

Electronic structure of III-V's semiconductors from B3LYP and PBE0 functionals

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Abstract. Details of the band gaps within semiconductor materials are of paramount importance to a wide range of technological applications. We present the results of two hybrid exchange, B3LYP and PBE0, approximations to density functional theory for the band gaps of zinc-blend and wurtzite structured III-V materials. Agreement with experimentally derived band gaps at characteristic points in the first Brillouin zone is at least as good as that obtained with correlated calculations, perturbation theories and screened exchange functionals. Using experimental lattice constants for unit cells we conclude that B3LYP functional provides results on energy gaps that are close to experimental values than with PBE0.

Keywords: Semiconductor bulk, electronic structure, density functional theory.

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INTRODUCTION

In order to study the electronic and optical properties of III-V zinc-blend and wurtzite semiconductor materials an approach providing a reliable estimate of band gaps while retaining an accurate and efficient method for computing the ground state energy surfaces required. The hybrid exchange approximation to density functional theory (DFT), embodied in the B3LYP and PBE0 functionals, was originally developed to improve the description of ground state energetics. Subsequently, these functionals have been demonstrated to be significantly more reliable than the best GGA functional for computing atomisation enthalpies, geometries and vibrational frequencies in molecular systems [1]. The implementation in solids is more recent but initial studies indicate a similar level of performance for geometries and vibrational frequencies [2, 3]. The hybrid exchange functionals used in the current study are B3LYP and PBE0 which have the following form: $E_X = E_X^{\text{LSDA}} + 0.2(E_X^{\text{Fock}} - E_X^{\text{LSDA}}) + 0.72 \Delta E_X^{\text{GGA}}$, and $E_{\text{XC}} = E_{\text{XC}}^{\text{PBE}} + 0.25(E_X^{\text{Fock}} - E_X^{\text{PBE}})$ respectively, where the LSDA, GGA, and PBE energies are taken from widely used functionals and E_X^{Fock} is the non local Fock exchange energy. While this is not convenient within the commonly used plane-wave basis sets it can be implemented readily and very efficiently within a Gaussian basis set as used in the

CRYSTAL code [4]. Within the CRYSTAL code hybrid functionals can be used to study surfaces [5], defects [6], and nanostructures [7] calculations. The main numerical approximation is the selection of the local Gaussian basis set.

RESULTS AND DISCUSSION

In our numerical calculations we use all electron 6-311G* basis sets (N, Al, P); and “m”-pVDZ-PP (for Ga, As, In, Sb) with relativistic effective core potential basis sets. The index “m” refers to the modification that in all basis sets exponents below 0.12 1/a.u. were removed to prevent numerical instabilities due to linear dependency problem [8]. The Brillouin zone integration was performed using 29 symmetry irreducible points in k-space for zinc-blend (ZB) structures and 50 k-points for wurtzite (WZ) structures. Band gaps were obtained as a Kohn-Sham eigenvalue differences at the Γ point for direct gap semiconductors and as a minimal energy difference between Γ point and X_1 point or minimum along Δ direction in the case of the indirect gap materials (AlP, AlAs, AlSb, GaP). Introduction of the exact exchange Fock term in the B3LYP and PBE0 functionals is the main factor that “opens” the E_g when compared to conventional LDA approach. The main reason for that behaviour is that in LDA each individual electron contribute to the total density. In fact, one electron in an occupied orbital interacts with

N other electrons in the system, when it should interact with $N-1$ electrons only (so called the *self interaction* problem [9]). In the DFT in the LDA approximation all occupied bands are pushed up in energy by this interaction which has for a consequence an on-site/diagonal Coulomb/Exchange repulsion. This leads to too small energy band gap in DFT-LDA. On the other hand, in Hartree-Fock (HF) theory the Coulomb and exchange interactions cancels exactly, i.e. $J_{ii} = K_{ii}$, so there is no self interaction. HF theory overestimates band gaps due to the lack of dynamical screening. It appears that energy gaps predicted with hybrid functionals with $\sim 20\%$ HF and $\sim 80\%$ DFT exchange, exactly the proportions optimised for use in the calculation of ground state energetics in the B3LYP functional, are also in good agreement with experimentally measured ones.

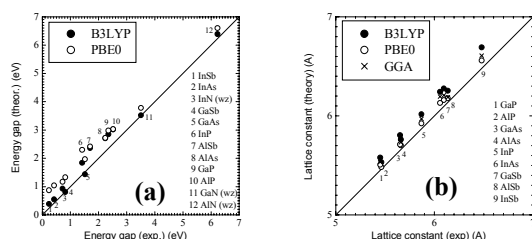


FIGURE 1. A comparison of experimental energy gaps (a) and experimental lattice constants (b), with those predicted using DFT with B3LYP, PBE0, and GGA functionals. The energy gaps are computed at the experimental lattice constant.

It has been shown previously, that the B3LYP functional, can provide a remarkable agreement with measured energy gaps, for most of the III-V semiconductor binaries [10]. In figure 1(a) the calculated energy gaps of 9 representative ZB binaries and 3 group III-N WZ materials are shown for the B3LYP and PBE0 hybrid functionals. The B3LYP functional provides slightly better agreement with the experiment then PBE0 when the calculation is performed assuming experimental lattice constants. In general the PBE0 functional results in an overestimate of the band gap. In figure 1(b) the optimized lattice constants of the nine ZB binaries is presented for calculations using the B3LYP and PBE0 functionals. The lattice constants predicted using the PBE0 functional are closer to the experimental values than the B3LYP results. The B3LYP calculations systematically overestimate values of the lattice constant by 1-2% and are in somewhat worse agreement with experiment than those predicted from the GGA functional.

The trends in the band gap and lattice constant can be understood from the proportion of Fock exchange retained in the functional, which is

25% in PBE0 and 20% in B3LYP. The larger exchange component opens a larger band gap as it compensates for electronic *self interaction*. Increasing the exchange also tends to decrease the lattice constant; in the limit of a pure HF calculation the lattice constant would be significantly underestimated in a covalently bonded system. One therefore expects the use of PBE0 to lead to higher band gaps and shorter bond lengths than B3LYP in covalent systems.

For wurtzite structures, with generally very small spin orbit splitting, it is observed here that there is remarkable agreement between ab-initio predicted and experimental energy gaps and optimized lattice constants for both B3LYP and PBE0 approaches. The overall agreement is competitive with that achieved by more sophisticated methods [11,12] and with empirical theories tailored for this purpose [13].

CONCLUSIONS

In conclusion, the hybrid exchange methodology provides an efficient and robust basis for large scale calculations of III-V semiconductors reliably predicting both the ground state energetics and the electronic structure.

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