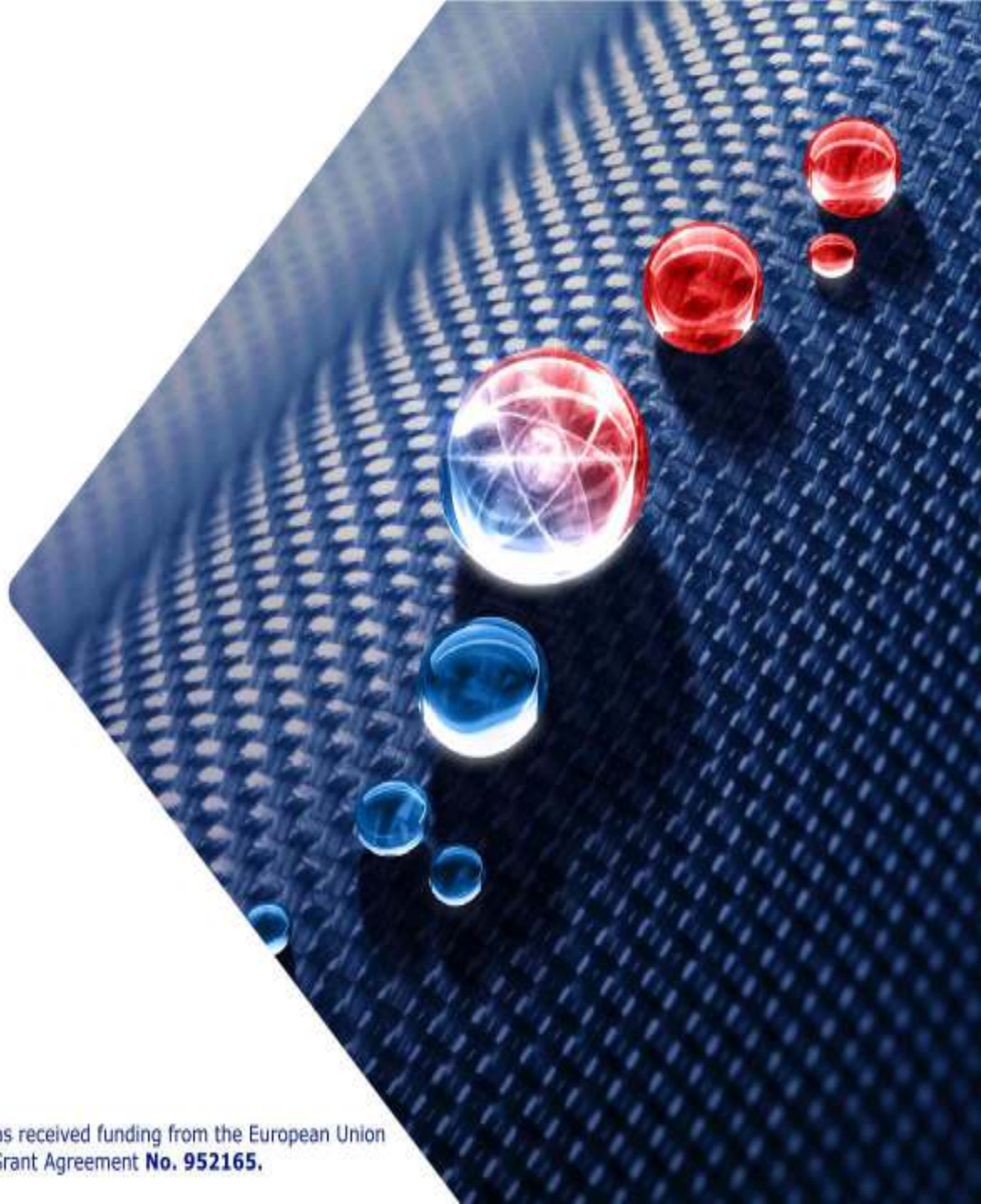
Targeting Real chemical accuracy at the EXascale

Quantum Monte Carlo study of straintronic response of 2D materials: monolayer phosphorene and MoS_2

I. Stich
Inst. of Informatics,
Slovak Academy of Sciences



Targeting Real Chemical Accuracy at the Exascale project has received funding from the European Union Horizoon 2020 research and innovation programme under Grant Agreement **No. 952165.**

2D materials project

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SLOVAK ACADEMY OF SCIENCES

Funding:

- **H2020**
- **APVV-21-0272**
- **VEGA 2/0070/21**
- **PRACE**
- **EuroHPC**

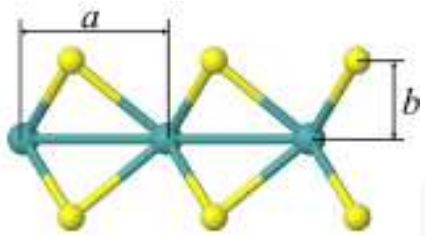
H2020 GA: 952165
SLOVAK RESEARCH AND DEVELOPMENT AGENCY
PRACE PARTNERSHIP FOR ADVANCED COMPUTING IN EUROPE
Call 24, Tier0: project no. 2021250026
EuroHPC

Outline

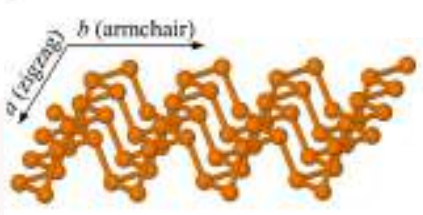
- Intro. 2D materials

quintessential
straintronic material

MoS_2

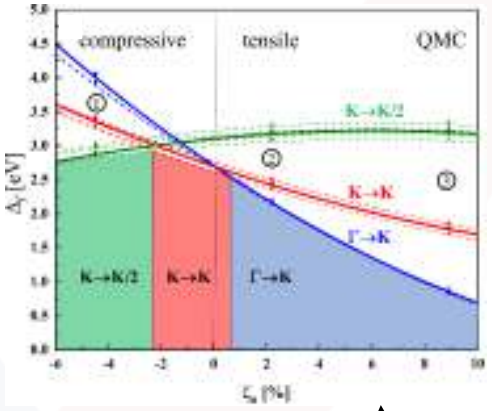


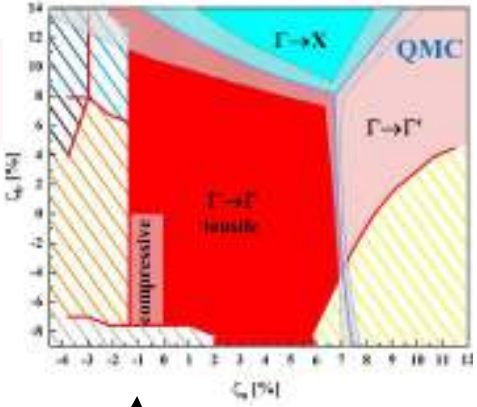
phosphorene



- Calculations: 1) band gap
  2) strain effects
  3) deformation energy

„phase diagrams“ of excitationas





- Summary

2D materials

Nobel prize for physics (2010)

Geim & Novoselov

- **a number of 2D materials prepared:**
  - **exfoliation**
  - **epitaxial growth**
- **electronic properties:**

metals ⇔ semimetal ⇔ semiconductor ⇔ wide gap insulator

Pd, Rh graphene

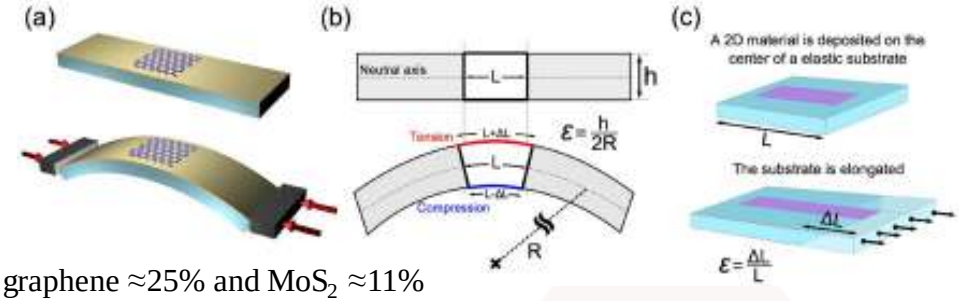
TMD
phosphorene

h-BN

- **high carrier mobility**
- **often direct gap**

2D materials tuning: phosphorene

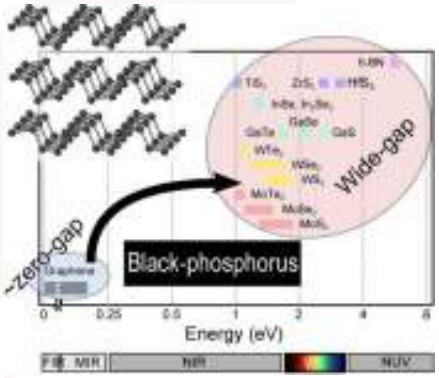
2D materials highly sensitive to **strain**



2D materials can **sustain strains** well in excess of **10%**: graphene ≈25% and MoS_2 ≈11%

R. Roldán, A. Castellanos-Gomez, E. Capelluti, and F. Guinea, J. Phys.: Condens. Matter **27**, 313201 (2015)

tuning properties via **strain** - **band gap** for given applications

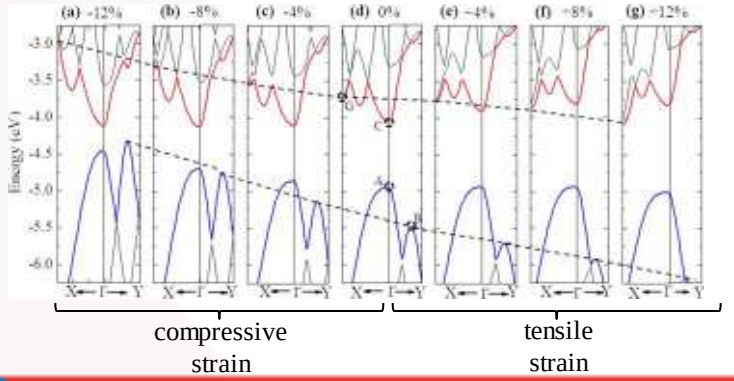


Castellanos-Gomez. A., J. Phys. Chem. Lett. **6**, 4280 (2015)

- **effective mass** ⇒ carrier mobility

$$m^* = \frac{1}{\frac{1}{\hbar^2}\frac{d^2E}{dk^2}}$$

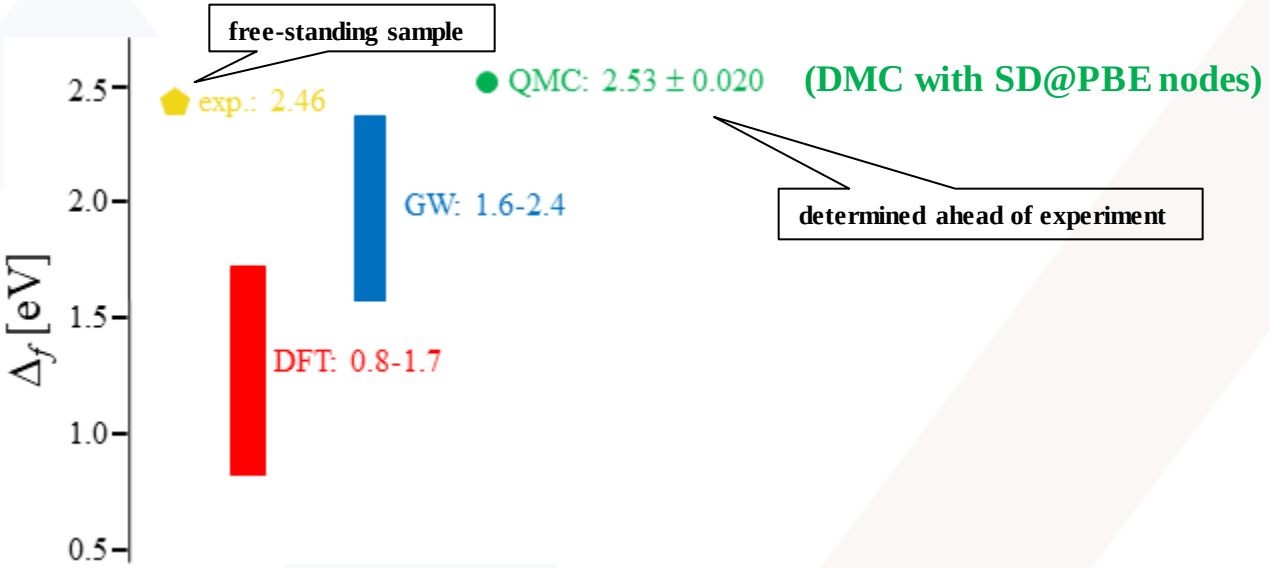
Y. S., Y. Chen, and C. Jiang, InfoMat. **3**, 397420 (2021)



2D materials: phosphorene gap

accuracy: quasiparticle band gap

example: monolayer phosphorene



E. Gaufrès, F. Fossard, V. Gosselin, L. Sponza, F. Ducastelle, Z. Li, S. G. Louie, R. Martel, M. Côté, and A. Loiseau, Nano Lett. 19, 8303 (2019).

T. Frank, R. Derian, K. Tokar, L. Mitas, J. Fabian, and I. Stich, Phys. Rev. X **9**, 011018 (2019).

2D materials: phosphorene gap

how can the band gap be calculated?

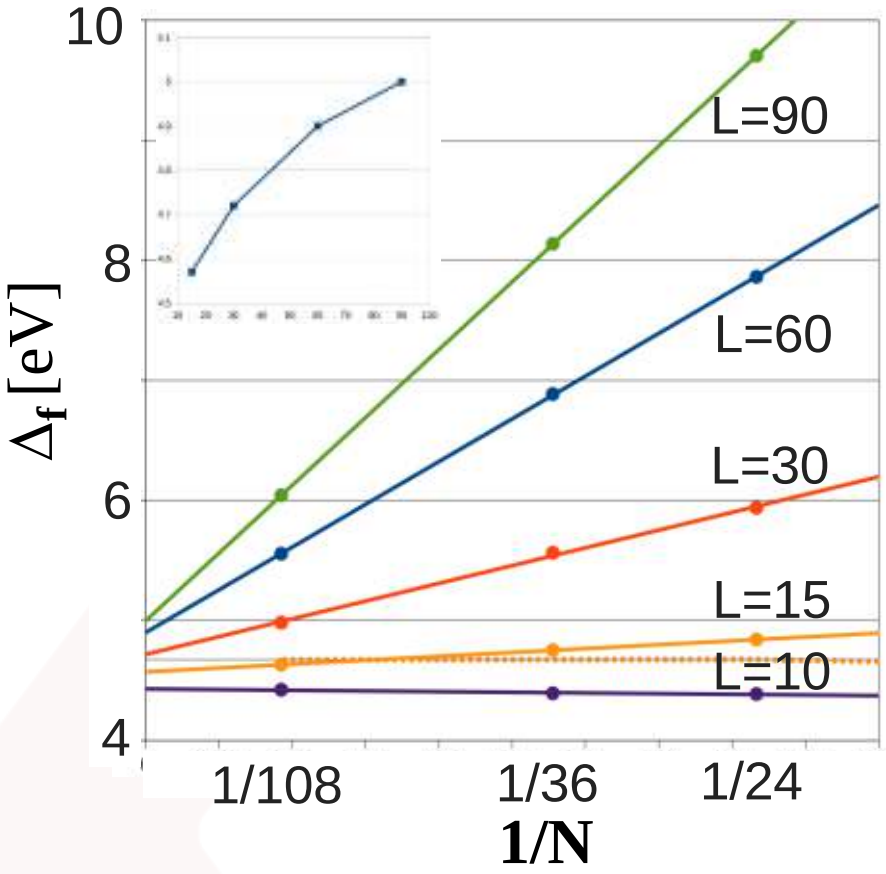
- quasiparticle band gap

$$\Delta_f = (E_{Ne+1} - E_{Ne}) - (E_{Ne} - E_{Ne-1})$$

how to calculate for a 2D crystal???

2D crystal is in reality 2D+h system

???how to apply
neutralizing background ???



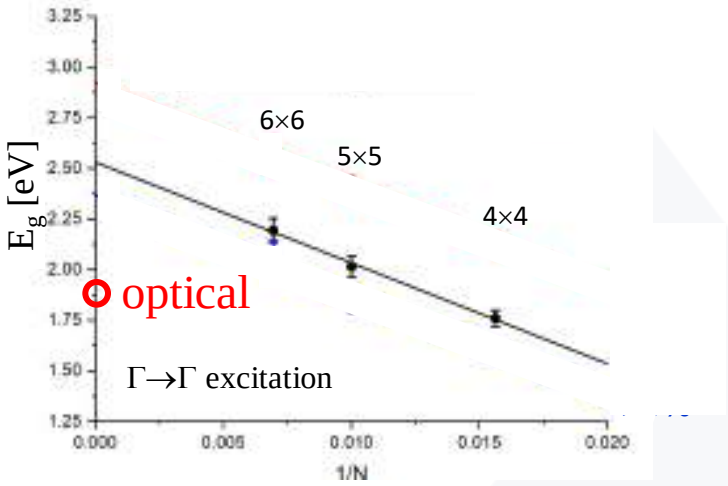
2D materials: phosphorene gap

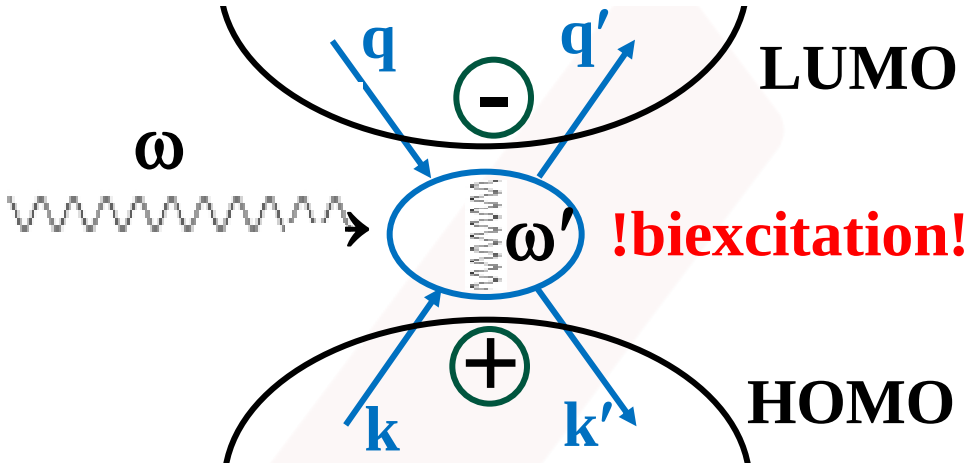
how can the band gap be calculated?

- excitation/neutral band gap

$$\Delta_e \approx E_v^s = E_1^s - E_0^s$$

what does that correspond to:
optical/quasiparticle





⇒ no exciton possible!!!

- in 2D size larger than supercell

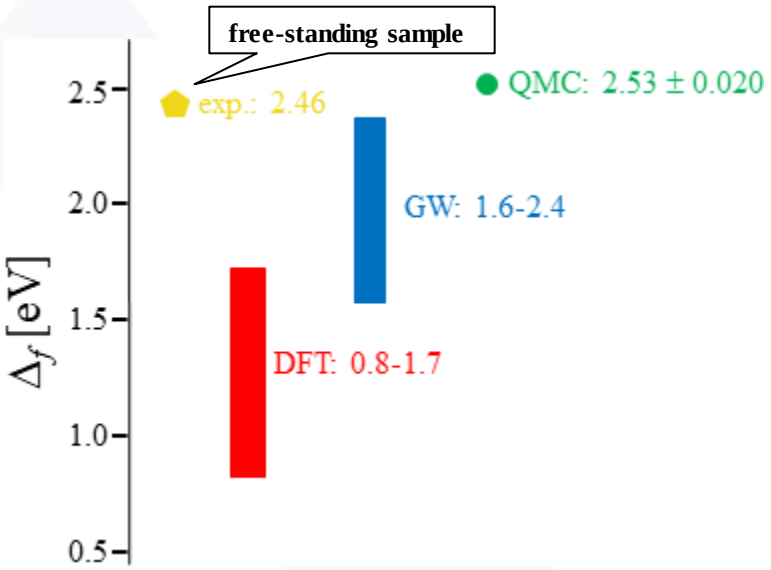
- e-h pair cannot be formed from single-particle Bloch states

- DMC gaps@PBE nodes
  gaps@hybrids equal

2D materials: phosphorene gap

accuracy: quasiparticle band gap

example: monolayer phosphorene



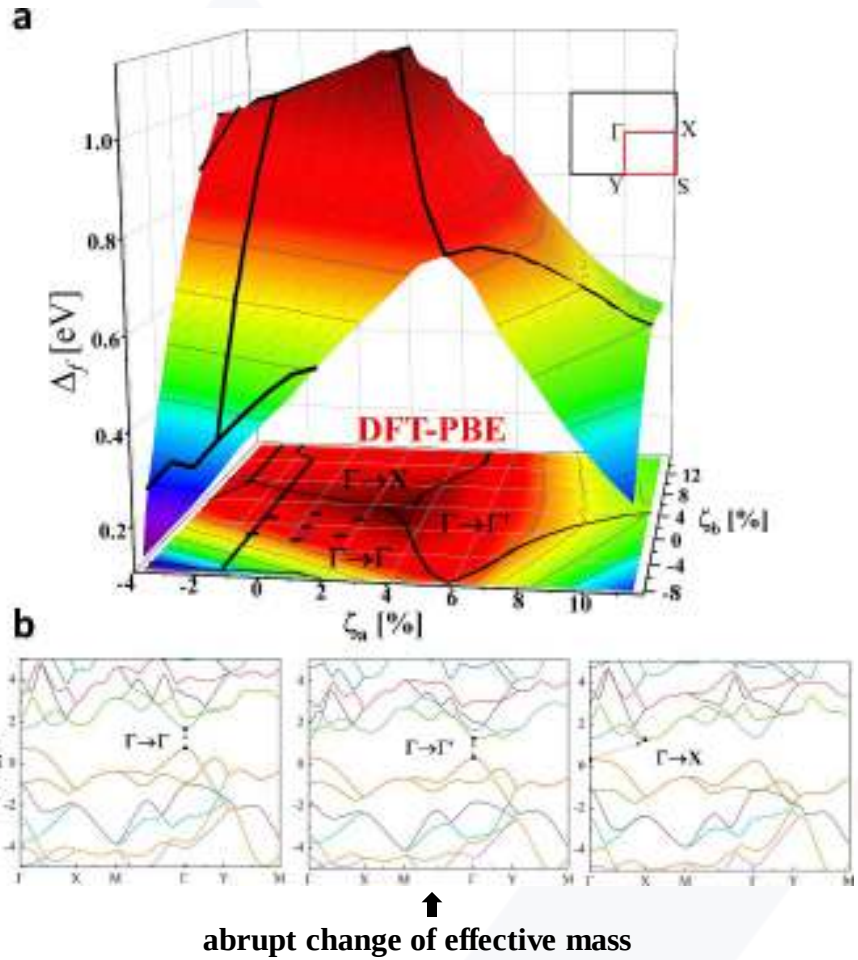
⇒ **need accuracy better than DFT & GW: quasiparticle gap ⇒ QMC**
GW-BSE: for excitons

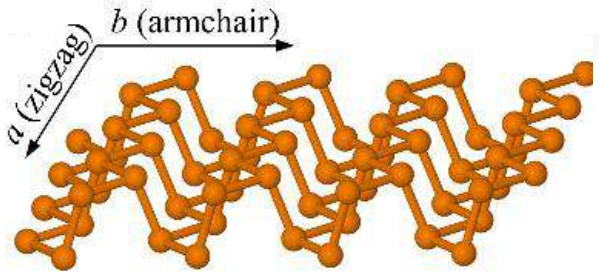
⇒ **under strain bias bound to increase theory & experiment**

E. Gaufrès, F. Fossard, V. Gosselin, L. Sponza, F. Ducastelle, Z. Li, S. G. Louie, R. Martel, M. Côté, and A. Loiseau, Nano Lett. 19, 8303 (2019).
T. Frank, R. Derian, K. Tokar, L. Mitas, J. Fabian, and I. Stich, Phys. Rev. X **9**, 011018 (2019).

strained phosphorene

qualitative picture: pre-screened by DFT-PBE DFT

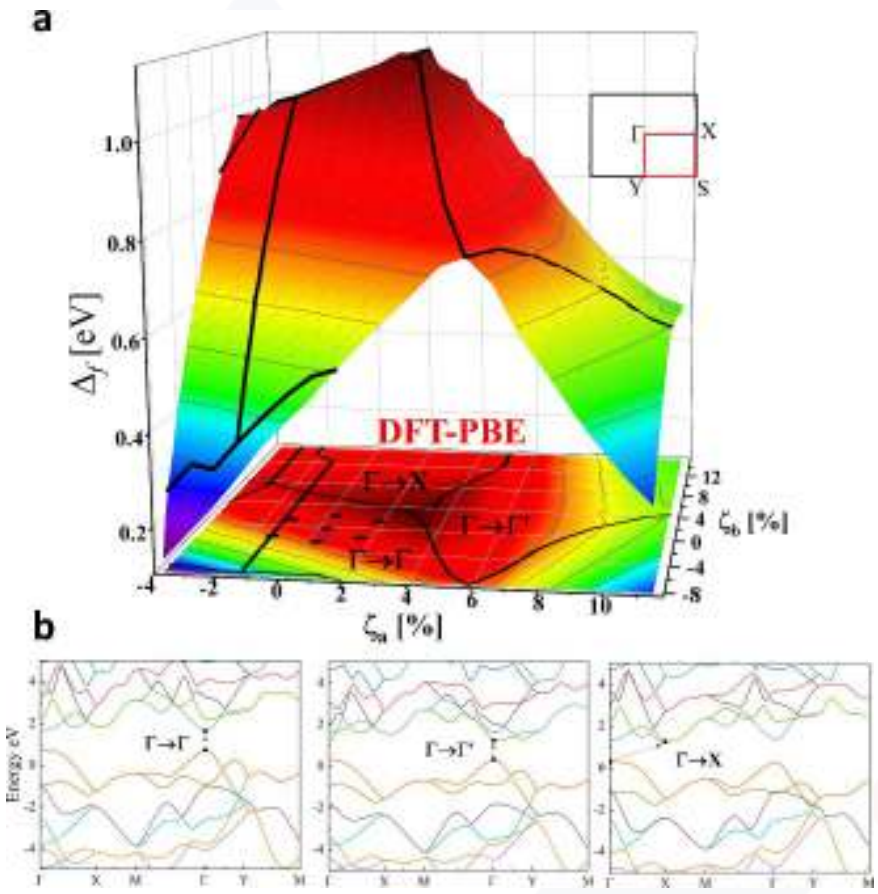




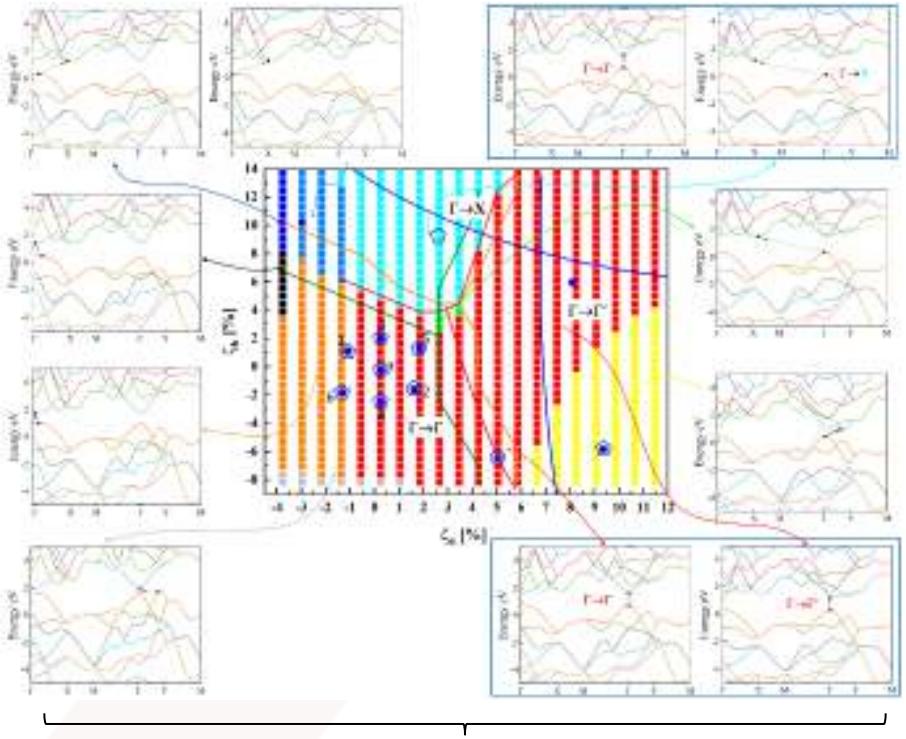
abrupt change of effective mass

strained phosphorene

qualitative picture: pre-screened by DFT-PBE DFT



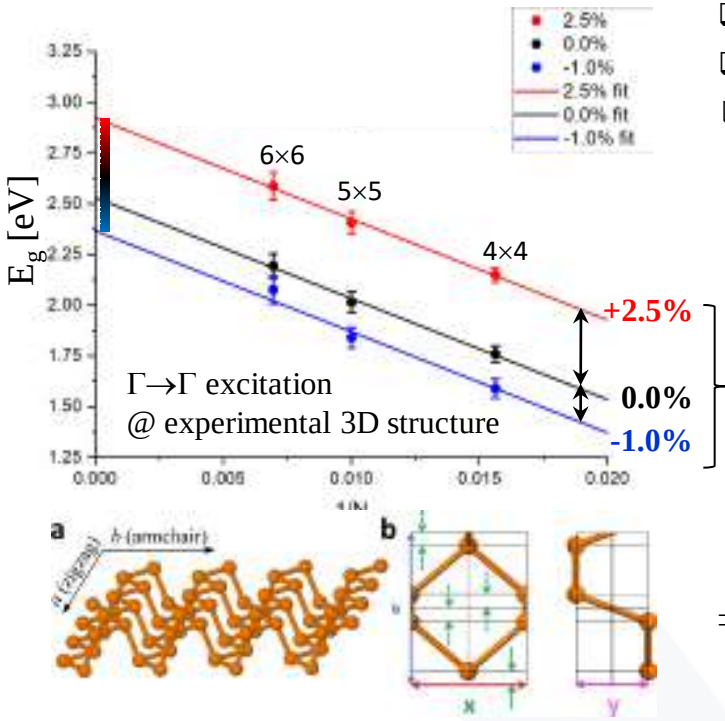
abrupt change of effective mass



plethora of other excitations

band gap: strain effects

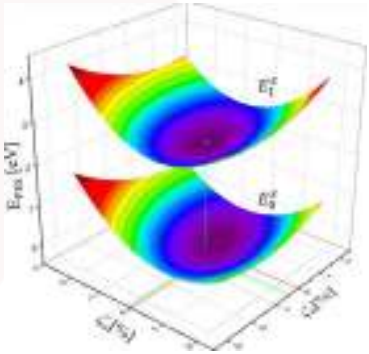
quantitative picture: FNQMC (SD with DFT-PBE nodes)



- ❑ the strain band gap tuning is quite strong
- ❑ quasiparticle band gap scales linearly with the applied strain
- ❑ highly nontrivial as the band gaps are differences between ground- and excited-state PESs.

converged ground- and excited-state PESs parallel; only vertical & lateral offsets

diagonal



⇒ 4 parameters a, b, x, and y

bracketted by at least 25 QMC points

⬇

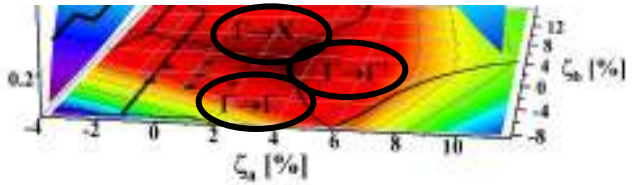
fixing all 4 parameters a, b, x, and y: quadrivariate paraboloid function $E_0(a, b, x, y)$, minimize w.r.t. x, and y for each (a, b) ⇒ $E_0(a, b)$

excited state E_1 only computed at the minimum w.r.t. x, and y ⇒ $E_1(a, b)$

Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

band gap: strain effects

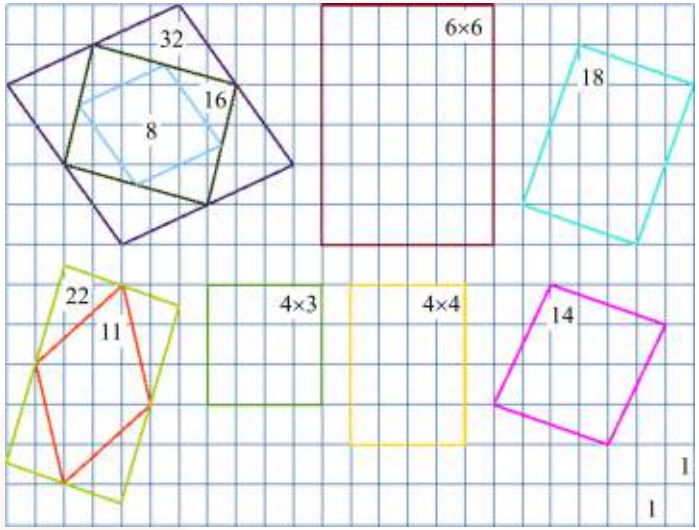
structural approximants & finite size scaling:
7 points bracketing the minimum



Γ→Γ/Γ→Γ':

approximants:

11 prim. u.c. | 4D
16 prim. u.c. | 4D
18 prim. u.c. | 4D
22 prim. u.c. | 4D



Γ→X:

approximants:

14 prim. u.c. | 4D
16 prim. u.c. | 4D
18 prim. u.c. | 4D
22 prim. u.c. | 4D

Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

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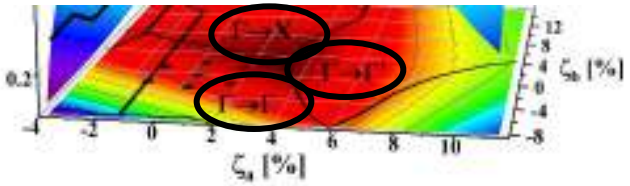

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Γ→X:

approximants:

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16 prim. u.c. | 4D
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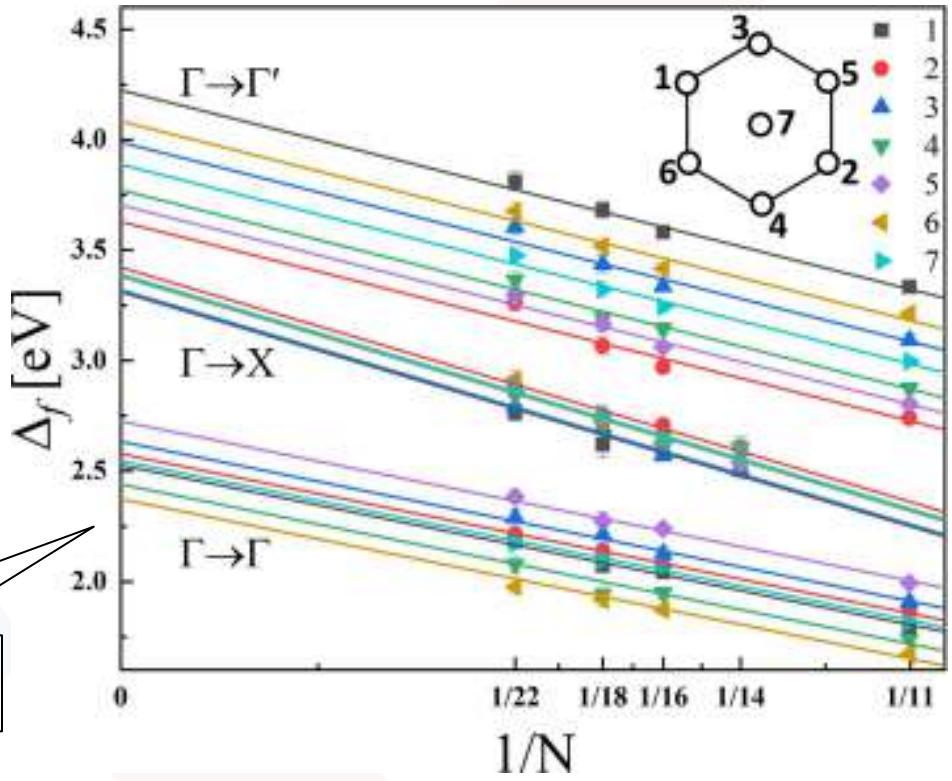
22 prim. u.c. | 4D

!no twist averaging possible!



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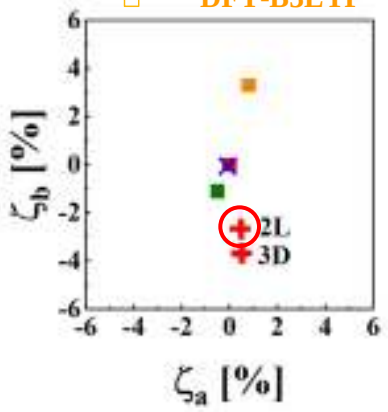
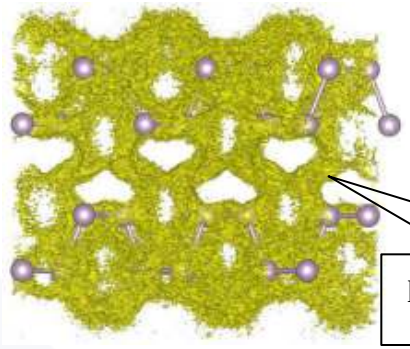
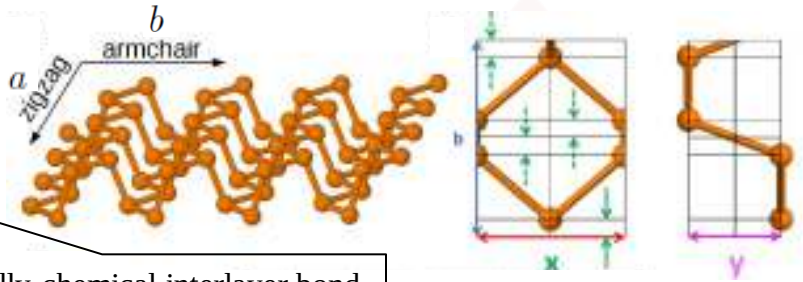
equilibrium properties

× QMC
□ DFT-PBE
□ DFT-HSE
□ DFT-B3LYP



2-layer phosphorene





partially chemical interlayer bond
(between loan pairs on P's)

expt.

	QMC 11-cell	QMC 16-cell	QMC 22-cell	DFT-PBE	3D-BP
	ground state				
a	6.229±0.008	6.238±0.002	6.230±0.002	6.235	6.2618
b	8.651±0.017	8.688±0.008	8.707±0.006	8.711	8.2700
x	0.748±0.005	0.759±0.002	0.765±0.001	0.770	0.6367
y	3.987±0.007	3.978±0.003	3.985±0.002	3.975	4.0280
E_0^s	-716.563±0.002	-716.498±0.0008	-716.469±0.0007	-717.711	NA
	excited state				
a	6.227±0.027	6.222±0.003	6.224±0.003	6.222	NA
b	8.515±0.178	8.607±0.012	8.664±0.010	8.543	NA
x	0.728±0.044	0.747±0.003	0.761±0.002	0.739	NA
y	4.053±0.018	4.031±0.002	4.020±0.002	4.051	NA
E_1^s	-716.415±0.005	-716.375±0.0007	-716.375±0.001	-717.643	NA

$a = 3.30 \pm 0.003$ Å
$b = 4.61 \pm 0.006$ Å
$x = 0.405 \pm 0.001$ Å
$y = 2.109 \pm 0.001$ Å

not known experimentally

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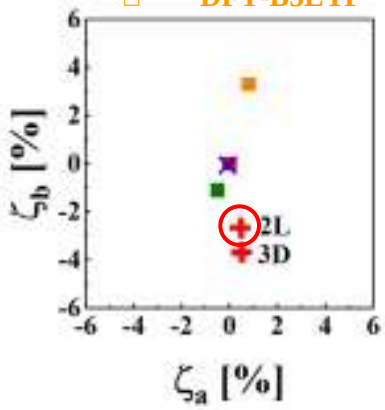
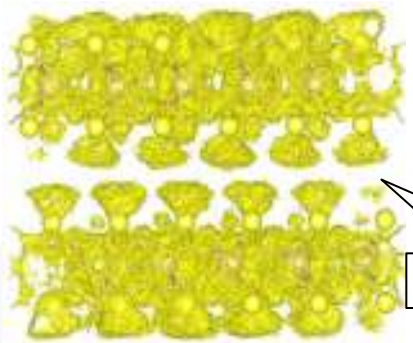
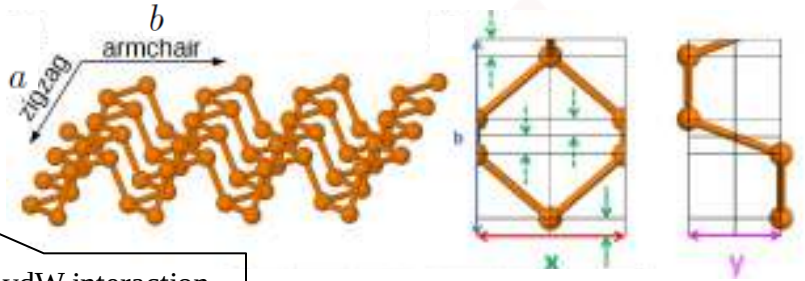


2-layer MoS_2



pure vdW interaction



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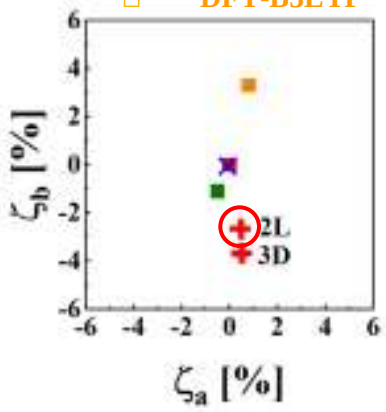
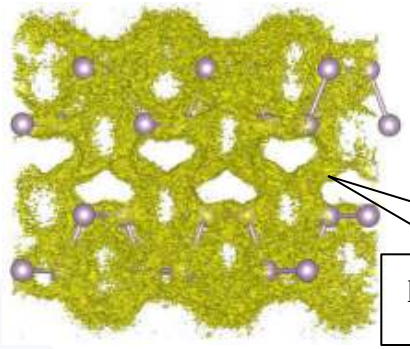
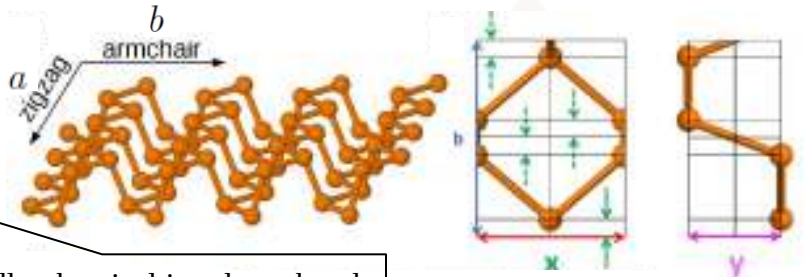


2-layer phosphorene





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not known experimentally

$$\Delta_f = 2.53\pm0.020\ \text{eV} \Leftrightarrow 2.46\ \text{eV}$$

experimental value for freestanding phosphorene

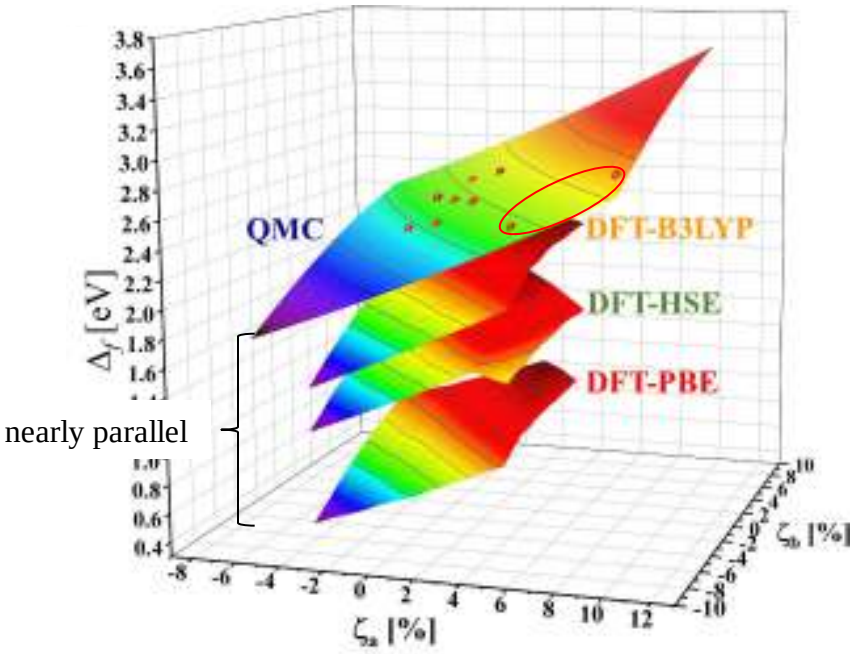
⇑

(almost) **chemical precision**
(no vibronic and zero-point corrections)

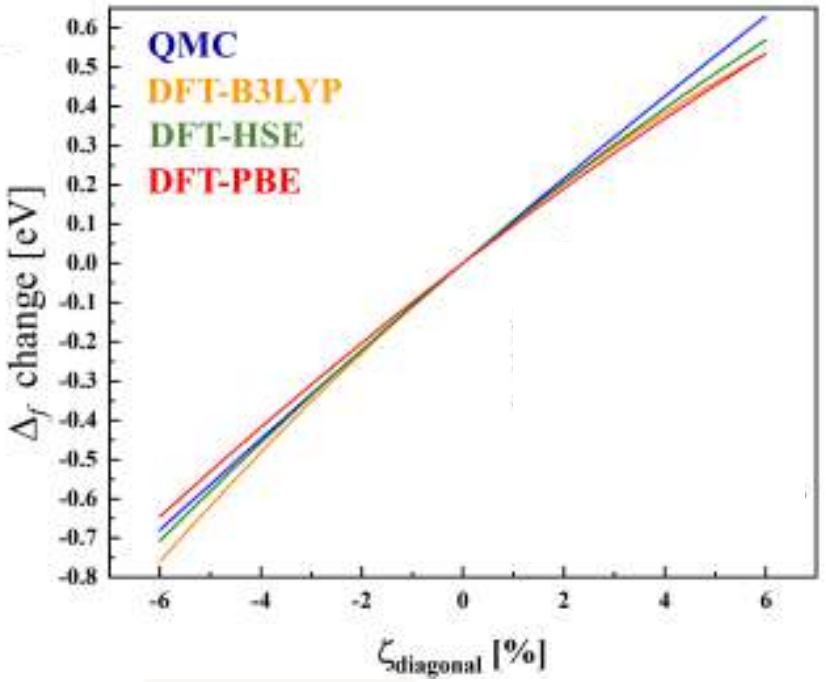
E. Gaufr`es, F. Fossard, V. Gosselin, et al., Nano Lett. **19**, 8303 (2019)
Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

strained gap

band gap **Γ→Γ excitatiion** **gauge factor**



nearly parallel



QMC consistently gives larger gap than any common DFT functional (PBE, HSE, B3LYP), !ζ = 0 agrees with experiment!

gauge factor (change of Δ_f) very similar to DFT (if computed against the respective minimum)

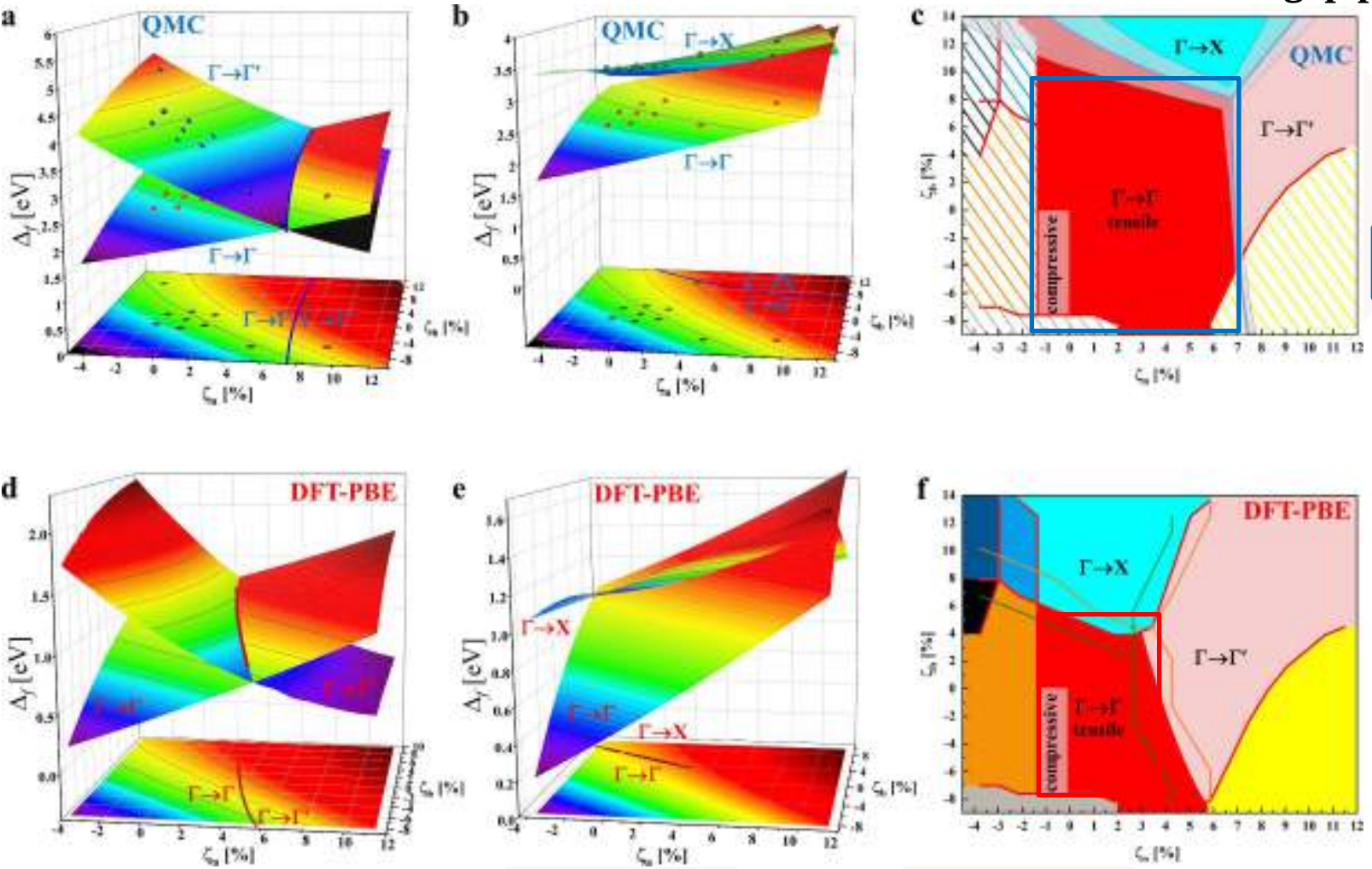
large gauge factor: ≈100 meV/%

main straintronic materials MoS_2: 64±5/68±5 meV/%

Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

strained gap

quantitative picture: QMC Γ→Γ Γ→Γ' Γ→X boundaries ⇒ band gap phase diagrams



large gauge factor
+
huge tuning area

colossal gap response to strain

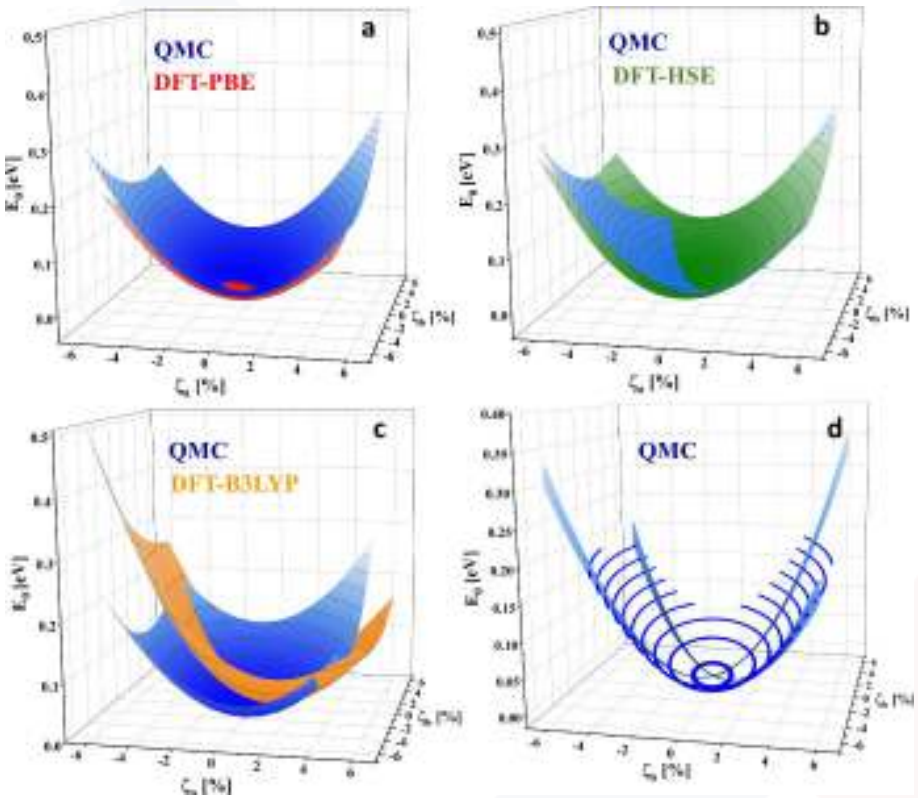
≈1 eV tuning mainly in tensile strain

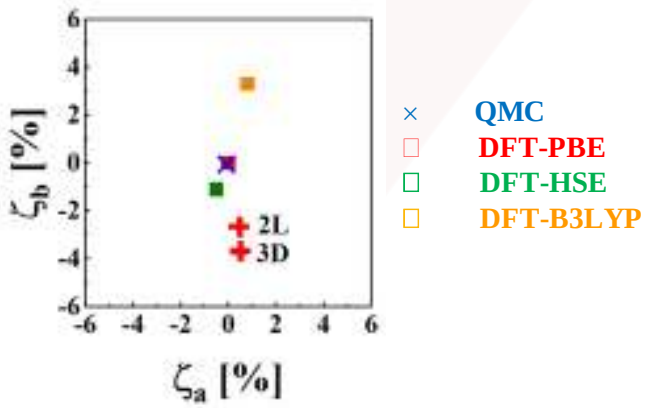
strain tuning area in DFT much smaller

- DFT-PBE
- DFT-HSE
- DFT-B3LYP

Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

deformation energies

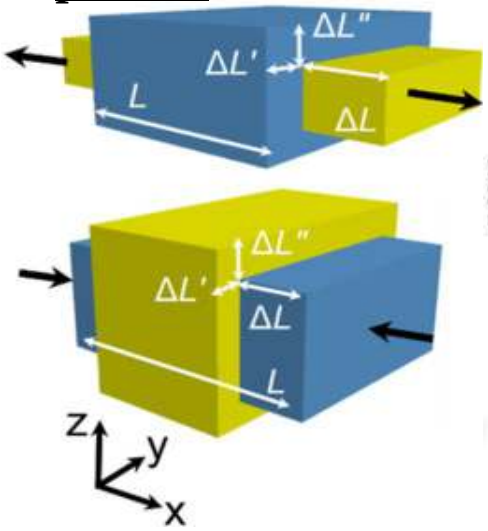


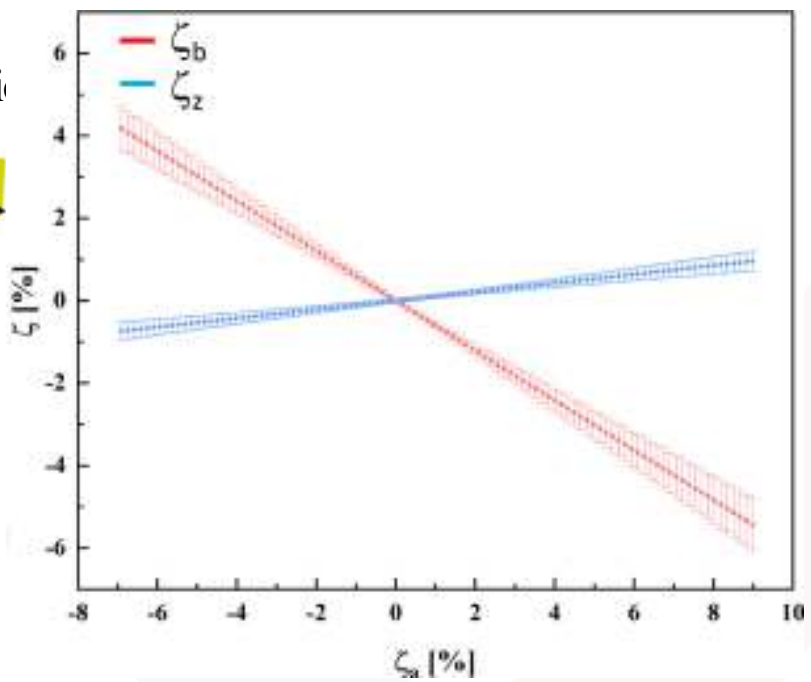


Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

Poisson's ratio

positive Poison's rati





positive in-plane

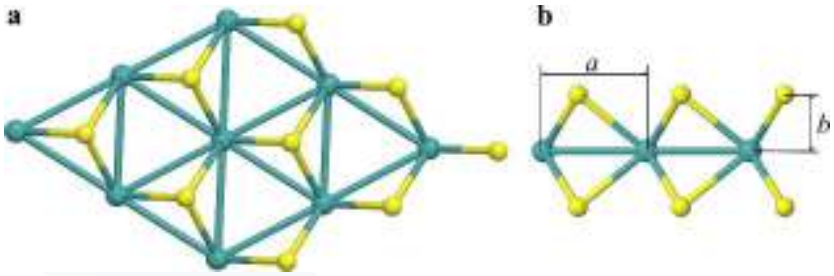
negative out-of-plane

Poisson's ratio

auxetic material

Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

monolayer MoS_2



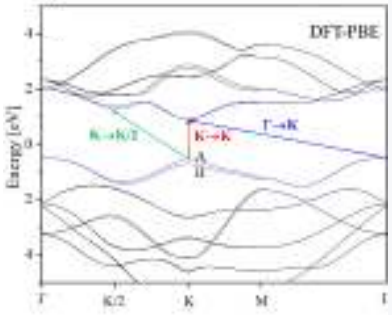
consider only diagonal strain (a)

$\Rightarrow$ 2 parameters a, b

fixing 2 parameters a, b: bivariate paraboloid function $E_0(a, b)$, minimize w.r.t. b for each a $\Rightarrow E_0(a)$

excited state E_1 only computed at the minimum w.r.t. b $\Rightarrow E_1(a)$

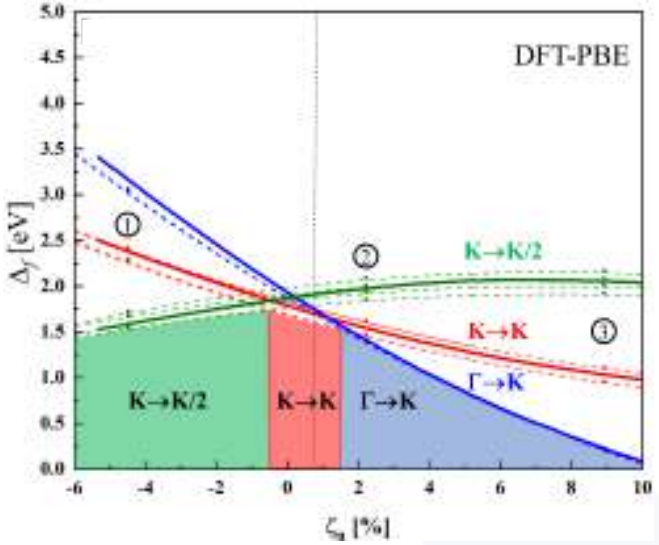
spin-orbit couplings (SOC) small but non-nebligible $\Rightarrow$ SOC added à posteriori perturbatively based on DFT-PBE



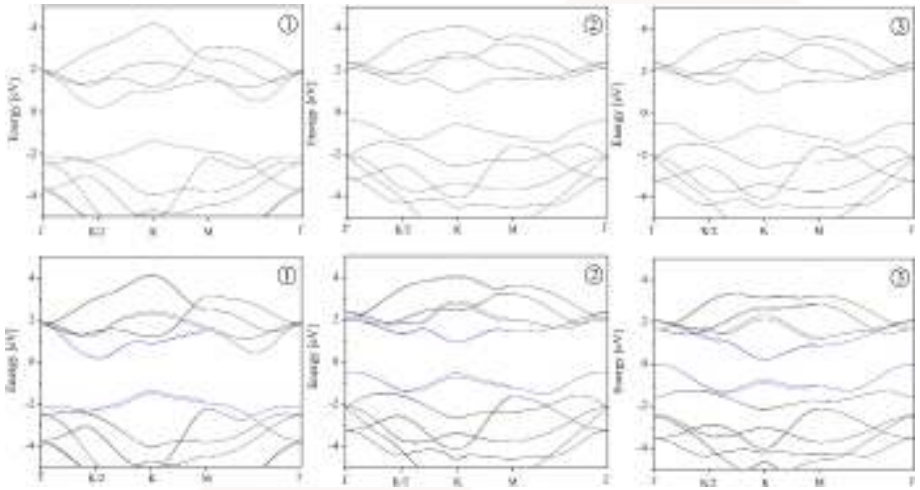
Y. Huang, M. Manzoor, J. Brndiar, and I. Štich, Phys. Rev. Research **6**, 013007 (2024).

qualitative picture: pre-screened by DFT-PBE DFT

band gap phase diagram



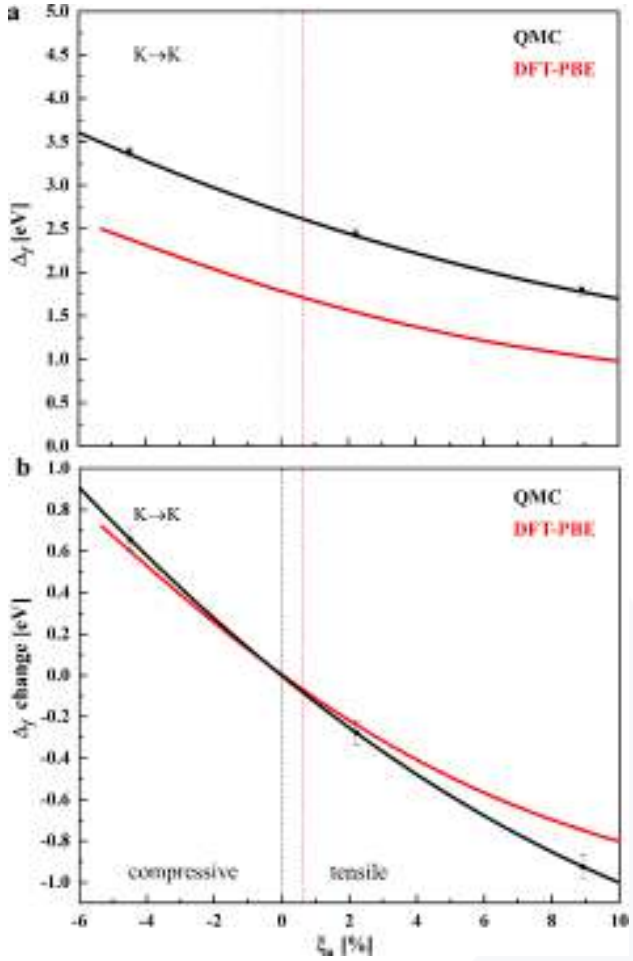
SOC splittings:



Y. Huang, M. Manzoor, J. Brndiar, and I. Štich, Phys. Rev. Research **6**, 013007 (2024).

band gap: strain effects

K→K exitation



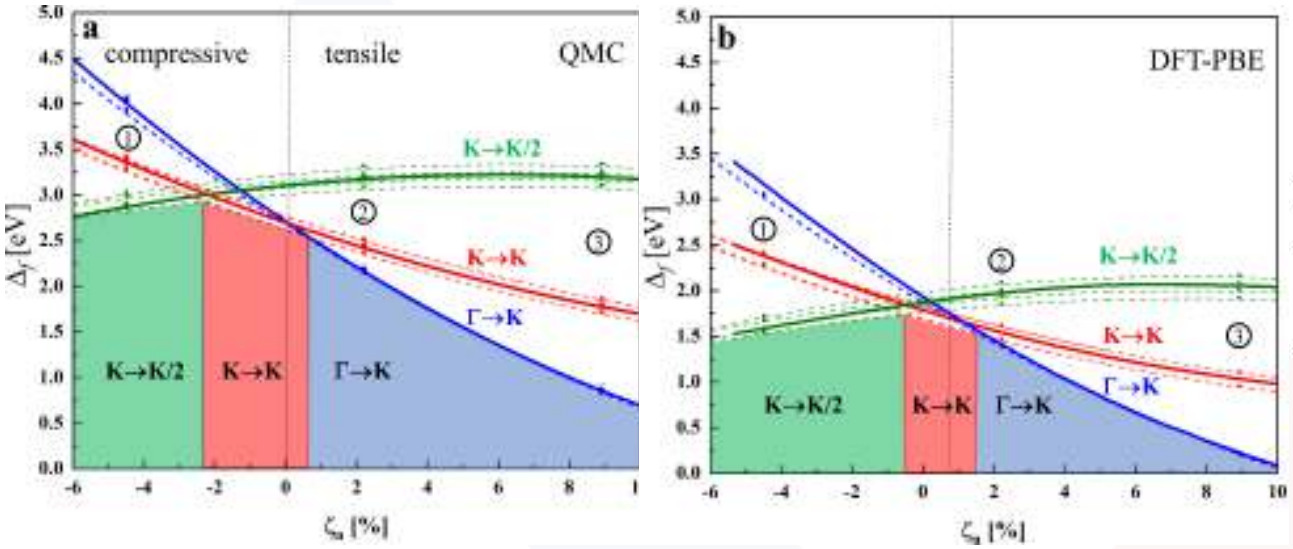
DFT-PBE rigid band gap offset by ≈1 eV

qualitativly similar results

Y. Huang, M. Manzoor, J. Brndiar, and I. Štich, Phys. Rev. Research **6**, 013007 (2024).

band gap: strained gap boundaries

band gap phase diagram



gauge factor						
transition	QMC	GW	PBE	HSE	B3LYP	exp
K→K	136/60	138/60	104/47	149	145	40–125
Γ→K	227	271	198	198	196	-
K→K/2	42	83	40	41	41	-

⇒ qualitativly similar results ⇒ ???coincidence or trend for ALL TMDs and TREATMENTS???

Y. Huang, M. Manzoor, J. Brndiar, and I. Štich, Phys. Rev. Research **6**, 013007 (2024).

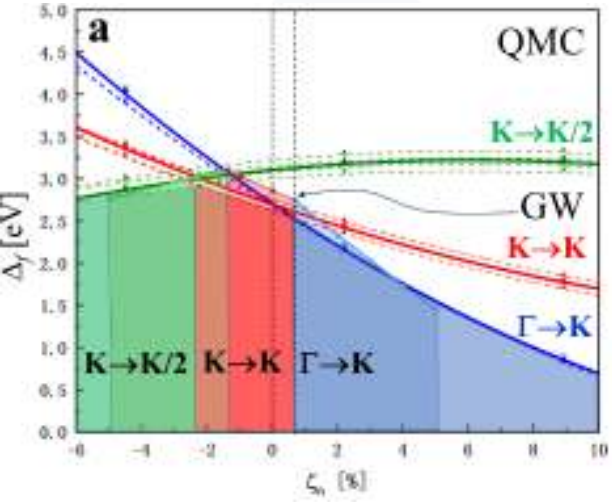
band gap: strained gap boundaries

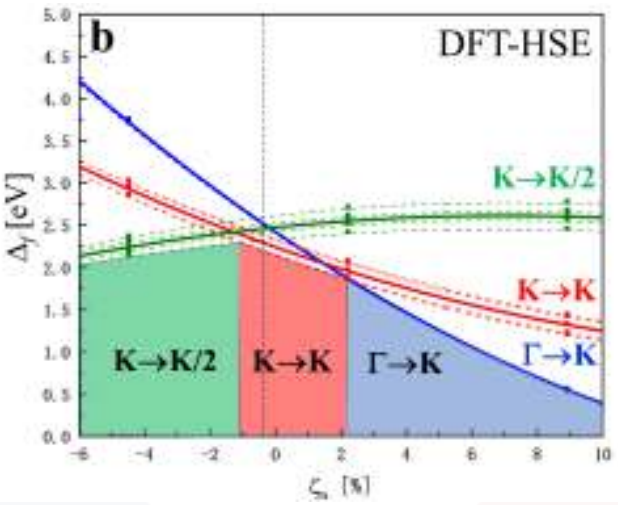
comparison of band gap phase diagrams

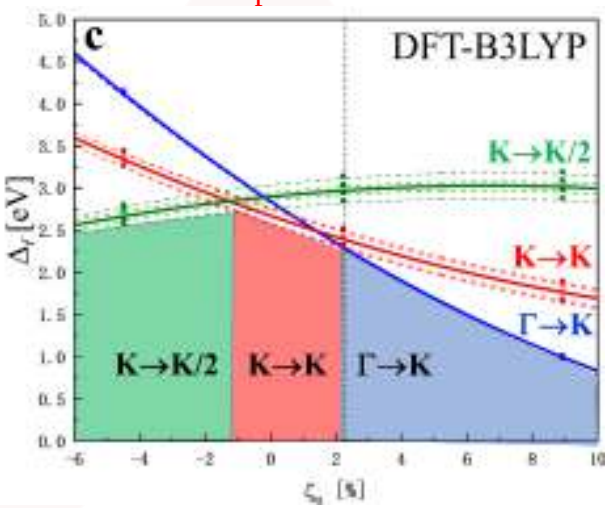
GW: tuning only in compressive strain

DFT-HSE: tuning mostly in tensile strain

DFT-B3LYP: tuning only in compressive strain







qualitatively similar phase diagrams

gauge factor						
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K→K	136/60	138/60	104/47	149	145	40–125
Γ→K	227	271	198	198	196	-
K→K/2	42	83	40	41	41	-

⇒ similar gauge factors

⇒ excitations similar response to strain

⇒ excitations different values

⇒ relation between different excitations different

extremely sensitive indicator of el. structure quality

Y. Huang, M. Manzoor, J. Brndiar, and I. Štich, Phys. Rev. Research **6**, 013007 (2024).

band gap: take home message

- excitation/neutral gap = quasiparticle gap

  optical gaps in 2nd order theory

- electronic & atomic structure of 2D materials can be studied ultra-accurately with FNQMC mehods
- direct band-gap tunability in tensile strain
- quintessential straintronic material MoS_2 tunability 10× smaller than in phosphorene
- tuability of phosphorene is colossal