Supplementary Information: Tunable optical properties of multilayers black phosphorus

Tony Low, A. S. Rodin, A. Carvalho, Yongjin Jiang, Han Wang, Fengnian Xia and A. H. Castro Neto

I. BANDSTRUCTURES AND EFFECTIVE MASSES CALCULATED FROM FIRST PRINCIPLES

A. Calculation method

We use first-principles calculations based on density-functional theory to obtain the bandstructure of monolayer, multilayer and bulk black phosphorus (Fig. 1). These were performed using the QUANTUM ESPRESSO code.[1] The core electrons were treated using the projector augmented wave method.[2] The exchange correlation energy was described by the PBE functional, as the PBEsol functional[3], used previously for the monolayer[5] was found to give a vanishing bandgap in the case of the bulk crystal. The Kohn-Sham orbitals were expanded in a plane-wave basis with a cutoff energy of 70 Ry. The Brillouin-zone (BZ) was sampled using 10×8 points following the scheme proposed by Monkhorst-Pack[4]. The lattice parameters thus found were 4.57, 3.51, and 11.69 Å along the x, y and z directions, respectively.

B. Effective masses

The energy derivatives were calculated using centered finite differences, with steps in the range $0.01\times(2\pi/a)$-$0.04\times(2\pi/a)$, where a is the lattice parameter along the x direction. Results are given in table I. The effective masses do not vary much with the number of layers, with exception of m_{vy}. For the monolayer, the derivative $\partial^2 E_v/\partial k_y^2$ is very small at Γ, and therefor the effective mass in this point could not be determined. As the number of layers increases, m_{vy} tends to $2.0m_0$.

TABLE I: Calculated effective masses for bulk black phosphorus. All masses are in units of the electron rest mass m_0.

bulk				
band	point	m_{xx}	m_{yy}	m_{zz}
E_v	Z	0.07±0.03	2.0±0.8	0.46±0.01
E_c	Z	0.07±0.02	1.3±0.1	0.25±0.01
E_c	Γ	0.15±0.01	1.2±0.1	1.60±0.03
tri-layer				
E_v	Γ	0.12±0.01	2.8±0.1	
E_c	Γ	0.12±0.06	1.27±0.02	
bi-layer				
E_v	Γ	0.13±0.01	4.3±0.1	
E_c	Γ	0.14±0.01	1.31±0.01	
monolayer				
E_v	Γ	0.13±0.04	very large	
E_c	Γ	0.18±0.04	1.23±0.01	

[1] P. Giannozzi et al., J. Phys.-Cond. Matter **21**, 395502 (2009).
[2] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[3] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).
[4] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[5] A. Rodin, A. Carvalho and A.H. Castro-Neto, submitted.

FIG. 1: (Color online) Band structure of monolayer (ML), bilayer (2L), trilayer (3L) and bulk black phosphorus as obtained from DFT calculations. Occupied and unoccupied bands are represented in blue and red, respectively.