I. Introduction

With the development of computer technology within the last decades, a new way of performing research has joined the traditional experimental and theoretical natural sciences: computational materials science. Among the different approaches are Monte-Carlo simulations, phase field models, the Green’s Functions formalism, the Boundary Element Method, finite element analysis and Density Functional Theory (DFT). The basis of this new field was mainly provided by theoretical physicists and chemists, and a clear distinction between these two cannot be made anymore. In 1998, this new science got its full
recognition with the dedication of the Nobel Prize in Chemistry to Walter Kohn, a theoretical physicist, for ”his development of the Density Functional Theory”.

Apart from the simulation of existing material properties and the comparison of these results with the ones obtained in experiments, modern computational materials science utilizing DFT can also be used to predict certain properties as well as whole classes of new, functional materials. One of the most prominent recent examples for its predictive power within the field of wide band gap semiconductors is the suggestion that hydrogen acts as a major donor in ZnO by van de Walle. This hypothesis has meanwhile attracted many scientists and could neither be finally proved nor rejected yet (see, for example, references 2–5). To obtain computational results for systems as wide band gap semiconductors, a huge variety of software packages applying different approximations and approaches is available. The ultimate goal of each of these projects should be the use of one and the same package using the numerically obtained ground state properties to gain a fully consistent picture of the material considered. However, since materials as ZnO and GaN exhibit several peculiarities compared to more conventional systems as Si or GaAs, a very careful look at the effects of the used method is needed. In the present chapter we would like to present aspects of the theoretical basics of most of the software packages, we will introduce the most common approaches and will then compare on how these approaches effect the results for bandstructures, band order at the valence band maximum, and the optical constants of ZnO and GaN. Furthermore, values for the band effective masses for ZnO and GaN will be presented.

II. Density functional theory

In the literature calculations obtained within DFT are often also labelled with total-energy calculations, ground-state-theory calculations, ab-initio calculations or first-principles calculations. The name total-energy calculation already indicates that the fundamental quantity is the total energy $E_{\text{tot}}$ of the considered system. The name ground-state-theory calculation reminds, that the results obtained are, strictly speaking, only valid for the ground state of this system (and, thus, $T = 0$), a restriction based on the fundamental theorem by Hohenberg and Kohn. The names ab-initio calculation and first-principles calculation reflect that the only input parameters are the number of atoms and their core charge number, whereas the material properties will be calculated using quantum theory. A comprehensive picture of the numerical concepts and a detailed derivation of the DFT can be found elsewhere. Here, only a short description will be given. The quantum mechanical wave function contains, in principle, all the information about a given system. For
the case of a hydrogen atom, one can solve the single-particle Schrödinger equation exactly in order to get the wave function of the system. One can then determine the allowed single-particle energy states of the system. However, it is impossible to solve the Schrödinger equation for a many-body system like a semiconductor crystal. Since in this case the number of degrees of freedom of the system is quite large, one has to introduce some approximations. The first simplification that one may make is the Born-Oppenheimer approximation, where the electronic and nuclear degrees of freedom are separated. The equation one has to solve is

\[ \sum_i \left( -\frac{\hbar^2}{2m_e} \nabla^2_{i e} + V^{\text{ext}}(R_i) + V^{e-e}(r_i) \right) \Psi = E\Psi \]  

(1)

where \(-\frac{\hbar^2}{2m_e} \nabla^2_{i e}\) is the kinetic energy operator, \(V^{\text{ext}}\) is the external potential imposed by the configuration of nuclei \(R_i\), and \(V^{e-e}\) is that caused by electron-electron interaction. In non-magnetic systems, the electron-electron interaction is simply given by the Coulomb interaction term \(\sum_{i>j} \frac{e^2}{|r_i - r_j|}\). \(\Psi\) represents the many-body wave function for the \(N\)-electron system, an antisymmetric function of the electronic coordinates \(r_i : i = 1...N\) and \(E\) is the total energy of the electron system.

In principle, this equation may be solved to arbitrary accuracy by representing \(\Psi\) as a linear combination of an infinite number of combinations of direct product wave functions (Slater determinants) and diagonalizing the Hamiltonian. However, the many-body electronic wave function is a function of at least \(3N\) variables (the coordinates of all \(N\) electrons in the system without consideration of spin) and is thus not solvable straightforward. In 1964, Hohenberg and Kohn suggested to use the electron density as the fundamental variable to define the ground state of the system. In principle, the use of the electron density significantly speeds up the calculation, since it is only a function of the three space variables \((x, y, z)\). The underlying theorem states that the ground state electron density \(n_0(r)\) minimizes the energy functional of the electronic system

\[ E[n] = F[n] + \int n(r) V^{\text{ext}}(r) d^3r \]  

(2)
where $F[n]$ is a universal functional. The minimum value of $E$ is the ground state electronic energy, $E_0$. This ground state energy is a unique functional of the ground state electron density $n_0$.

The form of the functional $F[n]$ in Equation 2 is not known. Kohn and Sham postulated that this functional could be separated in the following form:

$$F[n] = T[n] + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} \, d^3r \, d^3r' + E^{xc}[n].$$

Here, the first term $T[n]$ is the kinetic energy of a system of non-interacting electrons with density $n(r)$ and the second one represents the elasical electron - electron interaction, the Hartree contribution. The third term, $E^{xc}[n]$, denotes the exchange-correlation energy. With the use of the variational principle of the Hohenberg-Kohn theorem the ground state electron density $n_0$ may be determined by

$$\frac{\delta T}{\delta n(x)} + V^{\text{ext}}(x) + e^2 \int \frac{n(r')}{|r-r'|} \, d^3r' + V^{xc}[n(x)] - \mu_{n=n_0} = 0.$$

Here, $\mu$ represents a Lagrangian multiplier to guarantee the conservation of the particle number. $V^{xc}$ is the exchange-correlation potential that formally follows from the variation of the unknown exchange-correlation functional $V^{xc}(x) = \frac{\delta E^{xc}}{\delta n}(x)$. The functional $E^{xc}$ and, hence, $V^{xc}$ may be approximated with different approaches. The functional of the kinetic energy may be determined exactly with the assumption that a potential $V^{\text{eff}}$ exists, for which $n$ is the ground state charge density of a non-interacting electron gas. The electron density in terms of a set of single-particle wave functions $\psi_i$ of a non-interacting electron gas is then

$$n(r) = \sum_i f_i |\psi_i(r)|^2$$

with $f_i$ as the occupation numbers of the single-particle states. Minimizing $E[n]$ with respect to $n(r)$ under the constraint that the number of electrons
remains constant leads to a set of equations with the Kohn-Sham-Hamiltonian

\[ H_{KS} = \left( -\frac{\hbar^2}{2m_e} \nabla^2 + V^{\text{eff}}(r) \right), \]

\[ H_{KS} \psi_i(r) = \epsilon_i \psi_i(r), \tag{6} \]

where \( V^{\text{eff}} \) is an effective potential, consisting of the sum of the external potential, the electron-electron-interaction, and the exchange-correlation potential. Equation 6 can be interpreted as a set of Schrödinger-like equations for the single-particle Kohn-Sham orbitals.

Thus, the problem of a system of interacting electrons has been mapped onto a system of non-interacting electrons moving in an effective potential. Simultaneously, the many-body problem of the ground state is traced back to a set of single-particle equations. However, the expression of the density in terms of a set of single-particle orbitals has increased the complexity of the problem. The minimization must now be performed over \( N \) degrees of freedom where \( N \) is the number of basis functions used to represent all \( \{\psi_i\} \).

Since the effective potential itself depends on the density, Eqs. 5 and 6 have to be solved simultaneously (self consistency problem). This problem is treated by the application of an iteration cycle for these equations.

Within this chapter, we would like to focus on one main aspect of the utilization of DFT: the impact of the choice of the exchange-correlation energy functional.

A. Common approaches and approximations

As described above, the Kohn-Sham orbitals (~i in Equation 6) need to be developed in terms of a complete basis set. A wide choice of basis sets is available:

- Plane waves (PW) and ultrasoft pseudopotentials (US-PP)
- Projector-augmented waves (PAW)
- Full Potential Linearized Augmented Plane Waves (FP-LAPW)
- Tight Binding Linear Muffin-tin Orbitals (TB-LMTO)
- Full Potential Linear Muffin-tin Orbitals (FP-LMTO)
- Linear combinations of Gaussian Type Functions (GTF)

Another choice we have to take is for representing the exchange-correlation energy functional.
For many materials, the Local Density Approximation (LDA) provides a good description of ground-state properties. However, problems arise when the DFT–LDA approach is applied to materials with strong Coulomb correlation effects\textsuperscript{10–12}, due to the mean-field character of the Kohn–Sham equations as well as due to the poor description of strong Coulomb correlation and exchange interaction between electrons in the narrow $d$ band.

To overcome such problems, other approximations have been developed:

- **LDA plus self-interaction correction (LDA+SIC)\textsuperscript{13–17}**. It eliminates the spurious interaction of an electron with itself as occurring in the conventional DFT–LDA. This approach has been widely used to study compounds with completed semicore $d$ shells\textsuperscript{14–19}, and it is found to lower the Zn-$3d$ levels derived from the simple LDA and thus giving better agreement with the measured X-ray emission spectra (XES) and effective masses of carriers\textsuperscript{14–16,19}. The calculated value of the band gap ($E_g$) then falls within the established error limits for the LDA\textsuperscript{14–17,20}.

- **LDA plus multiorbital mean-field Hubbard potential (LDA+U)\textsuperscript{10–12}**. It includes the on-site Coulomb interaction in the LDA Hamiltonian. After adding the on-site Coulomb interaction to the L(S)DA Hamiltonian, the potential becomes spin and orbital dependent. The LDA+U, although being a mean-field approach, has the advantage of describing both the chemical bonding and the electron-electron interaction. The main intention of the LDA+U approach is to describe the electronic interactions of strongly correlated states. Such a computational procedure is widely used to study materials with ions that contain incomplete $d$ or $f$ shells, e.g., transition metal oxides, heavy fermion systems etc\textsuperscript{10–12}. Recently, such an approach has been applied to ZnO\textsuperscript{21–23} with completed semicore-Zn-$3d$ valence shell. However, it is concluded in Refs. 21 and 22 that LDA+U calculations, in principle, should not have improved the size of the $E_g$ because the Zn-$3d$ bands are located well below the Fermi level (EF).

- **Generalized Gradient Approximation (GGA)\textsuperscript{24}**. Complementary to the LDA, which uses the exchange-correlation energy for the uniform electron gas at each point, the GGA uses the gradient of the charge density to correct for the non-uniform charge densities. For systems with a slowly varying charge density, GGA has proved to be an improvement over LDA.

Apart from more advanced LDA models and the GGA, also the Green’s function formalism has been utilized:
GW approximation\textsuperscript{25,26}

Here, "G" stands for one-particle Green’s function as derived from many-body perturbation theory and "W" for Coulomb screened interactions. This approximation can take into account both non-locality and energy-dependent features of correlations in many-body system and can correctly describe excited-state properties of a system including its ionization potential and electron affinity. Band-structure studies using the GW correction show that $E_g$ is underestimated by 1.2 eV for ZnO\textsuperscript{27}. However, the GW calculations in Ref. 28 overestimated $E_g$ for ZnO by 0.84 eV. The combination of exact exchange DFT calculations in the optimized-effective-potential approach with GW (Ref. 29) is found to give better agreement with the experimental band gaps and the location of the Zn-3d levels. This approach demands heavy computations.

B. Available software packages

All these basis sets and different solutions to approximate the exchange and correlation functional are utilized in quite a huge number of different software packages. In the following, we would like to list the most widely used ones (this list can only be incomplete):

  VASP runs equally well on super-scalar processors, vector computers and parallel computers. Support is given for a huge range of platforms. It offers the PAW method or ultra-soft pseudopotentials as a basis set and most of the density approximations.

- **WIEN2k (http://www.wien2k.at/)**
  Strengthening the role of Vienna as the capital of DFT codes, it has nothing to do with VASP. It is based on the full-potential (linearized) augmented plane-wave and local orbitals method; LDA, GGA, and LDA+SIC can be applied.

- **FHI98md (http://www.fhi-berlin.mpg.de/th/fhimd/)** FHI98md is the follow-up to FHI96md. It uses norm-conserving pseudopotentials of the Hammann\textsuperscript{30} and Troullier-Martins\textsuperscript{31} types, employing common parameterizations of the local-density approximation and generalized gradient approximations for exchange and correlation.

- **CASTEP (http://www.tcm.phy.cam.ac.uk/castep/index.html)** CASTEP was originally created by M.C. Payne (University of Cambridge) and subsequently developed by various UK academics, primarily from the TCM group in Cambridge. Since 1999 it is commercially marketed by Accelrys.
• Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA, http://www.uam.es/departamentos/ciencias/fismateriaic/siesta/). Apart from the enjoyable name, it utilizes local density (LDA-LSD) or generalized gradient (GGA) approximations as well as norm-conserving pseudopotentials in its fully nonlocal (Kleinman-Bylander) form or linear combination of atomic orbitals (LCAO).

• AIMPRO (http://aimpro.ncl.ac.uk/) AIMPRO uses an internal representation of the charge density by expanding it in a basis of Gaussian functions.

• CRYSTAL 2003 (http://www.crystal.unito.it/) The CRYSTAL program computes the electronic structure of periodic systems within Hartree Fock, density functional or various hybrid approximations. The Bloch functions of the periodic systems are expanded as linear combinations of atom centred Gaussian functions.

• MindLab04 (http://physics.njit.edu/mindlab/index.html) MindLab is a scientific software for Windows systems which performs electronic structure calculations of crystalline solids.

A very nice overview over current developments and active groups in the field of computational materials science can be found on the homepage of the Ψk-network (http://psi-k.dl.ac.uk/).

III. Application to ZNO and GAN

A. Peculiarities and choice of pseudopotentials

Compared to silicon, silicon carbide and gallium arsenide, the crystal properties of zinc oxide and gallium nitride exhibit some peculiarities due to the energetical overlap between the Zn- and Ga-3d band with the O-2p and N-1s band, respectively. The hybridization with the p and s band increases the energy of the d-band and decreases the fundamental energy derived by LDA, the value of the band gap, and, furthermore, falsifies the band dispersion and the momentum matrix elements 32,33. The order of the states at the top of the VB is changed to anormalous order for ZnO, whereas for GaN the origin of the bands is changed from $p_z$ type to $p_x$ type. The semicore d electrons hybridizing with the s band can split it into two bands and change their origin (GaN). As a result, the states are neither pure s band nor pure d band, but a mixture of the s and d bands. Furthermore, p-like bands can be formed near the s band (Ref. 34, see also Ref. 19). Upon including the d electrons into the core, the exchange-correlation processes can become non-linear and the inclusion of the non-linear core correction is needed. Lattice constants are significantly underestimated and the band structure is falsified. Furthermore, at the topmost valence band d-like bands can be formed (see e.g. Ref. 33). In general, the inclusion of the d-
bands into the core increases the total energy and decreases the cohesive
energy (Refs. 35,36).

The above listed findings are more precisely explained in the description
of the order of states at the top of the valence band (see III B 1), the band
structures (see III B 2), and the density of states (see III B 3). As a
consequence, the completely filled semicore Zn-3d and Ga-3d states have been
considered as valence states for the investigation of the effective masses (see
III B 4) and the optical properties (see III B 5).

The electronic band structure of ZnO and GaN is studied using the VASP-
PAW package\(^40\). The use of the PAW pseudopotentials addresses the problem
of the inadequate description of the wave functions in the core region common
to other pseudopotential approaches\(^41\). The application allows constructing
orthonormalized all-electron-like wave functions for the cation-3d, -4s and
anion-s and -p valence electrons. Band-structure calculations have been
performed for w-ZnO using three different pseudopotentials for the oxygen
atom supplied with the VASP package: ordinary, soft, and high-accuracy
oxygen pseudopotentials.

Band dispersion, band gaps \([E_g, E_g(A), E_g(B), E_g(C),\text{ and } E_0]\), \(\Delta_{CF}\), and \(\Delta_{SO}\)
corresponding to these oxygen pseudopotentials do not differ significantly
from each other and the subsequent calculations were performed using the
ordinary oxygen pseudopotential. Self-consistent calculations were performed
using a 10×10×10 mesh frame according to the Monkhorst-Pack scheme for z-
type structures and a similar density of k-points in the \(\Gamma\)-centered grids for w-
type phases. For band-structure calculations the experimentally determined
crystal-structure parameters (Table I) are used for all phases considered. For
investigation of the order of the states at the top of the VB, band-structure
calculations have been performed using the MindLab package\(^42\), which uses
the full potential linear muffin-tin orbital (FPLMTO) method, and by the
WIEN2K code\(^43\), based on a full-potential linearized-augmented plane-wave
method.

A more extensive description of the computational details of the work
presented here can be found in Refs. 23, 34, and 44.

<table>
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<th>c (Å)</th>
<th>V (Å(^3))</th>
<th>u</th>
<th>(u_{\text{exp}})</th>
</tr>
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<td>47.62</td>
<td>0.3799</td>
<td>0.3825</td>
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<tr>
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<td>3.1891</td>
<td>5.1853</td>
<td>45.67</td>
<td>0.3761</td>
<td>0.3770</td>
</tr>
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</table>
B. Effect of different density approximations

Upto now, already a lot of computational studies of ZnO\textsuperscript{21–23,27,28,45} and GaN\textsuperscript{46–53} have been performed. However, LDA underestimates $E_g$ for ZnO\textsuperscript{21–23,27,28} by more than 50\% than expected for a typical LDA error. Also, the actual positions of the Zn-3$d$ levels\textsuperscript{21–23,27,28,45}, the band dispersion, the crystal-field splitting ($\Delta_{CF}$), and the spin-orbit coupling splitting ($\Delta_{SO}$)\textsuperscript{14,23} are not reproduced correctly. Neither the use of the generalized-gradient approximation (GGA) nor the inclusion of the spin orbit (SO) coupling into the calculations seems able to remedy the above shortcomings\textsuperscript{21,23,54}. Here, the effect of using LDA\textsuperscript{55}, GGA\textsuperscript{24}, and simplified rotationally invariant LDA+U\textsuperscript{10,11} approaches on the order of states at the top of the valence band (III B 1), the band structures (III B 2), the density of states (III B 3), the effective masses (III B 4), and the optical properties (III B 5) are discussed.

1. The electronic structure at the top of the valence band (VB)

Most of the global optical and transport properties for semiconductors are determined by the carriers close to $k = 0$ in the vicinity of the $\Gamma$-point. The VB spectrum near the $\Gamma$-point is different for $z$- and $w$-type materials. Without SO coupling, the top of the VB for phases with $w$-type structure is split into a doublet $\Gamma_5$ and a singlet $\Gamma_1$ state by the crystal field (Fig. 1). Inclusion of SO coupling gives rise to three twofold degenerate bands in the VB, which are denoted as $\text{hh}$ (heavy holes), $\text{lh}$ (light holes), and $\text{sh}$ (spin-split-off holes). These states correspond to A, B, and C exciton lines in photoluminescence experiments\textsuperscript{56}. The symmetry of two of these three bands are of $\Gamma_7$ character and one of $\Gamma_9$ character. For ZnO these bands are in the order of decreasing energy $\Gamma_7$, $\Gamma_9$, and $\Gamma_7$, which is referred to as anomalous order, resulting from a negative $\Delta_{SO}$\textsuperscript{57}.

The order of states at the top of VB in $w$-ZnO is a frequently debated topic at present (see, e.g., Refs. 14, 58, and 59). By inspection of the degeneracy of the eigenvalues it is found that the normal order $\Gamma_5 > \Gamma_1$ of the states at the top of VB is obtained by LDA without SO coupling for both $w$- and $z$-ZnO. The same order was obtained by calculations within GGA. The variations in the order of the states at the top of the VB on $U$ are systematically studied for $w$- and $z$-ZnO, with and without including SO coupling. It is found, that for $U \leq 9.0$ eV, the LDA+U without SO coupling interchanges the sequence of the VB states from $\Gamma_5 > \Gamma_1$ to $\Gamma_1 > \Gamma_5$. Furthermore, by including the semicore-Zn-3$d$ electrons in the core it could be revealed that the anomalous order of the states in this case can be traced back to the treatment of the Zn-3$d$ electrons, whereas inhomogeneities in the electron gas do not affect the order of the states at the top of VB, and only slightly change the band dispersion\textsuperscript{23,44}. On the involvement of the SO coupling, the $\Gamma_5$ and $\Gamma_1$ states in $w$-ZnO are split
Figure 1. Schematic presentation of the band mixing in zincblende and wurtzite type structures. In w-type structures the levels ~9, ~7 (upper), and ~7 (lower) are formed due to the combined influence (in the middle) of $\Delta_{CF}$ (on the left) and $\Delta_{SO}$ (on the right). In z-type phases the levels $\Gamma_8$ and $\Gamma_7$ are separated due to the SO interaction.

into two $\Gamma_7$ and one $\Gamma_9$ states (see Fig. 1). Orbital decomposition analysis was performed to establish the origin and order of these states. The order of the states was found to be $\Gamma_7 > \Gamma_9 > \Gamma_7$ for LDA, GGA, and LDA+U ($U = 9.0$ eV), viz. an "anomalous" order\textsuperscript{14,57,60}.\textsuperscript{62}

The above analysis shows that ZnO is very sensitive to Coulomb correlation effects. The values for $\Delta_{CF}$ extracted from the $\Gamma_5-\Gamma_1$ splitting according to the LDA without SO coupling are positive and decrease with increasing U\textsuperscript{23}. Correspondingly, $\Delta_{SO}$ obtained on including the SO coupling was found to be negative and increased in size with increasing U. The order of the states is in this case $\Gamma_7 > \Gamma_9 > \Gamma_7$, in agreement with the ab initio calculations of Ref. 60. For all cases considered, the GGA approximation did not influence the order. Hence, inhomogeneities in the distribution of the electron gas do not play a significant role for the order of the states at the top of VB.

For GaN, orbital decomposition analysis shows that the wavefunction of the A, B and C states at the top of the valence have significant contribution from $p_x$ and $p_y$ type orbitals with small contribution of the Ga-$3d$ orbitals. When the Ga-$3d$ electrons are included into the core, then the weight of the $d$-like orbitals increased. Also, the inclusion of the Ga-$3d$ electrons into the valence complex did neither change the order of states at the top of the VB nor the band dispersion, because the Ga-$3d$ electrons are well below the top of the valence band. However, the treatment of the Ga-$3d$ electrons as valence electrons changes the structure around the N-2$s$ band by splitting it into two bands. The origin of the splitted band is found to be a mixture of $s$ and $d$-type states.
Figure 2. Band dispersions for ZnO with Zn-3d electrons (a) included into the valence complex and (b) into the core calculated by LDA with SO coupling (solid lines) and without it (dotted lines). The Fermi level is set to zero.

2. Band structure

The resulting band dispersions for ZnO can be found in Fig.2, whereas the band structures for GaN are presented in Fig.3. Band-parameter values calculated with and without taking SO couplings into consideration are listed in Table II. Band gaps and the mean energy level of Zn-3d electrons $E_d$ from LDA calculations are underestimated, while the crystal field splitting is overestimated compared to the experimental data. The DFT-LDA error is quite pronounced for ZnO and the discrepancy exceeds the usual error for LDA calculations\(^ \text{44}\). The discrepancies in the calculated $\Delta CF$ values for ZnO compared to experimental values are unacceptably large, emphasizing that Coulomb correlation effects are very pronounced for ZnO.

The calculations show (Table II) that $\Delta SO$ is much smaller than 1.0 eV. The SO coupling energy calculated for $z$-ZnO and $w$-ZnO within LDA, GGA, and LDA+U for $U < 9.0$ eV, is negative. The numerical values of $\Delta SO$ for both $w$- and $z$-ZnO are close to each other within the three approaches considered, but are severely underestimated compared to experimental data.

For GaN, regardless of the inclusion of the Ga-$d$ electrons into the core or valence complex, the SO coupling does not change the dispersion, because the energy of spin-energy coupling is too small. The analysis of the band dispersion shows that if the $s$-$d$ coupling is freezed by including the Ga-$3d$ electrons into the core, a single $s$ band is found in the band structure. However, if the Ga-$3d$ electrons are included into the valence complex, the single $s$-band splits into two $s$-bands separated by the localized semicore Ga-$3d$ band.
Table II. Band gaps [$E_g$, $E_g(A)$, $E_g(B)$, $E_g(C)$, and $E_0$], crystal-field ($\Delta_{CF}^0$, $\Delta_{CF}$), and spin-orbit ($\Delta_{SO}$) splitting energies (all in eV) for ZnO with w- and z-type structure calculated within LDA, GGA, and LDA+U approaches. $E_g$ and $\Delta_{CF}^0$ refer to calculations without SO coupling, in all other calculations the SO interactions are accounted for. Experimental values are quoted when available.

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<th>$E_g(B)$</th>
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Figure 3. Band dispersions for GaN with Ga-3d electrons (a) included into the valence complex and (b) into the core calculated by LDA with SO coupling (solid lines) and without it (dotted lines). The Fermi level is set to zero.

3. Density of states

The analysis of the density of states (DOS) for ZnO, calculated within the LDA, shows that the Zn-3d states are inappropriately close to the CB, which contradicts the findings from XPS, XES, and UPS experiments\textsuperscript{63–65}. Furthermore, these states and the top of the VB are hybridized. ZnO shows in both, z- and w-type structure, artificially widened Zn-3d states. These discrepancies indicate a strong Coulomb correlation between narrow Zn-3d states which is not accounted for correctly in the LDA calculations. As a consequence, the interactions of the semicore-Zn-3d states with O-2p in VB are artificially enlarged, the band dispersions are falsified, the widths of the O-p and Zn-3d bands are altered, and the latter are shifted inappropriately close to
Figure 4. Total density of states for w- and z-ZnO calculated from the LDA (solid line) and LDA+U (broken line) approaches. $E_F$ is marked by the dotted line.

the CB. These findings indicate that correlation effects of the Zn-3d states should be taken into account to obtain a more proper description of the electronic structure of ZnO. The simplified rotationally invariant LDA+U approach\textsuperscript{10,11} employing semiempirically extracted values for U and J was used to correct the strong correlation of the Zn-3d electrons (Figure 4). For comparison, the values of U and J have been calculated for some of the compounds within the constrained DFT\textsuperscript{66} (Table III), showing that the calculated values to some extent agrees with those extracted semiempirically. Using the semiempirical values for the parameters U and J, band-structure calculations have been performed within LDA+U. Figure 5 shows the dependence of the Zn-3d mean level ($E_d$) and $E_g$ of ZnO on U. Analysis of the illustrations shows that the LDA+U-derived band gaps are more reasonable than the pure LDA-derived band gaps (see also Table II). Moreover, the deviation of the $E_g$ values obtained using LDA+U from those obtained by experiments are much smaller than those calculated using the pure LDA (Fig. 4 and Table II).
Table III. Values of U and J calculated within the constrain DFT\textsuperscript{66} for w- and z-ZnO and extracted within LDA+U by fitting the energy level of Zn-3d electrons to band locations from XPS, XES, and UPS experiments\textsuperscript{63–65}.

<table>
<thead>
<tr>
<th>Method</th>
<th>w-ZnO</th>
<th>z-ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA+U</td>
<td>U</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>J</td>
<td>1.00</td>
</tr>
<tr>
<td>Constrain DFT</td>
<td>U</td>
<td>11.10</td>
</tr>
<tr>
<td></td>
<td>J</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Figure 5. Band gap ($E_g$) and mean energy level of the Zn-3d states ($E_d$) relative to the VB maximum for z- and w-ZnO as a function of the parameter U. Open symbols correspond to calculated data, and filled symbols are experimental data from Refs. 63–65 and 67.

The values of the peaks in the DOS (Fig. 4), corresponding to the Zn-3d states calculated by the LDA+U, is much larger than those calculated by using the pure LDA. It indicates that according to the LDA+U the semicore-Zn-3d electrons become more localized than according to the pure LDA. The width of the Zn-3d bands for ZnO calculated by LDA+U become much narrower than that calculated by LDA (Fig. 4), which again leads to the conclusion that the Coulomb correlation effects for ZnO are very pronounced.

The analysis of the density of states of GaN (Fig. 6) shows that when the Ga-3d electrons are included into the core, a single s bands appears. If the Ga-3d electrons are included into the valence complex, then the former single s-band is split into two separated ones due to the localized semicore Ga-3d band.
Ulrike Grossner et al.

Figure 6. Density of states for GaN with Ga-3d electrons (a) included into the valence complex and (b) into the core calculated by LDA. The Fermi level is set to zero (dotted line).

Also, the two bands can not be considered as pure s-bands anymore. They present a mixture of the s and Ga-3d bands. This result is obtained within pure LDA calculations and is consistent with other LDA calculations in Ref. 19 and photoemission measurements in Ref. 68. It is also interesting to note that the s-d coupling creates a N-2p-like state within the Ga-3d states. This result is consistent with that of Ref. 19, which reported an N-2p state in zincblende GaN. However, if the s-d coupling is freezed out by including the Ga-3d electrons into the core, then Ga-4p-like states are formed within the Ga-3d states and Ga-3d-like states are formed at the top of the valence band. As it is seen from the band dispersion in Fig. 3, the SO coupling does not change the band dispersion, so the density of states is plotted only for the case without spin-orbit coupling.

4. Effective masses

Owing to low crystal quality only a few cyclotron resonance experiments have been performed for ZnO\textsuperscript{75,74}. The status for the present situation is that effective masses from different \textit{ab initio} packages and experiments scatter appreciably in publications on ZnO (Refs.\textsuperscript{14,70,73,74}, and \textsuperscript{60,71,75}).

The CB states with short wave vectors (k \approx 0) are doubly degenerate with respect to spin and can be characterized by one or two energy-independent effective masses for the z- and w-type arrangements. The effective masses are
calculated along the directions $\Gamma \rightarrow A$, $\Gamma \rightarrow M$, and $\Gamma \rightarrow K$ within the LDA, GGA, and LDA+U approaches with and without including the SO couplings (Tables IV). According to the conventional notations, the carrier masses for w-ZnO and w-GaN are distinguished by the indices e, A, B, and C.

The numerical values of $m_e$ for w-ZnO obtained by the LDA are underestimated by about 50% compared to experimental findings, $^{69,71,73,74}$ LDA+U calculations improved the LDA-derived $m_e$ values for ZnO. This indicates once again that correlation effects are rather pronounced for ZnO.

The electron effective mass is smaller along the direction $\Gamma \rightarrow A(\parallel)$ than along $\Gamma \rightarrow M(\perp)$ and $\Gamma \rightarrow K(\perp)$. This feature can be important in film and superlattice constructions of these phases $^{70}$.

Table IV. Effective masses of electrons and holes (in units of the free-electron mass $m_0$) for w-ZnO calculated within LDA, GGA, and LDA+U approaches. The results are compared with the calculated and experimental data from Ref. 69 (directions not specified) and those calculated by FP LMTO (Ref. 14), LCAO (Ref. 70) and determined experimentally (Ref. 71). Labelling of the effective masses is not changed with changed order of the states at the top of VB. For w-GaN, the effective masses are calculated within LDA only for two cases: (i) when the Ga-3d electrons included into the core (GaN) and (ii) included into the valence complex (GaN-d). The results are compared to calculated ones by FP-LMTO (Ref. 72).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Method</th>
<th>$m_e^\parallel$</th>
<th>$m_e^\perp$</th>
<th>$m_A^\parallel$</th>
<th>$m_A^\perp$</th>
<th>$m_B^\parallel$</th>
<th>$m_B^\perp$</th>
<th>$m_C^\parallel$</th>
<th>$m_C^\perp$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Without SO coupling</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w-ZnO</td>
<td>LDA</td>
<td>0.139</td>
<td>0.132</td>
<td>2.943</td>
<td>2.567</td>
<td>2.943</td>
<td>0.150</td>
<td>0.157</td>
<td>3.476</td>
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<tr>
<td></td>
<td>GGA</td>
<td>0.147</td>
<td>0.140</td>
<td>3.233</td>
<td>2.864</td>
<td>3.233</td>
<td>0.162</td>
<td>0.161</td>
<td>2.272</td>
</tr>
<tr>
<td></td>
<td>LDA+U</td>
<td>0.234</td>
<td>0.221</td>
<td>4.770</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w-ZnO</td>
<td>LDA+U</td>
<td>0.137</td>
<td>0.130</td>
<td>2.447</td>
<td>2.063</td>
<td>2.979</td>
<td>0.227</td>
<td>0.169</td>
<td>0.288</td>
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<tr>
<td>w-GaN</td>
<td>LDA</td>
<td>0.144</td>
<td>0.143</td>
<td>2.266</td>
<td>0.351</td>
<td>3.227</td>
<td>0.300</td>
<td>0.165</td>
<td>0.537</td>
</tr>
<tr>
<td>w-GaN</td>
<td>GGA</td>
<td>0.189</td>
<td>0.209</td>
<td>0.207</td>
<td>11.401</td>
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<td>3.111</td>
<td>0.330</td>
<td>0.270</td>
</tr>
<tr>
<td>w-GaN</td>
<td>FP LMTO., Ref 14</td>
<td>0.230</td>
<td>0.210</td>
<td>2.740</td>
<td>0.540</td>
<td>3.030</td>
<td>0.550</td>
<td>0.270</td>
<td>1.120</td>
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<tr>
<td>w-GaN-d</td>
<td>Expt., Ref 71</td>
<td>0.24</td>
<td>0.590</td>
<td>0.590</td>
<td>0.590</td>
<td>0.590</td>
<td>0.590</td>
<td>0.310</td>
<td>0.550</td>
</tr>
<tr>
<td>w-GaN</td>
<td>LCAO, Ref 70</td>
<td>0.280</td>
<td>0.320</td>
<td>1.980</td>
<td>4.310</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With SO

| w-ZnO   | LDA          | 0.159           | 0.184       | 0.337           | 2.248       | 0.423           | 1.283       | 1.681           | 0.185       |
| w-GaN   | LDA+U        | 0.151           | 0.188       | 0.336           | 2.578       | 2.100           | 1.230       | 1.575           | 0.155       |
| w-GaN   | FP-LMTO. [72] | 0.170           | 0.190       | 0.330           | 2.000       | 0.350           | 1.190       | 1.270           | 0.170       |
established large disparity between electron and hole mobilities (Ref. 69), and also may explain the large optical non-linearity in ZnO\textsuperscript{70}. The effective masses of the holes are more anisotropic than those of the electrons, which can be traced back to states at the top of VB associated with O-\textit{p} orbitals. This can give rise to anisotropy in parameters like carrier mobility\textsuperscript{76}. The present values for ZnO are in reasonable agreement with the experimental values\textsuperscript{69,71,73,74}, except for m\textsubscript{A}, m\textsubscript{B}, and m\textsubscript{C}, and in good agreement with those obtained\textsuperscript{14} by the FP-LMTO method.

For w-GaN, the effective masses are calculated within LDA only for two cases: (i) when the Ga-3d electrons included into the core (GaN) and (ii) included into the valence complex (GaN-d). The results are compared to calculated ones by FP-LMTO (Ref. 72).

5. Optical properties of ZnO and GaN

Although DFT represents a ground state theory, one can also extract the optical parameters if the matrix elements are known. However, due to the limitations of the theory, a very careful evaluation procedure is needed.

Figure 7. Optical constants of ZnO calculated by GGA for E\parallel\textit{c} (left column) and E\perp\textit{c} (right column) directions. Calculated data are plotted by dotted lines and experimental data (Ref. 77) by solid lines.
In general, all the peak positions for the optical constants (i.e. \(\varepsilon_1\), \(\varepsilon_2\), \(\alpha\), \(R\), \(n\), and \(k\)) are reproduced within LDA, GGA, and LDA+U. Comparative analysis of the dependence of the optical constants on the energy calculated within LDA, GGA, LDA+U, and the experimental data reveals that the optical data calculated within GGA (Fig. 7) shows a much better agreement with the experiment than the ones calculated within LDA and LDA+U.

In the LDA and GGA calculations the imaginary part of the dielectric function contains a peak at energies corresponding to the fundamental absorption. The magnitude of the peak is found to decrease with increasing \(U\) in the LDA+U calculations. Furthermore, the discrepancy of the optical parameters calculated by LDA+U is found to be larger than those of LDA and GGA.

For w-GaN, the calculated optical parameters obtained within LDA agree fairly well with the experimental ones of Ref. 35 (see Fig. 8).

**Figure 8.** Optical constants of GaN of wurtzite structure calculated by LDA including the Ga3d electrons into the valence complex for \(E\parallel c\) (left column) and \(E\perp c\) (right column) directions. Calculated data are plotted by dotted lines and experimental data from Ref. 35 by solid lines and those of Ref. 77 by dashed lines.
C. Conclusions

Within this chapter, the basic theory of modern computational materials science has been introduced. It has been shown, under which assumptions materials as zinc oxide and gallium nitride can be numerically investigated and which tools can be used. The effect of different approaches to model the core variable of modern ab-initio methods, the electron density, has particularly been investigated for zinc oxide. A main focus was hereby to distinguish between approaches leading to false results and the ones in coincidence with experimental results. Former studies of gallium nitride could be approved. As a main result, the importance of correlation effects especially for zinc oxide could be revealed.

Acknowledgements

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37. Inorganic Crystal Structure Database (Gmelin Institut, Karlsruhe, 2001).