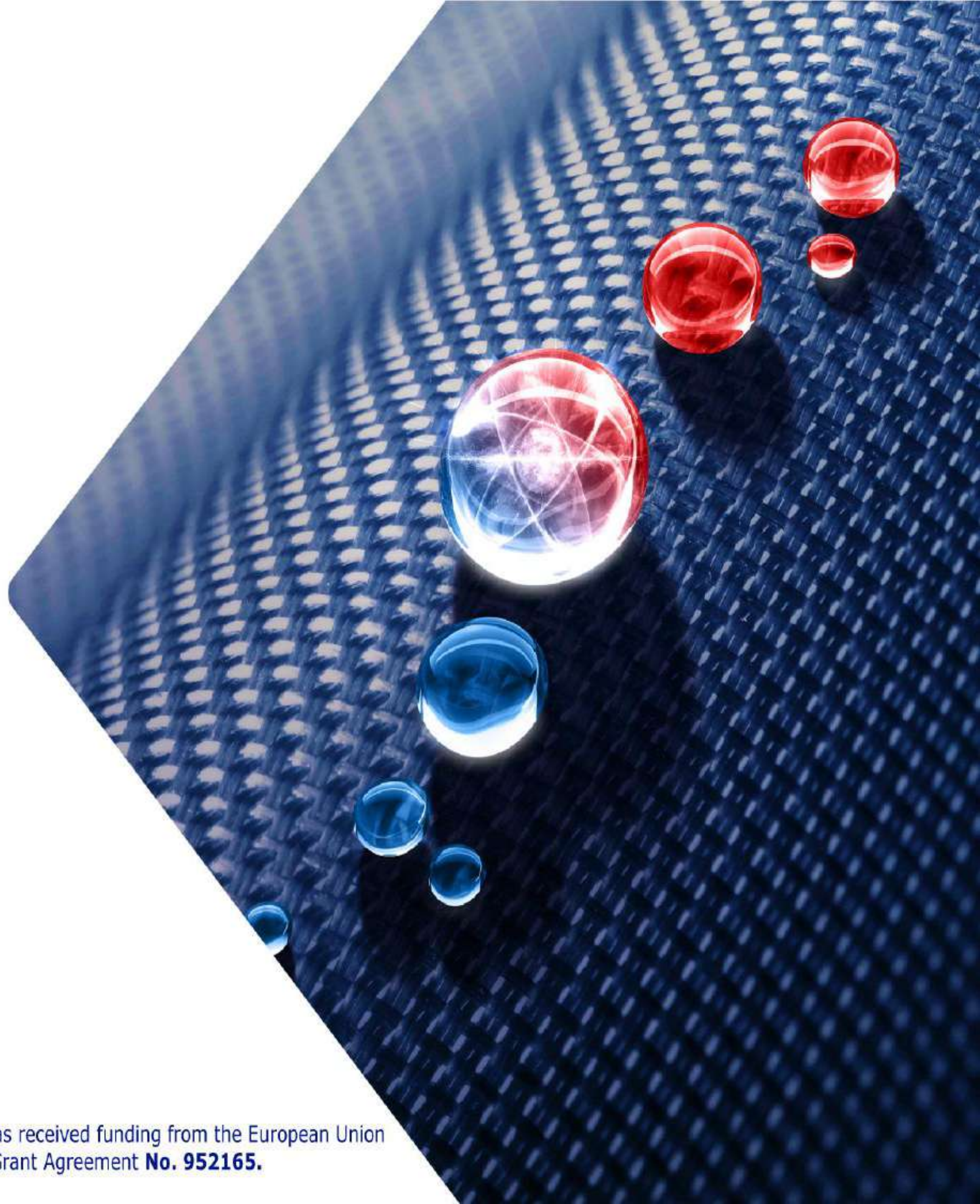
Targeting Real chemical accuracy at the EXascale

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

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

C|C|M|S
Center for Computational Materials Science



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

Y. Huang, J. Brndiar, M. Manzoor, I. Štich
L. Mitas, J. Fabian
CCMS, Inst. of Informatics, Slovak Academy of Sciences
Dept. of Physics, North Carolina State University, Raleigh, U.S.A.
University of Regensburg, Inst. for Theoretical Physics, Germany

SLOVAK ACADEMY OF SCIENCES

Center for Computational Materials Science

Funding:

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

H2020 GA: 952165

SLOVAK RESEARCH AND DEVELOPMENT AGENCY

PARTNERSHIP FOR ADVANCED COMPUTING IN EUROPE

Call 24, Tier0: project no. 2021250026

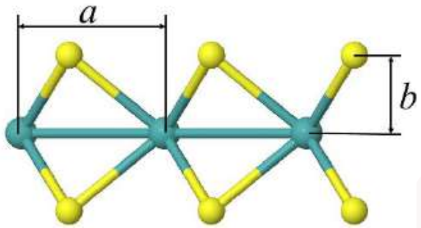
EuroHPC

Outline

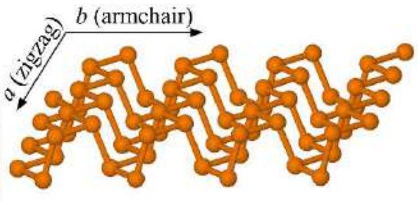
- ❑ **Intro. 2D materials**

quintessential
straintronic material

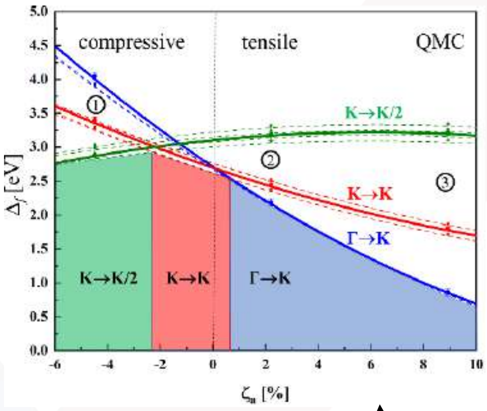
MoS_2

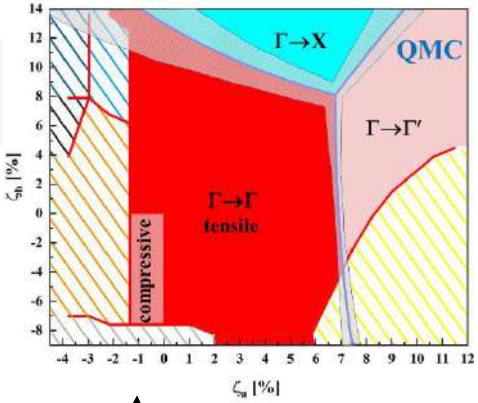


phosphorene



„phase diagrams" of excitationas

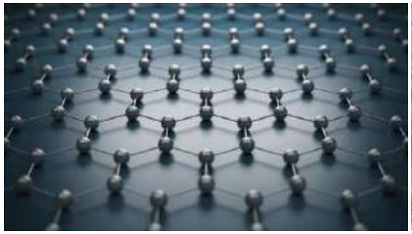




- ❑ **Calculations: 1) band gap**
  2) strain effects
  3) deformation energy

- ❑ **Summary**

2D materials



Nobel prize for physics (2010)

Geim & Novoselov

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

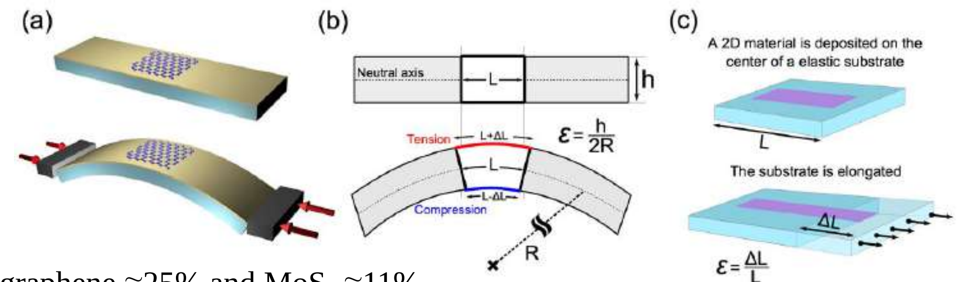
- **electronic properties:**

metals ⇔	semimetal ⇔	semiconductor ⇔	wide gap insulator
Pd, Rh	graphene	TMD phosphorene	h-BN

- **high carrier mobility**

- **often direct gap**

2D materials tuning: phosphorene

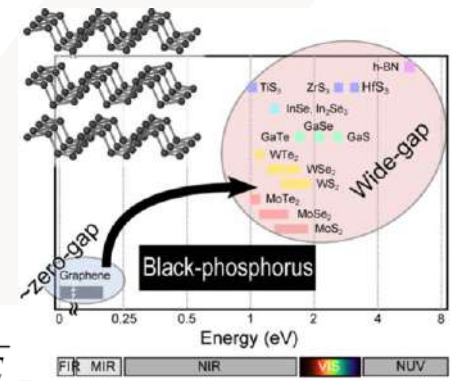


2D materials highly sensitive to **strain**

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

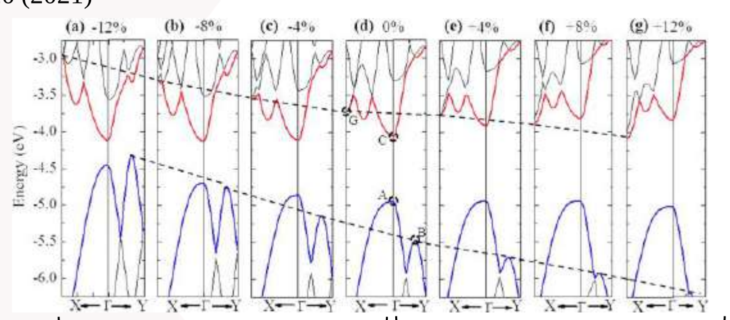


Castellanos-Gomez. A., J. Phys. Chem. Lett. **6**, 4280 (2015)

- **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)



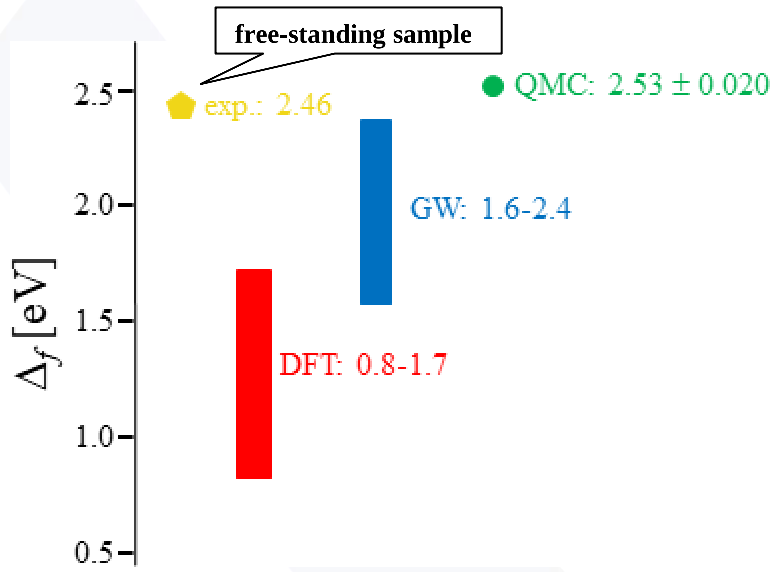
compressive strain

tensile strain

2D materials: phosphorene gap

accuracy: quasiparticle band gap

example: monolayer phosphorene



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

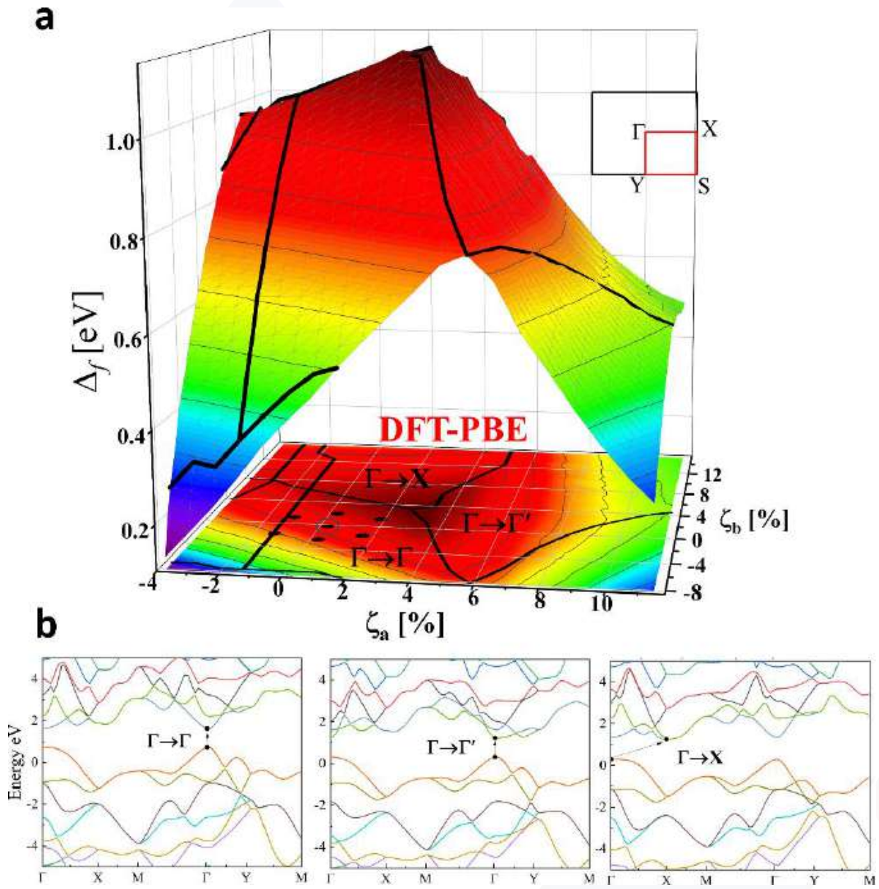
⇒ **under strain bias bound to increase theory & experiment**

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).

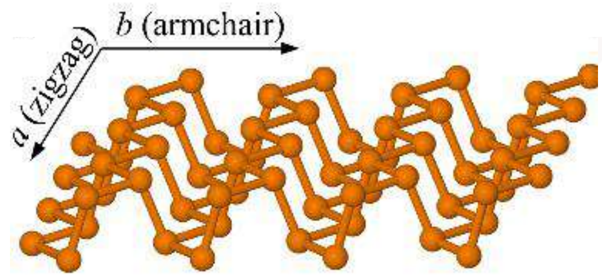
T. Frank, R. Derian, K. Tokar, L. Mitas, J. Fabian, and I. Stich, Phys. Rev. X **9**, 011018 (2019).

strained phosphorene

qualitative picture: pre-screened by DFT-PBE DFT

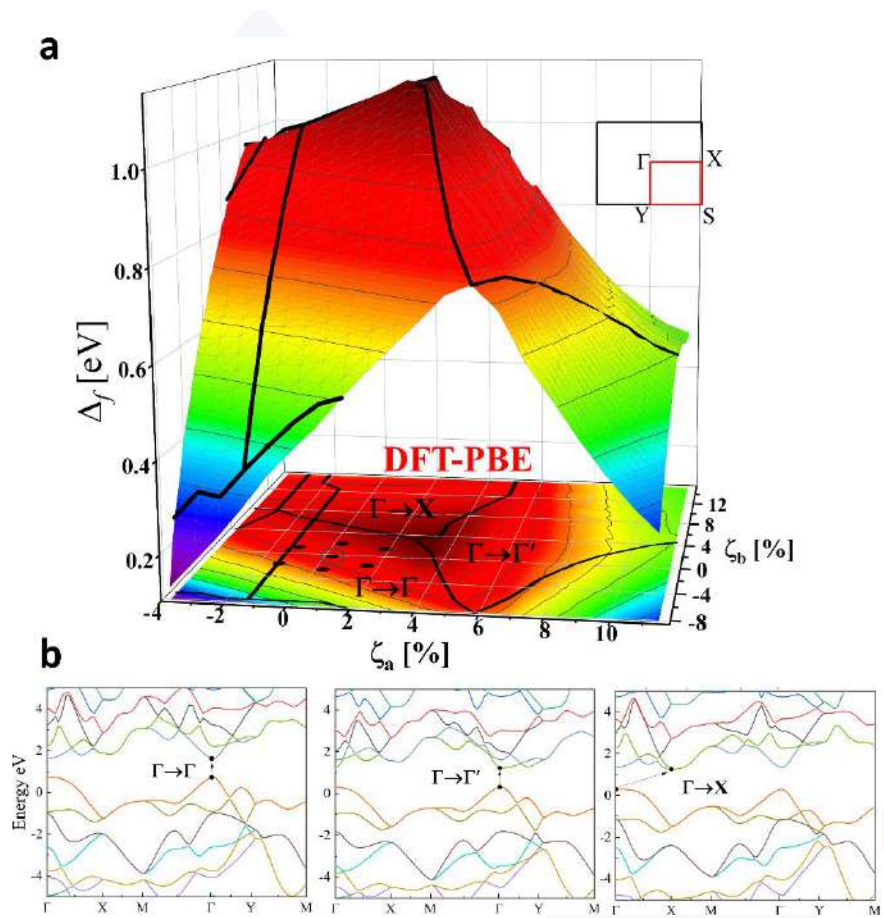


abrupt change of effective mass

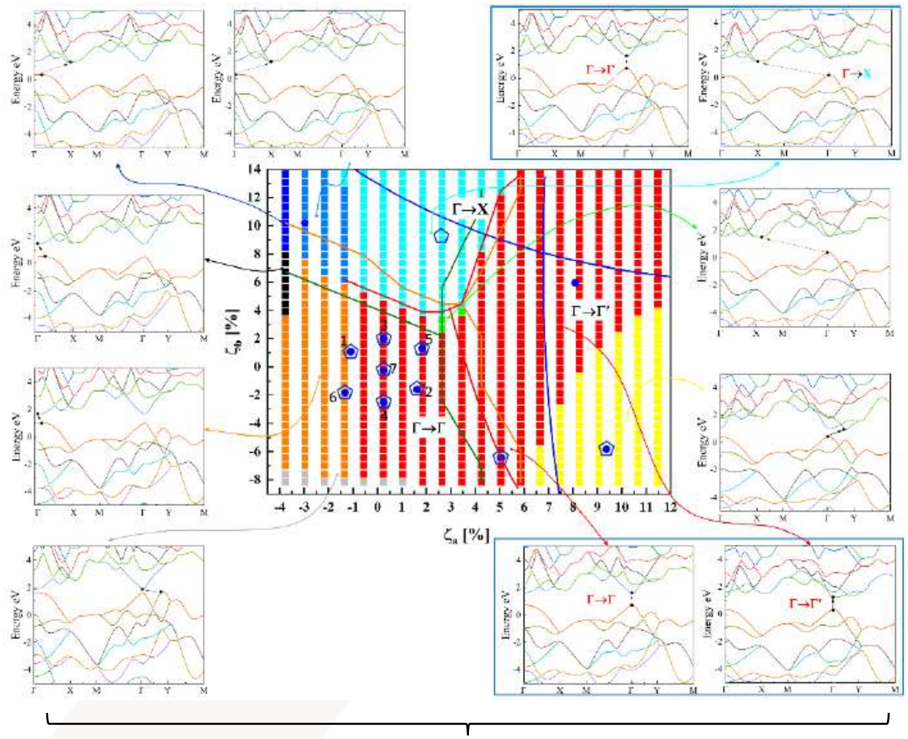


strained phosphorene

qualitative picture: pre-screened by DFT-PBE DFT



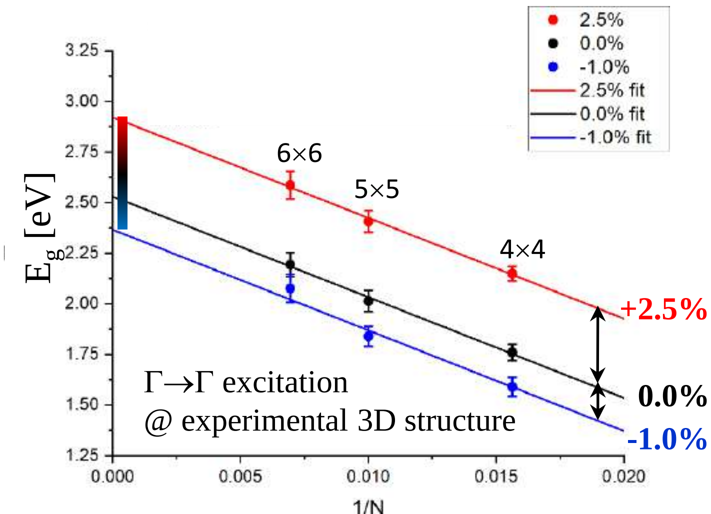
⬆
abrupt change of effective mass



plethora of other excitations

band gap: strain effects

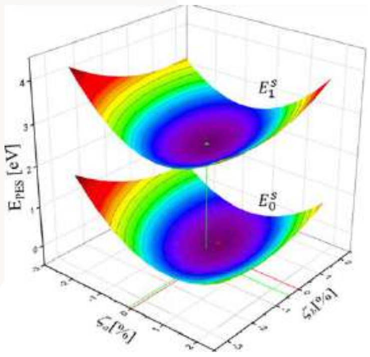
quantitative picture: FNQMC (with DFT-PBE nodes)

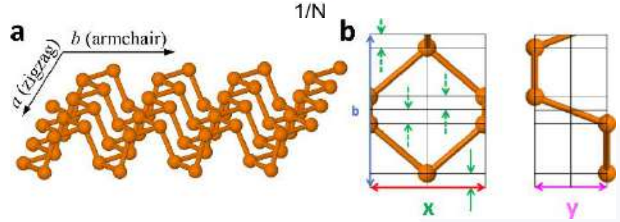


- the strain band gap tuning is quite strong
- quasiparticle band gap scales linearly with the applied strain
- highly nontrivial as the band gaps are differences between ground- and excited-state PESs.

converged ground- and excited-state PESs

parallel; only vertical & lateral offsets





⇒ 4 parameters *a*, *b*, *x*, and *y*

bracketted by at least 25 QMC points

⬇

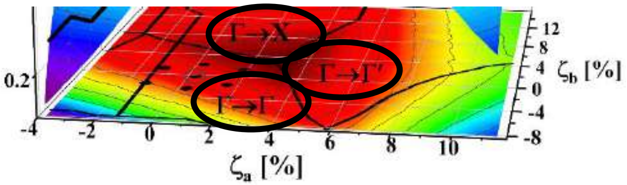
fixing all 4 parameters *a*, *b*, *x*, and *y*: quadrivariate paraboloid function $E_0(a, b, x, y)$, minimize w.r.t. *x*, and *y* for each $(a, b) \Rightarrow E_0(a, b)$

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

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 ':

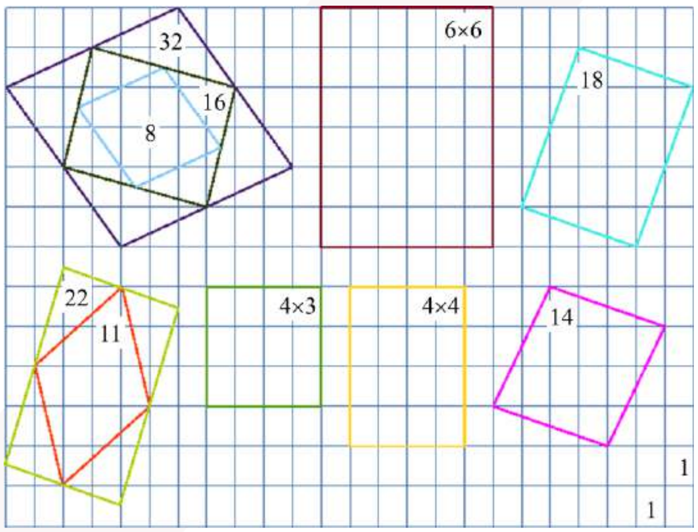
approximants:

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

Γ→X:

approximants:

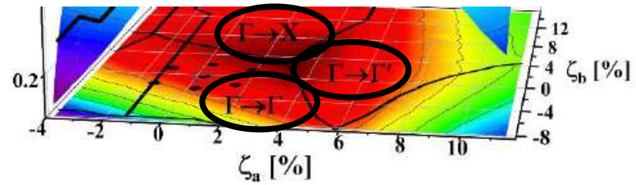
14 prim. u.c. | 4D
16 prim. u.c. | 4D
18 prim. u.c. | 4D
22 prim. u.c. | 4D



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

band gap: strain effects

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



Γ→Γ/ Γ→Γ ':

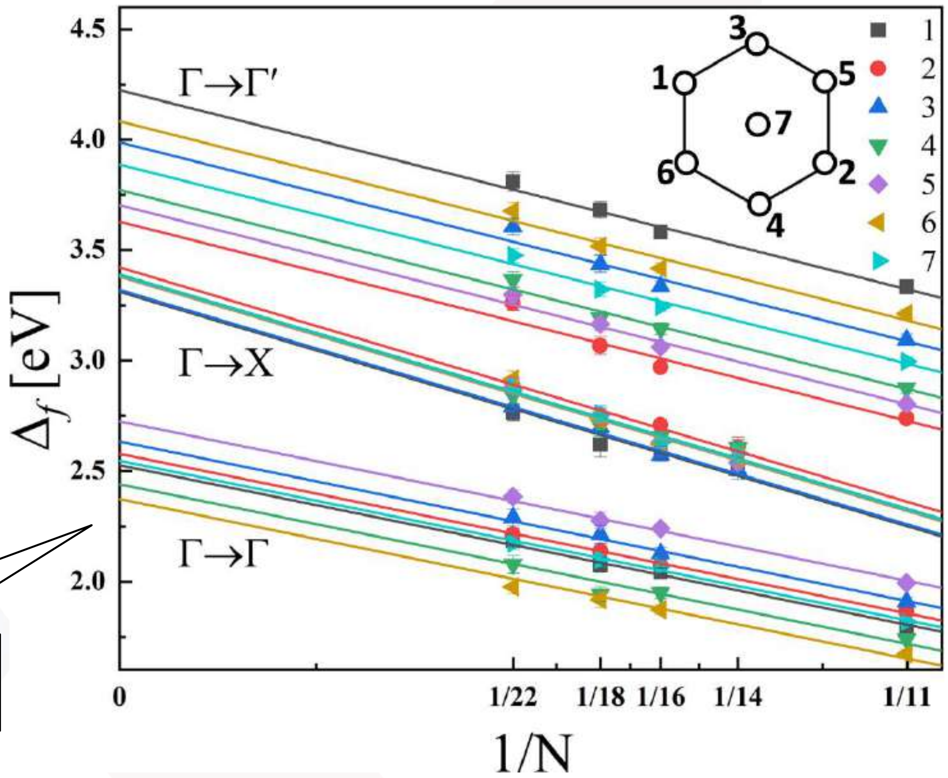
approximants:

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

Γ→X:

approximants:

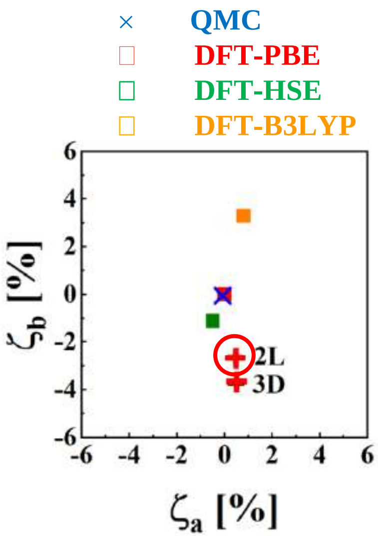
14 prim. u.c. | 4D
16 prim. u.c. | 4D
18 prim. u.c. | 4D
22 prim. u.c. | 4D



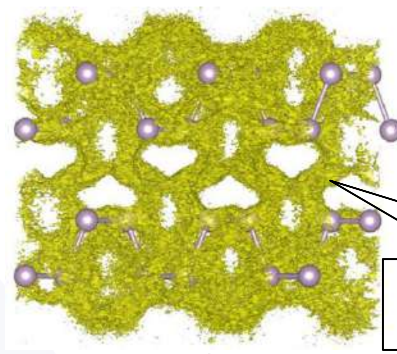
!no twist averaging possible!

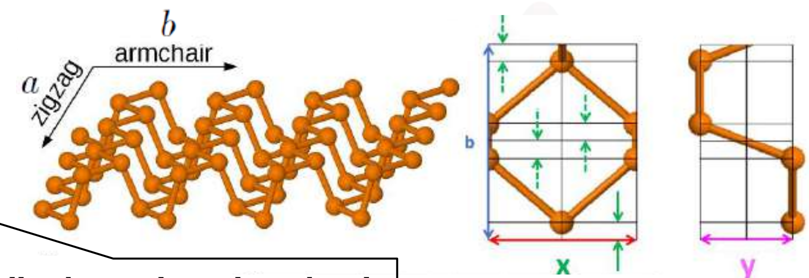
Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

equilibrium properties



2-layer phosphorene





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

expt.

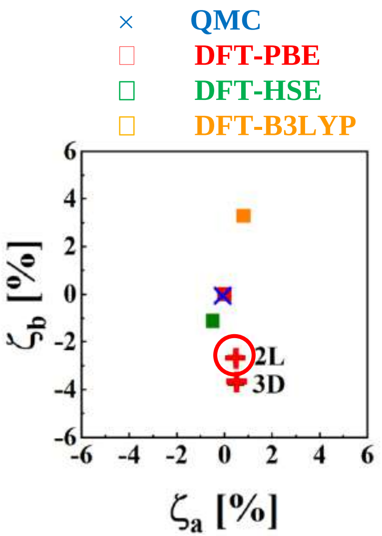
	QMC 11-cell	QMC 16-cell	QMC 22-cell	DFT-PBE	3D-BP
	ground state				
a	6.229±0.008	6.238±0.002	6.230±0.002	6.235	6.2618
b	8.651±0.017	8.688±0.008	8.707±0.006	8.711	8.2700
x	0.748±0.005	0.759±0.002	0.765±0.001	0.770	0.6367
y	3.987±0.007	3.978±0.003	3.985±0.002	3.975	4.0280
E_0^s	-716.563±0.002	-716.498±0.0008	-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

$a = 3.30\pm0.003$Å
$b = 4.61\pm0.006$ Å
$x = 0.405\pm0.001$ Å
$y = 2.109\pm0.001$ Å

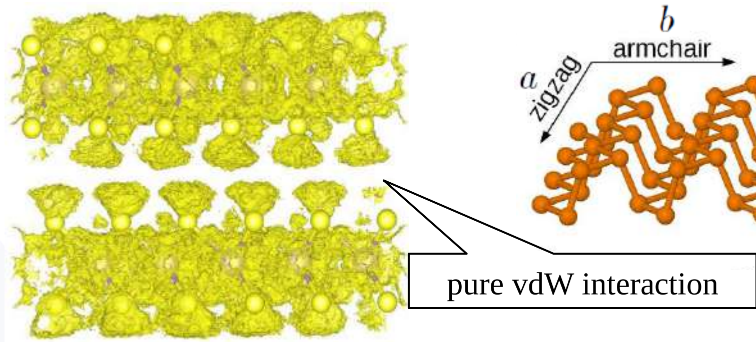
not known experimentally

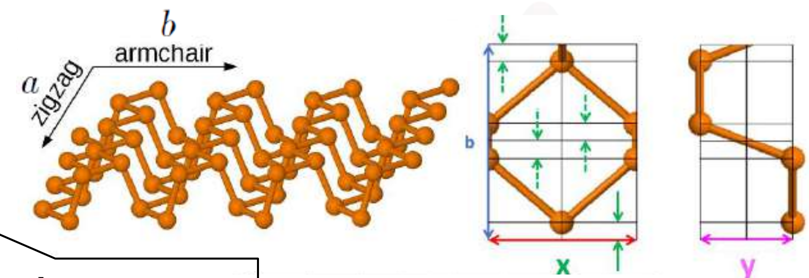
E. Gaufr`es, F. Fossard, V. Gosselin, *et al.*, Nano Lett. **19**, 8303 (2019)
Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

equilibrium properties



2-layer MoS_2





expt.

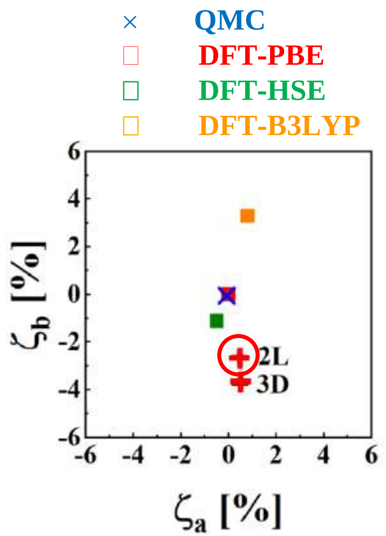
	QMC 11-cell	QMC 16-cell	QMC 22-cell	DFT-PBE	3D-BP
	ground state				
a	6.229±0.008	6.238±0.002	6.230±0.002	6.235	6.2618
b	8.651±0.017	8.688±0.008	8.707±0.006	8.711	8.2700
x	0.748±0.005	0.759±0.002	0.765±0.001	0.770	0.6367
y	3.987±0.007	3.978±0.003	3.985±0.002	3.975	4.0280
E_0^s	-716.563±0.002	-716.498±0.0008	-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

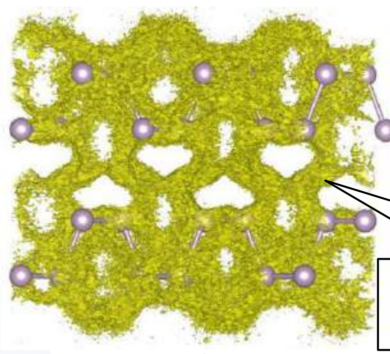
not known experimentally

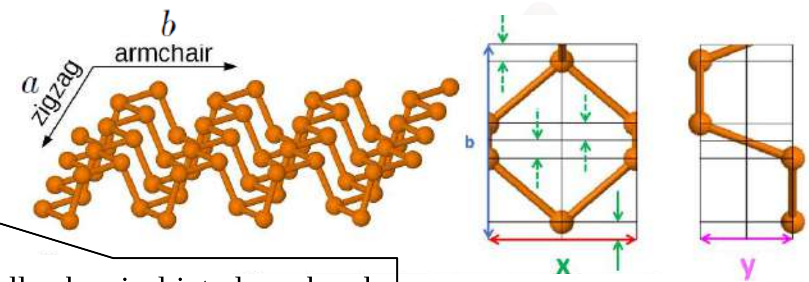
E. Gaufr`es, F. Fossard, V. Gosselin, *et al.*, Nano Lett. **19**, 8303 (2019)
Y. Huang, A. Faizan, M. Manzoor, J. Brndiar, L. Mitas, J. Fabian, and I. Štich, Phys. Rev. Reserach **5**, 033223 (2023).

equilibrium properties



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

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

not known experimentally

$$\Delta_f = 2.53 \pm 0.020 \text{ eV} \Leftrightarrow 2.46 \text{ eV}$$

experimental value for freestanding phosphorene

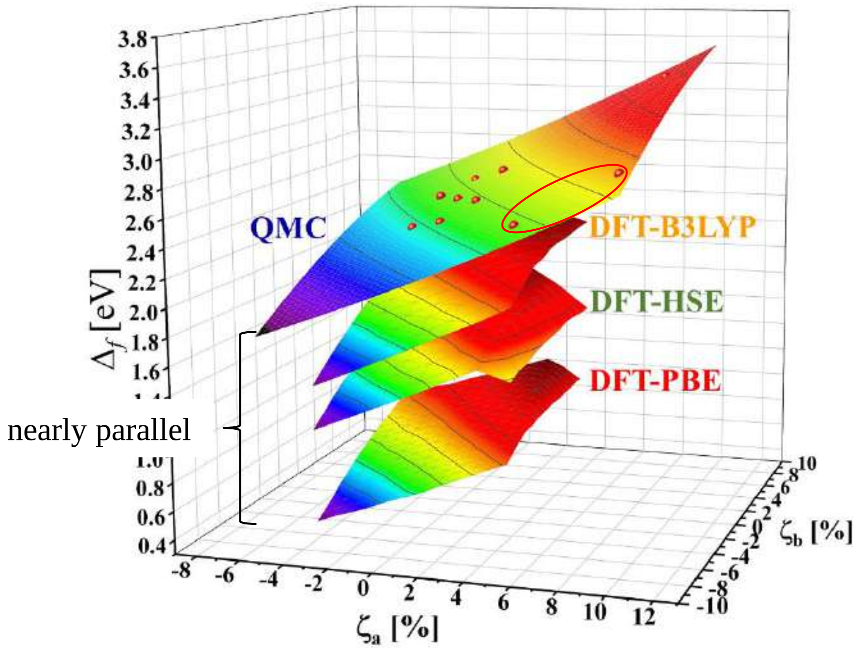
⇑

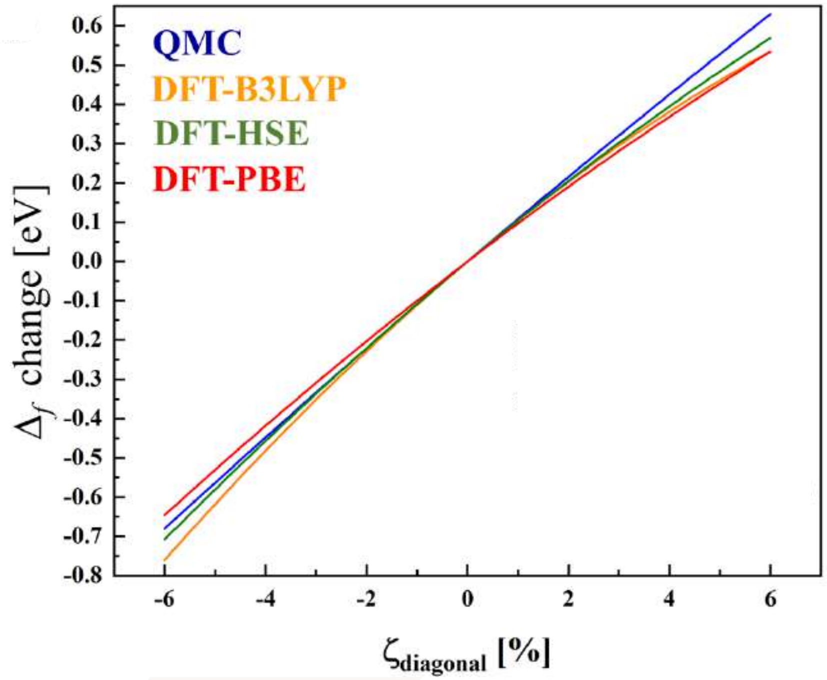
(almost) **chemical precision**
(no vibronic and zero-point corrections)

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**





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

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

large gauge factor: ≈100 meV/%

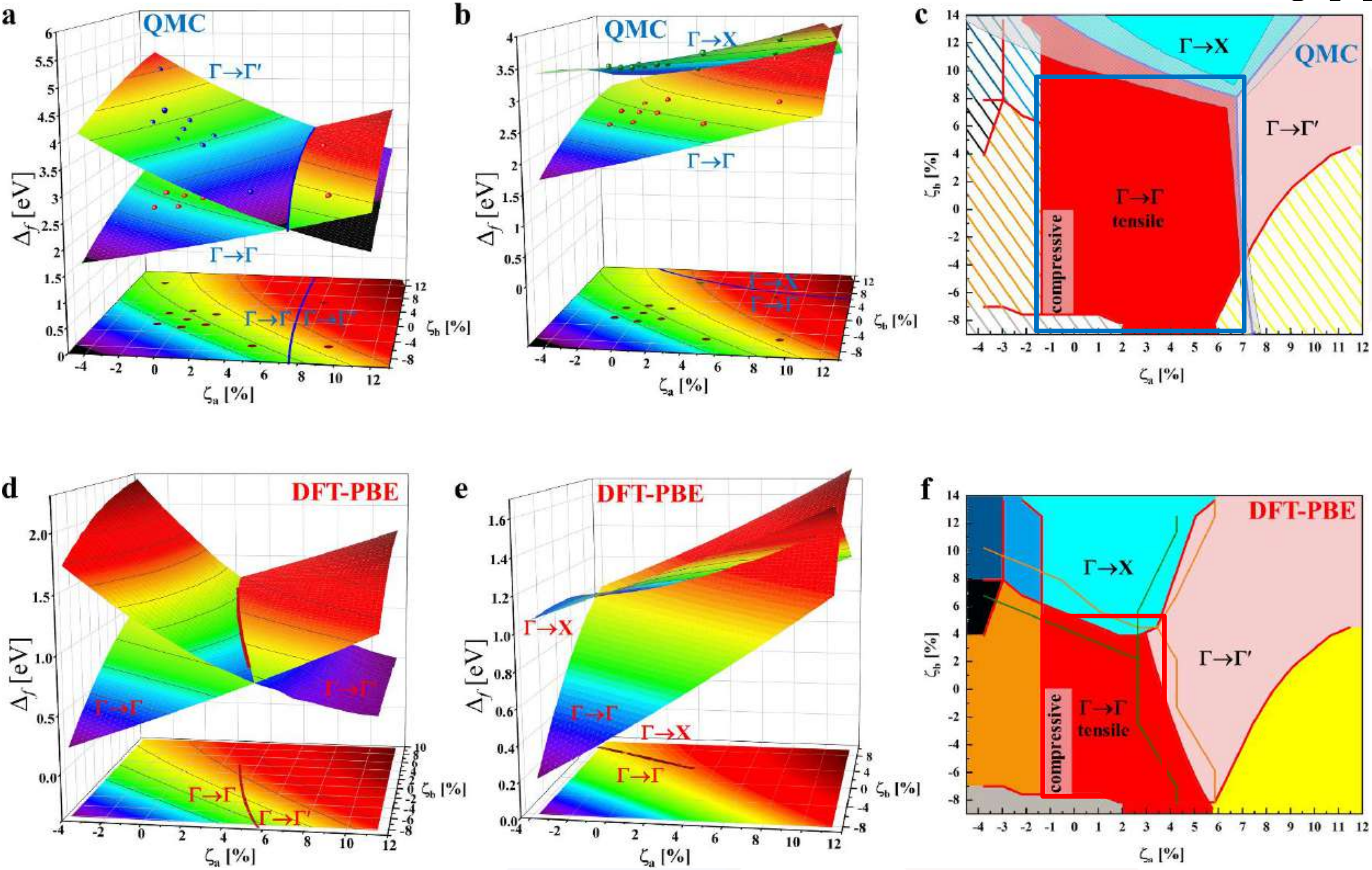
⬍

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

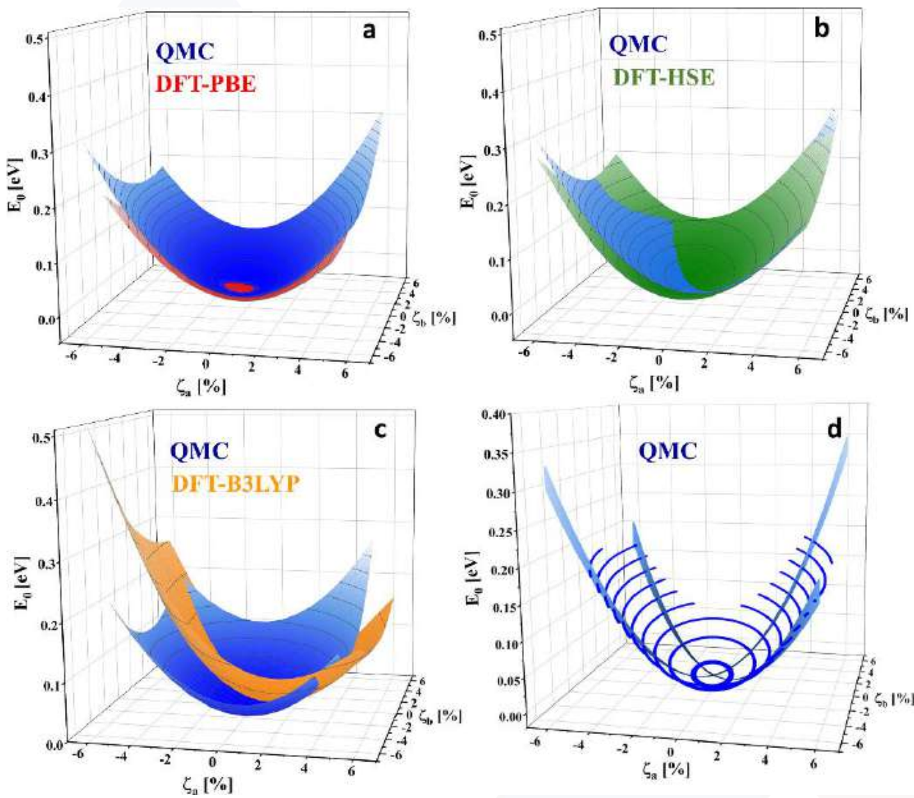
≈1 eV tuning mainly in tensile strain

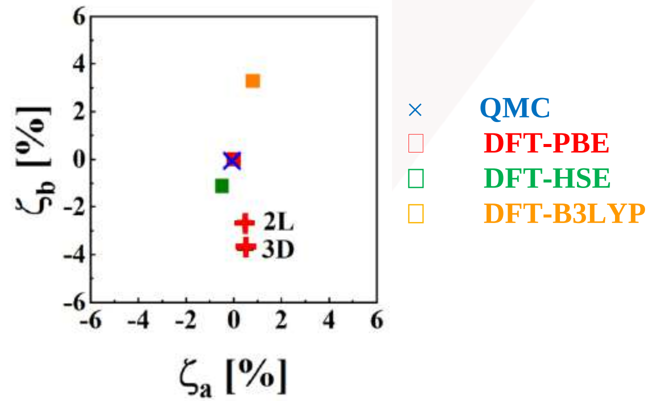
strain tuning area in DFT much smaller

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).

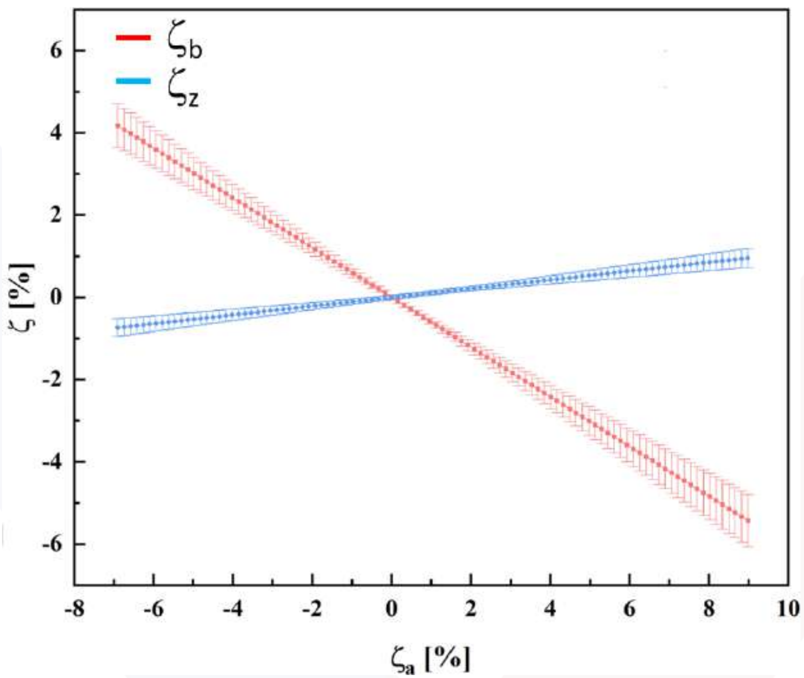
deformation energies





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 in-plane

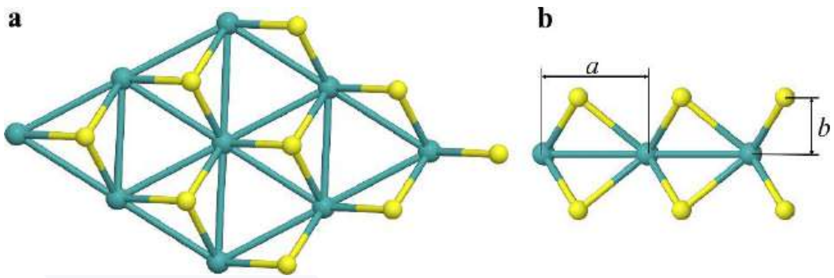
negative out-of-plane

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



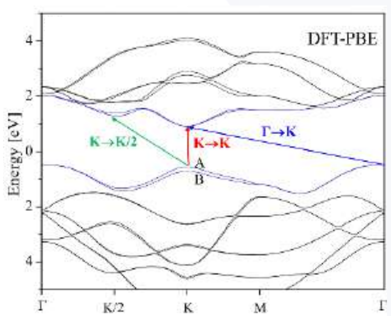
consider only diagonal strain (a)

$\Rightarrow$ 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

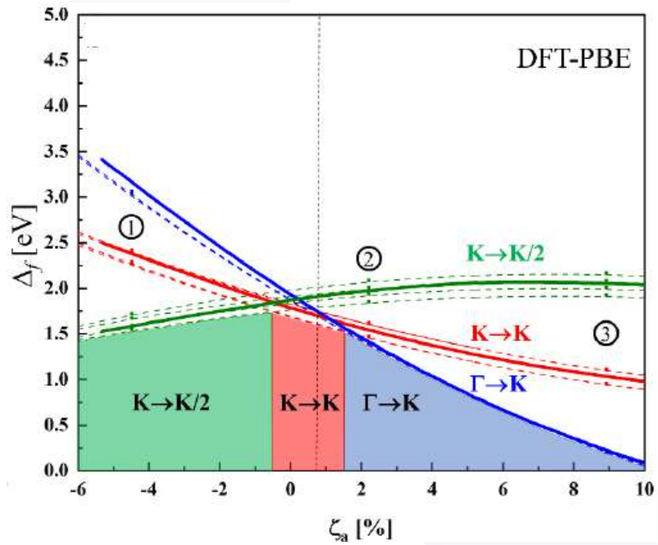


Y. Huang, M. Manzoor, J. Brndiar, and I. Štich, Phys. Rev. Research **6**, 013007 (2024).

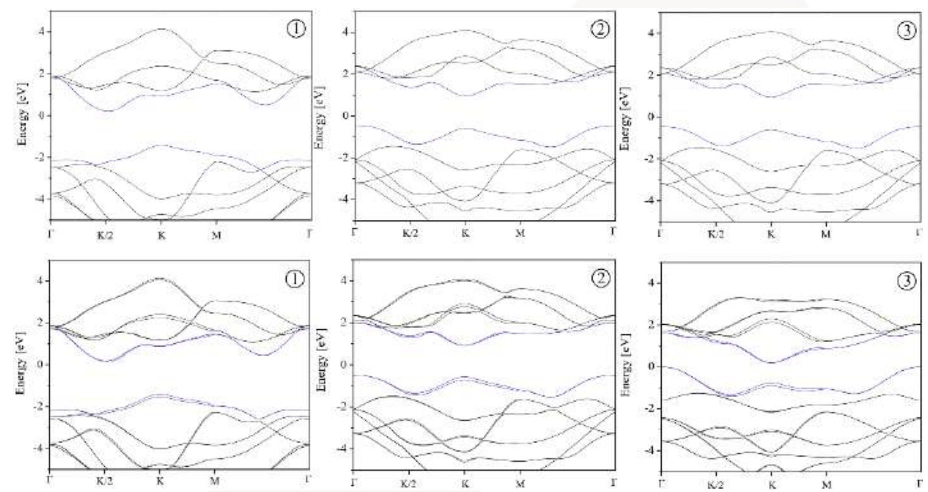
monolayer MoS_2

qualitative picture: pre-screened by DFT-PBE DFT

band gap phase diagram



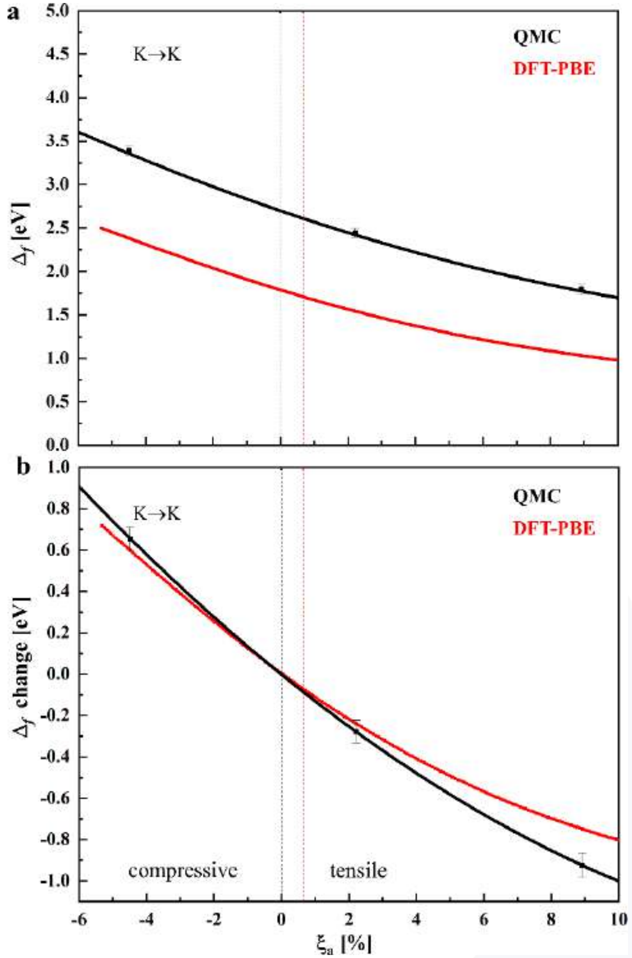
SOC splittings:



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

band gap: strain effects

K→K exitation



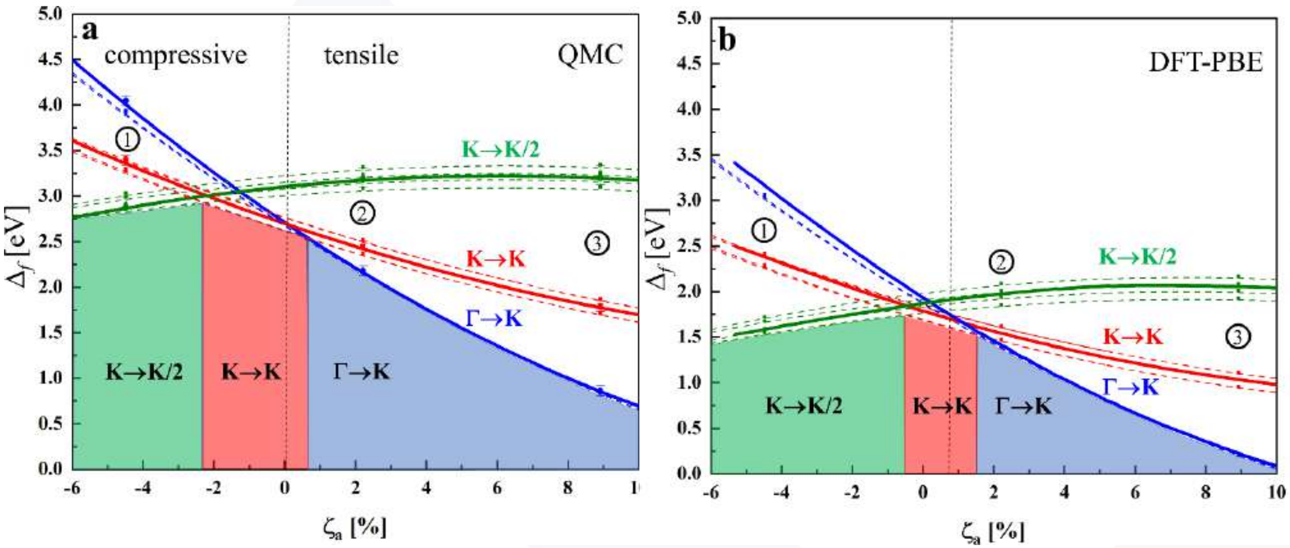
DFT-PBE rigid band gap offset by ≈1 eV

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



transition	gauge factor 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).

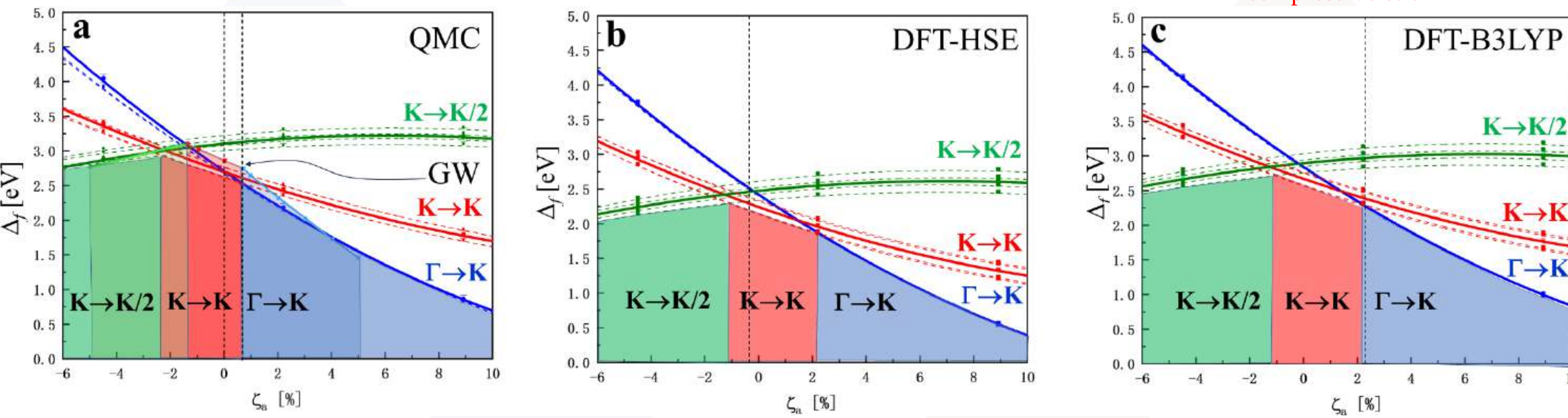
band gap: strained gap boundaries

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						
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	-

⇒ 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

- 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