have reached a high level of sophistication and are often useful 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 requirements and thus allow only the treatment of smaller unit cells than semi-empirical calculations. The advantage of first-principle (*ab initio*) methods lies in the fact that they do not require any experimental knowledge to carry out such calculations. The following presentation 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 must be antisymmetric when two electrons are interchanged. This situation leads to the phenomenon of exchange and correlation. There are two types of approaches for a full quantum mechanical treatment, HF and DFT. The traditional scheme is 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 such as configuration interaction (CI) but they progressively require 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 Density Functional Theory (DFT) that is commonly used to calculate the electronic structure of complex systems containing many atoms such as large molecules or solids. It is based on the electron density rather than on the wave functions and treats both, exchange and correlation, but both approximately.

The ideal crystal is defined by the unit cell which may contain several (up to about 100) 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 to simplify the calculations, which all correspond to the absolute temperature zero ( $T=0$ ).

## 2 Density Functional Theory (DFT)

### 2.1 The Kohn-Sham equations

The well-established scheme to calculate electronic properties of solids is based on density functional theory (DFT), for which Walter Kohn, who was born in Vienna, 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 with the same total density. Hohenberg and Kohn [1] have shown that the electron density  $\rho$  uniquely defines the total energy  $E$  of a system and is a functional  $E[\rho]$  of the density. The non-interacting particles of this auxiliary system move in an effective local one-particle potential, which consists of a classical mean-field

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

(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. Eqn.1 shows its form (written 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  $V_{xc}$ . It must be solved iteratively till self-consistency is reached. 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.

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

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 [3] (GGA), improved the LDA by adding gradient terms of the electron density and reached (almost) chemical accuracy.

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

There are many computer program available to solve the DFT equations. Essentially all use an LCAO (linear combination of atomic orbitals) scheme in one form or another but they differ in the basis sets. Some use Gaussian or Slater type orbitals (GTOs or STOs) others use plane wave (PW) basis sets with or without augmentations, and even others make use of muffin tin orbitals (MTOs) as in LMTO (linear combination of MTOs) or ASW (Augmented Spherical Wave). In the former cases the basis functions are given in analytic form, but in the latter the radial wave-functions are obtained numerically by integrating the radial Schrödinger equation.

Closely related to the basis sets used is the explicit form of the wave-functions, which can be well represented by them, whether they are node-less 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 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 face centered cubic metals) they become very approximate in all non-isotropic cases (e.g. layered compounds, semiconductors, or other open structures). Schemes that make no shape approximation in the form of the potential are termed full-potential schemes.

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 node-less 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 systems of interest contains heavier elements, relativistic effects can no longer be neglected. In the medium range of atomic numbers (up to about 54) so called scalar relativistic schemes 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 they omit spin-orbit splitting. The latter can be included in a second-variational treatment. For very heavy elements it may be necessary to solve Dirac's equation, which has all these terms included.

### 2.5 Properties

As a consequence of the aspects described above different methods have their advantages or disadvantages when it comes to compute 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 studies, in which the shape (and symmetry) of the unit cell changes, the knowledge of the corresponding stress tensor is needed for an efficient structural optimization. These tensors are presently only available in pseudo-potential schemes. Thus the choice of method could affect the accuracy, ease or difficulty to calculate a given property. The properties are e.g. energy band structure, densities of states, electron densities and the related static structure factors, forces acting on the atoms (for geometry optimization), strain tensor, or x-ray absorption or emission spectra.

### 2.6 Systems

The problems considered so far in QM calculations have covered a wide spectrum, including in particular insulators, semiconductors, metals, often transition metals up to f-electron systems, intermetallic compounds or highly correlated systems such as the high  $T_c$  superconductors or the often-discussed transition metal oxides. In some of them magnetism plays an important role and as long as the magnetic moments are ordered in a collinear arrangement (e.g. ferro-, ferri- or antiferromagnets) the systems can be well described. Extension to non-collinear systems became available recently.

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

One among the most accurate schemes for solving the Kohn Sham equations is the full-potential linearized-augmented-plane-wave (FP-LAPW) method (see e.g. [4]) on which our WIEN code is based. This FP-LAPW code has been developed in our group and is frequently used worldwide. The original version (WIEN) was the first LAPW code that was published [5] and thus was made available for other users.

#### 3.1 The linearized augmented plane wave (LAPW) method

In the LAPW method the unit cell is partitioned into (non-overlapping) atomic spheres centered around the atomic sites (type I) and an interstitial region (II). For the construction of basis functions 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, where in the former atomic-like functions and in the latter plane waves are used. Each plane wave is augmented by a corresponding atomic solution inside each atomic sphere. The energy dependence of these atomic radial functions can be treated in different ways. In APW this is done by choosing a fixed energy. This leads to a non-linear eigenvalue problem, since the basis functions become energy dependent. In LAPW a linearization of the energy dependence is used by solving the radial Schrödinger equation for a fixed linearization energy but adding an energy derivative of this function. The corresponding two coefficients can be chosen such as to match (at the atomic sphere boundary) the atomic solution to each plane wave in value and slope, which determine the two coefficients of the function and its derivative. In the APW plus local orbitals method the matching is only done in value, but this new scheme leads to a significant speed up of the method up to an order of magnitude while keeping the high accuracy of LAPW [6]. The details of this version, which is the basis for the new WIEN2k program [7]. A description of these three types of schemes (APW, LAPW, APW+lo) mentioned above is given in [8].

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

The MTA was frequently used in the seventies and works reasonable well in highly coordinated (metallic) systems such as face centered cubic (fcc) metals. 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)

$$\sum_{LM} V_{LM}(r) Y_{LM}(r) \quad (3)$$

and as a Fourier series (in the interstitial region):

$$\sum_K V_K e^{i\vec{K}\cdot\vec{r}} \quad (4)$$

Thus their form is completely general so that such a scheme is termed full-potential calculation. In order to have a small number of LM values in the lattice harmonics expansion a local coordinate system for each atomic sphere is defined according to the point group symmetry of the corresponding atom. This specifies a rotation matrix that relates the local to the global coordinate system of the unit cell. The choice of sphere

radii is not very critical in full-potential calculations in contrast to MTA, in which one would 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 but in full-potential calculations one can efficiently handle this problem.

### 3.3 Computational considerations

In the newest version WIEN2k [7] the alternative basis set (APW+lo) is used inside the atomic spheres [6,8]. In addition new algorithms for solving the computer intensive general eigenvalue problem were implemented. The combination of algorithmic developments and increased computer power has led to a significant improvement in the possibilities to simulate relatively larger systems on moderate computer hardware. Now PCs or a cluster of PCs can be efficiently used instead of the powerful workstations or supercomputers that were needed about a decade ago.

A modern software package needs a good graphical user interface (GUI). In WIEN2k this is implemented as a web-based GUI, called w2web. As one example the structure generator is illustrated below and is discussed with Fig.2 for the case of titanium carbide (TiC).

### 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 in addition to LDA the atomic sphere approximation (ASA) is made, i.e. within the self-consistency cycle a spherically averaged potential and charge density is assumed around each atomic site. (Note that a full-potential LMTO exists as well). Although these latter 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.

## 4 Applications

Titanium carbide is a refractory metal compound that crystallizes in the rock-salt structure (Fig.1) and has the unusual combination of properties, namely a melting point of about 3100°C, metallic conductivity and a hardness as diamond. It is used e.g. for cutting tools in the steel industry.

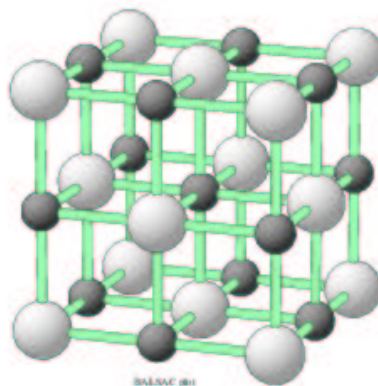


Figure 1: Titanium carbide crystallizes in the rock-salt structure

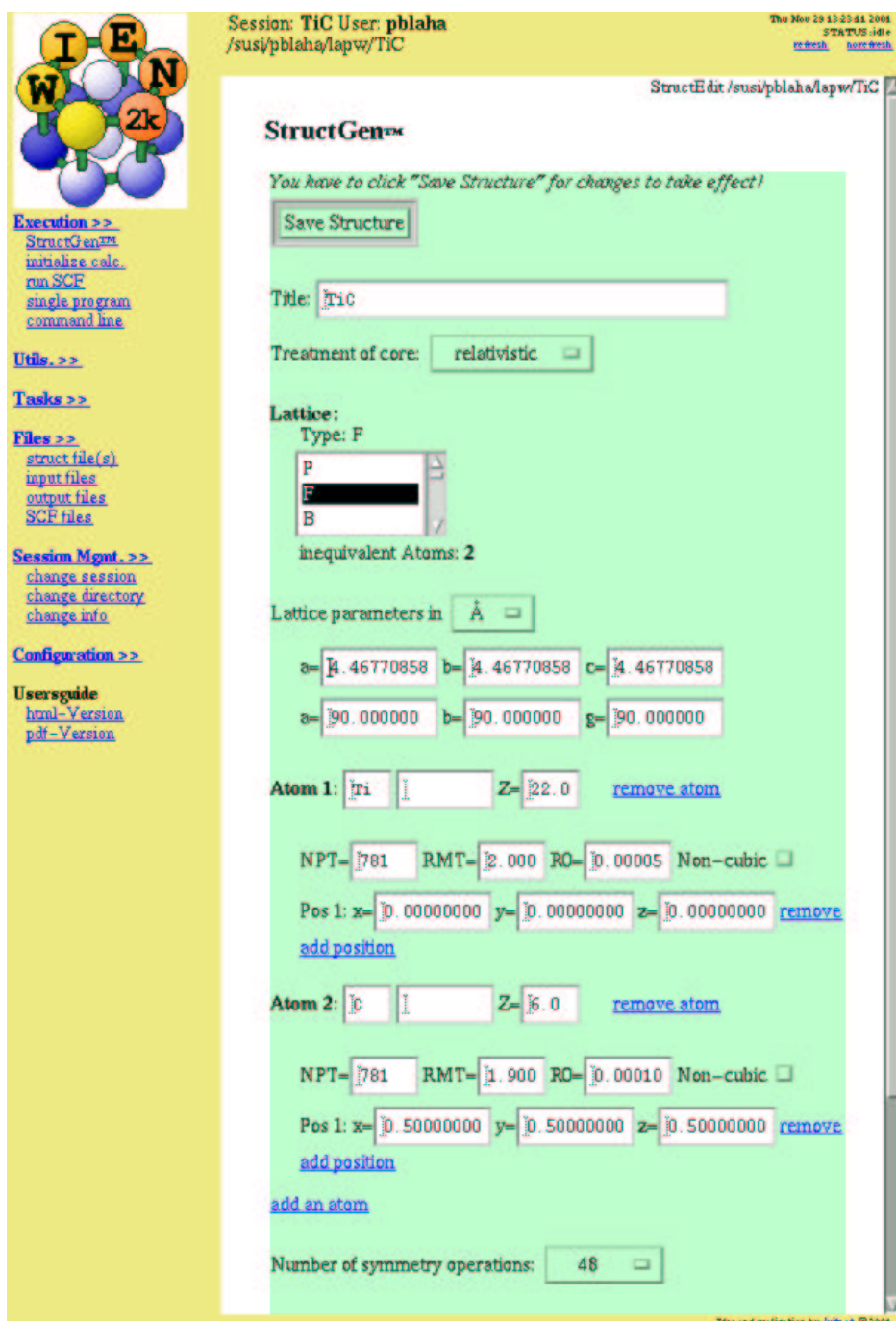


Figure 2: The graphical user interface w2web in WIEN2k: structure generator for TiC.

This figure 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  $90^\circ$ . Then the atoms, Ti and C, need to be specified, with the atomic number  $Z$ , the sphere radius  $RMT$  and the positions in the unit cell. This illustrates the first principles nature of such calculations. If the lattice constant is not known from experiment, then it can be varied (see below).

## 5 Mechanical properties

The calculation of mechanical properties require high accuracy and in particular a full-potential treatment. Both are given in WIEN2k. In DFT the total energy of a system is a well defined quantity that is mainly used to calculate the mechanical properties.

### 5.1 Equilibrium volume and bulk modulus

A series of total energy calculations as a function of volume can be fitted to an equation of states according to Murnaghan.

$$E(V) = \frac{B_0 V}{B_0'} \left[ \frac{(V_0/V)^{B_0'}}{B_0'} + 1 \right] + C \quad (5)$$

The equilibrium volume is given by the corresponding total energy minimum as shown in Fig.3.

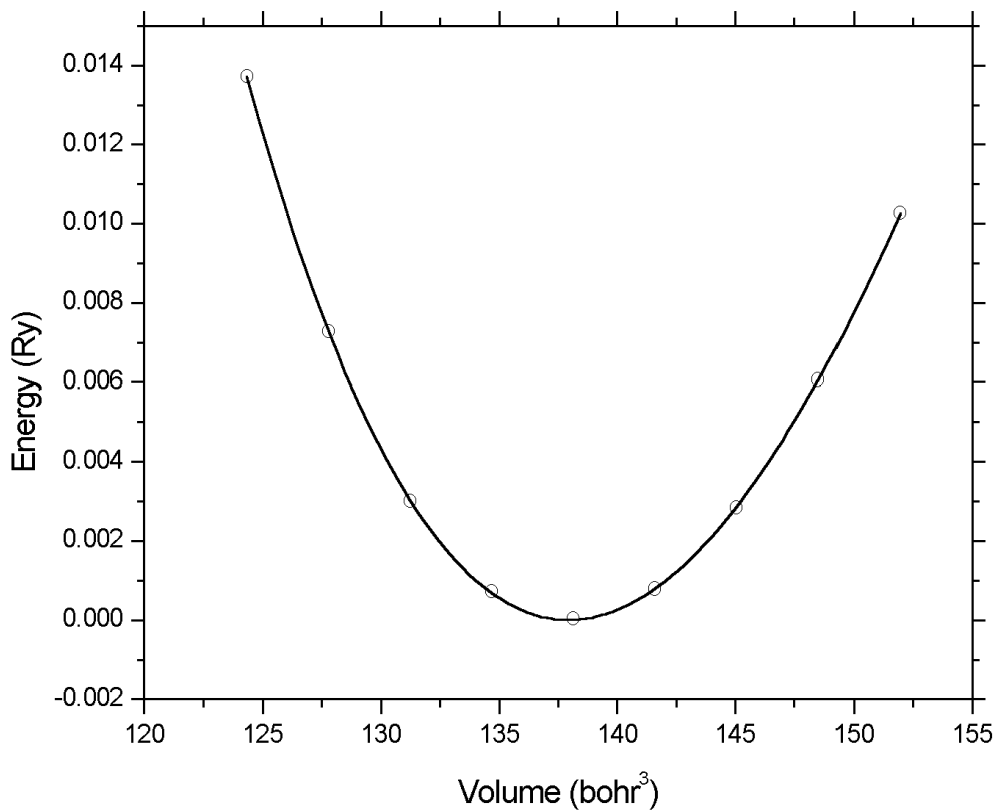


Figure 3: Total energy of TiC as a function of volume.



## 5.2 Elastic constants, theoretical background

Let  $E_{tot}^0$  be the total energy of an initial crystal, and  $V_0$  its volume. By deforming this crystal the energy  $E_{tot}$  of the resulting strained state can be expressed as

$$E_{tot} = E_{tot}^0 + P(V - V_0) + \Phi_{elast} \quad (6)$$

where  $V$  is the volume of the strained lattice,  $\Phi_{elast}$  the elastic energy, and  $P$  the pressure defined by

$$P = -\left(\frac{\partial E_{tot}^0}{\partial V}\right) \quad (7)$$

taken at  $V_0$ . To first order the strained lattice is related to the unstrained lattice by  $I+\varepsilon$ , where  $I$  is the identity matrix and  $\varepsilon$  the strain tensor. According to Hook's law, the linear elastic constants  $C_{ijkl}$  are then defined by using the second order development of the elastic energy

$$\Phi_{elast} = \frac{V}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \quad (8)$$

or in Voigt's two-suffix notation

$$\Phi_{elast} = \frac{V}{2} C_{ij} \varepsilon_i \varepsilon_j \quad (9)$$

the  $(V-V_0)$  term in eq. (6) is linear with respect to the strain, i.e.

$$V - V_0 = V_0 \cdot Tr(\tilde{\varepsilon}) = V_0 \sum_{i=1}^3 \varepsilon_i \quad (10)$$

Thus it is possible to derive elastic constants from the second order derivative of  $E_{tot}$

$$C_{ij} = \frac{1}{V_0} \cdot \frac{\partial^2 E_{tot}}{\partial \varepsilon_i \partial \varepsilon_j} \quad (11)$$

## 5.3 Application to TiC

In a cubic case as TiC it is sufficient to consider three different strains (volume, tetragonal, and rhomohedral strain) to determine all elastic constants. The required second derivatives are calculated numerically using about 5 to 10 different structures that represent the strained crystal. Here we show the results of WIEN2k calculations. Similar studies were done with other DFT codes [8,9].

Table 1: Experimental and theoretical bulk modulus B and elastic constants of TiC.

Results	Volume (bohr <sup>3</sup> )	Bulk modulus (Mbar)	C <sub>11</sub> (Mbar)	C <sub>12</sub> (Mbar)	C <sub>44</sub> (Mbar)
Experiment	136.7	2.5	5.145	1.060	1.788
WIEN2k	138.0	2.5	5.0	1.2	2.3 *
CASTEP [9]		2.42	5.39	0.94	1.92
FP-LMTO [10]		2.2	4.7	0.97	1.67

\* This value is sensitive to computational details that were not investigated intensively.

The comparison between theory and experiment is complicated by the fact that the stoichiometry, i.e. the composition, is not perfect in the real crystal, namely about  $\text{TiC}_{0.95}$ . Therefore about 5 per cent of carbon defects are present, which are ignored in the present calculation, that is based on the ideal NaCl structure.

## 6 Forces and structure optimization

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.

### 6.1 Application to crystal with many atoms per unit cell.

An example that was used to test the new APW+lo scheme, on which WIEN2k is based, is discussed below. It is sodium electro sodalite (SES) which contains 44 atoms per unit cell (Fig.4). This is an ordered aluminum-silicate in which the missing charge is compensated by sodium ions. The properties are discussed in [11], the use of forces is analyzed in [6].

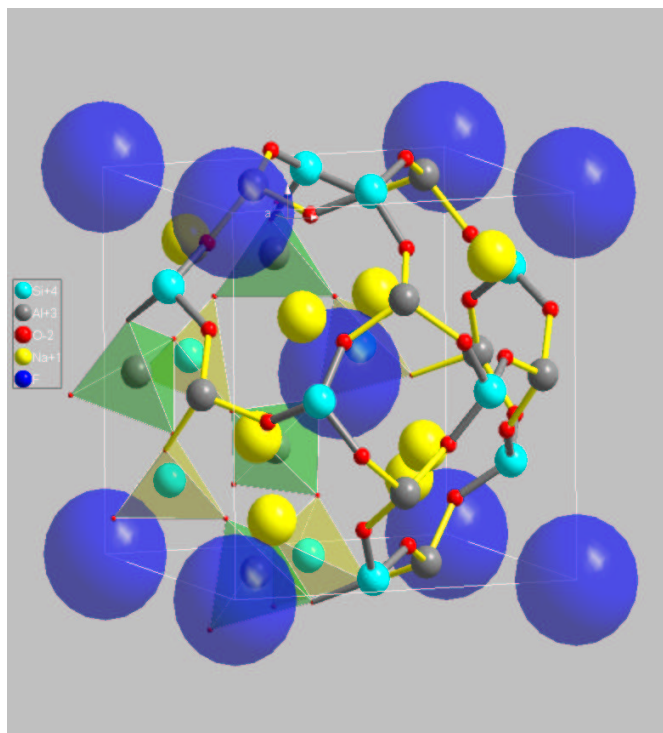


Figure 4: Structure of sodium electro sodalite (SES)  $\text{Na}_8(\text{AlSiO}_4)_6$ .

This example should illustrate the complexity of a system that nowadays can be treated efficiently on a PC. Increased computer power will let us study larger systems (up to a few hundred atoms per unit cell).

## 7 Summary and Conclusion

DFT calculations can provide useful information concerning the electronic structure of order crystal structures. The results depend on the choice of the exchange and correlation potential that is used in 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 a super-cell that consists (in a simple case) of  $2 \times 2 \times 2$  of the original unit cell. When one atoms 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. This example illustrates how theory can carry out computer experiments. Hypothetical or artificial structure can be considered and their properties, irrespective of whether or not they can be made, can be calculated. In addition to the mechanical properties that were discussed here, the complete information concerning the electronic, optic or magnetic properties are available too. Therefore calculations allow to predict a system to be an insulator, a metal or magnetic. The chemical bonding can be analyzed and allows to make predictions, of 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 is easier for experiment than for theory. Pressure and finite temperature effects can be included using lattice vibrations, which may be approximated from known phonon data. Such a procedure was recently illustrated for example for titanium under high pressure [12]. The examples given her are just a small selection to illustrate some possibilities DFT or the WIEN2k code can provide.

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