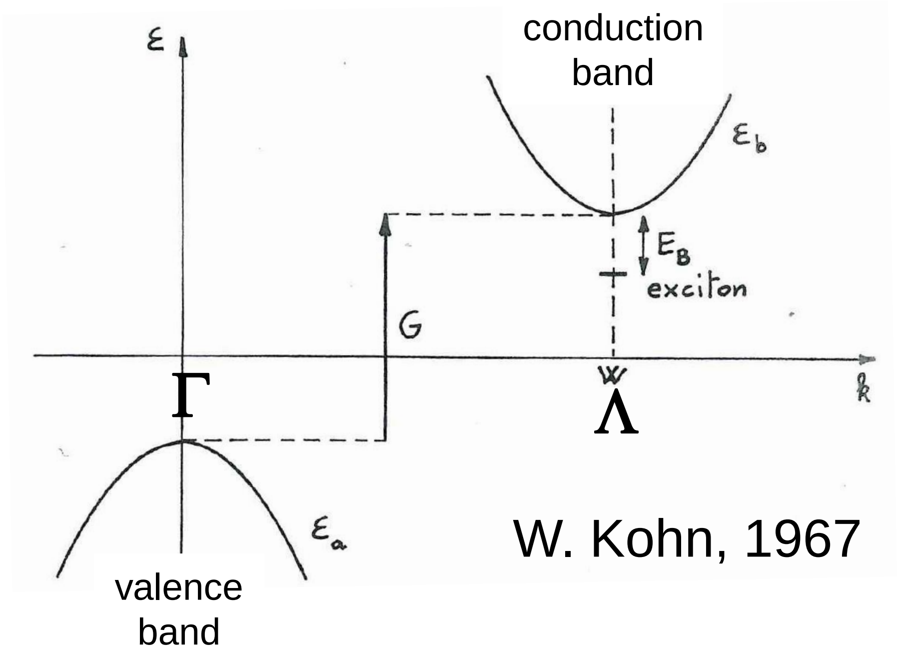
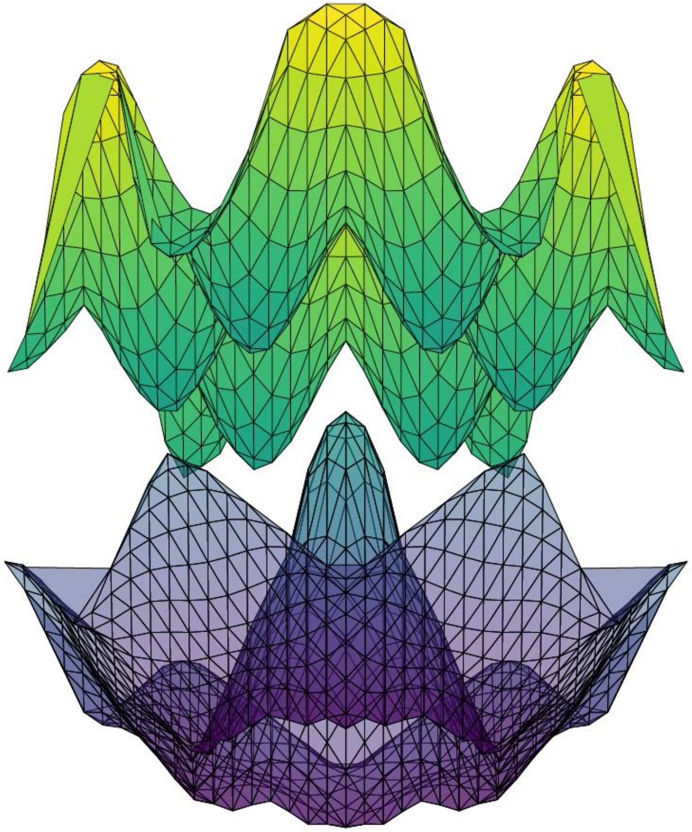
Monolayer WTe_2 and pressurized MoS_2 as ideal excitonic insulators

Massimo Rontani

CNR-NANO, Modena, Italy



W. Kohn, 1967



S. Ataei *et al.*, PNAS 2021

D. Varsano

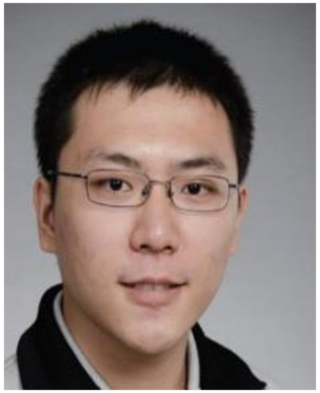
S. Ataei

E. Molinari

M. Palummo

first-principles many-body perturbation theory

B. Sun



D. Cobden

experiment in WTe_2

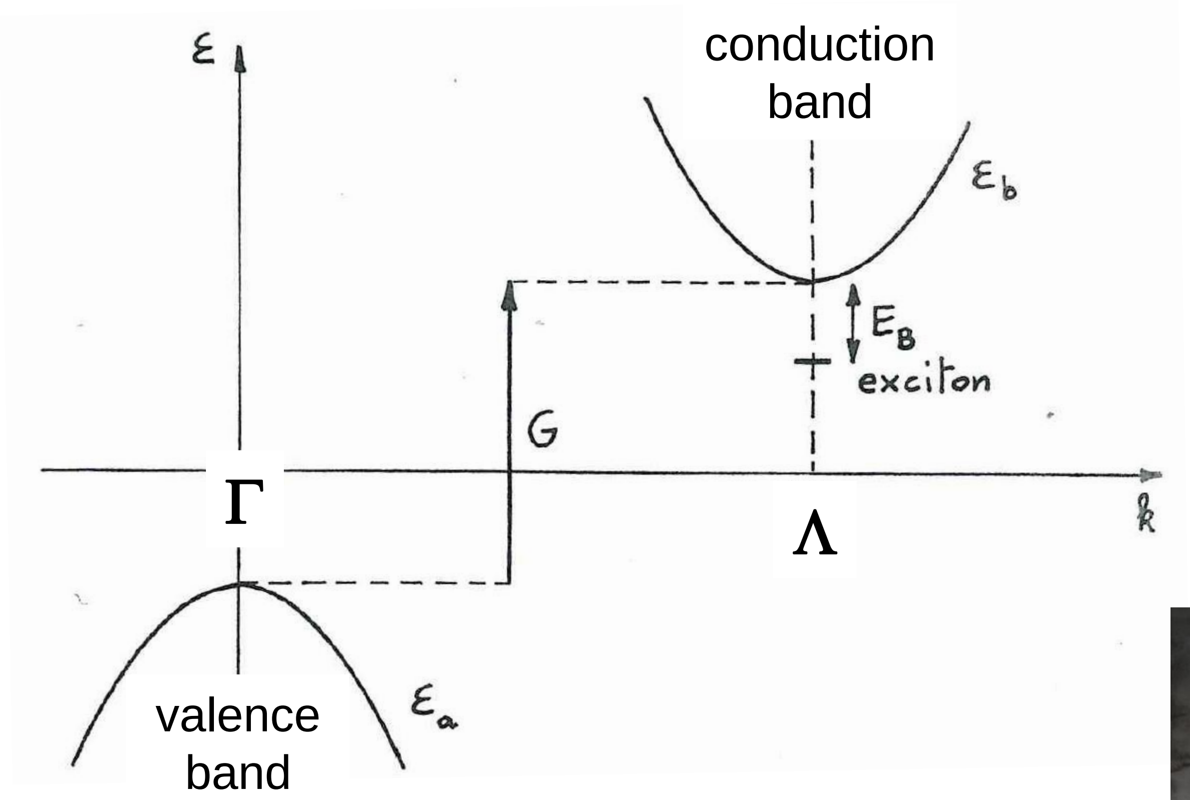
Cnr-Nano, Modena, Italy

Univ. Modena, Italy

Univ. Roma Tor Vergata, Italy

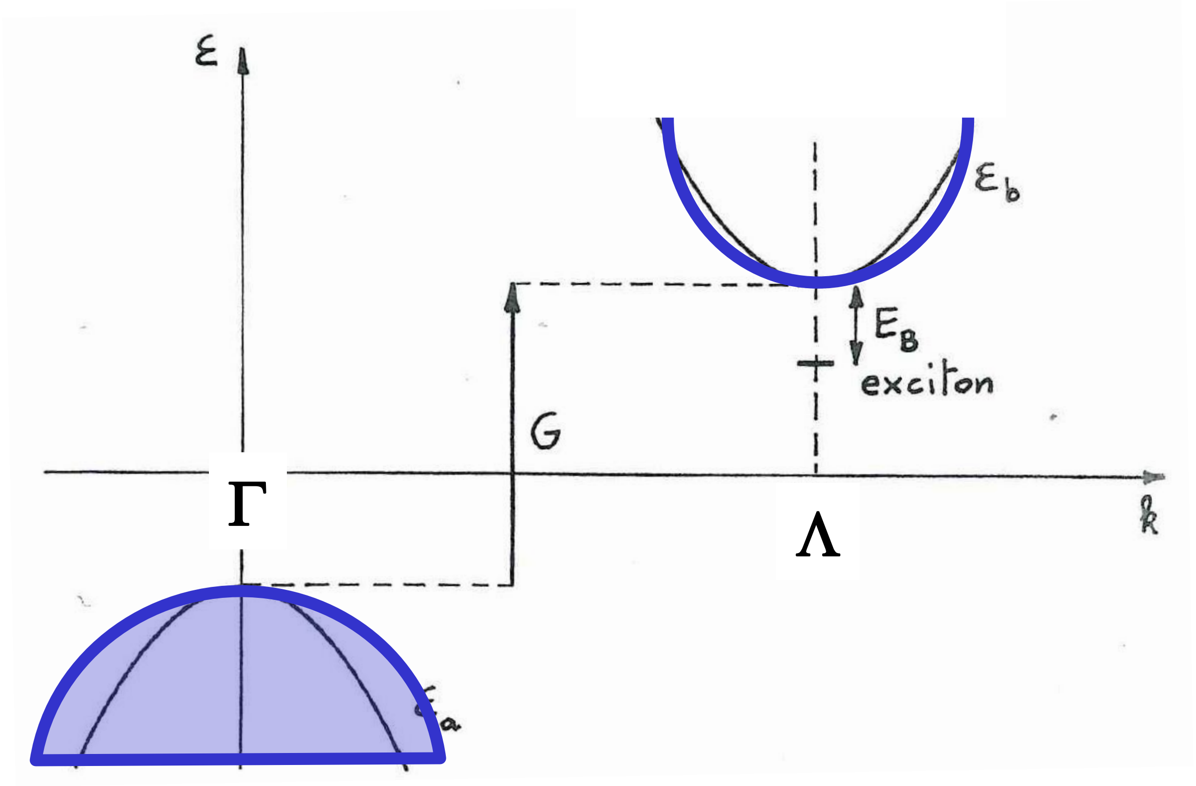
Univ. Washington, Seattle, USA

excitonic instability



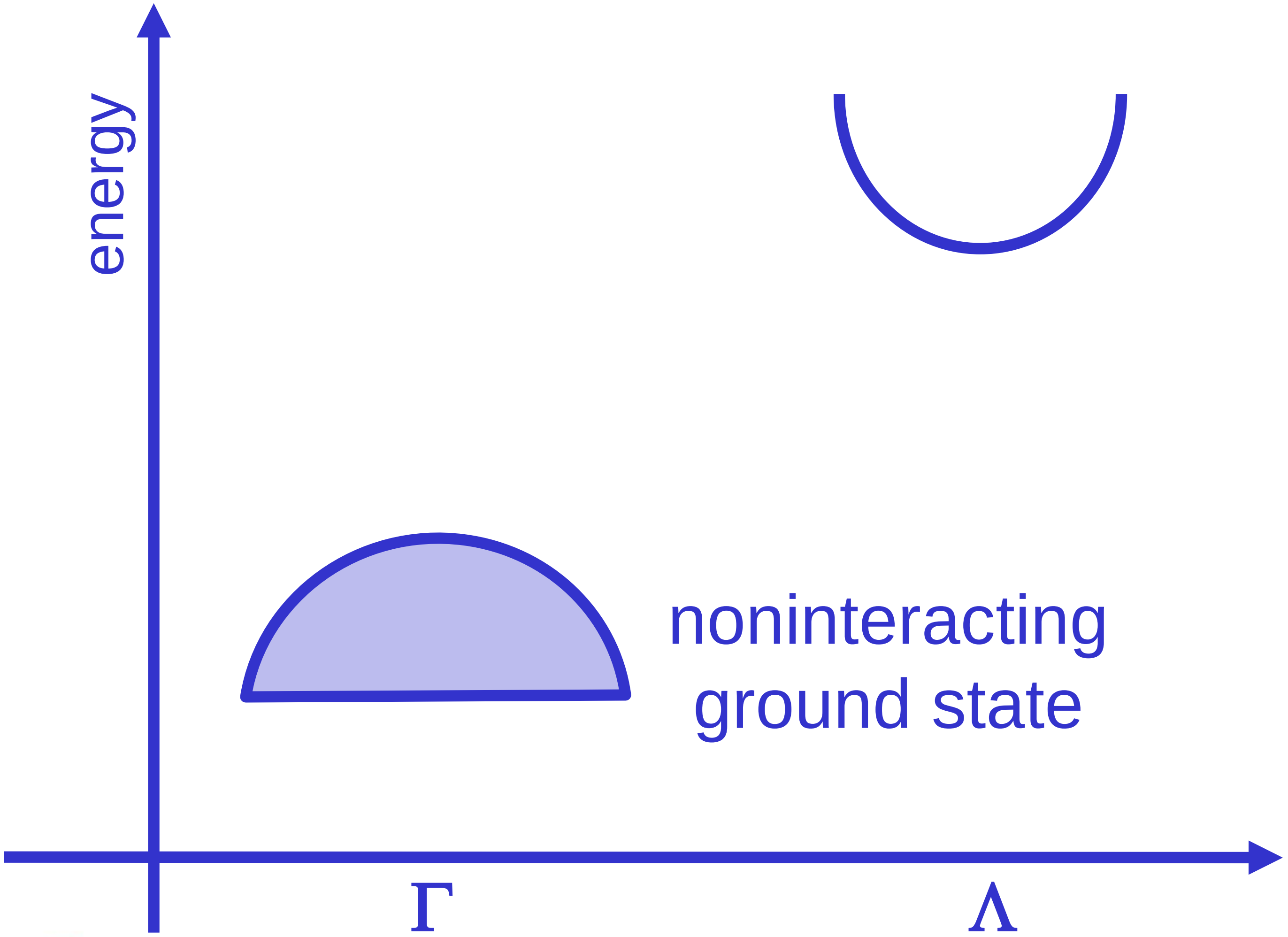
W. Kohn, 1967

excitonic instability

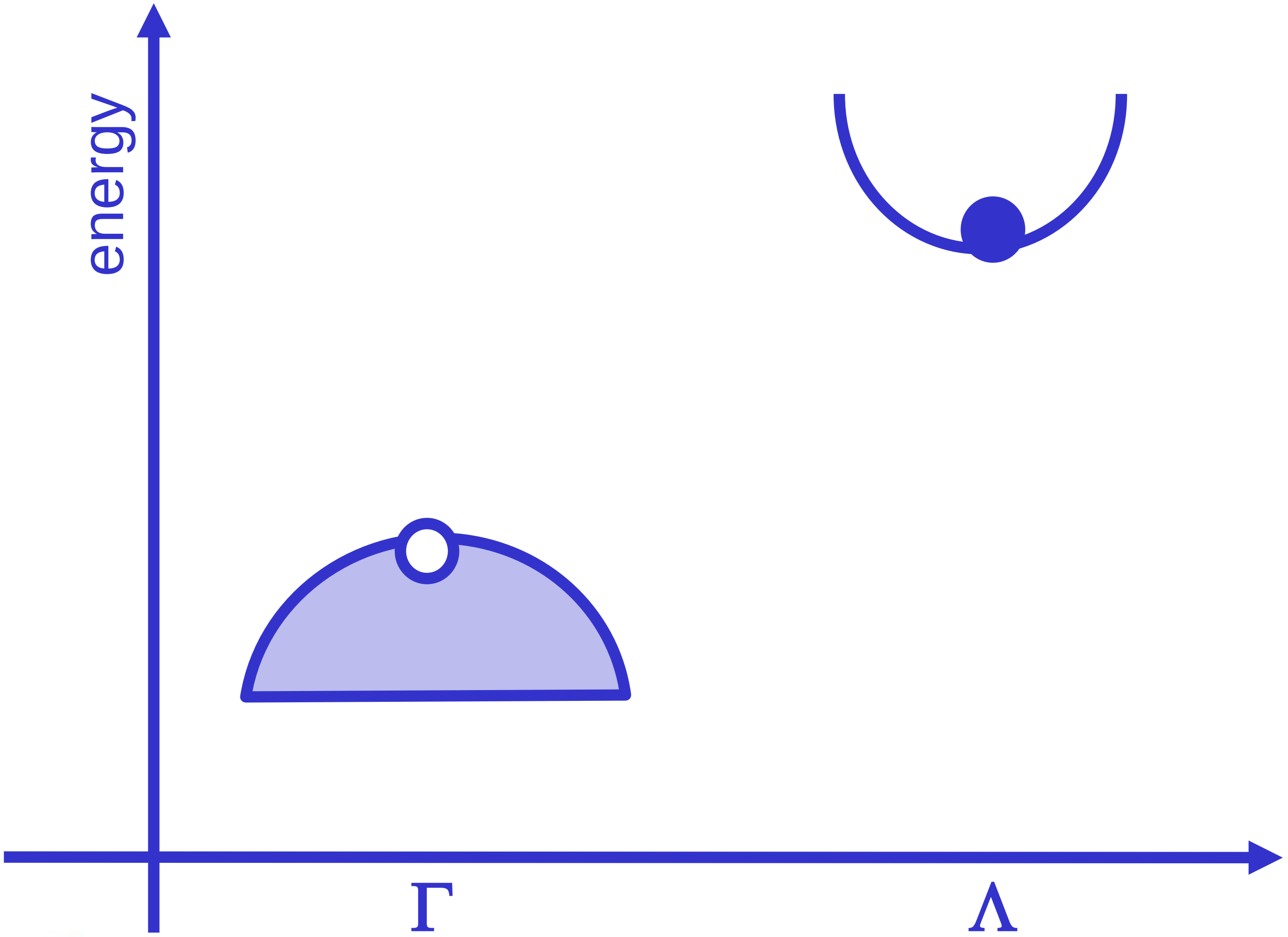


W. Kohn, 1967

excitonic instability

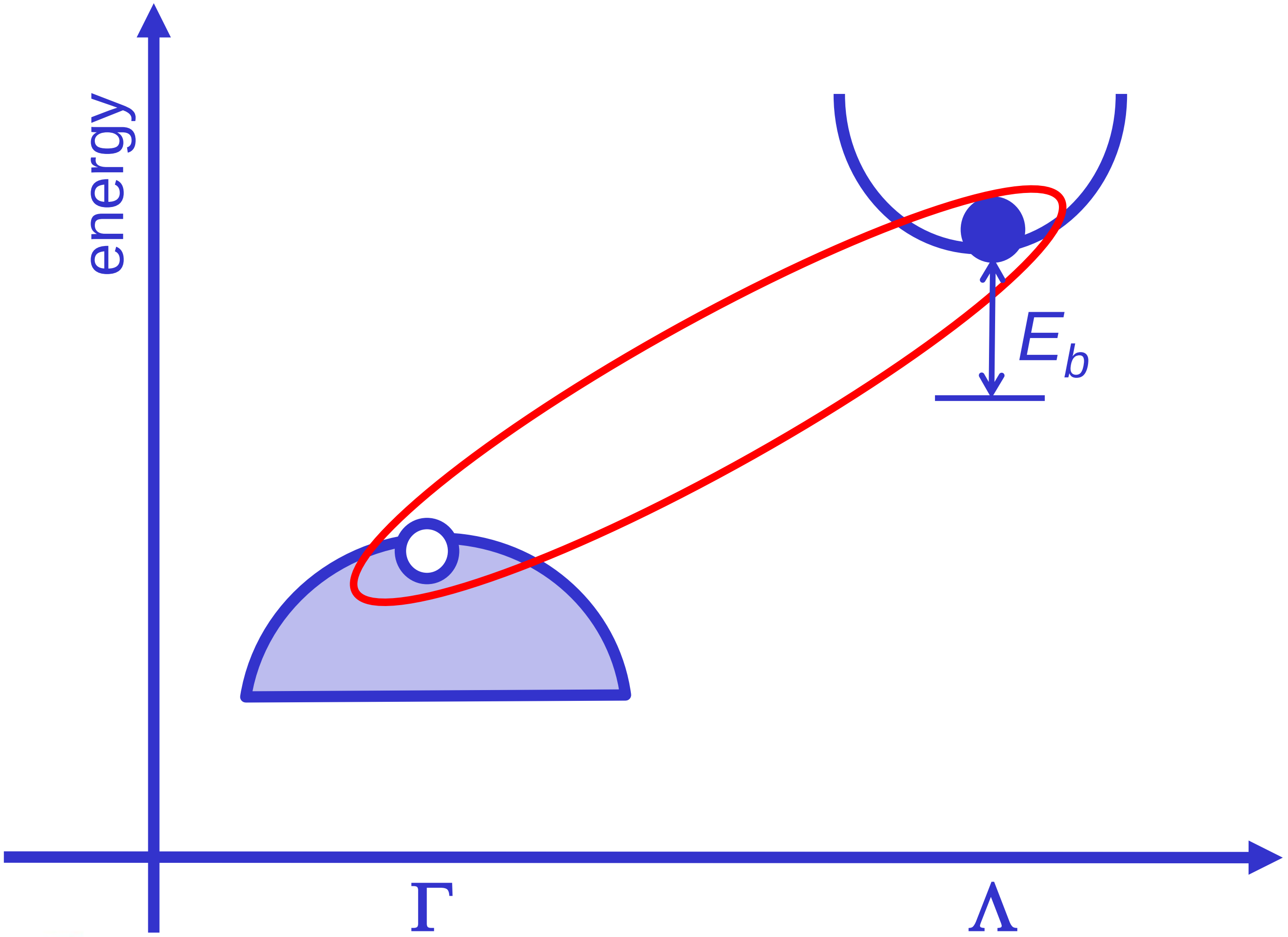


excitonic instability



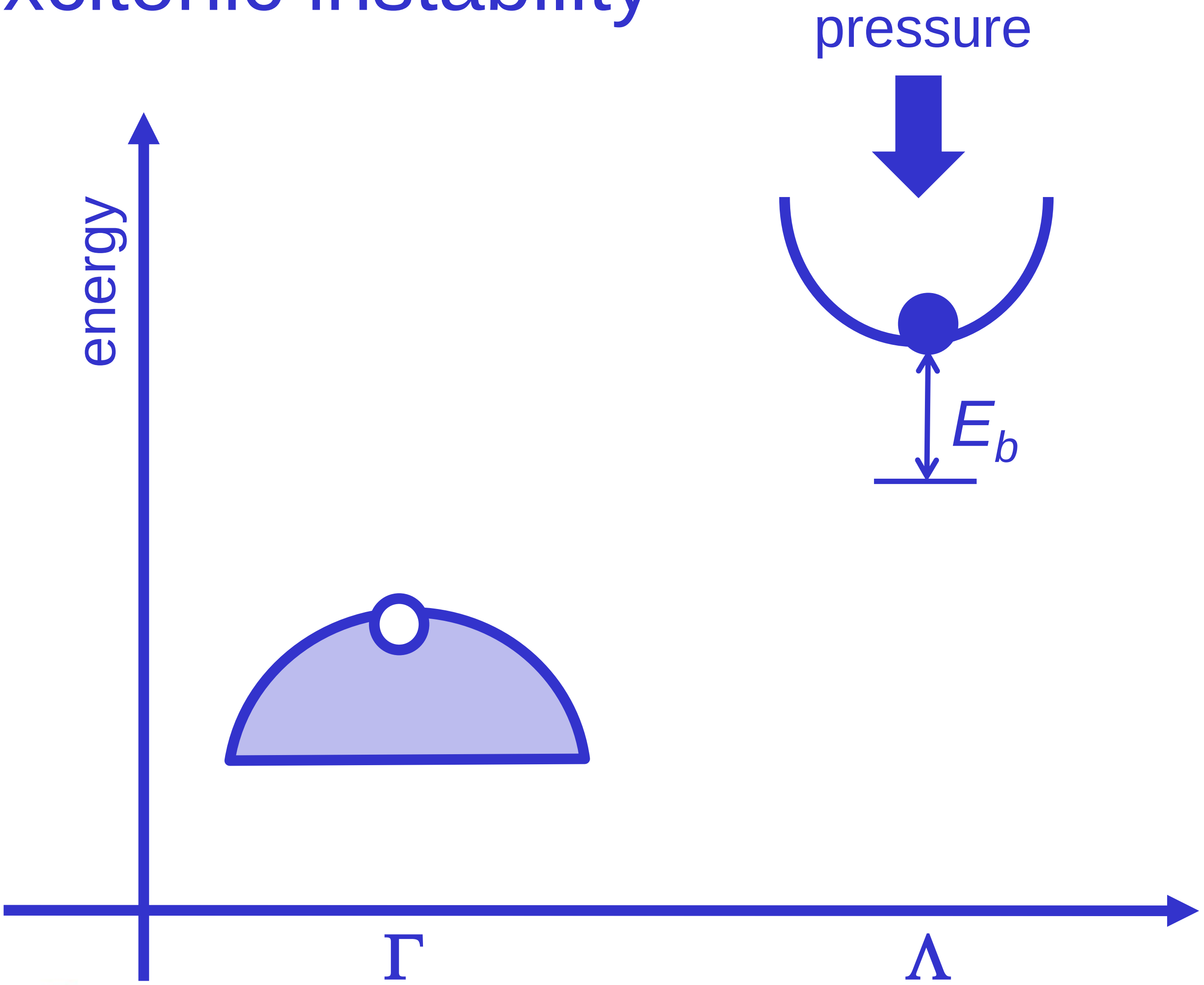
unbound
e-*h* pair

excitonic instability

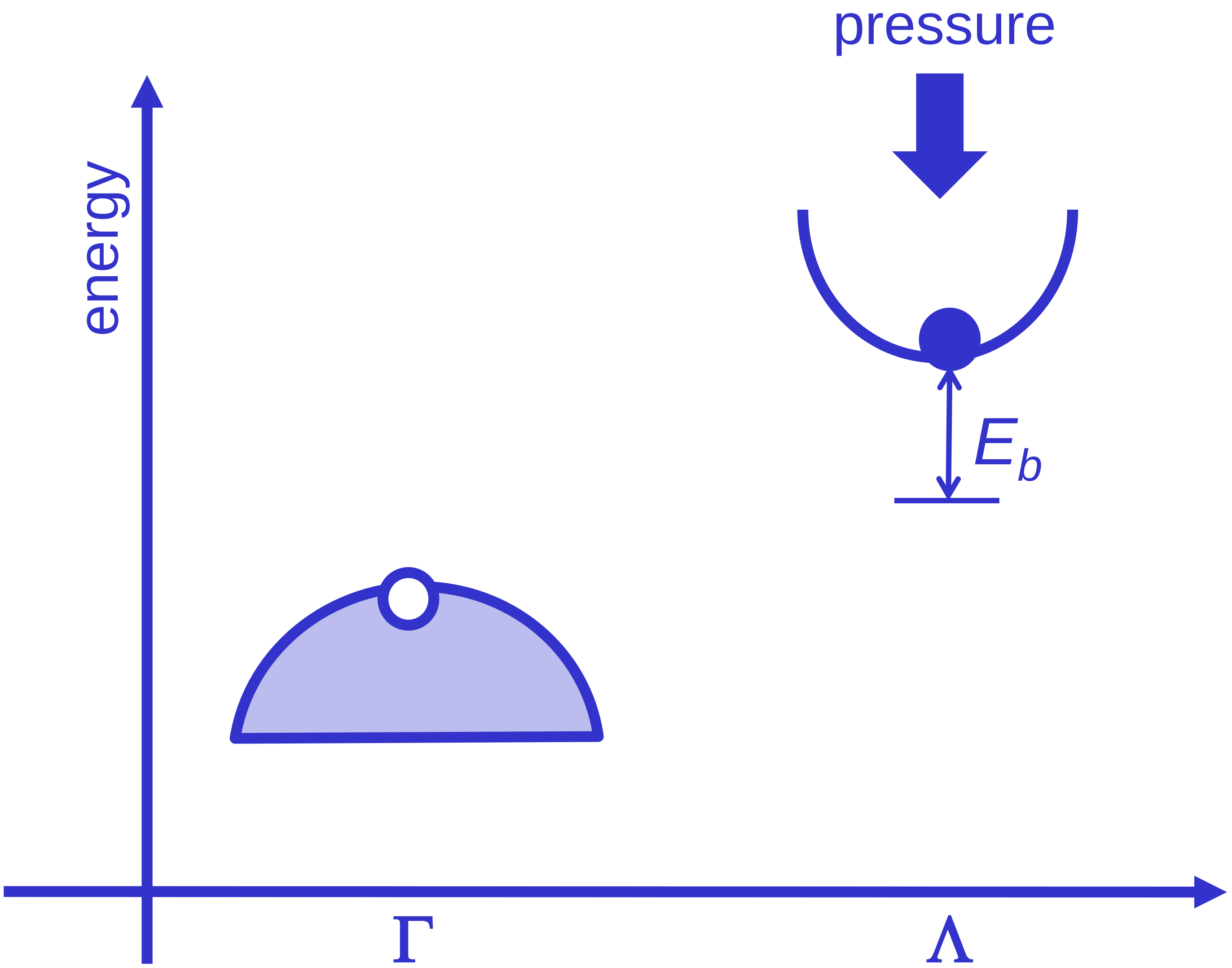


exciton

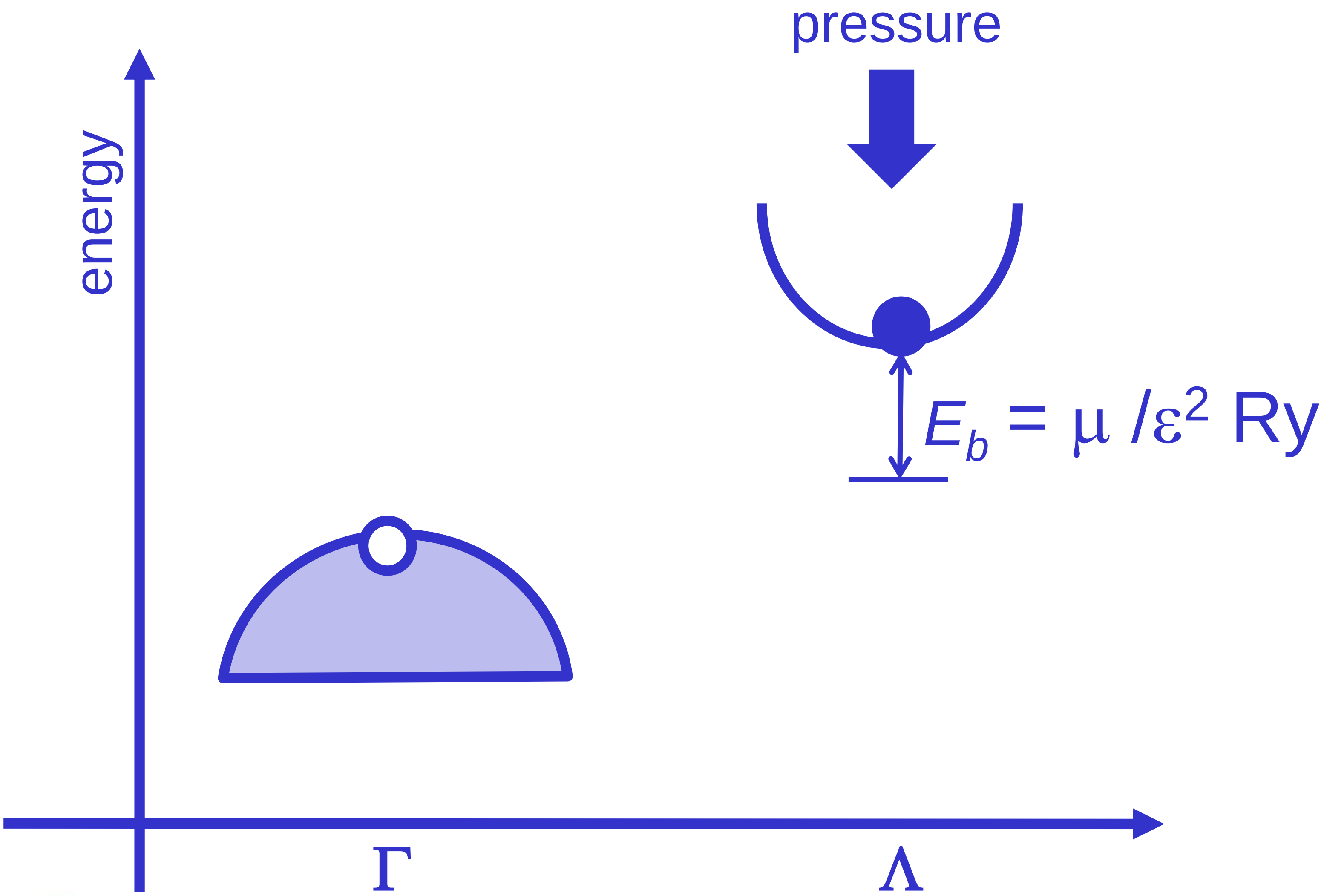
excitonic instability



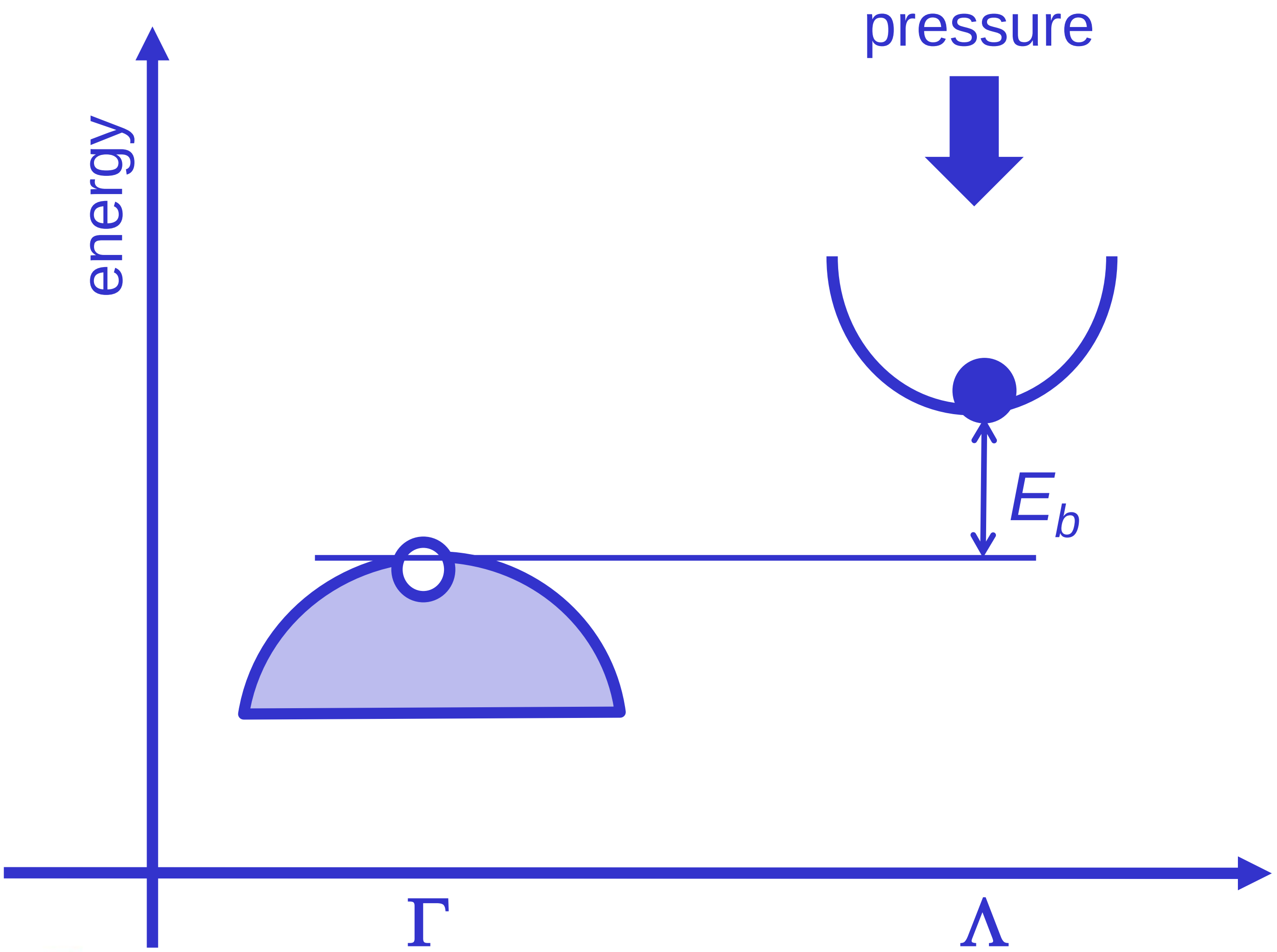
excitonic instability



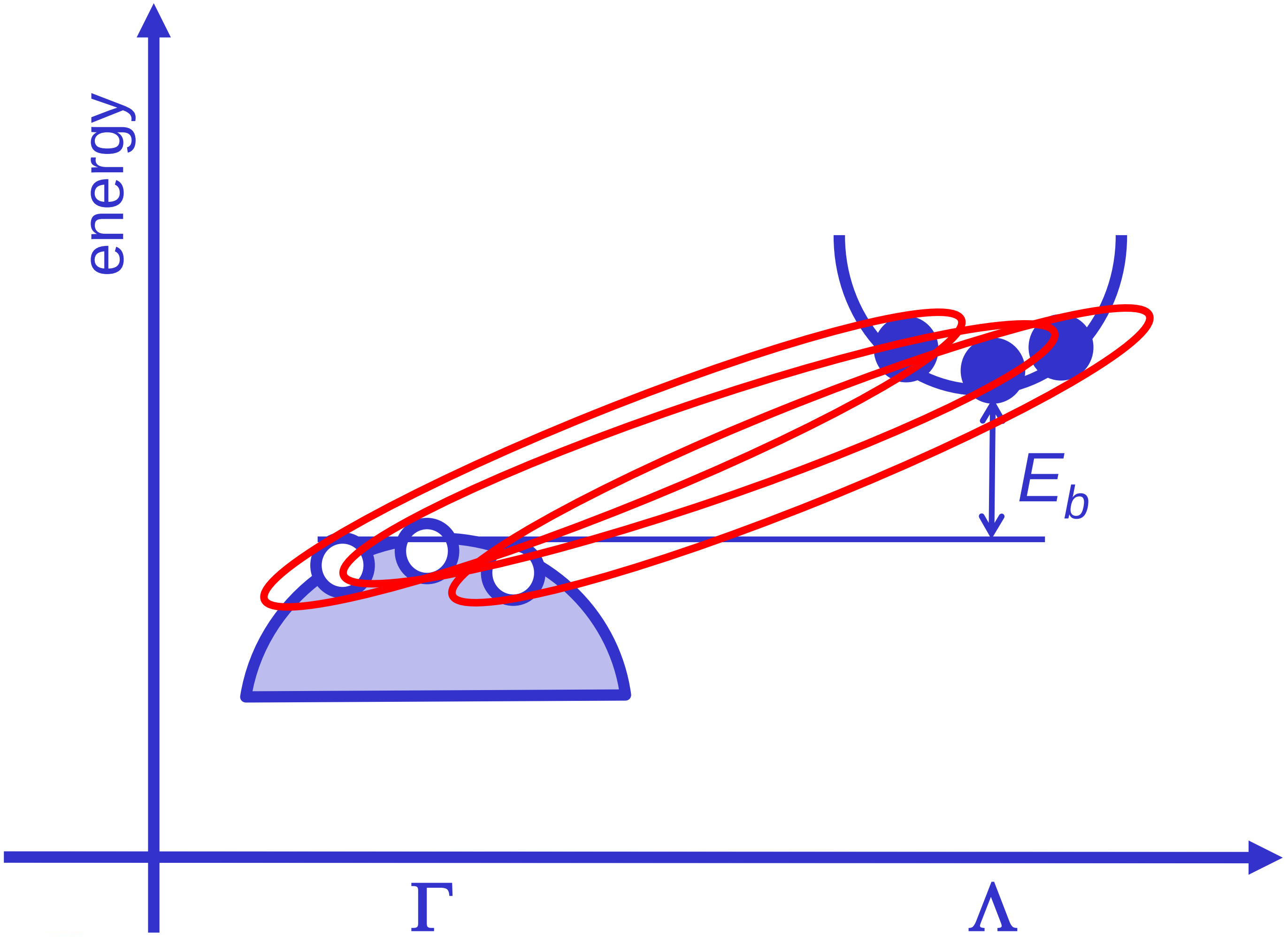
excitonic instability



excitonic instability

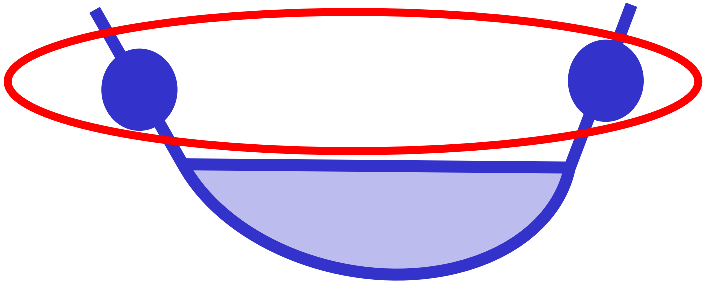


excitonic insulator



thermodynamic phase transition

Cooper problem

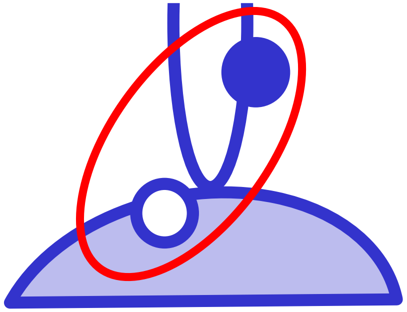


reconstructed ground state

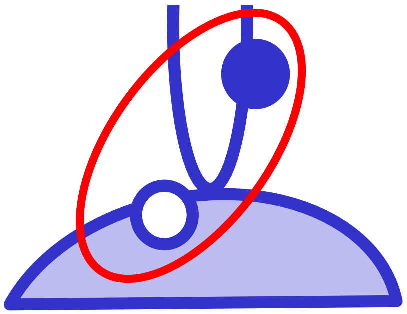
$$k_b T_c \approx E_b$$

many-body gap

exciton



excitonic insulator



excitonic insulator

strongly correlated semiconductor

broken symmetry inherited from exciton character

peculiar collective modes

Keldysh & Kopaev 1964; des Cloizeaux 1965;
Jèrome, Rice & Kohn 1967; Halperin & Rice 1968

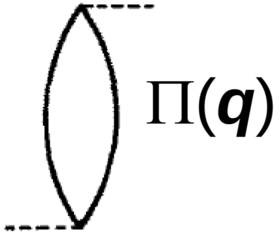
excitonic insulator hard to realize

$$k_b T_c \approx E_b = \mu / [\varepsilon(\mathbf{q} = 0)]^2 \text{ Ry}$$

$$\varepsilon(\boldsymbol{q}) = 1 + \frac{4\pi e^2}{\Omega q^2} \Pi(\boldsymbol{q})$$

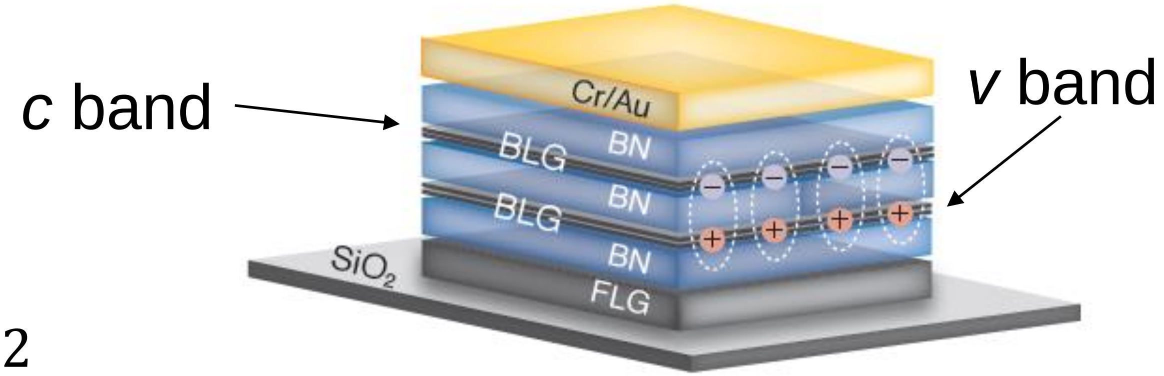
RPA polarizability $\Pi(\mathbf{q})$ **increases** with vanishing gap

$$\Pi(\boldsymbol{q}) = \sum_{\mathbf{k}} \frac{|\langle c|v\rangle|^2}{\varepsilon_c(\mathbf{k}+\mathbf{q}) - \varepsilon_v(\mathbf{k})}$$



c = conduction band
v = valence band
μ = exciton effective mass
Ω = volume

separate electrons from holes in real space



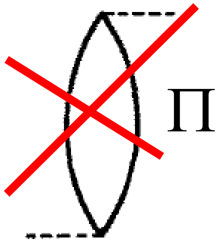
c band

v band

Li *et al*., Nat. Phys. **13,** 751 (2017)

$$\varepsilon(\boldsymbol{q}) = 1 + \frac{4\pi e^2}{\Omega q^2}\Pi(\boldsymbol{q})$$

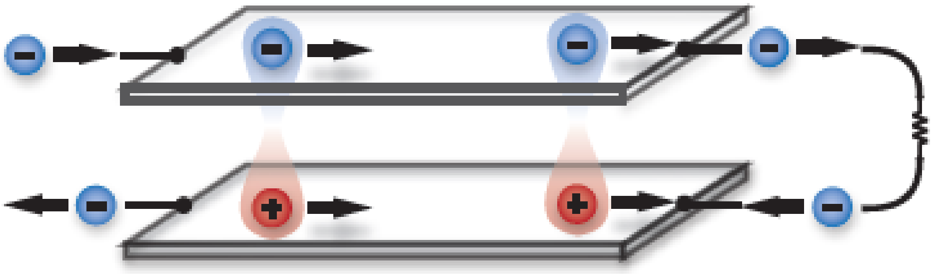
$$\Pi(\boldsymbol{q}) = \sum_{\mathbf{k}} \frac{\cancel{|\langle c|v\rangle|}^2}{\varepsilon_c(\mathbf{k}+\mathbf{q}) - \varepsilon_v(\mathbf{k})}$$



$\Pi(\boldsymbol{q})$

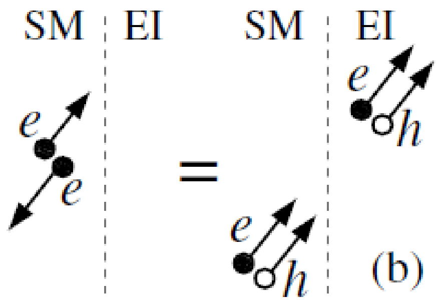
excitonic insulator in bilayers

Counterflow superconductivity

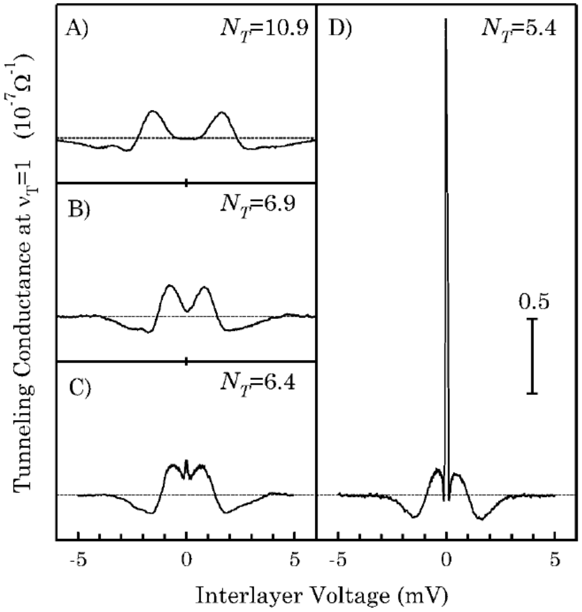


Lozovik & Yudson 1976

Andreev reflection



Rontani & Sham PRL 2005



Spielman *et al*. PRL 2000

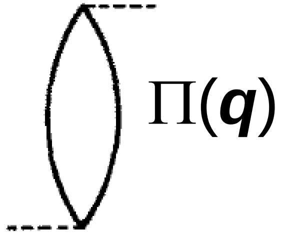
Eisenstein *et al*., Nature **432,** 691 (2004)
Nandi *et al*., Nature **488,** 481 (2012)
Li *et al*., Nat. Phys. **13,** 751 (2017)
Liu *et al*., Nat. Phys. **13,** 746 (2017)
Ma *et al*., Nature **598,** 585 (2021)
Liu *et al*., Science **375,** 205 (2022)

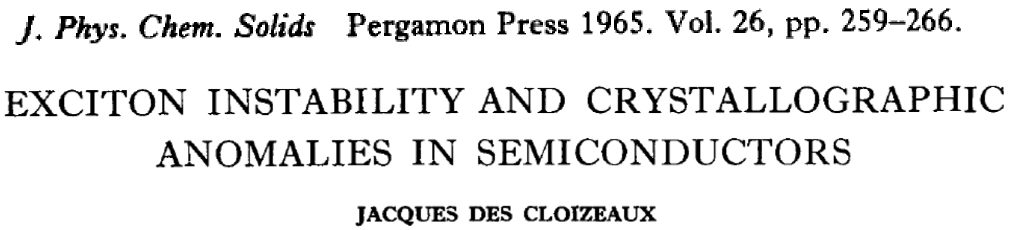
consider **indirect-gap** materials

$$\varepsilon(\boldsymbol{q}) = 1 + \frac{4\pi e^2}{\Omega q^2}\Pi(\boldsymbol{q})$$

$$\Pi(\boldsymbol{q}) = \sum_{\mathbf{k}} \frac{|\langle c|v\rangle|^2}{\varepsilon_c(\mathbf{k+q}) - \varepsilon_v(\mathbf{k})}$$

integration over **k**
regularizes **$\Pi(\mathbf{q})$**
for vanishing gap

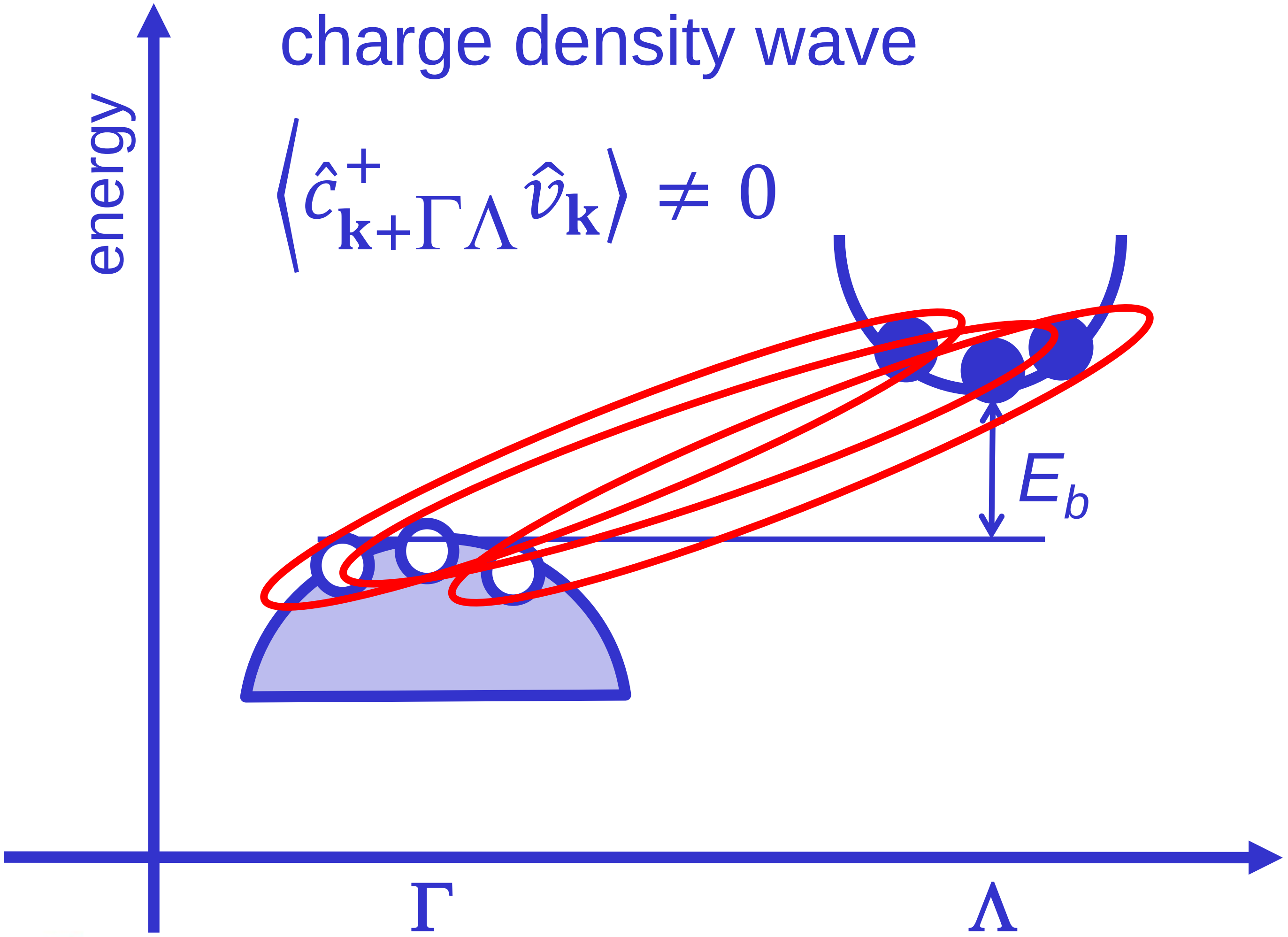



J. Phys. Chem. Solids Pergamon Press 1965. Vol. 26, pp. 259–266.

EXCITON INSTABILITY AND CRYSTALLOGRAPHIC
ANOMALIES IN SEMICONDUCTORS

JACQUES DES CLOIZEAUX

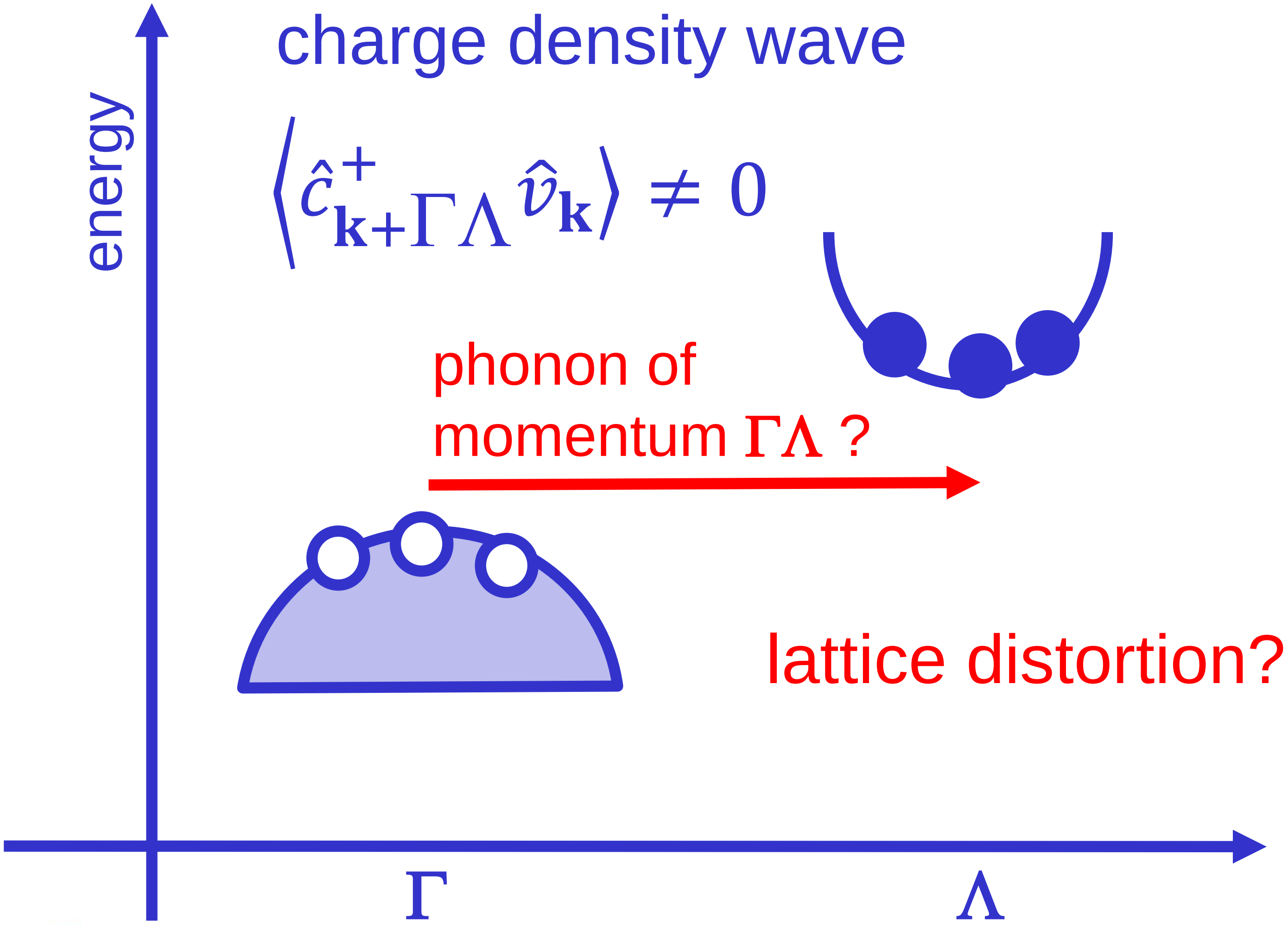
excitonic insulator



charge density wave

$$\left\langle \hat{c}^{+}_{\mathbf{k}+\Gamma\Lambda} \hat{v}_{\mathbf{k}} \right\rangle \neq 0$$

or Peierls insulator?



charge density wave

$$\left\langle \hat{c}^{+}_{\mathbf{k}+\Gamma\Lambda}\,\hat{v}_{\mathbf{k}} \right\rangle \neq 0$$

phonon of momentum $\Gamma\Lambda$?

lattice distortion?

excitonic or Peierls insulator in TMDs?

$TiSe_2$ indirect gap

DiSalvo *et al*., Electronic properties and superlattice formation in the semimetal $TiSe_2$. PRB **14,** 4321 (1976).
Rohwer *et al*, *Collapse of long-range charge order tracked by time-resolved photoemission at high momenta*. Nature **471,** 490 (2011).
Kogar *et al*., *Signatures of exciton condensation in a transition metal dichalcogenide.* Science **358,** 1314 (2017).
Hedayat *et al*., *Excitonic and lattice contributions to the charge density wave in 1T-$TiSe_2$ revealed by a phonon bottleneck*. Phys. Rev. Research **1,** 023029 (2019).

Ta_2NiSe_5 indirect exciton in real space

Lu *et al*, *Zero-gap semiconductor to excitonic insulator transition in Ta_2NiSe_5*. Nat. Commun. **8,** 14408 (2017).
Werdehausen *et al*., *Coherent order parameter oscillations in the ground state of the excitonic insulator Ta_2NiSe_5*. Sci. Adv. **4,** eaap8652 (2018).
Bretscher *et al., Imaging the coherent propagation of collective modes in the excitonic insulator Ta_2NiSe_5 at room temperature.* Sci. Adv**. 7,** eabd6147 (2021).
Windgaetter *et al*., *Common microscopic origin of the phase transitions in Ta_2NiS_5 and the excitonic insulator candidate Ta_2NiSe_5*. NPJ Comp. Mat**. 7,** 210 (2021).

this talk: excitonic insulators in TMDs with **no** lattice distortion

- MoS_2 under pressure

theory: S. Ataei *et al*., PNAS 2021

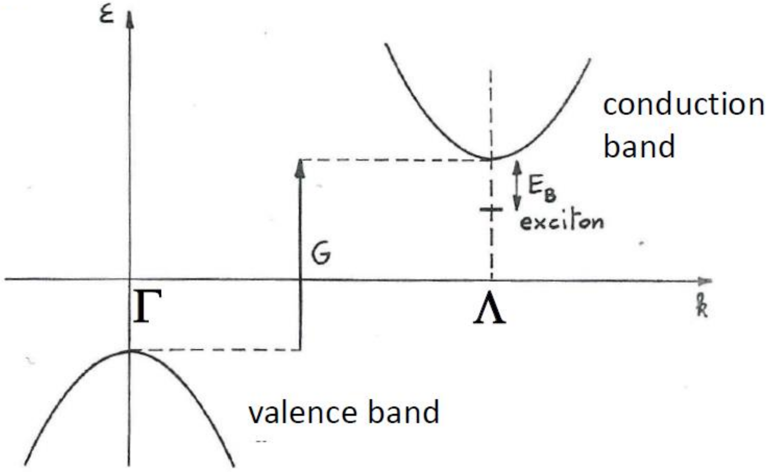
- monolayer WTe_2

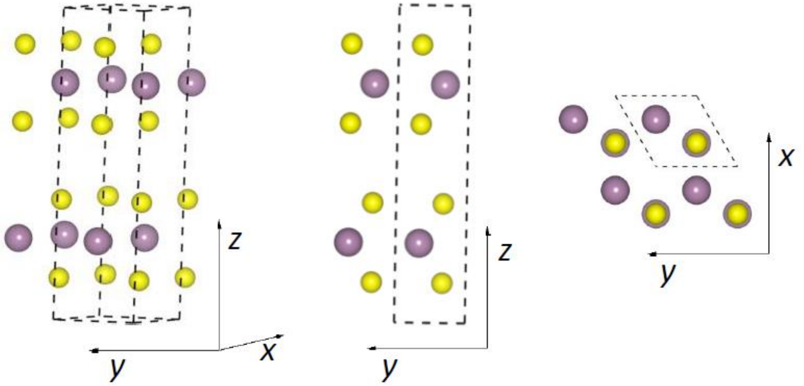
theory + exp: Sun *et al*., Nature Phys. 2022

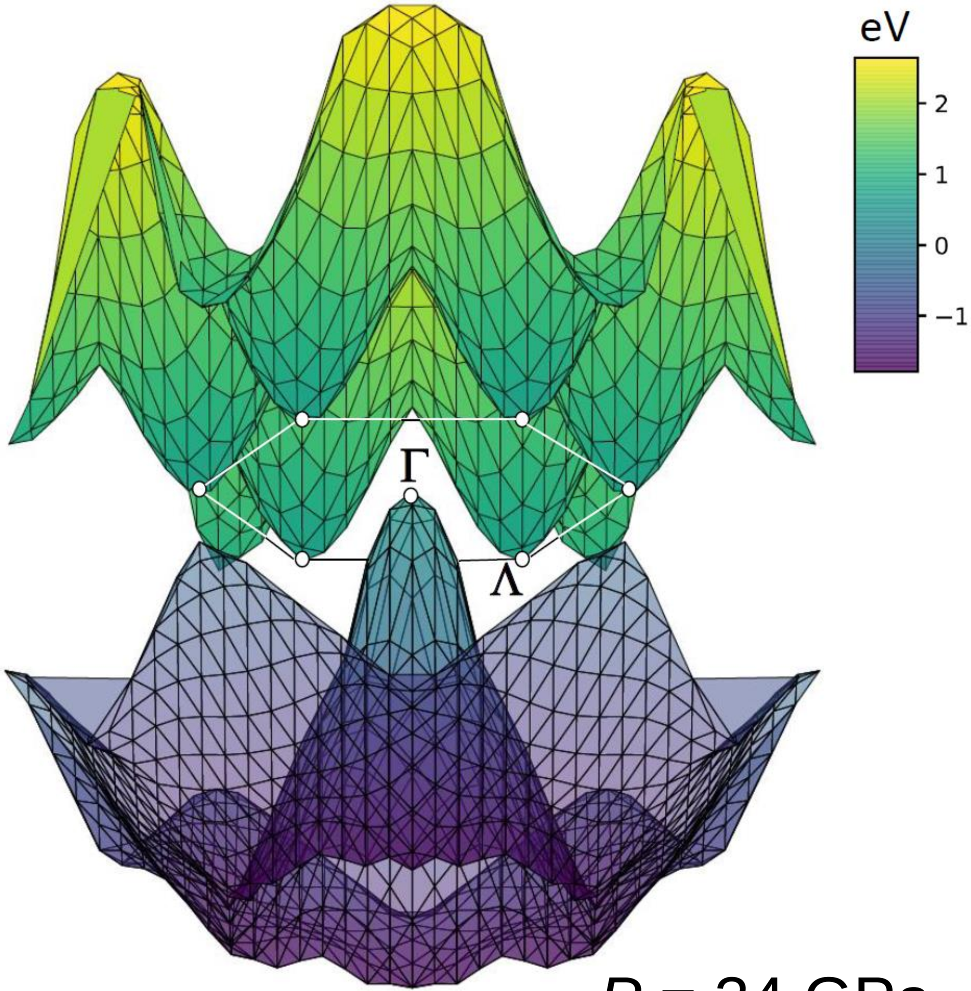
<u>lattice distortion ruled out experimentally</u>

indirect-gap MoS_2 as an ideal EI

seminal idea: Hromadova, Martonak, Tosatti, PRB **87,** 144105 (2013)







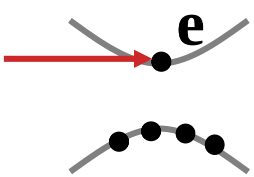
P = 34 GPa

Ataei, Varsano, Molinari & Rontani PNAS **118,** e2010110118 (2021)

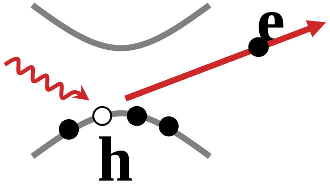
many body perturbation theory

Electron and hole states:

- Ground state within **Density Functional Theory (DFT)**
- Quasiparticle corrections: **GW approximation**



N + 1

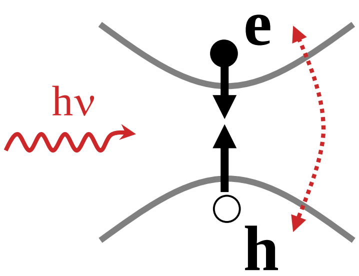


N - 1

STM
ARPES

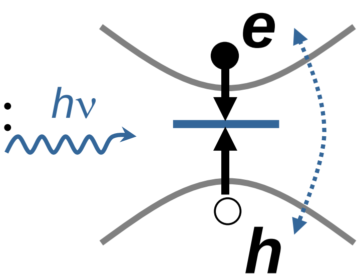
Optical excitations

- Electron-hole interaction included through the **Bethe-Salpeter equation**



OPTICS
RES. RAMAN

Optical properties:



Effective **two-particle (e-h)** Schrödinger-like equation:

Bethe-Salpeter equation

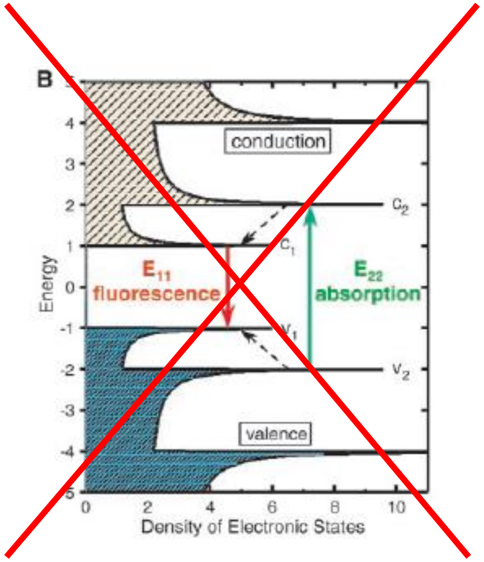
$$[(E_{ck}-E_{vk})\delta_{cc'}\delta_{vv'}\delta_{kk'}+K_{cvk,c'v'k'}]\Psi^{(n)}_{c'v'k'}=\Omega_n\Psi^{(n)}_{cvk}$$

Excitonic eigenvalues & eigenfunctions:

$$\phi^{(n)}(\mathbf{r}_e,\mathbf{r}_h)=\sum_{cvk}\Psi^{(n)}_{cvk}[\psi_{vk}(\mathbf{r}_h)]^*\psi_{ck}(\mathbf{r}_e)$$

Mixing of single particle transitions

$$\Omega_n \neq E_{ck}-E_{vk}$$

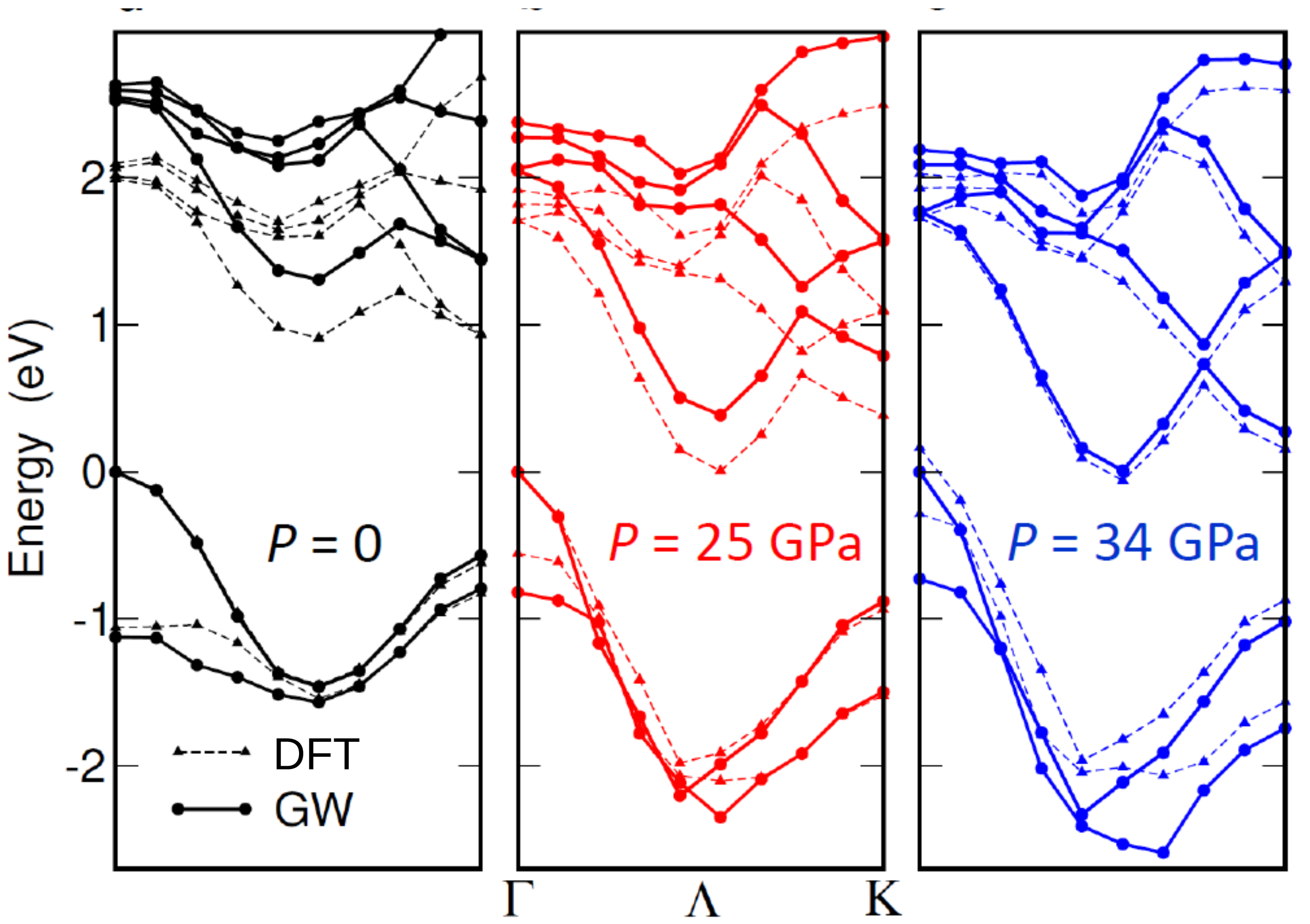


Hanke and Sham, PRL **33**, 582 (1974)

Extended systems:

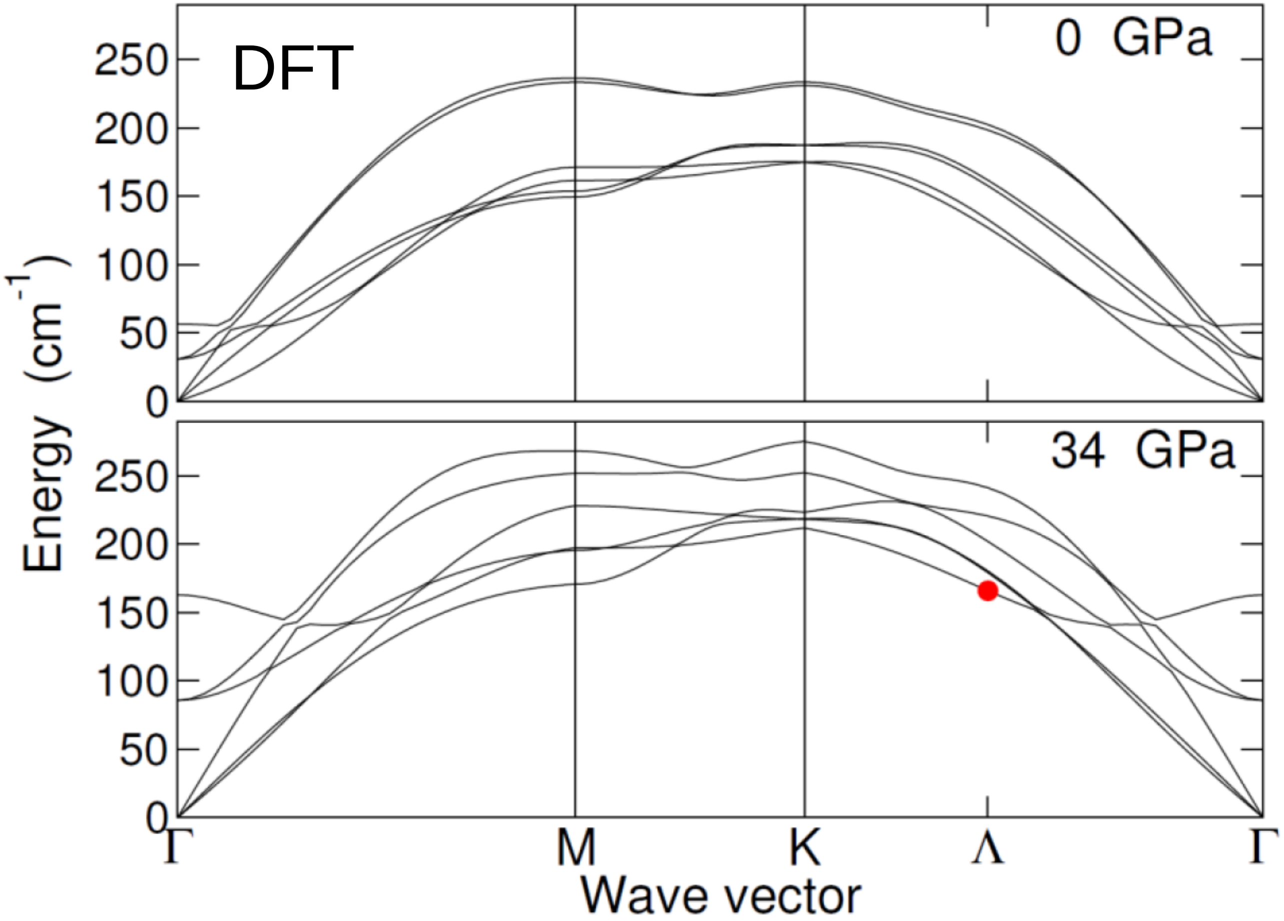
Albrecht et al., PRL **80**, 4510 (1998); *Benedict et al.*, PRL **80**, 4514 (1998); *Rohlfing et al*, PRL **81**, 2312 (1998)

closing the gap by applying pressure



S. Ataei *et al.*, PNAS **118,** e2010110118 (2021)

rule out lattice distortion

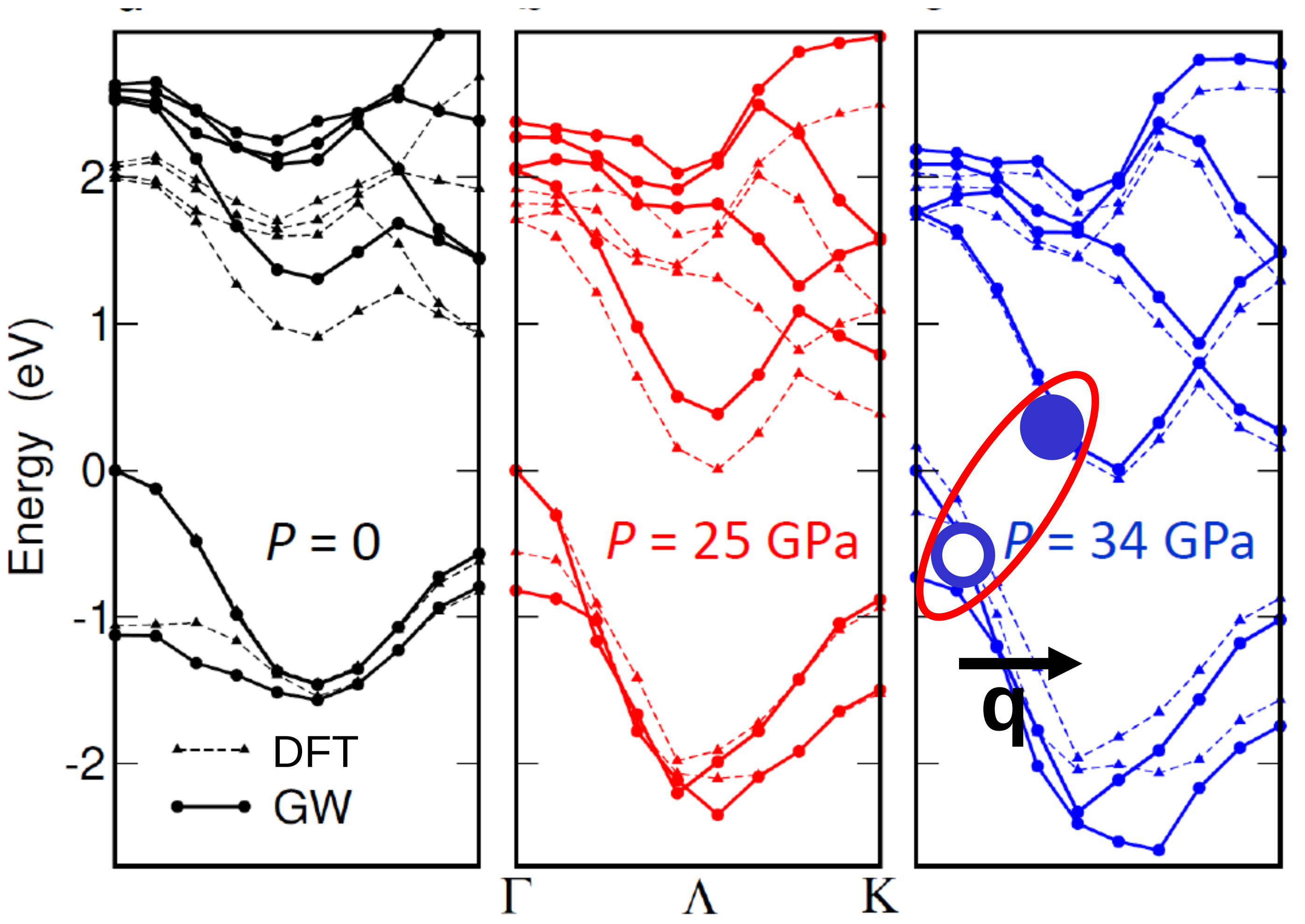


no evidence of lattice distortion:

Goncharov *et al.*, Structure and stability of *2H*$_a$-MoS$_2$ at high pressure and low temperatures. PRB **102**, 064105 (2020).

S. Ataei *et al.*, PNAS **118,** e2010110118 (2021)

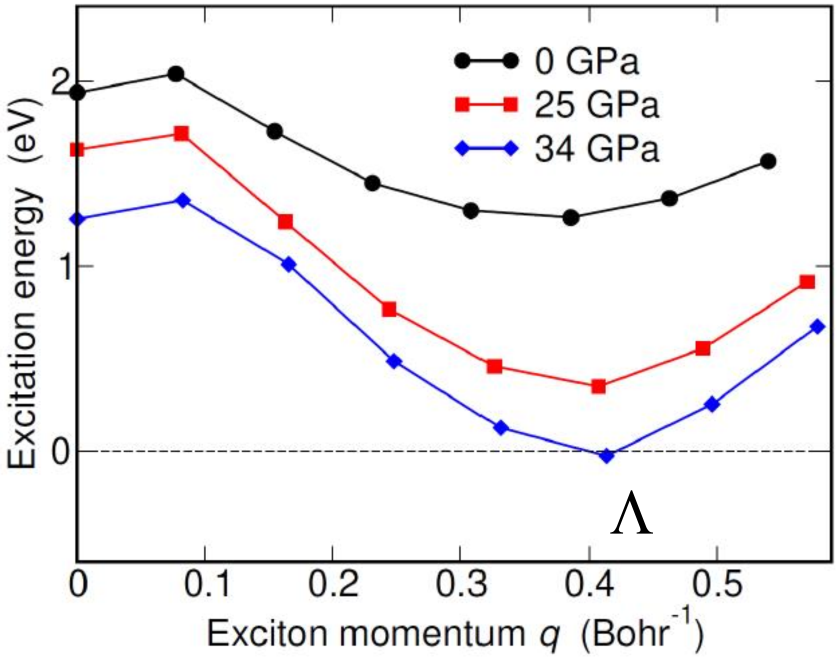
closing the gap by applying pressure

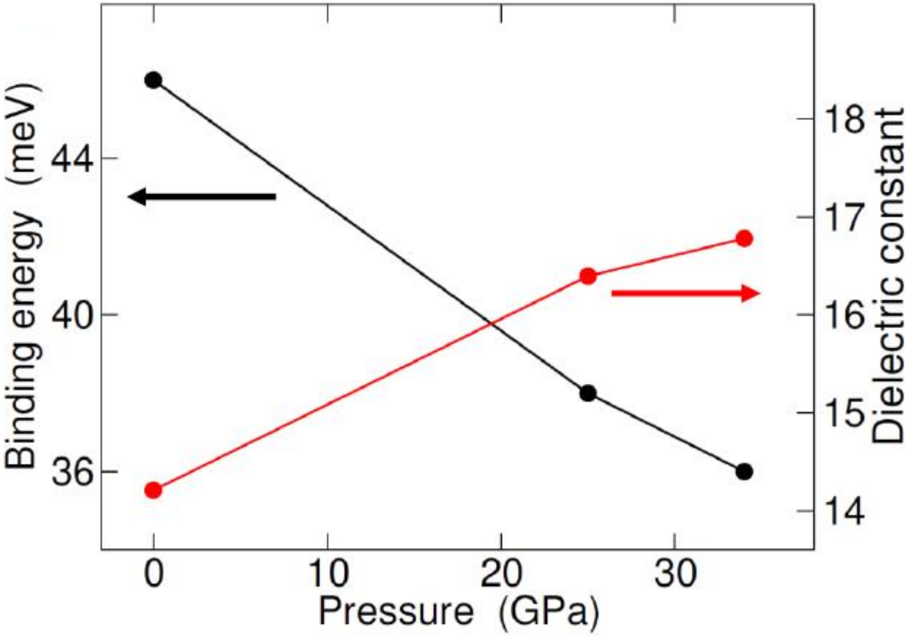


solve BSE for
exciton of momentum **q**

excitonic instability

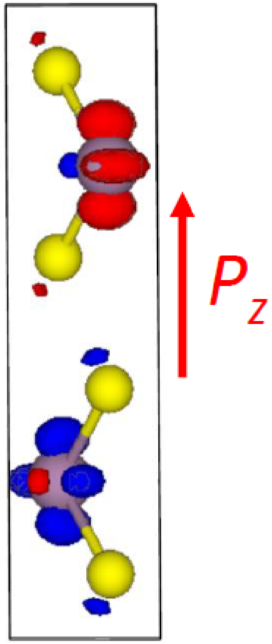
S. Ataei *et al*., PNAS **118,** e2010110118 (2021)

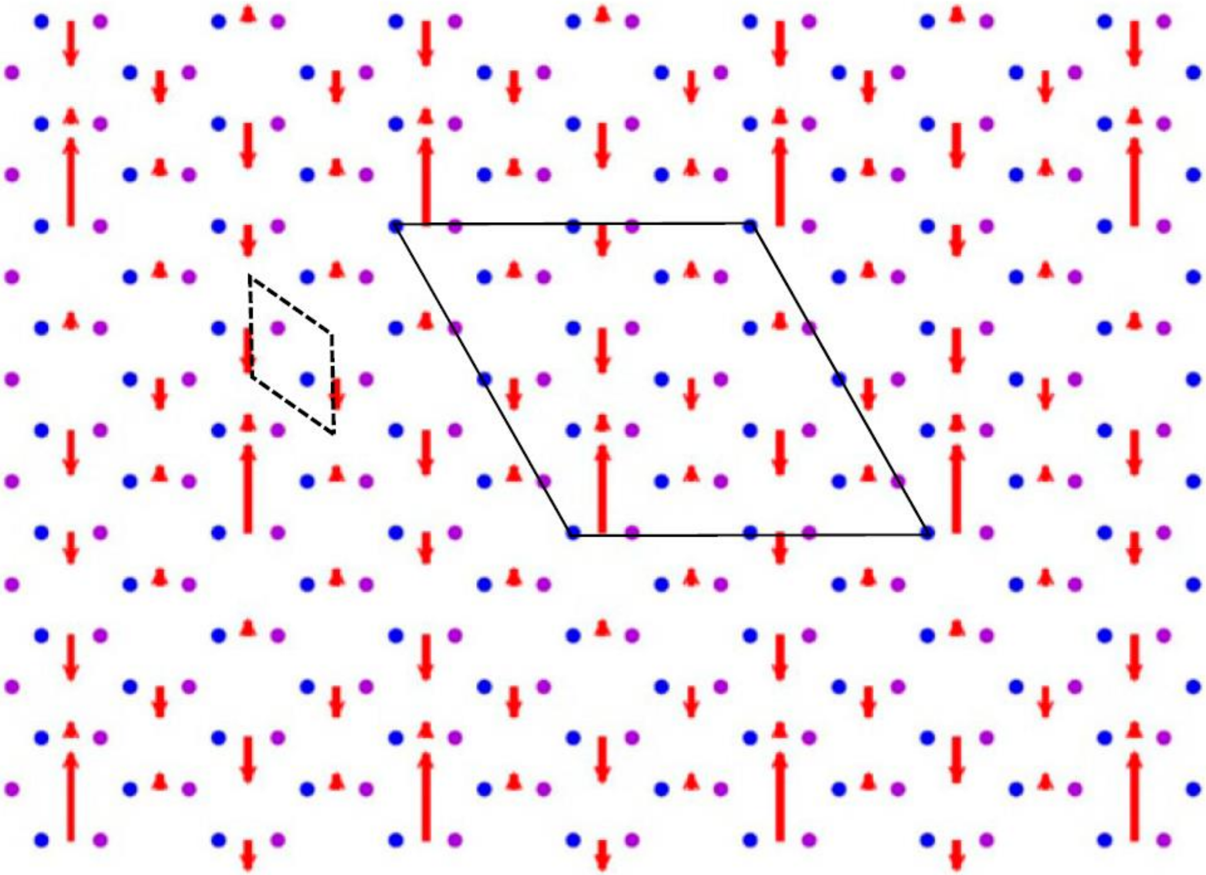




J. des Cloizeaux, *Excitonic instability and crystallographic anomalies in semiconductors*, J. Phys. Chem. Solids **26**, 259 (1965).

anti-ferroelectric EI





S. Ataei *et al.*, PNAS (2021)

multivalley EI:
Monney *et al.*
PRB **79,** 045116 (2009)

EI + ferroelectricity:
Portengen *et al.*
PRB **54,** 17452 (1996)

● top Mo atom
● bottom Mo atom

monolayer WTe_2 as an ideal excitonic insulator

Wu *et al.*, *Science* **359**, 76–79 (2018) 5 January 2018

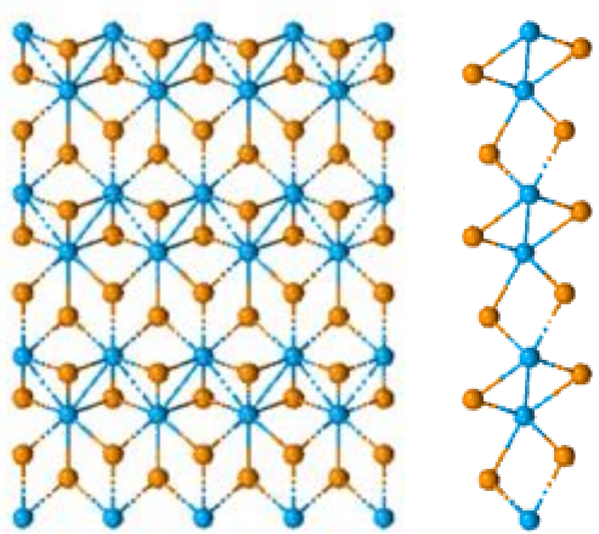
Observation of the quantum spin Hall effect up to 100 kelvin in a monolayer crystal

Sanfeng Wu,[1*†] Valla Fatemi,[1*†] Quinn D. Gibson,[2] Kenji Watanabe,[3] Takashi Taniguchi,[3] Robert J. Cava,[2] Pablo Jarillo-Herrero[1†]

Sajadi *et al.*, *Science* **362**, 922–925 (2018) 23 November 2018

Gate-induced superconductivity in a monolayer topological insulator

Ebrahim Sajadi[1], Tauno Palomaki[2], Zaiyao Fei[2], Wenjin Zhao[2], Philip Bement[1], Christian Olsen[1], Silvia Luescher[1], Xiaodong Xu[2,3], Joshua A. Folk[1*], David H. Cobden[2*]

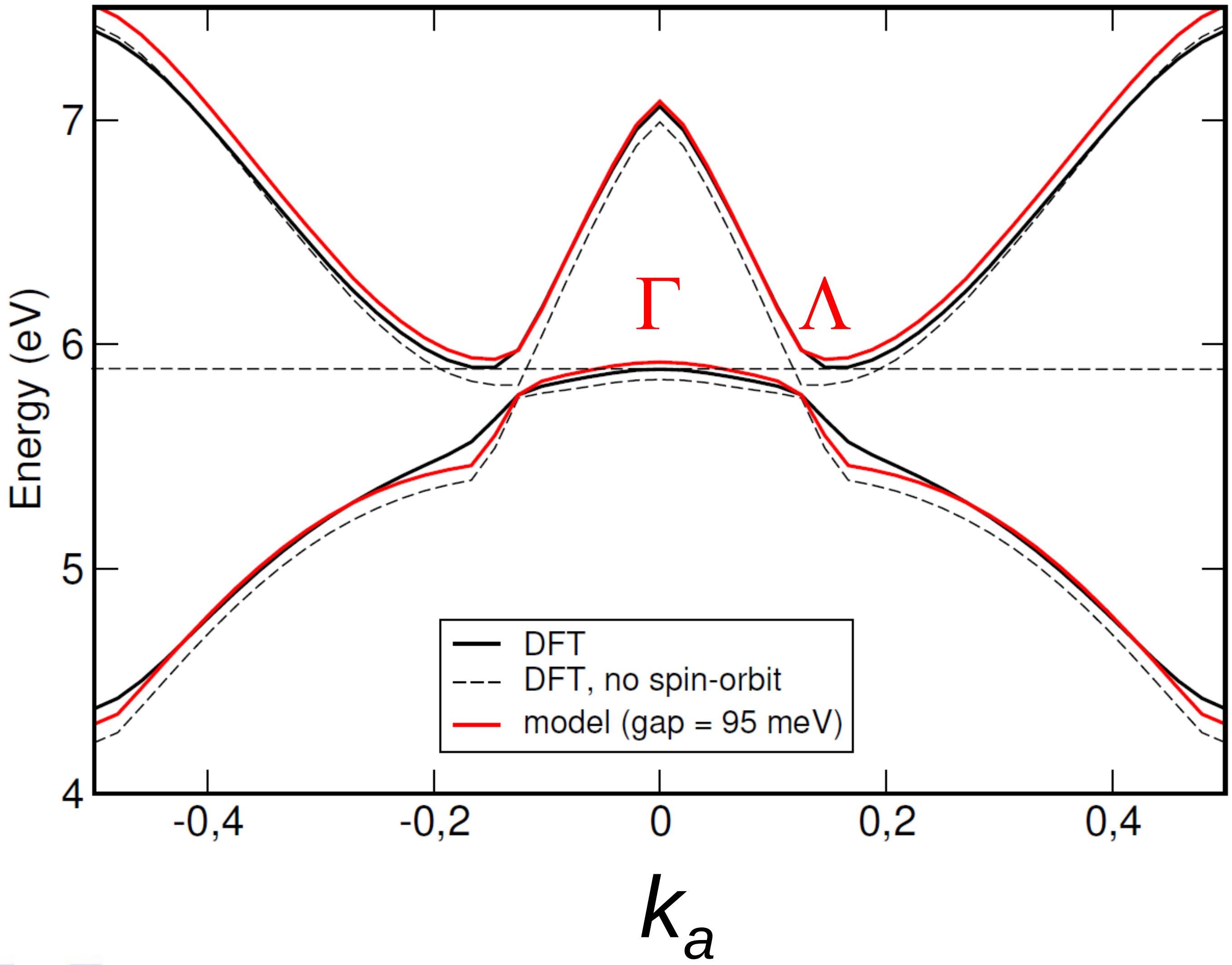


Fei *et al*., Nat. Phys. **13,** 677 (2017)
Tang *et al*., Nat. Phys. **13,** 683 (2017)

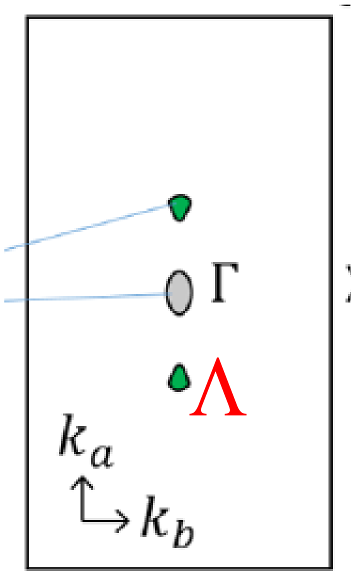
Fatemi *et al*., Science **362,** 926 (2018)

Varsano *et al*., Nature Nanotech **15,** 367-372 (2020).
Sun *et al*., Nature Physics **18,** 94-99 (2022).
See also: Jia *et al*., Nature Physics **18,** 87-93 (2022).

spinless WTe_2 as a topological metal

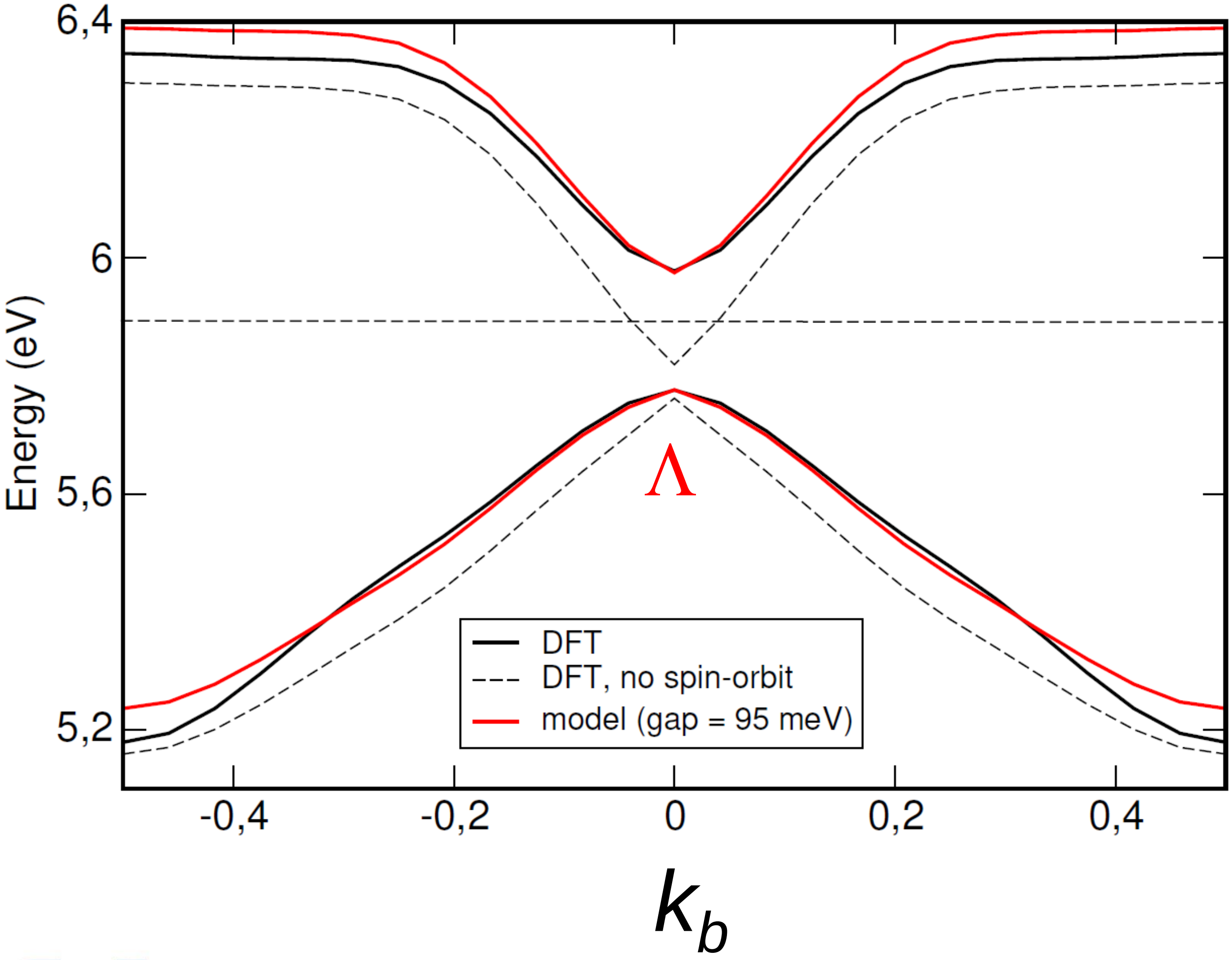


Nature Physics **18**, 94-99 (2022).

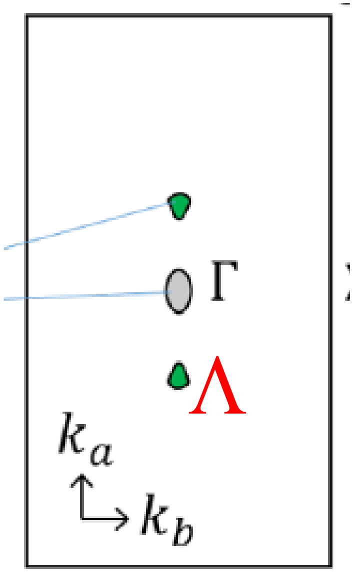


see Muechler *et al*., PRX **6**, 041069 (2016).

spinless WTe_2 as a topological metal



Nature Physics **18**, 94-99 (2022).



see Muechler *et al*., PRX **6**, 041069 (2016).

is bulk WTe_2 monolayer gapped?

photoemission

Tang *et al*., Nature Physics **13,** 683–687 (2017).
Cucchi *et al*., Nano Lett. **19,** 554–560 (2019).

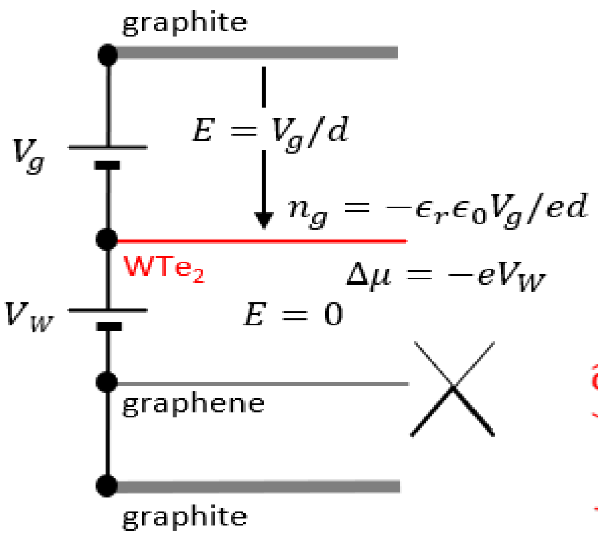
STM

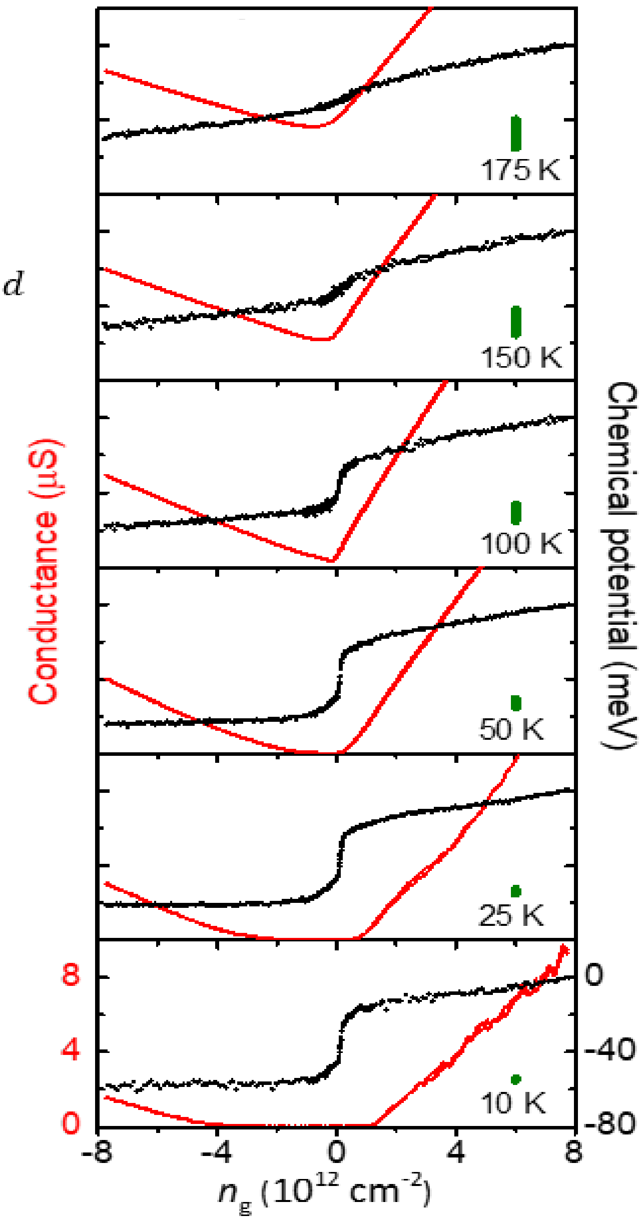
Tang *et al*., Nature Physics **13,** 683–687 (2017).
Song *et al*., Nature Commun **9,** 4071 (2018).

theory from first principles

Qian *et al*., Science **346,** 1344-1347 (2014).
Zheng *et al*., Adv. Mater. **28,** 4845-4851 (2016).
Ok *et al*., PRB **99,** 121105 (2019).
Cucchi *et al*., Nano Lett. **19,** 554–560 (2019).

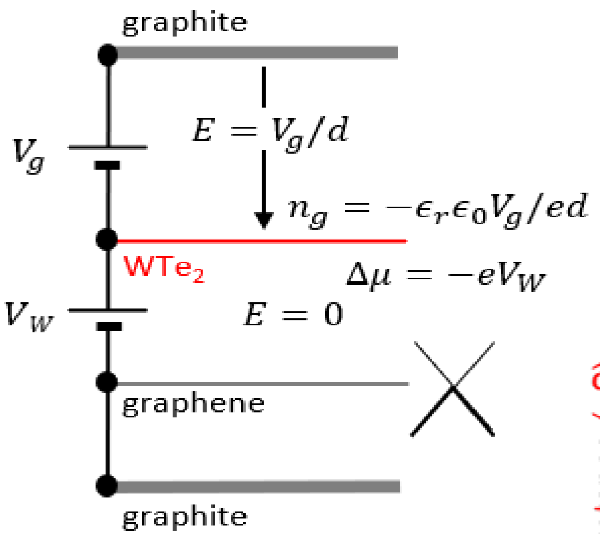
many-body bulk gap



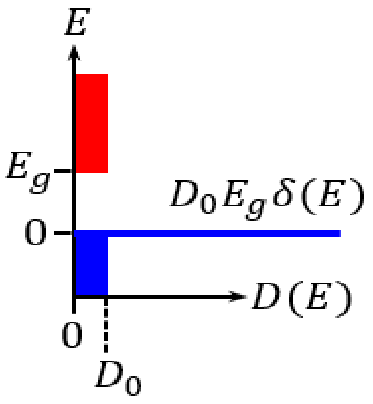


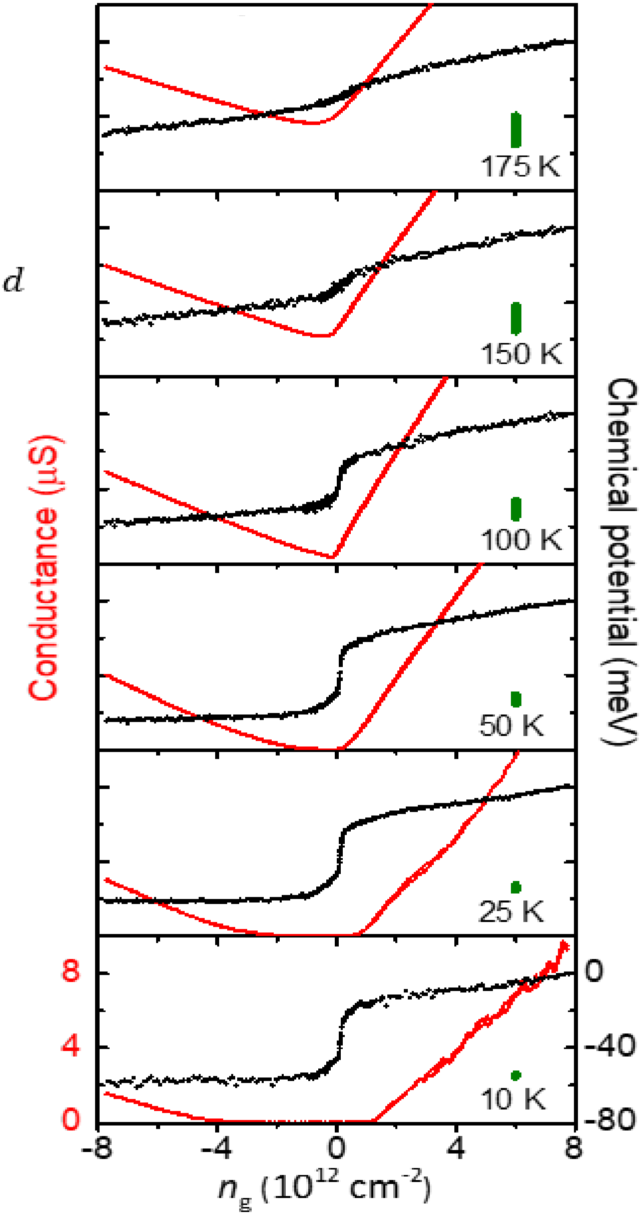
Nature Physics **18,** 94-99 (2022)

many-body bulk gap



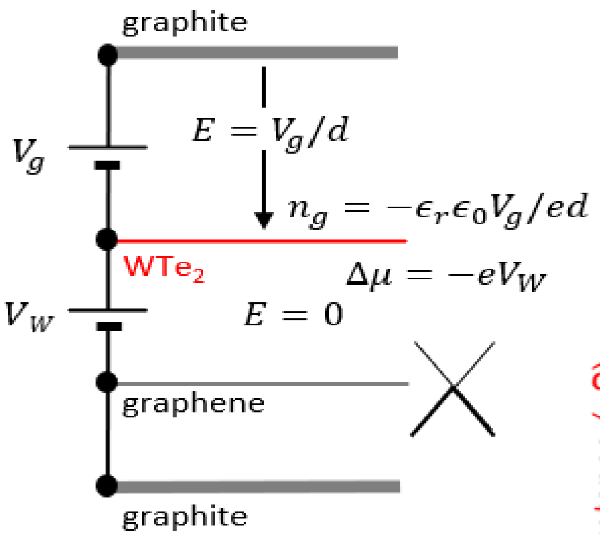
Single-particle model



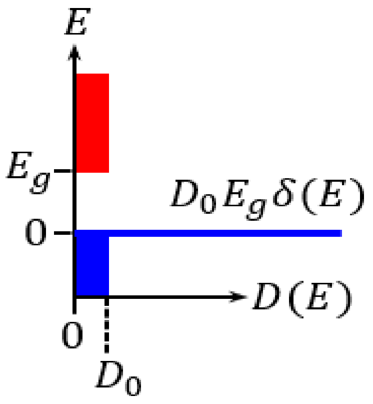


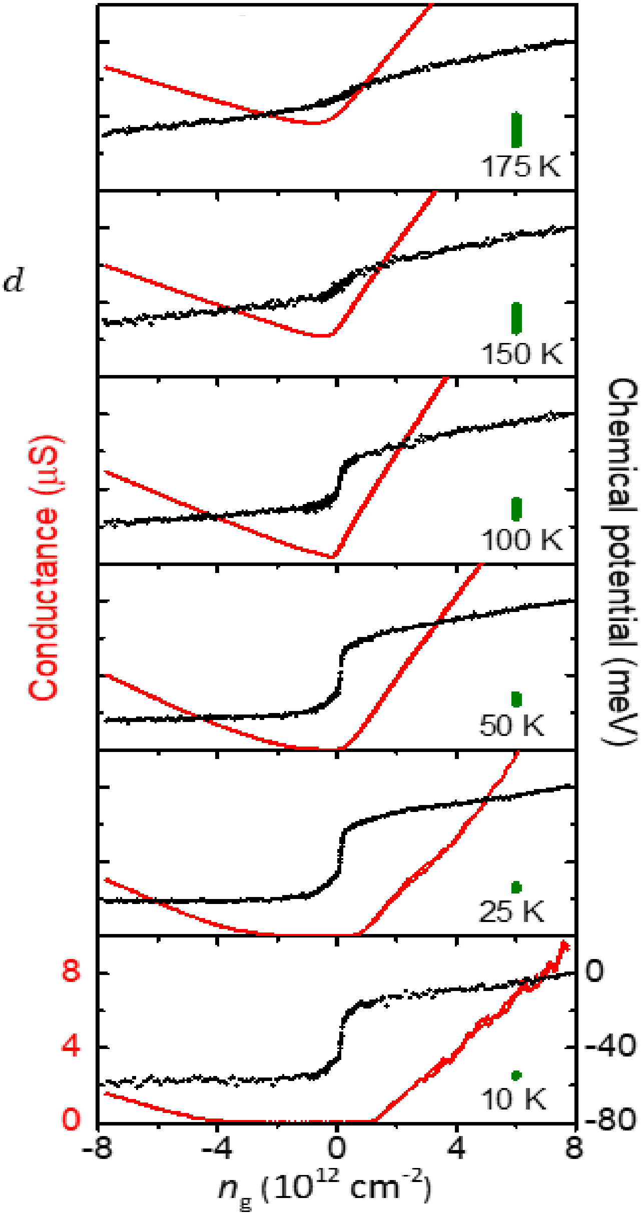
Nature Physics **18,** 94-99 (2022)

many-body bulk gap

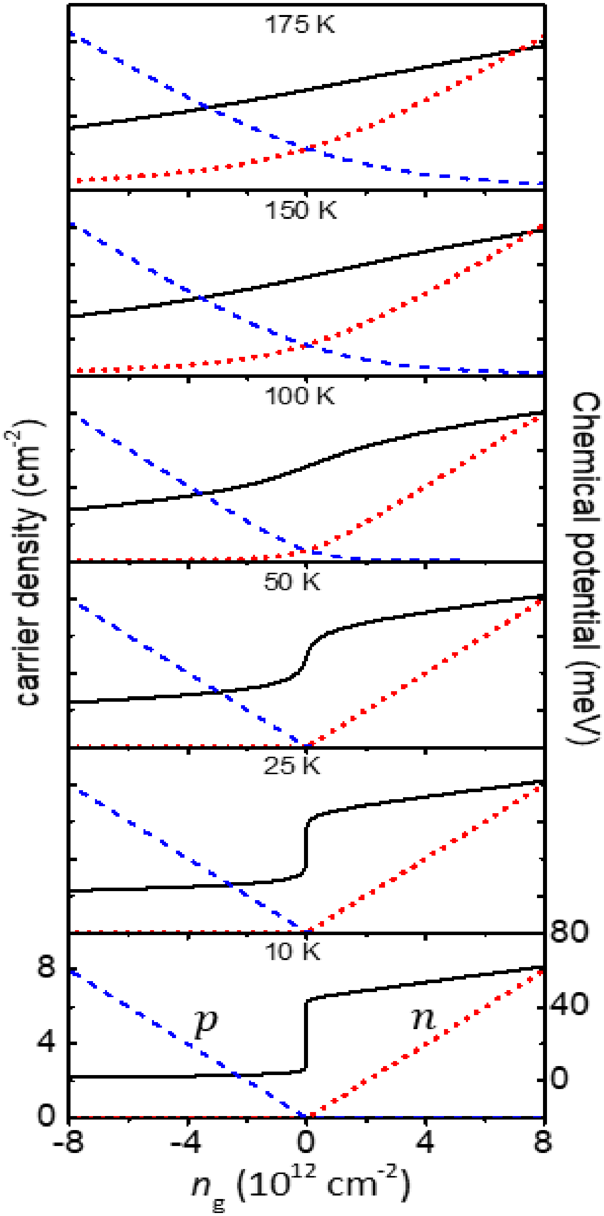


Single-particle model

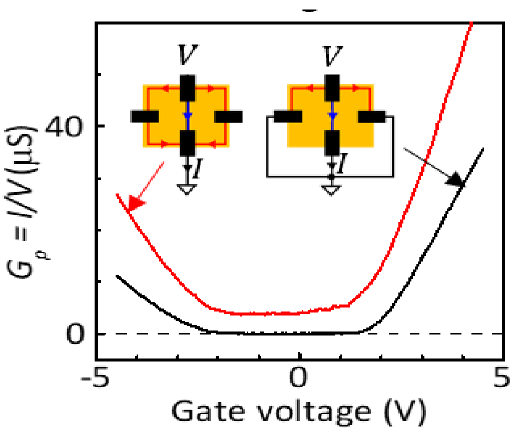


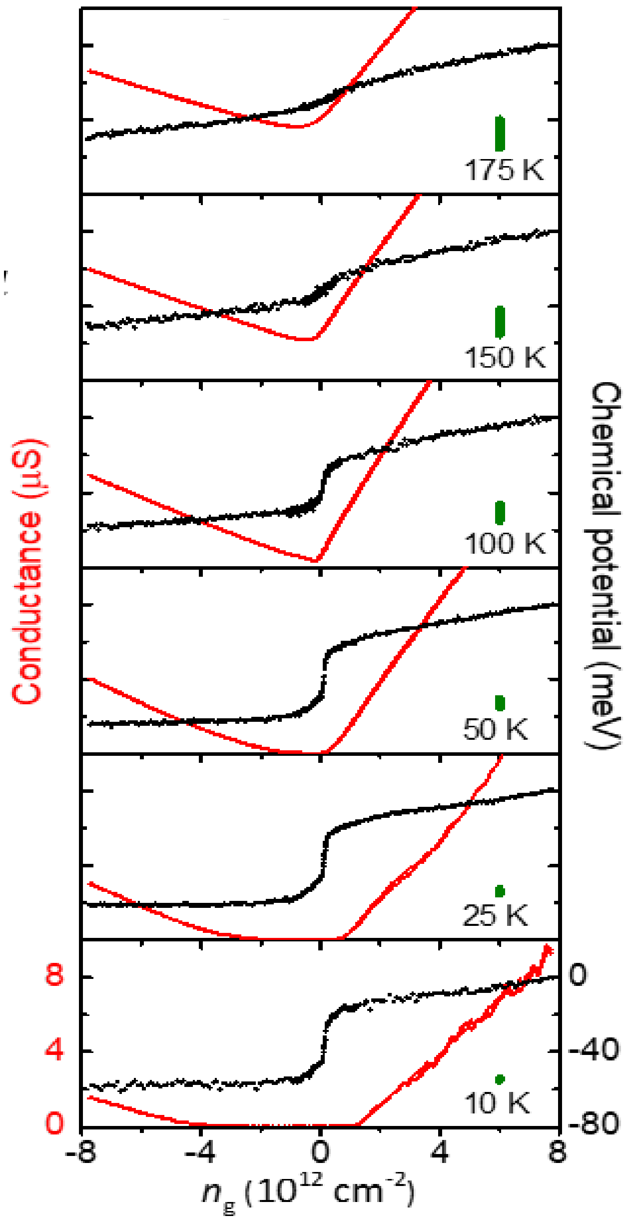


single-particle model



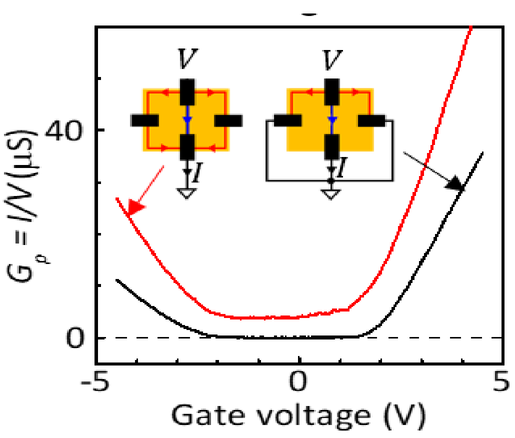
critical doping density

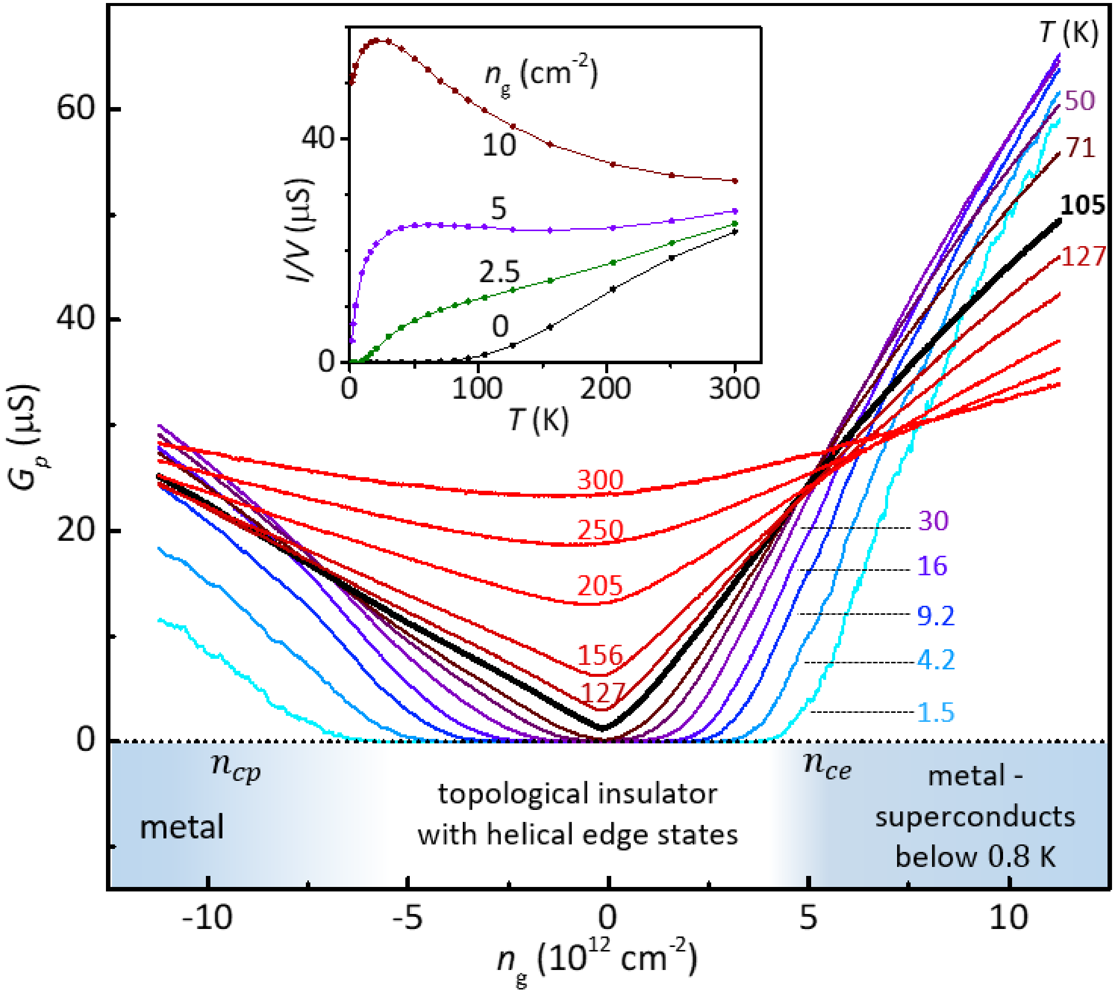




Nature Physics **18,** 94-99 (2022)

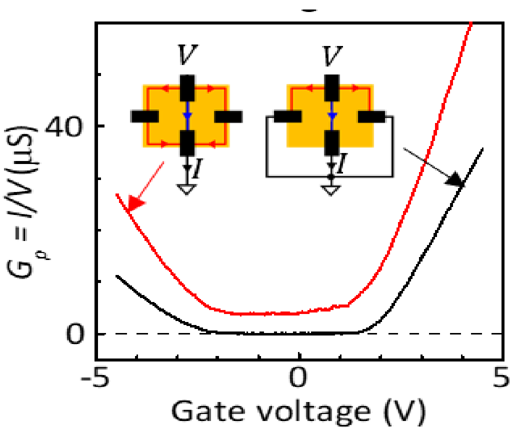
critical doping density

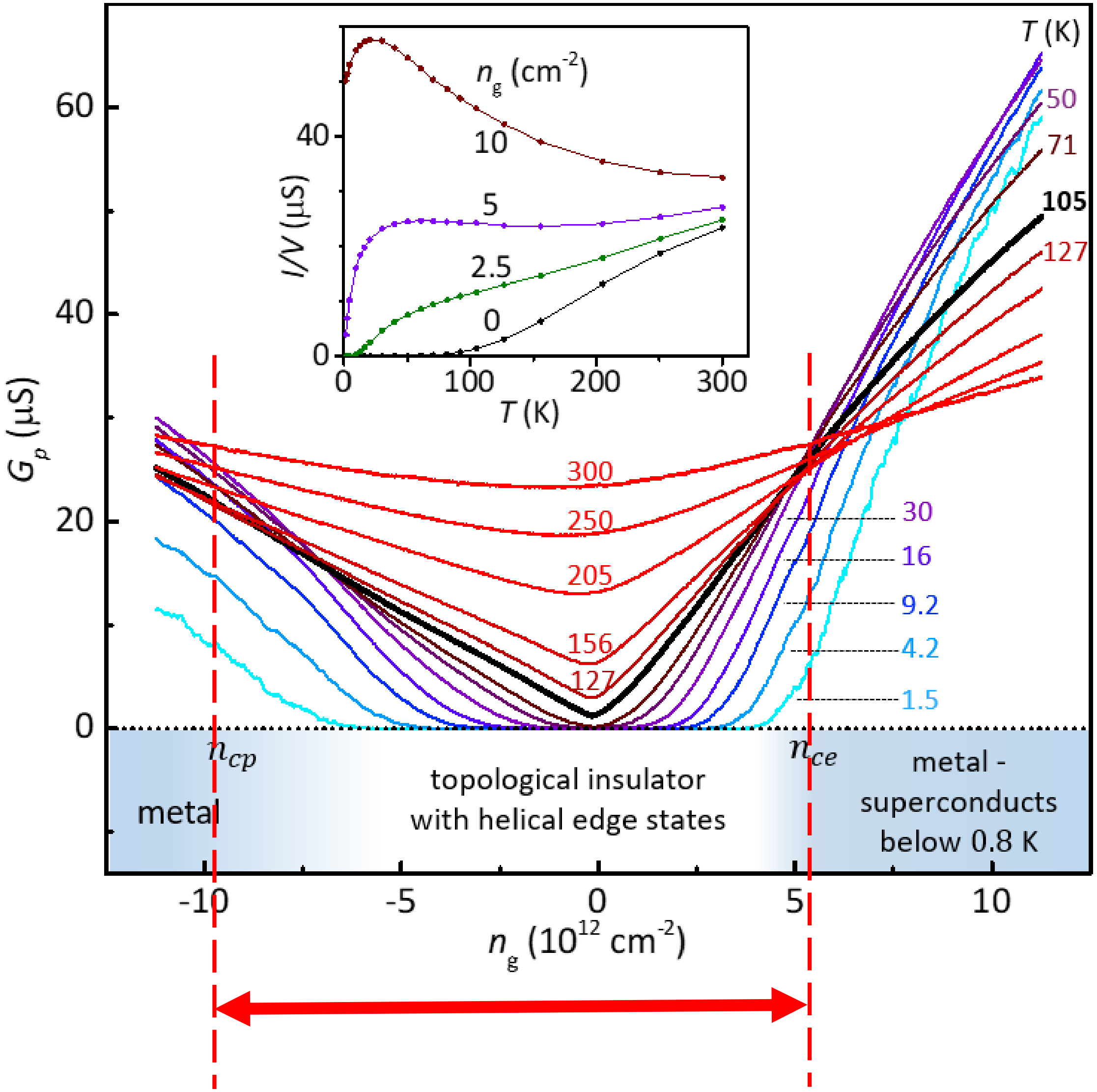




Nature Physics **18,** 94-99 (2022)

Mott criterion for the excitonic insulator?

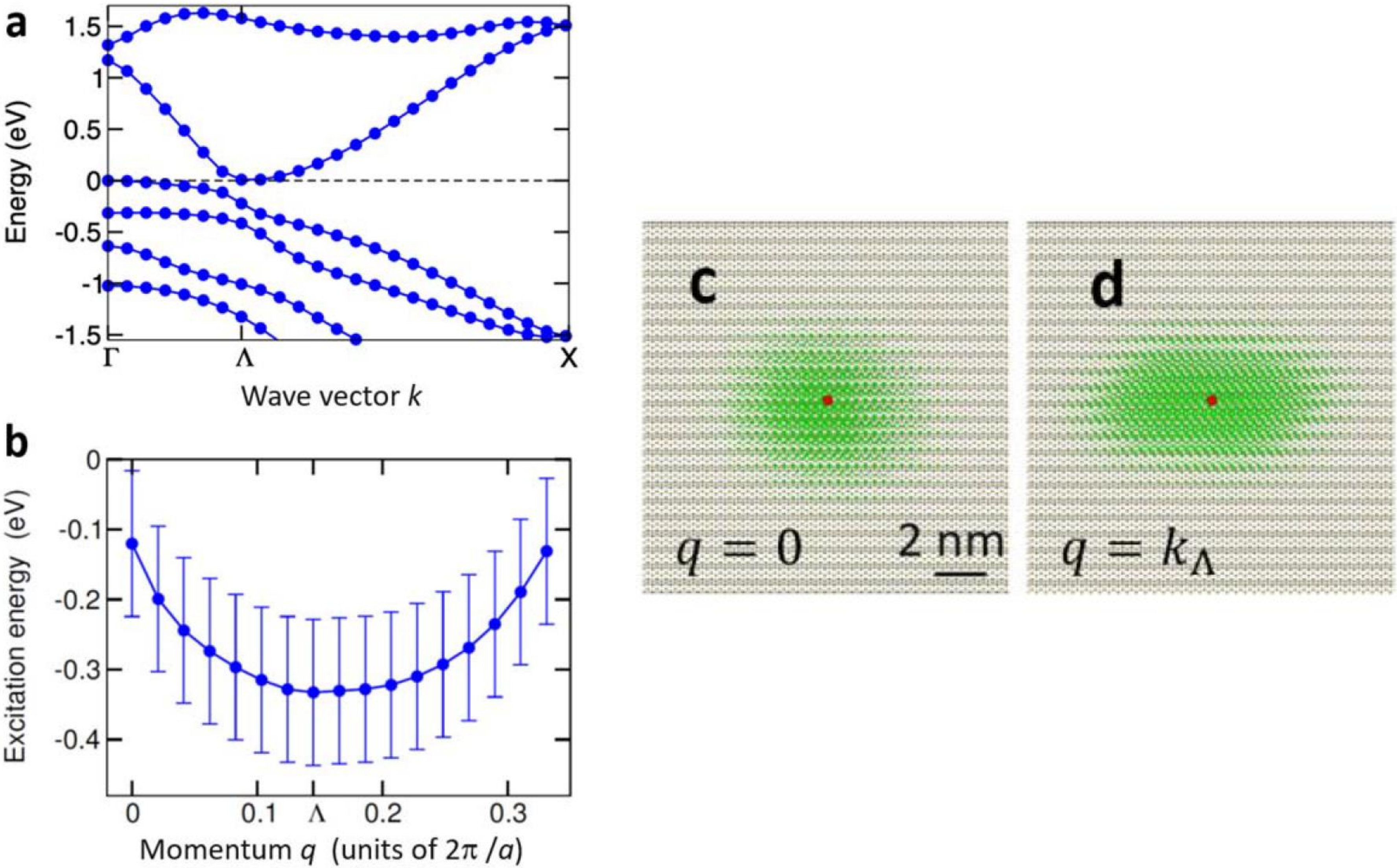




Nature Physics **18**, 94-99 (2022)

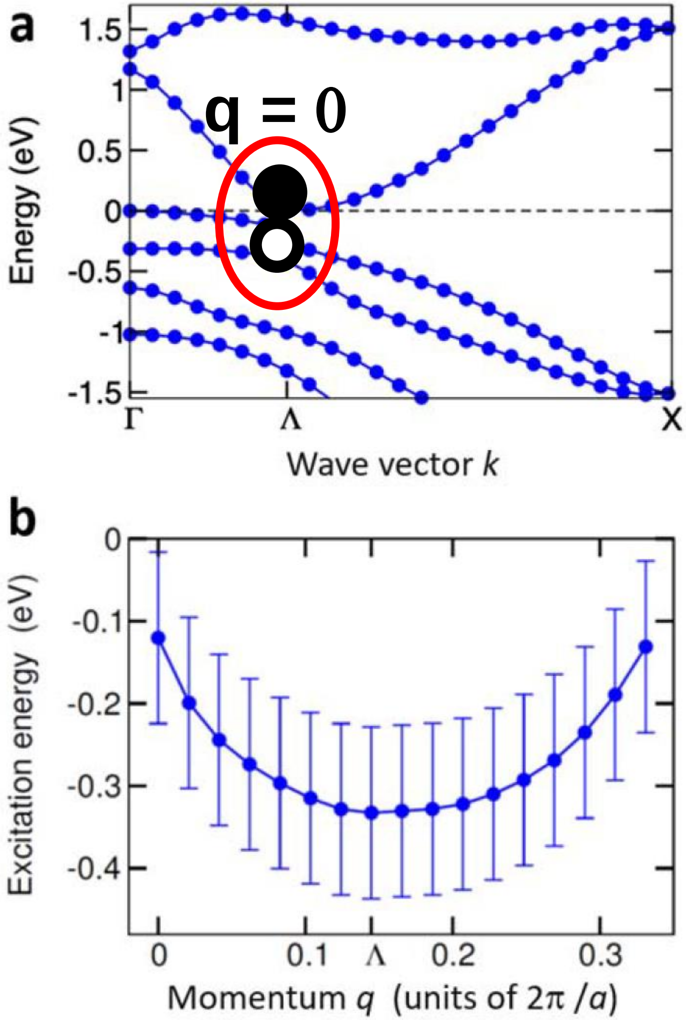
bulk excitonic insulator phase

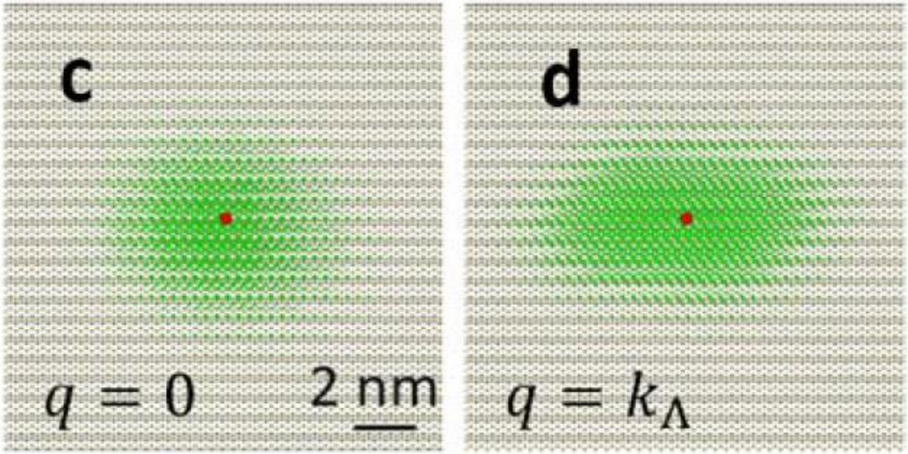
excitons from first principles



Nature Physics **18,** 94-99 (2022)

excitons from first principles

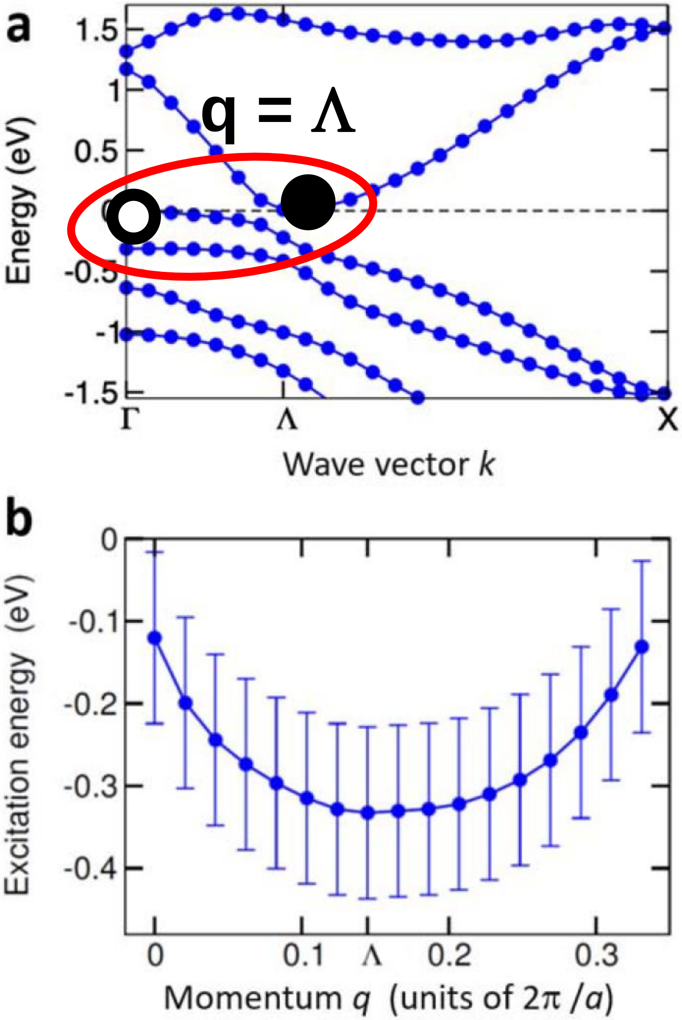


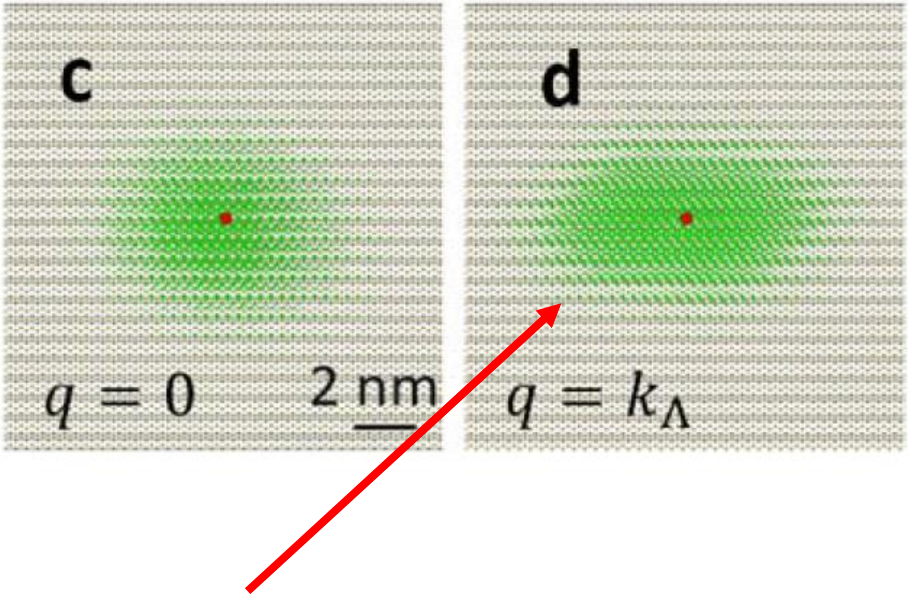


WTe$_2$ unstable against exciton condensation

Nature Physics **18,** 94-99 (2022)

excitons from first principles

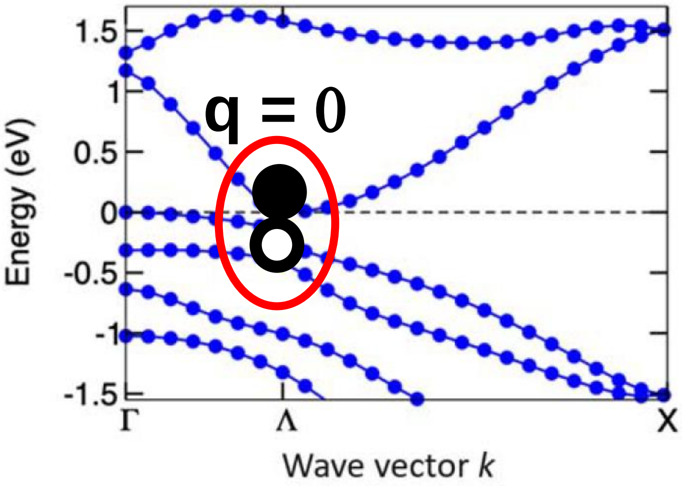


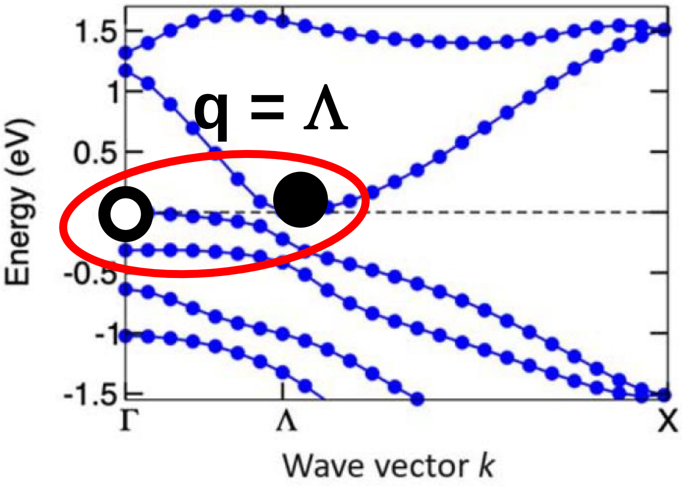


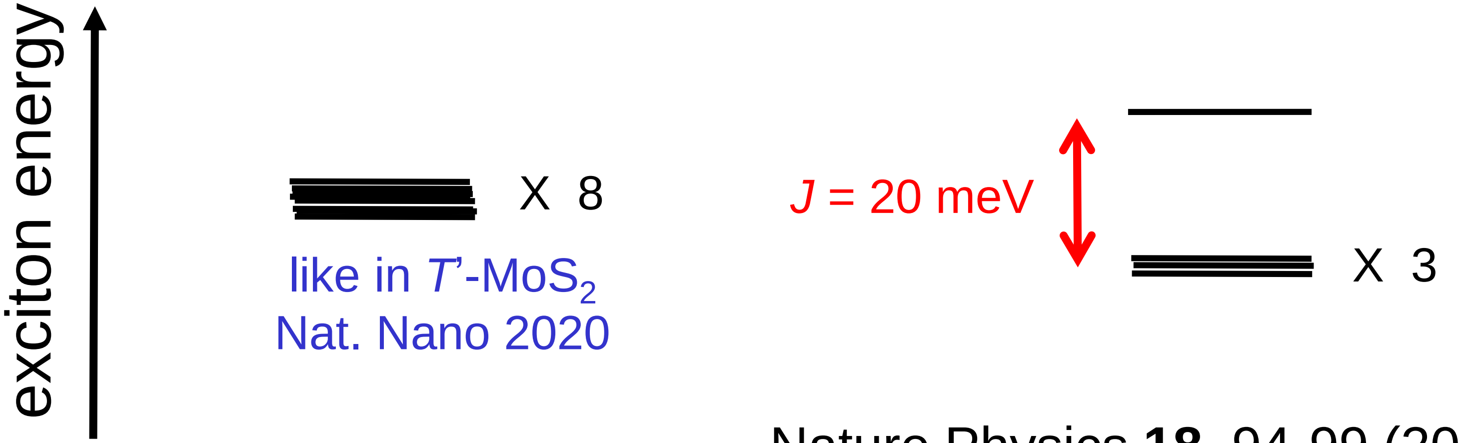
r_{Bohr} = 4 nm
critical doping $n_c^{-1/2}$ = 4.5 nm

Nature Physics **18,** 94-99 (2022)

lowest exciton partially spin-polarized → no CDW







like in T'-MoS$_2$
Nat. Nano 2020

Nature Physics **18,** 94-99 (2022)

see also: Kwan *et al*., PRB **104,** 125133 (2021)

conclusions & outlook

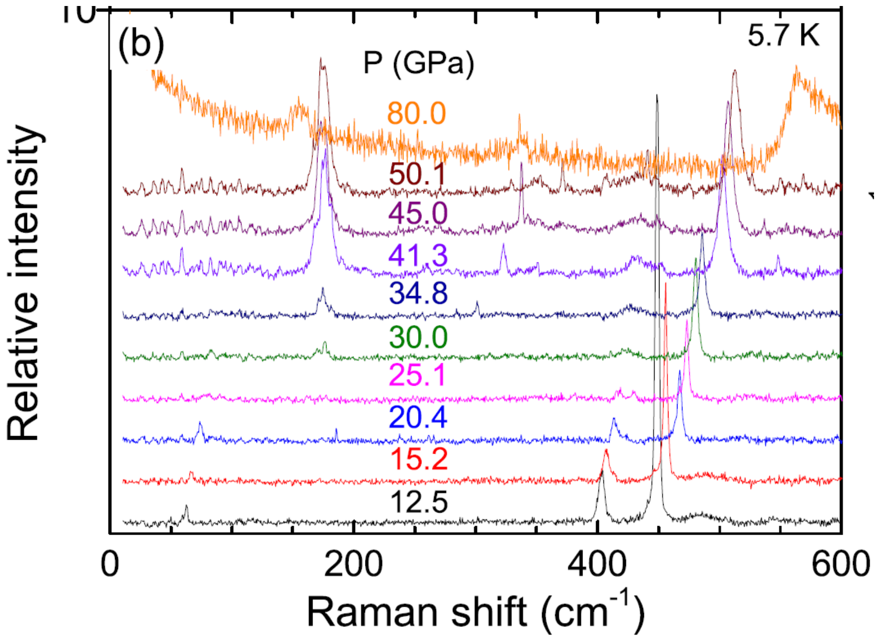
- ideal EI in pressurized MoS_2 and monolayer WTe_2
- macroscopic quantum coherence?
- relation with superconducting and topological orders?

Varsano *et al*., Nature Nanotechnology **15,** 367-372 (2020)
Ataei *et al*., PNAS **118,** e2010110118 (2021)
Sun *et al*., Nature Physics **18,** 94-99 (2022)

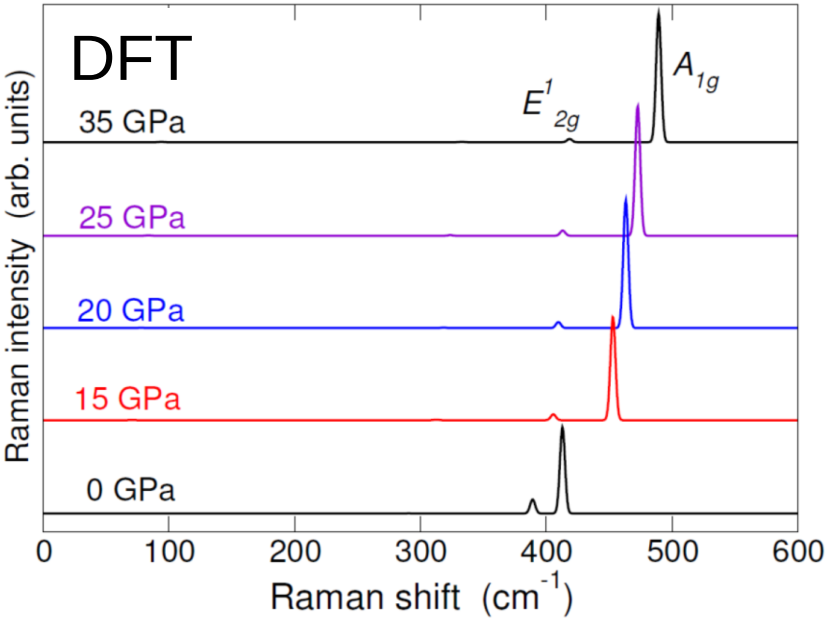
website: excitonic-insulator.nano.cnr.it

Raman fingerprint

Cao *et al*., PRB **97,** 214519 (2018)

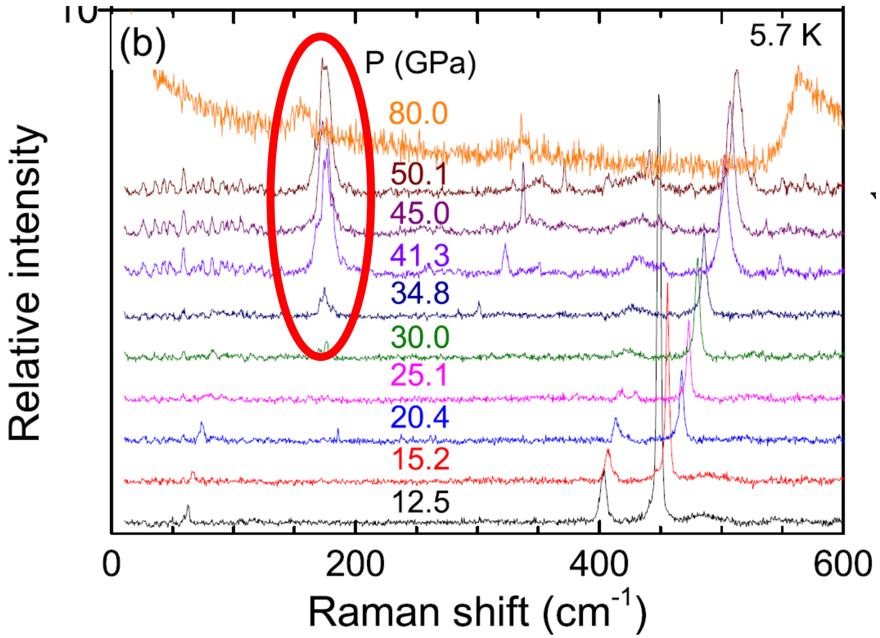


Ataei *et al*., PNAS (2021)

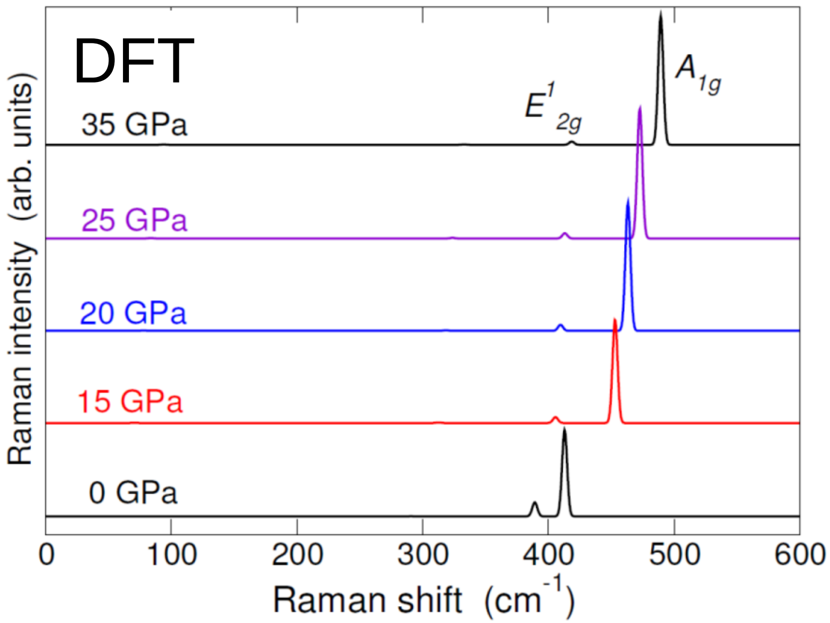


Raman fingerprint

Cao *et al*., PRB **97,** 214519 (2018)

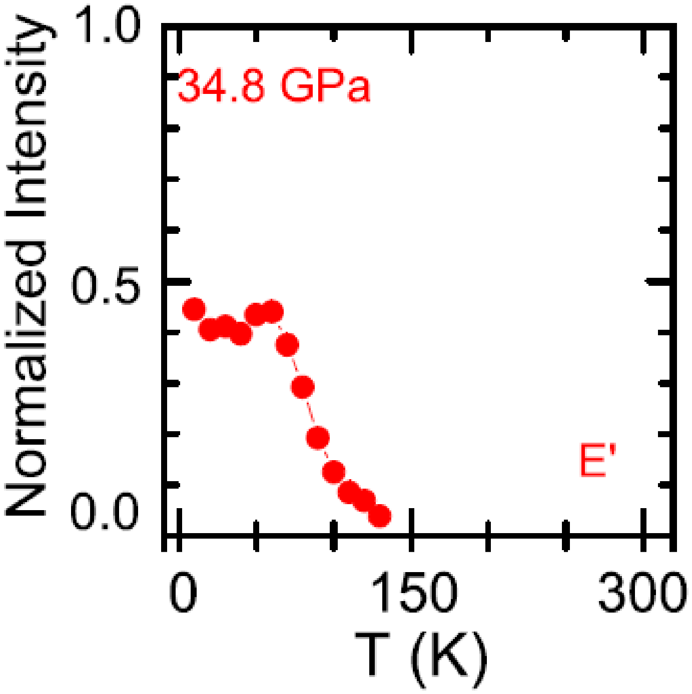


Ataei *et al*., PNAS (2021)

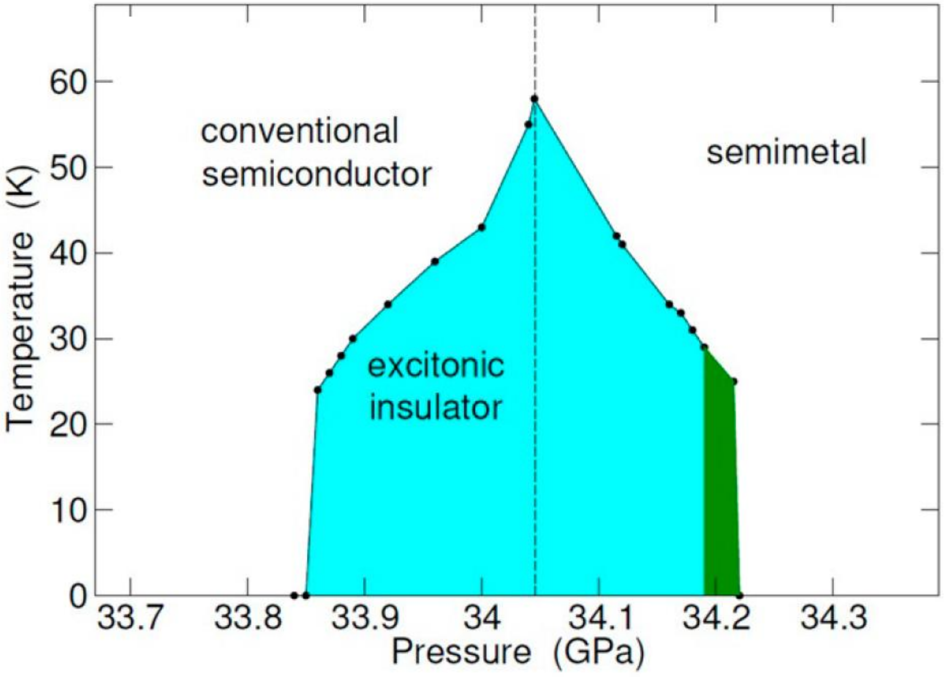


Raman fingerprint

Cao *et al*., PRB **97,** 214519 (2018)

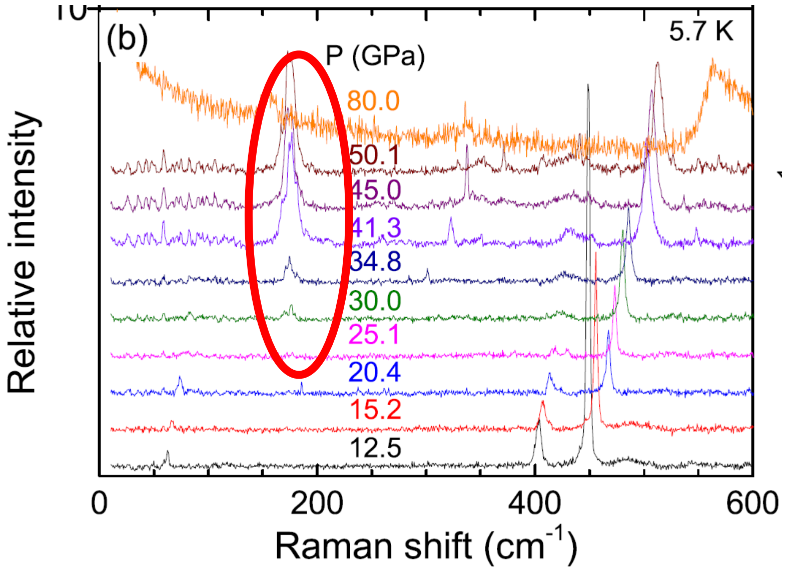


Ataei *et al*., PNAS (2021)

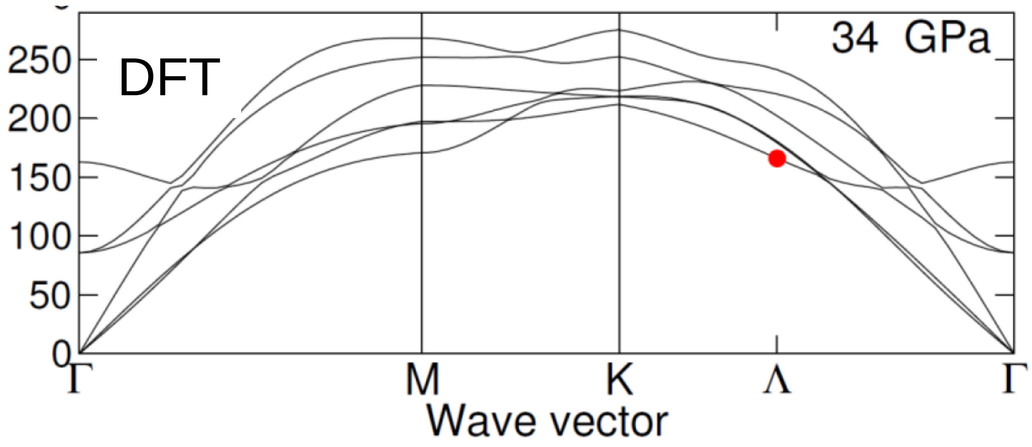


Raman fingerprint

Cao *et al*., PRB **97,** 214519 (2018)

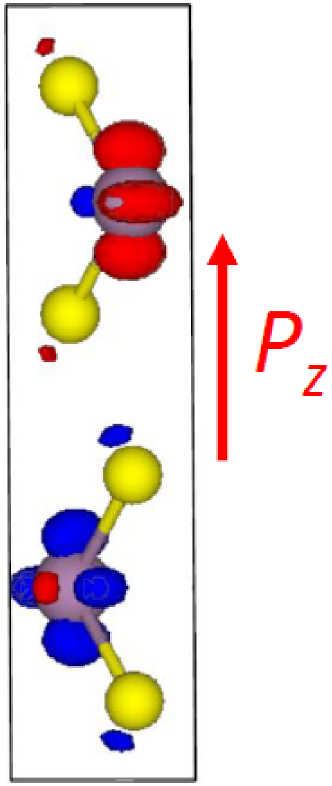


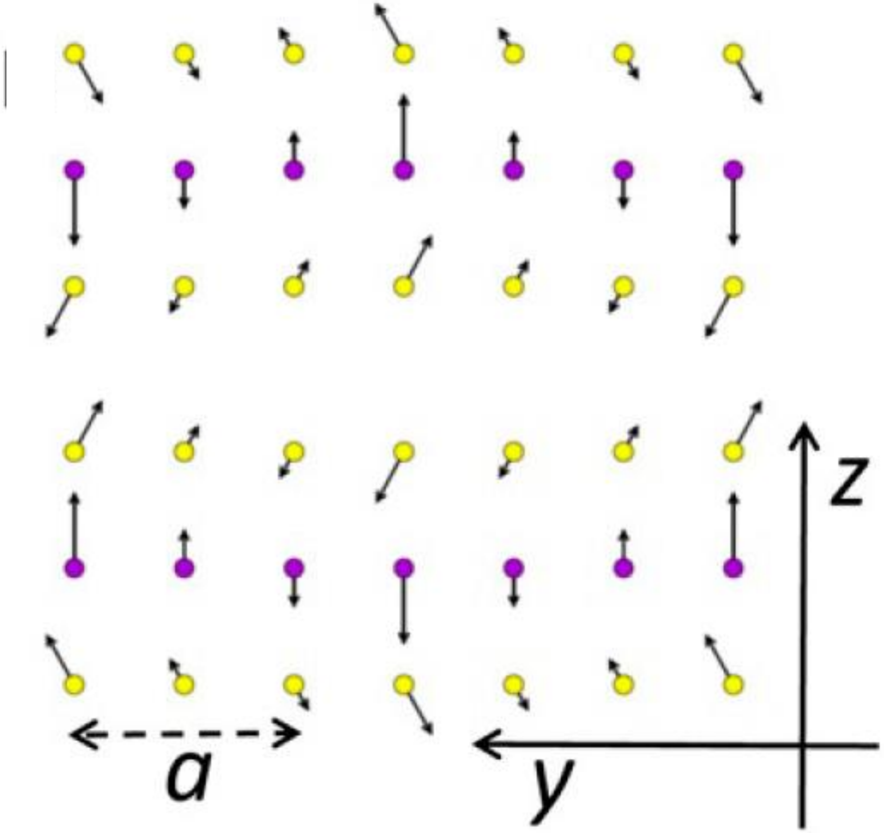
Ataei *et al*., PNAS (2021)



folding from Λ to Γ

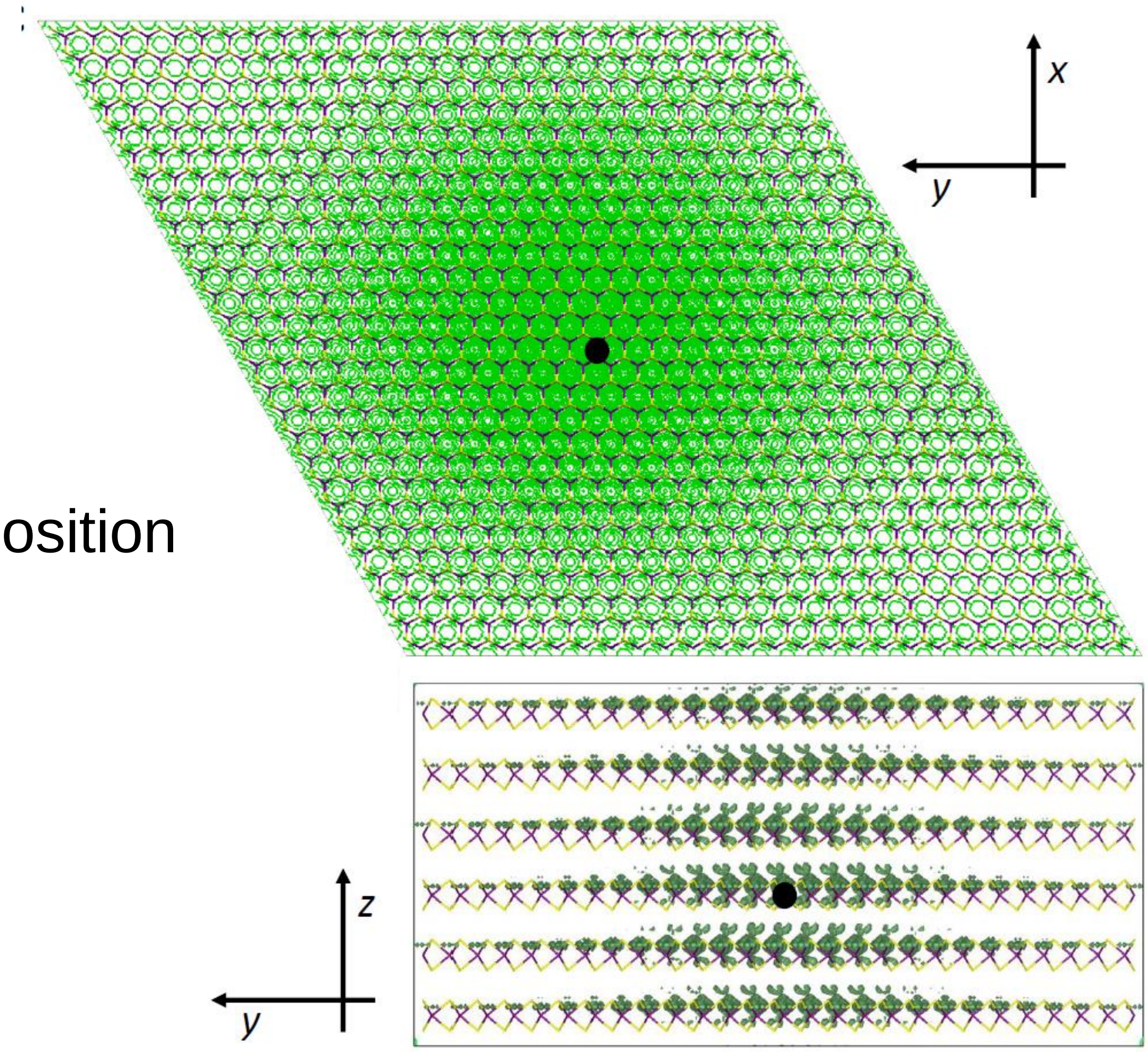
Raman fingerprint



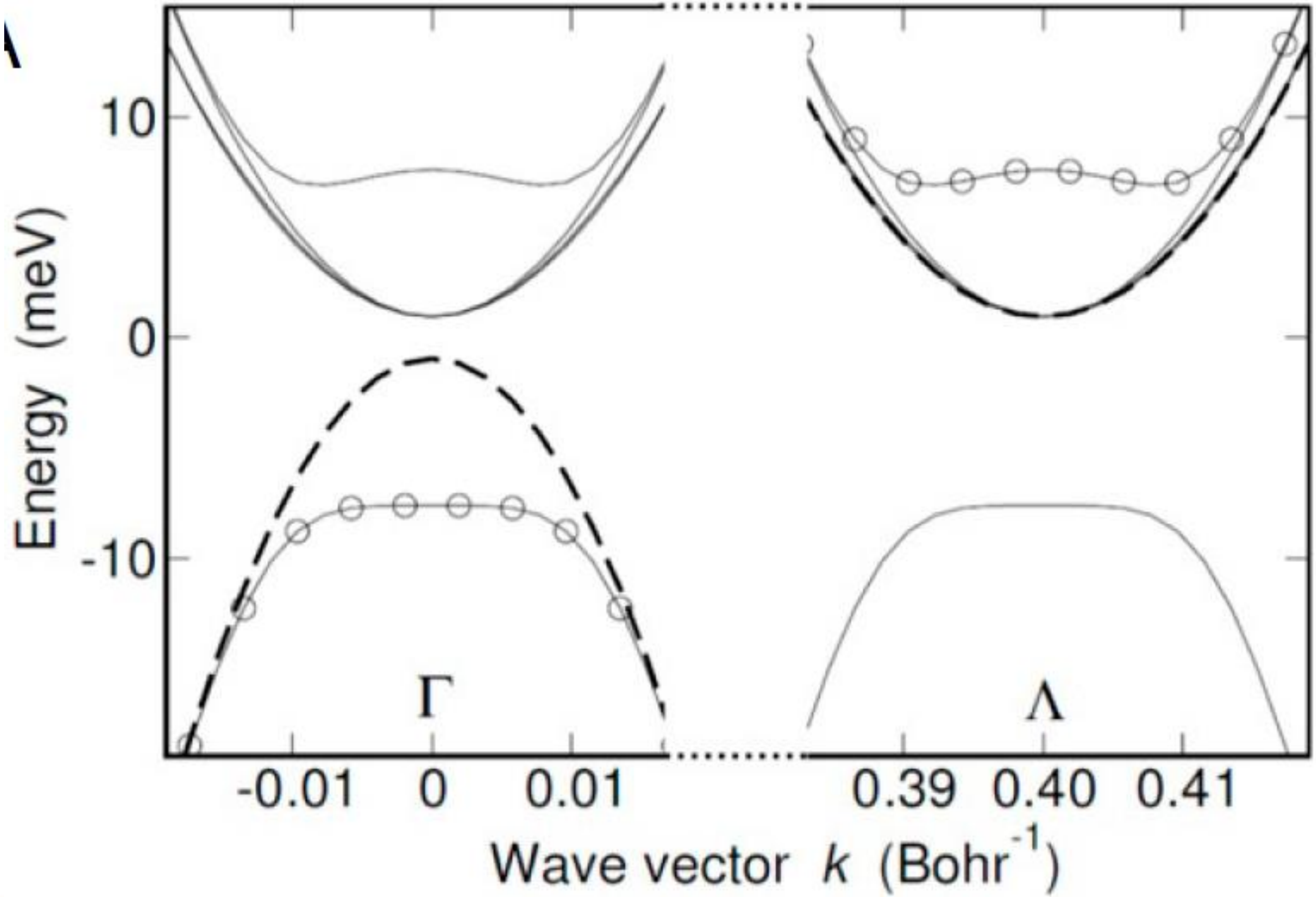


S. Ataei *et al*., PNAS **118,** e2010110118 (2021)

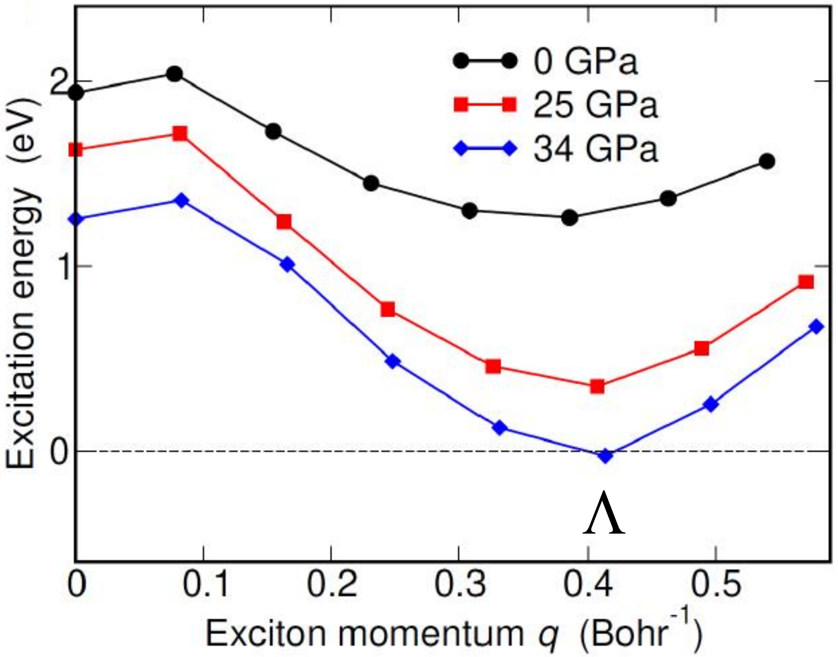
exciton wave function

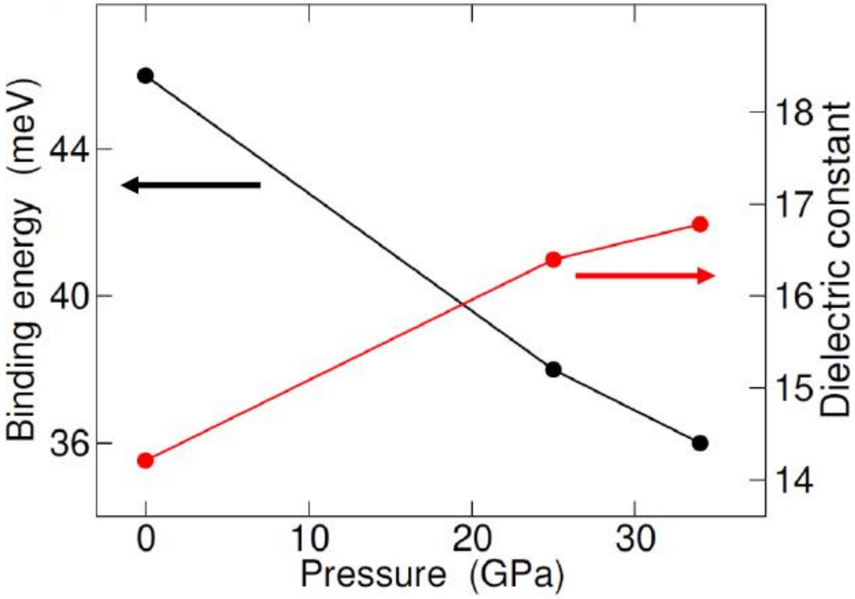


● fixed hole position


A
Energy (meV)
10
0
-10
Γ
Λ
-0.01
0
0.01
0.39
0.40
0.41
Wave vector k (Bohr^{-1})

excitonic instability



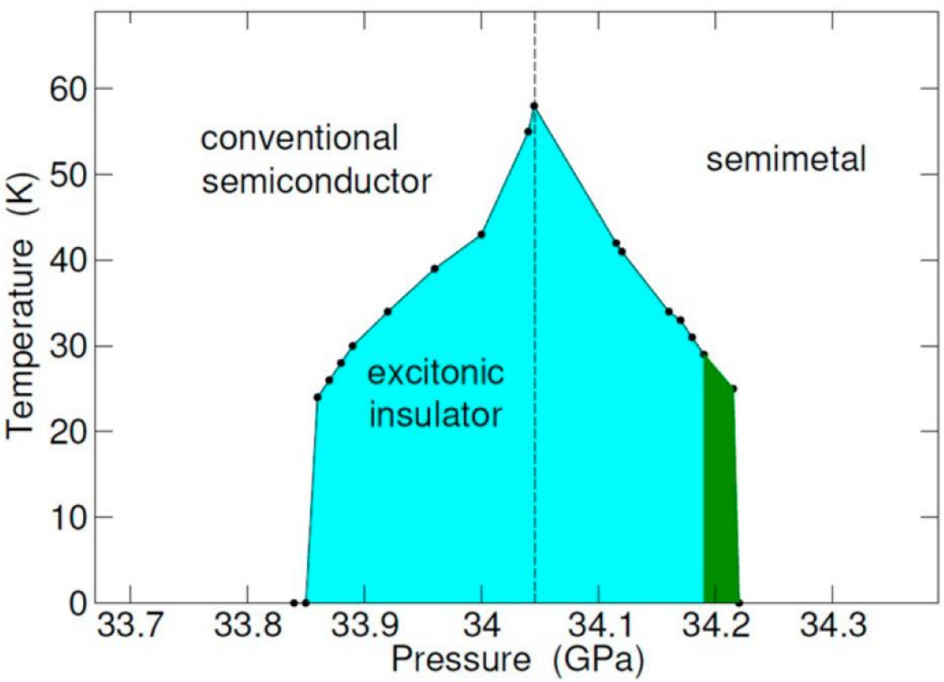


Quantum Espresso + **Yambo**
GGA PBE functional, 60 Ry cutoff
norm-conserving fully relativistic
pseudopotential (<u>spin-orbit included</u>)
GW and <u>finite-q</u> Bethe-Salpeter calculation:
2187 *k*-point sampling in full Brillouin zone
50 bands used to compute dielectric matrix

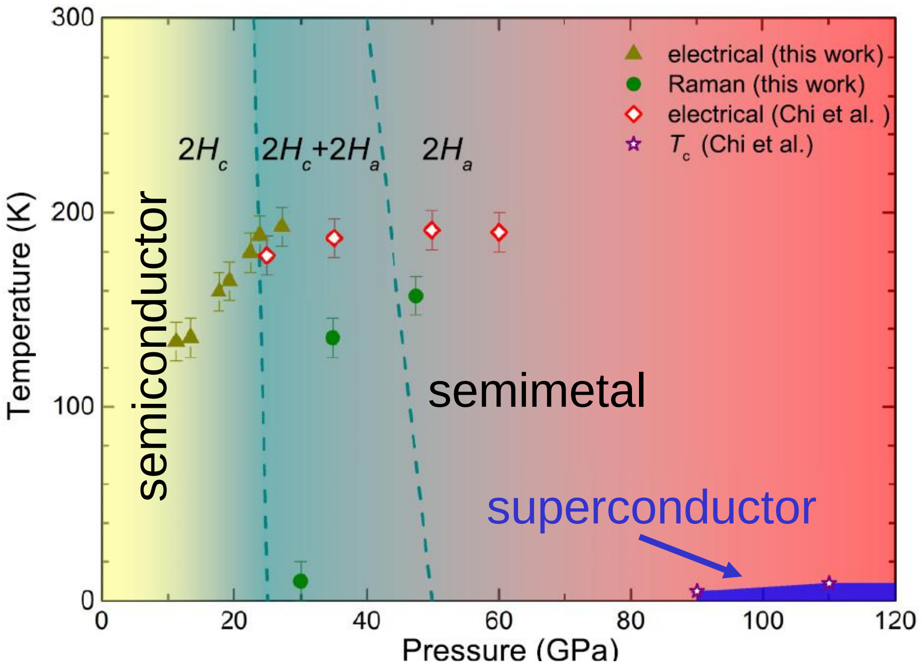
our theory

exp

Ataei *et al*., PNAS (2021)



PRB **97,** 214519 (2018)

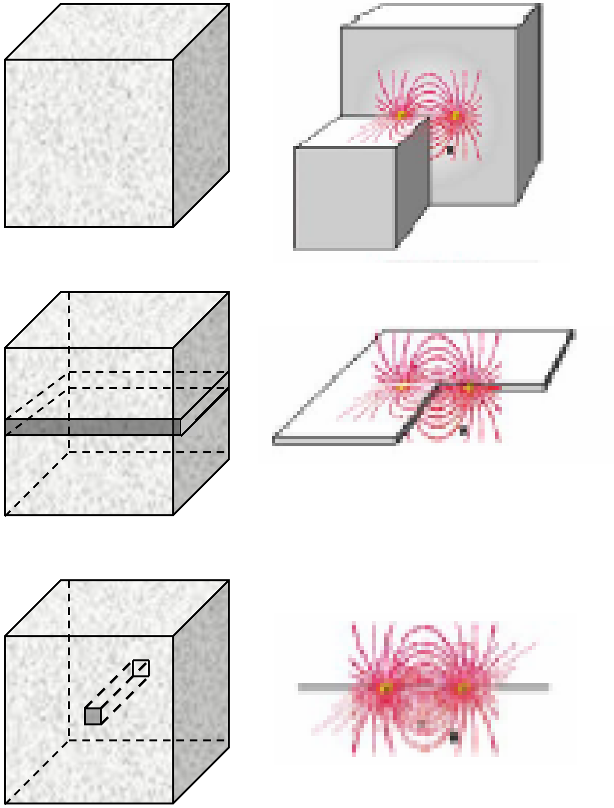


ideal low-D

3D $E_b = \mathrm{Ry}^*$

2D $E_b = 4\,\mathrm{Ry}^*$

1D $E_b \rightarrow \infty$

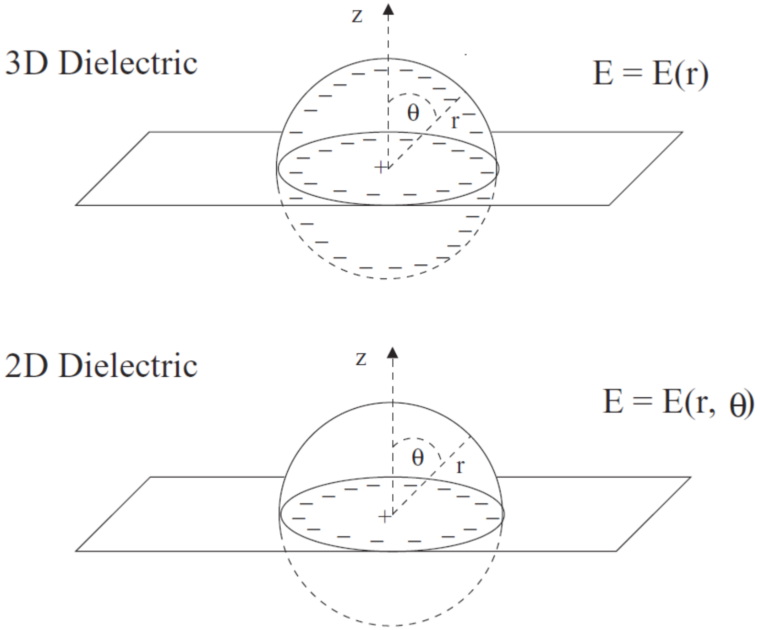


$$\boxed{\mathrm{Ry}^* = \mu / \varepsilon^2\,\mathrm{Ry}}$$

non local screening in low d

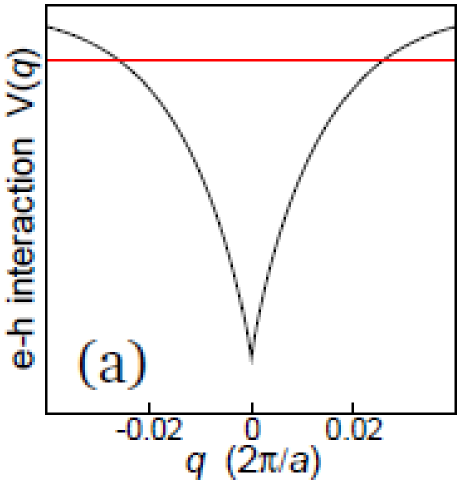
$\varepsilon(\mathbf{q}\rightarrow 0) = 1$

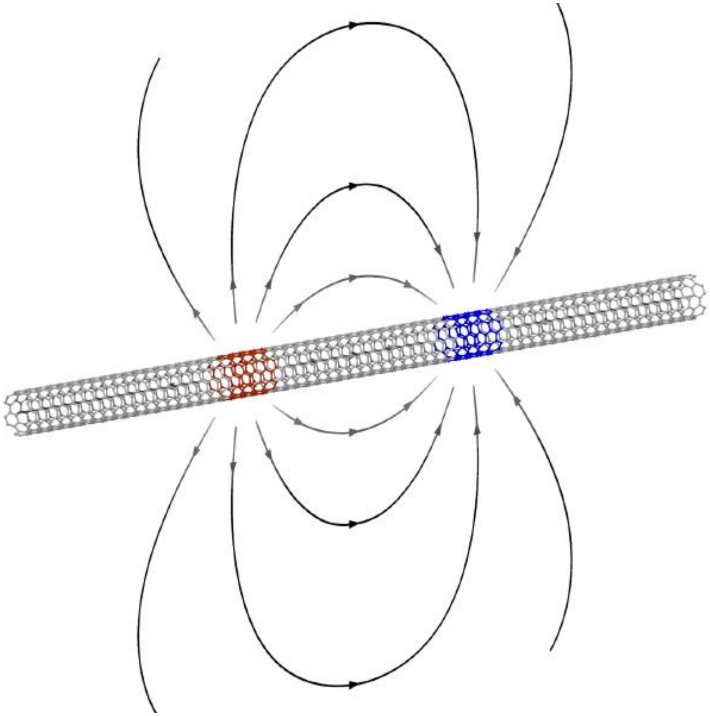
long-wavelength
interaction unscreened



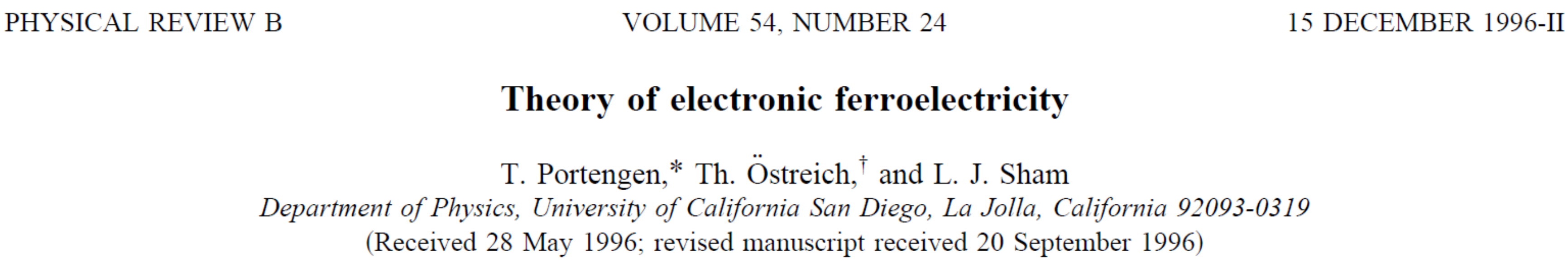
Cudazzo, Tokatly, Rubio 2011

carbon nanotubes





D.Varsano *et al.*, Nat. Commun. 2017



PHYSICAL REVIEW B VOLUME 54, NUMBER 24 15 DECEMBER 1996-II

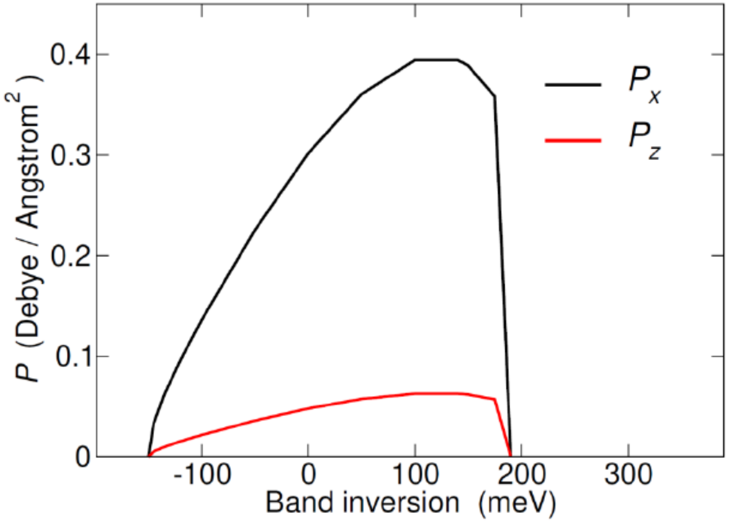
Theory of electronic ferroelectricity

T. Portengen,* Th. Östreich,† and L. J. Sham
Department of Physics, University of California San Diego, La Jolla, California 92093-0319

(Received 28 May 1996; revised manuscript received 20 September 1996)

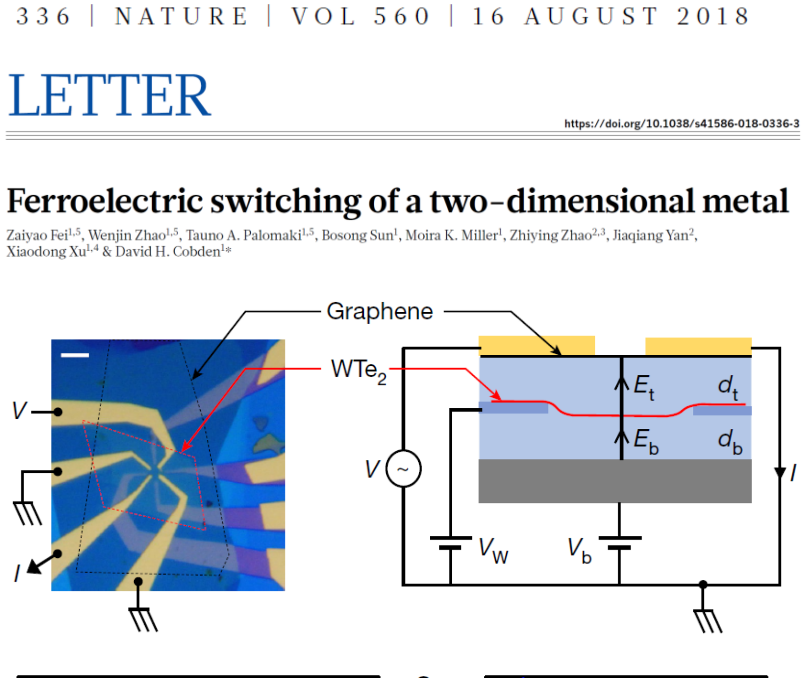
$$\mathbf{P} \sim \sum_{\mathbf{k}} \mathbf{p}_{\mathbf{k}} \langle \hat{c}^{+}_{\mathbf{k}} \hat{v}_{\mathbf{k}} \rangle$$

T'-MoS_2



arXiv:1906.07971

T'-WTe_2



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LETTER

https://doi.org/10.1038/s41586-018-0336-3

Ferroelectric switching of a two-dimensional metal

Zaiyao Fei[1,5], Wenjin Zhao[1,5], Tauno A. Palomaki[1,5], Bosong Sun[1], Moira K. Miller[1], Zhiying Zhao[2,3], Jiaqiang Yan[2], Xiaodong Xu[1,4] & David H. Cobden[1]*

mean field theory of the EI

$|\Psi_0> = \prod_k \hat{v}_k^+ |\text{vac}>$ ground state of energy E_0

$|\Psi_1> = \sum_k A(k)\, \hat{c}_k^+\, \hat{v}_k\, |\Psi_0 >$ exciton of energy E_1

$|\Psi_\gamma> = N(\gamma) \prod_k (\hat{v}_k^+ + \gamma\, A(k) \hat{c}_k^+)\, |\text{vac}>$ trial wave function

$|\Psi_\gamma> = |\Psi_0> + \gamma\, |\Psi_1>$ to first order

$$E_\gamma = \frac{\langle \Psi_\gamma | \hat{H} | \Psi_\gamma \rangle}{\langle \Psi_\gamma | \Psi_\gamma \rangle} = \frac{E_0 + \gamma^2\, E_1}{1 + \gamma^2} = E_0 + \gamma^2\, (E_1 - E_0)$$