Accurate many-body calculation of electronic and optical band gap of bulk hexagonal boron nitride

Miroslav Kolos, František Karlický

Department of Physics, Faculty of Science, University of Ostrava, Czech Republic

Introduction

Recent interest in two-dimensional (2D) materials has re-initiated intensive discussion on bulk layered materials' electronic and optical properties. The debate concerning the band gap of bulk hexagonal boron nitride (h-BN), its nature, and excitonic properties was re-opened by recent experiments. While graphite (and its 2D analog called graphene) is a zero band gap semi-metal, h-BN is a wide gap semiconductor with very high thermal and chemical stability, suitable in devices operating under extreme conditions. Experimental estimation of the bulk h-BN band gap has been a long-debated issue, and different experiments have varied. The nature of the band gap was controversial too. Still, this recent experimental studies brought a turning point in this consensus and showed the band gap's nature as indirect and reported very accurate values of the electronic and optical band gaps.

Benchmark GW and BSE study of h-BN band gaps

Figure 1. Convergence of h-BN (AA’) band gaps $E_{\text{gap}}$ (indirect, direct in M, optical) and exciton binding energy $E_{\text{exc}} = E_{\text{M}} - E_{\text{opt}}$ in eV. A) With respect to GW number of bands $N_{\text{B}}$ and energy cut-off $E_{\text{cut}}$ (indicated in the legend, in eV); B) With respect to number of iteration $i$ in G$_0$W$_0$ and G$_0$W$_0$ calculations. 12 x 12 x 4 k-grid was used. Green points are experimental values.

Table 1. Comparison of calculated gap values with experimental values.

<table>
<thead>
<tr>
<th>$N_{\text{B}}$</th>
<th>$E_{\text{cut}}$</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>$E_{\text{exc}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hack</td>
<td>6.04</td>
<td>6.53</td>
<td>5.71</td>
</tr>
<tr>
<td>Calc, AB</td>
<td>6.17</td>
<td>6.29</td>
<td>5.61</td>
</tr>
<tr>
<td>Exp, AB</td>
<td>6.08</td>
<td>6.42</td>
<td>5.69</td>
</tr>
</tbody>
</table>

Results

Figure 2. Conduction (top) and valence (bottom) bands of h-BN obtained from G$_0$W$_0$ calculation as cuts through the plane G–M–K in the first Brillouin zone.

Figure 3. Change in h-BN band gaps $E_{\text{gap}}$ (indirect, direct in M, optical) and exciton binding energy $E_{\text{exc}} = E_{\text{M}} - E_{\text{opt}}$ in eV with respect to c lattice parameter. Two h-BN stacking configurations are considered, AA’ and AB.

Conclusions

Our carefully converged results reveal h-BN as an indirect material (indirect gap $\approx$6.1 eV) with a huge excitonic effect ($\approx$0.8 eV) in agreement with recent experimental studies. Variability of previous theoretical predictions and our convergence tests indicate that many-body methods should be used carefully, and numerical convergence should always be performed. On the other hand, based on benchmark G$_0$W$_0$ results, we suggest a computationally cheap scissor corrected DFT approach providing band structure comparable with the G$_0$W$_0$ band structure. Time-dependent DFT with a suitable exchange-correlation kernel can provide absorption spectra that mimic the full G$_0$W$_0$+BSE spectra.

Simple scissor approximation of h-BN band structures

Figure 4. Electronic band structure of h-BN (AA’) from G$_0$W$_0$ calculation (black triangles) and electron-hole contributions to first excitonic peak from BSE calculation (reproduced by radius of colored circles). Scissor corrected DFT (PBE) band structure, DFT+(blue lines), seems a very good approximation to the G$_0$W$_0$ band structure. Fermi energy is set as zero.

Experimental lattice constants of $a = 2.502$ Å and $c = 6.617$ Å was used. The Vienna ab initio simulation package (VASP) implementing projector augmented-wave (PAW) method, G$_0$ set of PAWs, and cut-off energy $E_{\text{cut}} = 500$ eV are used in all calculations (2s1p electrons are explicitly treated). We use GW+ approximation with input orbitals from DFT and Perdew, Burke and Ernzerhof (PBE) functional for electronic structure calculations. The break condition for the electronic step is an energy difference of $1 \times 10^{-4}$ eV. Excitonic effects are accounted for by the Bethe–Salpeter equation.

Acknowledgments

This was supported by Czech Science Foundation (18-25128S) and Institutional Development Program of the University of Ostrava (RIF01762). M. K. acknowledges the institutional support from Technology Agency and Support for Science and Research in the Moravian - Silesian Region 04544/2017/RRC. The calculations were performed at local facility of University of Ostrava (purchased from EU funds, project No. CZ.1.05/2.1.00/03/0075 and IT4Innovations National Supercomputing Center LM2015070).

References

6. G. Cassabois, P. Valvin and B. Gil, Nat. Photonics, 2016, 10, 262–266.