Many-Body Quantum Monte Carlo Study of 2D Phosphorene

***K. Tokár*[1,2)], *I. Štich*[1)]**

[1]Center for Computational Materials Science, Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia
[2]Advanced Technologies Research Institute, Faculty of Materials Science and Technology, Slovak University of Technology, Trnava, Slovakia

Motivation

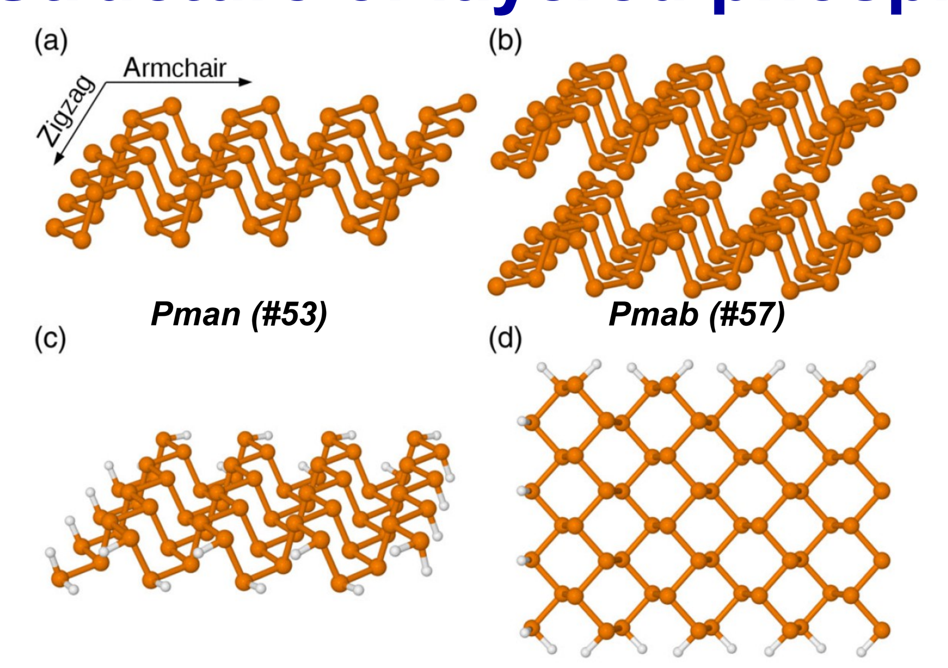
- Two-dimensional materials (**2D**) revolutionized science and technology due to their unique electronic, optical, thermal, spin, and magnetic properties and their tunability.
- The layered **black phosphorus (BP) 2D** structures feature **a direct band gap** at the **Γ-point** from single-layer structure up to bulk phosphorus in the range of **0.3–2 eV,** whereas standard **Density Functional Theory (DFT) functionals** or **GW** technique tend to **underestimate** these values systematically.
- Phosphorene material has particularly advantages in terms of the band gap manipulation:
  - varying with the number of layers and therefore band engineering techniques can be readily applied.
  - multilayer **2D** structure can sustain large in-plane compressive or tensile strains in excess of about 10%, compared to just some 2% in the bulk.
  - the band gap is predicted to be strongly susceptible to the dielectric environment of samples.

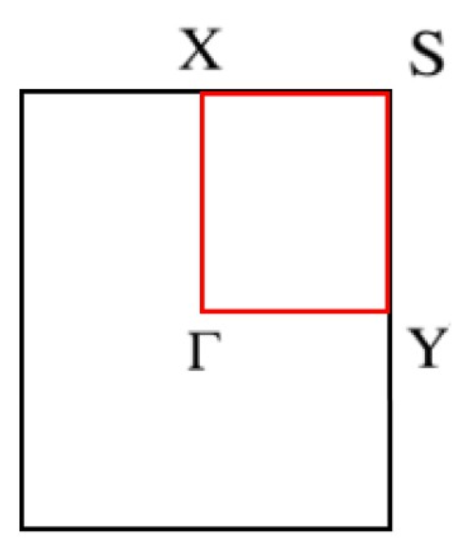
In this work:
We focused on precise simulations of **phosphorene** free-standing **monolayer electronic system** to obtain accurate bounds and reliable estimates of **the fundamental band gap** and **cohesion energy**. The quantum **Monte Carlo (QMC)** methodology was empoyed as an efficient tool to benchmark **electronic structure calculations** in **2D** layered systems.

Simulation methods

The fundamental gap Δ_f was determined from both extended and cluster approximants with the experimental values of lattice parameters in the black phosphorus crystal. The gap Δ_f was extracted as the singlet-singlet vertical excitation energy: $\Delta_f \approx E_v \equiv E_1 - E_0$, with E_0 and E_1 being, respectively, the ground and the first excited states obtained by the fixed-node **QMC** method not allowing any relaxation of the **DFT** nodal hypersurfaces due to the **HOMO → LUMO** electron excitation. No vibronic effects were included.
Periodic setup: E_0 and E_1 were computed from **DMC (diffusion Monte Carlo)** energies in the fixed-node approximation using the **VMC (variational Monte Carlo) trial wave functions** with the nodal hypersurfaces provided by the generalized gradient approximation **Perdew-Burke-Ernzerhof (PBE) (DMC@PBE)** and **hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) (DMC@B3LYP)** at the **Γ-point** of the **Brillouin** zone, optimizing the short-range correlations of **the Jastrow factor.** The consistency check using both **PBE** and **B3LYP DFT** nodal hypersurfaces was performed as at the **DFT** level the **HOMO-LUMO** gaps of the two **DFT** functionals differ by **≈ 1 eV**. The **Yeh-Berkowitz** modification in the **3D Ewald summation** technique for systems with a slab geometry periodic in two dimensions and have a finite length in the third dimension was adopted.
Cluster setup: The **B3LYP (DMC@B3LYP)** nodal hypersurfaces were used.The ground-state energy E_0 was also used to determine the **cohesion energy** E_{coh}.

Structure of layered phosphorene

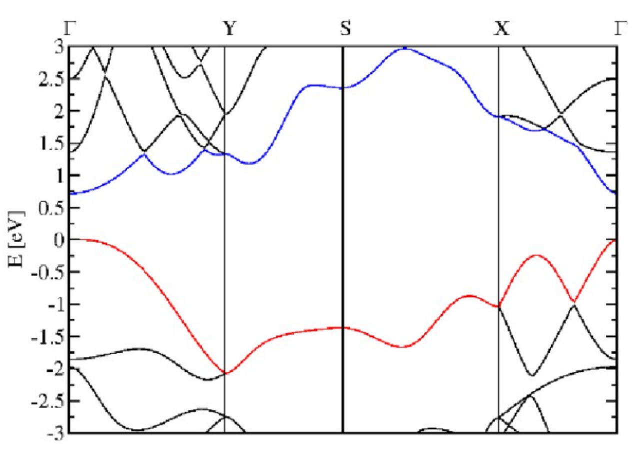




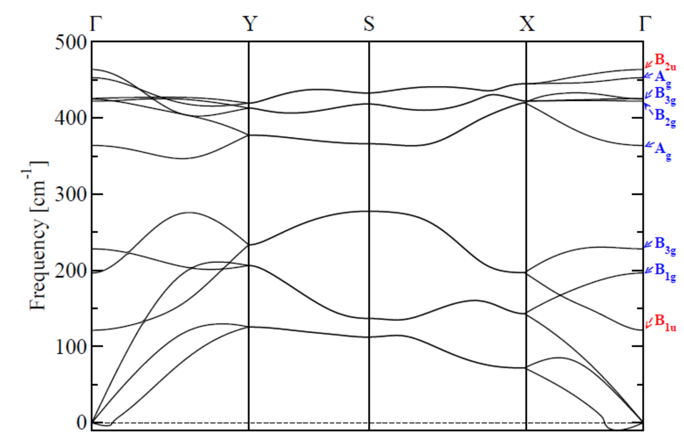
2D Brillouin zone of multilayer phosphorene

Atomic structure of **(a)** single-layer and **(b)** few-layer phosphorene. Characteristic armchair and zigzag directions are indicated in **(a)**. Side and top views of a **4 × 4 cluster approximant**, with saturated edge bonds, are presented in **(c)** and **(d)**, respectively.

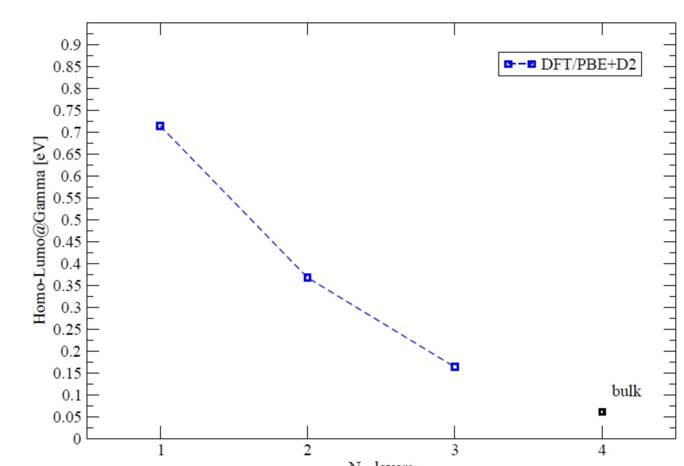
Electronic and dynamical properties of phosphorene - DFT



Electronic band structure of monolayer with direct band gap situtated at **Γ-point** at **GGA PBE-D2** level.Red/blue solid line denotes **Valence BandMaxima/Conduntance Band Minima** (**VBM**/**CBM**).

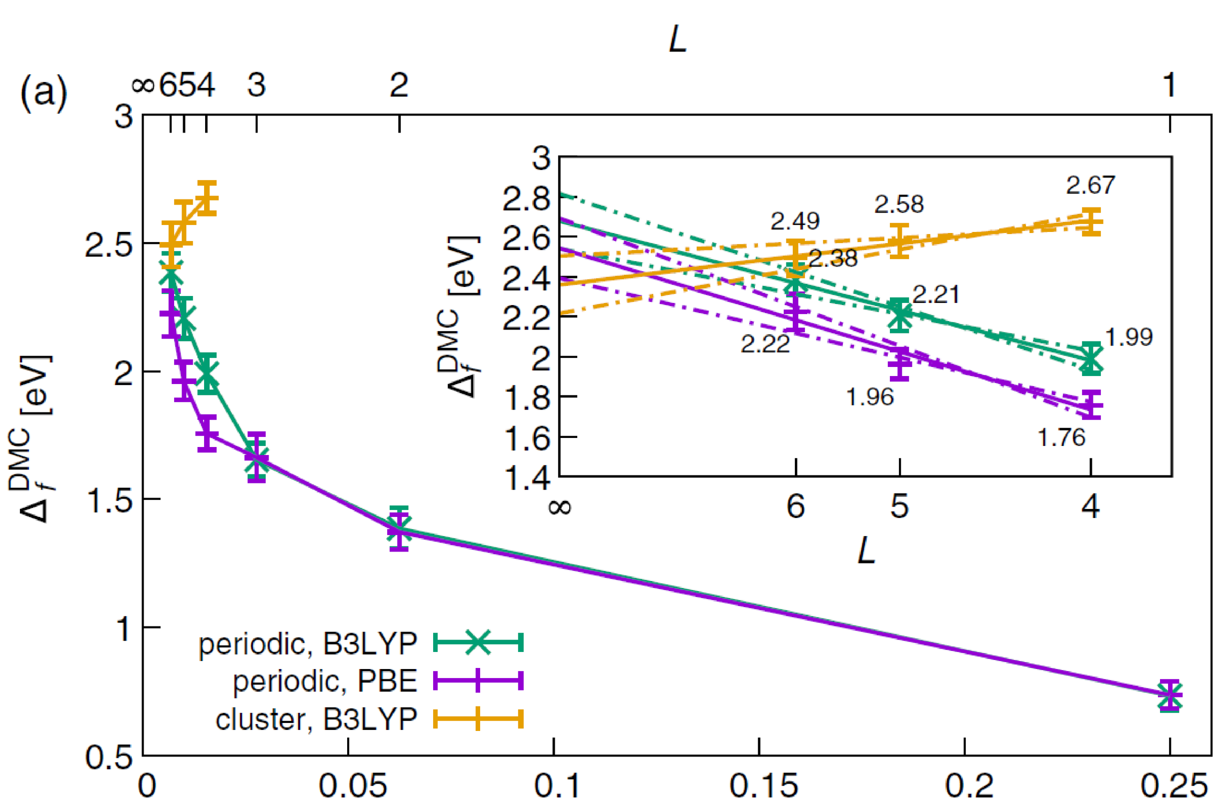


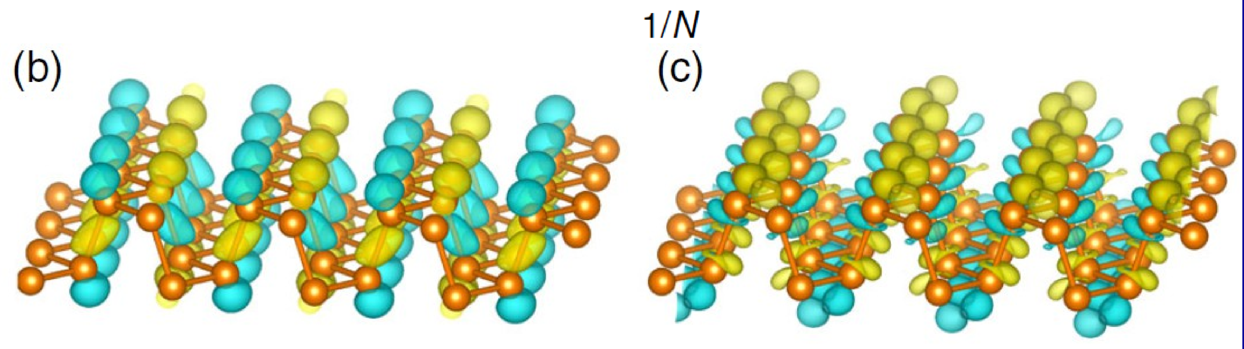
Phonon dispersion curves and optical **Raman** active vibrational modes in **monolayer** indicating the mechanical stability of **2D** lattice in unstrained state. (12 modes, Spg: ***Pman(#53)***).



Evolution of band gap with **the number** of layers as calculated in **GGA PBE-D2** functional. The standard DFT functionals tend to underestimate the experimental values by **> 1 eV**.

QMC finite-size scaling of fundamental gap





QMC Band gap extrapolations

Periodic system

DMC@B3LYP	**2.68 +/- 0.14 eV**
DMC@PBE	**2.54 +/- 0.15 eV**

Cluster approximants

DMC	**2.54 +/- 0.15 eV**

Optical gap (universal scaling)

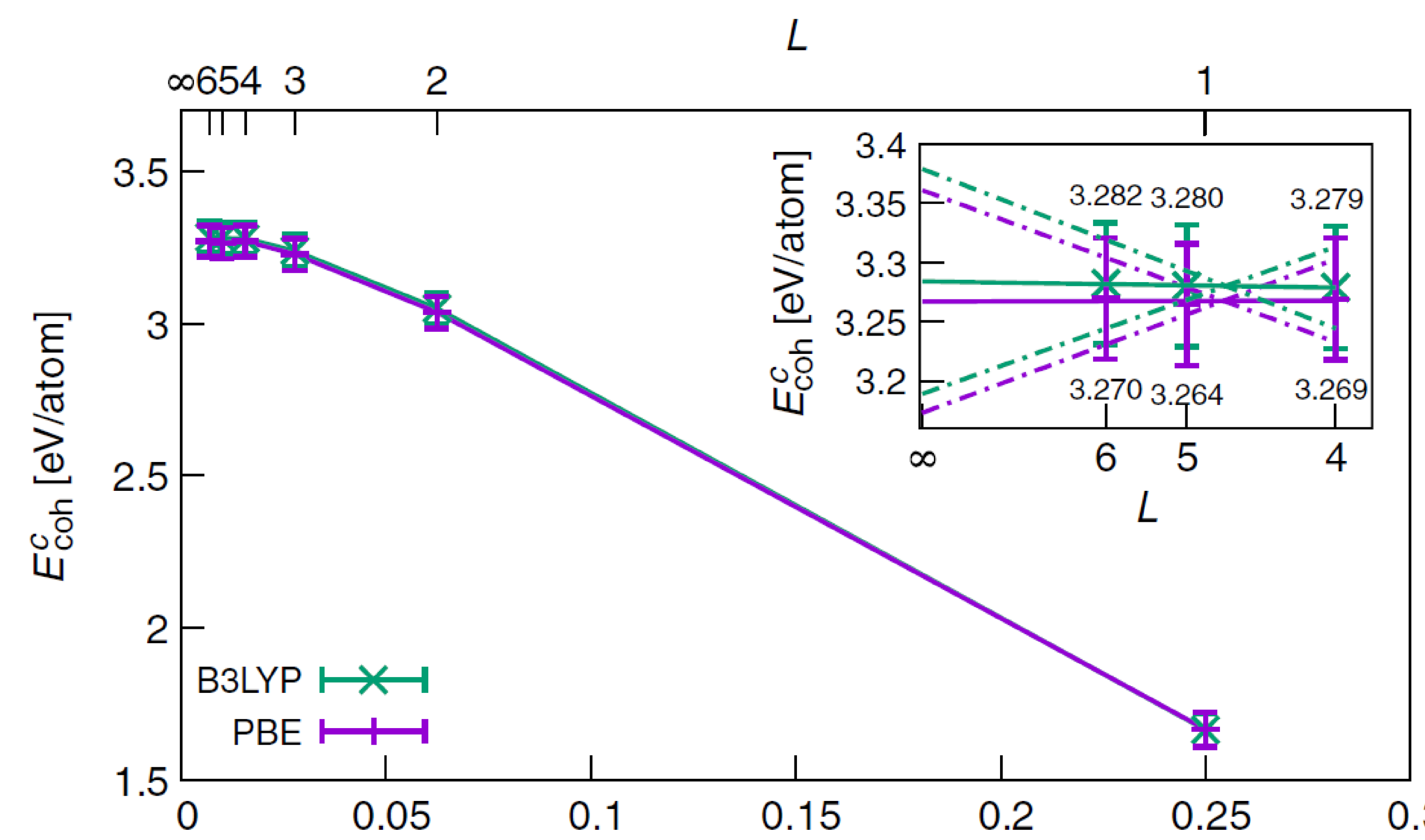
$\Delta_o = \Delta_f - \Delta_b = \Delta_f - 0.27\Delta_f \approx 1.75$ **eV**

Experimental values [eV]

STS	PLES	PL	OA
2.0	2.2 +/- 0.1	2.1 +/- 0.02	1.6
		2.0 +/- 0.04	1.5
		1.3 +/- 0.02	1.7

(a) Finite-size scaling of the **QMC** fundamental gap Δ_f, with the number of atoms N in the periodic supercell (green line, **DMC@B3LYP**; purple line, **DMC@PBE**) and in the cluster approach (yellow line, **DMC@B3LYP**) along the series of **L × L** supercell approximants, **L = 1–6** for the periodic setup and **L = 4–6** in the cluster approach. The inset shows an enlargement of the scaling for large N with the dashed lines showing the linear extrapolation to the infinite-size limit. **(b)** Localisation of **B3LYP DFT HOMO (left)** and **(c) LUMO (right)** orbitals. Both represent **Γ-point Bloch** states, **HOMO** being a superposition of bonding orbitals [mostly **σ(p_z)**] along the vertical **P–P** bonds while **LUMO** is its antibonding counterpart.

DMC fixed-node corrected cohesion energy



Cohesion energy E_{coh} in **DMC@PBE** (purple curve) and **DMC@B3LYP** (green curve) treatment. The error bars are smaller than the size of the points. The inset shows the enlargement of the linear scaling for large N with extrapolation to infinite system size.

Thermodynamic path model:
P_4 molecule → **bulk black phosphorus** →**monolayer** :: including also the **QMC** calculation of the **van der Waals** binding energy contribution.

Periodic calculations

E_{coh} **DMC@PBE**	**3.27 +/- 0.10 eV/atom**
E_{coh} **DMC@B3LYP**	**3.28 +/- 0.06 eV/atom**

Clusters

E_{coh} **DMC@B3LYP**	**3.26 +/- 0.05 eV/atom**

Bulk black phosphorus cohesion energy (experimental)

E_{coh} **= 3.43 eV/atom**

Conclusions and Outlook

- Systematic **fixed-node QMC** calculations of **the quasiparticle band gap** of freestanding single-layer phosphorene were performed (> 10^7 core hours).
- The optical gap of phosphorene monolayer extracted from universal scaling between the gap and optical binding energy is comparable with **photoluminiscence and optical absorption** experiments.
- Accurate **ground state** is limited only by the (corrected) fixed-node errors as evidenced from the calculated cohesion and its agreement with available indirect experimental data.
- **QMC fixed-node** cuttingedge calculations are **feasible** for a range of **2D** systems and **QMC** methods should be expected to pawe the way to the top of the list of the toolkit for studying **2D** systems.

References

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