Electronic structure and properties of a few-layer black phosphorus

Mikhail Katsnelson

Main collaborators:

Sasha Rudenko    Shengjun Yuan    Rafa Roldan    Sergey Brener    Clément Dutreix    Zhenya Stepanov    Edo van Veen
Zoo of 2D materials

Plenty of 2D materials starting from graphene

Graphene

Silicene, germanene

Buckling

Semimetals (graphene), semiconductors, metals, superconductors, broad-gap insulators...

**Topical Review**

**Germanene: the germanium analogue of graphene**

A Acun, L Zhang, P Bampoulis, M Farmanbar, A van Houwel, N Rudenko, M Lingenfelder, G Brocks, B Poelsema, M I Katsnelson, and H J W Zandvliet
Antimony

Electronic properties of single-layer antimony: Tight-binding model, spin-orbit coupling, and the strength of effective Coulomb interactions

A. N. Rudenko,¹* M. I. Katsnelson,¹ and R. Roldán²

The same buckled structure as for silicene or germanene

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_\Sigma^{\Gamma\Sigma}$</th>
<th>$E_\Sigma^{\Gamma\Gamma}$</th>
<th>$m_\Gamma^1$</th>
<th>$m_\Gamma^2$</th>
<th>$m_\Gamma$</th>
<th>$m_\Sigma^x$</th>
<th>$m_\Sigma^y$</th>
<th>$m_K$</th>
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<tr>
<td>DFT</td>
<td>1.26</td>
<td>1.57</td>
<td>0.08</td>
<td>0.45</td>
<td>0.09</td>
<td>0.14</td>
<td>0.45</td>
<td>0.39</td>
</tr>
<tr>
<td>TB</td>
<td>1.15</td>
<td>1.40</td>
<td>0.06</td>
<td>0.44</td>
<td>0.06</td>
<td>0.13</td>
<td>0.42</td>
<td>0.36</td>
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<tr>
<td>DFT+SO</td>
<td>0.99</td>
<td>1.25</td>
<td>0.10</td>
<td>0.19</td>
<td>0.08</td>
<td>0.14</td>
<td>0.46</td>
<td>0.40</td>
</tr>
<tr>
<td>TB+SO</td>
<td>0.92</td>
<td>1.14</td>
<td>0.09</td>
<td>0.11</td>
<td>0.06</td>
<td>0.13</td>
<td>0.43</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Semiconductor. Strong spin-orbit coupling

$\lambda = 0.34$ eV
What is BP?

For historical and basic review: Ling et al, PNAS 112, 4523 (2015)

Bridgman (1914)

Black P – stable allotrope of P at ambient conditions

Layered compound, 4 atoms per unit cell, bond lengths within layer 0.222 and 0.224 nm, between layers 0.53 nm

Tunable gap, depending on number of layers
Other allopropes of phosphorus

White phosphorus is most know to a general public (e.g., “phosphorescence”)
Gap problem: conventional density functional (LDA or GGA) usually strongly underestimates gaps in semiconductors – more advanced methods should be used like GW

Quasiparticle equation:

\[
(T + V_{n-e} + V_H) + \int \left[ \Sigma_{\mathbf{r}, \mathbf{r}', E_{nk}} \right] \psi_{nk}(\mathbf{r}') d\mathbf{r}' = E_{nk} \psi_{nk}(\mathbf{r})
\]

Self-energy in the GW approximation:

\[
\Sigma^{GW}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G(\mathbf{r}, \mathbf{r}'; \omega + \omega') W(\mathbf{r}, \mathbf{r}'; \omega') e^{i\omega'q} d\omega'
\]
Computations of electronic structure II

Bulk BP

GW fixes the band gap problem

And self-consistency makes the gap accurate, 0.35 eV!
### TABLE I. Band gaps (in eV) for monolayer ($n = 1$), multilayer ($n = 2, 3$), and bulk BP ($n = \infty$) calculated at different levels of theory.

In the notation of different methods, $G_0$ and $W_0$ imply that the Green’s function and screened Coulomb repulsion in the $GW$ approach are calculated non-self-consistently on the basis of wave functions derived from density functional (GGA) or hybrid functional (HSE) calculations, whereas $G'$ means a self-consistent calculation of the Green’s function. $W'_0$ and $W_0$ denote that the screened Coulomb interaction is calculated by using the general plasmon pole model [39] and RPA [40], respectively.

<table>
<thead>
<tr>
<th></th>
<th>$GW_0@GGA^a$</th>
<th>TB Model $^a$</th>
<th>$GW_0@GGA^b$</th>
<th>$GW_0@HSE^c$</th>
<th>$G_0W_0@GGA^d$</th>
<th>$G_0W'_0@GGA^e$</th>
<th>HSE $^f$</th>
<th>GGA $^g$</th>
<th>Expt.</th>
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<tr>
<td>$n = 1$</td>
<td>1.85</td>
<td>1.84</td>
<td>1.94</td>
<td>2.41</td>
<td>1.60</td>
<td>2.00</td>
<td>1.00–1.91</td>
<td>0.80–0.91</td>
<td>2.05$^h$</td>
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<tr>
<td>$n = 2$</td>
<td>1.16</td>
<td>1.15</td>
<td>$\sim 1.65$</td>
<td>1.66</td>
<td>1.01</td>
<td>$\sim 1.30$</td>
<td>1.01–1.23</td>
<td>0.45–0.60</td>
<td>—</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>0.84</td>
<td>0.85</td>
<td>$\sim 1.35$</td>
<td>1.20</td>
<td>0.68</td>
<td>$\sim 1.05$</td>
<td>0.73–0.98</td>
<td>0.20–0.40</td>
<td>—</td>
</tr>
<tr>
<td>$n = \infty$</td>
<td>0.35</td>
<td>0.40</td>
<td>0.43</td>
<td>0.58</td>
<td>0.10</td>
<td>0.30</td>
<td>0.18–0.39</td>
<td>0.00–0.15</td>
<td>0.31–0.35$^i$</td>
</tr>
</tbody>
</table>

$^a$This work.

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A very strong dependence of the gap on number of layers!
Cohesive energy: QMC calculations

VdW interactions: weak and can hardly be described by conventional density functional

How can it be? How weak cohesive energy is consistent with a huge dependence of interlayer hopping to the gap?!
Computations of electronic structure V

GW is qualitatively important also for single layer

GW predicts a *direct* band gap
Mapping on tight binding model I

Single layer BP

- Valence and conduction band edges are isolated
- ...and have predominantly $p_z$ character

$H_{GW}^k$ \rightarrow \rightarrow \rightarrow H_{TB}^R$

**multiorbital Hamiltonian** \rightarrow \rightarrow \rightarrow **single-orbital Hamiltonian**
Mapping on tight binding model II

Minimal model for single-layer BP (phosphorene)

\[ H = \sum_{i \neq j} t_{ij}^{\|} c_i^{\dagger} c_j \]

\[ \Delta_{g}^{(1)}(\Gamma) \approx 2t_2^{\|} + 4t_1^{\|} \]

Band gap appearance criterion: \( t_2^{\|} > 2|t_1^{\|}| \)

A. Rudenko, M. Katsnelson, PRB 89, 201408 (2014)
Mapping on tight binding model III

Minimal model for bilayer BP

\[ H = \sum_{i \neq j} t_{ij}^\parallel c_i^\dagger c_j + \sum_{i \neq j} t_{ij}^\perp c_i^\dagger c_j \]

- Intralayer term
- Interlayer term

\[ t_1^\parallel \approx -1.5 \text{eV} ; \quad t_2^\parallel \approx +3.7 \text{eV} ; \quad t_1^\perp \approx 0.5 \text{eV} \]

\[ \Delta_g^{(2)} \]

\[ \Gamma X S Y \Gamma \]

\( t_1^\perp \) accounts for the narrowing of a gap in multilayer BP

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A. Rudenko, M. Katsnelson, PRB 89, 201408 (2014)
The main difference with graphene: a very large and positive second-neighbour hopping in plane; interlayer hopping is roughly of the same order of magnitude
Effect of interlayer bias: anisotropic Dirac cones

Linear crossing in $x$ direction and parabolic in $y$ direction

Bias leads to gap opening and formation of anisotropic conical points

A. Rudenko, S. Yuan, M. Katsnelson, PRB 92, 085419 (2015)
Effect of interlayer bias: anisotropic Dirac cones II

Insulator-semimetal transition with formation of anisotropic Dirac cones

S. Yuan, MIK, R. Roldan, PRB 93, 245433 (2016)
Experiment: K deposite

Observation of tunable band gap and anisotropic Dirac semimetal state in black phosphorus

Jinmin Kim, Seung Su Bahn, Sae Hee Ryu, Yeongsup Sohn, Soohyung Park, Byeong-Gyu Park, Jonathan Denlinger, Yeonjin Yi, Hyoung Joon Choi, Keun Su Kim
High-frequency laser fields

Quickly oscillating strong electric field means quickly oscillating effective hopping

\[ t_{ij} \to t_{ij} \exp \left\{ \frac{ie}{\hbar c} \int_{\tilde{r}_j} d\tilde{r}' \vec{A}(\tilde{r}', t) \right\} \]

At very high frequency effective static Hamiltonian should exist

Classical analog: Kapitza pendulum

One needs to develop efficient perturbative theory in inverse frequency of the laser field

In classical mechanics: Bogoliubov, Krylov ...


http://butikov.faculty.ifmo.ru/Russian/ParamPendulumKIO.pdf
Laser-induced topological transitions

C. Dutreix, E. A. Stepanov & MIK, Phys. Rev. B 93, 241404(R) (2016)

In bilayer, electric bias creates insulator-semimetal transition; but with high-frequency laser field one can make it for the single layer

Averaging over high-frequency field:

High-frequency expansion (in $1/\Omega$) for the effective static Hamiltonian

$$
\tilde{H}_1 = H_0, \quad \tilde{H}_2 = -\frac{1}{2} \sum_{m \neq 0} \frac{[H_m, H_{-m}]}{m},
$$

$$
\tilde{H}_3 = \frac{1}{2} \sum_{m \neq 0} \frac{[[H_m, H_0], H_{-m}]}{m^2} + \frac{1}{3} \sum_{m \neq 0} \sum_{n \neq 0, m} \frac{[[H_m, H_{n-m}], H_{-n}]}{mn},
$$

$$
H_m = \int_{-\pi}^{+\pi} \frac{d\tau}{2\pi} e^{i m \tau} H(\tau)
$$

Very important: NN and NNN hopping are renormalized differently, and both are very relevant for the electronic structure!
Laser-induced topological transitions II

Single-particle Hamiltonian (only bands), Peierls substitution

\[ A(t) = (A_x \cos \Omega t, A_y \sin[\Omega t - \phi], 0) \]

Second-order effective static Hamiltonian

On can pass from band insulator to topological insulator or to semimetal

Elliptic polarization: topological insulator
Linear polarization: semimetal, no gap

Lowest-energy bands in semimetallic phase

FIG. 3. Phase diagrams for electric fields with elliptic (left) and linear (right) polarizations. Light purple areas refer to band insulating (BI) phases characterized by \( e^{i\gamma e} = +1 \). Dark purple areas correspond to semimetallic (SM) and topological insulating (TI) phases in which \( e^{i\gamma e} = -1 \). Components \( A_x \) and \( A_y \) are given in Å\(^{-1}\).
Optics

Two approaches for $\sigma_{xx}(\omega)$:

1. **k-space (based on GW approximation)**

$$\sigma_{\alpha\beta}(\omega) = \frac{i\hbar}{N_k \Omega} \sum_k \sum_{mn} \frac{f_{mk} - f_{nk}}{\epsilon_{mk} - \epsilon_{nk}} \frac{\langle nk|j_\alpha|m_k\rangle \langle m_k|j_\beta|nk\rangle}{\epsilon_{mk} - \epsilon_{nk} - (\hbar\omega + i\eta)}$$

2. **R-space (tight-binding propagation method)**

$$\sigma_{\alpha\beta}(\omega) = \lim_{\epsilon \to 0^+} \frac{e^{-\beta\omega} - 1}{\omega \Omega} \int_0^\infty e^{-\epsilon t} \sin \omega t \times 2 \text{Im} \langle \varphi|f(\mathcal{H}) J_\alpha(t) [1 - f(\mathcal{H})] J_\beta|\varphi\rangle \, dt$$

Chebyshev polynom expansion, etc. – up to $10^9$ sites

Successfully applied to graphene
Two approaches for $\sigma_{xx}(\omega)$:

- **GW (k-space)**
  - Primitive cell (four atoms)
  - $4.4 \, \text{Å}$

- **TB (R-space)**
  - Large supercell ($\sim 10^7$ atoms)
  - $0.7 \, \mu\text{m}$

Excellent agreement up to $\omega \sim 2.5 \, \text{eV}$

A. Rudenko, S. Yuan, M. Katsnelson, PRB 92, 085419 (2015)
Hyperbolic plasmons

Just to remind:
crystallooptics

\[ \vec{k} = k_0 \vec{n}, \quad k_0 = \frac{\omega}{c} \]

\[ \det |n^2 \delta_{ij} - n_i n_j - \varepsilon_{ij}(\omega)| = 0 \]

\[ \varepsilon_{ij}(\omega) = \delta_{ij} + \frac{4\pi i}{\omega} \sigma_{ij}(\omega) \]

Main axes \( \varepsilon_{ij} = \varepsilon_i \delta_{ij} \)

If \( \varepsilon_x \varepsilon_y < 0 \)

\[ n_z = 0 \]
\[ n^2 = \varepsilon_z \]
\[ \frac{n_x^2}{\varepsilon_y} + \frac{n_y^2}{\varepsilon_x} = 1 \]
\[ \frac{k_x^2}{\varepsilon_y} = \frac{k_y^2}{\varepsilon_x}, \quad k >> k_0 \quad (c \to \infty) \]
Hyperbolic plasmons in black P


Black P is anisotropic – one can find the region where $\varepsilon_x \varepsilon_y < 0$

Manipulations by strain

$$
t_{ij}(r_{ij}) = t_{ij}(r_{ij}^0) \left(1 - \beta_{ij} \frac{|r_{ij} - r_{ij}^0|}{|r_{ij}^0|}\right)
$$

Or by optical gain (nonequilibrium occupation)

Quasi-equilibrium distribution

$$
n_F(E) = \theta(E) f(E + \frac{E_g}{2} + \Delta\mu) + \theta(-E) f(E - \frac{E_g}{2} - \Delta\mu)
$$

$$
f(E - \mu) = \frac{1}{e^{(E-\mu)/kT} + 1}
$$

$T = 300$ K
Hyperbolic plasmons in black P II

One can manipulate black (hyperbolic) regions

\[ \sigma_0 = \frac{\pi e^2}{2h} \]

FIG. 2. (a) The optical conductivity of bilayer black phosphorus with photo-doping \( \Delta \mu = 0.5 \) eV. (b) A close-up of the region where \( \text{Re}(\sigma_{yy}) < 0 \), showing a new hyperbolic region (shaded) for \( \omega < 1.27 \) eV. (c) The corresponding band structure around the \( \Gamma \)-point, with the population-inverted pockets shown in blue and orange.

FIG. 3. The hyperbolic region (indicated in black lines) for different tuning parameters. The visual spectrum is indicated in color.
Large scale TB simulations for disordered BP

Transport and optical properties of single- and bilayer black phosphorus with defects

Shengjun Yuan, A. N. Rudenko, and M. I. Katsnelson

Point defects: missing atoms

Puddles: Gaussian electrostatic potential

\[ v_i = \sum_{k=1}^{N_{\text{imp}}} U_k \exp \left( -\frac{|r_i - r_k|^2}{2d^2} \right) \]
Probing Single Vacancies in Black Phosphorus at the Atomic Level
Brian Kiraly, Nadine Hauptmann, Alexander N. Rudenko, Mikhail I. Katsnelson, and Alexander A. Khajetoorians

STM observation of vacancy states

Comparison with calculations allows to attribute peaks to vacancies

Figure 2. (a) Three-dimensional representation of a constant-current STM image with a distribution of single vacancies in black phosphorus ($V_S = -0.1$ V, $I_t = 200$ pA, size = 62 nm x 48 nm, color bar = 0–0.2 nm). (Inset) Line profiles taken across the vacancies labeled 1L, 2L, and 3L in (a). Constant-current STM image of a single vacancy at (b) sublattice A and (c) at sublattice B ($V_S = -0.1$ V, $I_t = 200$ pA, scale bar = 2 nm). (d) Tight-binding calculations of the charge density of a single vacancy in black phosphorus located at (d) sublattice site A and (e) sublattice site B (scale bar = 1 nm).

STM image of bulk black P – atomically flat surface

Gap 0.32 eV
STM observation of vacancy states II

Vacancies in sublattice A and B, first and second layers

Friedel oscillations around vacancies
Several metastable configurations of Co atom, switching between them is possible between two states of hollow sites (top site is separated from them).

Fig. 1 Adsorption and switching of Co on BP. a Six Co species on BP as deposited at $T < 5$ K ($V_s = -400$ mV, $I_t = 20$ pA, scale bar = 1 nm). Boxed atoms show species related through mirror plane along [010]. b Four atoms from a have been switched into $J_{H,low}$ ($V_s = -400$ mV, $I_t = 20$ pA, scale bar = 1 nm). c Two atoms from b have been switched into $J_{H,high}$ ($V_s = 420$ mV and $J_{H,high}$ to $J_{H,low}$ with $V_s = -680$ mV. Approximate threshold biases for switching ($V_{th}$) are noted. Orange circles indicate the tip position during the switching sequence. The inset images showing before and after configurations are 4 nm x 4 nm in size. 

Schematic representation of adsorption energy curves for Co species on BP.
DFT+U calculations (U = 4 eV) confirm two metastable states for Co in hollow site
Co atom at black-P surface III

![Graph showing energy vs. Hubbard-U](image)

- **Energy (eV)**
- **Hubbard-U (eV)**

![Imaginary images of Co atom at different Hubbard-U values](images)

**a**

**b**

**c**

![DOS plots for Spin-Down and Spin-Up](plots)
Exchange interaction of Co atoms

D. Badrtdinov, A. Rudenko, MIK, V. Mazurenko (2020)

\[ \hat{\mathcal{H}}_{12} = J_{12} \hat{S}_1 \hat{S}_2 \]

Change of effective exchange interaction via orbital states of Co atoms

Different signs of interactions for high spin and low-spin configurations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>HH</th>
<th>HL</th>
<th>LL</th>
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</thead>
<tbody>
<tr>
<td>Exchange interaction (meV)</td>
<td>13.3</td>
<td>4.8</td>
<td>-51.2</td>
</tr>
<tr>
<td>Co-Co distance $R$ (Å)</td>
<td>4.34</td>
<td>4.47</td>
<td>4.37</td>
</tr>
<tr>
<td>Co-BP distance $d$ (Å)</td>
<td>1.37</td>
<td>1.34/1.00</td>
<td>1.01</td>
</tr>
<tr>
<td>Total magnetic moment ($\mu_B$)</td>
<td>4.20</td>
<td>3.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Adatoms moments ($\mu_B$)</td>
<td>1.91</td>
<td>1.91/0.55</td>
<td>0.81</td>
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</table>

STM switching (b)
Exchange interaction of Co atoms II

Distance dependence of $J$

Charge density distributions
(H – high spin, L – low spin)
Exchange interaction of Co atoms III

Model analysis in two-site Anderson model

\[ \hat{\mathcal{H}} = \hat{\mathcal{H}}_p + \hat{\mathcal{H}}_d + \hat{\mathcal{H}}_{pd}, \]

\[ \hat{\mathcal{H}}_p = \sum_{\sigma, i \neq j} t_{ij}^{\parallel} \hat{c}_i^{\sigma \uparrow} \hat{c}_j^{\sigma \downarrow} + \varepsilon_0 \sum_{\sigma, i} \hat{c}_i^{\sigma \uparrow} \hat{c}_i^{\sigma \downarrow}, \]

\[ \hat{\mathcal{H}}_{pd} = V \sum_{\sigma} \sum_{i, j} \left( \hat{d}_1^{\sigma \uparrow} \hat{\bar{c}}_i^{\sigma \downarrow} + \hat{\bar{c}}_i^{\sigma \uparrow} \hat{d}_1^{\sigma \downarrow} + \hat{d}_2^{\sigma \uparrow} \hat{\bar{c}}_j^{\sigma \downarrow} + \hat{\bar{c}}_j^{\sigma \uparrow} \hat{d}_2^{\sigma \downarrow} \right) \]

Magnetic force theorem

\[ J_{12} = \frac{1}{2 \pi S^2} \int_{-\infty}^{E_F} d\varepsilon \Im \left( \Delta G_{12}^{\uparrow}(\varepsilon) \Delta G_{21}^{\uparrow}(\varepsilon) \right) \]

Δ spin splitting

\[ \Delta = 1 \text{ eV in all calculations} \]
Screening and plasmons


FIG. 4. Macroscopic static dielectric function $\epsilon_M(q_x, q_y)$ calculated for electron-doped (left), undoped (middle) and hole-doped (right) 1L-BP. Each plot shows distribution of $\epsilon_M$ over the whole BZ. Doping in both electron- and hole-doped cases corresponds to $n = 10^{13}$ cm$^{-2}$.

FIG. 5. Diagonal element of the screened Coulomb interaction matrix $W$ calculated in real space along $x-$ (blue) and $y-$ (red) directions of 1L-BP. Unscrened (bare) interaction $V(r)$ is shown for comparison.

FIG. 6. On-site ($W_{00}$) and nearest-neighbor ($W_{01}$) screened Coulomb interaction in 1L-BP shown as a function of electron doping $n_e$. Red and blue lines are guide for the eye.
FIG. 7. Wave vector and frequency resolved loss function $L(q, \omega)$ (shown in color) calculated for 1L-, 2L-, and 3L-BP. Left and right part of each spectrum corresponds to $y-$ and $x-$ direction, respectively. Red horizontal line marks an energy gap for each system. Note different scales along vertical ($\omega$) axis. In all cases, electron-doping was used, corresponding to $n_e = 10^{13}$ cm$^{-2}$. 
Screening and plasmons III

EELS function for 1, 2, 3 layers of phosphorus: several plasmon branches are seen
Anisotropic screening: experiment

Alex Khajetoorians group (Nijmegen)

Ordering of K at black P surface

B. Kiraly et al, PRL 123, 215403 (2019)
Anisotropic screening: experiment II

Potassium atoms form chains in the directions where screening is the strongest.

**Figure 3. Density-dependent mean interaction potentials.** Mean interaction potentials for varying K adatom density ($n_K$) are shown after annealing the samples to 13.4 K (lowest density), 14.8 K (medium and high density), and approximately 18.0 K (highest density). (a) Mean interaction potential for lowest K density ($n_K = 7.0 \times 10^{11} \text{ cm}^{-2}$) showing isotropic screening behavior. (b) Mean interaction potential at $n_K = 1.4 \times 10^{12} \text{ cm}^{-2}$, revealing the onset of screening anisotropy. (c), (d) Mean interaction potential for $n_K = 2.0 \times 10^{12} \text{ cm}^{-2}$ and $n_K = 1.8 \times 10^{13} \text{ cm}^{-2}$, respectively.
Supplementary Figure 8. Comparison between theoretical and experimental Friedel oscillations. (a) Mean interaction potential with $n_k = 1.8 \times 10^{13}$ cm$^{-2}$ showing elliptical oscillatory envelope characteristic of free-carrier scattering on the Fermi surface. (b) Numerical calculation for charge-density redistribution around a single point charge on monolayer BP with $E_F$ located 0.05 eV above the CB minimum (corresponding carrier density $n_{2D} = 8.0 \times 10^{12}$ cm$^{-2}$).

Anisotropic screening in agreement with theoretical predictions
In graphene, two-phonon processes involving flexural phonons are more important than single-phonon processes involving in-plane phonons (except very low temperatures).
Kubo-Nakano-Mori formula (corresponds to variational solution of Boltzmann equation)
Phonon energies at $q = 2k_F$ are supposed to be much smaller than $k_B T$

$$\sigma_{xx} = \frac{e^2}{2S} \sum_k \tau_{xx} v_k^x \left( - \frac{\partial f}{\partial \varepsilon_k} \right)$$

$$\frac{1}{\tau_{xx}} = \frac{1}{\langle j_x^2 \rangle} \int_0^\infty \! dt \langle F_x(t) F_x^\dagger \rangle$$

$$F_x = [j_x, H']$$

$$H' = \sum_{kk'} V_{kk'}^{\text{eff}} c_k^\dagger c_{k'}$$

$$F_x = e \sum_{kk'} (v_k^x - v_{k'}^x) V_{kk'}^{\text{eff}} c_k^\dagger c_{k'}$$

$$k = k' + q$$

$$\frac{1}{\tau_{xx}} = \frac{\pi}{\hbar} \sum_{kk'} \delta(\varepsilon_k - \varepsilon_{k'}) \left( - \frac{\partial f}{\partial \varepsilon_k} \right) \frac{(v_k^x - v_{k'}^x)^2 \langle |V_{kk'}^{\text{eff}}|^2 \rangle}{\sum_k v_k^x \left( - \frac{\partial f}{\partial \varepsilon_k} \right)}$$

Parameters of interactions with in-plane and out-of-plane phonons are calculated from first principles

Continuum-medium description for in-plane and out-of-plane phonons
Intrinsic mobility in single-layer BP III

Energy dependence of effective masses are important (non-parabolic bands)

\[ \varepsilon_k = \frac{\hbar^2 k_x^2}{2m_x^E(\varepsilon)} + \frac{\hbar^2 k_y^2}{2m_y^E(\varepsilon)} \]

\[ v_k^{x(y)} = \frac{\hbar k_x^{x(y)}}{m_x^{x(y)}(\varepsilon)} \]

FIG. 5. (Color online) Energy dependence of the effective masses used in this work to approximate anisotropic dispersion \((m_x^E, m_y^E)\) and band velocities \((m_x^V, m_y^V)\) related to holes and electrons in monolayer BP.

FIG. 2. (Color online) (a,b) Energy dispersion of electrons and holes in monolayer BP along the armchair (\(x\)) and zigzag (\(y\)) directions with the related densities of states (DOS). (c,d) Fermi contours \(\varepsilon_F = \varepsilon(k_x, k_y)\) shown for the irreducible wedge of the Brillouin zone. Points and thick lines are the result of \(GW_0\) calculations [32], whereas thin black lines correspond to the model used in this work. Gray area marks the phonon cutoff wave vector \(q^*\) at \(T = 300K\) (see text for details).
**Intrinsic mobility in single-layer BP IV**

**Conclusions:**

1. Contrary to graphene, single-phonon processes are more important at RT;
2. Intrinsic limit of mobility for holes (electrons) contrary to 10,000 for graphene;
3. Anisotropy of mobility is much stronger for holes than for electrons

(2), (3) seem to be in qualitative agreement with experiments on a few-layer phosphorus.
Flexuron tail of density of states

At finite temperature, membranes are rippled

Snapshot: graphene @RT

Interaction with intrinsic ripples – the same as two-phonon processes

Average position of band edge is shifted and fluctuation tail appears (flexuron states)


Flexuron tail of density of states II

PHYSICAL REVIEW B 95, 041406(R) (2017)

Effect of flexural phonons on the hole states in single-layer black phosphorus

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Electron self-energy

$$\Sigma(E, p) = \int \frac{d^2 q}{(2\pi)^2} \gamma(p - q, p, q, E)K_2(q)G(E, p - q).$$

Without vertex corrections: self-consistent Born approximation. To take into account fluctuation tail (idea of L.V. Keldysh)

$$\gamma(p, p, 0, E) = 1 - \frac{\partial \Sigma}{\partial E} \quad \text{Ward identity} \quad \Sigma(E) = \left(1 - \frac{\partial \Sigma}{\partial E}\right) \int \frac{d^2 q}{(2\pi)^2} \frac{K_2(q)}{E - \epsilon_q - \Sigma(E)}$$

Applied to holes in phosphorene, parameters from ab initio calculations:

$$\epsilon_q = 2.9q_x^2 + 0.05q_y^2 + 13.2q_y^4$$ (atomic units)

Very anisotropic spectrum!
Flexuron tail of density of states III

FIG. 1. DOS per unit cell per spin for T = 100, 200, 300 and 400 K. For reference, the DOS corresponding to bare dispersion without the inclusion of the flexuron tail is shown. The Van Hove singularity in the latter manifests the aforementioned quasi-one-dimensionality of the holes in black phosphorus. It is to a large extent smeared by the flexural modes.

Smearing of Van Hove singularity near the band edge by interaction with intrinsic ripples

FIG. 2. Spectral function along $k_x$ and $k_y$ axis for $T = 300$ K. Note the different scale for the two plots.
Resume

(1) Completely different physics from both graphene and transition-metal dichalcogenides
(2) Strong difference of electronic structure from monolayer to bulk despite small cohesive energy
(3) Insulator-semimetal transition under bias/potassium doping with anisotropic Dirac cones in bilayer black phosphorus
(4) Very interesting defects, especially Co adatoms (single-atom orbital memory?!) 
(5) Tunable electronic structure by high-frequency fields?!
(6) Hyperbolic plasmons?!
(7) Mechanisms of intrinsic mobility quite different from graphene, much stronger interaction with acoustic phonons, strong limits on mobility

MANY THANKS
FOR YOUR ATTENTION