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

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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[1,2]. 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.

Methods

Experimental lattice constants of a = 2.502 Å and c = 6.617 Å[1] was used. The Vienna *ab initio* simulation package (VASP)[3] implementing projector augmented-wave (PAW) method, GW set of PAWs, and cut-off energy E_{cut} = 500 eV are used in all calculations (2s1p electrons are explicitly treated). We use GW[4] approximation with input orbitals from DFT and Perdew, Burke and Ernzerhof (PBE) functional[5] for electronic structure calculations. The break condition for the electronic step is an energy difference of 1 x 10^{-6} eV. Excitonic effects are accounted for by the Bethe–Salpeter equation[6].

Benchmark GW and BSE study of h-BN band gaps

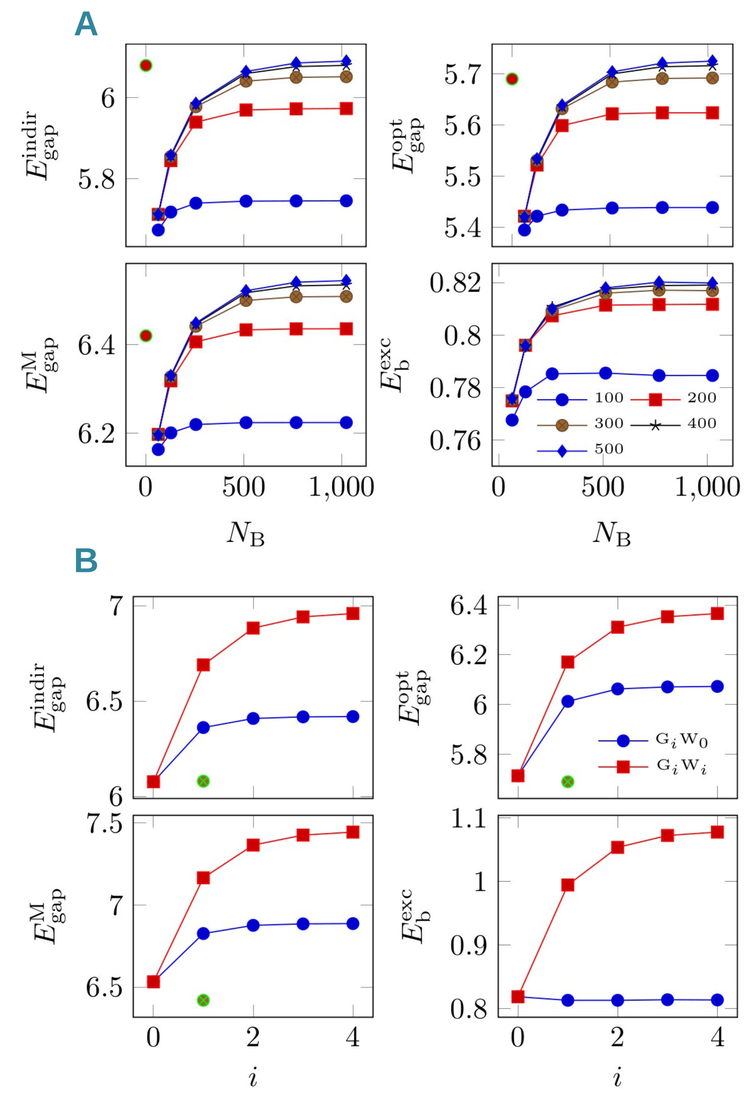

Figure 1. Convergence of h-BN (AA`) band gaps E_{gap} (indirect, direct in M, optical) and exciton binding energy $E_b^{exc} = E_{gap}^{M} - E_b^{opt}$ in eV. A) With respect to GW number of bands N_B and energy cut-off E cut (indicated in the legend, in eV); B) With respect to number of iteration i in G_iW_0 and G_iW_i calculations. 12 x 12 x 4 k-grid was used. Green points are experimental values.[1,2]

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

	E_{gap}^{indir}	$E_{gap}^{M/K}$	E_{gap}^{opt}	E_b^{exc}
Calc. AA′	6.08	6.53	5.71	0.82
Calc. AB	6.17	6.39	5.61	0.78
Exp.[1,2]	6.08	6.42	5.69	0.73

Results

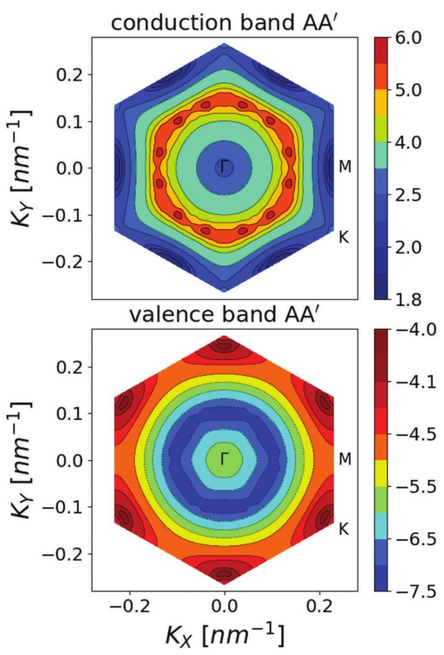

Figure 2. Conduction (top) and valence (bottom) bands of h-BN obtained from G_0W_0 calculation as cuts through the plane G–M–K in the first Brillouin zone.

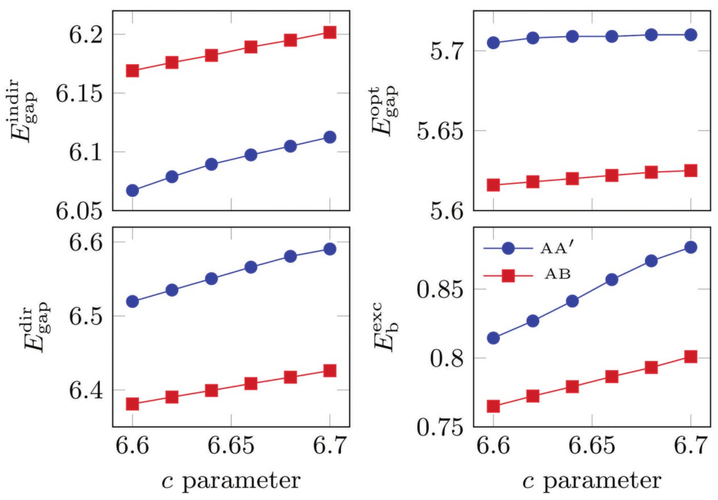

Figure 3. Change in h-BN band gaps E_{gap} (indirect, direct in M, optical) and exciton binding energy $E_b^{exc} = E_{gap}^{M} - E_b^{opt}$ in eV with respect to c lattice parameter. Two h-BN stacking configurations are considered, AA` and AB.

Simple scissor approximation of h-BN band structures

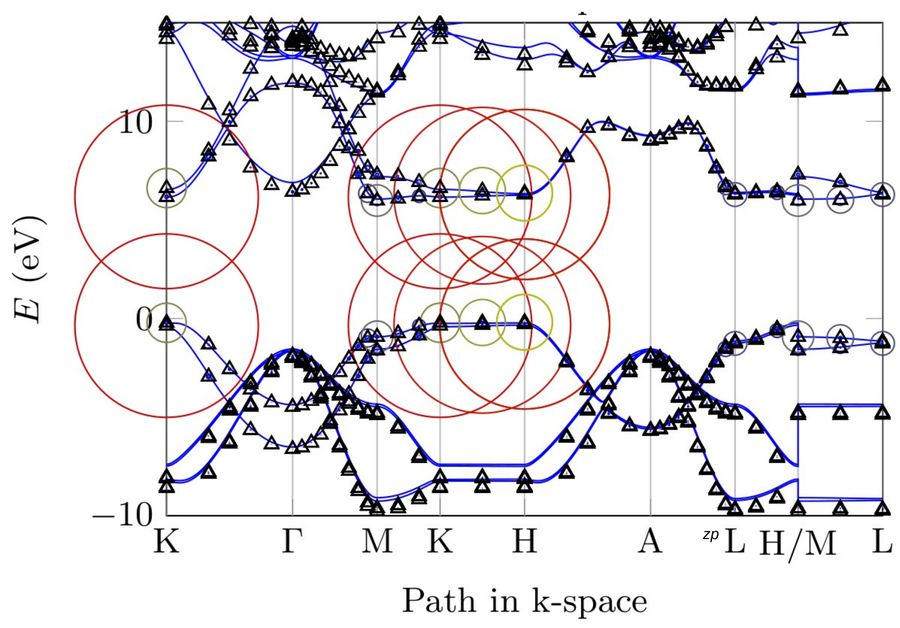

Figure 4. Electronic band structure of h-BN (AA`) from G_0W_0 calculation (black triangles) and electron-hole contributions to first excitonic peak from BSE calculation (represented by radius of colored circles). Scissor corrected DFT (PBE) band structure, DFT+Δ (blue lines), seems a very good approximation to the G_0W_0 band structure. Fermi energy is set as zero.

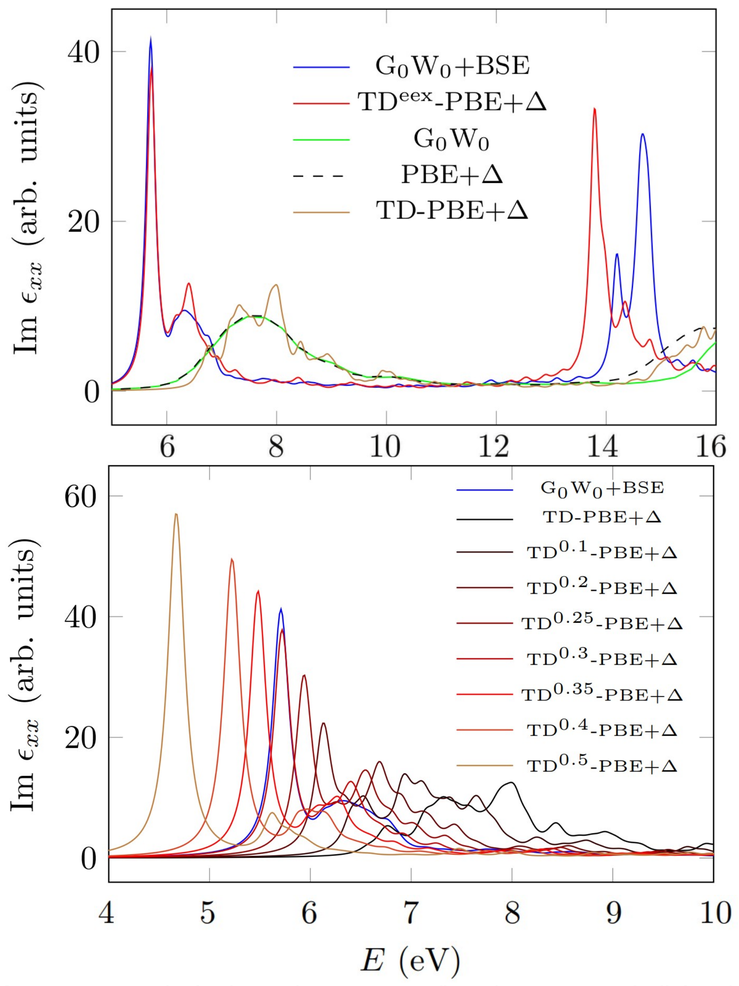

Figure 5. Optical absorption spectra (imaginary part of dielectric function) of h-BN (AA`) using various approximate methods and the reference and the reference G_0W_0+BSE curve (blue line). The electron-hole ladder diagrams in present TD-DFT calculations are approximated by the exact exchange (EEX) and different EEX/GGA ratio is evaluated (and labeled by the EEX part as TD_{EEX}-PBE+Δ). We achieve surprisingly good approximation with EEX/GGA ratio of 0.3/0.7.

Conclusions

Our carefully converged results reveal h-BN as an indirect material (indirect gap ≈6.1 eV) with a huge excitonic effect (≈0.8 eV) in agreement with recent revolutionary experiments[1,2]. 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_0W_0 results, we suggest a computationally cheap scissor corrected DFT approach providing band structure comparable with the G_0W_0 band structure. Time-dependent DFT with a suitable exchange-correlation kernel can provide absorption spectra that mimic the full G_0W_0+BSE spectra.

Acknowledgments

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