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An *ab initio* pseudopotential calculation of ground-state and excited-state properties of gallium nitride

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Abstract. In this work, the electronic, ground-state and vibrational properties of both α -GaN (i.e. wurtzite structure) and the recently fabricated β -GaN (i.e. zincblende structure) have been studied using the *ab initio* pseudopotential method within the local density approximation and a simple quasi-particle scheme. The calculated equilibrium lattice constants, bulk moduli, the pressure derivatives of the bulk moduli, and the A_1 TO(Γ) phonon frequency are in good agreement with available experimental and other recent *ab initio* theoretical results. The self-energy band gap corrections are found to be highly k -dependent. The calculated fundamental band gap is direct in both cases and for the experimental lattice constant is calculated to be 3.36 eV in β -GaN and 3.48 eV in α -GaN, in excellent agreement with experiment.

1. Introduction

Although members of the III–V family of semiconductors, gallium nitride and its related compounds aluminium nitride and cubic boron nitride have a number of remarkable properties which set them apart from other III–V compounds and make them particularly worthy of study. It has been noted that as a result of the short bonds characteristic of the nitrides these materials share many properties with diamond, notably exceptional hardness, high lattice thermal conductivity and a wide band gap [1]. GaN is proving to be particularly fascinating, largely because of the recent fabrication of a new structural phase of this material. The most usual form is the wurtzite structure (α -GaN) but in the last few years molecular-beam epitaxy (MBE) techniques have allowed films of zincblende structure GaN (β -GaN) to be grown on the β -SiC(100) surface [2], the Si(100) surface [3] and the GaAs(100) surface [4]. The experimental lattice constant of β -GaN is around 4.49 Å [3] while the experimentally determined direct band gap energy has a rather large scatter, lying between 3.2 eV [3] and 3.87 eV [4]. In the wurtzite structure, the c/a ratio is close to the ideal value of 1.633 with $a = 3.19$ Å [5] and the direct band gap energy is in the range 3.41–3.46 eV [1]. Both are thought to be direct gap materials. The wide band gap of α -GaN has led to interest in its potential use for the manufacture of optoelectronic devices operating in the blue-green region of the spectrum.

Until recently there have been relatively few theoretical studies of the electronic and structural properties of β -GaN [6–17]. The large scatter in the experimental results for the band gap in the zincblende phase has made it difficult to assess the accuracy of various different approaches. A few research groups have studied both phases [7–11, 14–17], but only a small number have attempted to include quasiparticle (many-body) corrections to their band gaps [11–14]. Only two groups, to our knowledge, have attempted quasiparticle

corrected calculations for both materials [11, 14] and it is a measure of the existing lack of consensus that their calculated band gaps in both phases are in substantial disagreement with each other. Indeed the confusion is not confined to quasiparticle corrected results; there is not even a consensus about the single-particle band gaps. Theoretical single-particle results for the direct gap in the zincblende phase range from 2.0 eV [12] to 2.65 eV [10], while in the wurtzite phase figures as different as 2.04 eV [11] and 2.76 eV [10] have been reported. Furthermore, the ground-state properties of the zincblende phase have been found to vary significantly depending on the choice between two reasonable pseudopotentials [10]. Clearly GaN is proving to be a particularly difficult material to investigate and there is a need for a comprehensive study of the ground-state and excited-state properties of both phases including many-body effects on the band gaps.

In this paper we present the results of systematic *ab initio* pseudopotential calculations on α -GaN and β -GaN, performed in the plane wave basis. For both phases, ground-state properties have been calculated using the local density approximation, and quasiparticle energies have been calculated by use of two tight-binding-based models [18, 19] within the so called GW approximation [20]. In section 2 we describe the methods we have used in calculating these properties and the results are described in section 3. It is hoped that our well converged results will be helpful in assessing the success of the plane wave pseudopotential approach for the structural and electronic properties of GaN.

2. Calculation

We have performed density functional [21] (DF) calculations on α -GaN and β -GaN within the local density approximation (LDA) using the Ceperley–Alder correlation form [22]. The interaction of valence electrons with the ion cores is accounted for by the use of *ab initio*, norm-conserving, pseudopotentials and the single-particle wavefunctions are expanded in a basis set of plane waves. There are two major difficulties in such a calculation on GaN. Firstly, the 3d electrons of Ga lie at an energy close to the nitrogen 2s level, and hence close to the valence bands of GaN. Strictly speaking these d electrons ought to be considered as valence electrons, because they may be hybridized with the p-like valence electrons. Recently it has been suggested that the error induced by not accounting for the effects of the Ga 3d electrons in the structural and electronic properties of GaN may be quite large [12]. However, a more recent study suggests [14] that the extent to which this really is true is an open question. In the present work, therefore, we have considered the Ga 3d electrons as inert core electrons.

The second problem is common to all nitrogen compounds. Compounds containing the elements C, N and O are notoriously difficult to deal with in pseudopotential calculations because these elements lack p-like core electrons. In other compounds, the p-like valence states orthogonalize to the p-like core electrons and thus occupy regions further from the core than they otherwise would. In C, N and O no such mechanism operates and the valence electrons are thus unusually close to the core region and experience an unusually deep and sharp pseudopotential. The choice of pseudopotential can be critical in such compounds. Even with the smoothest pseudopotentials we must still be prepared to use a much higher cut-off for these compounds than is usual.

In order to check this issue, we have performed convergence tests on both the total energy and the direct band gap of the zincblende phase using the Bachelet–Hamann–Schlüter [23] (BHS) pseudopotential for Ga and both the BHS and the much smoother Troullier–Martins [24] (TM) pseudopotentials for N. The TM ionic s and p pseudopotentials (only these non-localities were used in our calculation) for N were generated with core radii $r_s = r_p =$

1.5 a.u.. These are shown in figure 1 in both real space and Fourier space. Also shown for comparison are the BHS s, p and d pseudopotentials (all these were used in our calculation) for N. The TM pseudopotentials differ from the BHS potentials in two important respects; they are less 'deep' and satisfy the condition $V_1''(0) = 0$. The second aspect, meaning zero curvature of the potential at the origin, provides the criterion for the smoothness of the TM potentials. Furthermore, the amplitudes of the Fourier transforms of both the s and p pseudopotentials show a fast convergence rate in reciprocal space.

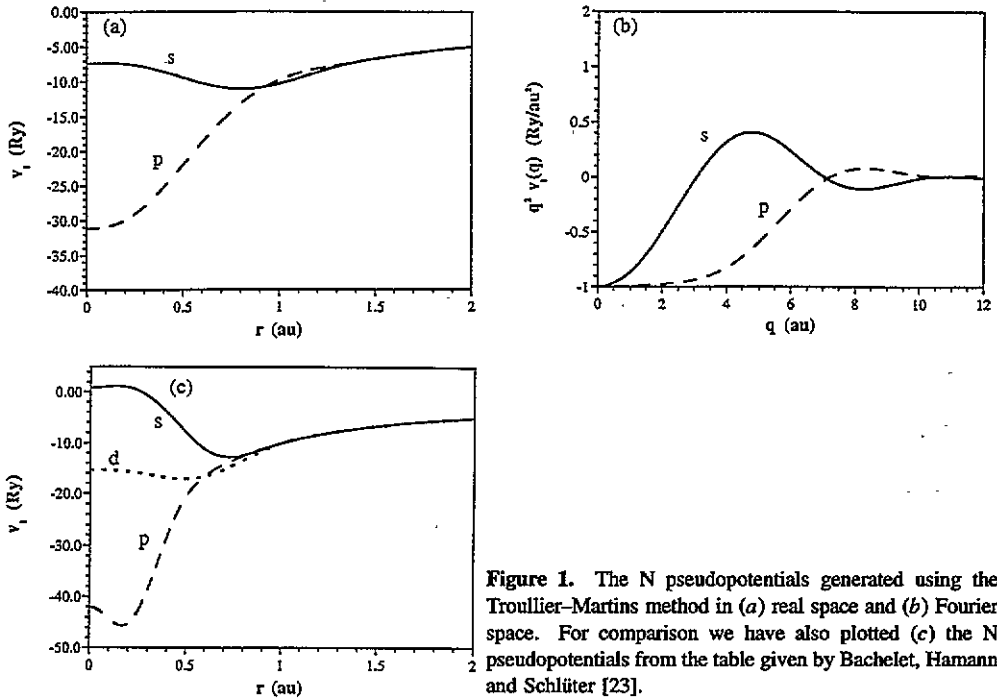


Figure 1. The N pseudopotentials generated using the Troullier–Martins method in (a) real space and (b) Fourier space. For comparison we have also plotted (c) the N pseudopotentials from the table given by Bachelet, Hamann and Schlüter [23].

In figure 2 we show the convergence of the calculated total energy and the direct band gap at Γ in the zincblende structure (β -GaN) using two special k -points [25] for the Brillouin zone summation. It is clear that the total energy based on the BHS potentials shows a poor convergence at least up to 100 Ryd kinetic energy cut-off. The same applies to the band gap. On the other hand, for the TM potentials, both the total energy and the band gap have reached a well converged value for 70 Ryd. We have noted that these converged results are reproduced by using 150 Ryd cut-off with the BHS potentials. We also note in passing that a similar calculation by Rubio *et al* [14] claims convergence at only 40 Ryd using the Troullier–Martins pseudopotential. We find that our results are still poorly converged at such a cut-off and suggest that 60 Ryd is really the absolute minimum acceptable cut-off for this pseudopotential.

We have also performed convergence tests on the total energy and the band gap, for both phases of GaN, with respect to the number of special k -points for Brillouin zone summation. In each case we have used a sample lattice constant (close to the eventual theoretical lattice constant). For the zincblende phase we made calculations with one (Baldereschi point [26]), two (Chadi–Cohen points [25]) and ten (Chadi–Cohen [25]) special k -points, and found that the band structure with the two points scheme was well converged (see table 1). However, the total energy values for two and ten points differed by about 18 meV per atom. For

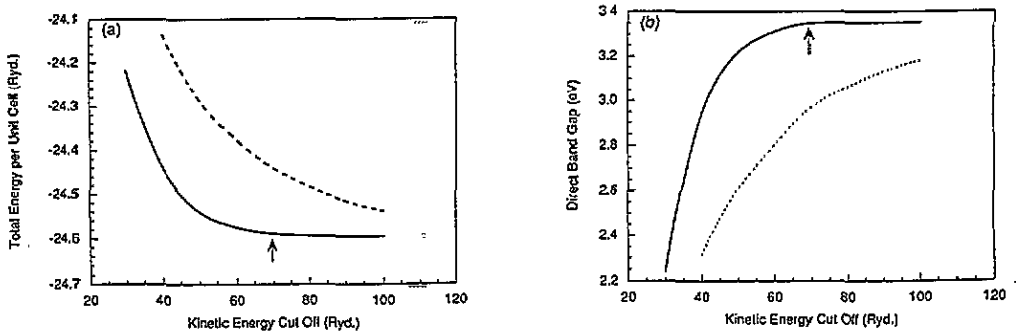


Figure 2. (a) Total energies (in Ryd) per Ga-N unit and (b) direct LDA band gaps (in eV) for the zincblende structure at a range of kinetic energy cut-offs using Troullier-Martins (full-line) and Bachelet-Hamann-Schlüter (dashed line) pseudopotentials for the nitrogen component. The arrow marks the cut-off used in all subsequent calculations.

the wurtzite structure we made calculations with two, six and nine independent special k -points which were obtained using the Monkhorst and Pack scheme [27], generated from meshes $2 \times 2 \times 2$, $4 \times 4 \times 2$ and $4 \times 4 \times 4$ respectively in reciprocal space. As seen from table 1, the band structure results are well converged with the choice of two points. Once again, however, the total energy results are not fully converged unless we take nine special k -points. In the light of these observations we suggest that for any detailed energetic comparison between the two phases at least ten k -points for the zincblende structure and nine for the wurtzite structure must be used. Since our aim was not to make such a detailed comparison of relative stabilities, we studied structural properties using 2 special k -points for both phases while 2 and 10 points were used in our band structure calculations for α - and β -GaN respectively.

Table 1. Convergence of total energy and band gap with increasing number of special k -points in the irreducible part of the Brillouin zone for α -GaN (at lattice constant 3.0 Å) and β -GaN (lattice constant 4.3 Å).

Number of k -points	Total energy per unit cell (Ryd)	Direct band gap (eV)
Wurtzite (α -GaN)		
2	-49.345 57	4.02
6	-49.279 91	3.96
9	-49.279 75	3.95
Zincblende (β -GaN)		
1	-24.616 51	3.42
2	-24.587 60	3.35
10	-24.585 04	3.35

It is well known that although the density functional theory within the LDA provides very good results for ground-state properties, it fails to reproduce accurately the band structures of semiconductors and insulators by systematically underestimating band gaps, often by several electronvolts [28, 29]. Many-body calculations involving self-energy techniques are capable of overcoming this problem [30–32] but they are, in general, rather complicated in comparison with DF calculations. A number of attempts have been made to provide

simple, easy-to-use corrections to LDA results based upon model calculations of the self-energy. Two particularly simple schemes are those of Bechstedt and Del Sole [19] and of Sterne and Inkson [18, 33, 34]. Both of these schemes are based upon a calculation of the self-energy of a model tight-binding system within the GW approximation [20].

The Bechstedt–Del Sole method is easier to apply since it takes the form of a constant gap correction Δ across the entire Brillouin zone which may be calculated very simply without the use of a computer. The gap correction in this scheme is given by [19]

$$\Delta = \frac{e^2 q_{TF}}{\epsilon_0(1 + 7.62x)} \tag{1}$$

where $x = q_{TF}[(1 - \alpha_p)r_A + (1 + \alpha_p)r_B]/2$, $r_H = a/4\pi\beta_H$, q_{TF} is the Thomas–Fermi wave number, α_p is the polarizability and $\beta_A = 1.6$, $\beta_B = 1.8$ for III–V materials.

In deriving their expression Bechstedt and Del Sole explicitly neglected dynamic screening and local field effects. In effect, the Bechstedt–Del Sole correction is a variation on the static COHSEX (coulomb hole plus screened exchange) approximation [35], excluding local fields. The neglect of local fields and dynamic screening offset each other somewhat. Additionally, since their gap correction is derived from the difference between the self-energies of the inhomogeneous and homogeneous electron gases within the same approximation, some further cancellation of errors may occur. Consequently the method has proved to be reasonably reliable in many semiconductors.

The Sterne–Inkson approach provides a pair of local potentials (one each for the valence and conduction bands) to be used in place of the LDA potential and requires a computer to evaluate the correction accurately, although the computational cost is not very high. The exchange–correlation potentials for valence and conduction bands are [18, 34]

$$V_{XC}^v(\mathbf{r}) = -e^2 \rho^{1/3}(\mathbf{r}) \left(\frac{3}{\pi} \right)^{1/3} - \frac{C}{2} \left(\frac{\epsilon_0 - 1}{\epsilon_0 + \sqrt{\epsilon_0}} \right) \tag{2}$$

$$V_{XC}^c(\mathbf{r}) = -e^2 \rho^{1/3}(\mathbf{r}) \left(\frac{3}{\pi} \right)^{1/3} \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 1} \right) - \frac{C}{2} \left(\frac{\epsilon_0 - 1}{\epsilon_0 - \sqrt{\epsilon_0}} \right) \tag{3}$$

where $\rho(\mathbf{r})$ is the electron density calculated within the LDA, ϵ_0 is the experimental static dielectric constant and C is a material dependent on-site exchange term.

$$C = \int d^3r d^3r' \phi_v^c(\mathbf{r} - \mathbf{R}) \phi_v^v(\mathbf{r} - \mathbf{R}) v(\mathbf{r} - \mathbf{r}') \phi_v^c(\mathbf{r}' - \mathbf{R}) \phi_v^v(\mathbf{r}' - \mathbf{R}). \tag{4}$$

The entity $\phi_v^{v/c}(\mathbf{r} - \mathbf{R})$ is a Wannier function for the valence or conduction band in the v th bond at the R th lattice site and $v(\mathbf{r} - \mathbf{r}')$ is the Coulomb interaction between electrons at \mathbf{r} and \mathbf{r}' . In [18] we estimated the value of C by re-writing the Wannier functions in terms of Slater atomic orbitals $\xi_{a,b}(\mathbf{r})$ from the two atoms, a and b , between which the bond v lies. The expression we found was

$$C = \frac{1}{(1 + f_c^2)^2} \left\{ I_{abab} + f_c^2 [I_{aaaa} + I_{bbbb} - 2I_{aabb} - 2I_{abab}] + f_c^4 I_{abab} \right\} \tag{5}$$

where the integrals I_{wxyz} were defined as

$$I_{wxyz} = \int d^3r d^3r' \xi_w(\mathbf{r}) \xi_x(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \xi_y(\mathbf{r}') \xi_z(\mathbf{r}') \tag{6}$$

and f_c , the fractional covalency, allowed us to take some account of the degree of ionicity in the bond. We calculated the values of these integrals for diamond using the analytical methods of [36] and [37], taking the effective nuclear charge to be $Z_{\text{EFF}} = 3.5$. This is lower than the actual nuclear charge because of screening by the core electrons. The calculated integrals in diamond (bond length 1.54 Å) are

$$\begin{aligned} I_{\text{aaaa}} &= I_{\text{bbbb}} = 18.63 \text{ eV} \\ I_{\text{aabb}} &= 10.76 \text{ eV} \\ I_{\text{abab}} &= 5.12 \text{ eV} \end{aligned} \tag{7}$$

This technique cannot easily be extended to materials beyond the first row of the periodic table, or to those containing two different atomic species. For such materials we estimate the integrals according to a set of simple scaling rules. The underlying concept is to identify the integrals I_{aaaa} and I_{bbbb} with the anion and cation respectively and consider the mixed integrals I_{aabb} and I_{abab} as covalent contributions. In order to account for size effects we then scale the ionic integrals inversely with the square of the ionic radii and the covalent integrals inversely with the square of the covalent bond length. Additionally we consider the effect of different choices for the effective nuclear charge for each of these integrals. Typically for the ionic integrals one might choose the effective nuclear charge to be 2.5 for a group III element, 3.5 for group IV and 4.5 for group V. A choice of 3.5 for Z_{EFF} would be reasonable for the covalent integrals of III–V or II–VI compounds. Fortunately the integrals I_{aaaa} , I_{bbbb} and I_{aabb} are linear in Z_{EFF} and so we can easily scale from the diamond results, but the integral I_{abab} must be recalculated for each different choice of Z_{EFF} . In [18] we have shown that this procedure leads to quasiparticle band structures in good agreement with experiment for a range of semiconductors. In the case of GaN we choose Z_{EFF} to be 2.5 for the Ga integral but we have tried various values between 4.75 and 5.0 for the N integral because the relative lack of core electrons means that there is likely to be less screening in N than in other group V materials. Similarly we have tried various figures between 3.75 and 4.0 for the covalent integrals for the same reason. In this manner we obtained a number of estimates for \mathcal{C} depending on the precise choice of Z_{EFF} for the various integrals. We believe that a good average would be $\mathcal{C} = 4.0$ eV, with an uncertainty of ± 0.2 eV. This introduces an uncertainty of less than ± 0.1 eV into our self energy corrections.

The compensation for the increased complexity in the Sterne–Inkson approach is that this method includes dynamic and local field effects ignored in the Bechstedt–Del Sole correction and also introduces a wavevector dependence into the gap correction. We have applied both methods to the results of our pseudopotential calculation in order to obtain the quasiparticle band structure of both phases of GaN in addition to ground-state properties such as bulk modulus and lattice constant.

3. Results

3.1. Ground-state properties

Ground state properties of β -GaN were calculated within the LDA using the Ceperley–Alder correlation scheme [22] with 2 special k -points at the energy cutoff of 70 Ryd. As stated in section 2, Bachelet–Hamann–Schlüter [23] and Troullier–Martins [24] pseudopotentials were used for the Ga and N components respectively. Total energy was calculated for a selection

of lattice constants from 3.0 Å to 5.0 Å. By fitting the total energy versus volume data to the non-linear Murnaghan equation of state [38] curve we have determined the theoretical lattice constant (i.e. the lattice constant at which the total energy has its minimum) to be 4.30 Å. From this fit we also calculated the value of the bulk modulus to be 2.51 Mbar and its pressure derivative to be 2.76. Our well converged pseudopotential results are at some variance with all-electron and other (less converged) pseudopotential calculations. For comparison, Lu, Zhang and Xie [11] using the LMTO/ASA method obtained a value of 4.40 Å for the lattice constant and 3.09 Mbar for the bulk modulus, while Fiorentini *et al* [12] performed a full-potential LMTO (FP-LMTO) calculation and obtained quite different values of 4.47 Å for the lattice constant and 1.98 Mbar for the bulk modulus. Muñoz and Kunc [7], whilst primarily interested in the high pressure phases of GaN, have also given some zero pressure results of their pseudopotential density functional calculations. They found the equilibrium lattice constant of β -GaN to be 4.47 Å and the bulk modulus and its pressure derivative to be 1.79 Mbar and 3.93 respectively.

Our results compare particularly well with those from two other similar *ab initio* pseudopotential calculations. Min *et al* [8] used a mixed basis set [39] and employed non-linear core corrections (NLCC) to account for errors caused by freezing the d states into the core. Their results were 4.30 Å and 2.4 Mbar for the lattice constant and bulk modulus respectively. Palummo *et al* [10] performed calculations with no NLCC using Stumpf, Gonze and Scheffler pseudopotentials [40]. They included only s and p non-localities (as we do in this work) for the nitrogen pseudopotential and used two special *k*-points for the zincblende structure. However, their results were calculated using a cut-off of 100 Ryd. They calculated the lattice constant and bulk modulus to be 4.45 Å and 1.76 Mbar. However, when they used the BHS [23] pseudopotentials including s, p and d non-localities for both Ga and N, they got results very similar to our own values and those of Min *et al*. We trust that the work of Min *et al* [8] presents well converged results on account of the use of the mixed basis set. The fact that our results (obtained without NLCC) agree so well with those of Min *et al* [8] (who did use NLCC) suggests that non-linear core corrections have only a fairly small effect on the structural properties of GaN. At any rate the effect seems to be far less than the variation seen by Palummo *et al* when using two different nitrogen pseudopotentials.

Table 2. Ground state properties of β -GaN (calculated at 70 Ryd cut-off).

	Present work	[7]	[8]	[9]	[10]	[11]	[12]	Expt ^a
a_0 (Å)	4.30	4.47	4.30	4.42	4.45	4.40	4.47	4.49
B_0 (Mbar)	2.51	1.79	2.4	1.73	1.76	3.09	1.98	
B'_0	2.76	3.93		3.64				

^a [3].

Table 2 summarizes the ground-state properties of β -GaN obtained in the present work and by other groups [7–12]. Whilst there is, in general, good agreement with other works, we note here that the disagreement between the present work and the work of Van Camp *et al* [6, 9] is presumably due to the use of a smaller plane wave basis in [6] and [9].

In our calculations for ground state properties of α -GaN (wurtzite structure) we have used 2 special *k*-points at a cut-off of 70 Ryd for a range of values of *a*, assuming the ideal *c/a* ratio (1.633) and the ideal value for the parameter *u* (0.375*c*). Once again we used BHS [23] and TM [24] pseudopotentials for the Ga and N components respectively. The atomic positions in the wurtzite structure are Ga:(0,0,0), ($2a/3$, $a/3$, $c/2$); N:(0,0,*u*), ($2a/3$, $a/3$, $c/2 + u$). Fitting to the Murnaghan equation of state we compute that the lattice constant *a*

takes the value 3.04 \AA , the bulk modulus is 2.34 Mbar and its pressure derivative is 3.55. These values compare well both with experiment [5] and with other recent calculations [7–10, 41], in particular with the work of Min *et al* [8] (see table 3). We also performed calculations at the theoretical lattice constant for seven different values of the wurtzite parameter u . From a polynomial fit to this data we determined the theoretical equilibrium value of u to be $0.384c$ (see figure 3) and found the frequency of the $A_1\text{-TO}(\Gamma)$ phonon to be 469 cm^{-1} from the second derivative of the curve. The experimentally observed frequency is 533 cm^{-1} measured by Raman spectroscopy [42].

Table 3. Ground state properties of α -GaN (calculated at 70 Ryd cut-off).

	Present work	[7]	[8]	[9]	[10]	[41]	Expt ^b
a_0 (\AA)	3.04	3.21	3.04	3.126	3.15	3.11	3.19
u	$0.384c$		$0.375c$			2.39	
B_0 (Mbar)	2.34		2.4	1.90		2.39	
B'_0	3.55			2.92			

^b [5].

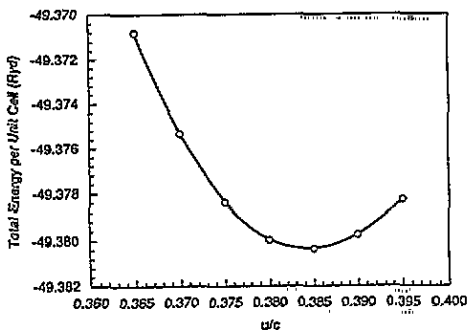


Figure 3. Total energies (in Ryd) per Ga-N unit for the wurtzite (α -GaN) structure at a range of values of the wurtzite parameter u/c (kinetic energy cut-off of 70 Ryd).

Whilst we have not attempted seriously to address the relative stability of the two phases it is nevertheless interesting to note that we find the wurtzite structure to be more stable than the zincblende structure, in agreement with several previous works [7, 9, 16, 17], although contrary to the results of Min *et al* [8]. There are three ways to obtain meaningful energy differences between the two structures; one can perform calculations for both structures within the same (non-primitive) unit cell and use the same set of special k -points, one can use the primitive unit cells but ensure that compatible special k -points are taken, or one can use the primitive unit cells and simply increase the number of special k -points to ensure convergence of the total energy. The first approach would undoubtedly give the most accurate total energy difference but in this case would require calculations on a much larger unit cell (four times the volume of the wurtzite primitive unit cell). The second approach would require careful consideration for the selection of k -points within the Brillouin zones of the two structures. The third approach is the most straightforward and is used here. Taking our optimized lattice constants from the calculations described above, considering ideal c/a and u parameters, and comparing the total energies for nine and ten k -points for the α - and β -phases respectively, we find the relative stability of the wurtzite structure over the zincblende structure to be 0.33 eV per atom. This figure is much larger than quoted in [7, 9, 16, 17] but we emphasize that this simply reflects the use of incompletely-optimised a , c/a and u parameters in this aspect of the present work.

3.2. Excited-state properties

As expected, the band gaps of both materials are severely underestimated by the LDA. However, our calculations do show that both α -GaN and β -GaN have direct band gaps, making them particularly promising for optoelectronic devices. Although the actual band gaps calculated within the LDA are unreliable, we find that even after quasiparticle corrections the prediction that the band gaps are direct is still valid.

In comparison with other reported LDA gaps for β -GaN our figures are quite reasonable. We calculate the direct gap to be 2.32 eV using Ceperley–Alder correlation [22] at the experimental lattice constant of 4.49 Å. Fiorentini *et al* [12] quote a similar LDA direct gap of 2.0 eV at 4.47 Å, while Lu *et al* [11] give a gap of 2.29 eV. Min *et al* [8] calculate an LDA gap of 2.8 eV at a lattice constant of 4.30 Å, rather smaller than our well-converged figure of 3.35 eV at the same lattice constant. The figure of 2.65 eV at 4.45 Å found by Palumbo *et al* [10] using the Stumpf, Gonze and Scheffler pseudopotentials [40] is inconsistent with all other reported values at similar lattice constants.

Using a cut-off of 70 Ryd we found the LDA direct band gap in α -GaN at the experimental lattice constant of 3.19 Å to be 2.37 eV. This is in quite good agreement with the results quoted by Rubio *et al* [14] (2.3 eV). Just as this group found, our α -GaN band gap is slightly higher than the band gap of β -GaN. The same qualitative result was also noted by Lambrecht and Segall [43] and by Min *et al* [8].

We have calculated quasiparticle band gaps for β -GaN at the experimental lattice constant, employing the self-energy techniques referred to in section 2. For our calculation of the Bechstedt–Del Sole self-energy correction to the LDA results we have taken $\beta_A = 1.6$, $\beta_B = 1.8$ [17], $\alpha_p = 0.6$ [44] and used the dielectric constant of the wurtzite phase, $\epsilon_0 = 5.2$, since that of the zincblende phase is unknown. In order to estimate the value of q_{TF} we have considered the approximate relation [45]

$$q_{TF} = \frac{2.95}{(r_s/a_B)^{1/2}} \text{Å}^{-1} \quad (8)$$

and taken the reasonable value of $(r_s/a_B) \simeq 2.5$ for GaN which gives

$$q_{TF} = 1.87 \text{Å}^{-1}. \quad (9)$$

The Bechstedt–Del Sole correction can then be evaluated, yielding a constant gap correction of 1.32 eV at the experimental lattice constant 4.49 Å. This value is not changed too much by reasonable choices of electron density (i.e. for (r_s/a_B) between 2 and 3).

The Sterne–Inkson corrections to the LDA results are evaluated by the method outlined in [18] using $\epsilon_0 = 5.2$ which yields rather varied corrections of 1.04 eV, 1.69 eV and 0.76 eV at the Γ , X and L points respectively when $a = 4.49$ Å and $C = 4.0$ eV. In these calculations we have used 229 G vectors in the sum over Fourier components at which level our results for the many-body correction are fully converged (see figure 4, noting the oscillatory behaviour of certain of the principal band gaps when the sum is severely truncated). Table 4 give the results of our LDA calculations at the experimental lattice constant of 4.49 Å and also shows the Sterne–Inkson corrected and Bechstedt–Del Sole corrected principal band gaps. Figure 5 shows the calculated Sterne–Inkson band structure. The non-rigid nature of the correction is highlighted by the enlarged scale of figure 5(b).

To our knowledge there have been only four reported experimental values for the direct band gap in β -GaN: 3.2 eV [3], 3.45 eV [46], 3.5 eV [2] and 3.87 eV [4]. Both our Sterne–Inkson corrected direct gap of 3.36 eV and our Bechstedt–Del Sole corrected direct gap

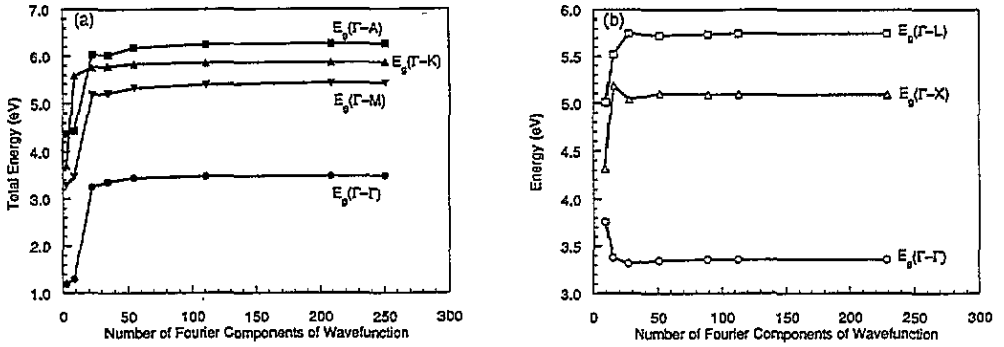


Figure 4. Convergence of the Sterne-Inkson-corrected band gaps (in eV) with increasing number of Fourier components of the wavefunction included in the Sterne-Inkson calculation. (a) Wurtzite structure (α -GaN), full circles are $E_g(\Gamma-\Gamma)$, full inverted triangles are $E_g(\Gamma-M)$, full upright triangles are $E_g(\Gamma-K)$, and full squares are $E_g(\Gamma-A)$. (b) Zincblende structure (β -GaN): open circles are $E_g(\Gamma-\Gamma)$, open triangles are $E_g(\Gamma-X)$ and open squares are $E_g(\Gamma-L)$.

Table 4. Principal band gaps in eV for β -GaN at the experimental lattice constant 4.49 Å (calculated at 70 Ryd cut-off).

	Present LDA	Present s-I	Present B-DS	[11] $a = 4.40$ Å	[12] $a = 4.47$ Å	[13] $a = 4.45$ Å	[14] $a = 4.45$ Å	Expt ^a Range
$E_g(\Gamma-\Gamma)$	2.32	3.36	3.64	3.90	3.55	3.60	3.1	3.2–3.9
$E_g(\Gamma-X)$	3.40	5.09	4.72	4.79			4.7	
$E_g(\Gamma-L)$	4.99	5.75	6.31	7.00			6.2	

^a See text.

of 3.64 eV lie within this experimental range. In particular, our Bechstedt–Del Sole figure agrees quite well with the theoretical results of Fiorentini *et al* [12] (direct gap 3.55 eV). The result quoted by Fiorentini *et al*, must, however, be regarded as no more than a crude estimate since it is based on the empirical approximation to the gap correction of $\Delta \simeq 9/\epsilon_0$ proposed by Fiorentini and Baldereschi [47].

The result of Lu *et al* [11] (direct gap 3.90 eV) is incorrect since they have wrongly assumed $7.62x \gg 1$ in their calculation of the Bechstedt–Del Sole correction. This leads them to overestimate the correction by approximately 0.3 eV and thus they should have found a gap of ~ 3.6 eV without this mistake, in fair agreement with our own Bechstedt–Del Sole corrected figures.

There is also, apparently, good agreement between our Bechstedt–Del Sole corrected results and a very recent calculation by Palummo *et al* [13] (direct gap 3.60 eV). However, their LDA band gaps are rather larger than all other calculations so this is coincidental. The self-energy corrections found by this group are actually very similar to those that we calculate using the Sterne–Inkson method. The Bechstedt–Del Sole and Fiorentini–Baldereschi [47] schemes yield corrections at the Γ point of 1.32 eV and 1.74 eV respectively (taking $a = 4.49$ Å and $\epsilon_0 = 5.2$). Palummo *et al* find a correction of 0.95 eV at the Γ point which matches our 1.04 eV correction quite closely. Our best agreement, however, is with the work of Rubio *et al* [14] (direct gap 3.1 eV). Not only is our correction in agreement with their correction of 1.0 eV, but since we calculate a similar LDA band gap our predicted quasiparticle band gap is also in reasonable agreement with theirs.

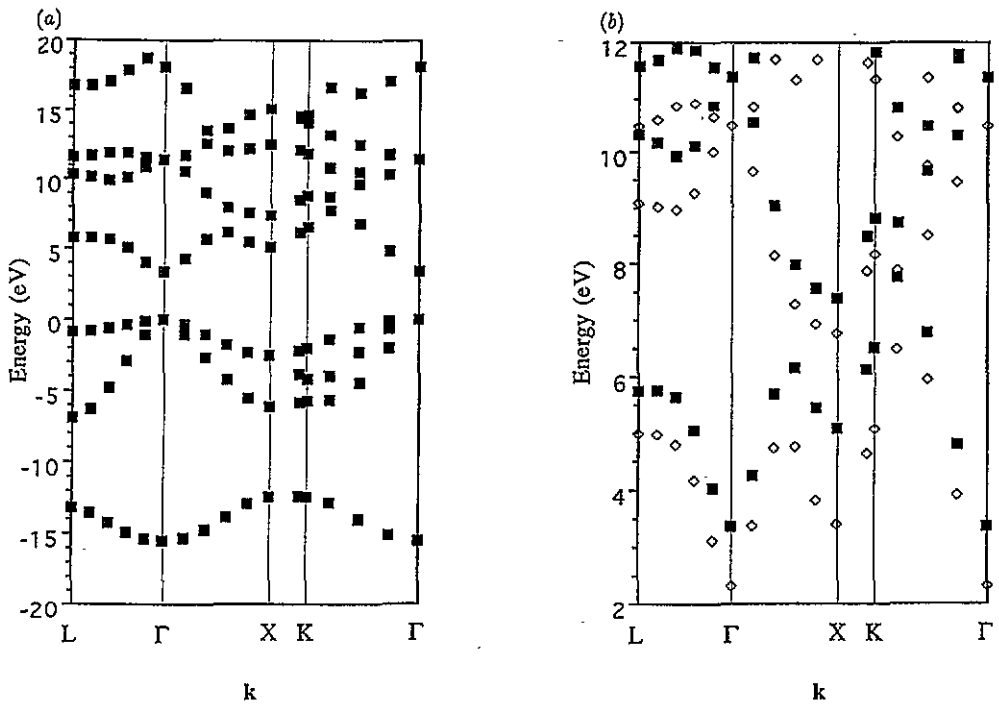


Figure 5. (a) Sterne-Inkson corrected band structure for β -GaN (zincblende structure) showing valence and conduction bands (b) LDA (open diamonds) and Sterne-Inkson corrected (full squares) conduction bands on an enlarged scale to emphasize the non-rigid shift from LDA to quasiparticle results.

Since both the Bechstedt-Del Sole and Sterne-Inkson methods are based on tight-binding models it is reasonable to apply essentially the same kind of correction to GaN in the wurtzite structure (α -GaN) as it only differs from the zincblende structure at the level of the next-nearest neighbours. In fact, since the bond length is almost unaltered in both phases we can even use the same value for \mathcal{C} as before. The sum over Fourier components is truncated at 233 G vectors, which is sufficient for complete convergence (see figure 4). Table 5 shows our LDA and self-energy corrected band gaps for α -GaN calculated at the experimental lattice constant. Figure 6(a) shows the Sterne-Inkson corrected band structure, while once again the non-rigid nature of the correction is highlighted by the enlarged scale of figure 6(b). The Sterne-Inkson corrected direct band gap of 3.48 eV at the experimental lattice constant is in excellent agreement with experimental results which show that the true band gap lies between 3.41 eV and 3.46 eV [1]. The corresponding Bechstedt-Del Sole figure of 3.69 eV is rather too large in comparison.

For both phases our Sterne-Inkson band-gap corrections are highly dependent upon the wavevector. In [18] we examined a number of materials (diamond, Si, Ge, GaAs and ZnSe) and saw no such large dependence. We suggest that it is an effect of the highly inhomogeneous electron distribution in GaN compared to these other materials. Similar wavevector dependence of the GW correction is seen in the calculations of Rubio *et al* [14] for both GaN phases. In particular the raising of the X-point conduction band in β -GaN relative to the Γ -point minimum is well reproduced. This kind of k -dependent shift cannot be modelled by the simple Bechstedt-Del Sole formula (1).

Table 5. Principal band gaps in eV for α -GaN at the experimental lattice constant of $a = 3.19 \text{ \AA}$ with the ideal c/a value of 1.633 and the ideal $u = 0.375c$ (calculated at 70 Ryd cut-off).

	Present LDA	Present S-I	Present B-DS	[11]	[14]	Expt ^a
$E_g(\Gamma-\Gamma)$	2.37	3.48	3.69	3.65	3.5	3.41–3.46
$E_g(\Gamma-M)$	5.27	5.86	6.59	6.22	6.5	
$E_g(\Gamma-K)$	5.03	6.27	6.35		6.6	
$E_g(\Gamma-A)$	4.64	5.42	5.96		6.1	

^a [1].

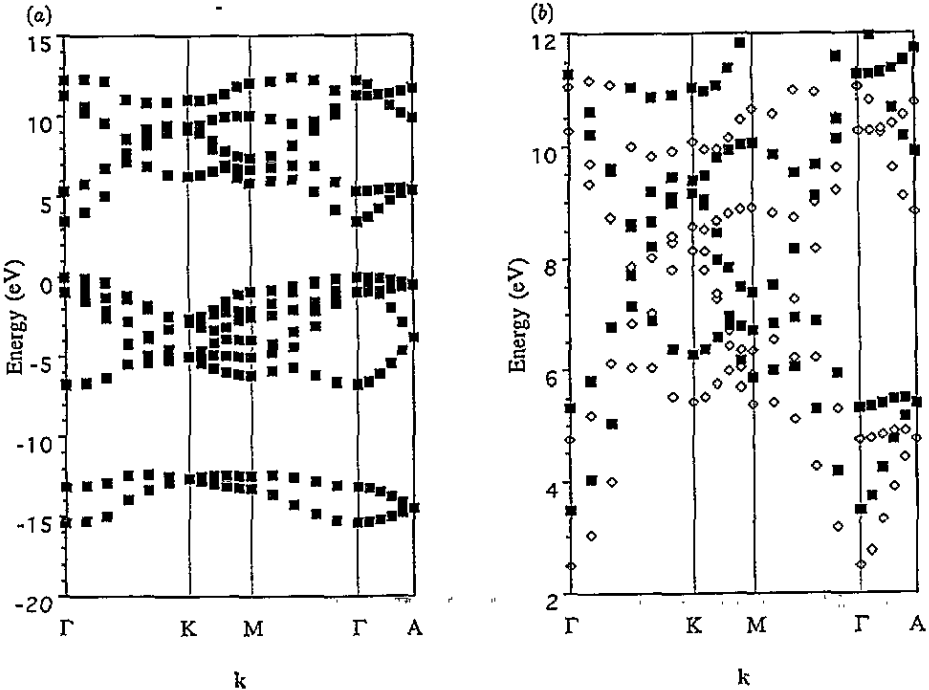


Figure 6. (a) Sterne-Inkson corrected band structure for α -GaN (wurtzite structure) showing valence and conduction bands (b) LDA (open diamonds) and Sterne-Inkson corrected (full squares) conduction bands on an enlarged scale to emphasize the non-rigid shift from LDA to quasiparticle results.

4. Summary

We have presented converged plane wave pseudopotential calculations within the LDA for the ground state properties of both α -GaN and β -GaN. We find that ground state properties are reproduced reasonably well by the LDA. In addition, we have investigated the excited state properties of the two phases of GaN. As expected, the band gaps obtained from the LDA calculation are severely underestimated, but we have shown that our simple GW scheme is capable of correcting this fault and yielding quasiparticle energies comparable with experiment. Notably, the corrections are extremely dependent upon wavevector. Even though the very much simpler approach of Bechstedt and Del Sole and the empirical model of Fiorentini and Baldereschi give band gap corrections of reasonable magnitude, they do not reproduce the wavevector dependence obtained from our scheme. The band gap corrections

predicted from this work can be favourably matched with those recently presented by Rubio *et al* using a model dielectric matrix for the evaluation of the electron self-energy. Our work suggests that the band gap measurement for β -GaN quoted in [4] is too large, and that the most plausible experimental range is 3.2–3.5 eV.

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