

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

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The band structure of the zinc-blende phase of AlN, GaN, and 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 band gaps 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 band gaps 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.

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I. INTRODUCTION

The modern computational methods applied to condensed matter systems are based mainly on Kohn-Sham¹ 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 band structures of solids display several limitations of this approach. The most serious shortcoming is the so-called *band gap problem*: the LDA band gaps 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 band gap, it is well known⁴ 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 band gaps as well as for binding energies of semicore states have been attributed⁵ 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-self-consistent GW approach based on LDA results (LDA-GW) is found to reproduce very well the experimental band gaps of standard sp semiconductors.⁸ For group-III nitrides and II-VI compounds, the pseudopotential^{9,10} and all-electron¹¹ LDA-GW methods are found to give good band gaps (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-interaction⁶ of the electron with its own charge density is eliminated. In the exchange-only KS-DFT formalism, the EXX potential is equivalent¹³ 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 Akai.¹⁶⁻¹⁹ This approximate EXX approach is found to highly improve the calculated band gaps of several semiconductors¹⁸ 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 give²¹ band-gap 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 solids²³ the pseudopotential EXX approach gives band gaps that 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-self-consistent GW (EXX-GW) calculations.²⁴

The purpose of this work is of threefold. (i) To perform pseudopotential EXX calculations of the electronic band-structure of the metastable²⁵ zinc-blende (ZB) phase of GaN, AlN, and InN. In these calculations, the Ga $3d$ and In $4d$ 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 band structure. To do that, an additional set of EXX band structures 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 band structure calculations employing LDA-PPs, and LDA calculations using both LDA- and EXX-PPs.

It is worth noting that the band gap of W-InN is still a matter of debate. The band gap of the recently grown single crystalline hexagonal InN epilayers is found²⁸ to be 0.7–1.0 eV, which is much smaller than the previous and widely accepted²⁹ experimental value of 1.9 eV. However, the smaller band gap is far from being well established.^{30,31} A very recent experimental study suggested³⁰ that this small band gap 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 band gap of 1.4 eV has been given in Ref. 30. Therefore, accurate theoretical studies of the band gap 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 formalism²¹ in the SPH-INGX code,³² which employs plane-wave basis sets and *ab initio* pseudopotentials. As noted above, EXX band-structure 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, respectively³³). 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 band gaps and to avoid shifts in the band gaps due to deformation potentials.

Norm-conserving scalar-relativistic EXX- and LDA-PPs of the involved elements are generated by using the Troullier-Martins optimization method.³⁴ The EXX-PPs are constructed as described in Ref. 35. The generated pseudopotentials are then transformed to the separable Kleinman-Bylander form.³⁶ The ground state electronic configuration is assumed for all the atoms considered. Following Ref. 26,

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 $4d$ and In $5d$ 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	$l=0$

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-Alder³⁹ exchange-correlation data as parametrized 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-Pack⁴⁰ mesh. The KS wave functions 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_0 (see Ref. 21), plane waves up to energy cutoffs 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_0 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_0 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 band structure when going from the ZB to W phases. The most prominent band-structure 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 band structures of ZB-GaN.

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

We focus here mainly on the differences in the band gap 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 band gap 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 band-gap 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 concentrate mainly 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. Band gaps 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 band gap (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. 1(a)]. This figure shows that the energetic position and dispersion of the valence band 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 band gap from 1.97 eV (LDA calculation

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

^aPresent work, using LDA pseudopotentials.

^bReference 8.

^cReference 41.

^dPresent work, using EXX pseudopotentials.

^eReference 21.

^fReference 42.

^gReference 10.

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

^aPresent work, using LDA pseudopotentials.

^bReference 10.

^cReference 45.

^dPresent work, using EXX pseudopotentials.

^eReference 11.

^fReference 46.

^gReference 48.

^hReference 47.

ⁱReference 28.

^jReference 29.

^kReference 27.

^lReference 49.

^mReference 50.

with EXX-PPs, see Table II) to 3.52 eV. This EXX band gap is in excellent agreement with previous EXX calculations,^{8,21} LDA-GW calculations¹⁰ (with Ga 3*d* 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. 1(b) the EXX and LDA band structures 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 band gap closes by 0.64 eV, leading to a band gap of 2.88 eV. This reduction can be easily understood as a consequence of the symmetry allowed anion p -cation d repulsion,⁴⁴ which

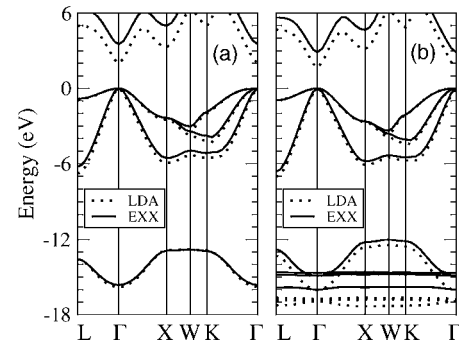


FIG. 1. Band structure of GaN calculated without (a) and with (b) treating the Ga 3*d* electrons as valence states. The EXX pseudopotentials have been used in both LDA and EXX calculations.

pushes the upper valence band states up in energy, leading to a smaller band gap. This EXX band gap is in remarkable agreement with the pseudopotential LDA-GW result (2.88 eV) of Rohlfling *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 potential³⁵ 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 approaches underestimate the band gap 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) gives²⁴ band gaps that are in very good agreement with experiment for GaN and some II-VI compounds.

Concerning InN, the experimental band gap (available only for W-InN) is still controversial, as noted above. Our results listed in Tables II and III for InN show a behavior

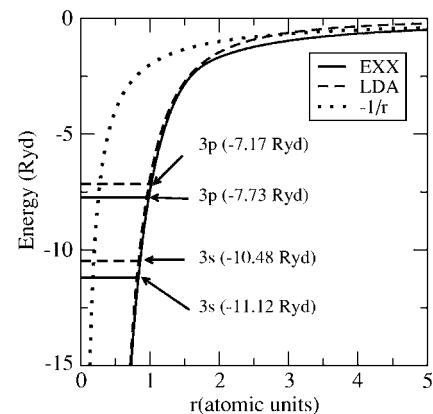


FIG. 2. The atomic EXX and LDA all-electron potentials of Ga. The right asymptotic $-1/r$ behavior of the EXX potential should be noted. The EXX and LDA eigenvalues of the Ga 3*s* and 3*p* are shown.

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 band gap to ~ 0.8 eV. Assuming a similar error as that of the band gap of GaN (of about 0.4 eV) and taking into consideration the difference in the band gap of InN when going from ZB to W phases (see Sec. III A), a direct fundamental band gap 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 band gaps 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 band gap of InN when including the semicore (In $4d$) states is significantly larger than in all-electron LDA-GW calculations,^{11,47} which give a band gap of ~ 0 eV, for the W phase. This is in contrast to the case of GaN wherein both approaches give almost identical results. The reason appears⁴⁷ 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 band gap, 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 band gap (about -0.1 eV). However, since this band gap 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 Furthmüller²⁷ have performed pseudopotential LDA-GW calculations with the semicore d -electrons included in the core. The reduction in the band gap 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 band gap 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 band gaps 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-PPs (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

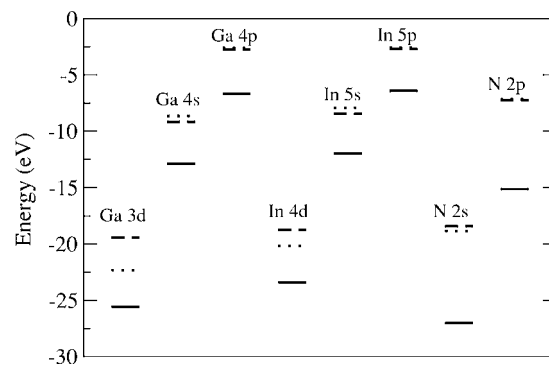


FIG. 3. Eigenvalues of the Ga, In, and N (pseudo)atoms. Dashed lines: LDA calculations using LDA-PPs. Dotted lines: LDA calculations using EXX-PPs. Solid lines: EXX calculations using EXX-PPs.

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-PPs 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 widths of the upper three valence bands, which originate mainly 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.

Figure 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. 1(a)] 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 explained²¹ 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 VBWs (see Refs. 8 and 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.

Figure 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 VBWs 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 shows that, unlike the case of the band gap, 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 cannot 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-PPs) 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 that leads to approximate quasiparticle or -hole energies, while the EXX method is a single-particle approach. As shown in this work and Refs. 8 and 22), there is a very good agreement between the band gaps 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 band 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 Slater transition state calculations show.^{2,52} This explains the good agreement between the EXX and LDA-GW results for the band gaps, 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 as to why the EXX approach yields highly improved band gaps, especially for the conventional sp semiconductors. Following Städele *et al.*,²¹ we write the band gap as

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

Here, $E_g^{\text{EXX(X)}}$ is the EXX band gap obtained without any correlation, and $\epsilon_{g,c}^{\text{KS}}$ is the change in the band gap due to the KS correlation potential. For conventional sp semiconductors it has been shown that $E_g \approx E_g^{\text{EXX(X)}}$, and $\epsilon_{g,c}^{\text{KS}}$ 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 band gaps of these systems.²¹ On the other hand, the random-phase approximation (RPA) investigations^{19,53,54} have shown that the KS band gaps derived from these GW calculations are very close to those of LDA, for bulk Si and C. This means that RPA $\epsilon_{g,c}^{\text{KS}}$ is quite large. Thus, according to these RPA calculations, the EXX approach provide improved band gaps because of a large cancellation between Δ_{XC} and the errors in the LDA (or GGA) $\epsilon_{g,c}^{\text{KS}}$.

The effects of employing consistent pseudopotentials in the EXX calculations (on the calculated band gaps 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 as follows. (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 of the employed pseudopotentials. (ii) For the three nitrides considered, these effects are quite small on the above properties, contrary to E_d , except 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 band gap 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 band gap 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 band gaps of sp semiconduc-

tors and the energetic position of the d -bands. For the latter the ell-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 for 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, and (ii) there are significant differences in the implementation of the EXX scheme in the two approaches (see Refs. 21 and 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 structure 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 band gap 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 band gaps, and the results are in excellent agreement with the pseudopotential (when the entire semicore shell is included as valence) and all-electron 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 band gaps 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 band gap for InN when the semicore d -electrons are included as valence, which provides the basis for more accurate GW calculations.

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