QUASIPARTICLE SELF-CONSISTENT $GW$ BAND STRUCTURES OF III-N, II-IV-N$_2$ SEMICONDUCTORS AND BAND OFFSETS

by

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Abstract

by

ATCHARA PUNYA

The group-III nitrides and their alloys are among the most intensively investigated semiconductors for optoelectronic and electronic applications. However, there are some problems such as high cost in Indium, phase segregation and phase separation of InN and GaN in their alloys. Thus, in this dissertation, we use the first-principles calculations to quantitatively predict the properties of a new family of II-IV-N$_2$ semiconductors. The main objectives of this study are to facilitate identifying the materials once they are first synthesized and to help understand which ones may be appropriately used for specific technical purposes. First, we use the new technique called Quasiparticle Self-consistent $GW$ (QSGW) to re-investigate the properties beyond the fundamental band gaps of III-N semiconductors, which ones may view as the closest relative of II-IV-N$_2$ semiconductors. We present the Rashba Sheka Pikus Hamiltonian parameters, which describe the valence band maximum splittings and effective masses. Next, the II-IV-N$_2$ semiconductors were proposed as heterovalent ternary compounds by replacing the group III elements of III-N semiconductors alternately by a group II elements, such as Mg, Zn, and Cd and a group IV elements, such as Si, Ge, and Sn. Their electronic band structures are reported comparing with available experimental results. Finally, we study band offsets between ZnGeN$_2$, ZnSnN$_2$, ZnO, and GaN by using DFT-LDA including quasiparticle corrections. Almost all of the band offsets among them are staggered except between ZnGeN$_2$/ZnSnN$_2$, and the potential benefits for photovoltaic cells are pointed out.
Chapter 1

Introduction

By using human reasons or philosophy, Empedocles (450 BC) proposed that all the structures in the world are constructed from four elements, i.e., earth, water, air, and fire. These four elements can be mixed and separated by two powers called love and strife. Now, by employing quantum mechanics, specific material phenomena can be predicted from two components, i.e., electrons and nuclei with only one interaction, the electromagnetic interaction. In this dissertation, we employ the first-principles calculations to quantitatively predict the properties of a new family of II-IV-N\textsubscript{2} semiconductors in terms of this basic interaction. The details of the calculation methods are reviewed in chapter 2. The main objectives of this study are to facilitate identifying the materials once they are first synthesized and to help understand which ones may be appropriately used for specific technical purposes.

In the first part of this thesis, we use the new technique called Quasiparticle Self-consistent \textit{GW} (QSGW) developed by van Schilfgaarde \textit{et al.} [2; 3] to investigate the properties beyond the fundamental band gaps of III-N semiconductors, which one may view as the parents of the new materials II-IV-N\textsubscript{2}. The group-III nitride semiconductors and their alloys are among the most intensively investigated semiconductors for optoelectronic and electronic applications. Although significant experimental and
theoretical work has been performed in the past, the basic parameters such as the Rashba Sheka Pikus (RSP) Hamiltonian parameters, which describe the valence band maximum splittings and effective masses, are still uncertain [4; 5; 1; 6; 7; 8; 9; 10]. For future progress in development of nanostructured devices, reliable material parameters are needed. The technique we use here has a distinct advantage for determining the fine structure of the energy bands. Thus, the electronic band structures, the RSP Hamiltonian parameters as well as the strain deformation potentials of the crystal field splittings for wurtzite AlN, GaN, and InN are presented in chapter 3. Compared with previous work on these parameters the QSGW results provide a more accurate prediction of the splittings and effective masses. As part of this work, we also developed a more accurate approach to fit the parameters taking into account the calculated bands in directions intermediate between parallel and perpendicular to the basal plane. We also studied the strain dependence in more detail than previous work.

Next, because of numerous applications in the semiconductor industry, not only existing materials have been improved but also new materials have been searched for. Starting from III-N semiconductors, the II-IV-N$_2$ semiconductors were proposed as heterovalent ternary semiconductors. They are obtained by replacing the group III element alternately by a group II, such as Mg, Zn, and Cd and a group IV, such as Si, Ge, and Sn. Although II-IV-N$_2$ compounds have been known since the 70s, most of their properties are still poorly known.

Here is a II-IV-N$_2$ literature in brief. ZnSiN$_2$, ZnGeN$_2$, and alloys of ZnSi$_x$Ge$_{1-x}$N$_2$ were grown in thin film form by a few different approaches such as vapor growth method [11], metalorganic chemical vapor deposition (MOCVD) [12], remote plasma MOCVD [13; 14; 15], and RF-sputtering [16]. Single crystal were grown at high pressure by Endo et al. [17] and polycrystalline as well as small single crystals were grown by Du et al. [18] Raman spectra were measured by Viennois et al. [19] on
polycrystalline powders and on small single crystal needles by Peshek et al. [20]. Optical absorption [21], index of refraction [22], infrared reflectivity [23], magnetic properties upon Mn doping [24], and fabrication of transistors on SiC [25], were investigated for the Zn(Si,Ge)N$_2$ films produced by Zhu et al. [12] Several papers have recently appeared [26; 27; 28] on the growth of ZnSnN$_2$ and pointed out the opportunities of this material for photovoltaics. Band structure calculations were carried out by Limpijumnong et al. [29], Misaki et al. [30], Shaposhnikov et al. [31], and Paudel et al. [32] for a number of these materials but left considerable uncertainty on the band gaps because of the shortcomings of the local density approximation (LDA). Recently, we first calculated the band structure of CdGeN$_2$ and found to have a gap at the edge of the blue-green region [33]. Because of their close relation to the group III-N, we expect similar but not identical properties, which will provide an alternative opportunity for band-structure and other property engineering to the usual III-N alloys. In chapter 4, we present the predicted properties, such as lattice parameters, energies of formation, QSGW band structures, and effective valence band Hamiltonian parameters, of these new materials II-IV-N$_2$. The main contributions from this work are that the band structures were obtained for the first time using the QSGW method. In comparison with previous work using LDA or GGA methods, the QSGW allows us to provide much more accurate predictions on the band gaps. The details of the band structure, such as valence band splittings and effective mass hamiltonian parameters were obtained for the first time. Other important contributions of this work are our determination of the energies of formation of these materials and their range of stability in terms of chemical potentials.

Besides fundamental properties of each material, behaviors at the interfaces between materials also play an important role in semiconductor devices. Thus, band alignments between group-III nitrides have been studied before [34] as well as between GaN and ZnO [35; 36; 37; 38; 39; 40]. In chapter 5, we then extended these
studies to band offsets between the ZnGeN$_2$, ZnSnN$_2$, ZnO, and GaN by using DFT-LDA including quasiparticle corrections. ZnGeN$_2$, GaN, and ZnO have almost equal band gaps of $\sim$3.4 eV and are closely lattice matched. The band offsets among them must be staggered and hence create a situation where an effectively smaller band gap exists across the interface. We take ZnSnZn$_2$ into account although it has a larger lattice constant than the other three materials. That is because it is a new material with a potential for solar cells [26; 27; 28]. Finally, the potential benefits of this alignment for photovoltaic cells are pointed out.
In this thesis, we used the existing methods which are Density Functional Theory (DFT) and Quasiparticle Self-consistent $GW$ Approximation (QSGW) to study electronic structure of III-N and II-IV-N$_2$ semiconductors. A brief introduction to each topic to specify what approximations are made and what basis functions we used is given in this chapter. First, let us begin with the basic concepts of the self-consistent electronic structure theory based on the DFT. These methods are often called “ab initio” or “first-principles” because they do not use any empirical inputs or adjustable parameters. To deal with the large system of $N_n$ nuclei and $N_e$ electrons explicitly, we start with writing the Hamiltonian as

$$H = -\frac{\hbar^2}{2} \sum_{i}^{N_n} \frac{\nabla_i^2}{M_i} + \frac{1}{2} \sum_{i,j}^{N_n} \frac{N_n}{4\pi\epsilon_0 |R_i - R_j|} - \frac{\hbar^2}{2m} \sum_{i}^{N_e} \nabla_i^2$$

$$+ \frac{1}{2} \sum_{i}^{N_e} \sum_{i,j}^{N_e} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{I}^{N_n} \sum_{i}^{N_e} \frac{Z_I e^2}{4\pi\epsilon_0 |r_i - R_I|}.$$  \tag{2.1}$$

Where the indices $i,j$ and $I,J$ are used for electrons and nuclei respectively. $M_I$ and $R_I$ denote nuclear masses and positions while $m$ and $r_i$ are for electron masses and positions. Although it is insurmountable to solve this many-particle problem,
we can use the Born-Oppenheimer Approximation to reduce this complication. One can consider that the nuclei do not move on the time scale of the electrons. It allows us to separate the Hamiltonian into electronic and nuclear parts.

The last term in eq. 2.1, the Coulomb interaction between the nuclei and the electrons, can be considered as an external potential $V_{\text{ext}}$ seen by electrons. Then, the electronic Hamiltonian of the interacting many-body system in the atomic unit ($\hbar = m = e = 1$) is written as

$$H_{\text{el}} = -\frac{1}{2} \sum_i N_e \nabla_i^2 + \frac{1}{2} \sum_{i,i\neq j} N_e \frac{1}{|r_i - r_j|} + \sum_i N_e V_{\text{ext}}(r_i). \quad (2.2)$$

Once we have the electronic energy for fixed nuclear positions, we can solve separately the nuclear motion problem. The eigenvalues of the electronic part together with the second term of eq. 2.1, which is just a constant for fixed positions, now become the effective potential energy landscape for the nuclei. We can then vary the positions of the nuclei and hence obtain properties of atomic bonding, energy changes under deformation, relaxations of the atoms etc.

### 2.1 Density Functional Theory (DFT)

Instead of solving the many-body Schrödinger equation directly, DFT was introduced as a method to determine the ground-state properties of a many-electron system by expressing its total energy as a functional of the electron density which has only three variables instead of straightforwardly dealing with $3N_e$ variables of a many-electron wavefunction. It is based on the two theorems of Hohenberg and Kohn (HK) [41]. The first theorem states that there is a one-to-one mapping relation between the electron density and the external potential, or in other words the electron density uniquely determines the Hamiltonian and the many-body wavefunctions. Thus, every
property of the many-body system is a functional of the ground state charge density. The second theorem establishes a variational principle for the total energy functional so that ones can get the ground state energy by minimizing the energy over all possible densities. Although the HK theorem is an existence proof that the many-electron wavefunction can be substituted by the electron charge density as a basic variable, it does not provide an explicit mathematical form. In 1965, Kohn and Sham [42] proposed to express the kinetic energy in terms of independent electron single particle wavefunctions. This fictitious non-interaction electron system in an effective potential consisting of the external potential and the exchange correlation interaction is equivalent to the actual interacting system in the sense that it provides the same density. Then one arrives at the following set of equations, named the Kohn-Sham (KS) equations.

\[
H_{\text{eff}} \psi_i(r) = \left( -\frac{\nabla^2}{2} + V_{\text{eff}}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r)
\]

\[
V_{\text{eff}} = V_{\text{ext}} + \int d^3r' \frac{n(r')}{|r-r'|} + V_{\text{xc}}[n]
\]

\[
n(r) = \sum_i N_e |\psi_i(r)|^2
\]

where \( n(r) \) is the electron density, and \( V_{\text{xc}} = \frac{\delta E_{\text{xc}}[n]}{\delta n(r)} \) is the functional derivative of the exchange correlation energy \( E_{\text{xc}}[n] \) with respect to \( n(r) \). Finally, once these equations are solved for \( n(r) \) then we can express the total energy as

\[
E[n] = \sum_i N_e \varepsilon_i - \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|} - \int d^3r V_{\text{xc}}[n]n(r) + E_{\text{xc}}[n].
\]

Although the KS-DFT is in principle an exact theory, the exact exchange-correlation functional is not known and requires further approximations. First, we should understand the physical meaning of \( E_{\text{xc}} \). Let us consider an electron sitting in the electron
cloud, it does not see simply an average charge density around itself. That is because
the other electrons try to avoid this spot first by the Pauli exclusion principle and
second by electron repulsion. So the region around this particular electron has a
so-called exchange-correlation hole around itself. The exchange-correlation energy is
essentially the interaction of the electron with its surrounding exchange-correlation
hole. In other words, we can say that the exchange energy is the quantum mechan-
cal energy resulting from the antisymmetry of the many-electron wavefunctions and
the correlation energy is the dynamical interaction energy between electrons in a
quantum system. Next, we provide a brief explanation of the Local Density Ap-
proximation (LDA) and Generalized Gradient Approximation (GGA) techniques to
obtain $E_{xc}$ in the ground state, as well as the $GW$ Approximation (GWA) method
to study the one-electron excitations of the system.

2.1.1 Local Density Approximation (LDA)
The local density approximation (LDA) corresponds to the assumption that the
exchange-correlation energy at each point in space depends only on the density at
that point. In a homogeneous electron gas, the density $n$ is constant and the exchange
correlation energy $E_{xc}[n]$ has been calculated in various limits, e.g. at low density
by Wigner [43] and high density by Gell-Mann and Brueckner [44], and interpolation
formulas between these regimes exist. LDA [45] starts from computing the ground
state of the homogeneous electron gas as accurately as possible and then constructing
the exchange-correlation energy per particle, $\varepsilon_{xc}(n) = E_{xc}(n)/N$ as a function of
electron density $n = N/V$. Then we apply the same expression at each point locally
in the actual inhomogeneous system and by integration we get

$$E_{xc}^{LDA} = \int d^3 r n(r) \varepsilon_{xc}(n(r)).$$  \hspace{1cm} (2.5)
The LDA exchange-correlation potential can be written as

\[ V_{xc}^{LDA} = \frac{\partial (n\varepsilon_{xc})}{\partial n}. \] (2.6)

Although the LDA is constructed based on the assumption of a slowly varying density, it works remarkably well even for some realistic systems where the density is not slowly varying. This has been shown to be related to the fulfillment of certain sum rules [46]. The exchange-correlation energy is an average property of the exchange-correlation hole and as such does not critically depend on the details of the pair-correlation function. LDA successfully predicts the total energy, lattice constant, equation of state and relaxations of atomic coordinates around defects and at surfaces within \( \approx 5\% \) of accuracy. Nevertheless, LDA fails to give a reliable electronic excitation energy because it is a theory for the ground state total energy, not for the excitations. Typically, the gaps in insulators or semiconductors are too small. The other problem is that even for ground state properties, LDA may fail for systems which have localized electrons such as \( d \) and \( f \) electrons. It also fails near surfaces or for molecules and free atoms because the electron density varies too rapidly from a typical density inside the material to a low density outside. That is because the homogeneous electron gas is no longer a good approximation due to the large charge fluctuations.

### 2.1.2 Generalized Gradient Approximation (GGA)

In the LDA, we obtained the exchange correlation energy from the uniform electron gas expression at every point in space, but in the real system, the charge density is nonuniform. Thus the \( E_{xc} \) can deviate significantly from the LDA results. This deviation can be expressed in terms of the gradient and higher spatial derivatives of the total charge density. So GGA [47] goes one step beyond LDA by taking the
density and also its gradient at each point in space. So we can write the exchange correlation energy as

\[ E_{xc}^{GGA} = \int dr^3 n(r) f(n, |\nabla n|) \] (2.7)

It has been shown that GGA gives a better description of the exchange-correlation hole and gives a more realistic account of energy barriers and adsorption energies for molecules. Although GGA produces very good results for molecular geometries, ground state total energies and surface energies, it is not clear that GGA is an improvement over LDA for all ground state properties. In contrast with LDA, GGA typically overestimates lattice constants and underestimates phonon energies.

LDA and GGA are basically designed to study ground state properties: there is no real justification to interpret the KS one-electron eigenvalues \( \epsilon_i \) of eq. 2.4) as excitation energies, i.e. the energy to extract or add an electron to the system. They are usually not applicable for systems with strongly correlated electrons and not completely self-interaction free. Thus in the next section we will discuss Green’s function methods as a tool to study both ground state and excited state properties of the many-body problem.

## 2.2 GW Approximation (GWA)

Because LDA and GGA suffer from an incomplete cancellation of artificial self-interaction and lack the discontinuity of the exchange-correlation potential with respect to the number of electrons, the KS eigenvalues cannot represent the quasiparticle band structure measured by direct and inverse photoemission. To overcome these deficiencies, the proper inclusion of both dynamical and non-local effects by the \( GW \) approach was introduced to improve LDA and GGA results [2]. It originally was
proposed by Hedin [48] and named after its construction of the electron self-energy from the Green’s function \((G)\) and the screened interaction \((W)\).

### 2.2.1 Green’s Function

In general, the Green’s function is a propagator or the probability amplitude for a particle to travel from position \(r\) at time \(t\) to another position \(r'\) at time \(t'\). First, let us define field operators, \(\Psi^\dagger (r', t')\) and \(\Psi (r, t)\) as creation and annihilation operators written in the time dependent position basis. When these field operators operate on an exact ground state wavefunction of \(N\) electron system \(|N, 0\rangle\), one will get \(N + 1\) or \(N - 1\) electron wavefunctions which are not necessarily in the ground state. \(\langle N, 0 \mid \Psi (r, t) \Psi^\dagger (r', t') \mid N, 0 \rangle\) defines a propagator \(iG^e (rt, r't')\) for an extra electron propagating from \((r', t')\) to \((r, t)\), in contrast, \(\langle N, 0 \mid \Psi^\dagger (r', t') \Psi (r, t) \mid N, 0 \rangle = iG^h (r't', rt)\) is a propagator measuring a missing electron (hole) which propagates from \((r, t)\) to \((r', t')\). Thus the one-electron Green’s function can be defined as

\[
iG (rt, r't') = \langle N, 0 \mid T [\Psi (r, t) \Psi^\dagger (r', t')] \mid N, 0 \rangle
\]

(2.8)

\[
= \langle N, 0 \mid \Psi (r, t) \Psi^\dagger (r', t') \mid N, 0 \rangle \quad \text{for} \quad t > t'
\]

\[
= - \langle N, 0 \mid \Psi^\dagger (r', t') \Psi (r, t) \mid N, 0 \rangle \quad \text{for} \quad t' > t
\]

Here \(T\) is the time-ordering operator which rearranges operators from right to left after increasing time and includes a minus sign for every interchange of fermion operators. Let us consider the field operator in the Heisenberg representation \(\Psi^\dagger (r, t) = e^{iHt} \Psi^\dagger (r) e^{-iHt}\) and insert the closure relation into eq. 2.8. Note that the limiting energy for injection of electrons or holes is the chemical potential \(\mu\). Thus we can
rewrite eq. 2.8 as

\[ iG(r, r', \tau) = \sum_n \langle N, 0 \mid \Psi(r) \mid N + 1, n \rangle \langle N + 1, n \mid \Psi^\dagger(r') \mid N, 0 \rangle e^{-iE_n \tau}, \tau > 0, E_n \geq \mu \]

\[ = -\sum_m \langle N, 0 \mid \Psi(r')^\dagger \mid N - 1, m \rangle \langle N - 1, m \mid \Psi(r) \mid N, 0 \rangle e^{-iE_m \tau}, \tau < 0, E_m < \mu. \]

(2.9)

Where \( \tau = t - t' \), \( n \) and \( m \) represent quantum numbers to specify the state which is not the ground state. \( E_n = E_n^{N+1} - E_0^N \) and \( E_m = E_0^N - E_m^{N-1} \) respectively. Eq. 2.9 can be Fourier-transformed into the frequency representation as

\[ iG(r, r', \omega) = \int_{-\infty}^{\infty} iG(r, r', \tau) e^{i\omega \tau} d\tau \]

\[ = \sum_n \langle N, 0 \mid \Psi(r) \mid N + 1, n \rangle \langle N + 1, n \mid \Psi^\dagger(r') \mid N, 0 \rangle \int_0^{\infty} e^{i(\omega - E_n + i\eta) \tau}, E_n \geq \mu \]

\[ = -\sum_m \langle N, 0 \mid \Psi(r')^\dagger \mid N - 1, m \rangle \langle N - 1, m \mid \Psi(r) \mid N, 0 \rangle \int_{-\infty}^{0} e^{i(\omega - E_m - i\eta) \tau}, E_m < \mu. \]

The positive infinitesimal \( \eta \) is for ensuring that \( G(r, r', \omega) \) has the correct analytic properties.

Let us define the quasiparticle amplitudes of any excited state \( s \) as

\[ f_s(r) = \langle N, 0 \mid \Psi(r) \mid N + 1, s \rangle \quad \text{for} \quad E_s = E_s^{N+1} - E_0^N, E_s \geq \mu \]  

\[ f_s(r) = \langle N - 1, s \mid \Psi(r) \mid N, 0 \rangle, \quad \text{for} \quad E_s = E_0^N - E_s^{N-1}, E_s < \mu \]  

(2.11)

and work out the integrals in the eq. 2.10. Then we get

\[ G(r, r', \omega) = \sum_s \frac{f_s(r)f_s^*(r')}{\omega - E_s \pm i\eta} \]

(2.12)

where now the sum is over both electrons and holes and the \( \pm \) signs correspond to electrons and holes respectively. The poles of the Green’s function represent the
single-particle excitations or the quasiparticle energies.

Next, an explicit expression for the single-particle Green’s function was derived by Hedin, starting from the Heisenberg equation of motion for the field operator.

\[ i \frac{\partial \Psi(x)}{\partial t} = [\Psi(x), H] \]  \hspace{1cm} (2.13)

\( x \) denotes space(\( r \)), spin(\( \sigma \)), and time(\( t \)). The Hamiltonian is split into the non-interaction part \( H_0 \) and the interaction part.

\[ H = \int dr \Psi^\dagger(x)H_0(x)\Psi(x) + \frac{1}{2} \int dr dr'\Psi^\dagger(r, t)\Psi^\dagger(r', t)\nu(r, r')\Psi(r', t)\Psi(r, t) \] \hspace{1cm} (2.14)

The problem is that the second part in eq. 2.14 when inserted in eq. 2.13 involves a two-particle Green’s function. Then, we need to somehow decouple this part, so the mass operator is defined by

\[ \int dx'' M(x, x'')G(x'', x') = \] \hspace{1cm} (2.15)

\[ -i \int dr''\nu(r, r'')\langle N[T[\Psi^\dagger(r'', t)\Psi(r', t)\Psi(r, t)\Psi^\dagger(r', t')]|N \rangle \]

and from the well-known eq. 2.13, an equation of motion for the Greens’s function can be derived as

\[ \left[ i \frac{\partial}{\partial t} - H_0(x) \right] G(x, x') - \int dx'' M(x, x'')G(x'', x') = \delta(x - x'). \] \hspace{1cm} (2.16)

One can put the average Coulomb interaction, \( V_H \), into the non-interacting part, and write the equation of motion for the Green’s function as

\[ \left[ i \frac{\partial}{\partial t} - H_0(x) - V_H(x) \right] G(x, x') - \int dx''\Sigma(x, x'')G(x'', x') = \delta(x - x') \] \hspace{1cm} (2.17)
The eq. 2.17 defines the self-energy, $\Sigma$. Hedin [49] used Schwinger’s functional derivative method to derive a set of equations for the self-energy in terms of the screened Coulomb interaction. The physical idea is that the electron-electron interaction itself is screened. Because the screening reduces the interaction, one may hope that expressing everything in the screened interaction will lead to a better-converging approximate method. Eventually, one arrives at the set of equations

$$
\begin{align*}
\Sigma(1,2) &= i \int d(34) G(1,3^+) W(1,4) \Lambda(3,2,4) \quad : 1 \equiv (r_1, \sigma_1, t_1) \\
G(1,2) &= G_0(1,2) + \int d(34) G_0(1,3) \Sigma(3,4) G(4,2) \\
W(1,2) &= \nu(1,2) + \int d(34) \nu(1,3) P(3,4) W(4,2) \\
P(1,2) &= -i \int d(34) G(2,3) \Lambda(3,4,1) G(4,2^+) \\
\Lambda(1,2,3) &= \delta(1-2) \delta(2-3) + \int d(4567) \delta \Sigma(1,2) \delta G(4,5) G(4,6) G(7,5) \Lambda(6,7,3)
\end{align*}
$$

where $W$, $\Lambda$ and $P$ are the screened Coulomb potential, the vertex function and the polarization function respectively. The $GWA$ is the first step in solving this formidable set of equations by assuming the vertex function $\Lambda(1,2,3) = \delta(1-2) \delta(2-3)$. Then we get

$$
\begin{align*}
\Sigma(1,2) &= iG(1,2^+) W(1,2) \quad (2.19a) \\
W(1,2) &= \nu(1,2) + \int d(34) \nu(1,3) P(3,4) W(4,2) \quad (2.19b) \\
P(1,2) &= -iG(2,1) G(1,2^+). \quad (2.19c)
\end{align*}
$$

These Hedin equations can be solved self-consistently until the resulting Green’s function coincides with the starting one. For more details, review articles about $GW$ method are in ref. [50; 49; 51].
2.2.2 GW correction to LDA energy

The GW A in practice is applied as a perturbation approach to calculate the excitation energy from KS-DFT eigenfunctions and eigenvalues. In simple words, it is just a one-shot correction to, for example, LDA. Although in the previous section quasiparticle excitations were defined in terms of the poles of the Green’s function, one can introduce also a quasiparticle wavefunction and energy. They obey the equation

$$\left(-\frac{\nabla^2}{2} + V_{\text{ext}}(r) + V_H(r)\right) \phi_i(r) + \int dr' \Sigma(r, r', \varepsilon_{\text{GW}}) \phi_i(r, r') = \varepsilon_{\text{GW}} \phi_i(r) \quad (2.20)$$

Although it looks very similar to the KS equation

$$\left(-\frac{\nabla^2}{2} + V_{\text{ext}}(r) + V_H(r)\right) \psi_{\text{LDA}}^LDA(r) + V_{xc}^{\text{LDA}}(r) \psi_{\text{LDA}}^LDA(r) = \varepsilon_{\text{LDA}} \psi_{\text{LDA}}^LDA(r) \quad (2.21)$$

the self-energy (\(\Sigma\)) is a non-local and energy-dependent operator. Thus the operator in eq. 2.20 is not a hermitian operator. For example, its energies can be complex. Their imaginary part represents the lifetime of the particle. Nevertheless we can find solutions of eq. 2.20 by means of perturbation theory if we assume the wavefunctions of eq. 2.20 are the same as those in eq. 2.21. Then one can correct DFT-LDA eigenvalues by a using first-order perturbation treatment.

$$\varepsilon_{\text{GW}}^i = \varepsilon_{\text{LDA}}^i + \left\langle \psi_{\text{LDA}}^LDA \left| \Sigma(r, r', \varepsilon_{\text{GW}}^i) - V_{xc}^{\text{LDA}}(r) \right| \psi_{\text{LDA}}^LDA \right\rangle \quad (2.22)$$

Using a Taylor expansion of \(\Sigma(r, r', \varepsilon_{\text{GW}}^i)\) around \(\varepsilon_{\text{LDA}}^i\), we get the GW eigenvalues as

$$\varepsilon_{\text{GW}}^i = \varepsilon_{\text{LDA}}^i + Z_i \left\langle \psi_{\text{LDA}}^LDA \left| \Sigma(r, r', \varepsilon_{\text{LDA}}^i) - V_{xc}^{\text{LDA}}(r) \right| \psi_{\text{LDA}}^LDA \right\rangle \quad (2.23)$$
Where $Z_i = (1 - \langle \psi_i^{LDA} | \frac{\partial}{\partial \varepsilon} \Sigma(r, r', \varepsilon_i^{LDA}) | \psi_i^{LDA} \rangle)^{-1}$ is a quasiparticle renormalization factor.

To summarize, eq. 2.23 gives us the energy shift of the one-particle excitations from the KS eigenvalues and also their imaginary parts. Within the $GW$ approximation, by Fourier transforming eq. 2.19a over time, the self-energy $\Sigma$ is given as

$$\Sigma(r, r', \varepsilon) = \frac{i}{2 \pi} \int d\varepsilon' e^{-i\delta \varepsilon'} G(r, r', \varepsilon - \varepsilon') W(r, r', \varepsilon')$$ (2.24)

In the so-called one-shot $G_0W_0$, $G$ can be approximated by the independent particle $G^0$

$$G^0(r, r', \varepsilon) = \sum_i \frac{\psi_i^{LDA} \psi_i^{LDA*}}{\varepsilon - \varepsilon_i^{LDA} \pm i\eta}$$ (2.25)

Then, by using the Random Phase Approximation (RPA), the screened Coulomb interaction $W$ can be estimated as $W^0$

$$W^0 = \nu \varepsilon^{-1} = \nu (1 - \nu P)^{-1}$$ (2.26)

Here, $W^0$ is expressed by a schematic notation. We should remember that all these quantities are actually $\nu(1, 2), W(1, 2)$ etc. and thus eq. 2.26 represents an integral equation. Instead of the time domain, one first switches to the frequency or energy domain so $P$ becomes a dynamic polarization $P(r, r', \omega)$. In practice, all quantities are expanded in a basis set so that these become matrix equations. $P$ given by eq. 2.19c is the proper polarization function and $\nu$ is the bare Coulomb interaction and $\varepsilon$ is the dielectric function. Although the GWA is an enormous step forward from the KS theory for calculating excitation energies, it still is not always sufficiently accurate. First, in practice, the results depend on other approximations made such
as pseudopotentials to describe the interaction between valence and core electrons. When using more accurate all-electron band structure methods, the corrections to band gaps still tend to be too small. The reason is that GW is in practice applied as a perturbation theory and therefore it depends on the accuracy of the starting point.

### 2.3 Quasiparticle Self-consistent GW Approximation (QSGW)

The GWA is usually applied as a perturbation theory and its success depends on the accuracy of the starting point. In the QSGW formalism, we search for the best possible starting point by redefining an effective independent particle Hamiltonian ($H^0 = H^{LDA} + \Delta V_{xc}$) with a correction to the exchange correlation potentials which must somehow be extracted from the self-energy.

Van Schilfgaarde et al. [2; 3] have proposed to do this by deriving the self-energy as a functional of $G^0$ and extracting $G^0$ initially from $V_{eff} = V_{ext} + V_H + V_{xc}^{LDA}$ and then determining $V_{eff}^{GW} = V_{ext} + V_H + \Sigma(G^0)$. To complete the self-consistency circle of the effective potential, $V_{eff}^{GW}$ is mapped back to $V_{eff}$. This is equivalent to requiring that the eigenvalues of eq. 2.20 become as close as possible to those of eq. 2.21 with the $\Delta V_{xc} = V_{xc}^{QSGW} - V_{xc}^{LDA}$ added to the potential. On the way back to $V_{eff}$, a non-local but energy independent exchange-correlation potential shown in eq. 2.27 is extracted from the self-energy,

$$V_{xc}^{QSGW} = \frac{1}{2} \sum_{ij} |\psi_i\rangle \Re[\Sigma_{ij}(\epsilon_i) + \Sigma_{ij}(\epsilon_j)] \langle \psi_j|$$

where $\psi$ are the one-electron KS eigenstates and $\Re$ means taking the Hermitian part.

Note that this is not the only method beyond single-shot $G_0W_0$. Some people would take the corrected eigenvalues of eq. 2.23, insert them into eq. 2.25 and
Thus obtain a new $G$ and then a new $\Sigma$ from $GW_0$ but still keeping $W_0$ in eq. 2.26 fixed. Others would also recalculate $W$ with the new Green’s function. This is more demanding because the calculation of the dynamic screening for $W$ is the most time-consuming part of the $GW$ calculation. However, in eq. 2.23 one only needs diagonal matrix elements of the self-energy, while in eq. 2.27 one needs also off-diagonal elements. This allows the states in the presence of the new potential to be mixed up or interact and is an important reason for the success of QSGW. In other words, it not only adjusts the eigenvalues but also the eigenstates of the $H_0$. In practice the method can become unstable for high energy states. It was also found that this problem can be cured by approximating the self-energy by a diagonal approximation above a certain cut-off ($E_{\text{cut}}$).

The performance of QSGW was demonstrated in a series of studies by van Schilfgaarde et al. [52; 2; 3] It was shown to give excellent agreement for band gaps for most semiconductors. It improves band widths and gives good agreement with photoemission for metals. Even for strongly correlated materials like transition metal oxides and rare earths it gives reasonable results although it is not able to explain fully the spectral functions of such complex materials. However, the method has systematic small remaining errors: it gives a slight overestimate of the gaps compared to experiment. This remaining discrepancy is thought to arise from the under-screening by the RPA. It can be corrected by scaling the final $\Delta V_{xc}$ by about 80 % as obtained empirically by comparing QSGW with experiment for a wide variety of semiconductors [2]. This correction is referred as the $0.8\Sigma$ approximation. Within this approximation most band gaps are obtained to better than 0.1 eV. In this thesis, we are not concerned with strongly correlated systems but with new semiconductors which have similar $sp$-covalent and ionic bonding as in other semiconductors.
2.4 Full-Potential Linear Muffin-Tin Orbital Method (FP-LMTO)

There are two major methods used to solve the single-particle Schrödinger equation of a periodic system. The first one is the variational method in which the eigenfunctions are expanded in terms of a fixed set of basis functions. An example is the plane wave method which is usually combined with a pseudopotential approximation to describe the interaction between valence and core electrons. This keeps the basis set to a reasonable number of functions because it avoids describing the rapid oscillations of the wavefunctions in the core region. The second one is the multiple scattering method. In this method, the potential is usually geometrically approximated by a muffin-tin potential. For accurate solutions, the former requires a large number of basis functions while the latter requires a high computational effort since it is no longer a simple matrix eigenvalue problem. Here, we use the Linear Muffin-Tin Orbital (LMTO) [53] which combines the advantages of both methods by using basis sets derived by the scattering method. It will lead to very small basis sets and is less time consuming.

To define the basis set, space is divided into spheres around the atomic sites called “muffin-tin spheres” and the interstitial region between the spheres. The Muffin-Tin Orbitals (MTOs) will be constructed from solutions of the Schrödinger equation in each region. They are given by the product between a spherical harmonic and a radial function centered on each of the atomic sites. Outside the sphere, the solution is for the constant potential, i.e. a decaying Hankel function corresponding to some energy a little below the constant potential. This is called the envelope function. Inside the sphere on which the orbital is centered, the solution is replaced by a matching linear combination of the solution of the Schrödinger equation at some chosen energy and its energy derivative. We call these $\phi$ and $\dot{\phi}$. The tail of
the envelope function is re-expanded in spherical harmonics about any other site wherever it intersects another sphere and is likewise matched to a linear combination of $\phi$ and $\dot{\phi}$. The expansion of a spherical wave centered on one site about another site is described in terms of the so-called structure constants, which also appear in the multiple scattering theory. Overall, the function is thus continuous and differentiable everywhere and is constructed out of solutions of the Schrödinger equation for the muffin-tin potential in each region but not necessarily at the correct energy. By containing both $\phi$ and $\dot{\phi}$ parts the functions can be expected to describe the actual solutions of the eigenstates of energy $\varepsilon_v$ in some range of energies where the Taylor expansion of the partial waves as functions of energy is valid. The eigenstates will be a superposition of these MTOs. To deal with the periodic boundary conditions in a solid, one needs to take Bloch sums over the lattice vectors. Then matrix elements of the Hamiltonian and the overlap matrices are calculated. The latter are diagonalized to give the eigenvalues and eigenvectors. Then a new charge density can be constructed by integrating over the Brillouin zone and hence the KS equations can be solved self-consistently. Calculating the integrals over the spheres is easy because one knows how the Hamiltonian acts on the $\phi$ and $\dot{\phi}$ but the integrals over the interstitial region are difficult because of its complicated shape. Therefore a fast computational scheme is obtained if one lets the spheres overlap a bit so they fill all space. The interstitial region then essentially disappears from the problem. This is done in the so-called atomic sphere approximation (ASA), in which one usually also assumes that the charge density is a superposition of spherical charge densities in the spheres. This method is fast but not sufficiently accurate for total energies in low-symmetry structures.

In order to avoid the restrictions of the muffin-tin shaped potential, the Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) was introduced [54; 55]. In FP-LMTO, the muffin-tin shape is only used for constructing basis sets, but there is no
shape approximation to the crystal potential or charge density. Inside each muffin-tin sphere, the Schrödinger equation is solved numerically. Here, the calculation is simple because the potential is very close to spherical, whereas the non-spherical terms are included later. In the interstitial region, the envelope function can be further improved from the original LMTO method by changing the Hankel function to a smoothed Hankel function. For the flat potential outside the spheres, the solution of the radial Schrödinger equation is a standard Hankel function with a singularity at the origin. However, the true potential of the system starts to feel the attractive nuclear potential outside the muffin-tin radius \( R_{mt} \) so the correct wavefunction bends over outside \( R_{mt} \). To include this behavior and remove the singularities, the smooth Hankel functions were defined by Methfessel et al. [56] as a convolution of Gaussians and standard Hankel functions. The shape of each smooth Hankel function can be controlled by two parameters. The first one is the function decay constant \( \kappa \), while another one is the smoothing radius \( R_{sm} \). \( R_{sm} \) is used to determine how strongly the function has been bent. Nevertheless, the difficult problem of a FP-LMTO method is how to calculate the matrix elements of the Hamiltonian over the interstitial region. We employ the method in ref. [55] to overcome this problem by using a dual representation of all the quantities needed: charge density, potential, and wavefunctions. Instead of strictly separating the muffin-tins and interstitial region, FP-LMTO beaded on smooth Hankel functions [55] splits the quantities in a smoothly varying function defined in the whole cell and a correction to this function inside the spheres. The latter is obtained by expanding the smooth function inside the spheres in spherical harmonics times a radial function. Only the low angular momentum components of this function need to be replaced by the actual rapidly varying functions obtained from the radial solutions of the Schrödinger equation of the true potential inside the spheres. Now, the charge density, \( n(r) \), can be represented as a smooth function throughout the whole unit cell, plus contributions from
inside the muffin-tin spheres.

\[ n(r) = \tilde{n}(r) + \sum_{R,L} \{n_{R,L}(r) - \tilde{n}_{R,L}(r)\} \quad (2.28) \]

\( \tilde{n}(r) \) and \( \tilde{n}_{R,L}(r) \) are the smooth charge densities throughout the unit cell and inside the muffin-tin spheres respectively, which are slowly varying. \( n_{R,L}(r) \) is a true density inside the muffin-tin sphere which is rapidly varying near the core. The smooth parts or the functions are given on a relatively coarse mesh. Their Fourier transform can be obtained by fast Fourier transform method (FFT) which allows one to easily find the corresponding electrostatic potential, i.e. solve Poisson’s equation. The method avoids some of the disadvantages of previous implementations of FP-LMTO, such as the need for high angular momentum expansions. Matrix elements are all relatively easily calculated because no cross terms occur between the smooth part and the intra-sphere parts and the integration over an awkwardly shaped interstitial region is avoided. In practice, the method is competitive in accuracy with the so-called linearized augmented plane wave (LAPW) method, which is in the community considered one of the most accurate band structure methods. In fact, the method has been recently generalized to allow mixing augmented plane waves with augmented LMTOs so that the convergence of the basis set can be studied more systematically \[54\]. Further additions to the method include the use of local orbitals. These are orbitals defined only inside the spheres. They add additional variational freedom to express the eigenstates more accurately. In particular they are used to include both high energy partial waves of a given angular momentum and low energy semicore states, e.g. Zn\(–3d\) and Cd\(–4d\).
2.5 Implementation of $GW$ and $QSGW$ within FP-LMTO

The eq. 2.19 are expressed in terms of functions which are continuous functions of the real space variables $r$ and $t$. In practice, these are not solved in the space and time domain but by means of basis function expansions. First, we always use the energy domain, so the Green’s function is given by eq. 2.25 and the self-energy is obtained as an integral over energy (eq. 2.24) which has to be carried out over a contour in the complex energy plane for efficient evaluation. Secondly, the polarizability is not obtained from the Green’s functions but by Fourier transforming to reciprocal space in which case it becomes a convolution in $k$-space and requires sums over occupied and empty bands as well as products of four eigenstates of the Schrödinger equation. To solve the integral eq. 2.19b or equivalently invert eq. 2.26, we need an efficient basis set to represent the screened and unscreened Coulomb interaction and the polarizability etc. All of these are two point quantities in real space that depend on $r$ and $r'$. In most $GW$ implementations, these are all expanded in plane waves. In the implementation by Kotani and van Shilfgaarde [52; 2; 3], an auxiliary basis set is used for these expansions which is more efficient because it requires fewer functions. The main idea is to use a so-called product basis set. Inside each sphere, these functions are products of the same partial waves also used in the LMTO basis set. They are spherical harmonics times radial functions. In the interstitial region, a plane wave expansion is added. Once these are constructed, all one needs is to know the coefficients which allow one to rotate between this product or mixed basis set and the products of muffin-tin orbitals. A full description of these aspects of the method can be found in ref. [52; 2; 3].

The results in ref. [52] shows the self-consistent cycle of $QSGW$. It starts within the $H^0 = H^{LDA}$ or $\Delta V_{xc} \equiv V_{xc}^{QSGW} - V_{xc}^{LDA} = 0$. The density and LDA potential are
made self-consistent keeping $\Delta V_{xc}$ constant. Then, the $V^{QSGW}_{xc}$ is constructed from the “QSGW” basis $\Psi_{kn}$ on the irreducible subset of $k_{mesh}$ points by using eq. 2.27. This $GW$ mesh is given by a discrete mesh in a primitive cell in the Brillouin zone. We can interpolate $V^{QSGW}_{xc}(k_{mesh})$ to other $k$ by Fourier transforming the basis $\Psi_{kn}$ to $\chi_{RLj}^k$ in real space. This transformation handles the problem of ambiguities near band crossings. Then $V^{QSGW}_{xc}(k)$ in the “LDA” basis for arbitrary $k$ points on a finer mesh than the $GW$ mesh can be built by Bloch sum and basis transformation. This procedure allows us to obtain accurate continuous energy bands which are essential for detailed properties such as effective masses.
Chapter 3

Heterovalent binary III-N compounds

3.1 Introduction

The group-III nitride semiconductors, AlN, GaN, and InN represent an important and promising class of materials for a variety of optoelectronic and electronic applications because of their direct band gaps which span the range 0.7 - 6.2 eV, including the whole of the visible region. To model electronic states, optical properties and transport in quantum well heterostructures, nanowires and nanoparticles of these materials, one often uses a description in terms of a six-band effective Hamiltonian describing the valence band maximum manifold of nearly degenerate states near the center of the Brillouin zone. Within the envelope function approximation, the states of these nanostructures are described as a linear combination of products of slowly varying envelope functions and the Bloch functions of the crystal near the valence band maximum. This effective Hamiltonian approach is also used in the theory of excitons and shallow acceptors. The effective Hamiltonian for semiconductors with zincblende structure was introduced by Luttinger and Kohn [57; 58]. Its form is
determined by the theory of invariants. Its generalization for wurtzite crystals was introduced by Rashba, Sheka and Pikus [59].

The parameters for these effective Hamiltonians include inverse effective mass parameters, describing all the terms of order $k^2$, crystal field and spin-orbit splittings at $\Gamma$ and some linear-in-$k$ terms. Strain dependent terms are added to the energy splittings. Several previous works have fitted these parameters to first-principles band structure results [4; 5; 1]. Because there were significant discrepancies on these parameters from different groups, and validation of these parameters by experimental methods is indirect, some efforts were made to arrive at a recommended set of values [6; 7]. Recently, there has been a resurgence of interest [8; 9; 10] in improving these valence band parameters because more accurate band structure methods have become available going beyond the local density approximation used in the work of the '90's. Among the group-III nitrides, InN requires perhaps the most important revisions because its band gap is now accepted [60; 61] to be 0.7 eV while it was long believed to be about 1.89 eV [62].

Rinke et al. [8] used $G_0W_0$ quasiparticle band structures starting from optimized effective potential exact exchange + LDA correlation, but focused on the fit only very near the $\Gamma$-point. de Carvalho et al. [10] use $G_0W_0$ starting from hybrid functional HSE calculations. Svane et al. [9] used QSGW calculations, very similar to the calculations reported here but did not extract effective Hamiltonian parameters. It focused only on the effective masses and splittings.

In this chapter, we revisit the problem once more with several differences to be mentioned from the previous work. First, we use QSGW which has an advantage for determining the fine structure of the band structure, such as effective masses. Second, we have reevaluated the process for most reliably extracting the effective Hamiltonian parameters. While some derive directly from the effective masses without spin-orbit coupling in or perpendicular to the basal plane, some of the parameters such as
required fitting the band structures in an intermediate k-space direction if one
does not wish to rely on quasi-cubic approximations. The linear-in-k-parameter $A_7$
also requires careful evaluation of the band anti-crossing behavior. These aspects
will be discussed in detail below. The determination of the spin-orbit and crystal
field splittings and the validity of the quasi-cubic approximation for the former also
requires some discussion. We show that in GaN and InN, relativistic terms linear in
$k$ need to be included to properly describe the spin-splittings. Finally, the crystal
field splitting at $\Gamma$ is particularly sensitive both to the $GW$ corrections to the band
structure and to the crystal structure, such as the $c/a$ ratio. This means in practice
the crystal field splitting is dependent on uniaxial strain. We therefore think it is
essential to include a description of the latter in terms of deformation potentials.

As our main new results, we mention that we find a crystal field splitting in GaN
much closer to experiment than in previous work. Secondly, we find a negative spin-
orbit splitting for InN. We also discuss the recent experimental work on AlN band
parameters in view of our results [63; 64].

### 3.2 Computational details

We use the DFT-LDA method [41; 42] to determine the equilibrium crystal structure
parameters. The quasiparticle band structures are calculated using the QSGW ap-
proach [2; 52]. For some specific details of our calculations, we use a double ($\kappa, R_{sm}$)
basis set consisting of $spdf$ and $spd$ functions for the first and the second set of group
III and N atoms. In addition we add 3$d$ and 4$d$ local orbitals of Ga and In atoms, and
also $spd$ floating orbitals. Floating orbitals only have an envelope function (smoothed
Hankel function) but no augmentation inside a sphere. They are centered on intersti-
tial sites of high symmetry. We use a $GW$ $k$-point set of $4 \times 4 \times 4$ for AlN and GaN.
In the case of InN, we found the results to be particularly sensitive to the $k$-point
convergence and therefore used $6 \times 6 \times 4$. We chose the cut-off energy ($E_{cut}$) to be 2 Ryd in GaN, AlN, and InN.

### 3.3 Results

#### 3.3.1 QSGW band structures

The structural parameters obtained from our LDA optimization are in good agreement with experiments and previous calculations and are given in table 3.1 for reference. For InN no experimental value is available for the internal parameter $u$ of Wurtzite structure, but our value agrees well with that of de Carvalho et al. [10], 0.378, Svane et al. [9], 0.379, and Rinke et al. [8], 0.380.

<table>
<thead>
<tr>
<th></th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>LDA</td>
<td>Expt.</td>
<td>LDA</td>
</tr>
<tr>
<td>$c$</td>
<td>4.975</td>
<td>5.143</td>
<td>5.166-5.185</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.599</td>
<td>1.601</td>
<td>1.629</td>
</tr>
<tr>
<td>$u$</td>
<td>0.382</td>
<td>0.382</td>
<td>0.376</td>
</tr>
</tbody>
</table>

*Expt. from Schulz et al. [65]*
*Expt. from Ueno et al. [66]*

Next, the LDA and QSGW band structures of AlN, GaN, and InN are compared with each other in fig. 4.4. The valence band maximum obtained from the LDA calculation is set to zero. Let us discuss the shifts of the individual band states due to $GW$. In an electron gas or metal, the $GW$ self-energy $\Sigma_{xc}(\epsilon_F) = 0$ at the Fermi level and furthermore one knows that near the Fermi level $|\text{Im}\Sigma_{xc}(\omega)| \propto (\omega - \epsilon_F)^2$ and leads to an increasing shift of the levels away from the Fermi level [49]. In a semiconductor we can no longer do this expansion around the Fermi level and the
Table 3.2: Band gaps of the III-N compounds and shifts between QS\textit{GW} and LDA relative to their own average electrostatic potentials for CBM and VBM in eV.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_g$ (LDA)</th>
<th>$E_g$ (QS\textit{GW})</th>
<th>$E_g(0.8\Sigma)$</th>
<th>$E_g$ (Expt.)</th>
<th>$\Delta$ CBM</th>
<th>$\Delta$ VBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>4.28</td>
<td>6.67</td>
<td>6.19</td>
<td>6.23\textsuperscript{a}</td>
<td>1.19</td>
<td>-0.73</td>
</tr>
<tr>
<td>GaN</td>
<td>2.11</td>
<td>3.97</td>
<td>3.60</td>
<td>3.51\textsuperscript{a}</td>
<td>1.16</td>
<td>-0.34</td>
</tr>
<tr>
<td>InN</td>
<td>0.00</td>
<td>0.87</td>
<td>0.70</td>
<td>0.69\textsuperscript{b}</td>
<td>0.65</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Expt. from Vurgaftman \textit{et al.} [7]  
\textsuperscript{b} Expt. from Wu \textit{et al.} [68]

zero of the $\Sigma_{xc}(\omega)$ is set by that of the Green’s function of the underlying one-electron Hamiltonian. Although there is no physical meaning to eigenvalues on an absolute scale in a periodic system, we can use the average electrostatic potential as the zero of energy. We can compare the shifts between the QS\textit{GW} quasi-particle energies and the LDA eigenvalues with respect to the average electrostatic potential, calculated in the same way by setting the reciprocal lattice vector $\mathbf{G} = 0$ component of the Madelung potential equal to zero. These absolute shifts are mainly useful in the context of band-offset calculations between two materials as will be considered in the final chapter of this thesis. Once we determine from an interface calculation, how the average electrostatic potentials in the two semiconductors are placed relative to each other, and assuming that far away from the interface, the material is bulk-like, we can then apply the shifts between LDA and QS\textit{GW} relative to this \textit{local} average electrostatic potential reference and thus obtain a $\text{GW}$ correction to the LDA band offset. One can also use core levels or any other “local potential marker” for this purpose, such as the potential at the muffin-tin radius, discussed later in chapter 5. These shifts also play a role in the understanding of defect levels and alloys [67]. The band gaps calculated at equilibrium lattice constants and the shifts of CBM and VBM are summarized in table 3.2.
3.3.2 Effective valence band Hamiltonian

The effective-mass Hamiltonian can be described in terms of the operators for $L = 1$ angular momentum representing the basis states of the three-fold degenerate valence band maximum (VBM) at $\Gamma$ without spin-orbit coupling, the Pauli matrices representing the spin, the wave vector $\mathbf{k}$, and the strain tensor $\epsilon$. The only allowed terms are those up to terms of second order in any of these quantities whose combination has the $A_1$ symmetry. In wurtzite, this Hamiltonian is described by [59]:

$$
H = \Delta_1 L_z^2 + \Delta_2 L_z \sigma_z + \sqrt{2} \Delta_3 (L_+ \sigma_- + L_- \sigma_+) \\
+ (A_1 + A_3 L_z^2) k_z^2 + (A_2 + A_4 L_z^2) (k_x^2 + k_y^2) \\
- A_5 (L_+^2 k_-^2 + L_-^2 k_+^2) \\
- 2i A_6 k_z (\{L_z, L_+\} k_+ - \{L_z, L_-\} k_-) \\
+ A_7 (k_- L_+ + k_+ L_-) + (\alpha_1 + \alpha_3 L_z^2) (\sigma_+ k_- + \sigma_- k_+) \\
+ \alpha_2 (L_+^2 k_- \sigma_- + L_-^2 k_+ \sigma_+) \\
+ 2\alpha_4 \sigma_z (\{L_z, L_+\} k_- + \{L_z, L_+\} k_+) \\
+ 2i \alpha_5 k_z (\{L_z, L_+\} \sigma_- - \{L_z, L_-\} \sigma_+) \\
+ (D_1 + D_3 L_z^2) \epsilon_{zz} + (D_2 + D_4 L_z^2) \epsilon_{\perp} \\
- D_5 (L_+^2 \epsilon_- + L_-^2 \epsilon_+) \\
- 2i D_6 (\{L_z, L_+\} \epsilon_{-z} - \{L_z, L_-\} \epsilon_{+z}) \quad (3.1)
$$

Here, $\{L_z, L_-\} = \frac{1}{2} (L_z L_- + L_- L_z)$ is the symmetrized product, $L_\pm = \frac{1}{\sqrt{2}} (\pm i L_x - L_y)$, $\sigma_\pm = \frac{1}{2} (\pm i \sigma_x - \sigma_y)$, $k_\pm = k_x \pm i k_y$, $k_\perp^2 = k_x^2 + k_y^2$, $\epsilon_\perp = \epsilon_{xx} + \epsilon_{yy}$, $\epsilon_{\pm z} = \epsilon_{xz} \pm i \epsilon_{yz}$, $\epsilon_\pm = \epsilon_{xx} - \epsilon_{yy} \pm 2i \epsilon_{xy}$. The parameters $\Delta_1, \Delta_2, \Delta_3$ are the crystal field splitting and spin-orbit coupling parameters. The $A_1 - A_6$ are inverse effective-mass type parameters.
and the $A_7$ is a non-relativistic (spin-independent) linear in $k$ term. Relativistic terms linear in $k$ and spin are described by the $\alpha_1 - \alpha_5$ terms. The parameters $A_1 - A_5$ are directly related to the hole masses in the plane and perpendicular to the plane by means of

$$-(m_h^\parallel)^{-1} = A_1 + A_3$$
$$-(m_s^\parallel)^{-1} = A_1$$
$$-(m_h^\perp)^{-1} = A_2 + A_4 + A_5$$
$$-(m_s^\perp)^{-1} = A_2 + A_4 - A_5$$
$$-(m_{sh}^\perp)^{-1} = A_2$$

(3.2)

Note that the masses here correspond to the bands without spin-orbit coupling.

The parameter $A_6$ only affects the bands in directions intermediate between the plane and perpendicular to it. While in Kim et al. [1] these were obtained by means of the quasi-cubic approximation from the previous parameters, we here determine it directly by fitting the bands in an intermediate direction. We will show explicitly that the quasi-cubic approximation is not sufficient.

As described in detail in Kim et al. [1] the $A_7$ parameter is related to the avoided band crossing of the light hole and crystal field split-off band. When it is set to zero the bands cross. The split-off band then has a large effective hole mass. When $A_7$ is switched on, the crossing is lifted. The light hole and split-off hole masses are changed respectively by

$$\pm 2A_7^2/|\Delta_1|.$$  

(3.3)

The parameter $A_7$ is determined by fitting the non-parabolic shapes of the bands near this crossing directly by manually adjusting $A_7$ until good agreement is obtained.
The crystal field splitting parameter at $\Gamma$ is directly obtained from the calculation without spin-orbit coupling. It is defined as the difference $\Delta_1 = E(\Gamma_5) - E(\Gamma_1)$ between the doublet and singlet of the VBM. When spin-orbit coupling is included the $\Gamma_5$ state splits in to a $\Gamma_9$ and $\Gamma_7$ state. The latter can then interact with the nearby crystal field split-off state $\Gamma_1$ because in double group notation, $\Gamma_1$ becomes $\Gamma_7$. This leads to the eigenvalues given by

\[
E_{9} = \Delta_1 + \Delta_2 \\
E_{7\pm} = \frac{\Delta_1 - \Delta_2}{2} \pm \sqrt{\left(\frac{\Delta_1 - \Delta_2}{2}\right)^2 + 2\Delta_3^2}
\] (3.4)

The two splittings allow us to determine the parameters $\Delta_2$ and $\Delta_3$ if we already know $\Delta_1$ or assume it is not changed by spin-orbit coupling. While in some other cases this procedure may lead to difficulties, (it may lead to an imaginary $\Delta_3$) it works fine for all nitrides considered here. On the other hand, one may assume a quasi-cubic approximation for spin-orbit coupling $\Delta_2 = \Delta_3$. In that case, there are only two parameters determining the two energy splittings and they can be determined directly.

The crystal field splitting $\Delta_c = E(\Gamma_5) - E(\Gamma_1)$ is sensitive to uniaxial strain. For a uniaxial volume conserving (traceless) strain in the $z$-direction, $\epsilon_{xx} = \epsilon_{yy} = -\epsilon_{zz}/2$. Eq. 3.1 then gives

\[
\Delta_c = \Delta_1 + (D_3 - D_4)\epsilon_{zz}
\] (3.5)

On the other hand, for an isotropic volume change, the strain tensor is $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = \epsilon/3$ with $\epsilon = dV/V$. In that case,

\[
\Delta_c = \Delta_1 + (D_3 + 2D_4)\frac{dV}{V}
\] (3.6)

By fitting $\Delta_c$ extracted from the band structure for isotropic and uniaxial strains,
we can determine both $D_3$ and $D_4$. In the quasi-cubic approximation $D_3 = -2D_4$, there would be no isotropic strain change in crystal field splitting, and the uniaxial effect reduces to $\frac{3}{2}D_3 \varepsilon_{zz}$. Thin films are often under biaxial strain, which has both a uniaxial and an isotropic component. By providing both $D_3$ and $D_4$, the change in crystal field splitting can be obtained easily for any biaxial strain situation that might occur depending on growth conditions, temperature, and film-thickness. The parameters $D_1$ and $D_2$ only lead to shifts of the bands and were not determined. The parameters $D_5$ and $D_6$ only enter when strains breaking the hexagonal symmetry are considered. We did not determine them here because they are of less interest for thin films. Finally, we also determine the band gap hydrostatic strain deformation potentials as

$$a_v = \frac{dE_g}{d \ln V}. \quad (3.7)$$

The band structures near the VBM without spin-orbit coupling are shown for AlN, GaN, and InN in fig. 3.2 for $\mathbf{k}$ along the c-axis ($k_\parallel$) and in the plane ($k_\perp$). The solid lines indicate the fits by means of the effective-mass Hamiltonian. Separately, in fig. 3.3 we show the bands for a direction between the two at an angle of 45° illustrating the inadequacy of using the quasi-cubic approximation for $A_6$.

The band structures including spin-orbit coupling are shown in fig. 3.4 together with the effective-mass Hamiltonian results. These include the same parameters as before plus the spin-orbit splitting parameters at $\Gamma$. It shows that now the bands become spin-split in the plane. Along the c-axis, they are still degenerate because by time reversal $\psi_{k_z \sigma} = \psi_{-k_z -\sigma}$ and by the glide mirror plane perpendicular to the c-axis $\psi_{k_z \sigma} = \psi_{-k_z \sigma}$. Hence there is a Kramer’s degeneracy. In order to fully adjust the spin-splittings in the plane, we also needed to add the small relativistic linear-in-$\mathbf{k}$ terms ($\alpha$) for GaN and InN. The fittings including $\alpha$-parameters are shown in fig. 3.5. For AlN, we notice that along $k_\parallel$, the upper band crosses the second band but
not the third band. This is because the upper band has \( \Gamma_7 \) symmetry along the line \( \Delta = \Gamma - A \), the second band has \( \Gamma_9 \) symmetry and the third band has \( \Gamma_7 \) symmetry. Bands of the same symmetry cannot cross because an interaction between the two avoids the crossing.

The parameters are summarized in table 3.3. Here we use \( \Delta_{so}^{\parallel} = 3\Delta_2, \, \Delta_{so}^{\perp} = 3\Delta_3 \). In the quasi-cubic approximation \( \Delta_{so}^{\parallel} = \Delta_{so}^{\perp} = \Delta_{so}^{ZB} \), the latter being the value in the zincblende structure. Using this approximation, we can extract \( \Delta_1 \) and \( \Delta_2 \) directly from the two band splittings using eq. 3.4.

Finally, we include the (spin-averaged) effective masses of the three separate valence band maxima, \( A, B, C \) when spin-orbit coupling is included as shown in table 3.4. Here, \( A \) means \( \Gamma_9 \), \( B \) means \( \Gamma_{7+} \), and \( C \) means \( \Gamma_{7-} \).

The crystal field and spin-orbit coupling parameters are compared with other recent calculations and experimental data in table 3.5. We note that the crystal field splitting is sensitive to strain. The experimental values quoted here for AlN are for bulk single crystals [73; 74]. For GaN, they correspond to 500 \( \mu \)m thick layers [75]. For InN, the only value we could find is for a rather thin film of only 670 nm on r-plane sapphire [76]. This value is likely to be influenced by some residual strain.

We can see in table 3.3 that the QSGW values differ significantly from the LDA values for the deformation potentials. While for AlN and GaN the quasi-cubic approximation \( D_3 + 2D_4 \approx 0 \) is reasonably well obeyed, the deviation from quasi-cubic is significant for InN. The band gap deformation potentials are all negative. The decrease of the band gap with increasing lattice constant is the usual behavior in covalent semiconductors. Our values are comparable to those of Rinke et al. [8]: \( -9.8 \) eV for AlN, \( -7.6 \) for GaN, and \( -4.2 \) for InN.

We found the crystal field splitting of InN to be very sensitive to computational details. For example, using a smaller \( GW \) \( k \)-point set, we obtained a negative crystal field splitting of \( -14.8 \) meV. A small compressive strain along the c-axis could easily
Table 3.3: Band structure parameters: inverse masses ($A_1 - A_6$) (in units $\hbar^2/2m_e$), energy splittings ($\Delta_1 - \Delta_3$) (in meV), $A_7$ and $\alpha_i$ (in units $e^2/2$), and deformation potentials (in eV). The value of $A_6$, $\Delta_1, \Delta_2, \Delta_3$ in parentheses are obtained in the quasi-cubic approximation. Electron effective masses (in units $m_e$). The hole masses correspond to the band structure without spin-orbit coupling. The hole masses obtained with $A_7$ from eq. 3.3 are in parentheses.

<table>
<thead>
<tr>
<th>parameter</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>-4.05</td>
<td>-5.98</td>
<td>-15.7</td>
</tr>
<tr>
<td>$A_2$</td>
<td>-0.28</td>
<td>-0.58</td>
<td>-0.63</td>
</tr>
<tr>
<td>$A_3$</td>
<td>3.71</td>
<td>5.44</td>
<td>15.2</td>
</tr>
<tr>
<td>$A_4$</td>
<td>-1.71</td>
<td>-2.46</td>
<td>-7.10</td>
</tr>
<tr>
<td>$A_5$</td>
<td>1.90</td>
<td>2.53</td>
<td>7.14</td>
</tr>
<tr>
<td>$A_6$</td>
<td>-1.05(-2.75)</td>
<td>-1.55(-3.31)</td>
<td>-5.03(-9.45)</td>
</tr>
<tr>
<td>$A_7$</td>
<td>0</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>$\Delta_1$</td>
<td>-245(-245)</td>
<td>12.2(18.2)</td>
<td>43.7(43.4)</td>
</tr>
<tr>
<td>$\Delta_{so}^\parallel = 3\Delta_2$</td>
<td>18.6(18.9)</td>
<td>11.7(5.4)</td>
<td>-9.5(-9.2)</td>
</tr>
<tr>
<td>$\Delta_{so}^\perp = 3\Delta_3$</td>
<td>22.5(18.9)</td>
<td>16.2(5.4)</td>
<td>-5.9(-9.2)</td>
</tr>
<tr>
<td>$m_e^\parallel$</td>
<td>0.32</td>
<td>0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>Expt.</td>
<td>0.29-0.4$^a$</td>
<td>0.20$^b$</td>
<td>0.05-0.07$^c$</td>
</tr>
<tr>
<td>$m_e^\perp$</td>
<td>0.31</td>
<td>0.22</td>
<td>0.09</td>
</tr>
<tr>
<td>$m_{hh}^\parallel = m_{th}^\parallel$</td>
<td>2.94</td>
<td>1.85</td>
<td>2.00</td>
</tr>
<tr>
<td>$m_{sh}^\parallel$</td>
<td>0.25</td>
<td>0.17</td>
<td>0.06</td>
</tr>
<tr>
<td>$m_{hh}^\perp$</td>
<td>11.11</td>
<td>1.96</td>
<td>1.69</td>
</tr>
<tr>
<td>$m_{th}^\perp$ w/o $A_7$</td>
<td>0.26</td>
<td>0.18</td>
<td>0.07</td>
</tr>
<tr>
<td>$m_{th}^\perp$ with $A_7$</td>
<td>-</td>
<td>0.30(0.28)</td>
<td>0.10(0.10)</td>
</tr>
<tr>
<td>$m_{sh}^\perp$ w/o $A_7$</td>
<td>3.57</td>
<td>1.72</td>
<td>1.59</td>
</tr>
<tr>
<td>$m_{sh}^\perp$ with $A_7$</td>
<td>-</td>
<td>0.36(0.39)</td>
<td>0.17(0.18)</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>-</td>
<td>0.0028</td>
<td>-0.0095</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>-</td>
<td>0.0080</td>
<td>0.0135</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>-</td>
<td>-0.0030</td>
<td>0.0110</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>-</td>
<td>0.0028</td>
<td>0.0035</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$D_3 - D_4$ (LDA)</td>
<td>6.04</td>
<td>5.43</td>
<td>2.70</td>
</tr>
<tr>
<td>$D_3 + 2D_4$(LDA)</td>
<td>0.23</td>
<td>-0.14</td>
<td>2.78</td>
</tr>
<tr>
<td>$D_3 - D_4$(QS GW)</td>
<td>14.3</td>
<td>4.71</td>
<td>2.98</td>
</tr>
<tr>
<td>$D_3 + 2D_4$(QS GW)</td>
<td>0.52</td>
<td>-0.04</td>
<td>-1.25</td>
</tr>
<tr>
<td>$a_v = dE_g/d\ln V$</td>
<td>-9.78</td>
<td>-8.41</td>
<td>-2.33</td>
</tr>
</tbody>
</table>

$^a$Expt. from Silveira et al. [69]
$^b$Expt. from Vurgaftman et al. [7] and references therein
$^c$Expt. from Wu et al. [70] and Fu et al. [71]
Table 3.4: Hole effective mass with spin-orbit coupling included. The masses obtained from directly fitting the effective-mass Hamiltonian bands near the Γ point are given in the first line for each material, the numbers in parentheses are obtained from second order perturbation theory as given in Eq. 10 in Kim et al. [1]. Only for GaN, a direct comparison to experimental values obtained from exciton binding energies is available.

<table>
<thead>
<tr>
<th>Material</th>
<th>$m_A^\parallel$</th>
<th>$m_B^\parallel$</th>
<th>$m_C^\parallel$</th>
<th>$m_A^\perp$</th>
<th>$m_B^\perp$</th>
<th>$m_C^\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>2.94</td>
<td>0.25</td>
<td>2.83</td>
<td>0.56</td>
<td>3.53</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>(2.94)</td>
<td>(0.25)</td>
<td>(2.89)</td>
<td>(0.50)</td>
<td>(3.53)</td>
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<td>GaN</td>
<td>1.85</td>
<td>0.55</td>
<td>0.20</td>
<td>0.69</td>
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<td>(0.51)</td>
<td>(0.22)</td>
<td>(0.33)</td>
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</tr>
<tr>
<td>InN</td>
<td>1.76</td>
<td>0.419</td>
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<td>0.349</td>
<td>0.512</td>
<td>0.676</td>
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<td>(1.81)</td>
<td>(0.06)</td>
<td>(0.13)</td>
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</tr>
</tbody>
</table>

*Expt. from Rodina et al. [72]

reduce the crystal field splitting and even make it negative. This is accompanied by a significant change in the band structure as illustrated in figs. 3.6 and 3.7. The VBM in that case moves away from Γ due to the repulsion between the crystal field split-off and light hole band. We can see that this off-Γ valence band maximum persists up to a positive crystal field splitting of about 15 meV. Given the deformation potentials, we can see that uniaxial compressive strain of order 1–2 % could cause the crystal field splitting to go from positive to negative and shift the valence band maximum away from Γ.

Our crystal field splitting for GaN is in better agreement with experiment than previous results. It was already pointed out by Kim et al. [1] that this value was likely overestimated by LDA (or GGA) because the Γ valence band is repelled by the Γ conduction band and hence, an underestimate of the gap results in an overestimate of the crystal field splitting. Clearly it is extremely sensitive to computational details, since it depends on the precise computational details of the GW method as well as the crystal structure, which must be truly strain-free.
We also note that we find here a negative value for the spin-orbit splitting in InN, in contrast to earlier reports [8; 10]. We note that in order to ascertain the sign of the spin-orbit coupling we need to examine the symmetry of the valence band states at \( \Gamma \). Whereas the \( \Gamma_{7+} \) state has a small \( p_z \) component in its wave function, the \( \Gamma_9 \) state has no \( p_z \) component by symmetry. We find definitely a \( \Gamma_{7+} > \Gamma_9 > \Gamma_{7-} \) ordering. The negative spin-orbit splitting arises from the contribution of the In-4\( d \) orbitals to the effective spin-orbit splitting. Because the latter lie below the VBM they give rise to a negative contribution. This is well known to be also the case for ZnO [77]. In that case, the Zn-3\( d \) states are closer to the VBM. The value in GaN is already small due to the coupling with the Ga-3\( d \) and the small value of the N-2\( p \) atomic spin-orbit coupling which tend to compensate each other. One may expect the In-4\( d \) contribution to be larger in magnitude because In is a heavier atom. Therefore it is plausible that it becomes negative in InN.

Next, we compare the \( A_i \) parameters to previous work. Our results agree quite closely with those of Rinke et al. [8] except for the parameter \( A_6 \). As we mentioned earlier, this parameter requires some care to extract it. Rinke et al. [8] used an automatic fitting to calculated band structures on a mesh of points near \( \Gamma \) but restricted themselves to obtaining a fit only very near \( \Gamma \). In contrast, our fitted band structures can be seen to fit very well over a rather extended region of \( k \)-space and down to energies of order 100 meV below the VBM. This is important if one wants to apply the method for calculating shallow acceptors which have binding energies of this order of magnitude.

For AlN, Gil [63; 64] recently reviewed how well the \( A_1, A_2 \) parameters fit the experimental data on the \( 1s-2s \) exciton splitting. In order to obtain a good fit, he found it is important to also include the anisotropy of the dielectric constants. The best fit corresponded to \( A_1 = -3.95 \) and \( A_2 = -0.27 \), in excellent agreement with our calculated values. The reason why only the \( A_1 \) and \( A_2 \) enter here is that in
Table 3.5: Comparison of the band gaps (in eV) and valence band splittings (in meV) to previous calculations and experiment.

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<td>$\Delta_{so}$</td>
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<tr>
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<td>$\Delta_{so}$</td>
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<td>$\Gamma_9 - \Gamma_{7+}$</td>
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<td>5.4</td>
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<td>$\Gamma_9 - \Gamma_{7-}$</td>
<td>40.7</td>
<td>47.4</td>
<td>21$^f$</td>
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</table>

$^a$ Expt. from Vurgaftman et al. [7]
$^b$ Expt. from Chen et al. [73]
$^c$ Expt. from Silveira et al. [74]
$^d$ Expt. from B. Gil et al. [75]
$^e$ Expt. from Wu et al. [68]
$^f$ Expt. from Goldhahn et al. [76]
AlN, the VBM has $\Gamma_1$ symmetry and thus the split-off hole band lies above the usual heavy and light hole. From eq. 3.2, we can see that then $A_1$ and $A_2$ are respectively the inverse masses for the directions parallel and perpendicular to the $c$-axis. They enter the reduced mass of the excitons that goes into the equation for the exciton binding energy.

For GaN, the most complete set of valence band effective masses is obtained again from a study of the exciton fine structure by Rodina et al. [72] Their values are included in the above table 3.4 for comparison. For InN, no reliable experimental data on the hole masses are available to the best of our knowledge.

The conduction band effective masses for AlN, GaN, and InN all agree well with experimental data and are only slightly anisotropic. The experimental values included in table 3.3 do not resolve the anisotropy.

### 3.4 Conclusions

The parameters of the valence band maximum effective Hamiltonian were determined for AlN, GaN, and InN from quasiparticle self-consistent $GW$ band structures. Because the crystal field splitting is strongly dependent on strain, the relevant strain deformation potentials are also determined. Good agreement is obtained with experiment for the band gaps and valence band maximum splittings at $\Gamma$ in AlN and GaN. Our calculated effective masses, including spin-orbit coupling effects also agree well with those extracted from exciton fine structure in AlN and GaN. For InN, it is concluded that experimental data for strain-free material are not yet available. We find the spin-orbit coupling parameter in InN to be negative and show that the band structure will be strongly dependent on strain. For both GaN and InN relativistic terms linear in $\mathbf{k}$ and spin need to be included to fully account for the spin-splitting of the bands away from $\Gamma$. 
Figure 3.1: Electronic band structure of AlN, GaN, and InN
Figure 3.2: Valence bands of AlN, GaN, and InN, dots represent QSGW results, full lines represent the Rashba-Sheka-Pikus (RSP) fit including $A_7$, dashed lines excluding $A_7$. The zero of energy is at the $\Gamma_5$-state.
Figure 3.3: Valence bands of AlN, GaN, and InN in the direction between in-plane and perpendicular to plane at angle 45°, LHS: using quasi-cubic approximation, RHS: using manual fitting. The zero of energy is at the doubly degenerate $\Gamma_5$-state. Dots represent QSGW results, full lines represent the RSP fits.
Figure 3.4: Valence bands of AlN, GaN, and InN including spin-orbit couplings, but neglecting the $\alpha_i$ spin-dependent terms. The zero of energy is at the valence band maximum, which is $\Gamma_9$ in GaN, $\Gamma_{7+}$ in AlN and InN. Dots represent QSGW results, full lines represent the RSP fits.
Figure 3.5: Valence bands of GaN and InN including spin-orbit couplings and the additional $\alpha_i$ spin-dependent terms. The zero of energy is at the valence band maximum. Dots represent QSGW results, full lines represent the RSP fits.
Figure 3.6: Valence bands of InN without spin-orbit coupling calculated from the effective mass Hamiltonian (a) $\Delta_1 < 0$, (b) $\Delta_1 = 0$, (c) $\Delta_1 > 0$.

Figure 3.7: Valence bands of InN without spin-orbit coupling calculated from the effective mass Hamiltonian, with various positive crystal field splitting.
Chapter 4

Heterovalent ternary II-IV-N$_2$ compounds

4.1 Introduction

The II-IV-N$_2$ compounds constitute a family of heterovalent ternary semiconductors with properties closely related to those of the III-Nitrides. These compounds have been synthesized already in the 70s, e.g., ZnGeN$_2$ [78; 17; 11], ZnSiN$_2$ [17], MgSiN$_2$ and MgGeN$_2$ [79]. We give below the literature of materials that we are interested in.

The earliest report on the synthesis of ZnGeN$_2$ is by Maunaye and Lang in 1970 [78]. They used a reaction of NH$_3$ with Zn$_2$GeO$_4$, the latter being separately obtained from reacting GeO$_2$ with ZnO. The initial reports on the crystal structure showed it to have a structure related to that of wurtzite but with a lower monoclinic symmetry. Because of the similarity in electron density of Zn and Ge, it was impossible using X-ray diffraction to determine whether the Zn and Ge atoms were ordered or disordered on the cation lattice. A neutron diffraction study [80] determined the ordering of the Zn and Ge atoms, and thus established the orthorhombic structure explained in the
next section. Larson et al. [11] used a vapor growth method for ZnGeN$_2$ starting from elemental Zn and Ge in NH$_3$ and reported an absorption onset at 2.67 eV, which is an underestimate resulting from defects. High-pressure synthesis of ZnGeN$_2$ and ZnSiN$_2$ starting from mixtures of Zn$_3$N$_2$ and Si$_3$N$_4$ or Ge$_3$N$_4$ was reported by Endo et al. [17]. Their reported a band gap of 3.64 eV for ZnSiN$_2$ based on the optical absorption onset. Their ZnGeN$_2$ crystals were opaque and black, indicating a high degree of contamination. Metal-organic chemical vapor deposition (MOCVD) was used by Zhu et al. [12] to synthesize thin films of ZnGeN$_2$. The same group also reported ZnSiN$_2$ growth and alloy growth of ZnSi$_{1-x}$Ge$_x$N$_2$. These materials were investigated by a number of other collaborators determining optical properties [21; 22], transistor devices on SiC [25], and even their suitability as magnetic semiconductor hosts by implantation of Mn [24]. Muth et al. [21] determined band gaps from optical absorption data as a function of alloy composition in ZnSi$_{1-x}$Ge$_x$N$_2$ and found them to vary between 3.1-3.2 eV for ZnGeN$_2$ to 4.4 eV in ZnSiN$_2$. Cook et al. [22] determined the indices of refraction and Mintairov et al. [23] determined the infrared reflection relating to the vibrational spectrum. Misaki et al. [13; 14; 15] used remote plasma enhanced MOCVD for thin film growth of ZnGeN$_2$ and reported a band gap of 3.3 eV. They also reported optical reflectivity in the UV up to 20 eV. Most of this work used r-plane sapphire as the substrate. Cloitre et al. [81] reported ZnSiN$_2$ growth by MOVPE on c-plane sapphire. Kikkawa and Morisaka [16] reported RF-sputter deposition of ZnGeN$_2$ thin films on Si and glass substrates and estimated the gap to be about 3.1 eV. Viennois et al. [19] performed the first Raman spectroscopy study on powder samples of ZnGeN$_2$, synthesized by a similar approach as used by Maunaye and Lang. A vapor-liquid-solid synthesis method was used by Du et al. [18] using pure Zn and Ge, and NH$_3$, at growth temperatures between 750°C and 900°C. Photoluminescence on these materials indicate a gap of 3.40±0.01 eV and a high ratio of band gap versus defect luminescence. Recently, several papers have appeared
on the growth of ZnSnN$_2$, by using a plasma-assisted molecular beam epitaxy [26], RF sputtered thin films [27], and a plasma-assisted vapor-liquid-solid technique [28]. Interest in ZnSnN$_2$ has increased because of its opportunities for photovoltaics based on earth-abundant elements due to its relatively low band gap, estimated in different papers to be between 1.4 and 2.0 eV. For MgGeN$_2$, it has been synthesized since 1970 [79] but only lattice parameters have been measured so far.

The first band structure calculations of ZnGeN$_2$ were presented in 1999 by Limpijumnong et al. [29] using LDA and LMTO method. They also investigated the linear and non-linear optical properties such as the index of refraction and second harmonic generation coefficients. Other groups also presented band structure calculations with pseudopotential plane wave approaches [30; 31] and included some other members of this family of II-IV-N$_2$ compounds. Recently, Lambrecht et al. [83; 84; 20; 85; 86] presented a series of papers mainly focusing on the lattice dynamics of ZnSiN$_2$, ZnGeN$_2$ and ZnSnN$_2$. As part of this work, the electronic band structures were also calculated using a pseudopotential plane wave approach [32]. Studies of the energy band structure of MgGeN$_2$ crystals were performed by different authors [87; 88; 89] using different program codes based on DFT. All of these previous works on the band structure however suffer from the limitations of LDA. Although some earlier estimates of the band gaps going beyond LDA were mentioned in Paudel et al. [85], there is still considerable uncertainty on the band structures both from the theory and experimental points of view.

In this Chapter, we present band structure calculations of ZnSiN$_2$, ZnGeN$_2$, ZnSnN$_2$, CdGeN$_2$, and MgGeN$_2$ [90; 91; 33] by using QSGW. The crystal structure and symmetry of ZnSiN$_2$, ZnGeN$_2$, ZnSnN$_2$, CdGeN$_2$ and MgGeN$_2$ is discussed first. We optimized crystal structure parameters using the FP-LMTO method in the LDA before proceeding with the GW calculations. After a discussion of the differences between LDA and GW and the atomic orbital character of the energy bands
over a wide energy range, we focus on the region near the band gap. Besides the
band gaps, it is of interest to determine some details of the VBM splittings and the
effective masses. We present a generalization of the Kohn-Luttinger Hamiltonian
suitable for crystals of orthorhombic symmetry based on the method of invariants
and determined the relevant inverse effective mass parameters in this model. We also
include and discuss the spin-orbit splittings of the VBM. We use our calculated effec-
tive masses to estimate exciton binding energies and estimate other corrections to the
band gaps such as the zero-point motion electron-phonon renormalization correction.

4.2 Crystal structure

The prototype for the crystal structure of the II-IV-N$_2$ compounds is $\beta$-NaFeO$_2$,
which is actually a I-III-VI$_2$ compounds. This crystal structure can be viewed as a
$2 \times \sqrt{3}$ superlattice of wurtzite along ortho-hexagonal axes as illustrated in fig. 4.1
showing a projection on the c-plane. It has 16 atoms per unit cell. The $b/a$ and $c/a$
can both adjust as well as the internal positions $x, y, z$ of each of the four types of
atoms, the group II, group IV and two inequivalent N positions : N$_{II}$ being on top
of the group II and N$_{IV}$ being on top of the group IV element.

The space group of our structure is $Pbn\overline{2}_1$, (space group No. 33, or $C_{2v}^9$) meaning
that there is a 2-fold screw axis along the z direction with translation $1/2c$, a diagonal
glide plane $n$ perpendicular to $b$ with translations $1/2(a+c)$ and an axial glide plane
perpendicular to the a-axis with translation $1/2b$. These symmetry elements are
indicated in the figure. In this setting, the origin is chosen to fall on the 2-fold screw
axis, the $a$ axis is equal to $2aw$ and $b \approx \sqrt{3}aw$ unlike the commonly found choice in
the International Tables of Crystallography (ITC) which interchanges $a$ and $b$ from
ours and has $Pan\overline{2}_1$ as a space group. In our case, $a$ is the longest lattice constant,
$b$ is the next longest one and $c = cw$, which is easier to relate to wurtzite structure.
Figure 4.1: Projection of crystal structure of Zn-IV-N$_2$ compounds on c-plane with symmetry elements. Large and small open circles indicate cations in bottom and top plane respectively, filled circles are N atoms above them as indicated. The symmetry elements are indicated and chosen so that the $2_1$ axes passes through the origin.

Table 4.1: Character table for the group $C_{2V}$, classes are in first row, basis functions, irreducible representations are in first and second column respectively.

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<th>$E$</th>
<th>$C_{2z}$</th>
<th>$\sigma_x$</th>
<th>$\sigma_y$</th>
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<td>$a_1$</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$x$</td>
<td>$b_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$y$</td>
<td>$b_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$xy$</td>
<td>$a_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The point group is thus $C_{2v}$. The character table for this group was given in table 4.1 [20]. We here note that the $a_1$, $b_1$ and $b_2$ irreducible representations correspond to $z$, $x$ and $y$ basis functions with $x$ along $a$, $y$ along $b$ and $z$ along the $c$-axes. The $a_2$ irreducible representation is even under the two-fold rotation but odd under both mirror-planes and corresponds to an $xy$ basis function.
4.3 Computational details

DFT-LDA and DFT-GGA [47] are used to calculate the energies of formation and to optimize the lattice constants and atomic positions inside the unit cell. These calculations are carried out using a FP-LMTO method [55; 54]. We use a $4 \times 4 \times 4$ $k$-point sampling for the Brillouin zone integration in the self-consistent LDA or GGA calculations. The basis set contains two sets of smoothed Hankel function decay parameters $\kappa$ and smoothing radii, $R_{sm}$ and includes $spd$ functions in the first and the second set for Zn and Cd. For Mg, Si, Ge, Sn and N, we include $spd$ functions in the first and $sp$ in the second set. In addition we add Zn-$4d$ and Cd-$4d$ as local orbitals. The quasi-particle band structure is calculated using the QS$GW$ approach implemented in the same FP-LMTO method as described in refs.[2; 3; 52]. We find it is important to take the cut-off energy sufficiently high for II-IV-$N_2$, say $E_{cut} = 3$ Ryd above the Fermi level to obtain well-converged results. The gaps for $E_{cut} = 2.5$ Ryd were still underestimated by 5-10 %. A $k$-point sampling set for the $GW$ self-energy we use a $2 \times 2 \times 2$ mesh.

4.4 Results

4.4.1 Energy of formation

Generally, the energy of formation is defined with respect to the elements in their equilibrium phase at room temperature and ambient pressure but in this calculation it is calculated at zero pressure and temperature. For example, it corresponds to the energy of the formation reaction between Zn in the hexagonal close packed structure, Ge in the diamond structure, and $N_2$ gas molecules, to the orthorhombic structure of ZnGe$N_2$. It is important to include the spin polarization contributions of the
spin-polarized atoms in determining the individual cohesive energies.

$$\text{Zn}(\text{hcp}) + \text{Ge}(\text{dia}) + \text{N}_2(\text{g}) \rightarrow \text{ZnGeN}_2(\text{orth})$$

The energies of formation and cohesive energies of the elements involved in this calculation are summarized in table 4.2. We note that formation energies of CdGeN2 and MgGeN2 have not yet been calculated by GGA. For comparison, we also calculated the formation energy of GaN where we can compare with experimental data [92]. We can see that LDA typically overestimates the cohesive energy by about 30% for all the solids and about 10% for the molecule. This is because primarily the LDA error occurs for the free atom and molecule. There is a large degree of compensation of errors when subtracting the energies. We find that all five components have exothermic energies of formation, including the new compounds ZnSnN2 and CdGeN2.

Table 4.2 does not include zero point motion corrections $\Delta(0)$, which we now estimate. They were calculated from the phonons for all three Zn-IV-N2 compounds in ref. [85] but these calculations have not yet been done for CdGeN2 and MgGeN2. $\Delta(0)$ can be estimated as $9/k_B \Theta_D$ from the Debye temperature for the other solids. The Debye temperatures were taken from an interactive periodic table online at :http://www.infoplease.com/periodictable.php. For the N2 molecule, we use simply $h\nu/2 = hc/2\lambda$ with $1/\lambda = 2360$ cm$^{-1}$ the vibrational frequency of the N2 molecule, obtained by Wathelet et al. [95] in the LDA and the harmonic approximation. The important point here is that the zero-point motion contribution of the gas molecule is significantly larger than that of the solids. The zero point motion corrections on the cohesive energy and molecular binding energy are given in table 4.3. We can see, however, that the zero-point motion corrections to the energies of formation amount to only $-0.13$, $-0.12$ and $-0.12$ eV for Zn-IV-N2 with IV=Si, Ge, Sn respectively, and they help to make the energies of formation more negative.
Table 4.2: Energies of formation (eV/per formula unit), cohesive energies (without zero point motion correction), and bonding energy of the N$_2$ molecule (in eV/formula unit)

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$-E_{coh}$

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$-E_B$

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<td>16</td>
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<td>23</td>
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$^a$Peshek at el.[92]

$^b$Gschneider [93]

$^c$Huber at el.[94]

$^d$Huber at el.[94]

Table 4.3: Zero-point motion contribution to the cohesive energy (in meV)

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<th>$E_{zpm}(meV)$</th>
</tr>
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<tbody>
<tr>
<td>Zn</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>146</td>
<td>31</td>
</tr>
<tr>
<td>Si</td>
<td>61</td>
<td>ZnSiN$_2$ $^a$</td>
</tr>
<tr>
<td>Ge</td>
<td>35</td>
<td>ZnGeN$_2$ $^a$</td>
</tr>
<tr>
<td>Sn</td>
<td>16</td>
<td>ZnSnN$_2$ $^a$</td>
</tr>
<tr>
<td>Ga</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The zero point motion of Zn-IV-N$_2$ was obtained from the phonon calculation by Paudel et al. [85] but this calculation has not yet been done for the CdGeN$_2$ and MgGeN$_2$. 

-------------------------
We caution that the energies of formation here are not sufficient to establish the thermodynamic stability of these compounds. It is necessary to also investigate the energies of formation of competing compounds such as Zn$_3$N$_2$, Si$_3$N$_4$, Ge$_3$N$_4$, Sn$_3$N$_4$ and other possible IV-N$_x$ compounds. Using these, we can construct maps of the available chemical potential region where the different compounds would be stable. These types of maps are usually used to determine the allowed ranges of the chemical potentials in the context of impurity calculations. We explain the procedure for ZnSnN$_2$.

For ZnSnN$_2$, the chemical potentials of the elements involved must obey:

$$\mu_{\text{Sn}} + \mu_{\text{Zn}} + 2\mu_{\text{N}} = E_f(\text{ZnSnN}_2) \quad (4.1)$$

Here $\mu_{\text{Sn}}$, $\mu_{\text{Zn}}$ and $\mu_{\text{N}}$ are excess chemical potentials. This means they are in principle Gibbs free energies relative to their value in the reference states, bulk Sn, bulk Zn and N$_2$ gas. We ignore here the pressure and temperature dependence of the N$_2$ gas and just focus on the energy of a N-atom in a N$_2$-molecule. In other words, it is half of the binding energy of a N$_2$-molecule. The energy of formation $E_f(\text{ZnSnN}_2)$ is the cohesive energy of ZnSnN$_2$ minus the cohesive energies of Zn and Sn per atom (in their solid form) and the binding energy of the N$_2$ molecule. Thus, when two of the chemical potentials are chosen, the third is defined by eq. 4.1. We choose $\mu_{\text{Sn}}$ and $\mu_{\text{Zn}}$ as the basic variables in fig. 4.2.

The diagonal line from the upper left to the lower right in fig. 4.2 shows $\mu_{\text{N}} = 0$ and corresponds to eq. 4.1. The chemical potential of N must lie above this line, otherwise the system becomes unstable to evolution of nitrogen gas. On the other hand, the chemical potentials of Sn and Zn must both be negative. If they became positive, it would be favorable to precipitate bulk Sn and bulk Zn. However, more severe restrictions apply if other compounds can form between Sn and N or Zn.
and N. Zn is known to form a compound Zn$_3$N$_2$ while for Sn and N, one might expect Sn$_3$N$_4$ but reports of other stoichiometries SnN$_x$ with 0.9 < $x$ < 3.3 exist in literature [96]. Most interesting is the report [97] that Sn$_3$N$_4$ has its lowest energy in a spinel structure, which for Si$_3$N$_4$ only exists as high-pressure phase. Using this stoichiometry, we require

$$3\mu_{Zn} + 2\mu_N \leq E_f(Zn_3N_2), 3\mu_{Sn} + 4\mu_N \leq E_f(Sn_3N_4).$$

(4.2)

Table 4.4: Formation energy of competing compounds calculated from equilibrium lattice constants in LDA

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$ spinel</td>
<td>-10.22</td>
</tr>
<tr>
<td>Si$_3$N$_4$ beta</td>
<td>-11.80</td>
</tr>
<tr>
<td>Ge$_3$N$_4$ spinel</td>
<td>-2.34</td>
</tr>
<tr>
<td>Ge$_3$N$_4$ beta</td>
<td>-3.36</td>
</tr>
<tr>
<td>Sn$_3$N$_4$ spinel</td>
<td>-0.94</td>
</tr>
<tr>
<td>Sn$_3$N$_4$ beta</td>
<td>-0.90</td>
</tr>
<tr>
<td>Zn$_3$N$_4$ antibixbyites</td>
<td>-1.05</td>
</tr>
</tbody>
</table>

$^a$ lattice constants and free parameters from Ref. [98]

These define two more lines and the region where ZnSnN$_2$ has a chance to be stable. We have calculated the energy of formation of the competing compounds in table 4.4. Fig. 4.2 shows that there is a wide range of stability of the chemical potentials where ZnSnN$_2$ would be stable. We can see that if $\mu_{Zn}$ becomes close to zero (Zn-rich) and $\mu_{Sn}$ is below a certain value, (Sn-poor) and above the $\mu_N = 0$ line, (nitrogen rich) Zn$_3$N$_2$ would prefer to form. Similarly, if we are at Sn-rich and Zn-poor, Sn$_3$N$_4$ might form in N-rich conditions. If the border line between ZnSnN$_2$ and Sn$_3$N$_4$ would shift down and to the right, conceivably, it could move past the Zn$_3$N$_2$/ZnSnN$_2$ border line. If that occurred it would mean ZnSnN$_2$ would have no
Figure 4.2: Chemical potential diagram for stability of ZnSnN$_2$

Figure 4.3: Chemical potential diagram for stability of ZnGeN$_2$
stability region at all. However, we see that this would require a much more negative energy of formation for Sn$_3$N$_4$. Similarly, if the Zn$_3$N$_2$ line move up and to the right, the range of allowable chemical potentials required for the stability of ZnSnN$_2$ could be reduced. Similar conclusion hold for ZnGeN$_2$ and ZnSiN$_2$. The corresponding diagram for ZnGeN$_2$ is obtained and shown in fig. 4.3.

### 4.4.2 Structural results

The lattice constants obtained by energy minimization in both LDA and GGA are presented in table 5.1 compared to experimental values where available. We note that even for ZnGeN$_2$, the most studied of these materials, there is still considerable variation between experimental results on the lattice constants obtained from different growth methods, reflecting for example film strain conditions, as discussed in more detail in Du et al. [18], and CdGeN$_2$ has not yet been synthesized. For example, Du et al. [18] obtain a $b/a_w$ ratio of 1.741 and $c/a_w$ of 1.627 with a lattice constant $a = 6.314$ Å. This gives $V = 178.24$ Å$^3$. We also compare our Zn-IV-N$_2$ results with those of a previous calculation by Paudel et al. [85]. The average deviation of the lattice constants from experiment is most easily seen by comparing the volumes. We see that, as usual, LDA slightly underestimates the volume while GGA overestimates it. For ZnSnN$_2$ the experimental lattice constants [28] are closer to Paudel’s results [85]. For ZnSiN$_2$, GGA appears closer to the experiment and for ZnGeN$_2$ and MgGeN$_2$ LDA is slightly closer but neither has a clear advantage. The ratios $b/a_w$, $c/a_w$ are slightly larger in our calculated results than in experiment and LDA seems closer to experiment for those than GGA. The remaining discrepancies in $b/a_w$ and $c/a_w$ with experiment are of order 1% comparable with the experimental uncertainty. Therefore, in the remainder of this chapter, we will calculate the band structures at the LDA equilibrium lattice parameters. Compared to the pseudopo-
tential plane wave calculations of Paudel et al. [85] the present results are slightly closer to the experimental values.

Table 4.6 gives the reduced coordinates \((x, y, z)\) of the atomic positions after relaxation. All atoms occur in 4(a) Wyckoff positions: (1) \(x, y, z\) (2) \(-x, -y, z + \frac{1}{2}\), (3) \(x + \frac{1}{2}, -y + \frac{1}{2}, z\), and (4) \(-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}\). Compared to the results given in Paudel et al. [85] we here use a different setting of the unit cell with the two-fold screw axes passing through the origin, as recommended in the International Tables of Crystallography. All coordinates are relaxed relative to the position of the two fold screw axes but one finds generally that the II and IV atoms are almost exactly shifted by \(0.5a\) from each other. The relaxation consists mainly in an adjustment of each N atom inside its surrounding tetrahedron, approaching the group-IV atom and moving away from the Zn atom. The average bond-lengths are summarized in table 4.7 and are in good agreement with Paudel et al. [85] and with experimental data for ZnGeN$_2$.  

In the process of obtaining the optimum lattice volume, we fitted the Vinet equation of state, given by

\[
E(V) = E_0 + \frac{2B_0V_0}{(B_0' - 1)^2} (2 - (5 + 3B_0'((V/V_0)^{1/3} - 1) \\
- 3(V/V_0)^{1/3}e^{\frac{3}{2}(B_0'-1)((V/V_0)^{1/3}-1)})
\]  

(4.3)

to the energy vs. volume relation and obtained from this fit, values for the static bulk modulus at zero pressure, \(B_0\), its first-order pressure derivative, \(B_0'\) and the equilibrium volume, \(V_0\). These are given in table 4.8 and are in good agreement with Paudel et al. [85; 86] This establishes that our FP-LMTO calculations describe the structure adequately so we can move on to a study of the electronic band structure in the next section.
Table 4.5: Lattice parameters $a$, $b$, and $c$ (Å), lattice volume $V$ (Å$^3$), the average error with respect to experiment ($\sigma = [\delta V/V] - 1)/3$), lattice constant ratio ($a_w = a/2$) in II-IV-N$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LDA</th>
<th>GGA</th>
<th>LDA-ABINIT $^a$</th>
<th>Expt $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiN$_2$</td>
<td></td>
<td></td>
<td>LDA-ABINIT $^a$</td>
<td>Expt $^b$</td>
</tr>
<tr>
<td>$a$</td>
<td>6.08</td>
<td>6.16</td>
<td>6.01</td>
<td>6.18</td>
</tr>
<tr>
<td>$b$</td>
<td>5.27</td>
<td>5.41</td>
<td>5.28</td>
<td>5.35</td>
</tr>
<tr>
<td>$c$</td>
<td>5.02</td>
<td>5.11</td>
<td>4.98</td>
<td>5.05</td>
</tr>
<tr>
<td>$V$</td>
<td>160.85</td>
<td>170.29</td>
<td>158.02</td>
<td>166.97</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>-0.012</td>
<td>0.007</td>
<td>-0.018</td>
<td></td>
</tr>
<tr>
<td>$b/a_w$</td>
<td>1.733</td>
<td>1.756</td>
<td>1.757</td>
<td>1.731</td>
</tr>
<tr>
<td>$c/a_w$</td>
<td>1.651</td>
<td>1.659</td>
<td>1.657</td>
<td>1.634</td>
</tr>
<tr>
<td>ZnGeN$_2$</td>
<td></td>
<td></td>
<td>LDA-ABINIT $^a$</td>
<td>Expt $^b$</td>
</tr>
<tr>
<td>$a$</td>
<td>6.38</td>
<td>6.42</td>
<td>6.33</td>
<td>6.44</td>
</tr>
<tr>
<td>$b$</td>
<td>5.45</td>
<td>5.54</td>
<td>5.36</td>
<td>5.45</td>
</tr>
<tr>
<td>$c$</td>
<td>5.22</td>
<td>5.27</td>
<td>5.11</td>
<td>5.19</td>
</tr>
<tr>
<td>$V$</td>
<td>181.50</td>
<td>187.44</td>
<td>173.38</td>
<td>182.16</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>-0.001</td>
<td>0.009</td>
<td>-0.349</td>
<td></td>
</tr>
<tr>
<td>$b/a_w$</td>
<td>1.708</td>
<td>1.726</td>
<td>1.693</td>
<td>1.693</td>
</tr>
<tr>
<td>$c/a_w$</td>
<td>1.636</td>
<td>1.641</td>
<td>1.614</td>
<td>1.612</td>
</tr>
<tr>
<td>ZnSnN$_2$</td>
<td></td>
<td></td>
<td>LDA-ABINIT $^a$</td>
<td>Expt $^b$</td>
</tr>
<tr>
<td>$a$</td>
<td>6.59</td>
<td>6.70</td>
<td>6.76</td>
<td>6.753±0.007</td>
</tr>
<tr>
<td>$b$</td>
<td>5.70</td>
<td>5.80</td>
<td>5.85</td>
<td>5.842±0.006</td>
</tr>
<tr>
<td>$c$</td>
<td>5.41</td>
<td>5.53</td>
<td>5.58</td>
<td>5.462±0.003</td>
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<tr>
<td>$V$</td>
<td>203.21</td>
<td>214.89</td>
<td>220.67</td>
<td>215.48</td>
</tr>
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<td>$\sigma$</td>
<td>-0.019</td>
<td>-0.001</td>
<td>0.008</td>
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<tr>
<td>$b/a_w$</td>
<td>1.730</td>
<td>1.731</td>
<td>1.731</td>
<td>1.730</td>
</tr>
<tr>
<td>$c/a_w$</td>
<td>1.642</td>
<td>1.651</td>
<td>1.651</td>
<td>1.618</td>
</tr>
<tr>
<td>CdGeN$_2$</td>
<td></td>
<td></td>
<td>LDA-ABINIT $^a$</td>
<td>Expt $^b$</td>
</tr>
<tr>
<td>$a$</td>
<td>6.74</td>
<td></td>
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</tr>
<tr>
<td>$b$</td>
<td>5.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$</td>
<td>5.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V$</td>
<td>210.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b/a_w$</td>
<td>1.694</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c/a_w$</td>
<td>1.633</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgGeN$_2$</td>
<td></td>
<td></td>
<td>LDA-ABINIT $^a$</td>
<td>Expt $^b$</td>
</tr>
<tr>
<td>$a$</td>
<td>6.58</td>
<td></td>
<td>6.61</td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>5.47</td>
<td></td>
<td>5.49</td>
<td></td>
</tr>
<tr>
<td>$c$</td>
<td>5.15</td>
<td></td>
<td>5.17</td>
<td></td>
</tr>
<tr>
<td>$V$</td>
<td>185.26</td>
<td></td>
<td>187.61</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>-0.004</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$From ref. [85]

$^b$For ZnSiN$_2$ from ref. [23], for ZnGeN$_2$ from ref. [80], for ZnSnN$_2$ from ref. [28], for MgGeN$_2$ from Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum, Eggenstein-Leopoldshafen 2, D-7514 Karlsruhe, Germany, http://icsd.fiz-karlsruhe.de.
Table 4.6: Wyckoff 4(a) positions (reduced coordinates) in the unit cell.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiN(_2)</td>
<td>Zn</td>
<td>0.623</td>
<td>0.089</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>0.126</td>
<td>0.074</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>NSi</td>
<td>0.102</td>
<td>0.057</td>
<td>0.346</td>
</tr>
<tr>
<td></td>
<td>NZn</td>
<td>0.649</td>
<td>0.109</td>
<td>0.402</td>
</tr>
<tr>
<td>ZnGeN(_2)</td>
<td>Zn</td>
<td>0.625 (0.620)(^a)</td>
<td>0.085 (0.083)</td>
<td>0.000 (0.000)</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>0.126 (0.125)</td>
<td>0.079 (0.083)</td>
<td>0.001 (0.000)</td>
</tr>
<tr>
<td></td>
<td>N(_{Ge})</td>
<td>0.113 (0.115)</td>
<td>0.069 (0.070)</td>
<td>0.360 (0.365)</td>
</tr>
<tr>
<td></td>
<td>NZn</td>
<td>0.637 (0.640)</td>
<td>0.096 (0.095)</td>
<td>0.389 (0.385)</td>
</tr>
<tr>
<td>ZnSnN(_2)</td>
<td>Zn</td>
<td>0.626</td>
<td>0.084</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>0.127</td>
<td>0.083</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>NSn</td>
<td>0.125</td>
<td>0.081</td>
<td>0.377</td>
</tr>
<tr>
<td></td>
<td>NZn</td>
<td>0.622</td>
<td>0.085</td>
<td>0.372</td>
</tr>
<tr>
<td>CdGeN(_2)</td>
<td>Cd</td>
<td>0.620</td>
<td>0.070</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>0.127</td>
<td>0.054</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>N(_{Ge})</td>
<td>0.098</td>
<td>0.047</td>
<td>0.284</td>
</tr>
<tr>
<td></td>
<td>NCd</td>
<td>0.651</td>
<td>0.101</td>
<td>0.336</td>
</tr>
<tr>
<td>MgGeN(_2)</td>
<td>Mg</td>
<td>0.624</td>
<td>0.072</td>
<td>0.000</td>
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<tr>
<td></td>
<td>Ge</td>
<td>0.126</td>
<td>0.060</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>N(_{Ge})</td>
<td>0.108</td>
<td>0.051</td>
<td>0.286</td>
</tr>
<tr>
<td></td>
<td>NMg</td>
<td>0.642</td>
<td>0.083</td>
<td>0.315</td>
</tr>
</tbody>
</table>

\(^a\)For ZnGeN\(_2\), the numbers in parentheses are the experimental values from Wintenberger et al. [80]

Table 4.7: Average bond lengths in Å.

<table>
<thead>
<tr>
<th>Compound</th>
<th>II-N (Å)</th>
<th>IV-N (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiN(_2)</td>
<td>2.02</td>
<td>1.74</td>
</tr>
<tr>
<td>ZnGeN(_2)</td>
<td>2.03 (2.01)(^a)</td>
<td>1.88 (1.88)</td>
</tr>
<tr>
<td>ZnSnN(_2)</td>
<td>2.04</td>
<td>2.02</td>
</tr>
<tr>
<td>CdGeN(_2)</td>
<td>2.24</td>
<td>1.88</td>
</tr>
<tr>
<td>MgGeN(_2)</td>
<td>2.07</td>
<td>1.86</td>
</tr>
</tbody>
</table>

\(^a\)For ZnGeN\(_2\), the numbers in parentheses are the experimental values from Wintenberger et al. [80]
Table 4.8: Bulk moduli and their pressure derivatives of Zn-IV-N$_2$ compounds obtained from fit to Vinet equation of state.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LDA</td>
<td>GGA</td>
</tr>
<tr>
<td>ZnSiN$_2$</td>
<td>234 (228)$^a$</td>
<td>208</td>
</tr>
<tr>
<td>ZnGeN$_2$</td>
<td>207 (197)</td>
<td>178</td>
</tr>
<tr>
<td>ZnSnN$_2$</td>
<td>177 (184)</td>
<td>150</td>
</tr>
<tr>
<td>CdGeN$_2$</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>MgGeN$_2$</td>
<td>182</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Values in parentheses from Paudel et al. [85]

4.4.3 QSGW band structures

The LDA and QSGW band structures of ZnSiN$_2$, ZnGeN$_2$, ZnSnN$_2$, CdGeN$_2$, and MgGeN$_2$ are compared with each other in figs. 4.4, 4.5, and 4.6. Before discussing the differences we discuss the atomic orbital character of the bands. The bands fall into three regions; the lower valence band near -15 eV is the N-2s like band, bands in the range from -5 to 0 eV are mostly N-2p but near $-7$ to $-5$ in LDA and about 2 eV lower in QSGW, we find the Cd-4d and Zn-3d bands overlapping with them. The N-2p bands are fairly strongly hybridized with cation s and p orbitals as can be seen in the partial density of states shown in figs. 4.7, 4.8 and 4.9. A more detailed examination of the orbital character of the conduction band minimum (CBM) indicates that the CBM has slightly higher group-IV than group-II cation-s character. Thus to maximally change the band gap it is more efficient to vary the group IV rather than group-II element.

First, we note that ZnSiN$_2$ has an indirect minimum gap slightly lower than the lowest direct gap. All compounds have their conduction band minimum (CBM) at $\Gamma$ but the valence band maximum (VBM) in ZnSiN$_2$ occurs at a point along the $\Gamma - Y$ direction close to $Y$. Before comparison with experiment, we add an estimated
Figure 4.4: Electronic band structure of ZnSiN$_2$ and ZnGeN$_2$. 
Figure 4.5: Electronic band structure of ZnSnN$_2$ and CdGeN$_2$. 
zero-point motion band gap renormalization correction $\Delta(0)$ and exciton binding energy correction $E_{xb}$. The former were tabulated by Cardona and Thewalt [99] for various semiconductors. We find that for the III-N semiconductors this correction is approximately proportional to the band gap itself and approximately given by $-50 - 31E_g \text{meV}$. This gives $\Delta(0)$ as $-227$, $-162$, $-117$, $-128$ and $-202 \text{meV}$ for ZnSiN$_2$, ZnGeN$_2$, ZnSnN$_2$, CdGeN$_2$ and MgGeN$_2$ respectively.

The exciton binding energies are estimated from

$$E_{xb} = \frac{\mu}{\varepsilon_0^2} \text{Rydberg} \quad (4.4)$$

where we use the reduced mass $\mu = m_cm_v/(m_c + m_v)$ with $m_c, m_v$ a directional averaged conduction and valence band hole mass as obtained in the next section. We here neglect the interaction of the different valence bands and take only the highest VBM into account (which is justified by the fairly large crystal field splittings) and average the inverse masses over direction. For ZnSiN$_2$, we use the actual VBM...
Figure 4.7: Total and partial densities of states: N-2s, 2p, Si-3s, 3p, Ge-4s, 4p, and Zn-4s, 4p, 3d of ZnSiN$_2$ and ZnGeN$_2$. 
Figure 4.8: Total and partial densities of states: N-2s, 2p, Sn-5s, 5p, Ge-4s, 4p, Zn-4s, 4p, 3d, and Cd-5s, 5p, 4d of ZnSnN$_2$ and CdGeN$_2$. 
not at Γ so the exciton binding energy corresponds to the indirect gap. For the direct gap we do not include an exciton binding energy. We use the static dielectric constants $\varepsilon_0$ from Paudel et al. [85] to calculate exciton binding energies shown in table 4.9. The use of static dielectric constants is consistent with the fact that the resultant exciton binding energies are significantly smaller than the optical phonon frequencies, so one may assume that lattice distortion contributes to the screening of the Coulomb interaction between electron and hole. The effective Bohr radius of the exciton is given by $(\varepsilon_0/\mu)a_0$, with $a_0$ the Bohr radius of hydrogen: 0.529 Å. The results are also given in table 4.9. We note that for ZnSiN$_2$ and ZnGeN$_2$ our values are comparable to the value in GaN of 25 meV [72]. For CdGeN$_2$, we used an interpolated static dielectric constant between ZnGeN$_2$ and ZnSnN$_2$ while for and MgGeN$_2$ we used interpolation between ZnSiN$_2$ and ZnGeN$_2$, assuming that dielectric constants are proportional to the gap. Our estimate of the static constant of CdGeN$_2$ and MgGeN$_2$ in this manner is 11.91 and 9.47. The gaps including both
Figure 4.10: Fine structure of the bands near the valence band maximum with symmetry labeling at $\Gamma$ for ZnSiN$_2$ and ZnGeN$_2$. 
Figure 4.11: Fine structure of the bands near the valence band maximum with symmetry labeling at Γ for ZnSnN$_2$ and CdGeN$_2$. 
zero-point motion renormalization correction and exciton binding energy are given in table 4.10.

For ZnGeN$_2$, our best converged QSGW calculations overestimates the gap by about 0.5 eV, which is typical for QSGW, while 0.8Σ is very close to the experimental value and is even closer after adding the above mentioned corrections. This experimental gap was determined by photoluminescence at 4 K and thus should be very close to our calculated gap. Spin-orbit corrections turn out to be negligibly small for these nitrides as will be discussed below. The LDA and GGA as usual underestimate the gap significantly. The GGA underestimates it a bit more than LDA but this is mostly because this calculation was done at the GGA lattice constants which are slightly larger and hence the gap is expected to be lower.

For ZnSiN$_2$, even our 0.8Σ gap is significantly larger than the experimental value. The zero-point motion and exciton binding energy corrections here are larger but even so, our value is about 1 eV larger than the experimental value. We note however,
Table 4.9: Zero-point motion band gap renormalization correction $\Delta(0)$, exciton binding energy correction $E_{xb}$ and related parameters: conduction band mass $m_c$, valence band mass $m_v$, reduced mass $\mu$, static dielectric constant $\varepsilon_0$, and effective Bohr radius $a^*$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta(0)$ (meV)</th>
<th>$E_{xb}$ (meV)</th>
<th>$m_c$</th>
<th>$m_v$</th>
<th>$\mu$</th>
<th>$\varepsilon_0$</th>
<th>$a^*$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiN$_2$</td>
<td>$-227$</td>
<td>$29$</td>
<td>$0.293$</td>
<td>$0.520$</td>
<td>$0.188$</td>
<td>$9.33$</td>
<td>$26$</td>
</tr>
<tr>
<td>ZnGeN$_2$</td>
<td>$-162$</td>
<td>$20$</td>
<td>$0.185$</td>
<td>$0.530$</td>
<td>$0.137$</td>
<td>$9.70$</td>
<td>$38$</td>
</tr>
<tr>
<td>ZnSnN$_2$</td>
<td>$-117$</td>
<td>$9$</td>
<td>$0.141$</td>
<td>$0.392$</td>
<td>$0.104$</td>
<td>$12.71$</td>
<td>$65$</td>
</tr>
<tr>
<td>CdGeN$_2$</td>
<td>$-128$</td>
<td>$12$</td>
<td>$0.165$</td>
<td>$0.491$</td>
<td>$0.124$</td>
<td>$11.91$</td>
<td>$50$</td>
</tr>
<tr>
<td>MgGeN$_2$</td>
<td>$-202$</td>
<td>$26$</td>
<td>$0.261$</td>
<td>$0.516$</td>
<td>$0.173$</td>
<td>$9.47$</td>
<td>$29$</td>
</tr>
</tbody>
</table>

that the latter is obtained from absorption measurements at room temperature. The temperature effect could be at most $0.2$ eV. So, even taking these corrections into account, there remains a significant discrepancy. Early absorption measurements for ZnGeN$_2$ also gave significantly lower values of the gap, e.g. $2.67$ eV in Larson et al. [11], $3.1$-$3.2$ eV [25], $3.3$ eV [13]. Defect band tails might be responsible for an experimental underestimate of the gap. Earlier work by Endo et al. [17] gave an even lower estimate of the onset of absorption in ZnSiN$_2$ of $3.64$ eV. Previous calculations also obtained an indirect gap for ZnSiN$_2$ [31] of $3.32$ eV in LDA. For ZnGeN$_2$ they obtained an LDA gap of $1.67$ eV close to ours. The small discrepancy in LDA values is likely to arise from the use of different band structure methods or slightly different lattice constants.

ZnSnN$_2$ has only very recently been grown in polycrystalline form. Lahourcade et al. [27] have reported optical absorption edge near $2$ eV which differs from their predicted band gap of $1.42$ eV. This is explained by the attribution of the Burstein-Moss effect, i.e. the large electron carrier concentrations and the low conduction band effective mass causes the effective band gap to be higher than the fundamental band gap. Quayle et al. [28] have used photoluminescence excitation spectroscopy (PLE) to determined $E_g$ of ZnSnN$_2$ as $1.7\pm0.1$ eV at room temperature. Single-
Table 4.10: Band gaps (in eV) of II-IV-N$_2$ compounds in various approximations. * 0.8Σ is refers QSGW correction [2]

<table>
<thead>
<tr>
<th>Compound</th>
<th>LDA</th>
<th>GGA</th>
<th>QSGW</th>
<th>0.8Σ</th>
<th>0.8Σ + Δ(0) + $E_{xb}$</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiN$_2$</td>
<td>3.60</td>
<td>3.23</td>
<td>6.01</td>
<td>5.70</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>direct</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.23</td>
</tr>
<tr>
<td>ZnGeN$_2$</td>
<td>1.66</td>
<td>1.57</td>
<td>3.99</td>
<td>3.60</td>
<td>3.42</td>
<td>3.40±0.01</td>
</tr>
<tr>
<td>ZnSnN$_2$</td>
<td>0.55</td>
<td>0.35</td>
<td>2.64</td>
<td>2.15</td>
<td>2.02</td>
<td>1.7±0.1</td>
</tr>
<tr>
<td>CdGeN$_2$</td>
<td>1.02</td>
<td></td>
<td>2.92</td>
<td>2.53</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>MgGeN$_2$</td>
<td>2.90</td>
<td>5.43</td>
<td>4.90</td>
<td></td>
<td>4.67</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Δ(0) is the estimated zero-point motion renormalization correction and $E_{xb}$ is the exciton binding energy.

$^b$Osinsky et al. [25]
$^c$Du et al. [18]
$^d$Quayle et al. [28]

Crystal thin films of ZnSnN$_2$ has been synthesized by Feldberg et al.[82] They show that the structures of two samples are monoclinic and optical absorption edges are slightly above 2 eV (2.12 and 2.38 eV). They claim that the absorption spectra are also influenced by the Burstein-Moss effect and a partially disordered cation sublattice can reduce the electronic band gap. However, their predicted lowest-energy structure is orthorhombic and predicted band gap is 2.09 eV. Our overestimate of the calculated gap (2.02 eV), comparing with PLE result [28], can in large part be explained by the change in the lattice constant. Our LDA lattice constant at zero temperature is about 6% smaller than the measured room-temperature lattice constant. We note that this difference is probably not only because of the thermal expansion but also because of the LDA underestimate of the lattice constant, even at 0 K. Using our calculated band-gap deformation potential $dE_g/dlnV$ of $-3.89$ eV, this effect reduces the gap by about $-0.2$ eV, giving a gap of $1.8±0.1$ eV. Thus, theory and experiment are consistent to within about 0.1 eV. For CdGeN$_2$ and MgGeN$_2$ there are no experimental data available.

We note that the direct gaps calculated here (including the various corrections)
Table 4.11: Absolute shifts \((E_i - \epsilon_i)\) in eV between QSGW and LDA relative to their own average electrostatic potentials and pure quasiparticle shift \(\Sigma_i\) (in parentheses) for various levels.

<table>
<thead>
<tr>
<th>level</th>
<th>ZnSiN_2</th>
<th>ZnGeN_2</th>
<th>ZnSnN_2</th>
<th>CdGeN_2</th>
<th>MgGeN_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBM</td>
<td>1.6 (1.5)</td>
<td>1.7 (1.5)</td>
<td>1.8 (1.6)</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>VBM</td>
<td>-0.5 (-0.5)</td>
<td>-0.1 (-0.4)</td>
<td>0.2 (-0.3)</td>
<td>0.0</td>
<td>-0.5</td>
</tr>
<tr>
<td>II-3d</td>
<td>-2.3 (-2.2)</td>
<td>-2.0 (-2.0)</td>
<td>-1.5 (-1.9)</td>
<td>-1.8</td>
<td>-</td>
</tr>
<tr>
<td>N-2s</td>
<td>-1.3 (-1.2)</td>
<td>-1.2 (-1.1)</td>
<td>-1.0 (-0.7)</td>
<td>-0.9</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

correspond to wavelengths of 218 nm, 362 nm, 614 nm, 521 nm, and 266 nm for ZnSiN_2, ZnGeN_2, ZnSnN_2, CdGeN_2 and MgGeN_2. For ZnSiN_2, the indirect gap corresponds to 228 nm. These values span the red-to-ultraviolet region, with ZnSnN_2 in the orange-red and CdGeN_2 very close to the green region of the spectrum.

Next, we discuss individual band state shifts due to GW. Quasi-particle shifts of eigenvalues between single-shot GW and the corresponding one-electron Hamiltonian are well defined, because they correspond to the same electron density. We obtain this shift by comparing the QSGW eigenvalues with the LDA eigenvalues obtained with the charge density generated by QSGW. We refer to it as the “pure quasiparticle shift” \(\Sigma_i\) for a given level \(i\). On the other hand, we also compare the shifts between the QSGW quasi-particle energies and the LDA eigenvalues for the LDA charge density. The QSGW and LDA eigenvalues were both determined relative to their average electrostatic potentials. In table 5.3, we include both the pure quasiparticle shifts and the shifts between QSGW and LDA. The difference in these two shifts provides an estimate of the error to expect in band offsets from 1-shot GW calculations based on the LDA.

Let us now inspect the results as given in table 5.3. We find the pure quasiparticle shifts of the VBM to be negative and of the CBM to be positive with the ratio of the CBM shift to the absolute value of the VBM shift increasing from Si to Sn. The
dominant shift is always in the CBM.

When considering the shifts relative to the pure LDA, which include a change in charge density between LDA and QSGW, we find also a downward shift of the VBM, except for ZnSnN$_2$, for which both the VBM and the CBM shift up relative to LDA. The CBM of ZnSnN$_2$ has a sizable Sn-s contribution. On an absolute scale one expects Sn-s levels to lie deeper than e.g. Ge-s levels because s-levels are non-zero at the nucleus. This is of course the underlying reason for the gap reduction from Si to Ge to Sn as well as from Mg to Zn to Cd. Apparently for ZnSnN$_2$, the Sn-s states are positioned relative to the electrostatic potential reference in such a way as to behave almost like a N-2p level and hence the VBM shift has the same sign as the CBM. The N-2s and Zn-3d bands shift considerably more down, showing that the GW shifts are orbital dependent: the Zn-3d shift down more than the N-2s even though the N-2s lie below the Zn-3d. These average band positions were taken as the peak in the corresponding partial density of states.

### 4.4.4 Effective valence band Hamiltonian

In this section, we examine the energy bands near the band gap in more detail. Figs. 4.10, 4.11, and 4.12 show the band structures near the VBM for the compounds. The states at $\Gamma$ are labeled according to the irreducible representations. We note that the CBM at $\Gamma$ has $a_1$ symmetry. Thus direct optical transitions are allowed from $a_1$ to $a_1$ for $\mathbf{E} \parallel \mathbf{c}$, from $b_1$ to $a_1$ for $\mathbf{E} \parallel \mathbf{a}$ and $b_2$ to $a_1$ for $\mathbf{E} \parallel \mathbf{b}$. We see that in these materials except ZnSiN$_2$ the VBM is split in three levels even without including spin-orbit coupling. The order of the different symmetry levels is different in each case. In ZnSiN$_2$ in addition, a level of $a_2$ symmetry lies in between these levels. This level has no allowed dipole transitions to the CBM. When adding spin-orbit coupling to the calculation, we find almost identical splittings. From the group theory point
of view, all transitions then become allowed because all of them belong to the \( \Gamma_5 \) irreducible representation of the double group, using Koster and Slater’s character table. However, the fact that spin-orbit coupling appears to have negligible effect on the VBM states indicates that we should discuss selection rules based on the single rather than the double group. The selection rules mentioned above imply that these materials might have opportunities for polarization sensitive detectors. Even for light incident normally to the basal plane, there should be a significant splitting between excitons or light absorbed for the two in-plane polarizations. This results from the low orthorhombic symmetry. At this point, however no such exciton fine structure has been observed. This will require high-quality films.

The effective masses of the valence bands at \( \Gamma \) are different in each direction \( x, y, z \) and for each separate valence band. Likewise the CBM has in principle an anisotropic mass tensor with three different diagonal components. The VBM manifold of states can be described by a generalization of the Kohn-Luttinger for zincblende or Rashba-Sheka-Pikus Hamiltonian for wurtzite. Using the theory of invariants, we can write the effective mass Hamiltonian as follows:

\[
H^{C_{2v}} = \Delta_1 e L_z^2 + \Delta_2 e (L_x^2 - L_y^2) + \Delta_1 s o L_z \sigma_z + \sqrt{2}(\Delta_2 s o L_x \sigma_x + \Delta_3 s o L_y \sigma_y) + \\
[A_1 + A_2 L_z^2 + A_3 (L_x^2 - L_y^2)]k_z^2 + [B_1 + B_2 L_z^2 + B_3 (L_x^2 - L_y^2)](k_x^2 + k_y^2) + \\
[C_1 + C_2 L_z^2 + C_3 (L_x^2 - L_y^2)](k_x^2 - k_y^2) + \\
D_1 \{L_x, L_y\} k_x k_y + D_2 \{L_z, L_x\} k_z k_x + D_3 \{L_z, L_y\} k_z k_y + E_1 L_x k_y + E_2 L_y k_x,
\]

(4.5)

where \( \{L_i, L_j\} \) are anti-commutators. This includes all terms up to second order that can be formed from the operators \( L_i, k_i \) and \( \sigma_i \) that are invariant (i.e. belong to the \( a_1 \) representation). At \( k = 0 \) we have two crystal field splittings and three spin-orbit splitting parameters. The remaining terms are inverse effective masses and the
parameters $E_1$ and $E_2$ are linear in $k_i$. We have neglected purely relativistic linear terms involving $\sigma_i$ and $k_i$. If $\Delta_{2c} = 0$, $\Delta_{2so} = \Delta_{3so}$, $A_3 = 0$, $B_3 = 0$, $C_1 = C_2 = 0$, $C_3 = 2D_1$, $D_2 = D_3$, and $E_1 = E_2$ the above Hamiltonian is reduced to the RSP Hamiltonian valid for $C_{6v}$ symmetry. If we denote the RSP Hamiltonian parameters as defined in Kim et al. [1] by $\tilde{A}_i$, we have the relations:

\[
\begin{align*}
A_1 &= \tilde{A}_1 & A_2 &= \tilde{A}_3 \\
B_1 &= \tilde{A}_2 & B_2 &= \tilde{A}_4 \\
C_3 &= \tilde{A}_5 & D_1 &= 2\tilde{A}_5 \\
D_2 &= D_3 &= \sqrt{2}\tilde{A}_6 \\
E_1 &= -E_2 &= \sqrt{2}\tilde{A}_7
\end{align*}
\] (4.6)

For $k = 0$ and without spin-orbit splitting, the Hamiltonian in the basis of $Y_l^m$ with $l = 1$ and $m = 1, 0, -1$ is of the form

\[
\begin{pmatrix}
\Delta_{1c} & 0 & \Delta_{2c} \\
0 & 0 & 0 \\
\Delta_{2c} & 0 & \Delta_{1c}
\end{pmatrix}
\] (4.7)

The eigenvalues are

\[
\begin{align*}
E_{a_1} &= 0, \\
E_{b_2} &= \Delta_{1c} + \Delta_{2c}, \\
E_{b_1} &= \Delta_{1c} - \Delta_{2c}
\end{align*}
\] (4.8)

where we have used the usual sign convention of the spherical harmonics

\[
Y_1^{\pm1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta \mathrm{e}^{\pm i\phi},
\]

so the $x$-orbital, which gives the state with $b_1 = x$ symmetry
corresponds to \(-Y_1^1 + Y_1^{-1}\), which indeed corresponds to the eigenvalue with the – sign in the above equation. Since in almost all cases except MgGeN\(_2\), we find \(E_{b_1} > E_{b_2}\) it means that \(\Delta_{2c} < 0\). The splittings \(\Delta_{1c}\) and \(\Delta_{2c}\) parameters are given in table 4.13. We find the hexagonal crystal field splitting \(\Delta_{1c}\) to be significantly larger than in GaN.

For arbitrary \(\mathbf{k}\) the \(3 \times 3\) Hamiltonian matrix without spin-orbit coupling terms is of the form

\[
\begin{pmatrix}
\Delta_{1c} + (B_1 + B_2 + C_1 + C_2)k_x^2 \\
+ (B_1 + B_2 - C_1 - C_2)k_y^2 \\
+ (A_1 + A_2)k_z^2 \\
(D_2k_xk_x + iD_3k_zk_y)/\sqrt{2} \\
+ E_1k_y + iE_2k_x \\
\Delta_{2c} + (B_3 + C_3)k_x^2 \\
+ (B_3 - C_3)k_y^2 + A_3k_z^2 \\
+iD_1k_xk_y
\end{pmatrix}
\]

\[
\begin{pmatrix}
(D_2k_xk_x - iD_3k_zk_y)/\sqrt{2} \\
+ E_1k_y - iE_2k_x \\
\Delta_{2c} + (B_3 + C_3)k_x^2 \\
+ (B_3 - C_3)k_y^2 + A_3k_z^2 \\
+iD_1k_xk_y
\end{pmatrix}
\]

\[
\begin{pmatrix}
(B_1 + C_1)k_2^2 + (B_1 - C_1)k_2^2 + A_1k_3^2 \\
+ E_1k_y - iE_2k_x \\
\Delta_{1c} + (B_1 + B_2 + C_1 + C_2)k_x^2 \\
+ (B_1 + B_2 - C_1 - C_2)k_y^2 \\
+ (A_1 + A_2)k_z^2
\end{pmatrix}
\]

\[
\begin{pmatrix}
\Delta_{2c} + (B_3 + C_3)k_x^2 \\
+ (B_3 - C_3)k_y^2 + A_3k_z^2 \\
iD_1k_xk_y
\end{pmatrix}
\]

(4.9)

If we now consider the bands in each of the orthogonal directions, e.g. \((k_x = k_y = 0)\), we can diagonalize the Hamiltonian in the same way as for \(\mathbf{k} = 0\) and read off the hole inverse masses. We will use the notation \(m_\alpha^\lambda\) where \(\lambda\) gives the irreducible representation of the level at \(\Gamma\) and \(\alpha\) gives the Cartesian direction \(x, y, z\). Thus, we
obtain the following relations for the inverse hole masses:

\[-(m_{a_1}^{a_1})^{-1} = A_1,\]
\[-(m_{b_2}^{b_2})^{-1} = A_1 + A_2 + A_3,\]
\[-(m_{b_1}^{b_1})^{-1} = A_1 + A_2 - A_3,\]
\[-(m_{a_1}^{a_1})^{-1} = B_1 + C_1,\]
\[-(m_{b_2}^{b_2})^{-1} = B_1 + B_2 + B_3 + C_1 + C_2 + C_3,\]
\[-(m_{b_1}^{b_1})^{-1} = B_1 + B_2 - B_3 + C_1 + C_2 - C_3,\]
\[-(m_{a_1}^{a_1})^{-1} = B_1 - C_1,\]
\[-(m_{b_2}^{b_2})^{-1} = B_1 + B_2 + B_3 - C_1 - C_2 - C_3,\]
\[-(m_{b_1}^{b_1})^{-1} = B_1 + B_2 - B_3 - C_1 - C_2 + C_3.\]

(4.10)

In table 4.12 we summarize the various VBM and CBM effective masses and in table 4.13 we summarize the \(A_i, B_i, C_i\) parameters. The remaining parameters \(D_i\) only enter if we look at bands in directions intermediate between in-basal-plane and out-of-basal-plane. Assuming the crystal is not too far from hexagonal, which we could call a quasi-hexagonal approximation, one would have the relation \(D_1 = 2C_3\). Furthermore, within the quasi-cubic relation, one has the approximate relation \(\tilde{A}_6 = (4\tilde{A}_5 - \tilde{A}_3)/\sqrt{2}\) in the wurtzite case. This leads here to the relation \(D_2 = D_3 = 4C_3 - A_2\). Thus the \(D_i\) parameters can be obtained approximately from the ones already determined. The \(E_i\) linear in k-parameters are related to the anti-crossing behavior of the bands one can observe for example for the \(b_2\) and \(a_1\) bands along \(\Gamma - Y\) in ZnGeN\(_2\). Since these occur well below the VBM, they are of limited interest and were not determined.

Now, we return to the case \(k = 0\) but add spin-orbit coupling. The \(6 \times 6\) Hamil-
Table 4.12: Effective masses (in units of free electron mass $m_e$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ZnSiN$_2$</th>
<th>ZnGeN$_2$</th>
<th>ZnSnN$_2$</th>
<th>CdGeN$_2$</th>
<th>MgGeN$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_x^c$</td>
<td>0.30</td>
<td>0.22</td>
<td>0.16</td>
<td>0.18</td>
<td>0.27</td>
</tr>
<tr>
<td>$m_y^c$</td>
<td>0.47</td>
<td>0.20</td>
<td>0.15</td>
<td>0.17</td>
<td>0.27</td>
</tr>
<tr>
<td>$m_z^c$</td>
<td>0.21</td>
<td>0.15</td>
<td>0.12</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>$m_x^a$</td>
<td>4.80</td>
<td>1.90</td>
<td>1.79</td>
<td>1.89</td>
<td>2.34</td>
</tr>
<tr>
<td>$m_y^a$</td>
<td>0.80</td>
<td>2.02</td>
<td>1.98</td>
<td>3.70</td>
<td>3.54</td>
</tr>
<tr>
<td>$m_z^a$</td>
<td>0.21</td>
<td>0.15</td>
<td>0.12</td>
<td>0.16</td>
<td>0.20</td>
</tr>
<tr>
<td>$m_x^b$</td>
<td>0.37</td>
<td>0.21</td>
<td>0.15</td>
<td>0.21</td>
<td>0.31</td>
</tr>
<tr>
<td>$m_y^b$</td>
<td>4.80</td>
<td>2.19</td>
<td>2.02</td>
<td>2.13</td>
<td>4.44</td>
</tr>
<tr>
<td>$m_z^b$</td>
<td>2.97</td>
<td>2.26</td>
<td>2.04</td>
<td>2.17</td>
<td>2.68</td>
</tr>
<tr>
<td>$m_x^c$</td>
<td>0.31</td>
<td>2.91</td>
<td>2.27</td>
<td>3.03</td>
<td>2.33</td>
</tr>
<tr>
<td>$m_y^c$</td>
<td>1.06</td>
<td>0.19</td>
<td>0.15</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>$m_z^c$</td>
<td>1.18</td>
<td>2.42</td>
<td>2.34</td>
<td>2.78</td>
<td>3.56</td>
</tr>
<tr>
<td>actual VBM</td>
<td>$m_x^v$</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in ZnSiN$_2$</td>
<td>$m_y^v$</td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$m_z^v$</td>
<td>1.09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.13: Parameters of Effective Hamiltonian: inverse mass ($\hbar^2/2m_e$), energy splitting (meV).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ZnSiN$_2$</th>
<th>ZnGeN$_2$</th>
<th>ZnSnN$_2$</th>
<th>CdGeN$_2$</th>
<th>MgGeN$_2$</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>-4.71</td>
<td>-6.87</td>
<td>-8.57</td>
<td>-7.39</td>
<td>-5.10</td>
<td>-5.98</td>
</tr>
<tr>
<td>$A_2$</td>
<td>4.11</td>
<td>6.44</td>
<td>8.10</td>
<td>6.95</td>
<td>4.78</td>
<td>5.44</td>
</tr>
<tr>
<td>$A_3$</td>
<td>-0.26</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
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<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>0.73</td>
<td>-0.51</td>
<td>-0.53</td>
<td>-0.52</td>
<td>-0.35</td>
<td>-0.58</td>
</tr>
<tr>
<td>$B_2$</td>
<td>-1.93</td>
<td>-2.19</td>
<td>-3.12</td>
<td>-2.06</td>
<td>-1.58</td>
<td>-2.46</td>
</tr>
<tr>
<td>$B_3$</td>
<td>0.04</td>
<td>0.09</td>
<td>0.11</td>
<td>0.24</td>
<td>-0.22</td>
<td></td>
</tr>
<tr>
<td>$C_1$</td>
<td>-0.52</td>
<td>-0.02</td>
<td>-0.03</td>
<td>-0.15</td>
<td>-0.07</td>
<td></td>
</tr>
<tr>
<td>$C_2$</td>
<td>-1.26</td>
<td>-0.05</td>
<td>-0.05</td>
<td>0.00</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>$C_3$</td>
<td>-0.32</td>
<td>2.30</td>
<td>3.18</td>
<td>2.15</td>
<td>1.61</td>
<td>2.53</td>
</tr>
<tr>
<td>$D_1$</td>
<td>-0.64</td>
<td>4.60</td>
<td>6.36</td>
<td>4.30</td>
<td>3.45</td>
<td>5.06</td>
</tr>
<tr>
<td>$D_2,D_3$</td>
<td>-5.41</td>
<td>2.76</td>
<td>4.62</td>
<td>1.65</td>
<td>1.66</td>
<td>2.19</td>
</tr>
<tr>
<td>$\Delta_{1c}$</td>
<td>160</td>
<td>115</td>
<td>82</td>
<td>97</td>
<td>-168</td>
<td>12</td>
</tr>
<tr>
<td>$\Delta_{2c}$</td>
<td>-20</td>
<td>-14</td>
<td>-94</td>
<td>-28</td>
<td>89</td>
<td>0</td>
</tr>
</tbody>
</table>
tonian breaks into two equivalent $3 \times 3$ Hamiltonians of the form

$$
\begin{pmatrix}
\Delta_{1c} + \Delta_{so1} & \Delta_{so2} - \Delta_{so3} & \Delta_{2c} \\
\Delta_{so2} - \Delta_{so3} & 0 & \Delta_{so2} + \Delta_{so3} \\
\Delta_{c2} & \Delta_{so2} + \Delta_{so3} & \Delta_{1c} - \Delta_{so1}
\end{pmatrix}
$$

(4.11)

The order of the basis function is $m = 1 \uparrow$, $m = 0 \downarrow$, $m = -1 \uparrow$ or equivalently $m = -1 \downarrow$, $m = 0 \uparrow$ and $m = 1 \downarrow$. The eigenvalues are indeed doubly degenerate in spin because of the Kramer’s theorem related to time reversal symmetry. If we assume that the spin-orbit coupling parameters are essentially isotropic, $\Delta_{so1} = \Delta_{so2} = \Delta_{so3} = \Delta_s$, which is usually a good approximation because spin-orbit coupling arises from the inner part of the atom where the potential is close to spherically symmetric, we can make some progress by first applying the unitary transformation that diagonalized the matrix without spin-orbit coupling. This leads to

$$
\begin{pmatrix}
\Delta_{c1} + \Delta_{c2} & \sqrt{2}\Delta_s & \Delta_s \\
\sqrt{2}\Delta_s & 0 & -\sqrt{2}\Delta_s \\
\Delta_s & -\sqrt{2}\Delta_s & \Delta_{c1} - \Delta_{c2}
\end{pmatrix}
$$

(4.12)

If we furthermore assume that the spin-orbit parameter is small compared to the crystal field splitting of the levels, then in second order perturbation theory we obtain

$$
\begin{align*}
E_{a1} &= -\frac{2\Delta_s^2}{\Delta_{c1} + \Delta_{c2}}, \\
E_{b2} &= \Delta_{c1} + \Delta_{c2} + \frac{2\Delta_s^2}{\Delta_{c1} + \Delta_{c2}} + \frac{\Delta_s^2}{2\Delta_{c2}}, \\
E_{b1} &= \Delta_{c1} - \Delta_{c2} + \frac{2\Delta_s^2}{\Delta_{c1} - \Delta_{c2}} - \frac{\Delta_s^2}{2\Delta_{c2}}
\end{align*}
$$

(4.13)

Strictly speaking all levels have symmetry $\Gamma_5$ but we still label them by the single
group label from which they are derived.

We carried out calculations including spin-orbit coupling and found that the splittings were essentially indistinguishable from the ones without spin-orbit coupling. This indicates that the spin-orbit coupling parameter is very small in these compounds and makes it at this point impractical and at the same time unimportant to try to extract these small parameters.

The reason for this small spin-orbit coupling is worth some discussion. For the parent compound, GaN, we find it is already rather small because (1) the N atom is a low-Z element for which relativistic effects are small, and (2) there is a negative contribution from the Ga-3d states lying below the VBM but which are nevertheless somewhat hybridized with the VBM. In ZnGeN$_2$, this negative contribution which now derives from the Zn-3d level must be even stronger. In fact, we know that in ZnO, the spin-orbit splitting becomes negative[77]. One expects it here to be intermediate between GaN and ZnO because only half the cation sites contribute. The Ge-3d or Sn-4d states lie significantly deeper so that their contribution must be significantly smaller. Apparently, the 3d contribution must almost perfectly cancel the N-2p contribution.

Now for ZnSiN$_2$, the $a_2$ valence band lies in between the $b_1$ and $b_2$. Along $\Gamma - Z$ the point group of the k-point is still $C_{2v}$ so the band emanating from $a_2$ retains $a_2$ symmetry and cannot interact with the other bands. Thus it is indeed seen to cross the $b_1$ band as it disperses upward in energy. Along $\Gamma - X$ or $\Gamma - Y$ the symmetry group is reduced to a single mirror plane, $\sigma_y$, $\sigma_x$ respectively. Along $\Gamma - Y$, for example, $a_1$ and $b_2$ derived bands are both even and $a_2$ and $b_1$ are odd under the $\sigma_x$. Thus one can see an anti-crossing behavior of the $a_2$ and $b_1$ derived bands along $\Gamma - Y$. However, the effective Hamiltonian describing the states near $\Gamma$ loses its usefulness. In fact, this Hamiltonian is mostly useful as a starting point for envelope function calculations of nanostructures or shallow acceptor impurities or excitons. But the
Γ-point VBM lies about 0.2 eV below the actual VBM. Thus it is more useful to give
the anisotropic effective mass tensor of the VBM at this \( k \)-point. The actual VBM
are also given in table 4.12.

Finally, it is instructive to compare these parameters with those in GaN. Using
eq 4.6 we can rewrite the RSP parameters of GaN derived in chapter 3 in our present
orthorhombic notation. These are included in table 4.13 as the last column. In that
case \( E_{b_1} = E_{b_2} \) and the masses in \( x \) and \( y \) directions are the same. We can see that
the inverse mass parameters in GaN are similar to those in ZnGeN\(_2\) but the crystal
field splitting is significantly smaller.

4.5 Conclusions

We presented FP-LMTO LDA and GGA calculations of the crystal structure pa-
rameters and QSGW band structures of the II-IV-N\(_2\) semiconductors with II=Zn,
Cd, and Mg, IV=Si, Ge, and Sn. Excellent agreement is obtained for the structural
parameters with experiment and previous calculations. As for the band structures,
we find ZnSiN\(_2\) to be an indirect gap semiconductor while the others are direct gap
semiconductors. The band gaps versus lattice constants are summarized in fig. 4.13
compared with the group-III nitride family and firmly establish that these compounds
are promising for similar optoelectronic applications as the III-N family. Gap correc-
tions such as exciton binding energy and zero-point motion phonon renormalization
of the gaps were included. Spin-orbit coupling was also taken into account and found
to have negligible effect on the valence band splittings.

The orthorhombic symmetry reduction compared to the III-nitrides, however, has
important consequences in splitting the valence band according to x, y, z-like states.
The bands near the valence band maximum were analyzed in detail by generalizing
the Kohn-Luttinger Hamiltonian for orthorhombic symmetry and the corresponding
Figure 4.13: Band gaps as function of wurtzite lattice constant of ZnSiN$_2$, ZnGeN$_2$, ZnSnN$_2$, CdGeN$_2$, and MgGeN$_2$ compared to AlN, GaN, and InN.

parameters were extracted by fitting to the band structure. Conduction band masses and exciton reduced masses and binding energies were estimated.
Chapter 5

Band offsets between II-IV-$\text{N}_2$ and III-N

5.1 Introduction

Band offsets at heterojunctions play an important role in semiconductor devices such as light emitting diodes (LED) and solar cells. They lead to built-in electric fields which allow one to control the spatial distribution of carriers. For an LED, carrier confinement of both holes and electrons in the same region is beneficial, while for photovoltaic applications, separation of photogenerated electrons and holes is required.

From chapters 3 and 4, we point out here the interesting opportunity that ZnGeN$_2$, GaN, and ZnO are closely lattice matched and have almost equal band gaps of $\sim$3.4 eV, which is far from optimal for photovoltaic applications. This means necessarily that the band offsets among them must be staggered or so-called type II. The offsets create a situation where an effectively smaller band gap exists across the interface. This leads to the possibility of absorption at lower photon energies and effective separation of electrons and holes in the different semiconductors joined at the interface.
In this chapter, we will show that if the materials are arranged from low to high valence band maximum (VBM), the valence band offsets are from 0.4–2.6 eV, predicting significantly lower effective gaps at the interfaces. This is of interest from a fundamental point of view because it highlights the role of Zn-3d, Ga-3d orbitals and the anion in affecting the VBM. ZnGeN$_2$, GaN, and ZnO indeed differ in that, in ZnGeN$_2$, the Zn-3d electrons lie at about 7 eV below the VBM, whereas in GaN, the Ga-3d states lie about 15 eV below the VBM. In ZnO, on the other hand, we have even shallower Zn-3d levels at about 6 eV, but now the anion O-2p states are also deeper than N-2p states. We include ZnSnN$_2$ although it has a larger lattice constant than the other three materials. That is because it has been viewed as a potentially useful material for solar cells [26; 27; 28]. Here, our best estimated band gap of ZnSnN$_2$ based on the QSGW method and using the experimental lattice constant [28] is 1.8±0.1 eV. This differs slightly from the value given in chapter 4 because in that chapter we use the slightly underestimated LDA lattice constant. Band offsets between group-III nitrides have been studied before [34] as well as between GaN and ZnO [35; 36; 37; 38; 39; 40].

### 5.2 Computational method

Our calculations of the structure and electrostatic potential at the interfaces are based on DFT-LDA while the calculation of the band structures themselves in each bulk material is based on the QSGW approach. We calculate the alignment of the electrostatic potential using the LDA method with a supercell approach for modeling the interface. The position of the bands relative to the potential is determined separately for each material including quasiparticle self-energy effects of the individual band edges. The band offsets are also strongly influenced by strain and depend on the particular arrangement at the heterostructure, the degree of epitaxy, etc. We first
study coherently strained interfaces. We assume that the in-plane lattice constant is dictated by the substrate, and relax the distance perpendicular to the interface based on continuum elastic theory. The internal positions of the atoms and the interface layer separations are determined by relaxing the total energy. Deviations from the specific structural models or strain situations handled explicitly here can (if required) be analyzed later in terms of the deformation potential induced changes to the VBM for each individual material. We study the importance of these effects by examining three different interface orientations. We then attempt to extract from this an average interface-independent and strain-free “natural” band offset which might apply to more random situations, for example, an array of nanoparticles in close contact with different interfaces.

The procedure is illustrated in fig. 5.1. The band offset is thus essentially sepa-
rated into a bulk and an interface contribution.

\[
\Delta E_v(A/B) = (E^b_v(B) - E^b_{\text{ref}}(B)) - (E^b_v(A) - E^b_{\text{ref}}(A)) \\
+ (E^a_{\text{ref}}(B) - E^a_{\text{ref}}(A)) \\
\equiv \Delta E^b_v + V_D \tag{5.1}
\]

The first two terms give the bulk valence band maximum relative to some suitable reference level in each material separately, and the third term gives the change in reference level across the interface. We call it the dipole potential \(V_D\) [100]. Several types of reference levels can be used.

All that is needed are some suitable markers of the potential in the materials that can be identified in the separate bulk as well as locally in the interface system, whose potential can be viewed as being bulk-like for the layers sufficiently far from the interface, except for a constant shift near the interface. In practice, for example, it is common for experimentalists to use a core level as a reference level. Here we use the average potential at the muffin-radius over the atoms in a layer. The average is taken weighted by the area of the spheres,

\[
\nabla = \frac{\sum_i V_i s_i^2}{\sum_i s_i^2} \tag{5.2}
\]

Here \(V_i\) is the potential at the sphere radius \(s_i\) of the \(i\)-th muffin-tin sphere and the sum is over all atoms in a given atomic layer.

It is convenient to focus first on non-polar directions such as the [100] and [010] directions. In this case, each layer is neutral in bulk. For the polar direction [001], because of the difference in spontaneous polarization, and the piezoelectric polarization due to the specific strain, a net charge can occur at the interface and this leads to an electric field in each different semiconductor region, in other words, a
sloped potential. This slope is then superposed on the dipolar shift that occurs also over a few atomic layers and this makes it a little more ambiguous to separate the in-principle abrupt dipole jump and the slope discontinuity. Paudel et. al. [86] have shown that the spontaneous polarizations of ZnGeN$_2$, GaN, and ZnSnN$_2$ are relatively close to each other, so that these effects are small, although they may be somewhat larger for the interfaces with ZnO. In reality, the surface charge resulting from the discontinuity in polarization, $\sigma = \Delta P \cdot \hat{n}$, which in a continuum model, is a strict two-dimensional charge per unit area, is distributed over some layers, and thus the potential is not really discontinuous in slope. The dipole discontinuity is likewise not abrupt at the atomic scale and this results in some difficulty in disentangling the two from each other.

So, to summarize, we set up a suitable supercell, modeling the interface with a few layers of each material, and calculate its self-consistent potential. Then we apply the above filtering and averaging procedure to extract the interface dipole profile and extract from this the $V_D$ term. The band edges with respect to the same type of average are determined separately in each material also within the local density approximation (LDA). However, a quasiparticle correction for each material is then applied to the band edges relative to the electrostatic potential. In other words, we take into account how much each band edge is shifted from its LDA to its $GW$ result relative to the same electrostatic potential average. As discussed earlier, [91] this makes sense within the quasiparticle self-consistent $GW$ method, in which our Kohn-Sham eigenvalues approach the quasiparticle energies once the exchange correlation potential is self-consistently determined from the $GW$ self-energy.

Our assumptions for a specific strain state assume that one of the materials, say GaN, is the substrate. We then adjust ZnGeN$_2$ to be biaxially strained to the substrate, i.e., to have the same in-plane lattice constants as the substrate. The
perpendicular lattice constant is obtained by minimizing the strain energy

\[ U = \frac{1}{2}(\eta_1, \eta_2, \eta_3) \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{12} & c_{22} & c_{23} \\ c_{13} & c_{23} & c_{33} \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \end{pmatrix} \] (5.3)

using the previously calculated elastic constants [86]. For the interface layer separation, we initially assume the average of the two bulk inter-planar distances and this sets the lattice constants of the supercell. Afterwards, all atomic positions as well as the interface layer separation (or equivalently, the lattice constant in the direction perpendicular to the interface) are relaxed to minimize the total energy. We find that this results primarily in adjustment of the interlayer separations right next to the interface.

The bulk contribution \( \Delta E^b_v \) is included the strain due to the lattice mismatch. It can be decomposed into an unstrained contribution \( \Delta E^0_v \) and a strain contribution: \( \Delta E^b_v = \Delta E^0_v + \Delta s \). To evaluate the importance of the \( GW \) correction, we further decompose \( \Delta E^0_v \) into the LDA part and its \( GW \) correction, \( \Delta E^0_v(GW) = \Delta E^0_v(LDA) + \Delta_{GW} \). In fact, these contributions can be given separately for each material, but the strain contribution depends on which strain situation is considered, and hence on the interface. Note that the strain here is biaxial and contains both a traceless as well as a hydrostatic component. The hydrostatic absolute deformation potential requires itself an interface calculation between unstrained and strained material because the reference level is not guaranteed to be the same between two separate bulk calculations. We have checked with separate calculations of the interface between strained ZnGeN\(_2\) and unstrained ZnGeN\(_2\) and found that this effect is less than 0.1 eV on the \( \Delta s \). By comparing the strained with the unstrained bulk ZnGeN\(_2\), we can undo the strain effect to extract a “natural” band-offset, i.e.
$\Delta E_{v}^{nat} = \Delta E_{v}^{0} + \bar{V}_{D}$, where the average of $V_{D}$ over different orientations is indicated by $\bar{V}_{D}$.

This would for example occur if we assume that the ZnGeN$_{2}$ is too thick to stay pseudomorphic and instead relaxes by introducing misfit dislocations. We have no way currently to take into account the effects of those misfit dislocations on the dipole, but we can easily estimate the changes in band edges due to the different strain states in the bulk. In principle, some other residual strain state might occur due to thermal expansion mismatch. For example, it is common to assume that at the growth temperature, the film is fully relaxed but after cooling a strain results from the different thermal expansion coefficients. Once we have a natural “strain-free” band offset, it would in principle be possible to add strain effects in terms of deformation potentials assuming the strain state is known or measured for a specific situation. For GaN/ZnGeN$_{2}$, these effects are all expected to be rather small.

### 5.3 Results

We start by illustrating the methodology for the GaN/ZnGeN$_{2}$ case. Fig. 5.2 shows the average potentials as discussed in the previous section for three different interface orientations and the dipole potential $V_{D}$ extracted from them. We used supercells consisting of four (or six) layers of GaN and four (or six) layers of ZnGeN$_{2}$. Only the results for the larger cells are shown in fig. 5.2. The dipoles extracted from the smaller cells agree with the larger ones within 0.1 eV and, therefore, for the other materials, we have used the smaller cells. The lattice constants obtained by minimizing the strain for the ZnGeN$_{2}$ region for each interface are summarized in table 5.1 and compared with the equilibrium lattice constants of unstrained ZnGeN$_{2}$ and GaN.

The separation of the valence band edges relative to the average electrostatic
Figure 5.2: Potential profiles for different interfaces for GaN/ZnGeN$_2$. The potential shown is the $\bar{V}$ of eq. 5.2.

Table 5.1: Orthorhombic structure lattice constants as strained for particular interfaces of GaN/ZnGeN$_2$, ZnO/ZnGeN$_2$ and GaN/ZnSnN$_2$

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnGeN$_2$ (unstrained bulk)</td>
<td>6.38</td>
<td>5.45</td>
<td>5.22</td>
</tr>
<tr>
<td>ZnSnN$_2$ (unstrained bulk)</td>
<td>6.59</td>
<td>5.70</td>
<td>5.41</td>
</tr>
<tr>
<td>GaN (unstrained substrate)</td>
<td>6.31</td>
<td>5.47</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnO (unstrained substrate)</td>
<td>6.41</td>
<td>5.55</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnGeN$_2$ [100] on GaN</td>
<td>6.40</td>
<td>5.47</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnGeN$_2$ [010] on GaN</td>
<td>6.31</td>
<td>5.49</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnGeN$_2$ [001] on GaN</td>
<td>6.31</td>
<td>5.47</td>
<td>5.31</td>
</tr>
<tr>
<td>ZnGeN$_2$ [100] on ZnO</td>
<td>6.36</td>
<td>5.55</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnGeN$_2$ [010] on ZnO</td>
<td>6.41</td>
<td>5.46</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnGeN$_2$ [001] on ZnO</td>
<td>6.41</td>
<td>5.55</td>
<td>5.19</td>
</tr>
<tr>
<td>ZnSnN$_2$ [100] on GaN</td>
<td>6.83</td>
<td>5.47</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnSnN$_2$ [010] on GaN</td>
<td>6.31</td>
<td>5.91</td>
<td>5.14</td>
</tr>
<tr>
<td>ZnSnN$_2$ [001] on GaN</td>
<td>6.31</td>
<td>5.47</td>
<td>5.56</td>
</tr>
</tbody>
</table>
Table 5.2: Decomposition of the band edge (relative to average electrostatic potential \( \bar{V} \) as defined in eq. 5.2) in each material in LDA, its \( GW \) shift and band gap (unit in eV).

<table>
<thead>
<tr>
<th>Material</th>
<th>( E^0_v(LDA) )</th>
<th>( \Delta_{ GW } )</th>
<th>( E_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>9.30</td>
<td>-0.34</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnGeN(_2)</td>
<td>9.40</td>
<td>-0.13</td>
<td>3.4</td>
</tr>
<tr>
<td>ZnSnN(_2)</td>
<td>10.42</td>
<td>0.20</td>
<td>1.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>6.45</td>
<td>-1.62</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 5.3: Dipole potentials and valence band offsets in each direction for the eight-layer supercell, units in eV. (Values in parentheses are obtained from the twelve-layer supercell.)

<table>
<thead>
<tr>
<th></th>
<th>GaN/ZnGeN(_2)</th>
<th>ZnO/ZnGeN(_2)</th>
<th>GaN/ZnSnN(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E^0_v(GW) )</td>
<td>0.31</td>
<td>4.44</td>
<td>1.66</td>
</tr>
<tr>
<td>( \Delta s^{[100]} )</td>
<td>0.15</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>( \Delta s^{[010]} )</td>
<td>0.19</td>
<td>0.29</td>
<td>0.33</td>
</tr>
<tr>
<td>( \Delta s^{[001]} )</td>
<td>0.14</td>
<td>0.21</td>
<td>0.34</td>
</tr>
<tr>
<td>( V_D^{[100]} )</td>
<td>1.15(1.29)</td>
<td>-2.21</td>
<td>0.18</td>
</tr>
<tr>
<td>( V_D^{[010]} )</td>
<td>1.04(1.17)</td>
<td>-2.10</td>
<td>0.18</td>
</tr>
<tr>
<td>( V_D^{[001]} )</td>
<td>1.10(1.24)</td>
<td>-2.43</td>
<td>0.23</td>
</tr>
<tr>
<td>( V_D )</td>
<td>1.10(1.23)</td>
<td>-2.25</td>
<td>0.20</td>
</tr>
<tr>
<td>( \Delta E_v^{[100]} )</td>
<td>1.61(1.75)</td>
<td>2.48</td>
<td>2.08</td>
</tr>
<tr>
<td>( \Delta E_v^{[010]} )</td>
<td>1.54(1.67)</td>
<td>2.63</td>
<td>2.17</td>
</tr>
<tr>
<td>( \Delta E_v^{[001]} )</td>
<td>1.55(1.69)</td>
<td>2.22</td>
<td>2.23</td>
</tr>
</tbody>
</table>

potential in the LDA, its \( GW \) correction, and the band gap for each material are given in table 5.2. The band gap given here is the low temperature experimental exciton gap rounded to 0.1 eV, which agrees well with QSGW after the 0.8\( \Sigma \) correction, the zero-point motion, and the exciton binding energy correction [91].

The extracted dipole potentials \( V_D \) and \( \Delta E_v^b \) including the strain effects are included in table 5.3 for each pair of interfaces calculated directly. The average over directions is also included.

In fig. 5.3, we show the total densities of states (DOS), resolved layer-by-layer.
Table 5.4: Natural valence and conduction band offsets, gap differences and effective interface gaps of heterostructures (in units of eV).

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta E_{val}^{nat}$</th>
<th>$\Delta E_{con}^{nat}$</th>
<th>$\Delta E_g$</th>
<th>$E_{g,av}^{i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN/ZnGeN$_2$</td>
<td>1.4(1.5)$^a$</td>
<td>1.3(1.4)</td>
<td>-0.1</td>
<td>2.1(2.0)</td>
</tr>
<tr>
<td>GaN/ZnSnN$_2$</td>
<td>1.9</td>
<td>0.2</td>
<td>-1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>ZnO/GaN</td>
<td>0.8(0.7)</td>
<td>0.9(0.8)</td>
<td>0.1</td>
<td>2.6(2.7)</td>
</tr>
<tr>
<td>ZnO/ZnGeN$_2$</td>
<td>2.2</td>
<td>2.2</td>
<td>0.0</td>
<td>1.2</td>
</tr>
<tr>
<td>ZnO/ZnSnN$_2$</td>
<td>2.7(2.6)</td>
<td>1.1(1.0)</td>
<td>-1.6</td>
<td>0.7(0.8)</td>
</tr>
<tr>
<td>ZnGeN$_2$/ZnSnN$_2$</td>
<td>0.5(0.4)</td>
<td>-1.1(-1.2)</td>
<td>-1.6</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$The values in parentheses correspond to the larger supercells.

One could in principle read off the band offsets directly from this figure by taking the difference between the VBM in the central layers in each half of the unit cell. However, the procedure discussed before is somewhat more accurate. The two are, in fact, in good agreement. The total DOS illustrates that the middle layers are indeed already bulk-like; in other words, that our supercell is large enough.

We can see that the band offsets between ZnGeN$_2$ and GaN depend only little on the interface direction. The variation is only 0.08 eV. This is because the materials are the closest lattice matched. For the other cases, the strain effects are somewhat larger and hence the band-offset variations with interface orientation are also larger.

By leaving out the strain contribution, we obtain an estimate of strain relaxed instead of coherently strained interfaces. The average of these over the three interfaces is what we defined as a “natural” band offset.

Finally, we summarize the valence as well as conduction band offsets and gap discontinuities in table 5.4 not only for the pairs directly calculated but also the other ones, which follows from the transitivity rule. The transitivity rule states that $\Delta E_v(A/C) = \Delta E_v(A/B) + \Delta E_v(B/C)$. Its validity has been discussed in many references in past literature, e.g. Interface-bond-polarity model for semiconductor heterojunction band offsets [101]. This rule follows immediately from any model in
which band offsets are obtained by aligning a reference level. In the past there has been ample discussion what reference level to align; e.g. a vacuum level [102], a so-called charge neutrality point [103; 104; 105; 106], a dielectric midgap point [107], and a dangling bond energy [101]. Our calculations do not make this assumption but calculate the interface potential line up explicitly. Nonetheless the transitivity rule is expected to hold at least for the natural band offsets which are designed to be independent of specific interface details and strain situations.

We can see that all heterostructures considered have a type-II alignment, except for ZnGeN$_2$/ZnSnN$_2$. For all type-II heterostructures, the lowest gap of the system is between the VBM of one and the CBM of the other material. This transition is spatially indirect and therefore we expect optical absorption at this smallest gap only near the interface. We therefore call it “the interface gap” $E_{g,\text{av}}^{i}$, average (av)
meaning with respect to different interface directions. It is included in table 5.4. On the other hand, ZnGeN$_2$ has a type-I alignment with ZnSnN$_2$, which means that ZnSnN$_2$ quantum wells could be created with ZnGeN$_2$ barriers for LED types of applications. The alignments of the valence bands and conduction bands between all four materials are also conveniently summarized in fig. 5.4. The interface gaps as well as the valence and conduction band offsets of each pair can be read directly from this figure.

![Figure 5.4: Natural band off-set alignment of ZnO, GaN, ZnGeN$_2$, and ZnSnN$_2$ and their effective interface gaps are displayed in unit of eV. GaN/ZnGeN$_2$, GaN/ZnSnN$_2$, and ZnO/GaN are calculated by using LDA supercell approach while ZnO/ZnGeN$_2$, ZnO/ZnSnN$_2$, and ZnGeN$_2$/ZnSnN$_2$ are obtained by using the transitivity rule.](image)

Considering the three materials with gaps near 3.4 eV, we note that the valence band offsets are of order 1–2 eV and we find the VBMs ordered from low to high from ZnO to ZnGeN$_2$. This result would imply that electrons will migrate from ZnGeN$_2$ to GaN to ZnO if all three were present in the same structure. Holes,
on the other hand, will migrate from ZnO to GaN to ZnGeN₂. This separation of carriers of different polarity in different regions is advantageous for photovoltaic applications. The band gaps of these materials are in the UV and hence not directly suitable for terrestrial solar-cell applications. One may expect light absorption at the smaller effective interface gap of these heterostructures. This absorption could be significant if a major portion of the material is near the interfaces, in other words if it is nanostructured. These gaps occur at 1.2 eV (infrared) at the ZnO/ZnGeN₂ interface, 2.0 eV (yellow) at the GaN/ZnGeN₂ interface, and at 2.7 eV (blue) at the ZnO/GaN interface, thus covering various portions of the visible spectrum and the near-infrared. We envision a solar cell of the type schematically shown in fig. 5.5. It would consist of nanosize columns of each of the materials, arranged in such a way that all three interfaces occur between them. We caution that the effective band gaps in these heterostructures could be larger than the interface gaps given in table 5.4 because of the size-quantization effect. By further varying the sizes of these nanocolumns and hence their band gaps, one could further improve the range of wavelengths for which light absorption can take place. Including ZnSnN₂ in the design of such a solar cell would further allow absorption at 1.8 eV (red) and even further in the near IR (0.8 eV). We note that the VBM of ZnSnN₂ is the highest of the four materials, so ultimately holes would migrate to ZnSnN₂ while the conduction band of ZnSnN₂ is above those of ZnO and GaN, so electrons would still accumulate in the ZnO. Of course, the growth of such a solar cell with well-separated materials and sharp interfaces presents a considerable challenge to thin-film and nanostructured growth method.
5.4 Discussion

The only case for which we are aware of previous results in the literature is the ZnO/GaN interface. Our valence band offset of 0.8 eV is in good agreement with the experimental results of Liu et al. [36] based on photoemission measurements of thin films of GaN grown on ZnO. They find 0.7±0.1 eV for polar and 0.9±0.1 eV for non-polar interfaces. On the other hand, Veal et al. [37] obtained the ZnO/GaN band offset of 1.37 eV in an indirect way by measuring the ZnO/AlN band offset and using the transitivity rule. McDermott et al. [39] studied mixed ZnO/GaN solid solution systems and proposed a 1.6 eV band offset between the ZnO and GaN phases in such systems. They found an effective gap of about 2.6−2.8 eV in such systems, in agreement with our proposed interface gap. However, the quantum size effects on the ZnO and GaN phases in such a mixed system are not completely clear. Their valence band offset is deduced from examining second derivatives of the O-K and N-K X-ray absorption and emission spectra in the mixed systems. They find evidence that such a mixed system is in fact phase separated at the nanoscale rather than forming a homogeneous superlattice oxynitride.
On the theory side, Huda et al. [38] found a band offset of 0.7 eV using the GGA+$U$ method, i.e., including a Hubbard $U$ for Ga-3$d$ and Zn-3$d$ orbitals. Wang et al. [40] also calculated a valence band offset of 1.04 eV using GGA+$U$. They in addition studied core-shell nanowire heterostructures. Wang et al. [35] find valence band offsets ranging from 0.455 to 1.588 eV depending on which exchange correlation functional is used. Using GGA functionals PBE or PW91, they find relatively small offsets while adding Hubbard $U$ for the Zn-3$d$ and Ga-3$d$, the band offset is increased. Their highest band offset is found for the hybrid functional HSE06 (Heyd-Scuseria-Ernzerhof [108]) in which they used a different fraction of Hartree-Fock mixing for both materials, so as to adjust the gaps. It is well known that HSE06 tends to shift down the valence band maximum and apparently in their calculation this occurs more strongly for ZnO than for GaN (maybe because of the larger Hartree-Fock fraction used). This result illustrates that obtaining a correct quasiparticle shift of the individual band edges is important. We note (from table 5.2) that among the materials studied here, the $GW$ correction is the most negative in ZnO and shows relatively smaller variation among the nitrides. Since these band offsets also depend strongly on strain, a detailed comparison between different results requires considering which strain state was assumed. For example, the results of Wang et al. [35] correspond to a coherently strained interface. Since the VBM is split in strained GaN, this splitting increases the valence band offset. It can also be seen in table 5.3 that the strain contribution is positive in all cases. Wang et al. [35] found that the dipole contribution is almost independent of the functional used. This result supports our approach of calculating the dipole at the LDA level, while the individual band edges in each material require the use of the $GW$ corrections. Our valence band offset for ZnO/GaN is also in good agreement with the embedded cluster approach calculations of Walsh et al. [109] which use a hybrid functional in the quantum mechanically treated region. Our calculations have assumed perfect crystals except
for strain effects. Point defects and cation disorder, especially in the ternary nitride, may affect their valence band offset [110].

5.5 Conclusions

We have studied the band alignment between ZnGeN$_2$, ZnSnN$_2$, GaN and ZnO. Calculations were carried out for coherent [100], [010], [001] interfaces of three pairs of the materials, GaN/ZnGeN$_2$, GaN/ZnSnN$_2$ and ZnO/ZnGeN$_2$. By separating out the strain contribution, we also deduced an averaged natural band offset for strain-relaxed materials. The $GW$ corrections to the band offset were found to be important for interfaces involving ZnO because among these materials, ZnO has a much larger downward valence band shift between LDA and $GW$ band edges.

The band offsets at the other three possible pairs are deduced from the transitivity rule. The results show that except for ZnGeN$_2$/ZnSnN$_2$, all other heterostructures considered are of type II, which is promising for charge separation at such interfaces. The effective “interface gaps” of these materials are in the visible to near-infrared making them much more attractive for photovoltaics than the individual materials, which have gaps in the UV except for ZnSnN$_2$. These materials’ valence bands are in increasing order from ZnO to GaN to ZnGeN$_2$ to ZnSnN$_2$. Their conduction bands are in decreasing order from ZnGeN$_2$ to ZnSnN$_2$ to GaN to ZnO. Thus, in a composite system comprising all four materials, holes would flow to ZnSnN$_2$ and electrons to ZnO. A columnar nanosize solar-cell concept was presented for how potentially these band offsets could be utilized in photovoltaic cells.
Chapter 6
Conclusions

In this thesis we applied the QSGW method mainly to the study of II-IV-N$_2$ semiconductors. We find that it gives band gaps in excellent agreement with experiment where good data are available and if various corrections are included carefully, such as zero point motion and exciton binding energies. The true value of the method however lies in that it allows us to make predictions for materials for which good data are not yet available. For example for ZnSnN$_2$ our calculations preceded the experimental synthesis. The gaps are of course also sensitive to the lattice constant and in that case we found that our LDA underestimated the lattice constants leading to an overestimate of the gap. Once we put in the experimental lattice constants, we obtained agreement to within 0.1 eV. We further highlight that our calculations provide predictions for the gaps of CdGeN$_2$ and MgGeN$_2$. By including these two materials we provide a roadway to extend the applications of these materials into the green and UV regions. Besides the overall band structure at the eV scale, we realize that for many future device modeling efforts a detailed understanding of the bands near the gap region is important. This includes the valence band splittings due to the lower crystals symmetry and the effective masses or in a more elaborate theoretical framework, the KL and RSP Hamiltonians. Therefore we have determined all these parameters for all these materials. We cannot yet ascertain how accurate
these will turn out to be for II-IV-N$_2$ semiconductors because no experimental data are available yet. But we have proven for the III-N semiconductors that they give very accurate results. In the process of this study we found important refinements of these parameters for the III-N semiconductors from previous work and we established the important fact of a negative SO splitting parameter for InN. Finally, we have started to study the interfaces between these various members of the family and other related materials, such as GaN and ZnO. We found these are of particular interest for solar cells because the staggered band offsets produce effectively lower gaps in the mixed system or interface system. As an outlook, much work remains to be done on these materials. Defects and doping need to be studied. Alloy band gap bowing for more complex mixtures such as ZnSi$_x$Ge$_{1-x}$N$_2$, ZnGe$_x$Sn$_{1-x}$N$_2$ etc should be calculated. We hope that the work described in this thesis provides a foundation for understanding their electronic structure.
References


[33] Atchara Punya and Walter R. L. Lambrecht. CdGeN$_2$ and ZnGe$_{0.5}$Sn$_{0.5}$N$_2$: Two new nitride semiconductors with band gaps in the blue-green. *Materials Science Forum*, 717-712:1331–1334, May 2012. 3, 48


[35] Zhenhai Wang, Mingwen Zhao, Xiaopeng Wang, Yan Xi, Xiujie He, Xiangdong Liu, and Shishen Yan. Hybrid density functional study of band alignment in


[66] Masaki Ueno, Minoru Yoshida, Akifumi Onodera, Osamu Shimomura, and


Excitonic structure of bulk AlN from optical reflectivity and cathodoluminescence 

[75] Bernard Gil, Olivier Briot, and Roger-Louis Aulombard. Valence-band physics 
and the optical properties of GaN epilayers grown onto sapphire with wurtzite 

W.J. Schaf. Critical points of the band structure and valence band ordering at 
the Γ point of wurtzite InN. J. Cryst. Growth, 288:273–277, 2006. 34, 38

[77] Walter R. L. Lambrecht, Anna V. Rodina, Sukit Limpijunnong, B. Segall, 
and Bruno K. Meyer. Valence-band ordering and magneto-optic exciton fine 

Bull, 5:793, 1970. 46


46, 59, 60

[81] T. Cloitre, A. Sere, and R. L. Aulombard. Epitaxial growth of ZnSiN₂ single-
47

Stampe, R. J. Kennedy, D. O. Scanlon, G. Vardar, R. L. Field, III, T. Y. Jen,


[90] Atchara Punya, Tula R. Paudel, and Walter R. L. Lambrecht. Electronic and
lattice dynamical properties of II-IV-N$_2$ semiconductors. *physica status solidi (c)*, 8(7-8):2492–2499, 2011. 48


[98] D.E. Partin, D.J. Williams, and M. O’Keeffe. The crystal structures of


