Electronic structure and optical properties of 2D hexagonal Boron Arsenide

Mathias Rosdahl Brems[1] and Morten Willatzen[1,2]

[1] *Technical University of Denmark, Department of Photonics Engineering, Kgs-Lyngby, 2800, Denmark*
[2] *Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China*

We examine the electronic structure of two-dimensional hexagonal boron arsenide using k.p theory, method of invariants, and density functional theory. The fundamental band gap occuring at the K point is 0.76 eV, however, this transition is not allowed in the dipole approximation. The conduction band at the Γ point is highly sensitive to strain or electric fields that renders transition into a metallic state possible. We investigate the optical absorption of boron arsenide and the possibilities of tuning by means of strain or electric field.

I. INTRODUCTION

After the discovery of graphene, a large number of two-dimensional materials have been fabricated[1]. Two-dimensional materials show great potential for applications in nanotechnology due to the plentitude of different material combinations, functionalizability, and structural properties possible.

Bulk boron arsenide forms a cubic structure with a remarkably high thermal conductivity and is a promising candidate as a coolant for optoelectronic devices[2]. Recently it was found theoretically that boron arsenide can form a stable two-dimensional hexagonal structure, analogous to the well-known hexagonal boron nitride monolayer[3].

In this work we use the method of invariants and k.p theory to derive analytical models for the band structure of 2D BAs and perform ab initio calculations using density functional theory for comparison and extraction of parameters. The effects of external electric fields and strain are investigated and it is shown that the conduction band at the Γ point is highly tunable allowing for a transition to a metallic state. We next use the derived models to calculate the optical absorption.

II. ELECTRONIC BAND STRUCTURE

We calculate the band structure using density functional theory (DFT) and the projector augmented wave method as implemented in GPAW and the PBE approximation of the exchange-correlation potential. The band structure is shown in Figure 1a, with labels indicating the orbital nature of the bands closest to the Fermi level. The fundamental band gap was found to be 0.76 eV and is located at the K point. We use the method of invariants to derive an analytical expression for the dispersion around the K point. To get a reasonable description of the dispersion without too many parameters we include all terms to fourth order in $\mathbf{q} = \mathbf{k} - \mathbf{K}$. The dispersions of the conduction and valence bands derived from the symmetry analysis are:

$$E_i = \epsilon_i + a_i q_{||}^2 + b_i(q_x^3 - 3q_x q_y^2) + c_i q_{||}^4. \qquad (1)$$

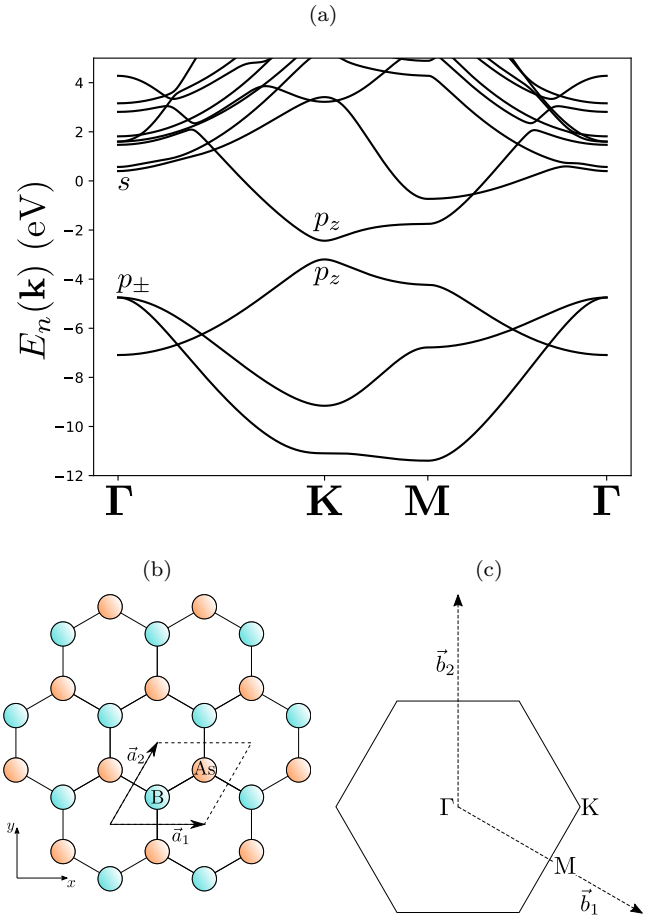

FIG. 1. (a) Electronic band structure of two-dimensional hexagonal boron arsenide. The fundamental band gap occurs at the K point where both conduction and valence band are p_z orbitals. At the Γ point there are two degenerate $p_\pm$ bands and two s states in the conduction band. (b) Crystal structure of hexagonal boron arsenide. The bond length after relaxation is 3.39 Å. (c) First brillouin zone and reciprocal lattice vectors.

where i denotes the band, (q_x, q_y) is the wave vector relative to K, $q_{||} = \sqrt{q_x^2 + q_y^2}$, and a_i, b_i, c_i are model parameters. By doing a polynomial fit to the DFT values on a grid close to $\mathbf{K}$ we extract the model parameters. In figure 2, the contours of the energy bands around K are

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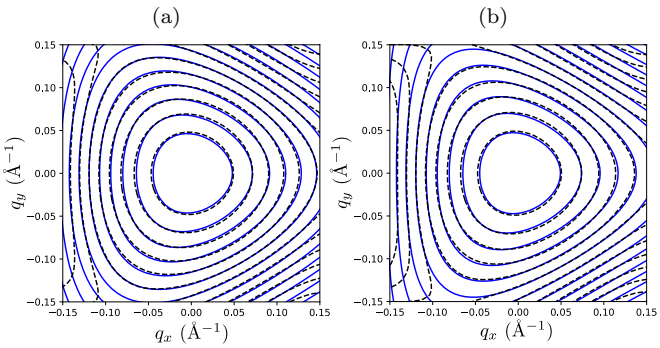

FIG. 2. Contour plot of the (a) valence and (b) conduction bands, around the K point. The blue lines are from the DFT result and the dotted are from the fitted model. Each contour line corresponds to 0.05 eV. The model is seen to fit reasonably well for a a range of energies of around 0.25 eV above/below the band extrema.

plotted with DFT values and the values obtained from the fit.

At the Γ point, the top valence band states have $|p_\pm\rangle$ symmetry while the lower conduction band states are nearly degenerate $|s\rangle$ states. Although the latter states are farther away from the Fermi level than the K point states this can be changed by applying either strain or an external electric field.

III. TUNING BY STRAIN OR ELECTRIC FIELD

A symmetry analysis reveals that at the K point only biaxial strain can affect the band gap. This is seen in Fig. 3a, where we clearly see a linear dependence allowed by the C_{3h} symmetry at the K point. For a high, but realistic strain $\epsilon_{xx} = \epsilon_{yy} = \pm 5\%$, the band gap can be tuned by ± 0.1 eV. However, the conduction band at the gamma point is much more sensitive to strain, and in Ref. 3 they report a transition to a metallic state at $\epsilon_{xx} = \epsilon_{yy} = \pm 14\%$.

We also investigate the band structure under an external electric field perpendicular to the sheet. We find that the conduction band at the Γ point is highly sensitive to electric fields, and for a electric field above $E_z \approx 0.75\,\mathrm{V\,Å^{-1}}$ the material becomes metallic, see Fig. 3b.

IV. OPTICAL PROPERTIES

Interestingly, our symmetry analysis shows that the lowest direct gap isa forbidden dipole transition, in agreement with the findings in Ref. 3, that the onset of optical absorption is at much higher energies. We then investigate two-photon absorption and the effect of excitonic coupling.

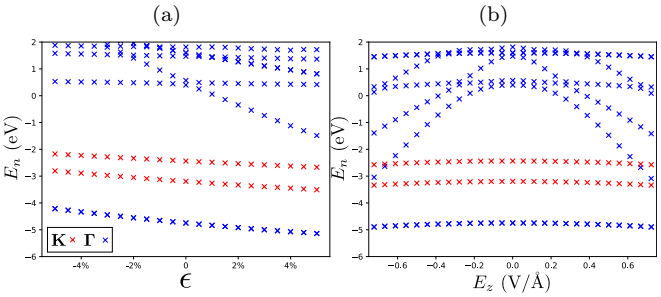

FIG. 3. Eigenvalues at Γ (blue) and K (red) as a function of biaxial strain $\epsilon_{xx} = \epsilon_{yy} = \epsilon$ in (a) and external electric field perpendicular to the atomic layer (b). We see a large sensitivity to external fields in the lowest conduction band at the Γ point.

Secondly, we investigate the optical absorption at large electric fields or strain where the lowest allowed dipole transition is at the Γ point. In this situation, the $|p_\pm\rangle$ bands couple optically to circular light polarization, and the onset of absorption can be effectively tuned.

V. CONCLUSION

We have developed analytic models for the electronic structure of two-dimensional hexagonal boron arsenide and extracted the parameters from DFT calculations. The effects of external fields have been investigated showing a transition from the semiconducting to a metallic state within realistic values of an external electric field. We also discuss the optical properties of 2D boron arsenide.

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