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Aalborg University

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Modelling zinc oxide for nanoscale applications

Modellering af zinkoxid med henblik på nanoteknologiske anvendelser

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Coverpage illustration: The wurtzite crystal with surfaces, an eigen state of the hexagonal quantum well, and a hexagonal zinc oxide nanowire.

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Foreword

This report summarizes my research as a Ph.D. student at the Department of Physics and Nanotechnology at Aalborg University. The work was done during the period of August 1st 2005 - November 13th 2008, under the skilled supervision of Prof. Thomas G. Pedersen, in collaboration with Prof. Kjeld Pedersen and Abbas Zarifi as well as the group of Prof. Dr. Friedhelm Bechstedt at the Friedrich-Schiller-Universität in Jena, Germany.

The numerical simulations were performed with support from the Danish Center for Scientific Computing at Aalborg University, on the Fyrkat supercomputer, as well as the High Performance Computing Center, Stuttgart (HLRS).

The publications documenting my research are enclosed in the appendices, and listed below.

List of publications for the thesis


Additional publications

5 T. G. Pedersen, C. Fisker and R. V. S. Jensen, ”Tight-binding parameterization of α-Sn quasiparticle band structure”, *J. Phys. Chem. Sol.*, vol. 71, pp. 18-23,
2010.

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Finally, I would like to thank my friends and family for their understanding when work took precedence over social life, and a special thanks to my girlfriend, Bettina, for her patience with me when I disappear in the world of research, and for sometimes calling me back to reality as well.

Aalborg, Denmark, August 2010

Christian Fisker
In the fast expanding field of nanotechnology, many well-known solids have had a revival through the appearance of nanostructures. One such material is zinc oxide (ZnO). Traditionally, ZnO has had its applications in the rubber industry, in concrete, paint and coatings, as well as as a component in sun screen due to its absorption in the ultra-violet spectrum [1–3]. Presently, the various new nanoscale forms of ZnO are generating a lot of scientific research, and both the solar cell and electronics industry are looking into their applications [4,5].

In the following, a short presentation of the properties of ZnO is given, as well as an overview of the status of current ZnO research, both experimentally and theoretically.

1.1 Zinc oxide in the bulk

Zinc oxide is a semiconducting material with a hexagonal crystalline structure known as the wurtzite structure. It consists of a crystal lattice defined by the lattice parameters \( a \) and \( c \) and a basis containing 4 atoms as illustrated in Figure 1.1. The basis defines a third parameter \( u \) as the ratio of the zinc-oxygen bond-length in the \( c \)-direction to the length of \( c \). In the ideal wurtzite structure, where all nearest neighbour bond-lengths and -angles are equal, the parameters \( c \) and \( u \) are given in terms of \( a \) as \( c = \sqrt{8/3} a \) and \( u = \frac{3}{8} \). Experimental values of the ZnO lattice parameters [6] are found to be \((a, c, u) = (6.15\text{au}, 9.85\text{au}, 0.382)\), with both \( c \) and \( u \) differing slightly from the ideal.

The wurtzite surfaces are typically described in a four-vector basis - three in the \( xy \)-plane defining the hexagonal geometry and one along the \( z \) axis as seen in Figure 1.1 (LEFT). A top view of the wurtzite structure is illustrated in Figure 1.2 (LEFT), with the lattice vectors denoted by \( \{1, 2, 3, 4\} \) and the red and grey spheres marking the positions of the two ZnO pairs in the wurtzite basis seen from above. The most commonly studied surfaces are the (0001) and (000\( \overline{1} \)) surfaces perpendicular to the \( z \)-axis, as seen in Figure 1.2 (RIGHT). These are terminated by either a layer of zinc or a layer of oxygen, making them polar. The orthogonal facets (10\( \overline{1} \)0), (1010) and (2110) are also well studied, all being non-polar due to the in-plane ZnO pairs [7–10].
Figure 1.1: The wurtzite geometry of ZnO with the hexagonal lattice (LEFT) and the unit cell containing 2 zinc and 2 oxygen atoms (RIGHT).

Figure 1.2: Illustration of typical wurtzite surfaces defined in a four-vector basis \{1, 2, 3, 4\}. LEFT: The non-polar facets parallel to the c-direction. RIGHT: The polar (0001) and (000̅1) surfaces.
Comparing the facets (10\(\overline{1}0\)) and (10\(\overline{1}0\)) in Figure 1.2 (LEFT), the first has two dangling bonds on each surface atom while the second has only one. Thus (10\(\overline{1}0\)) is expected to be a more stable. The blue hexagon on the left illustrates that a hexagonal wire can be made with only (10\(\overline{1}0\)) surfaces, which is why this surface is of special interest.

Zinc oxide is a II-IV semiconductor with a large band gap of \(\sim 3.4\text{eV}\) making it transparent in the visible spectrum but absorbing in the UV. This property makes it, along with titanium dioxide, one of the most common additives to sun screen lotions [1, 2]. In the electronics industry the optical properties of ZnO are of interest for the production of transparent electronics [5, 11, 12], possible applications in laser diodes and light emitting diodes [13], and as an absorbing medium in solar cells [4, 14, 15]. For these applications band gap engineering plays an important role. By doping with magnesium or cadmium the band gap is tunable in the 3–4\text{eV} range [16, 17], and by introducing hydrogen defects or vacancies in the material similar results have been achieved [18–20].

1.2 Zinc oxide nanostructures

On the nanoscale ZnO strongly favours crystalline growth in the \(c\)-direction, which results in the formation of many different nanostructures. The most studied is the hexagonal \textit{nanowire}, first reported by Kong \textit{et. al} [21]. The nanowires, synthesized by a physical vapour deposition (PVD) process, are very uniform in appearance, being single crystalline rods (see Figure 2.2 (LEFT) in chapter 2), with typical widths of 20–500\text{nm} and lengths in the \(\mu\text{m}\) range.

By varying growth conditions different nanostructures can be produced. One such is the \textit{nanobelt} (or nano-ribbon) [22] with the derived \textit{nanospiral} [26] and \textit{nanoring} [23] formed by the electrostatic surface potentials [27] (see Figure 1.3). Other structures are \textit{nanocombs} [24] created from the branching of nanowires (see Figure 1.4 (LEFT)), \textit{nanonails} created by a width-variation along the nanowire (see Figure 2.2 (RIGHT)), and the calthrop-like particles named \textit{octa-twin tetraleg} structures [25] (see Figure 1.4).
Due to the large bandgap, the potential application of ZnO in UV-lasing have received a lot of interest. An early result was achieved in thin films by Kawazaki et al. [28], followed by lasing in films of ZnO nanoparticles by Cao et al. [29]. Photoluminescence spectra of ZnO nanowires were presented in 2001 by Huang et al. [30], and the application of ZnO wires as waveguides with both spontaneous and stimulated emission at the end faces was demonstrated by Johnson et al. [13]. Their results are seen in Figure 1.5. To demonstrate the potential applications in opto-electronic components, Wang et al. [31] demonstrated how the strength of the surface plasmons increased with decreasing wire diameters from 100nm to 20nm. Applications for the solar cell industry have been demonstrated by Law et al. [14], and niobium-doped ZnO nanoparticles have been shown to increase the current output of solar cells as well [15].

As bulk ZnO is nearly isolating, surface states play the dominant role when nanowires are used as electrical conductors. Consequently the wire conductivity is very sensitive to changes in their surroundings. This makes the nanowire an ideal nanoscale sensor, as the density and nature of surface adsorbates directly affects the wire conductivity [32,33]. Likewise, T. H. Wang et al. have demonstrated a gas sensor made from ZnO nanowires, and applied it to detecting ethanol [34].

### 1.3 Theoretical modelling

Early theoretical treatment of zinc oxide consisted of modelling the bulk properties of the material. Empirical pseudopotential band structure parameters were presented by Bloom and Ortenburger [35] in 1973, by an empirical fitting of the form factors to band structure measurements, and a reasonable comparison with the reflectivity $R(\omega)$ was presented. Tight-binding parameters for ZnO were presented in 1981 by Ivanov and Pollmann [7], along with a treatment of the surface band structures of various cleavage surfaces. A more elaborate treatment was presented by Kobayashi et al. in 1983, with a full set of $sp^3$ tight-binding parameters for various wurtzite semiconductors, including ZnO [36]. In their scheme, both the low-lying oxygen $s$-type valence bands and the high zinc $p$-type conduction bands were reproduced. An
example of a pseudopotential band structure and the Kobayashi tight-binding band structure can be seen in Figure 1.6. An sp$^3$ treatment of the (10\(\overline{1}0\)) and (11\(\overline{2}0\)) surfaces was presented by Wang et al. [8] in 1987, including relaxation of the surface atoms. Their results included a comparison to the calculations by Ivanov and Pollmann.

In 1994 Prof. Pollmann’s group presented a treatment of the (10\(\overline{1}0\)) surface from density functional theory (DFT) in the local density approximation (LDA) [37]. It included surface relaxations and comparisons to the previous, non \textit{ab initio} results as well as experimental measurements. DFT modelling of ZnO is somewhat problematic, however, as it is a large bandgap II-IV semiconductor. As for most semiconductors the DFT bandgap is strongly underestimated, and one typically obtains a value around 0.75eV [38]. A DFT-LDA band structure for the experimental wurtzite geometry is seen in Figure 1.7, with a bandgap of $E_g = 0.91$eV.

The bandgap error can be corrected to some degree by the inclusion of the Hubbard potential in the LDA+U approximation [38, 39]. Another means of getting the correct DFT bandgap is through the GW method [40, 41]. Both methods, however, suffer from having a large numerical complexity, which makes them only really applicable to small systems. The complexity can be somewhat lessened by using the projector-augmented wave (PAW) method, as this reduces the set of basis functions needed [42].

During the late 2000’s, the number of publications reporting on DFT treatment of ZnO have exploded. In the bulk, DFT modelling has focused on electronic properties under the effects of material strain [43, 44], point defects and hydrogen interstitials [20, 45], and bandgap engineering by the substitution of Zn with Mn [46] or the introduction of phosphorous defects [47].
Figure 1.6: The Kobayashi tight-binding band structure for bulk ZnO (LEFT) with a bandgap of 3.3eV and the wurtzite Brillouin zone (LEFT INSERT), and the Bloom and Ortenburger pseudopotential band structure (RIGHT).

Figure 1.7: The DFT-LDA band structure of wurtzite ZnO calculated for the experimental lattice constants.
Clean ZnO surfaces have been extensively studied in DFT [37, 48] as have the effect of hydrogen adsorbates [49,50]. Single layers, having the well-known hexagonal honey-comb structure, have been modelled and ZnO nanotubes have been shown to be stable in theory [51]. The graphitic structure of stacked hexagonal layers have been shown to be more stable than the wurtzite structure for sufficiently thin ZnO films [52], and the strain dependence on film thickness have been reported [53]. The geometry and electronic properties of small ZnO nanowires have been reported by various groups [54–56] including the effect of hydrogen passivated wire surfaces [57].

The use of density-functional based tight-binding (DFTB) to model ZnO is somewhat less common. Self consistent charge-density functional based tight-binding (SCC-DFTB) have been successfully applied to zinc in the modelling of bio-molecules [58], and though crystalline ZnO had not been treated previously, SCC-DFTB parameters had been successfully applied to modelling other bulk semiconductors such as GaN by the group of Prof. Frauenheim [59].

There are two central challenges in the modelling of ZnO nanostructures. One is the challenge of size. Small ZnO nanowires have diameters of $\sim 20\text{nm}$, giving a unit cell with a number of atoms in the range of 10,000. This presents a huge numerical challenge, even in the most simple of models. But the size is still small enough that confinement effects and significant surface states are expected.

Another problem is the wavefunction complexity. The rapid spatial variation of the zinc $d$-orbitals requires basis functions with the same spatial variation to describe the wavefunctions correctly. In the case of plane waves this means a very large number of basis functions to reach numerical convergence. And the $d$-electrons are sufficiently important for the chemical bonding that they cannot simply be treated as core electrons.

Thus to theoretically study ZnO nanowires it can be useful to apply different models to highlight different wire properties. This is what will be presented in the following chapters.
Chapter 2

Experimental work

The following chapter describes the growth process of ZnO nanowires, and the equipment used for the growing of wires. In the second part of the chapter, an experimental study of the optical properties of ZnO nanowires is presented.

This chapter is based on the work presented in the article of appendix E.

2.1 Nanowire growth

The most common growth method of ZnO nanowires is by physical vapour deposition (PVD) [32, 60], where a powder of ZnO is evaporated in an oven at controlled pressure and temperature and deposited elsewhere in the oven. The schematics of the set-up is illustrated in Figure 2.1 (LEFT), and a photo of the actual equipment used is seen in Figure 2.1 (RIGHT). The source material was a mixture of zinc-oxide and carbon powder, both of 99.9% purity. It was placed in the center of a horizontal tube oven at a pressure of $1\times 3\text{mbar}$ and heated to $1050^\circ\text{C}$. The added carbon works to lower the evaporation temperature of ZnO from $\sim 1400^\circ\text{C}$ to $\sim 1000^\circ\text{C}$ [60]. A slight gas flow transports the vapour through the tube. A steady decrease in temperature is created by a water cooler, situated at the end of the oven next to a pressure gauge and a thermometer. A substrate for the wire deposition is placed in the temperature region of $900^\circ\text{C}$ to $700^\circ\text{C}$, where ZnO nanowires with diameters in the range of $20-500\text{nm}$ are formed and deposited randomly, if no means of growth control is applied. A scanning electron microscope (SEM) picture of ZnO nanowires grown on a silica wafer can be seen in Figure 2.2 (LEFT). As seen in the picture, there is no preferred growth direction or preferred wire diameter, and the collection of wires has a "hay stack" look to it. In Figure 2.2 (RIGHT) is seen a growth of "nanonails", with the characteristic that they have a wide "head" in one end and narrows down to a spike in the other.

A control of wire growth can been achieved by different means. Control of the wire diameter can be achieved by adding gold nanoparticles to the substrate surface [61]. In this case a Zn-Au alloy is formed in the gold droplet, and when saturated the ZnO wires form below the particles, limiting the wire diameter to that of the nanoparticle. Growth orientation has been shown to be controllable by choice of substrate, and
Figure 2.1: Schematic set-up of the horizontal tube oven for ZnO nanowire growth (LEFT), and a photo of the actual set-up (RIGHT).

Figure 2.2: Hexagonal ZnO nanowires grown by a PVD process (LEFT), and hexagonal ZnO nanonails, with a large hexagonal 'nail head' in one end and a slim point in the other (RIGHT).
epitaxial growth can e.g. be achieved on the (001) sapphire surface [61], where the ZnO and sapphire lattices line up well.

2.2 Optical properties

While the physical dimensions and composition of the nanowires can be identified through SEM imaging and X-ray and mass spectroscopy, the electronic properties are most often investigated by measuring the conductivity or absorption and emission spectra. To be able to compare the theoretical models to experiments one typically calculates either electrical or optical response functions, such as the susceptibility or dielectric function. The dielectric function $\epsilon_{ij}$ of ZnO is in fact a tensor-function due to the lack of symmetry in the wurtzite lattice structure. The $\epsilon_{zz}$ element as measured by Jellison et al. [62] is seen in Figure 2.3 on the left hand side. For comparison the same quantity calculated from the pseudopotential band structure of Bloom and Ortenburger [35] is presented on the right. The behavior of the real part is somewhat similar in both cases, with a peak at the bandgap, though the peak is broader in the calculated Re($\epsilon_{zz}$). For the imaginary part the difference is much bigger. The modelled Im($\epsilon_{zz}$) has the typical $\sqrt{E-E_g}$ absorption behaviour of a bulk material [63], while the measured quantity has a strong absorption peak. This is due to the fact that in real life ZnO has a large excitonic contribution at the bandgap, which isn’t modelled in the single-particle pseudopotential calculation.

Another means of investigating the electronic structure of a material is by two-photon photoluminescence or second harmonic generation (SHG). Both processes are illustrated in Figure 2.4. In both cases the sample is illuminated by a high intensity light source (typically a laser) with a photon energy below the bandgap. In the high-intensity field the simultaneous absorption of two photons is possible, momentarily creating a virtual electronic state above the bandgap. Now two things can happen. The intermediary virtual state can relax directly to the ground state emitting light of the double frequency, as illustrated in Figure 2.4 (LEFT). This is known as second harmonic generation. The second possibility is for the state to relax to a normal ex-
Figure 2.4: The principle of second harmonic generation (LEFT) and two-photon photoluminescence (RIGHT).

Figure 2.5: The experimental laser setup for the measurement of SHG and PL spectra of a ZnO wire sample.

cited state of the solid. The subsequent luminescence from the excited state is known as two-photon luminescence, and the process is illustrated in Figure 2.4 (RIGHT). Similarly, when the incoming photon energy is below half the bandgap, three photons give rise to a three-photon luminescence signal, and collectively this is known as multi-photon photoluminescence (PL).

The experimental setup used for the measurements is seen in Figure 2.5. The laser light is reflected off a silica wafer on which the ZnO wires are deposited. A filter removes the first harmonics from the signal, and a monochromator is used to scan the intensity spectrum for different wavelengths. The laser itself is equipped with an optical parametric oscillation system (OPO) to enable scanning of the incoming light frequencies as well. The strength of this approach is that all measured light is in fact coming from the sample, as the reflected laser light is filtered out. There is, however, a limit to the spectral range of the OPO.

A normal photoluminescence spectrum of a sample of ZnO nanowires is seen in Figure 2.6 (LEFT) with a pump wavelength of 300nm. The photoluminescence peak is dominant around 380nm with a small defect contribution to the spectrum around 500nm. The luminescence from the wires is directly visible, as can be seen from the photo in Figure 2.6 (RIGHT), of the luminescence from a silicon wafer covered with ZnO wires.
Figure 2.6: The photoluminescence of ZnO nanowires excited with 300nm light (LEFT), and second harmonic generation from the sample as photographed by a digital camera (RIGHT).

Figure 2.7: The emission spectrum from ZnO nanowires as a function of the pump wavelength (LEFT), and the decomposition of the spectrum into SHG and PL contributions (RIGHT).
Figure 2.8: Comparison of the SHG intensity for ZnO nanowires and a bulk ZnO crystal dependent on the pump wavelength.

An in-depth study of the optical properties of the nanowires has been performed by comparing the PL and SHG spectra from a wire sample to that of a ZnO crystal. A plot of the emitted light from the nanowires for varying pump light wavelengths is seen in Figure 2.7 (LEFT). For readability, the graph maxima have been normalised for each pump wavelength. The SHG signal is seen to follow the expected linear trend, while the PL signal remains fixed around the ZnO bandgap. Figure 2.7 (RIGHT) shows the spectra at pump wavelengths of 710nm and 1000nm. The first has a clearly dominant two-photon PL peak and a smaller SHG peak. When the pump wavelength grows higher than 750nm, as in the second case, SHG dominates as the PL signal now requires at least three photons.

From the Gaussian fittings, the intensity of the SHG signal as a function of the pump wavelength could be determined. A comparison to that of a ZnO crystal is seen in Figure 2.8. The behaviour is significantly different. The wires give the strongest signal when pumping at 750nm, whereas the crystal signal has the highest intensity above 850nm pump wavelength.

Thus, significant two-photon luminescence signals have been measured from ZnO nanowires and the much smaller three-photon luminescence was detected as well. The studied wires were too large to expect confinement effects on the spectrum, but still the SHG signal intensity from the nanowires was found to differ significantly from that of a bulk crystal.
Chapter 3

Theoretical methods

The purpose of this chapter is to treat the theoretical foundation of the quantum mechanical models used for the ZnO simulations. At the core is the Schrödinger equation, from which all non-relativistic quantum mechanics is derived. The following sections will describe the methods of Density Functional Theory (DFT), with the derivative Projector-Augmented Wave (PAW) method. Empirical Tight-Binding (TB) is presented to bridge the gap to Density Functional Based Tight-Binding (DFTB), including the Self-Consistent Charge (SCC) correction to the tight-binding system.

In a general molecular system, consisting of \( M \) nuclei and \( N \) electrons, the Hamiltonian is given by

\[
\hat{H}_{\text{tot}} = -\sum_{I} \frac{\hbar^2}{2m_I} \nabla^2_I - \sum_{i} \frac{\hbar^2}{2m_e} \nabla^2_i + \sum_{I<J} Z_I Z_J e^2 |R_I - R_J| + \sum_{I,i} Z_I e^2 |R_I - r_i| + \sum_{i<j} e^2 |r_i - r_j| + V_{\text{ext}}
\]

(3.1)

containing kinetic energy operators of the form \(-\frac{\hbar^2}{2m_J} \nabla^2\), and Coulomb interactions between all particle pairs. The nuclei are defined by their positions \( R_I \), charges \( Z_I e \), and masses \( m_I \), while the electrons have positions \( r_i \), charges \( e \), and masses \( m_e \). Finally, an external field \( V_{\text{ext}} \) may be present. The problem to be solved is the Schrödinger equation (ignoring spin-degeneracy),

\[
\hat{H}_{\text{tot}} \Phi_j(r_1, \ldots, r_N, R_1, \ldots, R_M) = E_j \Phi_j(r_1, \ldots, r_N, R_1, \ldots, R_M),
\]

(3.2)

where \( \Phi \) is the wave function describing the entire system. As this problem is practically intractable for even a small number of particles, some approximations are needed [64, 65].

3.1 The Born-Oppenheimer approximation

First step is the Born-Oppenheimer approximation. It states that, as the nuclei respond to potential changes on a timescale much larger than that of the electrons, the
nuclei can be considered fixed when calculating the electron dynamics. Equivalently the electrons can be considered always in the relaxed ground state of the system when treating motion of the nuclei. Consequently the electronic problem can be solved separately,

\[
\left[ \hat{T}_e + \hat{U}_{eI} + \hat{U}_{ee} + V_{\text{ext}} \right] \psi_{\mathbf{R}}(\mathbf{r}) = E_{\mathbf{R}} \psi_{\mathbf{R}}(\mathbf{r}),
\]

where \( \mathbf{r} \) represent the 3\( N \) electron coordinates and the short hand notations \( \hat{T}_e \) for the kinetic term and \( \hat{U}_{eI} \) and \( \hat{U}_{ee} \) for the electron-ion and electron-electron interactions have been introduced. The ground state energy \( E_{\mathbf{R}} \) and the all-electron ground state \( \psi_{\mathbf{R}} \) itself are obviously dependent on the ionic positions \( \mathbf{R} \) through \( \hat{U}_{eI} \). For a given geometry the total system energy \( E_{\text{tot}} \) can be calculated from the ionic problem,

\[
\left[ \hat{T}_I + \hat{U}_{II} + E_{\mathbf{R}} \right] \Phi(\mathbf{R}) = E_{\text{tot}} \Phi(\mathbf{R}),
\]

and the ideal geometry of a system can be found by minimizing \( E_{\text{tot}} \) through iterative solutions of (3.3) and (3.4).

### 3.2 Decoupling of electronic states

The electronic problem (3.3) is still a daunting task due to the electronic coupling term \( U_{ee} \). A central step in most modelling methods is therefore to decouple the electrons by rewriting the Hamiltonian

\[
\hat{H} = \sum_i \hat{H}_i,
\]

so that the \( i \)'th electron in the system obeys the eigen equation

\[
\hat{H}_i \psi_i(\mathbf{r}_i) = E_i \psi_i(\mathbf{r}_i), \quad \text{with} \quad \hat{H}_i = \hat{T}_i + V_{\text{eff}}(\mathbf{r}_i),
\]

where \( V_{\text{eff}} \) is an effective single electron potential. The initial 3\( N \) dimensional problem hereby reduces to solving \( N \) three dimensional problems, and the all-electron wave function can be formed as the product

\[
\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sqrt{N} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \ldots \psi_N(\mathbf{r}_N),
\]

or if an anti-symmetric solution is needed to satisfy the Pauli principle, a Slater determinant of the functions \( \psi_i(\mathbf{r}_i) \) [66].

For most chemical and electrical purposes the core electronic states are of no interest, as they are strongly localized on the atomic nuclei and do not interact with the surroundings. It is therefore useful to consider these states together with the nucleus to form a pseudo-atomic background potential, or pseudo-potential, seen by the valence electrons. This potential \( V_{\text{ps}} \) is included as part of the effective potential \( V_{\text{eff}} \), significantly reducing the number \( N \) of remaining valence electrons. The central problem remaining is how to handle the decoupling in (3.5). Several methods currently exist, each with their own strengths and weaknesses when it comes to precision, scalability and calculation of derived system properties.
Chapter 3. Theoretical methods

In the present work, density functional theory is applied for ab-initio studies of ZnO, and the extension to density functional based tight-binding is introduced for scalability and correct band structure calculations. The simpler method of studying a nanowire as a quantum well with an applied potential is used to study the confinement effects in hexagonal quantum wires.

3.3 Periodic systems, band structures, and the Bloch theorem

Periodic systems, such as bulk crystals (3D periodic), surfaces (2D periodic) and nanowires (1D periodic), are defined by introducing lattice vectors $\mathbf{T}_i$, $i \in \{1, 2, 3\}$, to describe the periodicity as well as the atomic position vectors $\mathbf{R}_i$ within the unit cell spanned by the $\mathbf{T}_i$. In such a system, with no external potential present, the effective single electron potential has the periodicity of the lattice,

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{eff}}(\mathbf{r} + \mathbf{T}),$$  \hspace{1cm} (3.8)

where $\mathbf{T} = n_1 \mathbf{T}_1 + n_2 \mathbf{T}_2 + n_3 \mathbf{T}_3$, $n_i \in \mathbb{N}$ is a lattice vector. Consequently the electron density must obey the same periodicity, and thus the single electron states calculated from (3.6) satisfy the equation

$$|\psi_i(\mathbf{r} + \mathbf{T})|^2 = |\psi_i(\mathbf{r})|^2.$$  \hspace{1cm} (3.9)

A consequence of the periodicity is the following, known as Bloch’s theorem:

The eigenfunctions $\psi_i$ of (3.6) satisfying the periodic boundary conditions of (3.8) can be rewritten in the form

$$\psi_{i,k}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{i,k}(\mathbf{r}), \quad \text{with} \quad u_{i,k}(\mathbf{r} + \mathbf{T}) = u_{i,k}(\mathbf{r}).$$  \hspace{1cm} (3.10)

$k$ is a reciprocal lattice vector appearing as a lattice quantum number in the reciprocal lattice defined by the $\mathbf{G}_i$.

The proof of the theorem is achieved by Fourier transform of $\psi_i$ and some simple manipulations.

Due to the crystal periodicity the equation must be solved for $\mathbf{k}$ only living on the smallest reciprocal lattice unit cell known as the Brillouin zone (BZ). The resulting $\mathbf{k}$ dependent energies $E_{i,k}$ give rise to what is known as the electronic band structure, a quantity most often portrayed along the high symmetry lines of the BZ [67].

3.4 Choice of basis

The typical approach when treating the one-electron Schrödinger equation is to expand the eigenfunction in a set of (possibly $\mathbf{k}$-dependent) basis-functions,

$$\psi_{i,k}(\mathbf{r}) = \sum_j c_{i,k,j} \phi_{k,j}(\mathbf{r}).$$  \hspace{1cm} (3.11)
and solve the matrix problem
\[ \sum_j c_{i,j} H_{i,j,k} = E_{i,k} \sum_j c_{i,j} S_{i,j,k}, \]
with Hamiltonian matrix elements \( H_{i,j,k} = \langle \phi_{k,j} | \hat{H} | \phi_{k,j} \rangle \) and overlap matrix elements \( S_{i,j,k} = \langle \phi_{k,i} | \phi_{k,j} \rangle \). If the \( \phi_{j,k} \) form a complete set this expansion is exact, but for numerical reasons a limited basis must be used, and the choice of basis functions becomes important. Some typical choices include the following [65,66]:

- **Plane wave basis (PW):** The Fourier basis \( \phi_{k,G}(r) = e^{i(k+G) \cdot r} \) with a finite set of reciprocal lattice vectors \( G \) defined by a cut-off energy \( E_{\text{cut}} = 2\pi^2(k+G)^2 \) has well known convergence properties. Another advantage is the simplification of the generalized eigenvalue problem, as the overlaps are simply \( S_{ij} = \delta_{ij} \). This basis is especially useful for smooth WF’s in continuous media, but large \( G \) vectors, and therefore a large basis set, are needed to describe strongly bound electrons or systems with large vacuum regions in the UC, such as isolated molecules.

- **Localized orbital basis:** Atomic orbitals, or orbital-like basis functions \( \phi_{i,\alpha} \), localized on all nuclei \( \alpha \) of the UC is another popular choice. It is often useful when treating strongly bound electrons, or molecular states that are localized in space. As the \( \phi_{i,\alpha} \) can be chosen to resemble the atomic orbitals of each atom, a smaller number of basis functions than in the PW case is usually needed. But convergence in the number of basis functions is harder to document.

### 3.5 Density functional theory

The currently most used method of modelling nanostructures is density functional theory (DFT). As the name implies, the Schrödinger equation in (3.3) is reformulated in terms of the electron density \( n(r) \), which in turn can be expressed from the \( N \) electron wave function as
\[ n(r) = \int dr_2 \ldots \int dr_N \psi^*(r, r_2, \ldots, r_N) \psi(r, r_2, \ldots, r_N). \]

Central to the method are two theorems by Hohenberg and Kohn, the first of which can be stated as [64,68]:

*In an electronic system described by the Hamiltonian in (3.2) there is a one-to-one correspondence between the external potential \( V_{\text{ext}} \) and the (possibly degenerate) ground state electron density \( n_0(r) \).*

That the external potential enables us to calculate the ground state density of a system is hardly surprising, seeing as this is what we do in the above-mentioned methods for solving the Schrödinger equation. What is central here is that the ground state density uniquely defines the potential, and thereby the eigenstate \( \psi \) itself, to within a complex phase. This enables the construction of a quantum mechanical theory operating on densities instead of wave functions, which is the purpose of the second
Hohenberg-Kohn theorem [64,68]:

Given an external potential $V_{\text{ext}}$ the energy of the system can be expressed as a functional $E[n_0]$ of a trial electron density $n_0(r)$, and the ground state density $n$ can be determined by the variational principle,

$$E[n] \leq E[n_0], \quad \forall n_0$$

(3.14)

where $n(r), n_0(r) \geq 0$ and $\int n(r)d^3r = \int n_0(r)d^3r = N$ the number of electrons in the system.

As the first Hohenberg-Kohn theorem states that the density uniquely defines $V_{\text{ext}}$, the energy functional can be expressed in the terms of (3.3),

$$E[n] = T[n] + V_{\text{ext}}[n] + U_{\text{ee}}[n],$$

(3.15)

For brevity the ionic background potential has been included in $V_{\text{ext}}$.

### 3.5.1 The Kohn-Sham method

As the electronic eigenfunctions are non-separable due to the electron-electron interaction, the terms $T[n]$ and $V_{\text{ee}}[n]$ in (3.15) are not easily treated. To avoid this coupling Kohn and Sham therefore proposed to study a de-coupled Hamiltonian with an effective potential $V_{\text{KS}}^{\text{eff}}$, chosen such that the ground state density $n_{\text{KS}}$ of the Kohn-Sham system is the same as $n$ in the original system [69]. In the KS system, the single electron eigen-value problems of equation (3.6) become

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}^{KS}(r) \right] \psi_i = E_i \psi_i.$$  

(3.16)

The $N$-electron density is calculated as

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

(3.17)

with $n_i$ being the occupation number of the electronic state $\psi_i$. To achieve the same density as the original system with electron interaction the effective potential must be chosen as

$$V_{\text{eff}}^{KS} = V_{\text{ext}}(r) + \int \frac{n(r)}{|r-r'|} dr' + V_{\text{xc}}(r),$$

(3.18)

where $V_H(r) = \int \frac{n(r')}{|r-r'|} dr'$ is the Hartree potential, and $V_{\text{xc}}(r)$, also a functional of the density, is a correction term known as the exchange-correlation potential.

The remaining problem lies in approximating the exchange-correlation potential as no exact solutions have been presented so far. Most common is the local density approximation (LDA) where the exchange-correlation potential is calculated on a homogeneous electron gas (HEG) [69, 70]. This is done for different electronic densities, generating the functional $V_{\text{xc}}^{\text{HEG}}[n]$. The LDA potential at a given point in the studied system is then defined as the HEG XC potential at the local electron density,

$$V_{\text{xc}}^{LDA}(r) = V_{\text{xc}}^{\text{HEG}}(n(r)).$$

(3.19)
Valence wavefunctions for Zn

Figure 3.1: Illustration of the all-electron and pseudo-atomic valence states of zinc, as generated by the Opium package [73]. The vertical bars indicate the core radius chosen for each state.

This way, the exchange-correlation potential is expanded to zeroth order in the density.

Higher order approximations have been developed, such as the generalized gradient approximation (GGA) by Perdew et al. [71, 72] taking into account the local gradient of the electron density. In a similar manner spin splitting has been introduced, as e.g. in the local spin-density approximation (LSDA) [72].

3.5.2 Pseudopotentials

As mentioned in section 3.2, the atoms are in fact treated as pseudo-atoms with an effective pseudopotential $V_{eff}$ generated by the nucleus and atomic core states. As the core states have different angular momenta, the potential is not spherically symmetric, but rather has a symmetry given by the $l$ quantum number of the electronic states. Thus a radial potential is generated for each value of $l$ in the core states.

The potentials are generated by an all-electron DFT calculation on an isolated atom. To keep consistency within the calculations, the choice of exchange-correlation potential in the all-electron problem must be the one used for the DFT calculation as well. The potential is generated such that the valence states of the pseudo-atom match the all-electron valence states outside a sphere with a given core radius $R_{core}$. Inside the sphere, the pseudo-atomic states are more smooth, thus requiring a smaller basis set. Popular software for generating LDA and GGA pseudopotentials include the Opium package by Eric J. Walter [73], and the fhi98PP code by M. Fuchs and M. Scheffler [74]. A comparison of the all-electron states, $\psi^{AE}$, and pseudo-atomic states, $\psi^{NL}$, of zinc is shown in Figure 3.1. The vertical bars at 1.9au and 2.2au are the core radii beyond which the pseudo-states should match the all-electron ones.
Chapter 3. Theoretical methods

3.5.3 The PAW method

As mentioned in the introduction, DFT calculations grow heavy when treating wave functions with a strong variation near the atomic nuclei. The projector-augmented wave (PAW) method was introduced to reduce this problem [77,78].

The main idea is to separate the electronic density in two parts - the density “near” a specific atom, say within a sphere of radius $R_{PAW}$, and the density “in between” atoms (see Figure 3.3). The electronic behavior near a nucleus is assumed to resemble the free atom orbitals due to the strong local Coulomb interaction, while the density in between atoms varies slowly with the weaker background potential.

The PAW method treats the “in between” region as usual in plane wave DFT, while making corrections to the density in the atomic region. A relatively small plane wave basis is used to generate a “smooth” density $\tilde{n}(r)$ over the entire unit cell. The eigenstates are then projected onto the radial eigenstates $|\phi_{i,\alpha}\rangle$ of the free atoms $\alpha$ inside the region of $R_{PAW}$. This generates a density $n_{\alpha}^A(r)$ around each atom $\alpha$, containing the “shapes” of the atomic orbitals, with their strong spatial variations, while keeping the overall electron count of $\tilde{n}(r)$. The original contribution from $\tilde{n}(r)$ in the $\alpha$ region is removed by projecting onto a smooth radial basis $|\tilde{\phi}_{i,\alpha}\rangle$, with the same boundary conditions as the $|\phi_{i,\alpha}\rangle$. This gives the densities $\tilde{n}_\alpha^A(r)$, and the total PAW density is defined as

$$n(r) = \tilde{n}(r) + \sum_\alpha \left( n_\alpha^A(r) - \tilde{n}_\alpha^A(r) \right).$$  (3.20)
Using the atomic wave functions in this way is known as the “frozen core” approximation, as the shape of the density near the cores cannot vary. But this allows the use of a much smaller plane wave basis, as only the density between atoms must be portrayed correctly.

3.6 Empirical tight-binding

Empirical tight-binding (TB) [79–81] is another approach to solving the Schrödinger equation, with the strenght that it does not contain a self-consistent step, and thus is much less heavy calculation-wise. Instead, it relies on a set of empirical parameters that must be obtained from external, often experimental, data.

As in DFT, the TB system contains a set of decoupled electronic states, as presented in (3.6). This is treated in a localized basis of atomic orbitals, and the matrix elements of (3.12) are obtained from the empirical tight-binding parameters.

In terms of single atom Hamiltonians $\hat{H}_{0,\alpha}$ the tight-binding system Hamiltonian is written as a sum over atoms $\alpha$,

$$\hat{H} = \sum_{\alpha} \hat{H}_{0,\alpha} + \Delta V,$$

(3.21)

where $\Delta V$ is the perturbation to the atomic potentials due to the proximity of the atoms in the material. The eigenstates $\phi_{i,\alpha}$ of the $H_{0,\alpha}$, that is the atomic orbitals, form the set of basis functions used. The eigenstates can thus be written

$$\psi_j(r) = \sum_{i,\alpha} c_{j,i,\alpha}\phi_{i,\alpha}(r - R_\alpha),$$

(3.22)

This expansion is known as a linear combinations of atomic orbitals (LCAO), central to the tight-binding method.

It is assumed in TB that the potential perturbation $\Delta V$ is small compared to the $H_{0,\alpha}$ so that the atomic states will only be slightly effected by the “binding” of
the atoms. This justifies reducing the basis to only the chemically active orbitals, that is the valence states and lower excited states. After determining the matrix elements $H_{ij}^{\alpha\beta}$ and $S_{ij}^{\alpha\beta}$ between two atomic orbitals $\phi_{i,\alpha}$ and $\phi_{j,\beta}$, the eigen states are calculated from (3.12). The matrix elements are presented in Appendix A.

The matrix elements $H_{ij}^{\alpha\beta}(R)$ are in general radially dependent, complicated quantities. But in TB the inter-atomic distances are assumed fixed, and the locality of the orbitals means that only interaction between nearest or possibly next-nearest neighbour atoms is taken into account. Thus only a limited number of parameters appear. As the parameters are typically obtained by fitting to bulk data, one must be careful when modelling different systems such as surfaces or strained geometries. Obviously, as TB only contains information on the electrons of the system, total energy calculations and geometrical relaxations are not possible.

3.7 Density functional based tight-binding

As the name implies, density functional based tight-binding (DFTB) tries to combine the efficiency of TB with the versatile ab-initio approach of DFT [59,82].

While tight-binding succeeds in treating the electronic problem of (3.6), the goal of density functional based tight-binding (DFTB) is to be able to treat the full problem of (3.4) with the electronic energy calculated from a tight-binding band structure. This is done by creating from DFT a set of parameters such that both the structural properties and electronic properties of a system can be determined within a TB scheme. In the present work an approach known as self-consistent charge DFTB (SCC-DFTB) is used.

The SCC-DFTB energy consists of 3 terms, 

$$E_{DFTB} = E_{0}^{TB} + \Delta E_{2nd}^{TB} + E_{rep},$$

(3.23)

that will be treated separately.

3.7.1 DFTB tight-binding energy

The first term is the tight-binding energy obtained by summing all electronic states

$$E_{0}^{TB} = \sum_{n} f_{FD}(E_{n})E_{n},$$

(3.24)

with $f_{FD}$ the Fermi-Dirac distribution and $E_{n}$ the TB eigen energies. In the case of a periodic system this expression becomes an integral over the band structure.

The calculation of the DFTB energy is a three-step process, the steps 1 through 3 in Figure 3.4. First atomic orbitals for the different types of atoms $\alpha$ in the system are calculated individually. This is done by solving the Kohn-Sham equations for all the electrons in a pseudo-atomic nuclear potential

$$\hat{H}_{0,\alpha}\phi_{nml}(r,\Omega) = E_{n}\phi_{nml}(r,\Omega).$$

(3.25)

The pseudo-atomic Hamiltonian is given by

$$H_{0,\alpha} = -\frac{1}{2}\nabla^{2} + V_{psat}(r),$$

(3.26)
\[ V_{\text{psat}}(r) = V_{\text{nuc}}(r) + V_H[n(r)] + V_{xc}^{\text{DA}}[n(r)] + \left( \frac{r}{r_0} \right)^2, \quad (3.27) \]

and \( \left( \frac{r}{r_0} \right)^2 \) is included to localize the orbitals. The parameter \( r_0 \) is typically chosen to be the covalent radius \( R_{\text{core}} \) of the atom, or some fraction thereof, to ensure that the spatial extent of the calculated orbitals is comparable to the typical bond-length of the material.

The orbital states are described by coefficients \( a_{j,nl,m} \) in a Slater type basis as

\[ \phi_{nlm}(r,\Omega) = \sum_j a_{nlj}^l \chi_{nlm}^j(r,\Omega), \quad (3.28) \]

\[ \chi_{nlm}^j(r,\Omega) = r^l e^{-k_{nlj}^2 r^2} Y_{l,m}(\Omega). \quad (3.29) \]

The next step is to calculate radially dependent tight-binding parameters directly from these DFT orbitals. This is done by re-expressing the two-atom Hamiltonian in terms of the atomic (DFT) Hamiltonians as

\[ \hat{H} = -\frac{1}{2} \nabla^2 + \sum_{\alpha} \psi^\alpha_{\text{psat}} - \sum_{\alpha} \left( \frac{r - R_{\alpha}}{r_{0,\alpha}} \right)^2. \quad (3.30) \]

Consequently the TB Hamiltonian matrix elements are of the form \( \langle \phi_{\alpha lm} | \hat{H} | \phi_{\beta l'm'} \rangle \). It is the assumed that only the pseudo-atomic potentials and the repulsive terms from atoms \( \alpha \) and \( \beta \) contribute significantly to the matrix elements, and that the rest of the terms can be neglected. This is known as the two-center approximation. In this case the matrix elements become of the form

\[ \langle \phi_{\alpha lm} | \hat{H} | \phi_{\beta l'm'} \rangle \approx \langle \phi_{\alpha lm} | E_{l'm'}^\alpha + E_{l'm'}^\beta - \frac{1}{2} \nabla^2 - \left( \frac{r - R_{\alpha}}{r_{0,\alpha}} \right)^2 - \left( \frac{r - R_{\beta}}{r_{0,\beta}} \right)^2 | \phi_{\beta l'm'} \rangle. \quad (3.31) \]

By a change of coordinates and applying (3.25) this reduces to

\[ \langle \phi_{\alpha lm} | \hat{H} | \phi_{\beta l'm'} \rangle \approx \langle \phi_{\alpha lm} | E_{l'm'}^\alpha + E_{l'm'}^\beta - \frac{1}{2} \nabla^2 - \left( \frac{r - R_{\alpha}}{r_{0,\alpha}} \right)^2 - \left( \frac{r - R_{\beta}}{r_{0,\beta}} \right)^2 | \phi_{\beta l'm'} \rangle. \quad (3.32) \]

As the \( \phi_{lm} \) and \( \chi_{lm} \) are Slater type functions, the above matrix elements can be re-expressed in terms of Slater-Koster integrals of the \( \chi_{lm} \). These integrals have analytic expressions, as shown in appendix B.

The last step is to calculate the tight-binding states and energies for the treated system in the basis of the DFT pseudo-orbitals, exactly as described in (3.22) for empirical tight-binding. But in this case we have the entire radially dependent parameters \( H_{xx}^{\alpha\beta}(R) \), so we are not limited to a few known atomic distances or configurations.
3.7.2 The self-consistent charge correction

The second order term in the total energy, $\Delta E_{2\text{nd}}^{\text{TB}}$, contains the Coulomb energy of the charge displacement between atoms in the studied material. Thus it is a sum over the Coulomb interaction between all the pairs of atoms in the studied system, with corrections for internal screening, overlap of electronic orbitals and such. In a periodic material it can be expressed in terms of a sum over the entire lattice relative to the unit cell as

$$\Delta E_{2\text{nd}}^{\text{TB}} = \frac{1}{2} \sum_{\alpha} \sum_{\beta} \gamma_{\alpha,\beta} \Delta q_{\alpha} \Delta q_{\beta}.$$  \hspace{1cm} (3.33)

$\Delta q_{\alpha}$ and $\Delta q_{\beta}$ are the charges of atoms $\alpha$ and $\beta$ respectively, and $\gamma_{\alpha,\beta}$ the correction parameter. The charges are calculated by projecting the electronic states of (3.22) onto the atomic orbitals located on the atom $\alpha$ as

$$\Delta q_{\alpha} = q_{\alpha}^{0} - \frac{1}{2} \sum_{k} n_{k} \sum_{i,j} \left[ c_{k,\alpha}^{*} e_{k,j,\beta} S_{\alpha,j} + e_{k,j,\beta}^{*} c_{k,\alpha} S_{\beta,i,\alpha} \right].$$  \hspace{1cm} (3.34)

Here $q_{\alpha}^{0}$ is the charge of the pseudo-atomic nucleus, $n_{k}$ is the occupation number of the $k$'th state and $c_{k}$ the corresponding eigen vector. This is known as a Mulliken charge analysis, and in the case of a periodic system must be extended to an integration over the Brillouin zone. The remaining parameter, $\gamma_{\alpha,\beta}$, expresses the strength of the charge interaction. When $\alpha \neq \beta$ in the long range limit, $\gamma_{\alpha,\beta}$ is just a Coulomb interaction with a correction for the effective dielectric screening $\epsilon$. When $\alpha = \beta$, the
parameter can be approximated by the Hubbard $U$ parameter of the material, and thus:

$$
\begin{align*}
\gamma_{\alpha,\alpha} &= U_{\alpha}, \\
\gamma_{\alpha,\beta} &\approx \frac{1}{\epsilon |R_\alpha - R_\beta|}, \text{ for } \alpha \neq \beta,
\end{align*}
$$

(3.35)

The $E_{2nd}^{TB}$ correction to the total energy can be interpreted as a perturbation to the Hamiltonian as [59]:

$$
H_{1\alpha,j\beta}^{2nd} = \langle \phi_{i\alpha} | \hat{\mathcal{H}} | \phi_{j\beta} \rangle + \frac{1}{2} S_{i\alpha,j\beta} \sum_\zeta (\gamma_{\alpha\zeta} + \gamma_{\beta\zeta}) \Delta q_\zeta.
$$

(3.36)

As the SCC-DFTB Hamiltonian becomes a functional of the electron density through $\Delta q_\zeta$, the Schrödinger equation must be solved self-consistently. This is illustrated on the left-hand side of figure 3.4 as the fourth step. The energy is calculated repeatedly until stability with respect to the charge shift is achieved - that is until the change in the charge shift $\Delta(\Delta q_\alpha)$ is sufficiently small.

### 3.7.3 The repulsive energy

The repulsive energy term $E_{rep}$ in (3.23) is a correction term introduced as the tight-binding energies are calculated from the band structure energy and charge shift energies only. The ion-ion and electron-electron interaction terms are lacking between atoms, as are the XC contributions from overlapping orbitals, and many other contributions due to approximations in the tight-binding. In the range of long inter-atomic distances these terms are negligible, but when packing the atoms close together the electron-ion binding terms of the TB must be compensated by a short-range repulsion.

The repulsive energy $E_{rep}$ is expressed in terms of short-range inter-atomic repulsive potentials $V_{\alpha\beta}^{rep}(R)$ between atoms $\alpha$ and $\beta$, assumed to be only dependent on the distance. The repulsive energy is the sum of these contributions, and in a periodic system the contribution pr. unit cell can be written

$$
E_{rep} = \frac{1}{2} \sum_{\alpha} \sum_{\beta \neq \alpha} V_{\alpha\beta}^{rep}(|R_\alpha - R_\beta|).
$$

(3.37)

The terms $V_{\alpha\beta}^{rep}$ are typically extrapolated from a reference DFT calculation. By treating the DFT energy as a functional of the set of atomic coordinates $\{R_\alpha\}$, and similarly the terms $E_{0}^{TB} + \Delta E_{2nd}^{TB}$, the repulsive energy can be expressed

$$
E_{rep}[\{R_\alpha\}] = [E_{0}^{TB} + \Delta E_{2nd}^{TB} - E_{DFT}] [\{R_\alpha\}].
$$

(3.38)

By constructing sufficiently many systems and varying their geometries around equilibrium the repulsive potentials can be extrapolated individually. One must, however, be careful to choose the reference systems to ensure as high a transferability of the potentials as possible.

After determining the repulsive potentials structural properties of the studied materials can be obtained as well. This is illustrated in Figure 3.4 in the right. The
iterative electronic calculation is inserted in an iteration to minimize the total energy of the system.

In the following, the here presented methods as well as a nearly-free electron model will be used to treat the electronic and optical properties of ZnO nanostructures.
Electronic properties of mesoscopic hexagonal wires

To reach an understanding of the nanoscale effects of electronic confinement and materials defects in ZnO nanostructures, it is useful to start off with a more simple approach, before treating the DFT and DFTB problems. For this, ZnO is studied as a continuous material with the relevant boundary conditions.

4.1 Mesoscopic systems

As previously mentioned, nanoscale materials such as ZnO nanowires are often in the $10 - 500\,\text{nm}$ size range. This mesoscopic size range is small enough that the objects show quantum properties, but in general too large for QM methods such as DFT or DFTB due to the numerical complexity. Therefore mesoscopic materials are studied as continuous media, with macroscopic materials properties, but subject to nanoscale effects such as electron confinement [83].

In such a system, the extended and confined dimensions are identified, and the wave functions expressed as the product of an extended state and a confined state, $\phi(\mathbf{r}) = \psi_{\text{ext}}(\mathbf{r})\psi_{\text{conf}}(\mathbf{r})$. The extended eigenfunctions are simply plane waves, so the interesting term is $\psi_{\text{conf}}$, the dimension of which depends on the type of system. A thin film is treated as a one-dimensional quantum well (QW), a nanowire as a 2D QW, and a quantum dot as a 3D QW.

To describe the confinement, and possibly the surrounding materials, a confining potential $U_{\text{conf}}$ is introduced. The specific material properties appear through the use of the bulk effective electron mass $m_e^*$, the bulk band gap, the dielectric properties of the material, or an internal field $U$. The electronic properties are determined from the Schrödinger equation,

$$-\frac{\hbar^2}{2m_e^*}\nabla_{\text{conf}}^2 \psi_n(\mathbf{r}) + (U(\mathbf{r}) + U_{\text{conf}}(\mathbf{r}))\psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r}),$$

where $\mathbf{r}$ has the dimension of the confinement, and $\nabla_{\text{conf}}^2$ is the Laplacian on the confined space. Internal potentials can arise due to materials defects or impurities, or...
through electronic depletion, in which case the Poisson equation [65] must be solved,

$$\nabla^2 U = \frac{e^2 \rho(r)}{\varepsilon \epsilon_0} - \frac{e^2 n(r)}{\varepsilon \epsilon_0}. \quad (4.2)$$

where $\rho(r)$ is the (positive) donor density and $n(r)$ the (negative) electron density.

The system size only appear through the length-scale of $r$ in (4.1) and (4.2), and thus the problem complexity is independent hereof.

### 4.2 Mesoscopic ZnO nanostructures

In the article presented appendix F, the effects of donor impurities, and the confinement effects due to the wire shape, were studied for ZnO nanostructures. The material constants used were an effective mass of $m^*_{e} = 0.24 m_0$ [84] and an average bulk dielectric constant of $\varepsilon \approx 8.15$, as well as the bulk band gap $E_g = 3.3 eV$ and the effective hole mass $m_h = 0.59 m_0$, corresponding to the experimental value for the heavy hole [85]. For the numerical solutions of the Poisson and Schrödinger equations, the hexagonal grid approach of J. Sun [86] was implemented. It defines the points on the unit hexagon as

$$p = \frac{1}{2} (t_1 \mathbf{n}_1 + t_2 \mathbf{n}_2 + t_3 \mathbf{n}_3), \quad t_1 + t_2 + t_3 = 0, \quad -1 < t_1, t_2, t_3 < 1, \quad (4.3)$$

with the unit vectors $\mathbf{n}_i$ equivalent to the first three of the wurtzite four-vector basis. The last constraint on the coefficients $t_i$ defines the hexagonal grid shape.

Analytic approximations were found, both to the Poisson equation and to the Schrödinger equation on a deformed hexagonal quantum well with no donor defects. The approximate analytic potentials are seen in Figure 4.1 (LEFT), compared for different electron-donor ratios $\alpha$. Good agreement with the numerical potentials is seen for sufficiently small $\alpha$, while the error grows with $\alpha$ due to the applied approximations.

![Figure 4.1](image.png)

**Figure 4.1:** LEFT: The approximate analytic potential $U_{ana}$ compared to the numeric result for varying electron to donor ratios $\alpha$. RIGHT: The energies of the approximate, analytic eigen-functions $\phi_{1-3}$ plotted against the real eigen values for varying deformation parameter $\gamma$. 


Chapter 4. Electronic properties of mesoscopic hexagonal wires

Figure 4.2: LEFT: Transformation of QW from hexagon to parallelogram by varying $\delta \in [0,1]$. RIGHT: Elongating the hexagon by varying $\gamma \in [0,2]$.

Figure 4.3: LEFT: The potential $U_0$ generated by a constant donor density $\rho = 0.1 \text{nm}^{-2}$ on the hexagon. RIGHT: The bound state energies on the hexagon relative to the potential minimum (black) and the energies of the paraboloid quantum well (red) as a function of the surface charge density.

The stretching of the hexagon, illustrated in Figure 4.2 (RIGHT), was treated analytically for the case with no defects. The stretching transforms the cross section from that of a nanowire to that of a nanobelt [22], by increasing the range of two of the $t_i$, with increasing parameter $\gamma$. The energies of the analytic approximate eigen functions are seen in Figure 4.1 (RIGHT), compared to the numerical results. The analytic states have slightly higher energies, but show the correct relative energies as well as stability under the transformation $\gamma$.

The potential generated by a constant donor density has a paraboloid-like shape around the center of the wire but stretches into the hexagonal shape near the wire border, as illustrated in Figure 4.3 (LEFT). An increase in donor density strengthens the potential and localizes the lower eigenstates more strongly in the center of the wire. Thus the eigen energies converge to those of the paraboloid for increasing donor densities, as seen in Figure 4.3 (RIGHT), where the energies are taken relative to the potential minimum. The non-degenerate energies defined by the hexagon shape for small $\rho$, are bundled into degenerate levels as the potential becomes more dominant. Regardless of shape, this behavior is to be expected for any highly doped quantum
The two transformations in Figure 4.2 were studied further using numerical methods. The energy spectrum of the transformations from hexagon to parallelogram, at constant area $A = 100\text{nm}^2$, is seen in Figure 4.4. This clearly shows the existence of degenerate states due to the high symmetry in both the hexagon and the parallelogram, while the symmetry is broken, and energies split off, in-between the two end-points. An illustration of two wave functions before and after the transformation is seen in Figure 4.5. In the top figures, the $\phi^H_8$ on the hexagon transforms into $\phi^P_6$ on the parallelogram. In the bottom, $\phi^H_5$ is transformed into $\phi^P_5$. As hinted by the number of extrema on each WF, the energies $E^H_5$ and $E^H_8$ on the hexagon are far apart, while on the parallelogram the level is degenerate $E^P_5 = E^P_6$.

The optical properties of the nanostructures were treated by the calculation of the complex part of the dielectric function, $\epsilon_I$. To do so, the donor energy $E_d = -61\text{meV}$ relative to bulk was introduced [87]. The charge balance equation [65] was solved iteratively for the the Fermi energy $E_f$, and $\epsilon_I$ was calculated for a wire with cross section $A = 300\text{nm}^2$ at temperature $T = 200\text{K}$, from the expression

$$\epsilon_I(\hbar\omega) \propto \frac{1}{\omega^2} \sum_{c,v} \int_{-\infty}^{\infty} |P_{cv}|^2 \delta(\hbar\omega - E_{cv})(f_v - f_c) dk. \quad (4.4)$$

Here $E_{cv} = E_{gcv} + \frac{\hbar^2 k^2}{2m_e}$, $E_{gcv} = E_g + E_c + E_v$ and $m_{ch}^{-1} = m_e^{-1} + m_h^{-1}$. $P_{cv}$ are the momentum matrix elements, and denoting by $f_{FD}(E)$ the Fermi-Dirac distribution, $f_c = f_{FD}(E_c + \frac{\hbar^2 k^2}{2m_e})$ and $f_v = f_{FD}(-E_g - E_v - \frac{\hbar^2 k^2}{2m_e})$.

The $\epsilon_I$ is calculated for the regular hexagon, as well as a slightly deformed hexagon, with $\delta = 0.1$. The result is seen in Figure 4.6 (RIGHT). The first three absorption peaks of the regular hexagon is seen, and for the deformed hexagon the higher peaks have split up due to symmetry breaking, as expected from the band structure in Figure 4.4 (LEFT).

The susceptibility as a function of the electron density was treated as well (Figure 4.6 (LEFT)). A slight shift of the absorption peaks was seen due to the electron
Figure 4.5: Eigenstates of the hexagon (LEFT) and their corresponding states on the parallelogram (RIGHT) through the transformation $\delta$. The parallelogram states are in fact degenerate, while the hexagon states are far apart in energy.

Figure 4.6: LEFT: Energies as a function of parameter variation $\delta \in [0, 1]$. RIGHT: Normalized imaginary part of the dielectric constant $\epsilon_I(\hbar \omega)$ of a hexagonal wire compared to that of a wire with deformation $\delta = 0.1$, both with cross-section $A = 100 \text{nm}^2$. 
dampening of the donor potential, and with the increasing electron occupation of the lowest levels, the peaks were diminished due to the Pauli blockade.

Thus both defects and geometry variations were found to have significant effect on the electron structure of ZnO nanomaterials, and consequently the optical properties are affected as well.
Chapter 5

DFT and DFTB modelling of ZnO structures

For a more precise understanding of the electronics of ZnO nanostructures, one needs to take into account the crystal structure and atomic configuration of the material. This is done using the DFT and DFTB methods described in chapter 3.

This chapter presents the treatment of ZnO within DFT-LDA, PAW-DFT and SCC-DFTB, with a focus on surfaces and wires with and without surface adsorbates. The surface geometries are treated, and the resulting band structures studied. The DFTB parametrization used is the one presented in the article of appendix G.

5.1 DFT modelling of ZnO

To determine DFT settings for calculations on nanostructures, a study of bulk ZnO is needed at first. The pseudopotentials used are the Troullier-Martins potentials generated by Khein and Allan described in section 3.5.2, and the calculations were performed using the ABINIT package by Gonze et al., with the Teter Padé XC parametrisation [76,88].

As a plane-wave basis is used, preliminary steps include determining the cut-off energy $E_{\text{cut}}$ described in section 3.4, and the necessary number of $k$-point in the shifted Monkhorst-Pack grid [89] on the Brillouin zone. The calculations are performed on the experimental geometry with $(a,c,u) = (6.15, 9.85, 0.382)$ with $a$ and $c$ given in atomic units [6].

The cut-off convergence was treated on a $(2 \times 2 \times 2)$ Monkhorst-Pack grid, shifted along 4 directions of the BZ, giving a total of 8 symmetrically distinct $k$-points. As an illustration, a graph of the DFT unit cell total energy for a fixed ZnO wurtzite geometry is plotted as a function of the plane wave cut-off energy is seen in Figure 5.1 (LEFT). A large $E_{\text{cut}}$ of about 40au to 45au is needed, to get a precision on the total energy of $\Delta E \approx 2 \cdot 10^{-3}$au, due to the electronic $d$-states of Zn. As the need for higher-energy plane waves only increases when treating surface states, a cut-off energy of $E_{\text{cut}} = 45$au will be used throughout the LDA-DFT calculations for consistency.

The Monkhorst-Pack grid is defined by a number of sub-divisions $(a \times b \times c)$ of the BZ along the three unit cell vectors, followed by a number of shifts of the entire grid. In fact, only a small $k$-point grid is needed for the calculations, as seen from
Figure 5.1: Wurtzite ZnO total energy of a fixed unit cell geometry. LEFT: As a function of the cut-off energy $E_{cut}$. RIGHT: as a function of the k-points grid size.

Figure 5.1 (RIGHT). Consequently, a grid of $(2 \times 2 \times 2) \times 4$ Monkhorst-Pack k-points will be used for all bulk wurtzite calculations made with ABINIT.

Performing a full relaxation of the unit cell, the DFT lattice parameters, in atomic units, are found to be

$$(a, c, u) = (6.034, 9.802, 0.376),$$

in good agreement with the experimental values.

5.1.1 PAW modelling using VASP

Surface calculations were performed using the PAW method in the Vienna Ab-initio Simulation Package (VASP), a plane wave DFT package developed by Prof. Kresse et al. [90–92]. The calculations were performed in collaboration with the group of Prof. Friedhelm Bechstedt at the Friedrich-Schiller university in Jena, using the work on ZnO by André Schleife and the PAW surface studies by Roman Leitsman as support [42,93].

The PAW pseudopotentials used have core radii of 2.3Å and 1.5Å for Zn and O respectively, and the calculations were made with $E_{cut} = 400eV$ on a 2D grid of 33 k-points. The PAW bulk lattice parameters were calculated to be

$$(a, c, u) = (6.070, 9.860, 0.377),$$

very close to the DFT-LDA values. These were then used to generate slabs for surface studies. The surface studied was the (1010) described in section 1.1. The atomic configuration is seen in the upper part of figure 5.2, where a clean crystal face is shown without relaxation. The surface UC contains two atoms, lying directly in the surface plane, and two lying slightly below the plane. The entire system studied was 12 atomic layers thick, and the symmetry of the system ensured that no charge build-up or internal polarization could affect the results. An illustration of the relaxed system, with projected electronic densities, is seen in Figure 5.3. The atomic positions
Figure 5.2: Relaxed geometry of the (1010) surface of ZnO with and without hydrogen termination of the dangling bonds. PAW calculation performed with the VASP package.

Figure 5.3: Plot of the electron density of the clean surface ZnO slab.
were fully relaxed, moving 5 layers on each side and fixing only the innermost two to the PAW geometry. The vacuum layer between slabs was 11.6Å wide.

In fact, two relaxations were made. In the first case a clean surface was studied, so that the dangling bonds of both Zn and O surface atoms were left free. In the second study, the surface states were terminated using hydrogen, having a PAW core radius of 1.1Å. The relaxed geometry in the two situations is illustrated in Figure 5.2 (BOTTOM) and the coordinates for the surface atoms are given in table 5.4, in terms of the coordinate system of Figure 5.2 (TOP-LEFT). In the case of the clean surface, the oxygen atoms move out of the plane, while the zinc atoms move further into the material. The opposite happened to the hydrogen terminated surface, in which case the Zn-H pair extend slightly from the surface, while the O-H pair is closer to the bulk. It is also noted that the O-H bond length of 0.99Å = 1.87au is much shorter than the Zn-H bond of 1.36Å = 2.37au. The calculated lengths are in good agreement with the typical O-H bond length found in molecules, and the Zn-H bond of zinc hydride [94,95].

A possible explanation is the charge build-up on the surface atoms. In the bulk there is a charge transfer of $\frac{1}{2}e^-$ from each nearest neighbour Zn atom to each O atom to fill the 2p shell of oxygen. The surface atoms, however, each have a dangling bond. This gives rise to an extra charge transfer between surface atoms, as illustrated in Figure 5.5 (LEFT). The negatively charged oxygen is slightly repelled by the other surface atoms, while the positively charged zinc is attracted. On the hydrogen-terminated surface the opposite happens, as seen in Figure 5.5 (RIGHT). As hydrogen supplies a charge of $1e^-$, the excess charge is returned to Zn, making it slightly negatively charged, and thus repelled.

The reason the (1010) surface is interesting, is that it is possible to generate hexagonal wurtzite nanowires with this face on all six sides, as illustrated in Figure 1.2 (LEFT). The smallest such wire is seen in Figure 5.9 (LEFT), and a comparison of its PAW and DFT-LDA band structures is seen in Figure 5.6. This wire is in fact semiconducting, with a bandgap of about 1.2eV for PAW and 1.6eV for DFT-LDA. The $d$-bands of the PAW band structure are also about 0.5eV higher than in the LDA-DFT band structure, even though in the bulk DFT-LDA already underestimates the split-off of the $d$-bands (see section 5.2.3).

A DFT-LDA relaxation of the same wire with hydrogen termination i seen in Figure 5.7 (LEFT), where, as in the PAW surface calculation, the Zn atoms are now extruding slightly more than the O atoms. The Zn-H and O-H bond lengths of 2.98au

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bulk coordinates:</th>
<th>Clean surface:</th>
<th>$H$ terminated surface:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn1</td>
<td>(0.0, 0.0, 0.0)</td>
<td>(−0.180, 0.0, 0.343)</td>
<td>(0.183, 0.0, −0.236)</td>
</tr>
<tr>
<td>Zn2</td>
<td>(2.654, 1.642, 0.948)</td>
<td>(2.669, 1.641, 0.839)</td>
<td>(2.590, 1.642, 0.992)</td>
</tr>
<tr>
<td>O1</td>
<td>(0.645, 1.642, 0.948)</td>
<td>(0.665, 1.642, 0.956)</td>
<td>(0.617, 1.642, 0.938)</td>
</tr>
<tr>
<td>O2</td>
<td>(3.299, 0.0, 0.0)</td>
<td>(3.289, 0.0, 0.014)</td>
<td>(3.355, 0.0, 0.020)</td>
</tr>
<tr>
<td>H1</td>
<td></td>
<td>(0.819, 0.0, −1.660)</td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td></td>
<td>(2.901, 0.0, −0.856)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.4: Coordinates of the surface atoms of the (1010) surface in Angstrom. The second column gives the bulk coordinates, while the relaxed coordinates of the two systems are given in columns 3 and 4.
Figure 5.5: Charge shift between surface atoms for the clean surface (LEFT) and the hydrogen terminated surface (RIGHT).

Figure 5.6: LEFT: PAW band structure of the smallest ZnO nanowire, illustrated in figure 5.11. RIGHT: The same band structure, calculated in LDA-DFT with the LDA-DFT relaxed geometry.

Figure 5.7: Relaxed geometry of the small wire of Figure 5.9 (LEFT), with hydrogen termination of the dangling bonds. The hydrogen positions related to the Zn and O are marked with black and red circles respectively.
and 1.91 au are similar to the PAW bond lengths as well. The band structure is seen in Figure 5.7 (RIGHT), with a much larger bandgap of 4.6 eV due to the hydrogen termination.

5.2 DFTB parametrization

As explained in section 3.7, the goal of DFTB is to create a set of versatile tight-binding parameters that are applicable to as many systems as possible. In the case of Zn and O, both have been studied independently for DFTB, zinc in the work by Elstner et al. on bio-molecules [58], and oxygen both in molecules [59,96] and in bulk materials such as SiO$_2$, Al$_2$O$_3$ and TiO$_2$ [97,98].

In the article in appendix G, a set of SCC-DFTB parameters for crystalline ZnO is presented and tested against various reference systems. SCC-DFTB was chosen to better handle the large charge transfer appearing in ZnO, and to take into account the difference in charge transfers at surfaces and around defects/adsorbates.

The all-electron DFT on individual atoms, and radially dependent Slater-Koster parameter calculations, were implemented in Fortran based on a code by Thomas Garm Pedersen. The program consisted of a Perdew-Zunger DFT-LDA calculation with the wave functions expressed in an expanded version of the Gaussian-type local orbital basis of Koga [99,100]. An SCC-DFTB code was written to handle general 3D, 2D and 1D periodic structures, with efficient BZ integration using the tetrahedron and triangle integration schemes [101–103], and using optimized Ewald summations for the periodic Coulomb potentials due to inter-atomic charge shifts [104,105].

5.2.1 Reference geometries, parameters and repulsive potentials

As described in section 3.7, some choices are to be made for the generation of DFTB parameters. Namely, what are the effective covalent radii $r_{0,\alpha}$, which crystal structures should be used to generate the parameters, and how should the repulsive potentials be expressed? A short motivation for each choice will be given in the following.

As the two constraint parameters $r_{0,Zn}$ and $r_{0,O}$ have the function of confining the atomic orbitals, they have a strong impact on the inter-atomic matrix elements - that is the atomic coupling. By inserting large values of $r_0$ the atoms decouple completely, while small values “smear” out the orbitals over several nearby lattice sites. As an initial guess, the covalent radii of $R_{cov}^{Zn} = 2.36$ au for zinc and $R_{cov}^{O} = 1.38$ au for oxygen, were used [106,107]. This, however, gave large orbital overlaps which resulted in a bulk bandgap of only a few eV. So smaller overlaps were needed. Re-expressing the constraint parameters $r_{0,\alpha} = \alpha_c R_{cov}^{\alpha}$ the wurtzite bandgap of the experimental geometry was plotted as a function of the parameter $\alpha_c$, in Figure 5.8. From the figure, a choice of $\alpha_c = 2.0$ was made, so that the bandgap was in the desired range. It is worth noting that the bandgap therefore is not a parameter that can be used for testing the model. But comparison of bulk and nanostructure band structures still makes sense.

The main goal was to generate a set of parameters that could equally well describe bulk and surface atoms. Thus both types of atoms were needed to generate the parameters. For the bulk was used wurtzite ZnO, and for the surface atoms was used
Figure 5.8: The bulk ZnO bandgap as a function of the constraint parameter $\alpha_c$.

Figure 5.9: LEFT: Geometry of a thin hexagonal ZnO nanowire, generated from a single hexagon of the crystal structure. RIGHT: A single honeycomb layer of ZnO with lattice parameters $a$ and $h$ defining the inter-atomic distances.

The thinnest possible hexagonal wire as illustrated in Figure 5.9 (LEFT), infinitely periodic along the $c$ direction. In both cases, a controlled variation of specific lattice parameters was made, and repulsive potentials calculated through comparison of the SCC-DFTB and LDA-DFT energies.

For the repulsive potentials, the first problem was to decide how far reaching the repulsive potentials should be. As an initial attempt, only nearest-neighbour (NN) interaction was considered, and the zinc-oxygen repulsion $V_{ZnO}^{rep}$ was extracted from simply scaling the wurtzite geometry. This parametrisation gave good results for the bulk, as could describe a single flat honeycomb-layer, as illustrated in Figure 5.9 (RIGHT), as well. But whenever two atoms of the same type were close to each other, they would collapse, as there were no zinc-zinc or oxygen-oxygen repulsion. This would most likely be problematic on surfaces and in vacancy sites, so this model was discarded.

Thus it was decided to include second-nearest neighbour (2NN) repulsion, giving a total of three potentials, $V_{ZnO}^{rep}$, $V_{ZnZn}^{rep}$, and $V_{OO}^{rep}$. With a growing number of potentials, a growing number of reference systems is needed, so the small wire was included as a reference as well.
The repulsive potentials are illustrated in Figure 5.10. It is seen that the main repulsion stems from the Zn-O bond in the typical range of the inter-atomic distances. Both the Zn-Zn and O-O potentials give only a small correction to the results, but the attractive nature of $V_{OO}^{rep}(r)$ for sufficiently small $r$ means that one should carefully examine results, where oxygen atoms sit close to each other. This, however, did not prove a problem in the studied systems.

### 5.2.2 SCC-DFTB geometries

With the parameters in place, tests were made against different systems, both with respect to the ideal relaxed geometry, and to the energetic behaviour of the systems around their total energy minima.

The bulk wurtzite geometry was very similar in DFT and DFTB, as this structure was the basis of the parametrisation. Relaxed wire geometries for two small wires are seen in Figure 5.11, where the dotted lines illustrate the bulk lattice. The atomic behaviour is found to be much the same in DFT and DFTB, with slightly more extruding oxygen atoms in DFTB than DFT. This again resembles the PAW results for the (10\(\bar{1}0\)) surface atoms. The charge shift is readily accessible from the SCC-DFTB calculation and found to be $\Delta q = 0.15e^-$ from Zn to O, supporting the double-
Figure 5.12: The rock salt phase of ZnO (LEFT), and the total energies calculated for varying lattice parameter $a$ in DFT (solid line) and DFTB (dashed line) (RIGHT).

Figure 5.13: LEFT: Total energy of a 2 dimensional hexagonal lattice ZnO as a function of the lattice constant $a$ from DFT (solid line) and DFTB (dashed line). RIGHT: slab thickness variation with constant nearest neighbour distance.

The energetics under lattice variations were studied on the honeycomb layer of Figure 5.9 (RIGHT), as well as the high-pressure rock salt phase of ZnO, as illustrated in Figure 5.12 (LEFT). The results for the rock salt phase is seen in Figure 5.12 (RIGHT), and results for the independent variation of the two honeycomb lattice parameters in Figure 5.13. The energy minima agree very well in both cases supporting the transferability of the parameters. Even more interesting, the energetic changes are on the same scale when varying the lattice parameters, for both DFT and DFTB. The honeycomb layer of figure 5.9 (RIGHT) is useful for testing the 2NN potentials, as varying $h$ for a fixed value of $d$ keeps the NN repulsion constant. This variation is seen in Figure 5.13 (LEFT), and the agreement with DFT indicates that even though $V_{OO}^{rep}(r)$ is attractive for sufficiently small $r$, nano structures will most likely not collapse in the DFTB calculation.

The similar energetic behaviour in DFT and DFTB also means that a reasonable treatment of e.g. vibrational spectra should be possible as well, assuming that the DFT energetics are correct.
5.2.3 Bulk and layer band structures

The DFTB band structure was calculated with a value of $\alpha_c = 1.85$ for the covalent radius correction, and is given in Fig. 5.14 (LEFT). The DFTB $d$-bands lie slightly lower, at $-6.2\text{eV}$ below the valence band edge, than those of DFT-LDA at $-5.1\text{eV}$. The experimental position [9] is reported to be around $-6.95\text{eV}$ supporting the strength of the DFTB band structure for use in electronic calculations. The valence band structure of the 2D hexagonal ZnO layer, calculated in both DFTB and DFT, is seen in Figure 5.14 (RIGHT). The valence bands are seen to be of the same shape and spanning the same energy range in both cases, again with the $d$-bands of the DFTB band structure lying slightly lower than the $d$-bands of the DFT calculation.

5.2.4 Effect of surface relaxation on ZnO nanowires

As the scalability of the SCC-DFTB model is much better than DFT, it can be applied to three larger nanowires as seen in Figure 5.15. These are denoted “Wire 2”, “Wire 3” and “Wire 4”, as they consist of two, three and four rings of hexagons respectively. They are generated with only (1010) surfaces as described in chapter 1 of the thesis.

The effect of surface relaxation is studied by comparing the band structure of a wire with bulk geometry to that of the same wires with surface relaxation. For the relaxed wires, the surface atom positions are extrapolated from the relaxation of the wire in Figure 5.11 (LEFT). This is done by simply calculating the correction to the position of the outermost atoms (denoted by $R_1$ in the article) and applying this correction to all wire surface atoms.

The results for Wire 2 are seen in Figure 5.16. The bandgap grows significantly in the relaxed wire, as the surface atoms, and thus surface orbitals, are more tightly bound to the bulk material. The wire with bulk geometry has a bandgap of $E_{g,W2}^{\text{bulk}} = 1.89\text{eV}$, well below the bulk value of 3.3eV due to the surface states. But in the relaxed case, the surface states are absorbed, and the bandgap of $E_{g,W2}^{\text{relax}} = 4.33\text{eV}$ is above the bulk value due to the electronic confinement.
Chapter 5. DFT and DFTB modelling of ZnO structures

Figure 5.15: Geometries of the three larger ZnO nanowires studied, denoted “Wire 2” (LEFT), “Wire 3” (CENTER) and “Wire 4” (RIGHT), as they have radii of two, three and four hexagons, respectively.

Figure 5.16: The band structures of Wire 2 generated from the bulk lattice (LEFT) and with surface relaxation (RIGHT).

The relaxed geometry band structures of Wire 3 and Wire 4 are seen in Figure 5.17, with decreasing bandgaps as the confinement weakens.

5.2.5 Hydrogen termination of surfaces

Terminating the surface with hydrogen is expected to increase the bandgap even more, as the dangling bonds of the surface are replaced with Zn-H and O-H bonds. The relaxed geometry of the surface is generated by extrapolating from the PAW calculations. The surface Zn and O positions are shifted from the bulk values with the same amount as found in the PAW calculations, and the H atoms are placed in the direction given by PAW, at the distances of 2.95 au for Zn-H and 1.87 au for O-H. Given the good agreement between methods, this is a reasonable guess. A covalent radius for hydrogen of $R_{H}^{cov} = 0.70$ au is used [107].

The Hydrogen terminated geometry of Wire 2 is seen in Figure 5.18 (LEFT), and the corresponding band structure in Figure 5.18 (RIGHT). Comparing to the band
Figure 5.17: The band structures of Wire 3 (LEFT) and Wire 4 (RIGHT) in the relaxed geometries of the clean surfaces.

Figure 5.18: The hydrogen terminated band structures of Wire 2 (LEFT) and (RIGHT).
structure of the clean surface wire, the surface bands have moved out of the band gap, and only a single low-lying conduction band is left. This resembles the single low conduction band of the bulk band structure, but again due to confinement, the bandgap is much larger than in the bulk.

As the wire grows thicker the bandgap approaches the bulk, as seen for Wire 3 and Wire 4 in Figure 5.19. The confinement effect is still significant, but the trend evident.

5.2.6 Metallic nanowires by partial hydrogen termination

As reported by Wang et al. in a study of the (2110) surface [50], metallicity can be induced in the nanowires by a partial hydrogen coverage.

An example of Wire 2 with hydrogen termination of only the surface oxygen atoms is seen in Figure 5.20 (LEFT). The ZnO geometry is generated from the bulk values,
and the terminating hydrogen placed at the same relative position as for the fully
terminated wire. The band structure is seen in Figure 5.20 (RIGHT). The H fills the
dangling O bonds, leaving the surplus Zn electrons to form a metallic surface band.
The band structure shape somewhat resembles that of the un-relaxed clean Wire 2,
but in partially covered wire the surface oxygen levels are lowered slightly, while the
now filled Zn HOMO levels have slightly higher energies than the LUMO levels of the
clean wire.

As the surface has not been fully relaxed, the actual band structure is expected
to be slightly different, but the general trends of band shifts and metallicity should
still hold true.

Thus, with the three methods of DFT-LDA, DFT-PAW and SCC-DFTB it was
shown possible to treat geometries and electronics of ZnO surfaces and nanowires. The
three methods can to some degree be seen to represent a progression, from the purely
*ab-initio* plane-wave DFT, over the plane-wave and orbital mixing of the frozen-core
PAW, to the LCAO method of DFTB with it’s parameter-dependence through the
choice of $\alpha_c$. Surely, DFT is most versatile, but the inclusion of AO’s enables the
study of larger systems, and in the case of DFTB improves the energy levels of the
band structure. And with the good agreement between methods on so many test
systems, the DFTB approach can easily be justified.
Chapter 6

The Franz-Keldysh effect

In the presence of a strong electric field, the optical properties of a material are affected due to a change in the electronic states. This is seen in the response functions, such as the susceptibility, by a splitting or shifting of the absorption peaks, and for strong fields higher-order oscillations appear on the peak-tail. This is known as the Franz-Keldysh (FK) effect [108,109].

The Franz-Keldysh effect has been documented for general confined systems [110–112], as well as studied for its effect in piezoelectric materials [113]. Cylindrical ZnO quantum dots have been treated in a simple two-band model by Xia and Spector [114], showing that the FK effect lowers the absorption threshold, but weakens the absorption as well. Presently we study how the FK effect in ZnO nanowires depend on the field direction due to the UC assymmetry, an effect that has also been documented in conjugated polymers [115]. Finally, the FK effect in carbon nanotubes is treated with focus on the quadratic electro-optic effect, as presented in the article in appendix D.

6.1 Theory

With a permanent electric field \( \mathbf{E} = eE_z \) along the \( z \) direction in a given system, the decoupled Hamiltonian of eqn. 3.6 becomes

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + eE_z + V_{\text{eff}}(\mathbf{r}).
\]

(6.1)

In the present case, a tight-binding model is applied, so \( V_{\text{eff}} \) is the tight-binding potential. The electronic eigenstates are of the form 3.22.

To calculate a macroscopic property of the material, such as the susceptibility, a macroscopic amount of nanowires is needed. This is done by introducing a super-lattice of wires, each aligned along the field direction. For a super-lattice of nanowires with a wire concentration of 1/Ω the susceptibility along the \( z \) axis is given by

\[
\chi(\omega) = \frac{\varepsilon_0^2}{\varepsilon_0 \Omega} \sum_{m,n} (f(E_n) - f(E_m)) \frac{\langle \psi_m | z | \psi_n \rangle^2}{E_{mn} - \hbar \omega - i\hbar \Gamma}.
\]

(6.2)
Here \( f(E) \) is the Fermi function, \( E_{mn} = E_m - E_n \) the energy difference of the states and \( \Gamma \) a broadening term. A derivation of the susceptibility is presented in appendix C.

### 6.2 The Franz-Keldysh effect in ZnO nanowires

The tight-binding model presently used is the \( sp^3 \)-parametrization of Kobayashi et al. [36]. To simplify the expression of \( \chi(\omega) \) we limit the calculations to the electronic states around the bandgap. Surface states are terminated by hydrogen adsorbates, and thereby moved well into the valence and conduction bands, so these can be neglected. In the applied \( sp^3 \) parametrisation the largest contribution to the states near the bandgap comes from the zinc \( s \) and \( p \) states. Therefore reducing the problem to only include the intra-atomic contributions from zinc is justified. Thus the dipole matrix elements in (6.2) are reduced to a sum over the zinc orbitals

\[
\langle \psi_m | z | \psi_n \rangle = \sum_{\mu z_n} (c_{m,\mu p_z}^* c_{n,\mu s} + c_{m,\mu s}^* c_{n,\mu p_z}) p_{cv}^{Zn},
\]

with \( p_{cv}^{Zn} = \langle \phi_{sZn}^* | z | \phi_{Zn}^p \rangle \) and the \( c_{m,\mu} \) the coefficients of the eigenfunctions in the orbital basis. In the low temperature regime the susceptibility is thus given by a sum over valence and conduction states,

\[
\chi(\omega) = \frac{e^2}{\epsilon_0 \Omega} \sum_{n\in\text{val.}} \sum_{m\in\text{cond.}} \left[ \frac{|\langle \psi_m | z | \psi_n \rangle|^2}{E_{mn} - \hbar \omega - i\hbar \Gamma} + \frac{|\langle \psi_m | z | \psi_n \rangle|^2}{E_{mn} + \hbar \omega + i\hbar \Gamma} \right]
\]

The dipole matrix element \( p_{cv}^{Zn} \) is determined from a bulk calculation, by fitting the real part of \( \chi(\omega) \) to measurements done by Jellison et al. [62] in the low frequency limit. The obtained value of \( |p_{cv}^{Zn}|^2 = 1.8\text{Å}^2 \), and the wire volume \( \Omega \) in the bulk geometry, are used in the calculation of the susceptibilities in the following. \( \hbar \Gamma = 0.07\text{eV} \) is introduced as the system dampening.

With the materials parameters in place, the variables to be studied are the physical dimensions of the ZnO wires, and the electric field strength. The wire length is fixed at 40\( UC \) and the effect of the applied fields is studied for different wire diameters, as illustrated in figure 6.1. The wires are generated from the bulk geometry illustrated in Figure 6.1 (INSERT), watching along the \( z \)-axis. The study of both field directions is important, as the wurtzite wire structure is non-symmetric with respect to a 180° rotation. The studied wires are those of Wire 1-4 of section 5.2.4 with purely \((10\overline{1}0)\) surfaces and hydrogen adsorbates on all surface atoms.

In the complex susceptibility, \( \chi(\omega) = \chi'(\omega) + i\chi''(\omega) \), the imaginary \( \chi''(\omega) \) determines the absorption of the material. Therefore the imaginary part of the susceptibility, as a function of photon energy \( \hbar \omega \), is presented for four different wires in figures 6.2 and 6.3. In Figure 6.2 (LEFT) is seen the smallest ZnO wire, with a diameter of 5.3Å. The susceptibility was calculated for zero field, as well as with an applied field of \( \pm 0.01\text{V}/\text{Å} \). As expected for a thin wire, the first absorption peak lies well above the bulk bandgap, at an energy of about 6.85eV. When applying the field, the peak is shifted slightly higher in energy, with a shift of 0.06eV for the positive field direction.
Figure 6.1: Schematic illustration of a ZnO nanowire with diameter $D$ and length $L$, and the optical properties in the presence of an applied field $F$. INSERT: The bulk basis used.

Figure 6.2: LEFT: Susceptibility of the first thin ZnO nanowire with zero applied field (Black) as well as applied fields of $F = \pm 0.01 \text{eV}$ (Green and Magenta). RIGHT: Susceptibility of the second ZnO nanowire.
Figure 6.3: LEFT: Susceptibility of the third ZnO nanowire with zero applied field (Black) as well as applied fields of $F = \pm 0.01\text{eV}$ (Green and Magenta). RIGHT: Susceptibility of the fourth ZnO nanowire.

and a shift of 0.04eV for the negative. Furthermore, the field induces oscillations on the previously smooth tail of the peak.

In Figure 6.2 (RIGHT) a slightly larger wire is seen. The bandgap is significantly lower than in Figure 6.2 (LEFT) due to the weaker QW confinement and the appearance of more “bulk-like” states. The effect of the applied field to $\chi''$ is however much the same as in the first wire, though the oscillations here are notably larger than for the first wire.

For the larger wires in Figures 6.3 (LEFT) and (RIGHT), the first absorption peak slowly approaches the bulk bandgap, with a lowest peak at 4.06eV for the 24.8Å wire of Figure 6.3 (RIGHT). The peak shifts are slightly larger, being 0.10eV and 0.07eV for positive and negative field directions respectively. The third peak in the spectrum is found to be degenerate. The oscillations of the FK effect is such that the stronger, second half-peak of the field-free system actually becomes the weaker in the presence of the field.

### 6.3 The F-K effect in carbon nanotubes

The same approach is taken in the article of appendix D, for the calculation of the FK effect in a special type of carbon nanotubes (CNT) known as armchair CNT’s [116]. It combines an analytical and numerical approach to the problem using a simple $\pi$-electron TB model [117]. It focuses on the quadratic electro-optic effect to facilitate the analytic modelling.

Expanding the susceptibility in terms of the field $F$ yields

$$\chi(\omega) = \chi^{(1)}(\omega) + F\chi^{(2)}(\omega) + F^2\chi^{(3)}(\omega) + F^3\chi^{(4)}(\omega) + O(F^4).$$

(6.5)

In an armchair carbon nanotube, unlike the previously treated ZnO wires, the odd coefficients such as $\chi^{(2)}$ and $\chi^{(4)}$, are zero due to symmetry. This leaves $\chi^{(3)}(\omega)$ the first field dependent term, and this contribution is known as the quadratic electro-optic (QEO) effect.
In a $\pi$-type tight-binding scheme, $\chi^{(3)}(\omega)$ can be calculated analytically in the low-field limit, with the method of Aspnes and Rowe [118]. The expressions are presented in full in the article in terms of the inter-band gaps, and the effective electron mass associated with each gap.

Examples of the analytically obtained $\chi^{(3)}(\omega)$ for various CNT’s are shown in Figure 6.4, calculated with a broadening of $\hbar\Gamma = 0.15\text{eV}$. The tubes are defined by parameters $(x, 0)$, where the wire radius increases for increasing $x$. The results show that while the first QEO peak does indeed increase with the tube diameter as reported by others [119], this does not hold true for the higher peaks. In stead, the degeneracy of bands and the band curvature seem to play the important role.

Numerically, the low-field quadratic electro-optic effect can be approximated by calculating $\Delta\chi(\omega) = \frac{\chi^{(3)}(\omega) - \chi^{(1)}(\omega)}{F^2}$ for a sufficiently small $F$. A comparison of the analytical result and the numerical one is given in figure 6.5. As is seen from the figure, there is very good agreement between the two approaches, supporting the analytical form. In the low field limit, there are no oscillations on the peak tail, as these stem from the higher order terms of (6.5) that vanish for small fields. But they do appear
Figure 6.6: The $\Delta \chi$ of figure 6.5, in a stronger field of $F = 5.5 \text{mV}/\text{Å}$. The oscillations above the bandgap are due to the higher-order terms in $\chi(\omega)$.

in the non-perturbative Franz-Keldysh regime at higher fields. An illustration hereof is seen in figure 6.6, where $\Delta \chi(\omega)$ has been calculated for $F = 5.5 \text{mV}/\text{Å}$. The oscillations are similar to those on the peak tails of the ZnO wire model, though in this case $\chi^{(1)}(\omega)$ has been removed.
This Ph.D. report presents both theoretical and experimental studies of zinc oxide (ZnO) nanostructures, with a special focus on nanowires. These are of interest, firstly as they are relatively easy to manufacture and mechanically quite stable, and secondly as their electronic properties have many likely applications both in the electronic and optical industry. As a large bandgap semiconductor the conductivity of zinc oxide nanostructures depends to a large degree on the surface electrons. This means that on one hand, one can control the conductivity of a ZnO nanowire by controlling the surface or the surroundings, and on the other that the conductivity can be used to identify the wire surroundings. In effect, the nanowire might work as a nanoscale adjustable resistor, as well as a nanoscale detector.

The optical consequences of the large bandgap is that ZnO interacts strongly with ultraviolet light, while the material is clear in the visible spectrum. ZnO nanostructures therefore have several promising applications, both in the field of solar cells and in transparent electronics.

The experimental work here presented treats the controlled growth of ZnO nanowires in a PVD process. The grown wires have been deposited on silicon wafers, and the second harmonic and multi-photon photoluminescence spectra have been measured and studied for varying wavelengths of incoming light. The wire response was found to differ significantly from that of bulk ZnO, as the second-harmonic signal strength had a peak-behaviour not found in the bulk.

The majority of the work lies in the theoretical treatment, where several different quantum mechanical methods have been applied to illuminate different aspects of the properties of ZnO nanostructures.

Mesoscopic nanowires and nanobelts have been studied in an effective mass electron model, subject to the physical properties of ZnO. The effect of donor impurities and the electronic confinement have been treated with both analytical methods and through numerical modelling, and from the electronic structure the optical spectra have been analysed as well. The absorption peaks were shown to split up when the wire cross section deviated from the perfect hexagon, and to diminish and shift with increasing electron density due to a change in the wire potential and a Pauli blockade.

A more complete quantum mechanical treatment of ZnO surfaces and wires was
presented using DFT and DFTB models. A PAW-DFT model was used to study the electronic properties of a ZnO surface, and the effect of surface adsorbates to the surface band structure. Hereby, it was illustrated how the adsorbed hydrogen shifted surface atoms, bound the surface electrons, and increased the bandgap. As DFT is limited to small systems due to calculation complexity, a SCC-DFTB model was presented. The versatility of the parametrisation was documented by studying the transferability to several test systems. The model was successfully used on the high-pressure rock salt phase of bulk ZnO, as well as wire and layer systems containing different atomic positions known to exist in ZnO nanostructures. The band structure of wurtzite ZnO was found to agree with experimental measurements of the valence band positions, as well as with the bandgap, and the model was applied to various nanowires to illustrate the effect of confinement, surface relaxation, and hydrogen termination of wire surfaces. Furthermore, a partially terminated wire presented conduction properties due to surplus Zn dangling bonds.

Finally, the optical properties of ZnO nanowires and carbon nanotubes in the presence of a strong electric field were studied using a tight-binding model. In the ZnO nanowires, the Franz-Keldysh effect was found to be directionally dependent due to the asymmetry of the wurtzite structure. Thus spectra for both field directions were presented. For the nanotubes, the quadratic electro-optic effect was studied separately in the low-field limit, and modelled both from an analytical approximation and a numerical implementation. The higher-order effects were illustrated numerically as well.

Though many goals have been achieved, an application of the DFTB model to a full relaxation of larger nanostructures, and a treatment of optical and conduction properties within this model, are still to come. Likewise, the scalability of the model encourages the study of different wire faces, different types and densities of surface adsorbates, and defects. But these are all interesting applications to pursue in the future.
I denne Ph.D. afhandling præsenteres både teoretiske og eksperimentelle undersøgelser af zinkoxid (ZnO) nanostrukturer, med specielt fokus på nanowires. Disse strukturer er interessante, da de for det første er forholdsvis lette at fremstille og meget mekanisk stabile, og for det andet har elektroniske egenskaber med flere anvendelsesmuligheder både i den elektroniske og optiske industri. Som kraftigt halvledende materiale afhænger zinkoxids ledningsevne på nanoskala i høj grad af elektronerne i materialets overflade. Dette betyder, at man på den ene side kan styre ledningsevnen ved at styre overfladen eller omgivelserne, og at man på den anden side kan bruge ledningsevnen til at identificere omgivelserne. Man har således en variabel modstand på nanometer skala, der kan fungere som detektor.

De optiske konsekvenser af denne elektroniske struktur er, at ZnO vekselvirker kraftigt med ultraviolet lys, mens materialet er næsten gennemsigtigt i det synlige spektrum. Nanostrukturerne har derfor flere lovende anvendelsesmuligheder, både indenfor solcelle-paneler og indenfor gennemsigtig elektronik.

Indenfor det eksperimentelle arbejde er der blevet dyrket ZnO nanostrukturer ved hjælp af en PVD proces. De dyrkede wires er studeret i opløsning og aflejret på silicium wafers, og spektre for andenharmonisk generation og multi-foton luminiscens er blevet målt og studeret. Den anden-harmoniske emission fra nanowirerne viste en markant anderledes intensitetfordeling end den man målte for et ZnO krystal under de samme forhold.

Størstedelen af arbejdet har ligget i den teoretiske behandling, hvor flere forskellige kvantemekaniske metoder er blevet anvendt til belysning af forskellige egenskaber ved ZnO nanostrukturer.


En mere fuldstændig kvantemekanisk behandling af ZnO overflader og wires blev


En naturlig fortsættelse af dette arbejde ville være en fuld relaxering af større nanolstrukturer i DFTB, samt en behandling af elektriske og optiske egenskaber i samme model. Tilsvarende åbner modellens gode skalering op for studier af flere overflader, forskellige typer og tætheder af overfladeadsorbater, og defekter. Perspektiverne for et videre studie af ZnO er derfor mange, og værd at forfolge i fremtiden.
Appendix A

Slater-Koster parameters

The tight-binding matrix elements of Slater and Koster [79] between two atoms depend on a small set of fixed parameters, as well as the positions of the atoms. In an orbital basis, the φ_i’s have the types s, p, d, f etc. defined by their angular momentum quantum number l. It was shown by Slater and Koster that the matrix element generated by arbitrarily located orbitals could be reduced to a limited number of parameters, by projections with respect to the connecting line between the atoms. Their initial work covered orbital types s, p and d, while f-orbital expressions were later included [120].

**Example:** Let φ_{i,α} be a p_x type orbital located at the origin and φ_{j,β} a p_x type at R as illustrated in figure A.1 (LEFT). Then \( R/|R| = (l, m, n) \) is the unit vector in the direction R.

Denote by \( \hat{P}_R \) the projector onto a p type orbital along the direction of R and by \( \hat{P}_{\perp R} \) the orthogonal projector. Then

\[
H_{\alpha\beta}^{\alpha\beta}_{p_x p_x} = \langle \phi_{i,\alpha} | \hat{H} | \phi_{j,\beta} \rangle = \langle \phi_{i,\alpha} | \hat{P}_R \hat{H} \hat{P}_R | \phi_{j,\beta} \rangle + \langle \phi_{i,\alpha} | \hat{P}_{\perp R} \hat{H} \hat{P}_{\perp R} | \phi_{j,\beta} \rangle = l^2 H_{pp\sigma}^{\alpha\beta}(R) + (1 - l^2) H_{pp\pi}^{\alpha\beta}(R),
\]

Figure A.1: LEFT: Two p_x orbitals located at the origin and at R respectively. RIGHT: The ppσ and ppπ projections of the orbitals onto the direction \( R/|R| \) between the two atoms.
with the parameters $H_{\sigma \sigma}^{\alpha \beta}(R)$ and $H_{\sigma \pi}^{\alpha \beta}(R)$ the energy integrals of the $\sigma$ and $\pi$ type bonding as illustrated in figure A.1 (RIGHT). The overlap integrals can be re-expressed in the exact same way, simply substituting $H_{\sigma \sigma}^{\alpha \beta}$ with $S_{\sigma \sigma}^{\alpha \beta}$ in the above calculation. The matrix elements between $s$, $p$ and $d$ orbitals in terms of the $\sigma$, $\pi$ and $\delta$ type bonding and the directional cosines are given in tables A.1 and A.2.

$$
H_{\sigma \sigma}^{\alpha \beta} = H_{\sigma \sigma}^{\alpha \beta}(R)
$$
$$
H_{\sigma \pi}^{\alpha \beta} = lH_{\sigma \pi}^{\alpha \beta}(R)
$$
$$
H_{\sigma \delta}^{\alpha \beta} = l^2H_{\sigma \delta}^{\alpha \beta}(R) + (1 - l^2)H_{\sigma \delta}^{\pi \pi}(R)
$$
$$
H_{\pi \pi}^{\alpha \beta} = lmH_{\pi \pi}^{\alpha \beta}(R) - lmH_{\pi \pi}^{\pi \pi}(R)
$$
$$
H_{\pi \delta}^{\alpha \beta} = lnH_{\pi \delta}^{\alpha \beta}(R) - lnH_{\pi \delta}^{\pi \pi}(R)
$$
$$
H_{\delta \delta}^{\alpha \beta} = \sqrt{3}lmH_{\delta \delta}^{\alpha \beta}(R)
$$
$$
H_{\delta \delta}^{\alpha \beta} = \frac{1}{2}\sqrt{3}(l^2 - m^2)H_{\delta \delta}^{\alpha \beta}(R)
$$
$$
H_{\delta \delta}^{\alpha \beta} = (n^2 - \frac{1}{2}(l^2 + m^2))H_{\delta \delta}^{\alpha \beta}(R)
$$
$$
H_{\sigma \sigma}^{\alpha \beta} = \sqrt{3}l^2mH_{\sigma \sigma}^{\alpha \beta}(R) + m(1 - 2l^2)H_{\sigma \pi}^{\alpha \beta}(R)
$$
$$
H_{\sigma \delta}^{\alpha \beta} = \sqrt{3}mnH_{\sigma \delta}^{\alpha \beta}(R) - 2mnH_{\sigma \pi}^{\alpha \beta}(R)
$$
$$
H_{\pi \pi}^{\alpha \beta} = \sqrt{3}lnH_{\pi \pi}^{\alpha \beta}(R) + n(1 - 2l^2)H_{\pi \pi}^{\alpha \beta}(R)
$$
$$
H_{\pi \delta}^{\alpha \beta} = \frac{1}{2}\sqrt{3}(l^2 - m^2)H_{\pi \delta}^{\alpha \beta}(R) + l(1 - l^2)H_{\pi \pi}^{\alpha \beta}(R)
$$
$$
H_{\delta \delta}^{\alpha \beta} = \frac{1}{2}\sqrt{3}ln(l^2 - m^2)H_{\delta \delta}^{\alpha \beta}(R) - m(1 + l^2 - m^2)H_{\delta \pi}^{\alpha \beta}(R)
$$
$$
H_{\sigma \sigma}^{\alpha \beta} = n(l^2 - \frac{1}{2}(l^2 + m^2))H_{\sigma \pi}^{\alpha \beta}(R) - \sqrt{3}mnH_{\pi \pi}^{\alpha \beta}(R)
$$
$$
H_{\sigma \delta}^{\alpha \beta} = m(n^2 - \frac{1}{2}(l^2 + m^2))H_{\sigma \delta}^{\alpha \beta}(R) - \sqrt{3}mnH_{\pi \pi}^{\alpha \beta}(R)
$$
$$
H_{\pi \pi}^{\alpha \beta} = n(m^2 - \frac{1}{2}(l^2 + m^2))H_{\pi \pi}^{\alpha \beta}(R) + \sqrt{3}lm(l^2 + m^2)H_{\pi \pi}^{\alpha \beta}(R)
$$
$$
H_{\delta \delta}^{\alpha \beta} = 3l^2m^2H_{\delta \delta}^{\alpha \beta}(R) + (l^2 + m^2 - 4l^2m^2)H_{dd\pi}^{\alpha \beta}(R)
$$
$$
+ (n^2 + l^2m^2)H_{\delta \delta}^{\alpha \beta}(R)
$$
$$
H_{\sigma \sigma}^{\alpha \beta} = 3lmH_{\sigma \sigma}^{\alpha \beta}(R) + ln(4mn)H_{\sigma \pi}^{\alpha \beta}(R) + ln(m^2 - 1)H_{\sigma \pi}^{\alpha \beta}(R)
$$
$$
H_{\sigma \delta}^{\alpha \beta} = 3lnH_{\sigma \delta}(R) + mn(1 - 4l^2)H_{\sigma \pi}^{\alpha \beta}(R) + mn(l^2 - 1)H_{\sigma \pi}^{\alpha \beta}(R)
$$
$$
+ \frac{1}{2}ln(l^2 - m^2)H_{\delta \delta}^{\alpha \beta}(R)
$$
$$
H_{\pi \pi}^{\alpha \beta} = \frac{1}{2}ln(l^2 - m^2)H_{\delta \delta}^{\alpha \beta}(R) - mn(1 + 2(l^2 - m^2))H_{\pi \pi}^{\alpha \beta}(R)
$$
$$
+ mn(1 + \frac{1}{2}(l^2 - m^2))H_{\delta \delta}^{\alpha \beta}(R)
$$

<table>
<thead>
<tr>
<th>Table A.1: Tight-binding matrix elements, part I.</th>
</tr>
</thead>
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---
\[
H_{d_{x^2-y^2}d_{x^2-y^2}}^{\alpha\beta} = \frac{3}{2}nl(l^2 - m^2)H_{dd\sigma}(R) + nl(1 - 2(l^2 - m^2))H_{dd\sigma}(R)
\]
\[
- nl(1 - \frac{1}{2}(l^2 - m^2))H_{dd\sigma}(R)
\]
\[
H_{d_{x^2-y^2}d_{x^2-y^2}}^{\alpha\beta} = \sqrt{3}lm(n^2 - \frac{1}{2}(l^2 + m^2))^2 - \frac{1}{2}dd\sigma(R) - 2\sqrt{3}lmn^2H_{dd\sigma}(R)
\]
\[
+ \frac{1}{2}\sqrt{3}lm(1 + n^2)H_{dd\sigma}(R)
\]
\[
+ \frac{1}{2}\sqrt{3}mn(l^2 - m^2)H_{dd\pi}(R)
\]
\[
- \frac{1}{2}\sqrt{3}mn(l^2 + m^2)H_{dd\delta}(R)
\]
\[
H_{d_{x^2-y^2}d_{x^2-y^2}}^{\alpha\beta} = \sqrt{3}ln(n^2 - \frac{1}{2}(l^2 + m^2))^2 - \frac{1}{2}dd\sigma(R) + \frac{1}{2}\sqrt{3}ln(l^2 + m^2 - n^2)H_{dd\sigma}(R)
\]
\[
- \frac{1}{2}\sqrt{3}ln(l^2 - m^2)H_{dd\sigma}(R)
\]
\[
H_{d_{x^2-y^2}d_{x^2-y^2}}^{\alpha\beta} = \sqrt{3}ln(n^2 - \frac{1}{2}(l^2 + m^2))^2 - \frac{1}{2}dd\sigma(R) + \frac{1}{2}\sqrt{3}ln(l^2 + m^2 - n^2)H_{dd\sigma}(R)
\]
\[
- \frac{1}{2}\sqrt{3}ln(l^2 - m^2)H_{dd\sigma}(R)
\]
\[
H_{d_{x^2-y^2}d_{x^2-y^2}}^{\alpha\beta} = \frac{1}{2}(l^2 - m^2)^2H_{dd\sigma}(R) + (l^2 + m^2 - (l^2 - m^2)^2)H_{dd\sigma}(R)
\]
\[
+ (n^2 + \frac{1}{2}(l^2 - m^2)^2)H_{dd\sigma}(R)
\]
\[
H_{d_{x^2-y^2}d_{x^2-y^2}}^{\alpha\beta} = \frac{1}{2}\sqrt{3}(l^2 - m^2)(n^2 - \frac{1}{2}(l^2 + m^2))H_{dd\sigma}(R)
\]
\[
+ \sqrt{3}ln(m^2 - l^2)H_{dd\sigma}(R)
\]
\[
+ \sqrt{3}lm(1 + n^2)(l^2 - m^2)H_{dd\sigma}(R)
\]
\[
+ \frac{1}{2}\sqrt{3}ln(l^2 + m^2 - n^2)H_{dd\sigma}(R)
\]
\[
+ \frac{1}{2}\sqrt{3}ln(l^2 - m^2)H_{dd\sigma}(R)
\]

Table A.2: Tight-binding matrix elements, part II.
Appendix B

Slater-Koster integrals

In the DFTB approach, the tight binding matrix elements are not simply expressed in terms of a set of fixed constants. Instead, the former constants become radially dependent, and are determined as integrals over the Slater type basis functions. The Slater-Koster symmetries are still in effect, however, so an integral for each of the σ, π and δ type bonds between each type of orbital i sufficient.

An example of the integrations, and a list of the integrals for s, p and d type orbitals, are given in the following.

B.1 Example: The $sp\sigma$ integrals

We take as an example the Hamiltonian and overlap terms of an $s$-type orbital $\chi_s$ located at the origin and a $p$-type orbital $\chi_p$ located at the distance $R$ along the $z$-axis and oriented along the same axis. This is the $sp\sigma$ configuration in TB.

The overlap term is given by

$$S_{sp\sigma}(R) = \int Y_{00}(\Omega_r)e^{-b_1 r^2} |\mathbf{r} - \mathbf{R}| Y_{10}(\Omega_{R-r})e^{-b_2 (\mathbf{r} - \mathbf{R})^2} d^3 \mathbf{r},$$

with $r$ and $\Omega_r$ denoting the length and angles of vector $\mathbf{r}$ respectively. To treat this expression some series expansions of the orbital at $\mathbf{R}$ are needed [121]. The Gaussian part can be rewritten

$$\exp\{-\alpha |\mathbf{r} - \mathbf{R}|^2\} = 4\pi \exp\{-\alpha (r^2 + R^2)\} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l (2\alpha r R) Y_{lm}(\Omega_r) Y_{lm}^*(\Omega_{R}),$$

with $i^l (2\alpha r R)$ a modified spherical Bessel function. The angular term is expanded

$$|\mathbf{r} - \mathbf{R}|^l Y_{LM}(\Omega_{\mathbf{r} - \mathbf{R}}) = \sum_{l_1,l_2=0}^{L} \delta_{l_1+l_2, L} G(l_1, l_2, L) \times$$

$$\sum_{m_1, m_2} \langle l_1 l_2 m_1 m_2 |LM\rangle r^{l_1} Y_{l_1 m_1}(\Omega_r) R^{l_2} Y_{l_2 m_2}(\Omega_{\mathbf{R}}),$$

(B.3)
with \( \langle l_1 l_2 m_1 m_2 | LM \rangle \) a Clebsch-Gordan coefficient and
\[
G(l_1, l_2, L) = (-1)^{l_2} \left( \frac{4\pi (2L + 1)!}{(2l_1 + 1)!(2l_2 + 1)!} \right)^{1/2}.
\] (B.4)

From (B.3) it follows that
\[
|r - R| Y_{10}(\Omega_{r-R}) = r Y_{10}(\Omega_r) - \sqrt{\frac{3}{4\pi}} R,
\] (B.5)
as all but two of the Clebsch-Gordan coefficients are zero. Consequently the overlap integral is rewritten
\[
S_{spsp}(R) = \int Y_{60}(\Omega_r) e^{-b_1 r^2} \left( r Y_{10}(\Omega_r) - \sqrt{\frac{3}{4\pi}} R \right) 4\pi \times
\]
\[
\exp\{-\alpha(r^2 + R^2)\} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i_l(2\alpha r R) Y_{lm}(\Omega_r) Y_{lm}^*(\Omega_R) d^3r.
\] (B.6)
The orthogonality of spherical harmonics ensure that only the two terms survive, and performing the angular integration \( S_{spsp}(R) \) reduces to
\[
S_{spsp}(R) = \sqrt{3} e^{-b_2 R} \int r^3 e^{-(b_1 + b_2)r^2} i_1(2b_2 r) dr
-
\sqrt{3} Re^{-b_2 R} \int r^3 e^{-(b_1 + b_2)r^2} i_0(2b_2 r) dr.
\] (B.7)
As \( i_0(x) = \frac{\sinh x}{x} \) and \( i_1(x) = \frac{x \cosh x - \sinh x}{x^2} \) the integral can be performed analytically, giving
\[
S_{spsp}(R) = -\sqrt{3\pi} \frac{b_1 R}{4 \left(b_1 + b_2\right)^{5/2}} \exp\left(-\frac{b_1 b_2 R^2}{b_1 + b_2}\right).
\] (B.8)

The Hamiltonian matrix element is given from (3.32) in the Dirac notation by
\[
H_{spsp}(R) = \langle \chi_s | E_s + E_p + \frac{1}{2} \nabla^2 - \left(\frac{r}{r_s}\right)^2 - \left(\frac{r - R}{r_p}\right)^2 | \chi_p \rangle.
\] (B.9)

The \( \left(\frac{r}{r_s}\right)^2 \) term simply introduces a higher power of \( r \) in the integrals of (B.7), while the \( \left(\frac{r - R}{r_p}\right)^2 \) integral after a change of origin can be treated as well. After some calculations similar to those of \( S_{spsp} \), the terms are expressed
\[
\langle \chi_s | r^2 | \chi_p \rangle = -\sqrt{3\pi} \frac{R(3b_2 + 2b_1 + b_2)}{4 \left(b_1 + b_2\right)^{7/2}} \exp\left(-\frac{b_1 b_2 R^2}{b_1 + b_2}\right),
\] (B.10)
\[
\langle \chi_s | (r - R)^2 | \chi_p \rangle = -\sqrt{3\pi} \frac{R(5b_2 + b_1 + 5b_2 R)}{8 \left(b_1 + b_2\right)^{9/2}} \exp\left(-\frac{b_1 b_2 R^2}{b_1 + b_2}\right).
\] (B.11)

From a direct calculation \( \nabla^2 | \chi_s \rangle = (4b_1^2 r^2 - 6b_1) | \chi_s \rangle \), and the Laplacian term can be expressed in terms of (B.7) and (B.10) as
\[
\langle \chi_s | \nabla^2 | \chi_p \rangle = 4b_1^2 \langle \chi_s | r^2 | \chi_p \rangle - 6b_1 S_{spsp}(R),
\] (B.12)
The \( E_s \) and \( E_p \) terms of (B.9) are simply the overlap integral times the energies.
B.2 List of integrals

Introducing the notation:

\[ H_{12} = \langle \chi_1 | E_1 + E_2 + \frac{1}{2} \nabla^2 + \left( \frac{r}{r_{c1}} \right)^2 + \left( \frac{r - R}{r_{c1}} \right)^2 | \chi_2 \rangle \]

\[ = (E_1 + E_2) S_{12} + H_{12}^s + \frac{1}{r_{c1}} H_{12}^p + \frac{1}{r_{c2}} H_{12}^{R-r}, \]  

(B.13)

the calculated matrix-element terms for s, p and d type orbitals are given in the list below. Note that for symmetry reasons the \( H^p \) and \( H^{R-r} \) contributions are the same for similar orbitals.

The \( ss\sigma \) case:

\[ S_{ss\sigma} = \frac{e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{4(b_1 + b_2)^{3/2}} \sqrt{\pi} \]  

(B.14)

\[ H_{ss\sigma}^p = \frac{e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{8(b_1 + b_2)^{3/2}} \sqrt{\pi} (3b_1^2 + b_2^2 (3 + 2b_2 R^2)) \]

\[ H_{ss\sigma}^{R-r} = H_{ss\sigma}^p \]

\[ H_{ss\sigma}^\Delta = \frac{b_1 b_2 e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{4(b_1 + b_2)^{3/2}} \sqrt{\pi} (-3(b_1 + b_2) + 2b_1 b_2 R^2) \]

The \( sp\sigma \) case:

\[ S_{sp\sigma} = -\frac{b_1 e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{4(b_1 + b_2)^{3/2}} \sqrt{\pi} R \]  

(B.15)

\[ H_{sp\sigma}^p = -\frac{e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{8(b_1 + b_2)^{3/2}} \sqrt{\pi} R (3b_1^2 - 2b_2^2 + b_1 b_2 (1 + 2b_2 R^2)) \]

\[ H_{sp\sigma}^{R-r} = -\frac{b_1 e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{8(b_1 + b_2)^{3/2}} \sqrt{\pi} R (5b_1 + 5b_2 + 2b_1^2 R^2) \]

\[ H_{sp\sigma}^\Delta = -\frac{b_1 b_2 e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{4(b_1 + b_2)^{3/2}} \sqrt{\pi} R (-5(b_1 + b_2) + 2b_1 b_2 R^2) \]

The \( pp\sigma \) case:

\[ S_{pp\sigma} = \frac{3e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{8(b_1 + b_2)^{3/2}} \sqrt{\pi} (b_1 + b_2 - 2b_1 b_2 R^2) \]  

(B.16)

\[ H_{pp\sigma}^p = \frac{3e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{16(b_1 + b_2)^{11/2}} \sqrt{\pi} (5(b_1 + b_2)^2 - 2(5b_1 - 3b_2) b_2 (b_1 + b_2) R^2 - 4b_1^2 b_2^3 R^4) \]

\[ H_{pp\sigma}^{R-r} = H_{pp\sigma}^p \]

\[ H_{pp\sigma}^\Delta = \frac{3b_1 b_2 e^{-\frac{\lambda_1 \lambda_2 R^2}{3}}}{8(b_1 + b_2)^{11/2}} \sqrt{\pi} (-5(b_1 + b_2)^2 + 16b_1 b_2 (b_1 + b_2) R^2 - 4b_1^2 b_2^3 R^4) \]
The $pp\pi$ case:

\[
S_{pp\pi} = \frac{3e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}}}{8(b_1 + b_2)^{5/2}}, \quad (B.17)
\]
\[
H'_{pp\pi} = \frac{3e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{\pi} (5b_1 + b_2 (5 + 2b_2 R^2))}{16(b_1 + b_2)^{9/2}},
\]
\[
H^{R-r}_{pp\pi} = H'^r_{pp\pi},
\]
\[
H^{\Delta}_{pp\pi} = \frac{3b_1 b_2 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{\pi} (-5(b_1 + b_2) + 2b_1 b_2 R^2)}{8(b_1 + b_2)^{9/2}}.
\]

The $sd\sigma$ case:

\[
S_{sd\sigma} = \frac{b_1^2 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{5\pi} R^2}{4(b_1 + b_2)^{7/2}}, \quad (B.18)
\]
\[
H'^r_{sd\sigma} = \frac{b_1 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{5\pi} R^2 (3b_1^2 - 4b_1^2 + b_1 b_2 (-1 + 2b_2 R^2))}{8(b_1 + b_2)^{11/2}},
\]
\[
H^{R-r}_{sd\sigma} = \frac{b_1^2 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{5\pi} R^2 (7b_1 + 7b_2 + 2b_2 R^2)}{8(b_1 + b_2)^{11/2}},
\]
\[
H^{\Delta}_{sd\sigma} = \frac{b_1^3 b_2 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{5\pi} R^2 (-7(b_1 + b_2) + 2b_1 b_2 R^2)}{4(b_1 + b_2)^{11/2}}.
\]

The $pd\sigma$ case:

\[
S_{pd\sigma} = \frac{b_1 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{15\pi} R (-b_2 + b_1 (-1 + b_2 R^2))}{4(b_1 + b_2)^{9/2}}, \quad (B.19)
\]
\[
H'^r_{pd\sigma} = \frac{e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{15\pi} R ((b_1 + b_2)^2 (-5b_1 + 2b_2) + b_1 (5b_1 - 6b_2) b_2 b_1 + b_1 b_2 R^2 + 2b_1^2 b_2 R^4)}{8(b_1 + b_2)^{13/2}},
\]
\[
H^{R-r}_{pd\sigma} = \frac{b_1 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{15\pi} R (-7(b_1 + b_2)^2 - b_1 (4b_1 - 7b_2) b_2 (b_1 + b_2) R^2 + 2b_1^2 b_2 R^4)}{8(b_1 + b_2)^{13/2}} \times
\]
\[
H^{\Delta}_{pd\sigma} = \frac{b_1^2 b_2 e^{-\frac{b_1 b_2 R^2}{\pi (b_1 + b_2)^{5/2}}} \sqrt{15\pi} R (7(b_1 + b_2)^2 - 11b_1 b_2 (b_1 + b_2) R^2 + 2b_1^2 b_2 R^4)}{4(b_1 + b_2)^{13/2}}.
\]
The $pd\pi$ case:

$$S_{pd\pi} = \frac{3b_1 e^{-\frac{b_1 R^2}{b_1^2 + b_2^2}} \sqrt{3\pi} R}{8(b_1 + b_2)^{7/2}}, \quad (B.20)$$

$$H_{pd\pi}^r = \frac{3e^{-\frac{b_1 R^2}{b_1^2 + b_2^2}} \sqrt{3\pi} R (5b_1^2 - 2b_2^2 + b_1b_2 (3 + 2b_2 R^2))}{16(b_1 + b_2)^{11/2}},$$

$$H_{pd\pi}^{R-r} = \frac{3b_1 e^{-\frac{b_1 R^2}{b_1^2 + b_2^2}} \sqrt{3\pi} R (7b_1 + 7b_2 + 2b_2 R^2)}{16(b_1 + b_2)^{11/2}},$$

$$H_{pd\pi}^\Delta = \frac{3b_1^2 b_2 e^{-\frac{b_1 R^2}{b_1^2 + b_2^2}} \sqrt{3\pi} R (-7(b_1 + b_2) + 2b_1 b_2 R^2)}{8(b_1 + b_2)^{11/2}}.$$

The $dd\sigma$ case:

$$S_{dd\sigma} = \frac{5e^{-\frac{b_1 R^2}{b_1^2 + b_2^2}} \sqrt{\pi} (3(b_1 + b_2)^2 - 8b_1 b_2 (b_1 + b_2) R^2 + 4b_1^2 b_2^2 R^4)}{16(b_1 + b_2)^{11/2}}, \quad (B.21)$$

$$H_{dd\sigma}^r = \frac{5e^{-\frac{b_1 R^2}{b_1^2 + b_2^2}} \sqrt{\pi} (21(b_1 + b_2)^3 + 2b_2(b_1 + b_2)^2 (-28b_1 + 11b_2) R^2 + + 4b_1 (7b_1 - 8b_2) b_2^2 (b_1 + b_2) R^4 + 8b_1^2 b_2^2 R^6)}{32(b_1 + b_2)^{13/2}},$$

$$H_{dd\sigma}^{R-r} = H_{dd\sigma}^r,$$

$$H_{dd\sigma}^\Delta = \frac{5b_1 b_2 e^{-\frac{b_1 R^2}{b_1^2 + b_2^2}} \sqrt{\pi} (-21(b_1 + b_2)^3 + 78b_1 b_2 (b_1 + b_2)^2 R^2 - -60b_1 b_2^2 (b_1 + b_2) R^4 + 8b_1^2 b_2^2 R^6)}{16(b_1 + b_2)^{15/2}}.$$

The $dd\pi$ case:

$$S_{dd\pi} = \frac{15e^{-\frac{b_1 b_2 R^2}{b_1^2 + b_2^2}} \sqrt{\pi} (b_1 + b_2 - 2b_1 b_2 R^2)}{16(b_1 + b_2)^{9/2}}, \quad (B.22)$$

$$H_{dd\pi}^r = \frac{15e^{-\frac{b_1 b_2 R^2}{b_1^2 + b_2^2}} \sqrt{\pi} (7(b_1 + b_2)^2 - 2(7b_1 - 3b_2) b_2 (b_1 + b_2) R^2 - 4b_1^2 b_2^2 R^4)}{32(b_1 + b_2)^{11/2}},$$

$$H_{dd\pi}^{R-r} = H_{dd\pi}^r,$$

$$H_{dd\pi}^\Delta = \frac{15b_1 b_2 e^{-\frac{b_1 b_2 R^2}{b_1^2 + b_2^2}} \sqrt{\pi} (-7(b_1 + b_2)^2 + 20b_1 b_2 (b_1 + b_2) R^2 - 4b_1^2 b_2^2 R^4)}{16(b_1 + b_2)^{13/2}}.$$
The $dd\delta$ case:

\[
S_{dd\delta} = \frac{15 e^{-\frac{b_1 b_2 R^2}{b_1 + b_2}} \sqrt{\pi}}{16 (b_1 + b_2)^{7/2}},
\]

\[
H_{dd\delta}^r = \frac{15 e^{-\frac{b_1 b_2 R^2}{b_1 + b_2}} \sqrt{\pi} (7b_1 + b_2 (7 + 2b_2 R^2))}{32 (b_1 + b_2)^{11/2}},
\]

\[
H_{dd\delta}^{r-r} = H_{dd\delta}^r,
\]

\[
H_{dd\delta}^{s} = \frac{15 b_1 b_2 e^{-\frac{b_1 b_2 R^2}{b_1 + b_2}} \sqrt{\pi} (-7(b_1 + b_2) + 2b_1 b_2 R^2)}{16 (b_1 + b_2)^{11/2}}.
\]
Appendix C

The optical susceptibility

The optical properties of a material can be expressed through the dielectric function \( \epsilon(\omega) \), or the susceptibility function \( \chi(\omega) \), of the material. Expressions for these can be calculated from a quantum mechanical viewpoint by treating the time dependent Schrödinger equation in the presence of an electric field \([63, 122, 123]\). Introducing a monochromatic linearly polarized electric field

\[
E = E_0 \cos \omega t, \tag{C.1}
\]

the time-dependent Schrödinger equation is written

\[
i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi, \tag{C.2}
\]

where \( \hat{H} = \hat{H}^0 + \hat{H}^\omega \), and \( \hat{H}^0 \) in the decoupled case is the Hamiltonian of equation 3.6. In the dipole-approximation the perturbation is written \([122]\)

\[
\hat{H}^\omega = -\mathbf{\mu} \cdot \mathbf{E}_0 \cos \omega t, \tag{C.3}
\]

with the electric dipole moment operator given by

\[
\mathbf{\mu} = -e \mathbf{r}, \ e > 0.
\]

In a system of multiple particles \( \mathbf{r} = \sum_{i=1}^{N} \mathbf{r}_i \), the sum of all particle position vectors. The average dipole moment is calculated

\[
\mathbf{p} = \int \psi^* \mathbf{\mu} \psi d^3r, \tag{C.4}
\]

where \( \psi \) is the solution to (C.2).

For \( \mathbf{E}_0 = 0 \) the stationary solutions \( \psi_n(\mathbf{r}, t) = \varphi_n(\mathbf{r})e^{-i\omega t} \) form a complete set, in which the general solution can be expanded

\[
\psi = \sum_n a_n(t)\varphi_n(\mathbf{r})e^{-i\omega t} \tag{C.5}
\]
Inserting this superposition in the Schrödinger equation,
\[ i\hbar \sum_n \dot{a}_n(t) \varphi_n(r)e^{-iE_n t / \hbar} + \sum_n E_n a_n(t) \varphi_n(r)e^{-iE_n t / \hbar} = \]
\[ \sum_n H^0 a_n(t) \varphi_n(r)e^{-iE_n t / \hbar} + \sum_n H^\omega a_n(t) \varphi_n(r)e^{-iE_n t / \hbar}. \]
As \( \varphi_n \) satisfies \( H^0 \varphi_n = E_n \varphi_n \) the two of the terms cancel, whereby
\[ i\hbar \sum_n \dot{a}_n(t) \varphi_n(r)e^{-iE_n t / \hbar} = \sum_n H^\omega a_n(t) \varphi_n(r)e^{-iE_n t / \hbar}. \]

By orthogonality of the basis functions
\[ i\hbar \dot{a}_m(t)e^{-iE_m t / \hbar} = \sum_n a_n(t) H^\omega_{mn} e^{i\omega_{mn} t}, \] with the matrix elements
\[ H^\omega_{mn} = \int \varphi_m^*(r) H^\omega \varphi_n(r) d^3r. \] (C.6)

Introducing the Bohr frequency \( \omega_{mn} = \frac{E_m - E_n}{\hbar} \), the coefficients satisfy
\[ \dot{a}_m(t) = \frac{1}{i\hbar} \sum_n a_n(t) H^\omega_{mn} e^{i\omega_{mn} t}, \]
and by integration
\[ a_m(t) = a_m(-\infty) + \frac{1}{i\hbar} \int_{-\infty}^t \sum_n a_n(t') H^\omega_{mn} e^{i\omega_{mn} t'} dt'. \] (C.7)

As the solutions to the time dependent problem depends on the strength of the electric field \( E \), the coefficients can be Taylor expanded in the field.
\[ a_m(t) = a^{(0)}_m(t) + a^{(1)}_m(t) + a^{(2)}_m(t) + \ldots \] (C.8)
where each \( a^{(p)}_m(t) \) is proportional to \( (E_0)^p \). Similarly \( H^\omega \propto E_0 \), so each term of the above sum must satisfy
\[ a^{(p)}_m(t) = a^{(p)}_m(-\infty) + \frac{1}{i\hbar} \int_{-\infty}^t \sum_n a^{(p-1)}_n(t') H^\omega_{mn} e^{i\omega_{mn} t'} dt'. \] (C.9)

In linear optics, the coefficients are approximated to be linear in \( E_0 \), that is \( a_m(t) \approx a^{(0)}_m(t) + a^{(1)}_m(t) \). This approximation will be used in the following.

In the unperturbed system \( a_m = a^{(0)}_m \), as \( E_0 = 0 \), and assuming that the system is in the ground state \( a_0 = 1 \), while \( a_m = 0 \) for \( m \neq 0 \). Applying the electric field at \( t = -\infty \) these are the starting conditions and it follows that
\[ a^{(1)}_m(t) = a^{(1)}_m(-\infty) + \frac{1}{i\hbar} \int_{-\infty}^t a^{(0)}_n(t') H^\omega_{mn} e^{i\omega_{mn} t'} dt' \]
\[ = \frac{1}{i\hbar} \int_{-\infty}^t H^\omega_{mn} e^{i\omega_{mn} t'} dt'. \]
Introducing $H_{mn} = e r_{mn} \cdot E_0 \cos \omega t$, the expression can be rewritten

$$a^{(1)}_m(t) = \frac{e}{i\hbar} r_{m0} \cdot E_0 \int_{-\infty}^{t} \cos \omega t' e^{i \omega_{m0} t'} dt'$$

$$= \frac{e}{2i\hbar} r_{m0} \cdot E_0 \int_{-\infty}^{t} \left( e^{i (\omega_{m0} + \omega) t'} + e^{i (\omega_{m0} - \omega) t'} \right) dt'$$

$$= \frac{e}{2i\hbar} r_{m0} \cdot E_0 \left( \frac{e^{i (\omega_{m0} + \omega) t}}{i(\omega_{m0} + \omega)} + \frac{e^{i (\omega_{m0} - \omega) t}}{i(\omega_{m0} - \omega)} \right).$$

Re-expressing the polarisability in terms of the $a_m$’s,

$$p = \int \psi^* \mu \psi d^3r$$

$$= -e \sum_{n,m} a_n^*(t) a_m(t) \int \varphi_n^* r_{m0} \varphi_m e^{i \omega_{nm} t} d^3r$$

$$= -e \sum_{n,m} a_n^*(t) a_m(t) \exp\{i \omega_{nm} t\} r_{nm}.$$ 

The zero order terms is given by

$$p^{(0)} = -e \sum_{n,m} (a_n^{(0)}(t))^* a_m^{(0)}(t) \exp\{i \omega_{nm} t\} r_{nm} = -e r_{00}. \quad (C.12)$$

This is the permanent dipole moment, as it is the only term independent of the applied field. Similarly we get for the first order term

$$p^{(1)} = -e \sum_{n,m} (a_n^{(0)}(t))^* a_m^{(1)}(t) \exp\{i \omega_{nm} t\} r_{nm} - e \sum_{n,m} (a_n^{(1)}(t))^* a_m^{(0)}(t) \exp\{i \omega_{nm} t\} r_{nm}$$

$$= -e \sum_{n,m} a_n^{(1)}(t) \exp\{i \omega_{nm} t\} r_{0n} - e \sum_{n} (a_n^{(1)}(t))^* \exp\{-i \omega_{nm} t\} r_{0n}$$

$$= -e \sum_{n} a_n^{(1)}(t) \exp\{-i \omega_{nm} t\} r_{0n} + c.c. \quad (C.13)$$

where $c.c.$ stands for the complex conjugate. In terms of the derived values of $a_n$,

$$p^{(1)} = \frac{e^2}{2\hbar} \sum_{n} r_{0n} \cdot E_0 \left( \frac{\exp\{i \omega t\}}{\omega_{n0} + \omega} + \frac{\exp\{-i \omega t\}}{\omega_{n0} - \omega} \right) r_{0n} + c.c. \quad (C.14)$$

As the macroscopic quantity connecting the polarization $P(\omega)$ and the electric field is the susceptibility tensor $\chi(\omega)$,

$$P(\omega) = \epsilon_0 \frac{\chi(\omega)}{\omega} E_0, \quad (C.15)$$
and the polarization is the electric dipole moment per volume $\Omega$, it appears from (C.14) as

$$\vec{\chi}(\omega) = \frac{e^2}{\epsilon_0 \hbar \Omega} \sum_n \left[ \frac{r_{n0}r_{0n}}{\omega_{n0} - \omega} + \frac{r_{n0}^*r_{0n}^*}{\omega_{n0} + \omega} \right]$$

(C.16)

$$= \frac{e^2}{\epsilon_0 \Omega} \sum_n \left[ \frac{r_{n0}r_{0n}^*}{E_{n0} - \hbar \omega} + \frac{r_{n0}^*r_{0n}}{E_{n0} + \hbar \omega} \right].$$

Now only two corrections are needed. In a decoupled electronic system, with $N$ occupied states, the sum runs over position matrix elements between occupied and unoccupied states. Additionally, there are inevitably internal losses, which appears as a dampening of the electric field. With a dampening term $\Gamma$ we get

$$\vec{\chi}(\omega) = \frac{e^2}{\epsilon_0 \Omega} \sum_{n=1}^N \sum_{m>N} \left[ \frac{r_{mn}r_{mn}^*}{E_{mn} - \hbar \omega - i\hbar \Gamma} + \frac{r_{mn}^*r_{mn}}{E_{mn} + \hbar \omega + i\hbar \Gamma} \right].$$

(C.17)

In a system of temperature $T > 0$, the sum over occupied and unoccupied levels can instead be expressed in the form of Fermi functions $f_F(E)$, and the susceptibility becomes [63]

$$\vec{\chi}(\omega) = \frac{e^2}{\epsilon_0 \Omega} \sum_{m,n} (f(E_m) - f(E_n)) \frac{r_{mn}r_{mn}^*}{E_{mn} - \hbar \omega - i\hbar \Gamma}.$$  

(C.18)
References


[73] “Open-source pseudopotential interface and unification module.”


Appendix D

“Theoretical study of quadratic electro-optic effect in semiconducting zigzag carbon nanotubes”
Theoretical study of quadratic electro-optic effect in semiconducting zigzag carbon nanotubes

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Using the perturbation treatment developed by Aspnes and Rowe [Phys. Rev. B 5, 4022 (1972)], an analytic expression for the third-order nonlinear optical susceptibility \( \chi^{(3)}(\omega; 0, 0, 0) \) is computed and analyzed for single walled zigzag carbon nanotubes. By improving their method, our calculations based on a tight-binding model take into account the transitions between all pairs of valence and conduction bands and thereby the contributions to the third-order susceptibility associated with different energy bands are investigated. With increasing radius of the nanotube, a nonmonotous increase of the quadratic electro-optic effect has been demonstrated except for the fundamental peak. The nonuniformity is a result of the overlap between two energy bands as well as the reduced effective masses associated with each pair of conduction and valence bands. A nonperturbative numerical calculation is applied to obtain the high-field response as well as to assess the applicability of the low-field perturbation expression.

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I. INTRODUCTION

The physical properties of carbon nanotubes (CNs), as quasi-one-dimensional systems, have been intensively studied theoretically and experimentally.1–8 Of considerable interest are the nonlinear optical (NLO) properties of semicon-ductor CNs not only because the nonlinear spectrum gives information on their electronic structure but also in view of the possible device applications. Along with third-harmonic generation, electro-optic (EO) or dc Kerr effect studies have been used to investigate the origins of the optical nonlinearities in CNs as well as CN-based composite materials. Several experimental results on the NLO properties of CNs have been reported so far9–14 and some papers have studied theoretically the third-order nonlinear optical susceptibility and EO effect in semiconducting CNs.15–19 All previous theoretical approaches to NLO properties in CNs are based on numerical calculations and rely on the two-band approximation. In this paper, we derive an analytic expression for the third-order nonlinear optical susceptibility of semiconducting zigzag CNs in the presence of a uniform electric field directed along the nanotube axis. Our calculations are based on a tight-binding model and include all energy bands of the semiconducting zigzag CNs. Therefore, it is possible to study closely the contribution to the quadratic electro-optic (QEO) effect from different energy bands. The obtained results generally agree with those previously reported for the fundamental resonance peak. However, for higher resonance peaks, a more complicated behavior follows from our calculations. We do not see a monotonous increase of \( \chi^{(3)}(\omega; 0, 0, 0) \) for higher resonances.

The outline of the paper is as follows. In Sec. II, we derive an analytic expression for the QEO function of semiconducting zigzag CNs. In Sec. III, the physical reason for a nonuniform behavior of \( \chi^{(3)}(\omega; 0, 0, 0) \) for higher resonances is discussed. Furthermore, the apparent displacement of fundamental resonance peaks between two groups of semiconducting CNs reported in some papers is analyzed and shown to be simply a question of taking an approximate rather than exact value of the band gap for semiconducting zigzag CNs.

In order to obtain the high-field response and to assess the applicability of the perturbation approach, we study numerically the response of a long but finite length CN placed in a uniform electric field in Sec. IV before summarizing our conclusions in Sec. V.

II. THEORY AND ANALYTICAL DERIVATIONS

Single walled CNs, constructed by rolling up a graphite sheet into a cylinder, are characterized by two integers \((n, m)\). For a more detailed classification of zigzag CNs \((m = 0)\) as a subclass of CNs, we introduce two integer parameters \(p\) and \(q\) which are connected with \(n\) by means of the relation \(n = 3p + q\). The zigzag tubes with \(q = 0\) are known as narrow gap semiconductors (metallic) whereas the tubes with \(q = 1, 2\) and arbitrary \(p\) are moderate-gap semiconductors (MSs). Among these, the MS with index \(q = 1\) are defined as MS1 and those with index \(q = 2\) are defined as MS2. In our previous work20 (hereafter referred to as I) using an orthogonal \(\pi\)-orbital tight-binding model, we obtained the electronic structure, electric dipole matrix elements, and subsequently linear susceptibility of zigzag CNs. In the present work, we obtain an analytic expression for the QEO effect in zigzag CNs. We utilize the perturbation expression obtained by Aspnes and Rowe21 in their derivation of the third-order nonlinear optical susceptibility caused by a uniform electric field using time-dependent perturbation theory. The same method has been applied in Ref. 22 to find the QEO effect in the conjugated polymer poly(para-phenylene). The \(\gamma\) component of the EO function in the vicinity of each band gap is given by

\[
\chi_{\gamma}^{(3)}(\omega; 0, 0, 0) = \frac{1}{\hbar \Omega^3} \frac{\epsilon^2 \hbar^2 \Omega^2}{8m} \frac{\epsilon [\hbar \Omega \chi_{\gamma}(\omega)]}{\delta \Omega^2},
\]

where \(\epsilon > 0\) is the elementary charge, \(m^*\) the reduced effective mass, \(\Omega^2\) the dc field directed along the nanotube axis, \(\epsilon\), and where \(\delta \Omega = \hbar \omega + \hbar \Gamma\) includes the photon energy and the phenomenological broadening parameter \(\Gamma\). As in I, we have introduced the dimensionless “susceptibility” \(\chi_{\gamma}(\omega)\) ob-
tained by normalizing the polarizability (per unit length) by the cross-sectional area $A = \pi a^2$, where $R = n a / 2 \pi$ is the radius of a zigzag CN and $a$ is the lattice constant of graphene. We notice that Eq. (1) only includes transitions between single pairs of bands while the linear susceptibility $\chi_{\text{lin}}^{(a)}(\omega)$ in our calculations includes contributions from many pairs of bands. Consequently, to include all pairs of conduction ($c$) and valence ($v$) bands, the reduced effective mass $m^*$ associated with each pair is applied separately.

It follows from Eq. (1) that to compute $\chi^{(a)}_{\text{lin}}(\omega;0,0,\omega)$, the third derivative of $\chi_{\text{lin}}(\omega)$ with respect to $\Omega$ should be taken. However, the third derivative of the final result for the linear susceptibility obtained in I gives a rather complicated form of the QEO function. Therefore, we first derive a more useful albeit approximate form for the linear susceptibility.

We start with Eq. (15) in I written in the following form:

$$\chi^{(a)}_{\text{lin}} = \frac{1}{6} \int d^2 p \frac{\chi_{\text{lin}}}{(4p^2 - \hbar^2 \Omega^2)^{3/2}}\left(\rho^2 - \frac{\rho_0^2}{4} + \frac{\rho_0^2}{2} - \rho^2\right),$$

where $\gamma = 2.89$ eV is the nearest-neighbor overlap integral and the integral bounds as normalized band-gap parameters are given by $\rho_0 = 2\sqrt{3} + 2 \cos(2\mu \pi n) - 4 \cos(\mu \pi n)$ and $\rho_0 = 2\sqrt{3} + 2 \cos(2\mu \pi n) + 4 \cos(\mu \pi n)$, defined by Eq. (13) in I, where $\mu = 1, 2, \ldots, n$. A factor of 1/6 was missing in Eq. (15) in I due to a typographical error. In evaluating the linear susceptibility on the basis of Eq. (2), we apply the following approximate method. First, we note the fact that

$$\begin{align*}
\rho_0 &> \rho_0 &\text{if } 1 \leq \mu \leq (n-1)/2, \\
\rho_0 &< \rho_0 &\text{if } (n+1)/2 \leq \mu \leq n, \\
\rho_0 &= \rho_0 &\text{for odd } n, \\
\rho_0 &> \rho_0 &\text{for even } n.
\end{align*}$$

Hence, in the case $\rho_0 < \rho_0$, the factor $\sqrt{4p^2 - \rho_0^2}$ in Eq. (2) can be approximated by $\rho_0 / 2$ since $\rho_0$ is much smaller than $\rho_0$ in the dominant part of the integration. After introducing this approximation, Eq. (2) finally yields the following analytic result for the long-axis linear susceptibility of zigzag CNs. For odd $n$,

$$\chi^{(a)}_{\text{lin}}(\omega;0,0,\omega) = \frac{4e^2 a}{3 \pi \varepsilon_0 a_0} \left[ \sum_{\mu = 1/2}^{n-1} \chi^{(a)}_{\text{lin}}(\omega) + \chi^{(a)}_{\text{lin}}(\omega)/2 \right].$$

and for even $n$,

$$\chi^{(a)}_{\text{lin}}(\omega;0,0,\omega) = \frac{4e^2 a}{3 \pi \varepsilon_0 a_0} \left[ \sum_{\mu = 0}^{n-1} \chi^{(a)}_{\text{lin}}(\omega) \right] + \chi^{(a)}_{\text{lin}}(\omega)/2 + \chi^{(a)}_{\text{lin}}(\omega)/2.\]$$

Here,

$$\chi^{(a)}_{\text{lin}}(\omega;0,0,\omega) = \frac{3}{2\hbar^2 \mu \pi n} \left[ \sum_{\mu = 0}^{n-1} G^{(c)}(\omega) + G^{(v)}(\omega)/2 \right].$$

Above, $\varepsilon_0$ is the vacuum permittivity. In Eq. (6), a small frequency-independent term has been ignored since it makes a vanishing contribution to the QEO function. The simplified expression obtained for the linear susceptibility of semiconducting zigzag CNs is in excellent agreement with the full expression, Eq. (16), obtained in I. Introducing the results of Eqs. (4)-(7) into Eq. (1), one obtains the QEO function. It is noticed that upon multiplication by $h^2 \Omega^2$, the first term of Eq. (6) becomes independent of $\Omega$ and thus its derivative is zero. In addition, we find an infinite effective mass for the flat energy bands associated with $\mu = n/2$ and consequently a vanishing nonlinear susceptibility. Therefore, the only nonzero contribution to Eq. (1) comes from the second term of Eq. (6).

For the calculation of $\chi^{(c)}_{\text{lin}}(\omega;0,0,\omega)$, we need the reduced effective mass related to each pair of $c$ and $v$ bands. According to the tight-binding model, the band gaps and the reduced effective masses for a $(n,0)$ CN are given by $E_n = 2y_n(1 + \cos(\pi n)/n)$ and $m^*_n = h^2 / (3\gamma a_0^2) \times [2 + 1/\cos(\pi n)/n]$, respectively, where $\mu = 1, 2, \ldots, n$. The values of $\mu$ for the fundamental band gap ($\Delta_n$) of each CN are given by $\mu(n+1)/3$ and $(2n+1)/3$ for MS1 and MS2, respectively. After using the only nonzero term of Eq. (6) as well as the obtained reduced effective mass and assuming that the slowly varying factors are constant during differentiation, one obtains the following result

$$\chi^{(c)}_{\text{lin}}(\omega;0,0,\omega) = \frac{i e^2 a^2 F^2}{12 \pi \varepsilon_0 a_0} \left[ \sum_{\mu = 0}^{n-1} G^{(c)}(\omega) + G^{(v)}(\omega)/2 \right].$$

where $n' = (n+2)/2$ and $(n+1)/2$ for semiconducting zigzag CNs with even and odd $n$, respectively, and the function $G^{(c)}(\omega)$ is given by
Together with Eq. (9), this relatively simple equation allows us to compute analytically the QEO function for all semiconducting zigzag CNs while still including transitions between all pairs of valence and conduction bands. Importantly, as shown in Eq. (10), the position and magnitude of resonances associated with different transitions are accounted for using separate band gaps and effective masses for each term.

\[ G^{\omega}(\omega) = \frac{-y^2 x}{\rho_{\parallel}^2 + 1/\cos(\pi \mu h)} \left\{ \arctan(\omega)(2x^3 + 3x^2) + 8\omega^2 (1 + \mu^2) \right\} \]

\[ + 15(\Omega)^4 + \frac{8\omega^2}{1 + \mu^2}(3x^4 - 2\omega^2 \epsilon_x^2) + \frac{9\epsilon_x^2 (\Omega)^4 - 24\epsilon_x^2 (\Omega)^4 + 13(\Omega)^4)}{1 + \mu^2} \left\{ \frac{y^2 x}{\rho_{\parallel}^2 + 1/\cos(\pi \mu h)} \right\} \]

The imaginary (Im) and real (Re) parts of \( \chi^{(3)}(\omega;0,0,\omega) \) for some semiconducting zigzag CNs are illustrated in Fig. 1, where the broadening parameter \( \Gamma = 0.15 \text{ eV} \). A monotonous increase of the third-order optical nonlinearity as well as QEO effect with the increasing CN radius has been reported in Refs. 15, 16, and 19 and some papers have reported a monotonous increase within each group of MS1 and MS2. In fact, this is not the case for all resonance peaks. For example, the graphs plotted in Fig. 1 demonstrate that the magnitude of the third resonance peak around \( g = 4 \) for \( n = 14,0 \) is much larger than that of \( n = 14,0 \). This difference can be understood from the band structure of the two species. Thus, the large magnitude resonance peak of the \( n = 14,0 \) nanotube can be attributed to a near degeneracy between third and fourth bands counted from the Fermi level at \( k = 0 \) as well as a small effective mass of the fourth energy band. The same is the case for the fourth resonance peak of \( n = 13,0 \) illustrated in Fig. 1 for \( n = 42,0 \) which is much larger than that of \( n = 19,0 \) as a result of the overlap between the fourth and fifth energy bands around \( k = 0 \) as well as the small effective mass of the fifth energy band. Thereby, the difference between magnitudes of the first resonance peaks for the two MS groups with nearly the same radius is reasonable. By considering the values of \( \mu \) for the highest \( v \) band and lowest \( c \) band, it is found that the effec-
tive mass of MS1 is smaller than that of MS2 and, besides, the dipole matrix elements of MS1 are larger than those of MS2, when they have nearly the same radius. Therefore, they result in a very pronounced peak of $\chi^{(3)}(\omega, 0, 0, a)$ for MS1. Again, we notice that this is not the case for all resonance peaks. For example, as shown in Fig. 1, the magnitude of the second peak of MS2 is larger than that of MS1, because of the smaller effective mass and larger dipole matrix elements associated with the second $\sigma$ band and $c$ band of MS2 in comparison with that of MS1. All in all, except for the fundamental resonance, we do not see a monotonous increase of QEO effect with increasing tube radius.

When plotted as a function of the normalized photon energy $\hbar\omega/\Delta_g$, the fundamental resonance is expected to be at an identical position for all CNs. However, a displacement of the $\chi^{(3)}(\omega, 0, 0, a)$ resonance peaks of MS1 with respect to those of MS2 has been reported in Ref. 18. The authors claimed that the shift resulted from the curvature effects and $\pi$-$\sigma$ hybridization. The same displacement has been reported in Ref. 24 in a theoretical study of the third-order nonlinearity in CNs exposed to intensive electromagnetic fields based on a perturbative and a nonperturbative model. We express that this is not a characteristic feature of these two groups of semiconducting CNs. The reason for the apparent displacement is simply that an approximate rather than exact value of the band gap has been applied. In both papers, the dispersion energy as well as electric dipole matrix elements are obtained based on a tight-binding model and then to normalize the photon energy with the band gap, the authors of Refs. 18 and 24 have taken an approximate value of the band gap given by $2\gamma_0/\sqrt{3}$. If the exact value of the band gap obtained by the tight-binding model is used, as in the present work and in Ref. 23, no shift will appear as is apparent from Fig. 1. By taking the approximate value of the band gap, the same shift of $0.03$ appears in our plots, which do not contain the curvature effects or $\pi$-$\sigma$ hybridization. In addition, an incorrect factor of 4 has been included in the second term of the transition matrix elements by Xu and Xiong,17 which changes the transition matrix elements for zigzag CNs appreciably. Therefore, using this form of transition matrix elements, one cannot get a reliable result for QEO function. Regarding the second and higher resonances, the peaks appear at different positions for different CNs even when plotted versus the normalized photon energy $\hbar\omega/\Delta_g$.

To show the limiting behavior of the QEO effect with increasing CN radius, Fig. 2 illustrates that the imaginary real parts of $\chi^{(3)}(\omega, 0, 0, a)$ of (38,0) and (50,0) CNs belonging to MS2 display an equal peak magnitude. By considering CNs with even larger radii, we observed a decrease in the magnitude of the QEO effect.

IV. NUMERICAL RESULTS

For comparison with the analytical result, a numerical tight-binding calculation is made as well. A long nanotube is modeled as a sequence of $N$ unit cells and a constant electric field $F = F_z$ is applied in the direction of the nanotube axis. The elements of the $4nN \times 4nN$ dimensional Hamiltonian matrix are defined by

$$H_{ij} = \begin{cases} -eF_z & \text{if } i = j \\ \gamma_0 & \text{if } i \text{ and } j \text{ are nearest neighbors} \\ 0 & \text{otherwise.} \end{cases}$$

The third-order nonlinear optical susceptibility in the weak-field limit is approximated as

$$\Delta \chi(\omega, 0, 0, a) = \frac{\chi(F, a) - \chi(0, a)}{F^2}.$$

Using molecular electronic states $\Phi(\vec{r})$, the field-dependent susceptibility $\chi(F, a)$ is defined as

$$\chi(F, a) = 2\gamma_0 \sum_{i,s} \sum_{\alpha, \beta, \gamma, \delta} E_{\alpha}(F) \langle \Phi(\vec{r}) | s_z \Phi(\vec{r}) \rangle^2 \frac{E_{\beta}(F) - E_{\gamma}(F)}{E_{\delta}(F) - E_{\gamma}(F)}.$$

Here, $V = \frac{3N}{\sqrt{2}}a/\pi$ is the CN volume, $E_{\alpha}(F)$ are field-dependent eigenvalues of the Hamiltonian matrix, and $\langle \Phi(\vec{r}) | s_z \Phi(\vec{r}) \rangle = \sum_{\alpha, \beta, \gamma, \delta} c_{\alpha s}^* c_{\beta s}^* \phi(\vec{r}) | \gamma(\vec{r}) \rangle - \sum_{\alpha, \beta, \gamma, \delta} c_{\alpha s} c_{\beta s} \phi(\vec{r}) | \delta(\vec{r}) \rangle$, where $c_{\alpha s}^*$, $c_{\beta s}^*$ are expansion coefficients of the molecular eigenstates in the basis of atomic $\sigma$ orbitals $\phi(\vec{r})$ and the upper summation limit corresponds to the number of atoms in a zigzag CN. Studying a (7,0) CN limited in length to 180 unit cells, the weak-field limit in Eq. (12) is found to be reasonably approximated for $F=0.1\text{ mV}/\text{Å}$. We compare the approximate analytical result with the full numerical calculation and find virtually indistinguishable results, as demonstrated in Fig. 3. Although the Aspnes perturbation expression has been derived for transitions in the vicinity of the band gap, it is surprisingly good even far from the band gap.

For strong fields, higher-order terms in the expansion of $\chi(F, a)$ become important which give rise to oscillating tails...
FIG. 4. Numerically obtained $\Delta \chi (F=5.5 \text{mV/Å})$ for a (7,0) CN taking $\Gamma = 0.1 \text{eV}$. The oscillations above the band gap demonstrate that higher-order terms in the expansion of $\chi (F, \omega)$ are significant for such large fields.

of the peaks above the band gap. As an example, Fig. 4 shows a plot of $\Delta \chi (F=5.5 \text{mV/Å})$. We find that for fields larger than $-1 \text{mV/Å}$, oscillations above the band gap emerge, which is a characteristic of the nonperturbative Franz-Keldysh regime.

In order to address the possibility of experimental verification of the present results, a number of issues need to be considered. First, experimental samples invariably contain a mixture of CNs differing by diameter and chirality. The precise composition depends on the method of production. Second, the spectral width of all field-induced features is obviously very sensitive to the line broadening $\Gamma$. Hence, ideally an experimental sample should be (1) dominated by relatively few CN species and (2) characterized by small line broadening. The latter is typically obtained in micelle-wrapped CNs (Ref. 26) for which broadening as low as $\Gamma = 25-50 \text{meV}$ has been observed. In this type of samples, the linear absorption of each CN species is clearly resolved and, hence, we clearly believe that the electro-optic response predicted in the present work should be observable as well.

V. CONCLUSIONS

Using a tight-binding model, the quadratic electro-optic (QEO) effect in moderate-gap semiconducting (MS) zigzag CNs has been calculated analytically including contributions from the entire energy band structure. Although the prominent resonance peak of QEO for MS1 is larger than that of MS2 for nearly the same radius, this is not the case for the second peak. Moreover, it is shown that the monotonous increase of the QEO with CN radius within each group of MS is not a general case for all resonance peaks. As a result of the overlap between two energy bands around $E=0$ as well as small reduced effective mass, a large magnitude peak for a small radius CN can appear which is much larger than that of a large radius CN. To assess the applicability of our analytical results obtained in a perturbative approach, a nonperturbative numerical calculation has been performed for comparison. The comparison demonstrates a good agreement between the two approaches for fields weaker than approximately $F=0.1 \text{mV/Å}$.

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Appendix E

“Second-harmonic generation from ZnO nanowires”
Second-harmonic generation from ZnO nanowires

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1 Introduction

Zinc oxide has very promising potentials for a broad range of practical applications, such as transducers, transparent conductive oxides, various types of sensors, and UV-light emitters [1, 2]. The optical applications are interesting due to the wide band gap (3.37 eV) and the high exciton binding energy (60 meV). Furthermore, a variety of ZnO nanostructures such as wires, rods, and ribbons can be grown with very good crystalline structure. Nanostructures can thus have applications as compact photonic devices such as modulators, light emitting diodes, and lasers.

Together with photoluminescence optical Second Harmonic Generation (SHG) is a very useful optical characterization tool. As ZnO is without centrosymmetry it has a large bulk second-order optical nonlinearity with an exciton resonance near the band gap [3]. Several investigations of the nonlinearity of thin films prepared under different conditions have been reported [4-6]. Also nanowires have been studied with SHG [7] and the nonlinear signals from single wires have been imaged with near-field microscopy [8]. Resonantly enhanced SHG and two-photon photoluminescence from nanowires excited at a few discrete pump wavelengths have been reported [9, 10].

In this work SHG spectra from a bulk ZnO crystal are compared to those obtained from a thin layer of nanowires and the problems of isolating the SHG response from the detected signals are addressed. Spectra recorded for fixed pump photon wavelengths show that the emitted light is dominated by SHG with only a very small contribution from two photon photoluminescence when the SH frequency is well below the band gap. Near the band gap, on the other hand, multiphoton luminescence has to be taken into account. The wavelength dependence of the nonlinear response of bulk and nanowire ZnO is deduced using available linear optical constants and an effective medium approximation for the nanowire film. It is shown that the major difference in the spectra of nanowires and the bulk crystal can be explained through an effective refractive index for the layer of nanowires.

2 Experimental details

Experiments were performed on a 0.5-mm thick (0001)-oriented bulk crystal and on wires grown on an oxide covered Si wafer and on a quartz glass substrate. The ZnO nanowires are grown in a horizontal tube oven at a pressure of 2-3 mbar over a period of 2 hours. The source of ZnO is a mixture of powders of ZnO and C as a catalyst for evaporation, both of 99.9% purity, placed at the center of the oven at 1050 °C. A constant gas flow ensures transport to a cooler part of the oven where the wires are formed in the 700-900 °C temperature region and collected on silica wafers. Depending on the gas flow and growth temperature different amounts of defects and impurities are expected, well known defects being oxygen vacancies and nitrogen or hydrogen impurities.

Figure 1 shows a photoluminescence spectrum excited by 300 nm pump light. The spectrum is dominated by lum...
nescence at the band gap with very little intensity in the defect region around 500 nm [11]. The inset shows a section of a SEM image of wires grown on the Si wafer. Typical diameters of the wires are in the range from 200 nm and down below 20 nm while typical lengths are several micrometers. The hexagonal cross sections appearing on all wires indicate that they have a well ordered crystal structure. SEM images taken at different places on the samples show no preferred growth direction of the wires, i.e. they have random orientations.

Figure 1 Photoluminescence from ZnO nanowires excited with 300 nm pump light. The inset shows a SEM image of the wires.

The SHG experiments were performed with an optical parametric oscillator pumped by the third harmonic of 6-ns pulses from a Q-switched Nd:YAG laser. Experiments on the ZnO crystal and on wires grown on a substrate have been performed at 60° angle of incidence with the light polarized in the incidence plane. SHG was detected in a narrow angular range around the specular direction by a photo multiplier tube mounted either at the exit of a monochromator or behind a set of coloured glass filters and connected to a box-car integrator. The SH signals have been normalized against those generated from a wedge shaped quartz crystal.

3 Results and discussion

In order to distinguish between SHG and various luminescence processes a set of scans have been recorded where a monochromator has been scanned over a broad region around the SH wavelength for a series of pump wavelengths between 710 and 1000 nm with 10 nm intervals. Figure 2 shows a contour plot generated from these data. Before the contour plot was generated the individual scans were normalized to the same peak height. Two structures forming straight lines in the figure are seen. The structure with highest intensity is the SHG signal at half the pump wavelength while the weaker horizontal structure is multiphoton excited luminescence from the ZnO band gap. When the photoluminescence appears at shorter wavelengths than SHG (below the SHG line) it is presumably three-photon luminescence while the much stronger two-photon process is seen above the SHG line.

Figure 2 Contour plot showing light emission intensity as a function of pump emission wavelength. Structures due to SHG and multi-photon photoluminescence are marked.

Figure 3 shows scans taken at pump wavelengths 710 and 1000 nm, respectively. At 1000 nm the SHG signal dominates completely while only a very small contribution is seen at the band gap. At 710 nm on the other hand, a relatively broad emission from the band gap dominates the signal though the SHG signal is clearly seen.

A decomposition of the spectrum generated by 710 nm pump light into two Gaussian contributions representing SHG and band gap luminescence is shown. In the two-photon luminescence region a broad emission can be seen in the green defect part of the spectrum around 500 nm. It was noticed during the experiments that the green emission has a fast decay component beyond the time resolution of the detection system (~10 ns) followed by a much slower decay of ~300 ns.

Figure 3 The emitted intensity is shown as a function emission wavelength from 710 and 1000 nm pump light. The 710-nm data have been fitted with two Gaussians contributions.
Figure 4 shows SHG spectra recorded in reflection from ZnO nanowires together with corresponding results recorded in transmission from a bulk ZnO crystal. The large difference in refractive index at the pump and SH wavelengths leads to very fast Maker fringe oscillations as a function of wavelength that are not resolved in these experiments. Such effects are only seen as larger spread in the data at the shorter wavelengths for both the ZnO crystal and the nanowire film. During recording of these spectra the monochromator has been exchanged with a set of filters transmitting in the whole SH scan range. Thus, they also allow band gap luminescence to be detected. However, from inspection of the scans in Fig. 2 we know that luminescence contributions are only significant for wavelengths below 750 nm. Extraction of the SHG part of the signal near the band gap has been done by separating spectra as shown in Fig. 3 into SHG and luminescence contributions. It should be noted that a procedure where data of the type shown in Fig. 3 into SHG and luminescence contributions. Extraction of the SHG part of the signal should be multiplied by $d_p$, where $d_p$ is the effective second order nonlinear susceptibility, $L$ is the thickness of the nonlinear film and $\theta_p$ and $\theta_w$ are angles of refraction related to the angle of incidence via Snell’s law. The transmittance-prefactor $T^*(2\omega)T^*(\omega)$ accounts for transmission of pump light into the film and SH light out of the film. In the case of the nanowire sample, SHG obtained via reflection of the SH light at the Si/SiO$_2$ interface, in which case the above expression should be multiplied by $R(2\omega)$, the reflectance at $2\omega$. The effective nonlinear response $d_p$ is calculated by correcting the experimental spectra using the expression above. To this end, the linear optical constants obtained by Jellison et al. [13] are applied. As ZnO is optically uniaxial, the appropriate refractive index for $p$-polarization is an angle-dependent combination of ordinary and extraordinary indices. We treat the thin layer of nanowires as a homogeneous film of thickness $L=1\mu m$. To account, however, for the large air fraction in the thin layer, an effective medium description is applied. Hence, we model the refractive index as $n=fn_{ZnO}+(1-f)n_{air}$, where $n_{ZnO}$ and $n_{air}$ are the refractive indices of ZnO and air, respectively, and $f$ is the ZnO volume fraction.

**Figure 4** Wavelength dependence of the SHG intensity from a ZnO bulk crystal and a nanowire film grown on a Si/SiO$_2$ wafer. In the data from the nanowires the contribution from luminescence has been subtracted with the help of the data in Fig. 2.

Even after removal of the luminescence contribution as it has been done in Fig. 4 the SHG spectrum of the nanowires is quite different from that of the bulk crystal. However, in order to evaluate the nonlinear response effects of the strong variation in linear optical properties to have be taken into account. The intensity of the SHG signal can be expressed by the results by Maker et al. [12] generalized to complex refractive indices in order to incorporate losses

$$\frac{I_p}{I_p} = d_p^2 T_p^2 (\cos\theta_p)$$

$$\times \left[ \frac{\sin^2 \theta_w \cos \theta_w}{\sin^2 \theta_w(\cos \theta_w - n_{air} \cos \theta_w)} \right]$$

where $d_p$ is the effective second order nonlinear susceptibility, $L$ is the thickness of the nonlinear film and $\theta_p$ and $\theta_w$ are angles of refraction related to the angle of incidence via Snell’s law. The transmittance-prefactor $T_p^*(\omega)T_p^*(\omega)$ accounts for transmission of pump light into the film and SH light out of the film. In the case of the nanowire sample, SHG obtained via reflection of the SH light at the Si/SiO$_2$ interface, in which case the above expression should be multiplied by $R(2\omega)$, the reflectance at $2\omega$. The effective nonlinear response $d_p$ is calculated by correcting the experimental spectra using the expression above. To this end, the linear optical constants obtained by Jellison et al. [13] are applied. As ZnO is optically uniaxial, the appropriate refractive index for $p$-polarization is an angle-dependent combination of ordinary and extraordinary indices. We treat the thin layer of nanowires as a homogeneous film of thickness $L=1\mu m$. To account, however, for the large air fraction in the thin layer, an effective medium description is applied. Hence, we model the refractive index as $n=fn_{ZnO}+(1-f)n_{air}$, where $n_{ZnO}$ and $n_{air}$ are the refractive indices of ZnO and air, respectively, and $f$ is the ZnO volume fraction.

**Figure 5** Normalized effective nonlinear response of (a) bulk ZnO and (b) nanowires as functions of the pump wavelength. The results are calculated on the basis of the spectra in Fig. 3 using Eq. (1). For the nanowires results based on different fractions of ZnO in the film are shown.

For SHG with the SH photon energy close to the band gap of ZnO the dominant frequency dependent factor besides $d_p$ is the refractive index $n_{ZnO}$. Figure 5a shows the frequency dependence of $d_p$ for the ZnO single crystal. The sharp peak at 743 nm corresponds to a resonance at the SH wavelength 372 nm, which coincides with resonance structures in the linear properties around the band gap. This observation is in agreement with the first obser-
evaluations of SHG from a ZnO crystal by Haueisen and Mahr [3].

Figure 5b shows normalized effective nonlinear susceptibilities as functions of pump wavelength for the nanowire film calculated from Eq. (1) with different ZnO fractions in the film. It is expected that the nonlinear optical properties of the wires are the same as for the bulk crystal since the wires have diameters much larger than the exciton diameter. Size effects are thus not expected [14]. By introducing an effective medium treatment as described above the layer of randomly oriented wires is treated as homogeneous thin film. The conditions for that may not be fully satisfied since the average diameter of the wires (of the order of 50 nm) is not much smaller than the wavelength of the SH light. However, direct inspection of the film does show signs of an interference pattern and the spread in the nanowire data at longer wavelengths in Fig. 4 is a result of weak Maker fringes. A ZnO volume fraction of about 20% gives a close resemblance to the data of the bulk crystal. The large difference in the raw SHG spectra from nanowire and bulk samples (Fig. 4) is thus caused by the reduced effect of the linear properties on the SH intensity (from the nanowire sample). This makes the dispersion of the nonlinear susceptibility the main source of the spectral variation of the SH intensity from the nanowire film.

4 Summary

In summary, it is shown that SHG from nanometer sized ZnO structures appear together with multiphoton excited photoluminescence. For SH wavelengths near the band gap two-photon luminescence dominates the emission spectrum. By analyzing emission spectra taken at different pump wavelengths covering two photon energies across the band gap it is possible to isolate the SH contribution to the spectra. The raw SH intensity spectra from a nanowire film and a bulk crystal are quite different. It is shown that the data can be analyzed with an effective medium model of the linear optical properties of the nanowire film.

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References

Appendix F

“Quantized electron states in nearly depleted hexagonal nanowires”
Quantized electron states in nearly depleted hexagonal nanowires

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Abstract

The hexagonal quantum well (QW) is studied as a model for hexagonal nanowires, and the effects of donor impurities and geometrical deformations of the well are treated. By use of the Poisson equation the donor potential is calculated and the eigenspectrum of the hexagonal QW is shown to converge to that of a paraboloid quantum well with increasing donor density. Small deformations of the hexagon are shown to change the eigenspectrum significantly and give strong splittings of degenerate eigenvalues. Analytical approximations for the potential and eigenfunctions on the deformed hexagons are given.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The growth of nanowires of different materials and with different properties is one of the biggest current subjects in materials science due to their possible applications in the optical and electronics industry [1]. Nanowires appear in many shapes depending on which facets of the material minimize the surface energy. The facets are important as the cross section and resulting confinement defines the electronic energy levels of the wire. An example of a material forming nanowires is zinc oxide [2], giving long straight uniform wires with hexagonal cross sections, as illustrated by the SEM picture inset in figure 1.

Bulk studies have shown that ZnO invariably contains donor impurities in the form of oxygen vacancies or hydrogen or nitrogen impurities [3–5]. Accordingly, electrons in ZnO nanowires must be described taking the geometric confinement as well as interaction with the positive donors into account. In a first approximation, the donors may be replaced by a uniform positive background charge. In addition, we will consider the nearly depleted regime in which electron–electron interaction can be treated by perturbation methods. Physically, depletion of conduction electrons may occur in transistor geometries due to external gates. Also, gating by surrounding charges and electron accepting species on the nanowire surface may lead to electron depletion in chemical nanowire sensors (chemFETs). Hence, the nearly depleted regime is relevant to both electrically and ‘chemically’ gated nanowires.

In the following we apply a discrete numerical model to treat hexagonal quantum wells (QWs) including the constant background charge \( \rho \). Furthermore we vary the length of the six facets independently (keeping all corner angles fixed at 120°) to study how different growth rates, and thus shapes of the cross section, affects the energy spectrum. An isotropic effective mass model with effective electron mass \( m_e \) is applied to describe the quantized electron states.

2. Hexagonal quantum wells with donor impurities

For a sufficiently long nanowire with a non-varying cross section, the eigenstates are products of hexagonally confined parts and free-electron like longitudinal parts \( \propto e^{ikz} \).
Correspondingly the energy separates into discretized confined levels and a continuous longitudinal part $E_z = \frac{\hbar^2}{2m_e} \nu$.

A convenient way of describing the regular hexagonal QW is by introducing a three-direction partitioning scheme, as done by Sun [6]. Following his method we introduce the three unit vectors $e_1 = (1, 0)$, $e_2 = (-1/2, \sqrt{3}/2)$ and $e_3 = (-1/2, -\sqrt{3}/2)$ defining the hexagon and their normal vectors $n_1 = 1/2(e_1 \times e_2) \times e_3$, with $S = (e_1 \times e_2)(e_1 \times e_3) = 3/4$ (see figure 1). Hence every point on the unit hexagon is uniquely given by

$$p = \frac{1}{3}(t_1 n_1 + t_2 n_2 + t_3 n_3), \quad t_1 + t_2 + t_3 = 0,$$

and when discretizing the hexagon by taking a finite number of equidistant coefficients $t$, the Laplacian can be approximated

$$-\nabla^2 f(p) = \frac{4}{\hbar^2} f(p) - \frac{2}{3\hbar^2} \sum_{i=1}^3 (f(p + \hbar e_i) + f(p - \hbar e_i)) \approx \frac{\hbar^2}{2m_e} \nu n,$$

with $h$ being the distance between points in the grid. In terms of the area $A$ of the hexagon and the number $n$ of grid points on the hexagon side, the total number of grid points $N_g = 3n^2 + 3n + 1$ and the point distance $h = \frac{\sqrt{3}a}{N_g^{1/2} - n}$, and a constant area $A = 100 \text{ nm}^2$ is used henceforth. Unless otherwise noted $N_g = 2977$ is used throughout the calculations. The electron affinity of ZnO is sufficiently large (~5 eV) that penetration of carriers into vacuum can be neglected and Dirichlet boundary conditions can be applied. In this case, the energy levels for different size QWs can be found by simple scaling as they are inversely proportional to the area. Denoting by $V_{\text{hex}}$ the Laplacian with Dirichlet boundary conditions on the hexagon border, the Schrödinger equation to be studied is

$$-\frac{\hbar^2}{2m_e} V_{\text{hex}} \psi(r) + U_0(r) \psi(r) = E \psi(r),$$

with $m_e = 0.24 m_0$ [7] the effective electron mass of ZnO and $U_0(r)$ being the electrostatic potential energy created by the uniform donor density $\rho$.

This is calculated by solving the Poisson equation $\nabla^2 U = \frac{\rho}{\epsilon \epsilon_0}$ with the condition that $U_0$ is zero on the hexagon border and assuming each donor contributes with the charge $e$. The dielectric constant for ZnO is in fact anisotropic due to the hexagonal wurzite geometry of the material and therefore a directional average $e = \frac{\epsilon_{\parallel} + \epsilon_{\perp}}{2} = 8.15$ [8] is used. An example of the calculated potential is shown in figure 2. It is seen to approach a paraboloid near the centre of the well, but with more hexagonally shaped equipotential lines near the edge of the well. An analytical approach to the Poisson equation with sixfold symmetry yields in polar coordinates

$$U(r, \theta) = \frac{e^2 \rho}{4 \epsilon_0} r^2 + \sum_{n=0}^{\infty} A_n r^n \cos n \theta,$$

where the $A_n$ are to be determined by the zero potential boundary condition on the circumference of the hexagonal.

The domain term for small $x$ is in fact the parabolic term as expected from the numerical plot. Given a positive charge distribution the eigenstates will be more localized near the centre of the slab as opposed to the case where there is no charge distribution. Illustrations of the ground state with and without charges are given in figure 3. Due to the localization the lowest energy eigenstates of the charged hexagon will not interact as strongly with the bounds of the hexagonal slab, and increasing the charge density thus reduces the effect of both the boundary conditions and the higher order terms in $U(r)$. Effectively, this means that the eigenstates and energies approach those of the paraboloid QW, given by $E_n = \hbar^2 n(n + m + 1)$ where $n, m \in \mathbb{N}$ and $\omega = \sqrt{\frac{m_e e^2}{\epsilon_0 \epsilon}}$. An illustration that this is the case is given in figure 4 where the first 20 eigenvalues of the hexagon taken relative to the bottom of the potential $E_{\text{min}} = U(0, 0)$ are plotted as a function of the applied charge density. The energies are seen to go from the nontrivial solutions on the hexagon to the equidistant energies of the paraboloid with degeneracy $N = [1, 2, 3, 4, \ldots]$.

A natural expansion of the model is to include the contribution to the potential from the electron density $\rho_n$. In the non-degenerate limit, the electron density varies exponentially with the local potential and the Poisson equation becomes [9]

$$\nabla^2 U = \frac{e^2 \rho}{\epsilon \epsilon_0} - \frac{e^2 \rho_n}{\epsilon \epsilon_0}.$$
which can be solved iteratively by a self-consistent calculation. In the scope of this article it is assumed that $n_0 \ll \rho$. In this case, (5) can be approximated to first order in $\rho$ to

$$ \nabla^2 U = \nabla^2 (U_0 + U_1) = \frac{\varepsilon^2 \rho}{\varepsilon_{\text{eff}}} - \frac{\varepsilon^2 n_0}{\varepsilon_{\text{eff}}} \mathbf{E} + O(n_0^2), \quad (6) $$

so the correction satisfies $\nabla^2 U_1 = -\hbar^2 e^2 / m_0 \mathbf{E}$, with $\hbar = c / \sqrt{2\pi\epsilon_0\epsilon_{\text{eff}}}$. Taking $U_0$ to be zero in the corners of the hexagon and on the mid-point of each side, an expansion of (4) to $r^6$ yields

$$ U_0 \approx \frac{\hbar^2 kT}{4 \pi} - \frac{75}{364} \frac{\hbar^2}{\pi^2} \rho \cos \theta. \quad (7) $$

where $l$ is the hexagon side length and $\rho = \frac{\hbar kT}{e}$. Neglecting the small $r^6$ term and inserting in (6), $U_1$ has the particular solution

$$ U_1 = \frac{\hbar^2 kT}{\pi} \left[ E_i \left( -\frac{\hbar^2}{\pi^2} - 2 \log r \right) \exp \left( \frac{75}{364} \frac{\hbar^2}{\pi^2} r^6 \right) \right], $$

where $E_i$ is the exponential integral function. It diverges as $\log r$ at the origin ensuring that in total $U_1$ stays finite. This yields the analytic approximation of the potential

$$ U_{\text{ana}} = \frac{\hbar^2 kT}{4 \pi} \left[ E_i \left( -\frac{\hbar^2}{\pi^2} - 2 \log r \right) \exp \left( \frac{75}{364} \frac{\hbar^2}{\pi^2} r^6 \right) \right] + \sum_{n<0} A_n \rho^n \cos nt \theta. \quad (8) $$

Expanding the series to $r^n$, the coefficients $A_n$ and $A_1$ are calculated so that the potential is zero in the same symmetry points as in the above expansion of $U_0$,

$$ A_0 = -\frac{\hbar^2}{\pi^2} \frac{\hbar^2 kT}{\pi} \left[ E_i \left( -\frac{\hbar^2}{\pi^2} - 2 \log r \right) \exp \left( \frac{75}{364} \frac{\hbar^2}{\pi^2} r^6 \right) \right] + A_1 r^6, $$

$$ A_1 = \frac{4 \hbar^2}{\pi^2} \frac{\hbar^2 kT}{\pi} \left[ E_i \left( -\frac{\hbar^2}{\pi^2} - 2 \log r \right) \exp \left( \frac{75}{364} \frac{\hbar^2}{\pi^2} r^6 \right) \right] + A_0 r^6, $$

$$ \times \left[ E_i \left( \frac{3 \hbar^2}{16 \pi^2} - \frac{75}{364} \frac{\hbar^2}{\pi^2} \right) \right] + A_0 r^4. $$

To ensure convergence of the numerical potential, $N_{\text{QW}} = 17557$ was used in this calculation. The inclusion of electrons is seen to dampen the effect of the ionic background by reducing the depth of the potential. The analytical potential agrees well with the numerical calculations for small electron to donor charge ratios, being slightly below the numerical potential with no electron contribution, and slightly above at $\alpha = 0.2$. For higher ratios the analytical expression produces too shallow potentials as the assumption that the QW is nearly depleted is no longer valid.

3. Deformation of hexagonal quantum wells

Another aspect to consider when treating hexagonal nanowires is that real wire cross sections in most cases deviate from a perfect hexagon. The wire facets are due to ZnO having a hexagonal lattice structure, and the assumed equal length of the sides minimizes the number of surface atoms, thereby minimizing the total energy of the wire. But during growth it is unlikely that the atoms are deposited homogeneously, and hexagons with different side lengths are likely to appear.

In the presented model the shape of the hexagon is defined by the conditions on equation (1) that $-1 < t_1, t_2, t_3 < 1$. Reducing the restriction on one coefficient to $|t_1| < 1 + \delta$ gives a transformation of the QW from a hexagon to a parallelogram by varying $\delta \in [0, 1]$. A change of conditions on two coefficients, $-1 - \gamma < t_2, t_3 < 1 + \gamma$ gives an angle preserving stretching of the QW for $\gamma > 0$, elongating two sides compared to the rest. Both transforms are illustrated in figure 6, where the area of each polygon is kept at $A = 100 \text{nm}^2$ through
the transforms by varying $\gamma$ with the number of grid points $N_{\text{pt}}$. The following calculations are all started with $N_{\text{pt}} = 2977$ for the hexagon and increasing with parameters $\gamma$ and $\delta$.

The effects of the deformations are studied for $\mu = n_0 = 0$. A plot of the energies as a function of the stretching $\gamma$ is given in figure 7, showing that even a slight deviation from the ideal hexagon gives a significant change in the spectrum. The degenerate eigenvalues split up as the sixfold symmetry of the system is broken, and the stretching gives a stronger confinement in the direction of the $y$-axis and a weaker confinement along the $x$-axis as seen in figure 6. Accordingly the eigenstates with many nodes in the $y$-direction increase in energy, while states with many nodes in the $x$-direction decrease in energy. To illustrate this, the three lowest eigenstates are treated analytically. The analytic approximations of the eigenfunctions on the regular hexagon given in [6] are expanded here to include the stretching parameter $\gamma$ as

$$\phi_1 = 4 \cos \frac{\pi t_1}{2a} \cos \frac{\pi t_2}{2b} \cos \frac{\pi t_3}{2a}$$

$$\phi_2 = 4 \sqrt{3} \cos \frac{\pi t_1}{2a} \sin \frac{\pi t_2}{2b} \cos \frac{\pi t_3}{2a}$$

$$- 4 \sqrt{3} \cos \frac{\pi t_1}{2a} \cos \frac{\pi t_2}{2b} \sin \frac{\pi t_3}{2a}$$

$$\phi_3 = 4 \cos \frac{\pi t_1}{2a} \sin \frac{\pi t_2}{2b} \cos \frac{\pi t_3}{2a} + 4 \cos \frac{\pi t_1}{2a} \cos \frac{\pi t_2}{2b} \sin \frac{\pi t_3}{2a}$$

$$- 8 \sin \frac{\pi t_1}{2a} \cos \frac{\pi t_2}{2b} \cos \frac{\pi t_3}{2a}$$

Figure 6. Transformation of QW. Left: from hexagon to parallelogram by varying $\delta \in [0, 1]$ Right: elongating the hexagon by varying $\gamma \in [0, 2]$.

Figure 7. Eigenspectrum as a function of parameter variation $\gamma \in [0, 2]$ as the QW is stretched. The number of grid points vary from $N_{\text{pt}}(\gamma = 0) = 2977$ to $N_{\text{pt}}(\gamma = 2) = 10\,789$.

Figure 8. The energies of the approximate eigenfunctions $\phi_{n+1}$ plotted against the real eigenvalues.

Figure 9. The initial hexagonal eigenfunction $\phi_{\text{hex}}^{\text{init}}$ compared to the final $\phi_{\text{paral}}^{\text{init}}$ of the $\delta$-transform.

where $a$ and $b$ (illustrated in figure 6) are given by

$$a(\gamma) = \frac{\sqrt{3} A}{\sqrt{\gamma + 6/2}}$$

$$b(\gamma) = (\gamma/2 + 1)a(\gamma).$$

The energies $E_i = \langle \phi_i | -\Delta | \phi_i \rangle$ follow closely the behaviour of the numerical eigenvalues, as illustrated in figure 8. The ground state increases in energy due to confinement in the $y$-direction. $\phi_1$ initially decreases in energy because of the decrease in energy of the high frequency terms $\sin \phi_6$ and $\sin \phi_8$ as $b$ grows with $\gamma$, but the $y$-direction confinement takes over around $\gamma = 0.85$. $\phi_1$ grows strongly in energy due to the term $\sin \phi_6$ as $a$ decreases with $\gamma$.

The eigenspectrum of the $\delta$-transform is given in figure 11. There is again a split of degenerate states initially, but new degenerate states are formed at $\delta = 1$. Interestingly the new degenerate states are not the same as for the original hexagon, as the non-degenerate eighth eigenstate of the hexagon, $\phi_{\text{hex}}^{\text{eig}}$, becomes the sixth degenerate eigenstate of the parallelogram $\phi_{\text{paral}}^{\text{eig}}$. These states are illustrated in figure 9 where it is seen that two pairs of the initial six peaks of $\phi_{\text{hex}}^{\text{eig}}$ recombine into four peaks along the long axis in $\phi_{\text{paral}}^{\text{eig}}$, explaining the decrease in energy. An interesting property of $\phi_{\text{paral}}^{\text{eig}}$ is that its energy can be determined analytically, as it is the same as that of the ground state of a regular triangle with $1/6$ the area. The
ground state of the triangular quantum well of unit area has the energy \[ E_{\text{Tri}}^{\text{hex}} = \frac{6E_{\text{Tri}}}{m_e A_{\text{hex}}} = 0.217 \text{ eV}. \] (10)

If compared to the calculated energies in figure 11 where \( E_{\text{Tri}}^{\text{hex}} = 0.214 \) the numerical error on the energy \( \Delta E < 1.5\% \), an error that only decreases with \( \gamma \) and \( k \) as \( N_{\text{pt}} \) increases. In figure 10, \( \phi_{\text{hex}}^{\text{final}} \) largely maintains the same shape through the transformation to \( \phi_{\text{paral}}^{\text{final}} \) and the increase in energy is solely due to the symmetry changes.

4. Optical properties of doped and deformed wires

As a straightforward method of studying experimentally the effects covered in this work, we now consider the influence on the optical response. Generally, increasing the conduction electron density will reduce the intensity of optical transition across the gap due to Fermi blocking. In addition deviations from perfect hexagonal symmetry will change the spectrum due to splitting of degenerate energy levels.

To calculate the optical properties of the doped hexagonal nanowires the charge balance equation [9] is solved iteratively for the Fermi energy \( E_F \), the confinement correction to the conduction and valence band energies \( E_c \) and \( E_v \), and the ionized donor density \( p \). Here \( \{c, v\} = 1, 2, 3, \ldots \) are indices running over the hexagon wavefunctions for the conduction and valence states respectively. The calculations are done for a fixed total donor density \( N_d = 10^{17} \text{ cm}^{-3} \) and a donor energy \( E_D = -61 \text{ meV relative to bulk} \) [11], assuming a bulk band gap \( E_g = 3.3 \text{ eV} \) and using the effective hole mass \( m_h = 0.59 \) corresponding to the experimental value for the heavy hole [12]. The ratio of conduction electrons to ionized donors is introduced by replacing \( N_d \) by \( \alpha N_d \) in the charge balance equation.

As the electron donor ratio \( \alpha \) increases the lowest peaks of the spectrum are dampened and shifted slightly lower in energy due to the reduction of the potential \( U \) as found in figure 5. We note, however, that the visibility of the effect is strongly dependent...
Figure 13. Normalized imaginary part of the dielectric constant $\varepsilon_1(\hbar\omega)$ of a hexagonal wire compared to that of a wire with deformation $\delta = 0.1$, both with $A = 100$ nm$^2$. The effect of wire deformation on the dielectric function is seen in figure 13 where the perfect hexagonal wire is compared to a wire with deformation $\delta = 0.1$, both of area $A = 100$ nm$^2$. A significant splitting of the spectrum is seen for even this slight deformation, and should again be discernible at low temperatures.

5. Summary

Hexagonal nanowires were treated as nearly depleted quantum wells with a constant background charge due to positive donors. To obtain the electrostatic potential, the Poisson equation was solved numerically on the hexagon, and the presence of an electron density was included perturbatively. Without the electronic contribution the eigenspectrum was calculated for varying donor densities, and shown to converge to that of the two-dimensional parabolic potential when the donor charge density was sufficiently large. An analytical approximation of the potential was derived for small electron densities, and a comparison with numerical calculations showed good agreement for an electron to donor charge ratio below 0.2. We also considered deviations from the perfect hexagonal symmetry and even slight deformations were found to give notable splittings of the degenerate eigenvalues due to the breaking of symmetry. Approximate analytic expressions for the eigenfunctions under the deformations were presented, and their energies were shown to agree well with the numerical results. Finally the effects of dopants and deformations on the optical properties of the wires were treated by a calculation of the dielectric function for different wires.

References

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Appendix G

“Density-functional based tight-binding modelling of ZnO structures”
Density-functional based tight-binding modelling of ZnO structures

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1 Introduction

As a large band gap semiconductor, zinc oxide has received a lot of attention from the scientific community, due to its potential applications in electronics and optics [1]. Lately, the controlled growth of ZnO nanostructures, such as nanowires, -belts and -combs, has become a very active field of research with promising applications such as gas sensors, nanoscale light sources and solar cells [2–4].

Density functional theory (DFT) has been successfully applied to geometric relaxation of both wurtzite and rock salt phases of bulk ZnO and to small nanowires [5, 6] and except for slightly high-lying d-bands the DFT valence band structures correspond well with the experimental data [1]. Unfortunately the DFT band gap is typically strongly underestimated [7] and the complexity of treating d-electrons makes treating larger systems such as nanowires and clusters of reasonable dimensions hard. The band gap can be corrected using e.g. GW methods [8] but this only increases the computational demands.

In this paper a treatment of ZnO will be presented using self-consistent charge density-functional based tight-binding (SCC-DFTB) parametrisation for structural optimisation and electronic properties of zinc oxide is presented. Repulsive potentials are obtained from the ZnO wurtzite geometry and a thin nanowire and applied to the bulk rock salt phase, a (0001) oriented slab and nanowires of different sizes. The parametrisation is shown to reproduce geometries in agreement with DFT calculations. A different set of parameters is generated for electronic calculations giving band structures with a bulk band gap of 3.3 eV and a strong split-off of the d-bands in agreement with experiments.

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2 SCC-DFTB parametrization  The SCC-DFTB energy consists of 3 terms,
\[ E_{\text{SCC-DFTB}} = E_{\text{TB}} + \Delta E_{\text{rep}} + E_{\text{crys}} \]  

(1)

The first term is the non-SCC tight-binding energy given by
\[ E_{\text{TB}} = \sum_{\alpha \beta} f_{\alpha \beta}(E_{\alpha}) E_{\alpha} , \]

with \( f_{\alpha \beta} \) the Fermi–Dirac distribution and \( E_{\alpha} \) the eigen energies. The eigenfunctions are expressed in a basis of pseudo-atomic orbitals, in turn generated from an all-electron calculation on the individual atoms using a Perdew–Zunger DFT-LDA implementation and the orbital basis of Koga [12]. A confining potential \( V_{\text{conf}} = \alpha(R_{\alpha \beta})^\gamma \) on the pseudo-atoms ensures the localization of the orbitals, with \( R_{\alpha \beta} \) the covalent radius of the studied atom and the constraint parameter \( \alpha \) to be chosen as to give the best energetic and electronic behaviour of the system.

The second order term in the total energy, \( \Delta E_{\text{rep}} \), contains the Coulomb energy of the charge displacement between atoms in the solid and can be expressed in terms of a sum over the entire crystal relative to the unit cell as
\[ \Delta E_{\text{rep}}^{\text{TB}} = \sum_{\alpha \beta} \sum_{\alpha \beta} \gamma_{\alpha \beta} \Delta q_{\alpha} \Delta q_{\beta} . \]  

(2)

\( \Delta q_{\alpha} \) and \( \Delta q_{\beta} \) are the charges of atoms \( \alpha \) and \( \beta \) respectively calculated from a Mulliken analysis. The coefficient \( \gamma_{\alpha \beta} = \gamma_{\alpha \beta}(U_{\alpha}, U_{\beta}, c, |R_{\alpha} - R_{\beta}|) \) is a functional of the Hubbard \( U \) parameters of the atoms, the effective dielectric screening \( c \) of the material, and the inter-atomic distance. It can be approximated by
\[ \gamma_{\alpha \beta} = \frac{U_{\alpha} c}{c|R_{\alpha} - R_{\beta}|}, \]  

(3)

for sufficiently large inter-atomic distances \( |R_{\alpha} - R_{\beta}| \). In the case of large dielectric screening the off-site matrix elements \( \gamma_{\alpha \beta} = 0 \) for \( \alpha \neq \beta \) is a good approximation. It is used in the present work as it is found to give better results than calculations using the static dielectric constant [13] of \( c = 8.15 \) or the high frequency dielectric constant [1] of \( c = 3.7 \). Consequently the tight-binding terms in \( E_{\text{SCC-DFTB}} \) can be calculated self-consistently.

The repulsive energy term \( E_{\text{crys}} \) in (1) is a correction term introduced as the tight-binding energies are calculated from the band structure energy and charge shift energies only, and is to be extrapolated from a reference DFT calculation. This contribution is treated in detail below.

3 Repulsive potentials  As the repulsive energy \( E_{\text{crys}} \) is due to the overlap of atomic orbitals and of core potentials it is expressed in terms of short-range inter-atomic repulsive potentials \( V_{\text{rep}}^{\text{u}} \) between atoms \( \alpha \) and \( \beta \). The repulsive energy pr. unit cell is
\[ E_{\text{crys}} = \frac{1}{2} \sum_{\alpha \beta \gamma \delta} V_{\alpha \beta}^{\text{u}} |R_{\alpha} - R_{\beta}| . \]  

(4)

As reference for the calculation of repulsive potentials the bulk wurtzite geometry of ZnO, as is illustrated in Fig. 1, and the thin infinite periodic hexagonal wire, as illustrated in Fig. 2. The wurtzite geometry is given by lattice parameters \( a \), \( c \), and \( \gamma \), and the wire geometry by the radii \( R_{\alpha} \) and \( R_{\gamma} \) and lattice parameters \( a \) and \( \gamma \). As the repulsive potentials are short-range, it is assumed that only nearest neighbour and next-nearest neighbour interactions contribute to (4). As there are three repulsive potentials, three reference calculations are needed. One is the ideal wurtzite lattice, where \( a = 0.32 \) and \( c = 0.49 \), in which case the repulsive energy can be expressed in terms of the repulsive potentials as
\[ E_{\text{crys}}^{\text{estim}} = 8V_{\text{rep}}^{\text{u}}(3\sqrt{3}a) + 12V_{\text{rep}}^{\text{u}}(a) + 12V_{\text{rep}}^{\text{u}}(a) . \]

The other two are calculated from the wire. Introducing an initial radius \( R \) and fixing the wire unit cell length \( L = \sqrt{8R} \) and \( u = \sqrt{3/8} \) the repulsive energy of the wire is
can be expressed as
\[
E^{\text{rep}} = 6E_{\text{rep}}^{(0)(0)} \left( \frac{1}{2} R_i^2 + (R_i - R_j)^2 \right) \\
+ 12r \sum_{ij} \left( \sqrt{R_i^2 + R_j^2 + R_i R_j} - (R_i R_j)^{1/2} \right) \\
+ 12r \sum_{ij} \left( \frac{1}{2} (R_i^2 + R_j^2) + 6E^{\text{rep}}^{(0)(0)} (\sqrt{3} R_i) \right) \\
+ 12r \sum_{ij} \left( \frac{1}{2} (R_i^2 + R_j^2) + 6E^{\text{rep}}^{(0)(0)} (\sqrt{3} R_i) \right).
\]

The second reference calculation is made by keeping \( R_i = R_j \) fixed and varying \( R_i, R_j \), and the third by varying the wire radius \( R_i = R_j \). The initial radius is taken as the bulk value \( R_i = 3.58 \) au, where the lattice constant \( a_0 = 6.03 \) au is used.

The repulsive energies are determined by comparing DFT and TB calculations as
\[
E_{\text{rep}} = E_{\text{DFT}} - E_{\text{TB}}^{(0)} - \Delta E^{\text{rep}}(0).
\]

The tight-binding parameters are calculated using the covalent radii of \( \text{Zn}^{\text{cov}} R = 2.36 \) au for zinc and \( \text{O}^{\text{cov}} R = 1.38 \) au for oxygen, and the constraint parameter is chosen to the value \( \alpha = 10^{-6} \) to ensure that the spatial extent of the pseudo-atomic wave functions is sufficiently large. This is done at \( T = 0 \) K, using the Hubbard \( U \) parameters of \( \text{Zn}^{\text{u}} U = 0.2667 \) au and \( \text{O}^{\text{u}} U = 0.4954 \) au for the SCC correction. Throughout the following these parameters will be used for the DFTB calculations unless otherwise noted.

The tight-binding energies are determined using the tetrahedron method on 1536 tetrahedrons in the irreducible Brillouin zone for bulk calculations, and from a 20 \( k \)-point mesh for wire calculations. The DFT calculations were performed on the FYRKAT [19] grid using the ABINIT [20] package in the local density approximation (LDA) using Troullier–Martins pseudo-potentials and the Teter Pade XC parametrisation [21]. These were carried out on a grid of \( 8 \times 8 \times 8 \) Monkhorst–Pack \( k \)-points for bulk and a \( 1 \times 1 \times 8 \) grid for the wire. For the wire, a supercell with an inter-wire distance of 20 au is used. All DFT calculations are performed with a plane wave cut-off energy of 45 au.

Fitting the repulsive potentials to exponentially localised polynomials of the form
\[
V_{\text{rep}}(r) = e^{-b + cr + dr^2},
\]
leads to the coefficients given in Table 1.

<table>
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<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
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<tr>
<td>OO</td>
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</table>

Plots of the calculated repulsive potentials are found in Fig. 3. The strong variation of \( V^{\text{rep}}_{\text{ZnO}} \) in the studied ranges ensures that this is the dominant repulsive term and supports the assumption of short-range repulsion.

4 Bulk, layer and wire geometries

The agreement between the DFT and DFTB treatment in the case of wurtzite \( \text{ZnO} \) is illustrated in Figs. 4 and 5 where \( E_{\text{tot}}(a_u) \) is plotted for \( a_u = 3.58 \) au. A full relaxation in DFTB yields the parameters \( (a_u, c_u) = (6.05 \text{ au}, 9.96 \text{ au}, 0.388) \) closely resembling the \( (a_u, c_u) = (6.034 \text{ au}, 9.802 \text{ au}, 0.376) \) of the DFT treatment, but with slightly larger values of \( c_u \) and \( u \). Experimental values of the parameters \( (a_u, c_u) = (6.15 \text{ au}, 9.85 \text{ au}, 0.382) \), fall in between the DFT and DFTB results.

The total energy of the rock salt phase of \( \text{ZnO} \) is treated in Fig. 6 for varying lattice parameter \( a \) in DFTB and DFT. The ideal lattice constants are found to be \( a_{DFTB} = 8.05 \text{ au} \) and \( a_{DFT} = 8.00 \text{ au} \). Though there is a slight
difference in the calculated lattice constants both fall within the range of values reported by others [5], and there is good agreement between the energetic behaviour of the two total energy curves. In comparison with the wurtzite phase the rock salt phase is seen to be less stable, with a phase transition energy per ion pair of \(E_{\text{DFTB}}^{\text{trans}} = 1.3 \text{ eV} \) compared to the DFT value of \(E_{\text{DFT}}^{\text{trans}} = 0.3 \text{ eV}\). Although the transition energy is higher the stability of the wurtzite phase is ensured, supporting the transferability of the parameters.

For the transferability to surfaces, a single layer of the (0001) surface of wurtzite is studied. The slab is illustrated in Fig. 7 where a purely two dimensional honeycomb layer appears for slab thickness \(h = 0\) corresponding to \(d = 1/2\) in the bulk. The hexagonal geometry appearing for \(d = 1/2\) is in fact the ideal structure for sufficiently thin slabs [23] and the single layer has been studied for the potential formation of ZnO nanotubes [24].

We study two variations of the honeycomb layer, namely one where the lattice constant \(a\) is varied for fixed \(h = 0\) and another where \(h\) is varied for fixed nearest-neighbour distance \(d = a\sqrt{3}\).

The DFTB energies are calculated by the triangle method [25] on a mesh of 64 triangles and DFT energies are calculated on a 12 \times 12 \times 1 Monkhorst–Pack grid with an inter-layer distance of 30\(\text{au}\). For the \(a\)-variation a temperature of \(T = 1000 \text{ K}\) is introduced in the DFTB calculation as the layer turns metallic for \(a > 8 \text{ au}\). The resulting total energy curves are given in Figs. 8 and 9. The calculated lattice constants are very close, with \(a_{\text{DFTB}} = 6.07 \text{ au}\) and \(a_{\text{DFT}} = 6.06 \text{ au}\), and in both cases the energetics of the lattice variations appear on the same scale. As the \(h\) variation is for constant \(V_{\text{rep}}^{\text{ZnZn}}(d)\) this calculation shows that the \(V_{\text{rep}}^{\text{ZnO}}(d)\) and \(V_{\text{rep}}^{\text{Zn}}(d)\) behave as intended for surface atoms as well. Thus surfaces with dangling bonds are equally well reproduced in the SCC-DFTB scheme as are bulk geometries.

A full relaxation of the small wire from Fig. 2 is performed and the resulting geometries for DFT and DFTB are shown in Fig. 10. The lattice parameters are given in Table 2 with the bulk values for comparison. In both DFT and DFTB the relaxed oxygen radius is slightly larger than the zinc radius resulting in a buckling of the surface. The unit cell is slightly stretched compared to bulk and subsequently the parameter \(u\) is lowered due to the attraction of the dangling bonds. The same overall behaviour is seen in both DFT and DFTB but with a slightly more pronounced variation from the bulk in the DFTB case.
Figure 9  Single layer slab thickness variation with constant nearest neighbour distance. Total energies from DFT (solid line) and DFTB (dashed line).

Figure 10  Relaxed geometries of the small wire determined from DFTB (left) and DFT (right) calculations, the Zn atoms illustrated by larger circles and O by the smaller, darker ones.

Table 2  Lattice parameters of the small nanowire.

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<th>DFTB bulk</th>
<th>DFT</th>
<th>DFT bulk</th>
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<td>3.470</td>
<td>3.484</td>
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</table>

Table 3  Lattice parameters of the larger nanowire.

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<th>DFTB bulk</th>
<th>DFT</th>
<th>DFT bulk</th>
</tr>
</thead>
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<tr>
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<td>6.05</td>
<td>5.97</td>
<td>6.034</td>
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</tbody>
</table>

Figure 11  (online colour at: www.pss-b.com) Geometry of a larger ZnO nanowire and the lattice parameters describing the surface atoms.

As the small nanowire takes part in the parametrization, a larger wire, as illustrated in Fig. 11, is studied as well. Only the outermost atoms, the ones with dangling bonds, are relaxed while the inner atoms are fixed to bulk values. The DFT calculations are performed on a hexagonal supercell with a distance of 25 au between wires. The resulting geometry is shown in Fig. 12 and the relaxed lattice parameters are given in Table 3. Due to symmetry only the lengths of the radial vectors $|\vec{R}_i|$ are given. As in the case of the small wire, both DFT and DFTB gives a buckling at the surface with the zinc atoms moving into the material and the oxygen protruding slightly more. Similarly the two $u$ parameters $u_x$ and $u_y$ (Fig. 11) are lowered, and in general the relaxation pattern is the same for both DFT and DFTB. Thus the presented SCC-DFTB parametrization has been tested against both bulk, surface and nanowire systems, giving relaxed geometries close to the DFT values, and the transferability of the parametrization has been verified.

5 Band structure calculations

With the radial constraint on the basis functions of $\alpha_0 = 2$ the band gap in the relaxed wurtzite geometry is found to be too large. The band gap of wurtzite ZnO at the ideal DFTB geometry as a function of $\alpha_0$ is illustrated in Fig. 13, and to get a band gap close to $E_g = 3.3$ eV a value $\alpha_0 = 1.85$ is used. The DFTB band structure is given in Fig. 14. The DFTB relaxed geometry DFT relaxed geometry

Figure 12  Relaxed geometries of the larger nanowire determined from DFTB (left) and DFT (right) calculations, Zn positions given by the larger brighter circles and O by the smaller ones.
d-bands lie slightly lower, at –6.2 eV below the valence band edge, than those of DFT-LDA at –5.1 eV. The experimental position [26] is reported to be around –6.95 eV supporting the strength of the DFTB band structure for use in electronic calculations.

The valence band structure of the 2D hexagonal ZnO layer is calculated in both DFTB and DFT, as shown in Fig. 15, again using \( \alpha = 1.85 \) for the DFTB calculation. The valence bands are seen to be of the same shape and spanning the same energy range in both cases, again with the d-bands of the DFTB band structure lying slightly lower than the d-bands of the DFT calculation.

Given the excellent results for both bulk ZnO and the \((0001)\) surface, the parameters presented here are expected to be transferable to the many and varied nanostructures formed by ZnO. With the scalability of DFTB, the calculation of both atomic geometries and confinement effects on the electronic structure is feasible, even in ZnO nanowires of large diameter.

6 Summary
A self-consistent charge density functional-based tight-binding parametrisation of zinc oxide was presented, based on DFT and SCC-TB calculations for bulk wurtzite ZnO and a small hexagonal nanowire. Repulsive potentials were presented for both nearest neighbour and next-nearest neighbour interaction to ensure transferability of the parametrisation to various systems including different crystal structures and low dimensional geometries.

This was demonstrated in the bulk by the treatment of the rock salt phase of ZnO, and for the surface systems by calculations for a single layer of the wurtzite \((0001)\) facet as well as a full relaxation of the surface atoms of two small nanowires. Both geometries and lattice parameter dependence of the total energies were found to be in good agreement with DFT calculations.

The correct band gap for wurtzite ZnO was achieved by the choice of a slightly stronger constraint parameter \( \alpha \). The band structures of wurtzite and honeycomb ZnO were presented, and the d-band split-off in the bulk was found to be slightly larger than that of DFT, closer to the experimental value.

References
[19] Fyrkat Supercomputer Grid, Dept. of Computer Science, AAU.