

Comment on “Band structures and optical spectra of InN polymorphs: Influence of quasiparticle and excitonic effects”

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In a recent paper, Furthmüller *et al.* [Phys. Rev. B **72**, 205106 (2005)] reported results of calculations of the band structure and optical spectra of InN polymorphs that included influence of quasiparticle and excitonic effects. We show below calculated results that disagree with their utilization of the *pd* repulsion to make significant corrections to band gaps obtained with their *ab initio* density-functional calculations.

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Furthmüller *et al.*¹ first performed *ab initio*, density-functional calculations of the band structures of wurtzite, zinc-blende, and rocksalt InN, i.e., w-InN, c-InN, and rs-InN, respectively. They found negative band gaps and the wrong orderings of states around the Fermi level for w-InN and c-InN. They argued that a perturbative approach for quasiparticle corrections cannot remedy these incorrect results and that self-consistent quasiparticle calculations, with an update of the quasiparticle wave functions, were needed. The authors then proceeded to claim that an understanding of the physics of the wrong orderings could permit a correction without full, self-consistent quasiparticle computations.

Furthmüller *et al.*¹ then performed calculations in which the *4d* bands are included in the core, even though they are taken into account in the construction of the pseudopotentials. They reportedly took self-interaction corrections into account in the underlying atomic calculations. These calculations yielded positive band gaps and the correct orderings of the states around the Fermi energy for both w-InN and c-InN. They reported differences between the band gaps when the *4d* bands are outside and in the core to be 0.76 and 0.79 eV for w-InN and c-InN, respectively. They then assumed that these differences are measures of the upward shift of the top of the valence band due to the *pd* repulsion suggested by Wei and Zunger.² Further, Furthmüller *et al.*¹ assumed that the ratios of the calculated minimum of the *4d* bands (i.e., 13.5 eV) to the measured minima of these bands, 14.9 eV (Ref. 3) and 16.7 eV,⁴ represent the correct proportions of *pd* repulsion to be included in a gap-opening schemes of the type of the scissors approximation. Hence, instead of performing the needed, self-consistent quasiparticle calculations, they applied the above ratios to obtain quasiparticle band gaps of 0.82 (0.89) and 0.59 (0.67) eV for w-InN and c-InN, respectively. The two numbers result from applying 81% (91%) of the *pd* repulsion. These results, contrary to their claim of predictions, are outcomes of *ad hoc* calculations by virtue of the above assumptions and of the use of the experimental minima of the *4d* bands to determine some presumed correct proportions of *pd* repulsion.

In contrast to the above results, our *ab initio*, self-consistent, density-functional calculations led to the correct band gap and electron effective mass at Γ for w-InN (Ref. 5) and predicted these quantities for c-InN (Ref. 6) from first principles. We summarize below a comparison of the above^{5,6} all-electron calculations with those of *ab initio*, self-

consistent, local-density approximation BZW calculations of the electronic structures of w-InN and c-InN with the *4d* bands in the core. The differences between these results point to a total lack of evidence for *pd* repulsion, for both for w-InN and c-InN, as an explanation¹ for the wrong band gaps and the wrong orderings of states around the Fermi level. Our present and previous^{5,6} calculations employed lattice parameters of $a=3.544$ Å, $c=5.718$ Å, and $u=0.3790$ for w-InN and 5.017 Å for c-InN.

The net results of the comparison of the two sets of calculations, in going from *4d* in the core to all-electron calculations, for both w-InN and c-InN, are an extensive hybridization of the In *4d* and N *2s* bands,^{5,6} a significant broadening of the group of *4d* and *2s* bands, and the consequent lowering and upward shift of the minimum and maximum of the group, respectively. When the *4d* bands are moved from the core to the valence, the band gaps only decrease by 0.13 eV, for both systems, and the minima of the *4d* and *2s* group of bands are lowered by 1 and 0.71 eV, for w-InN and c-InN, respectively, while the maxima are shifted upward by 0.64 eV for both. A clear indication that these changes cannot be ascribed to *pd* repulsion resides in the fact that the distance between the maximum of the mostly *4d* bands and the minimum of the dominant *p* valence bands remains the same for c-InN and only decreases from 8.71 to 8.69 eV for w-InN. For InN, these results support the key finding of Wei and Zunger² relative to the need for treating the *4d* bands properly as valence bands, and not the suggested *pd* repulsion.

The Bagayoko, Zhao, and Williams (BZW) method has been thoroughly described in the literature.⁵⁻⁹ It ensures the completeness of the basis set, *for the description of the ground state*, by methodically increasing its size until the occupied energy levels converge, within the computational errors, with respect to the size of the basis set. As stated in these papers, the method has resolved the problem of the theoretical underestimation of the band gaps of semiconductors by 30%–50% or more. The authors have underscored^{5,6} the need to determine the actual limitations of density-functional theory and of approaches that purport to correct it or to go beyond it. They do not claim that excitations, including exciton formation and relaxation, can be described by the ground-state theory of density functional. They do assert that the above theoretical underestimation that has been routinely ascribed to failures of density-functional

theory is not part of its intrinsic limitations. Extensive, *ab initio*, self-consistent results⁵⁻¹⁰ corroborate this assertion. Even for an exact theory of the ground state or of excited states, one still has to contend with the fact that comparisons⁸ with experiment should be done cautiously. Indeed, real materials have defects and impurities that complicate compari-

sons between theory and experiment, in addition to obvious factors that include temperature and pressure (and hence the lattice parameters). These factors partly explain the rather small differences between density-functional theory BZW results and experiments.

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¹J. Furthmüller, P. H. Hahn, F. Fuchs, and F. Bechstedt, *Phys. Rev. B* **72**, 205106 (2005). See also F. Bechstedt and J. Furthmüller, *J. Cryst. Growth* **246**, 315–319 (2002).

²S. H. Wei and A. Zunger, *Phys. Rev. B* **37**, 8958 (1988).

³Q. X. Guo, M. Nishio, H. Ogawa, A. Wakahara, and A. Yoshida, *Phys. Rev. B* **58**, 15304 (1998).

⁴Y. Bu, L. Ma, and M. C. Liu, *J. Vac. Sci. Technol. A* **11**, 2931 (1993).

⁵D. Bagayoko and L. Franklin, *J. Appl. Phys.* **97**, 123708 (2005).

Also, see references therein for the BZW method.

⁶D. Bagayoko, L. Franklin, and G. L. Zhao, *J. Appl. Phys.* **96**, 4297 (2004).

⁷G. L. Zhao and D. Bagayoko, *New J. Phys.* **2**, 16 (2000).

⁸G. L. Zhao, D. Bagayoko, and T. D. Williams, *Phys. Rev. B* **60**, 1563 (1999).

⁹D. Bagayoko, G. L. Zhao, J. D. Fan, and J. T. Wang, *J. Phys.: Condens. Matter* **10**, 5645 (1998).

¹⁰H. Jin, G. L. Zhao, and D. Bagayoko, *Phys. Rev. B* **73**, 245214 (2006).