Accurate \textit{ab initio} predictions of III–V direct-indirect band gap crossovers

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We report the compositional dependence of the electronic band structure for a range of III–V alloys. Standard density functional theory is insufficient to mimic the electronic band energies at different symmetry points of the Brillouin zone. The Heyd–Scuseria–Ernzerhof hybrid functional with screened exchange accurately reproduces the experimental band gaps and, more importantly, the alloy concentration of the direct-indirect gap crossovers for the III–V alloys studied here: AlGaAs, InAlAs, AlInP, InGaP, and GaAsP. © 2010 American Institute of Physics. [doi:10.1063/1.3485297]

The “band gap versus lattice constant” map is a popular model used to aid in the design of all optoelectronic devices but suffers from inaccuracies in band gap energies and crossover compositions where the alloy switches from a direct to an indirect band gap. Consequently a correct quantitative assessment of the electronic structure of semiconducting alloys is vital to improve upon this map. Most theoretical studies focused on density functional theory (DFT) calculations using the local density approximation (LDA) or the generalized gradient approximation (GGA) which do poorly on excited states. Only recently have hybrid functionals been used in predicting accurate excited states in individual semiconducting alloys.\textsuperscript{1,2}

The Heyd–Scuseria–Ernzerhof (HSE) hybrid functional,\textsuperscript{3} which combines the screened exchange with the Perdew–Burke–Ernzerhof (PBE) GGA functional,\textsuperscript{4} outperforms previous DFT methods in reproducing bulk band gaps.\textsuperscript{5} We report HSE reproduces not only the band gaps across the entire composition range of each alloy studied here but also the direct-indirect band gap crossovers seen experimentally.

Figure 1(a) demonstrates this significant improvement of HSE over PBE in predicting the direct-indirect ($\Gamma$–$X$) crossover (denoted by vertical arrows) for the AlGaAs alloy compared with experiment.\textsuperscript{6} HSE reproduces the direct-indirect crossover within 5\% Al concentration from the most recent experimental value published by Yi et al.\textsuperscript{1} The PBE functional which does not take into account screened exchange overestimates this crossover by 23\% Al concentration.

The disordered zinc-blende (cubic) alloys are best modeled by special quasirandom structures (SQSS),\textsuperscript{8} ordered structures designed to reproduce the most important pair-correlation functions of a random alloy. The best possible 32-atom SQS’s we construct for concentrations of $x=0.25$ and 0.50 match the pair-correlation functions of a random alloy up to third and seventh nearest neighbors, respectively.\textsuperscript{9,10} The SQS with concentration $x=0.25$ can be used interchangeably with that of $x=0.75$.

Table I gives the lattice vectors for each SQS used to describe the optical transitions as seen in the zinc-blende primitive cell through folding relations in the Brillouin zone. The SQS with concentration $x=0.50$ has a base-centered orthorhombic space group symmetry with the following folding relations in reciprocal coordinates:

\begin{align*}
\Gamma'^ZB(0,0,0) &\rightarrow \Gamma(0,0,0), \\
X'^ZB\left(\frac{1}{2},\frac{1}{2},0\right) &\rightarrow \Gamma(0,0,0), \quad 2 \times \bar{Z}(0,0,\frac{1}{2}), \\
L'^ZB\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right) &\rightarrow 2 \times \bar{Z}(0,0,0), \quad 2 \times \bar{Z}(0,0,\frac{1}{2}),
\end{align*}

where the bar denotes superlattice states and the coefficient denotes degeneracies. The SQS with concentration $x=0.25$ has a triclinic space group symmetry with folding relations given by.

\begin{align*}
\Gamma'^ZB(0,0,0) &\rightarrow \Gamma(0,0,0), \\
X'^ZB\left(\frac{1}{2},\frac{1}{2},0\right) &\rightarrow \Gamma(0,0,0), \quad 2 \times \bar{Z}(0,0,\frac{1}{2}), \\
L'^ZB\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right) &\rightarrow 2 \times \bar{Z}(0,0,0), \quad 2 \times \bar{Z}(0,0,\frac{1}{2}),
\end{align*}

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![Image](https://example.com/image1.png)

**FIG. 1.** (Color online) (a) Band gap energy for Al\textsubscript{x}Ga\textsubscript{1-x}As calculated using HSE (solid line) and PBE (dashed line) in comparison with the experimental fit (dotted line) taken from Ref. 6. A direct-indirect band gap crossover (vertical arrows) occurs as the Al concentration is increased. (b) A detailed plot of the individual direct (squares), $\Gamma$, and indirect (circles), $X$, gap energy fits using the HSE (solid symbols) and PBE (open symbols) values. The vertical lines denote the direct-indirect band gap crossover.
The calculations are performed using the projector augmented-wave (PAW) method. The functionals included are the PBE and the HSE06 (Ref. 3) hybrid functional in the VASP code. The Ga 3d and In 4d electrons are treated as valence and the wave functions are expanded in plane waves up to an energy cutoff of 500 eV. The Brillouin-zone integrations have been carried out on $10 \times 10 \times 10$, $6 \times 4 \times 4$, and $4 \times 4 \times 8$ f-centered $k$ meshes for the face-centered cubic primitive cell and SQS supercells for $x=0.25$ and $x=0.50$, respectively.

The lattice constants are linearly interpolated between the experimental parent compound lattice constants taken from Vurgaftman et al. Relaxations are not taken into account after observing only a slight shift of 1% Al concentration in the direct-indirect crossover in the AlInP alloy using the PBE functional. The compositional dependence of the band gap is described by a quadratic fit to the data, whereas a cubic fit is taken for only the direct gap of AlGaAs.

Figure 1(b) supplements Fig. 1(a) by showing the computed direct gap ($\Gamma$–$\Gamma$) and indirect gap ($X$–$\Gamma$), conduction to valence band energies, across the entire composition range of AlGaAs. The direct and indirect gap energies computed using HSE quantitatively agree better with experiment than using PBE. Figure 2 displays the band gap energies and the direct-indirect crossovers for four different III–V alloys. A detailed comparison of the crossovers is given in Table II.

For Al$_{1-x}$In$_x$As, Fig. 2(a) displays the band gap energy for HSE, PBE, and the recommended experimental fits taken from Ref. 6. HSE continues its success in predicting the direct-indirect ($\Gamma$–$X$) crossover at a concentration of 4% Al higher than experiment, again PBE overestimates by as much as 12% Al. Additionally, PBE predicts the alloy to be metallic up to 10% Al.

For Al$_{1-x}$In$_x$P, Fig. 2(b), HSE predicts a crossover at 37% Al concentration underestimating the early experimental value by Onton et al. ($x=0.44$) (Ref. 13) but shows relatively good agreement with the later results for strained AlInP by Ishitani et al. ($x=0.34$). More studies of the AlInP alloy could provide a better comparison with theory.

### Table I. The lattice vectors of the triclinic $x=0.25$ and the base-centered orthorhombic $x=0.50$ SQS’s in units of $a/2$ where $a$ is the lattice constant of the alloy A$_x$B$_{1-x}$C.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Lattice vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0.25$</td>
<td>(1,1,−2)</td>
</tr>
<tr>
<td>$x=0.50$</td>
<td>(4,2,2)</td>
</tr>
</tbody>
</table>

### Table II. Direct-indirect crossover points for five semiconducting alloys obtained using HSE and PBE compared alongside experimental measurements. HSE outperforms PBE at reproducing accurate crossover points for all the alloys other than Al$_{1-x}$In$_x$P.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crossover</th>
<th>HSE</th>
<th>PBE</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_{1-x}$Ga$_x$As</td>
<td>$\Gamma$–$X$</td>
<td>0.47</td>
<td>0.65</td>
<td>0.38$^a$, 0.42$^b$</td>
</tr>
<tr>
<td>Al$_{1-x}$In$_x$As</td>
<td>$\Gamma$–$X$</td>
<td>0.68</td>
<td>0.76</td>
<td>0.64$^a$</td>
</tr>
<tr>
<td>Al$_{1-x}$In$_x$P</td>
<td>$\Gamma$–$X$</td>
<td>0.37</td>
<td>0.44</td>
<td>0.44$^a$, 0.34$^d$</td>
</tr>
<tr>
<td>Ga$<em>x$In$</em>{1-x}$P</td>
<td>$\Gamma$–L</td>
<td>0.72</td>
<td>0.86</td>
<td>0.67$^a$, 0.68$^c$</td>
</tr>
<tr>
<td>Ga$<em>x$As$</em>{1-x}$P</td>
<td>$\Gamma$–L</td>
<td>0.73</td>
<td>0.90</td>
<td>0.746$^d$</td>
</tr>
<tr>
<td>$xL$–X</td>
<td>0.75</td>
<td>0.96</td>
<td>0.77$^a$</td>
<td></td>
</tr>
<tr>
<td>$xL$–X</td>
<td>0.56</td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$xL$–X</td>
<td>0.57</td>
<td>0.84</td>
<td>0.45$^a$</td>
<td></td>
</tr>
<tr>
<td>$xL$–X</td>
<td>0.58</td>
<td>0.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$From Ref. 6.
$^b$From Ref. 7, ballistic carrier spectroscopy.
$^c$From Ref. 13, cathodoluminescence.
$^d$From Ref. 14 for strained Al$_{1-x}$P.
$^e$From Ref. 15, piezomodulation spectroscopy.
$^f$From Ref. 16, photoluminescence.
For GaIn1−xP, Fig. 2(c), experiments utilizing optical luminescence measurements see only a single crossover for \( \Gamma - X \) whereas high pressure electrical measurements and piezoreflectance measurements observed two-point crossovers for \( \Gamma - L \) and \( L - X \). Both HSE and PBE yield two point crossovers as seen in Fig. 2(c) with only HSE reproducing crossover points that lie nearly on top of experiment as well as reproducing the band gap to within 8% accuracy throughout the entire Ga concentration.

For GaAs1−yP, Fig. 2(d), the HSE direct-indirect crossover shows the largest discrepancy with experiment of 12% atomic composition seen in Table II. This suggests the actual crossover may lie at a slightly higher P concentration than the thirty year old experimental value, \( x = 0.45 \).

To conclude, HSE reproduces accurate direct-indirect crossovers within 7% atomic composition for all the alloys except GaAsP, whereas PBE overestimates crossover points by as much as 39% atomic composition. More relevantly, HSE predicts GaAsP to remain direct up to P concentrations of 56% improving on the “band gap versus lattice constant” map. HSE emerges as the ab-initio method of choice when studying electronic properties of semiconducting alloys.

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SQS was generated with the gensqs program in the alloy-theoretic automated toolkit. A. van de Walle, M. Asta, and G. Ceder, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 26, 539 (2002).

See supplementary material at http://dx.doi.org/10.1063/1.3485297 for SQS supercell and band bowing parameters.


