

Role of semicore states in the electronic structure of group-III nitrides: An exact exchange study

A. Qteish and A. I. Al-Sharif

Department of Physics, Yarmouk University, 21163-Irbid, Jordan

M. Fuchs and M. Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

S. Boeck and J. Neugebauer

Department of Theoretical Physics, University of Paderborn, D-33095 Paderborn, Germany

(Dated: February 2, 2008)

The bandstructure of the zinc-blende phase of AlN, GaN, InN is calculated employing the exact-exchange (EXX) Kohn-Sham density-functional theory and a pseudopotential plane-wave approach. The cation semicore d electrons are treated both as valence and as core states. The EXX bandgaps of AlN and GaN (obtained with the Ga $3d$ electrons included as core states) are in excellent agreement with previous EXX results, GW calculations and experiment. Inclusion of the semicore d electrons as valence states leads to a large reduction in the EXX bandgaps of GaN and InN. Contrary to common belief, the removal of the self-interaction, by the EXX approach, does not account for the large disagreement for the position of the semicore d electrons between the LDA results and experiment.

PACS numbers: 71.15.Mb, 71.20.Nr

I. INTRODUCTION

The modern computational methods applied to condensed matter systems are mainly based on Kohn-Sham [1] formalism of density-functional theory (KS-DFT). When used in conjunction with both the local-density (LDA) and generalized gradient approximations (GGA) for the exchange-correlation (XC) potential, the KS-DFT approach provides a very efficient and successful tool to compute the total energy and other related ground state properties. However, calculated KS bandstructures of solids display several limitations of this approach. The most serious shortcoming is the so-called *bandgap problem*: the LDA bandgaps of semiconductors and insulators are between about 30 to more than 100% smaller than the corresponding experimental values. Another problem is the underestimation of the binding energies of the semicore electrons. For the group-III nitrides and II-VI compounds, currently intensely studied materials due to their potential technological applications, the LDA results for the position of the d bands are higher than experiment by 2 to 4 eV. The GGA electronic structures of these materials differ marginally from those of LDA. It should be noted that these deficiencies reflect on the one hand a fundamental issue: even the (unknown) exact single-particle KS eigenvalues will not directly correspond to excitation energies of the interacting electron system, except in special cases [2, 3]. As to the bandgap, it is well known [4] that there is a discontinuity in the *exact* XC potential (Δ_{XC}) when an electron is added to the system. In general the magnitude of Δ_{XC} is however unknown. The second, separate, issue is the effect of the (inevitable) *approximation* for the XC functional. The LDA errors for bandgaps as well as for binding energies

of semicore states have been attributed [5] to a spurious self-interaction in LDA and GGA calculations [3, 6].

The best available technique for calculating the electronic structure of solids is the quasiparticle theory, within Hedin's *GW* approximation [7]. The non-selfconsistent *GW* approach based on LDA results (LDA-GW) is found to reproduce very well the experimental bandgaps of standard *sp* semiconductors [8]. For group-III nitrides and II-VI compounds, the pseudopotential [9, 10] and all-electron [11] LDA-GW methods are found to give good bandgaps (few tenths of an eV smaller than experiment), provided that the *entire* semicore shell is considered as valence in the pseudopotential approach. The positions of the d bands are markedly improved within LDA-GW [10, 11], although they remain systematically higher than experiment by about 1 eV.

A very interesting recent development is the application of the exact-exchange (EXX) approach [12], within the KS-DFT approach, to calculate the electronic structure of solids. In this approach the local – KS – exchange potential is treated exactly, i.e., the spurious self-interaction [6] of the electron with its own charge density is eliminated. In the exchange-*only* KS-DFT formalism, the EXX potential is equivalent [13] to the variationally best local approximation (i.e., the optimized effective potential) to the nonlocal Hartree-Fock operator [14, 15]. The EXX approach was first applied to crystalline solids by introducing a spherical shape approximation of the potential by Kotani and co-worker [16, 17, 18, 19]. This approximate EXX approach is found to highly improve the calculated bandgaps of several semiconductors [18] and the electronic structure of transition metals [19], with respect to the LDA results. More recently, a pseudopotential EXX approach has been introduced [20, 21]. The

pseudopotential approach is free from the above shape approximation of the potential and the convergence with respect to the computational parameters can be easily controlled. The pseudopotential EXX approach is found to give [21] bandgap energies in good agreement with experiment and GW results [8, 22], for a large variety of semiconductors studied – except for diamond. On the other hand, for noble-gas solids [23] the pseudopotential EXX approach gives bandgaps which are larger than those of LDA, but they are still much smaller than the experimental values. Thus, in addition to their own fundamental and practical importance, the EXX results provide a very good starting point for the non-selfconsistent GW (EXX-GW) calculations [24].

The purpose of this work is of threefold: (i) To perform pseudopotential EXX calculations of the electronic bandstructure of the meta-stable [25] zinc-blende (ZB) phase of GaN, AlN, InN. In these calculations the Ga 3*d* and In 4*d* electrons are treated as valence states. The electronic structure parameters of the ground state wurtzite (W) phase of the considered nitrides can be inferred from those of the corresponding ZB structure [26, 27]. (ii) To systematically analyze the effects of the semicore states on the bandstructure. To do that, an additional set of EXX bandstructures for GaN and InN are calculated, with the semicore states included in the core. (iii) To analyze and separate the changes that are due to the use of EXX pseudopotentials (PPs) from those due to the EXX treatment of the valence electrons. This is done by performing EXX bandstructure calculations employing LDA-PPs, and LDA calculations using both LDA- and EXX-PPs.

It is worth noting that the bandgap of W-InN is still a matter of debate. The bandgap of the recently grown single crystalline hexagonal InN epilayers is found [28] to be of 0.7-1.0 eV, which is much smaller than the previous and widely accepted [29] experimental value of 1.9 eV. However, the smaller bandgap is far from being well established [30, 31]. A very recent experimental study suggested [30] that this small bandgap is a misinterpretation of the Mie resonances due to scattering or absorption of light in InN samples containing clusters of metallic In. Moreover, a tentative bandgap of 1.4 eV has been given in Ref. 30. Therefore, accurate theoretical studies of the bandgap of InN are in order.

The paper is organized as follows. Sec. II contains a description of the computational method. Our results are reported and discussed in Sec. III. A summary of our main results and conclusions is given in Sec. IV.

II. COMPUTATIONAL METHOD

To perform EXX band structure calculations, we implemented the pseudopotential EXX formalism [21] in the SPHInX code [32], which employs plane wave basis sets and *ab initio* pseudopotentials. As noted above, EXX bandstructure calculations are performed for only

the ZB phase of the considered nitrides. This is done at the experimental lattice constants (4.37, 4.50 and 4.98 Å for AlN, GaN and InN, respectively [33]). We use the experimental rather than the theoretical lattice constants (which can be obtained by minimizing the EXX or LDA total energy) to allow for a direct comparison with the experimental bandgaps and to avoid shifts in the bandgaps due to deformation potentials.

Table I: Pseudopotential parameters. The local part of the ionic pseudopotential is chosen to be one of its components, referred to by its orbital angular momentum (*l*). For the Ga⁺³ and In⁺³ LDA-PPs, reference energies for the Ga 4*d* and In 5*d* states of 20 and 25 eV are used, respectively.

Ion	approach	core radius (a_0)			local part
		$l = 0$	$l = 1$	$l = 2$	
N ⁺⁵	EXX	1.5	1.5		$l = 1$
N ⁺⁵	LDA	1.5	1.5		$l = 0$
Al ⁺³	EXX & LDA	1.9	1.9	1.90	$l = 2$
Ga ⁺¹³ & In ⁺¹³	EXX	2.2	2.2	2.20	$l = 0$
Ga ⁺¹³ & In ⁺¹³	LDA	2.2	2.2	2.20	$l = 1$
Ga ⁺³	EXX	2.1	2.1	2.50	$l = 0$
Ga ⁺³	LDA	2.1	2.1	2.20	$l = 0$
In ⁺³	EXX	2.2	2.2	2.90	$l = 0$
In ⁺³	LDA	2.2	2.2	2.35	$l = 0$

Norm-conserving scalar-relativistic EXX- and LDA-PPs of the involved elements are generated by using the Troullier-Martins optimization method [34]. The EXX-PP's are constructed as described in Ref. 35. Then, the generated pseudopotentials are transformed to the separable Kleinman-Bylander form [36]. The ground state electronic configuration is assumed for all the atoms considered. Following Ref. 26, only *s* and *p* components are included for N. The pseudopotential parameters used are listed in Table I. The transferability of the pseudopotentials has been carefully tested, and they are found to be free from ghost states [37]. The construction of the LDA-PPs and the testing of both the EXX- and LDA-PPs are performed by using the FHI98PP code [38].

In the LDA calculations we used the Ceperley-Alder [39] exchange-correlation data as parameterized by Perdew and Zunger [6]. In the present EXX calculations, the exchange energy and potential are treated exactly and the above LDA functional is used for those of the correlation. Hereafter, unless otherwise specified, this combination (exact-exchange plus LDA correlation) will be referred to simply as EXX. Brillouin zone integration is performed on a regular $4 \times 4 \times 4$ Monkhorst-Pack [40] mesh. The KS wavefunctions are expanded in terms of plane waves up to a cutoff energy of 60, 65 and 70 Ryd for AlN, InN, and GaN, respectively. To calculate

the independent particle polarizability, χ_o (see Ref. 21), plane waves up to an energy cutoff of 35, 45 and 55 Ryd are included for AlN, InN, and GaN, respectively. The energy cutoffs used for the EXX calculations for GaN and InN, with the semicore d electrons included in the core, are exactly as those of AlN. The k-point sampling and the energy cutoffs are carefully tested, and are found to give an excellent convergence. For example, reducing the χ_o energy cutoff of GaN from 55 to 45 Ryd, keeping the other cutoff fixed at 70 Ryd, changes the calculated eigenvalues by less than 0.01 eV. The calculation of the exact exchange potential involves also the unoccupied KS states, through χ_o and the Green's functions of the orbital shifts. To ensure convergence, we fully diagonalize the Hamiltonian in the plane wave representation and include all conduction states.

III. RESULTS AND DISCUSSION

In this section we report and discuss our EXX and LDA electronic structures of the ZB form of AlN, GaN and InN. We will also briefly address the modifications of their bandstructure when going from the ZB to W phases. The most prominent bandstructure parameters of the ZB phase of the three nitrides considered, obtained with the semicore d electrons treated as part of the frozen core, are listed in Table II. Whereas, those of GaN and InN, obtained with the semicore d electrons treated as valence states, are listed in Table III. The available experimental results for GaN are also shown in Table III. As an example, we show in Fig. 1 the LDA and EXX bandstructures of ZB-GaN.

A. Comparison between the electronic structures of ZB and W phases

We focus here mainly on the differences in the bandgap and the position of the shallow d bands (E_d) by going from the ZB to W phases, studied at the LDA level. For the W phase, we have also considered the experimental structural parameters [33]. The obtained results can be summarized as follows. (i) In agreement with previous LDA calculations [26, 27], the direct bandgap at the Γ -point (E_g^Γ) of the W phase of GaN and InN are larger than that of the corresponding ZB phase by about 0.2 eV. (ii) The ZB-AlN is an indirect bandgap semiconductor with conduction bands minima at the X-points, in agreement with experiment and previous calculations [8, 21, 26]. (iii) The values of E_g^Γ are almost identical in both ZB and W phases of AlN, in agreement with a recent LDA study [26]. (iv) The value of E_d remains almost the same by going from the ZB to W phases, for both GaN and InN. For instance, the LDA results for E_d of GaN (obtained using EXX-PPs), with respect to the valence bands maximum, are of -16.84 eV for the ZB phase and -16.87 eV for the W phase. In the following we will mainly

concentrate on the EXX and LDA electronic structure of only the ZB phase of the considered nitrides. For this reason, the reference to the ZB phase will be suppressed, and that to the W form will be explicitly stated.

B. Bandgaps and the effects of the semicore d electrons

We will start our discussion with AlN where no semicore states are present. Table II shows that the EXX results for the fundamental indirect bandgap (E_g^X) are in very good agreement with the experimental value (5.11 eV, see Ref. 8), and with the GW results [8]. For E_g^Γ , experimental results are only available for the W phase, and the most recent value is of 6.033 eV (Ref. 43). Since the values of E_g^Γ are almost identical in the ZB and W structures of AlN, one can conclude that the EXX and GW results for E_g^Γ are in good agreement with each other, and with the above experimental value.

We turn now to the electronic structure of GaN, obtained without the semicore d states and using EXX-PPs (Fig. 1a). This figure shows that the energetic position and dispersion of the valence bands are weakly affected when going from the LDA to EXX. The most noticeable difference is in the upper valence bandwidth. The conduction bands, however, are significantly shifted upward in energy in the EXX calculations, with respect to the valence bands maximum. This upward shift increases the bandgap from 1.97 eV (LDA calculation with EXX-PPs, see Table II) to 3.52 eV. This EXX bandgap is in excellent agreement with previous EXX calculations [8, 21], LDA-GW calculations [10] (with Ga $3d$ electrons were included in the frozen core) and experimental data (3.2 – 3.3 eV, see Table. III).

To analyze the effects of the semicore electrons, we show in Fig. 1b the EXX and LDA bandstructures of GaN, obtained by treating these electrons as valence states. In this case a rather different behavior is found: Compared to the EXX calculation without semicore states, the bandgap closes by 0.64 eV — leading to a bandgap of 2.88 eV. This reduction can be easily understood as a consequence of the symmetry allowed anion p -cation d repulsion [44], which pushes the upper valence bands states up in energy, leading to a smaller bandgap. This EXX bandgap is in remarkable agreement with the pseudopotential LDA-GW result (2.88 eV) of Rohlfing *et al.* [10], obtained with the entire Ga semicore shell considered as valence. Furthermore, these pseudopotential EXX and LDA-GW results agree well with the mixed basis all-electron LDA-GW result (3.03 eV) for W-GaN [11], after subtracting the difference in E_g^Γ between the W and ZB phases of GaN (~ 0.2 eV, see above). This indicates that the inclusion of the entire semicore shell as valence is not necessary in the EXX and EXX-GW (see Ref. 24) calculations. This is largely due to the linearity of the EXX potential [35] and the improved description of the semicore atomic s and p states of Ga by the EXX

approach. The binding energies of these states are appreciably increased by the removal of self-interaction, as shown in Fig. 2. Compared to experiment, both EXX and LDA-GW approaches underestimate the bandgap of GaN (by about 0.4 eV). However, it has already been shown that a combination of these two methods (i.e., the EXX-GW approach) gives [24] bandgaps that are in very good agreement with experiment for GaN and some II-VI compounds.

Concerning InN, the experimental bandgap (available only for W-InN) is still controversial, as noted above. Our results listed in Tables II and III for InN show a behavior which is qualitatively very similar to that of GaN: Inclusion of the semicore (In $4d$) states in the core gives an EXX value for E_g^Γ of ~ 1.5 eV, while considering them as valence lowers significantly this bandgap to ~ 0.8 eV. Assuming a similar error as that of the bandgap of GaN (of about 0.4 eV) and taking into consideration the difference in the bandgap of InN when going from ZB to W phases (see Sec. III.A), a direct fundamental bandgap for W-InN of ~ 1.4 eV is estimated. This result is smaller than the previously accepted experimental value of ~ 1.9 eV, and larger than the very recent results (0.7-1.0 eV, Ref. 28). Incidentally, it agrees well with the (tentative) experimental value of 1.4 eV suggested by Shubina *et al.* [30]. However, it should be noted that the EXX-GW approach does not always give bandgaps that are larger than those of EXX (Ref. 8), and, hence, the present estimate should be also treated as tentative.

It is interesting to note that the EXX bandgap of InN when including the semicore (In $4d$) states is significantly larger than in all-electron LDA-GW calculations [11, 47], which give a bandgap of ~ 0 eV, for the W phase. This is in contrast to the case of GaN where both approaches give almost identical results. The reason appears [47] to be related to the fact that the dielectric function (which enters the GW) is calculated using LDA, which gives a semimetallic ground-state (negative bandgap, see Table III) for InN. Thus, the calculated dielectric function is rather different from the real one which should be that of a semiconductor. It is well known that Ge has also a negative LDA bandgap (about -0.1 eV). However, since this bandgap is smaller than that of W-InN and the overlap between the conduction and valence bands is localized in a very small region around the Γ point, this does not seem to affect the application of the LDA-GW method to Ge (see for example Ref. 8). To address this issue in the case of InN two indirect LDA-GW approaches have been adopted in the literature: (i) Bechstedt and Furthmüller [27] have performed pseudopotential LDA-GW calculations with the semicore d electrons included in the core. The reduction in the bandgap due to the inclusion of these semicore electrons as valence is taken into account *a posteriori*: assuming the same value as found by LDA calculations. (ii) In the work of Usuda *et al.* [47], the bandgap has been opened by applying hydrostatic pressure, i.e., by reducing the InN lattice constant. The accuracy of these indirect LDA-GW approaches is difficult

to assess. They lead to LDA-GW bandgaps of ZB-InN of 0.52 eV (Ref. 27) and ~ 0.4 eV (Ref. 47, obtained by subtracting 0.2 eV from the reported result for the W phase), which are smaller than the EXX result, of 0.81 eV.

C. Energetic position of the d bands

our LDA results for E_d obtained using LDA-PP's, see Table III, are significantly higher than the corresponding experimental data, in agreement with previous LDA calculations. This deficiency has been attributed to the incomplete cancellation of the self-interaction [5]. It is therefore tempting to speculate that the EXX calculations, which are self-interaction free, would give improved d band energies. A remarkable finding of the present study is that this is not the case: the EXX results are very close to those of LDA. In GaN the EXX result is only 1 eV lower than the LDA results, while in InN it is about 0.1 eV higher. The LDA-GW approach, on the other hand, is found to lead to a significant downward shift in energy of the d bands in many II-VI and group-III nitrides [11]. However, the GW results for E_d are systematically higher than experiment by about 1 eV.

In order to understand the above unexpected EXX results for E_d let us inspect the LDA and EXX eigenvalues of the isolated Ga, In, and N (pseudo)atoms, shown in Fig. 3. These results are obtained by using the same pseudopotentials and XC functionals as those used for the corresponding bulk calculations, see Sec. II. The important features to note from Fig. 3 are as follows. (i) All the eigenvalues shown are shifted downward in energy due to the removal of the unphysical self-interaction by the EXX approach. (ii) The downward shifts in the eigenvalues of the N $2s$ and $2p$ states are comparable to those of Ga $3d$ states, and larger than that of the In $4d$ states. This explains why in the GaN and InN compounds, the EXX d bands remain roughly speaking at the same energetic position with respect to the N $2s$ and $2p$ derived valence bands as in the LDA. (iii) In the LDA calculations using EXX-PP's only the eigenvalues of the Ga $3d$ and In $4d$ states are appreciably shifted downward in energy, compared to the LDA calculations for all electrons (i.e., using LDA-PPs). It is interesting to note that these shifts (which are of 3.0 and 1.5 eV, respectively) closely match the downward shift of the d bands in the corresponding bulk calculations (see Table III). This leads to values for E_d in a rather good agreement with experiment. Similar results are obtained for some II-VI compounds by Moukara *et al.* [35], who suggested that further improvements might be achieved if the EXX approach is applied to all electrons. The results of the present work show that this is not correct.

D. Valence band-widths

We will focus mainly on (i) the width of the upper three valence bands, which mainly originate from the N $2p$ states, referred to as "upper VBW". (ii) The width of the total valence bands (referred to as "total VBW"), defined as the energy difference between the top of the valence bands and the minimum of the lowest energy valence band which originates from the N $2s$ states. This means that the cation semicore d bands are not considered as part of the main valence bands.

Fig. 1 and Tables II and III show that the upper VBW decreases (by about 0.5 eV) by going from LDA to EXX calculations. The width of the lowest valence band (see Fig. 1a) also decreases, but by a much smaller amount. The reduction of the upper VBW is consistent with previous EXX calculations [8, 21, 22]. This feature can be explained [21] as a direct consequence of the increase in strength of the effective potential seen by the valence electrons, due to the removal of the self-interaction by the EXX approach. The LDA-GW upper VBW's [8, 41] are larger than those of EXX by about 1 eV, for both AlN and GaN. For a discussion about the comparison between the EXX and LDA-GW results see the following subsection.

Fig. 1 and Tables II and III show that the total VBW is weakly affected by going from LDA to EXX calculations. The total VBW is affected through the reduction of the upper and lower VBW's and the difference in the downward shifts in energy of the involved bands, and these two contributions seem to cancel each other to a large extent. Table II show that, unlike the case of the bandgap, quasiparticle corrections have sizable effects on both the upper and total VBW's, in the case of both LDA (i.e., LDA versus LDA+GW results) and EXX (EXX versus EXX+GW results) approaches. The LDA-GW results [8, 41] for the total VBW are appreciably larger than those of EXX. For GaN, both the EXX and GW results deviate significantly from the experimental value for the total VBW. The reason for such bad disagreement is unclear, but experimental uncertainties can't be ruled out.

E. Further discussion

In this subsection we discuss our EXX results in comparison with those of GW, from the point of view of the conceptual difference between the two approaches. Furthermore, we discuss the role of using consistent pseudopotentials (i.e., EXX-PP's) in the EXX calculations, and comment on the discrepancies between the pseudopotential and all-electron EXX results.

We start with the comparison between the EXX and LDA-GW results. These two approaches provide different approximations to the XC self-energy operator. The LDA-GW approach is a many-body technique which leads to approximate quasi-particle or -hole energies, while the EXX method is a single-particle approach.

As shown in this work and Refs. [8, 22] there is a very good agreement between the bandgaps calculated by both methods for wide range of semiconductors. This may suggest that for these systems the XC potential in the EXX approach (including LDA correlation) can be considered as a very good approximation to the LDA-GW self-energy operator, in the optimized effective potential sense [51]. The conduction and upper valence-bands states are highly delocalized states and, thus, the effects of charge density relaxation by the removal (addition) of an electron from (to) these states are expected to be small. This is not the case for the more localized valence and semicore d states, as the ΔSCF calculations show [2, 52]. This explains the good agreement between the EXX and LDA-GW results for the bandgaps, and the appreciable discrepancies between their results for E_d and the valence band widths. Furthermore, this also implies that one should be careful when comparing the calculated EXX (or LDA) binding energies of the semicore d electrons with the experimental photoemission data, since the latter include electronic relaxation effects.

Now we address the question of why the EXX approach yields highly improved bandgaps, especially for the conventional sp semiconductors. Following Städele *et al.* [21], we write the bandgap as

$$E_g = E_g^{KS} + \Delta_{XC} = E_g^{EXX(X)} + \epsilon_{g,c}^{KS} + \Delta_{XC}. \quad (1)$$

Here, $E_g^{EXX(X)}$ is the EXX bandgap obtained without any correlation, and $\epsilon_{g,c}^{KS}$ is the change in the bandgap due to the KS correlation potential. For conventional sp semiconductors it has been shown that $E_g \approx E_g^{EXX(X)}$, and $\epsilon_{g,c}^{KS}$ is quite small at the LDA or GGA levels (~ 0.1 eV). These results have led Städele *et al.* [21] to conclude that Δ_{XC} is quite small, although the corresponding discontinuity in the EXX potential alone is very large, compared to the bandgaps of these systems [21]. On the other hand, the Random-phase approximation (RPA) investigations [19, 53, 54] have shown that the KS bandgaps derived from these GW calculations are very close to those of LDA, for bulk Si and C. This means that RPA $\epsilon_{g,c}^{KS}$ is quite large. Thus, according to these RPA calculations, the EXX approach provide improved bandgaps because of a large cancellation between Δ_{XC} and the errors in the LDA (or GGA) $\epsilon_{g,c}^{KS}$.

The effects of employing consistent pseudopotentials in the EXX calculations (on the calculated bandgaps and valence band-widths) can be easily seen by comparing the EXX or LDA results obtained using both LDA- and EXX-PPs, listed in Tables II and III. The interesting features to note are: (i) if the same set of pseudopotentials (LDA or EXX) is used in both calculations, the band-structure modifications by going from LDA to EXX calculations are almost independent on the employed pseudopotentials. (ii) For the three nitrides considered, these effects are quite small on the above properties, contrary to E_d , expect for the total VBW of InN obtained with the semicore d electrons included as core states. This

can be easily understood from the shifts in the eigenvalues of the pseudoatoms shown in Fig. 3. It should be noted that this is not always the case: the use of EXX-PPs in the LDA calculations leads to an increase in the bandgap of GaAs by about 0.6 eV, and to a correct ordering of the conduction band minima of Ge [21]. (iii) However, the advantages of using consistent pseudopotentials in the EXX calculations of the considered nitrides are clear: the comparison between EXX results obtained using EXX-PPs with experiment is better than those obtained employing LDA-PPs, especially for the the bandgap of GaN and E_d of both GaN and InN.

After the completion of this work, all-electron full-potential EXX results have been reported [55]. These results are considerably different from those of pseudopotential EXX calculations, especially for the bandgaps of *sp* semiconductors and the energetic position of the *d* bands. For the latter the all-electron EXX results are in very good agreement with experiment, contrary to our results (see above and Ref. 24). These discrepancies have been attributed mainly to the core-valence interaction [55]. We strongly believe that such a conclusion is misleading because of two reasons: (i) We have shown (in Sec. III.B) that our pseudopotential EXX results for E_d can be easily explained in terms of the eigenvalues of the corresponding isolated atoms, where core-valence interaction is not an issue. (ii) There are significant differences in the implementation of the EXX scheme in the two approaches (see Refs. 21, 55 for details), which may account for the above discrepancies. However, the reason behind these discrepancies can be clarified by performing pseudopotential EXX calculations with the entire semicore shell included as valence, which is currently under consideration.

IV. CONCLUSIONS

The exact-exchange (EXX) Kohn-Sham density-functional theory is used to calculate the electronic struc-

ture of the zinc-blende (ZB) form of AlN, GaN and InN, with and without including the cation semicore states. The effects of using consistent (i.e., EXX) pseudopotentials in the EXX calculations are also investigated. The changes in the bandgap and energetic position of the shallow *d* bands by going from the ZB to wurtzite (W) forms have been studied, at the LDA level. Our EXX results for AlN and GaN, obtained with the semicore *d* electrons treated as part of the core, are found to be in good agreement with similar previous EXX calculations, GW results and experiment. Treating the semicore *d* electrons as valence leads to a large reduction in the calculated EXX bandgaps, and the results are in excellent agreement with the pseudopotential (when the entire semicore shell is included as valence) and all-electrons GW results. This may indicate that the inclusion of the entire semicore shell as valence is not necessary in the EXX and EXX+GW approaches. Contrary to common belief, the removal of the self-interaction by the EXX approach, does not account for the large discrepancy for the position of the semicore *d* bands between the LDA results and experiment. Most of the opening of the bandgaps of the considered nitrides in the EXX approach is due to its application to the valence electrons, and its application to the core electrons has pronounced effects on the position of the *d* bands. The EXX method gives an appreciable bandgap for InN when the semicore *d* electrons are included as valence, which provides the basis for more accurate GW calculations.

Acknowledgments

we acknowledge stimulating discussions with Patrick Rinke and thank J. A. Majewski and P. Vogl for making their code for generating EXX pseudopotentials available to us. This work has been supported by the Volkswagen-Stiftung/Germany and the Deutsche Forschungsgemeinschaft (Research Group Nitride based quantum dot lasers).

-
- [1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
 - [2] A. R. Williams and U. von Barth, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum Press, New York, 1983), p. 276.
 - [3] Within the LDA, accurate bandgaps as well as semicore *d* band energies may be obtained, instead of from the KS bandstructure, from Slater's transition state method [52, 56] which as such provides (approximately) the LDA *total energy difference* associated with a particular excitation process. Justification and limitations of this approach are discussed e.g. in Ref. [2].
 - [4] See for example, R. W. Godby, M. Schlüter and L. J. Sham, Phys. Rev. B **37**, 10159 (1988).
 - [5] See for example, A. Qteish J. Phys.: Condens. Matter **12**, 5639 (2000), and references therein.
 - [6] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
 - [7] For a recent review see, W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Phys. **54**, 1 (1999).
 - [8] W. G. Aulbur, M. Städele, and A. Görling, Phys. Rev. B **62**, 7121 (2000).
 - [9] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **75**, 3489 (1995).
 - [10] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B **57**, 6485 (1998).
 - [11] T. Kotani and M. van Schilfgaarde, Solid State Comm. **121**, 461 (2002).
 - [12] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).
 - [13] V. Sahni, J. Gruenebaum and J. P. Perdew, Phys. Rev. B **26**, 4371 (1982).
 - [14] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953)
 - [15] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36

- (1976)
- [16] T. Kotani and H. Akai, Phys. Rev. B **50**, 14816 (1994).
- [17] T. Kotani and H. Akai, Phys. Rev. B **52**, 17153 (1995).
- [18] T. Kotani and H. Akai, Phys. Rev. B **54**, 16502 (1996).
- [19] T. Kotani, J. Phys.: Condens. Matter **10**, 9241 (1998).
- [20] M. Städele, J. A. Majewski, P. Vogl, and A. Görling, Phys. Rev. Lett. **79**, 2089 (1997).
- [21] M. Städele, M. Moukara, J. A. Majewski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10031 (1999).
- [22] A. Fleszar, Phys. Rev. B **64**, 245204 (2001).
- [23] R. J. Magyar, A. Fleszar, and E. K. U. Gross, Phys. Rev. B **69**, 045111 (2004).
- [24] P. Rinke, A. Qteish, J. Neugebauer, C. Freysoldt, and M. Scheffler, New Journal of Physics **7**, 126 (2005).
- [25] For a recent review, see S. C. Jain, M. Willander, J. Narayan and R. Van Overstraeten, Appl. Phys. Rev. **87**, 965 (2000).
- [26] C. Stampfl and C. G. Van de Walle, Phys. Rev. B, **59**, 5521 (1999).
- [27] F. Bechstedt and J. Furthmüller, J. Cryst. Growth **246**, 315 (2002).
- [28] J. Wu *et al.*, Appl. Phys. Lett. **80**, 3967 (2002); T. Takashi *et al.*, Appl. Phys. Lett. **81**, 1246 (2002); V. Y. Davydov *et al.*, Phys. Status Solidi (b) **230**, R4 (2002).
- [29] *Intrinsic Properties of Group IV Elements and III-V, II-VI and I-VII compounds*, edited by K. H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. **22**, Pt. a (Springer, Berlin, 1987).
- [30] T. V. Shubina *et al.*, Phys. Rev. Lett. **92**, 117407 (2004).
- [31] F. Bechstedt and J. Furthmüller, O. Ambacher and R. Goldhahn, Phys. Rev. Lett. **93**, 269701 (2004).
- [32] See, www.sfhingx.de.
- [33] *Properties of Group-III Nitrides*, edited by J. H. Edgar, EMIS Data reviews Series (IEE, London, 1994).
- [34] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
- [35] M. Moukara, M. Städele, J. A. Majewski, P. Vogl, and A. Görling, J. Phys.: Condens. Matter **12**, 6783 (2000).
- [36] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
- [37] X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **84**, 8503 (1999).
- [38] M. Fuchs and M. Scheffler, Comput. Phys. Commun. **119**, 67 (1999).
- [39] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [40] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5189 (1976).
- [41] A. Rubio, J. L. Corkill, M. L. Cohen, E. L. Shirley, and S. G. Louie, Phys. Rev. B **48**, 11810 (1993).
- [42] M. Palumbo, L. Reining, R. W. Godby, C. M. Bertoni, and N. Börnsen, Europhys. Lett. **26**, 607 (1994).
- [43] J. Li, K. B. Nam, M. L. Nakarmi, J. Y. Lin, and H. X. Jian, Appl. Phys. Lett. **81**, 3365 (2002).
- [44] See for example, S.-H. Wei and Zunger, Phys. Rev. B **37**, 8958 (1988).
- [45] T. Lei *et al.*, J. Appl. Phys. **71**, 4933 (1992); T. Lei *et al.*, Appl. Phys. Lett. **59**, 944 (1992); C. R. Eddy, T. Moustakas and J. Scanlon, J. Appl. Phys. **73**, 448 (1993).
- [46] M. J. Paisly *et al.*, J. Vac. Sci. Technol. A **7**, 701 (1989); Z. Sitar *et al.*, J. Mater. Sci. Lett. **11**, 261 (1992).
- [47] M. Usuda, N. Hamada, K. Shiraishi, and A. Oshiyama, Jpn. J. Appl. Phys. **43**, L407 (2004).
- [48] S. A. Ding *et al.*, J. Vac. Sci. Technol. A **14**, 819 (1996).
- [49] Q. X. Guo, M. Nishio, H. Ogawa, A. Wakahara, A. Yoshida, Phys. Rev. B **58**, 15304 (1998).
- [50] Y. Bu, L. Ma, M. C. Lin, J. Vac. Sci. Technol. A **11**, 2931 (1993).
- [51] M. E. Casida, Phys. Rev. A **51**, 2005 (1995).
- [52] F. Aryasetiawan and O. Gunnarsson, Phys. Rev. B **54**, 17564 (1996).
- [53] R. Godby, M. Schlüter and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986); Phys. Rev. B **37**, 10159 (1988).
- [54] Y. M. Niquet and X. Gonze, Phys. Rev. B **70**, 245115 (2004).
- [55] S. Sharma, J. K. Dewhurst and C. Ambrosch-Draxl, arXiv:cond-mat/0501353 v1 (2005).
- [56] D.A. Liberman, Phys. Rev. B **62**, 6851 (2000).

Table II: Selected EXX and LDA electronic structure properties of the ZB phase of the nitrides considered, obtained with the semicore d electrons treated as core states. All tabulated quantities are in eV.

	LDA	EXX	LDA-GW	EXX-GW
AlN				
E_g^I	4.27 ^a , 4.03 ^b 4.20 ^{c,d,e}	5.99 ^a 5.76 ^b 5.66 ^{c,e}	6.0 ^{c,d}	5.98 ^c
E_g^X	3.27 ^a 3.16 ^b 3.20 ^{c,d} 3.24 ^e	5.18 ^a 5.08 ^b 5.03 ^{c,e}	4.9 ^{c,d}	4.89 ^c
upper VBW	5.91 ^a 5.96 ^b 6.0 ^{c,d}	5.27 ^a 5.33 ^b 5.24 ^c	6.7 ^{c,d}	6.29 ^c
total VBW	14.81 ^a 15.16 ^b 15.10 ^{c,d} 14.74 ^e	14.59 ^a 14.95 ^b 14.85 ^c 14.86 ^e	17.00 ^{c,d}	15.32 ^c
GaN				
E_g^I	2.20 ^a 1.97 ^b 2.00 ^c 2.10 ^d 1.9 ^e 1.88 ^g	3.68 ^a 3.52 ^b 3.49 ^{c,e}	3.59 ^f 3.10 ^{c,d} 2.76 ^g	3.44 ^c
upper VBW	6.85 ^a 6.82 ^b 6.8 ^c 7.4 ^d	6.30 ^a 6.23 ^b 6.23 ^c	6.88 ^f 7.6 ^c 7.8 ^d	7.17 ^c
total VBW	15.85 ^a 15.82 ^b 15.50 ^c 16.30 ^d 15.75 ^e	15.35 ^a 15.63 ^b 15.64 ^{c,e}	16.70 ^c 17.80 ^d	16.05 ^c
InN				
E_g^I	0.17 ^a -0.13 ^b	1.89 ^a 1.49 ^b	1.31 ^h	
upper VBW	5.52 ^a 5.67 ^b	4.88 ^a 5.09 ^b		
total VBW	13.98 ^a 14.50 ^b	13.82 ^a 14.37 ^b		

^aPresent work, using LDA pseudopotentials.

^bPresent work, using EXX pseudopotentials.

^cRef. [8]; ^dRef. [41]; ^eRef. [21]; ^fRef. [10];

^gRef. [42]; ^hRef. [27].

Table III: Selected EXX and LDA electronic structure properties of the ZB phase of GaN and InN, with the semicore d electrons treated as valence states. For comparison some results for the W phase are shown, denoted by the superscript w. All tabulated quantities are in eV.

	LDA	EXX	LDA-GW	Expt.
GaN				
E_g^I	1.65 ^a 1.66 ^b	2.67 ^a 2.88 ^b	2.88 ^c 3.03 ^{w,g}	3.2 ^d 3.3 ^e
E_d	-13.8 ^a -16.9 ^b -13.8 ^{w,f}	-12.2 ^a -14.8 ^b	-15.7 ^c -16.4 ^{w,g}	-17.7 ^h
upper VBW	7.32 ^a 7.03 ^b	7.03 ^a 6.63 ^b	7.33 ^c	
total VBW	16.00 ^a 16.04 ^b	16.04 ^a 16.00 ^b		14.2 ^d
InN				
E_g^I	-0.43 ^a -0.39 ^b -0.36 ⁱ	0.61 ^a 0.81 ^b	~ 0.0 ^{w,j,g}	0.7-1.0 ^{w,j} 1.9 ^{w,k}
E_d	-13.5 ^{a,i} -14.9 ^b -13 ^{w,f}	-12.2 ^a -13.4 ^b		-14.9 ^{w,l} -16.7 ^{w,m}
upper VBW	6.10 ^a 5.85 ^b	5.82 ^a 5.48 ^b		
total VBW	14.60 ^a 14.71 ^b	14.67 ^a 14.73 ^b		

^aPresent work, using LDA pseudopotentials.

^bPresent work, using EXX pseudopotentials.

^cRef. [10]; ^dRef. [45]; ^eRef. [46]; ^fRef. [47]; ^gRef. [11].

^hRef. [48]; ⁱRef. [27]; ^jRef. [28]; ^kRef. [29]; ^lRef. [49].

^mRef. [50].

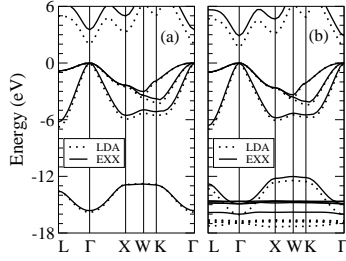


FIG. 1: Band structure of GaN calculated without (a) and with (b) treating the Ga 3d electrons as valence states. The EXX pseudopotentials have been used in both LDA and EXX calculations.

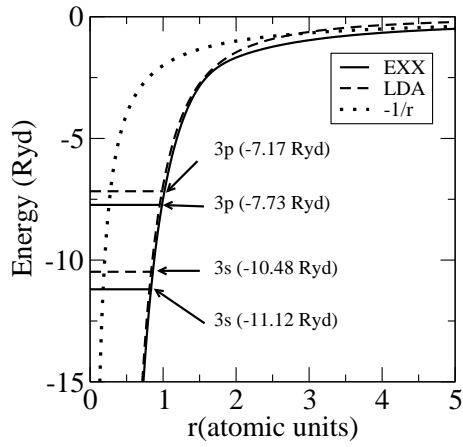


FIG. 2: The atomic EXX and LDA all-electrons potentials of Ga. The right asymptotic $-1/r$ behavior of the EXX potential should be noted. The EXX and LDA eigenvalues of the Ga 3s and 3p are shown.

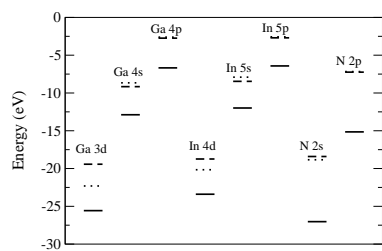


FIG. 3: Eigenvalues of the Ga, In and N (pseudo)atoms. Dashed lines: LDA calculations using LDA-PP's. Dotted lines: LDA calculations using EXX-PP's. Solid lines: EXX calculations using EXX-PP's.