Superconductive functional materials for advanced quantum technologies

at Moscow Institute of Physics and Technology@2023.09.27

Excitonic Insulators from First-principles

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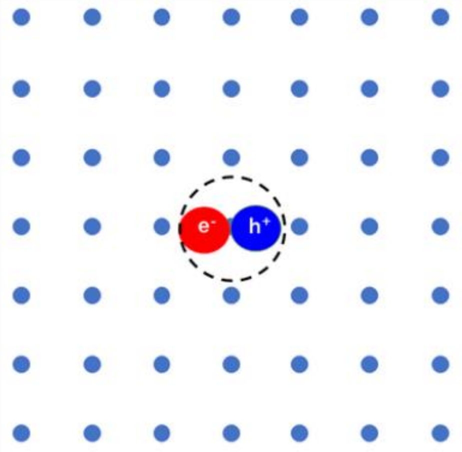
Outline

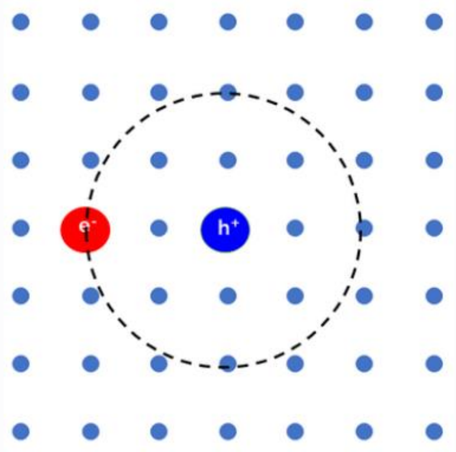
- What is the excitonic insulator?
- Development status and bottlenecks
- Our research: Dark exciton strategy and Materialization
- Conclusion, Perspective and Acknowledgements

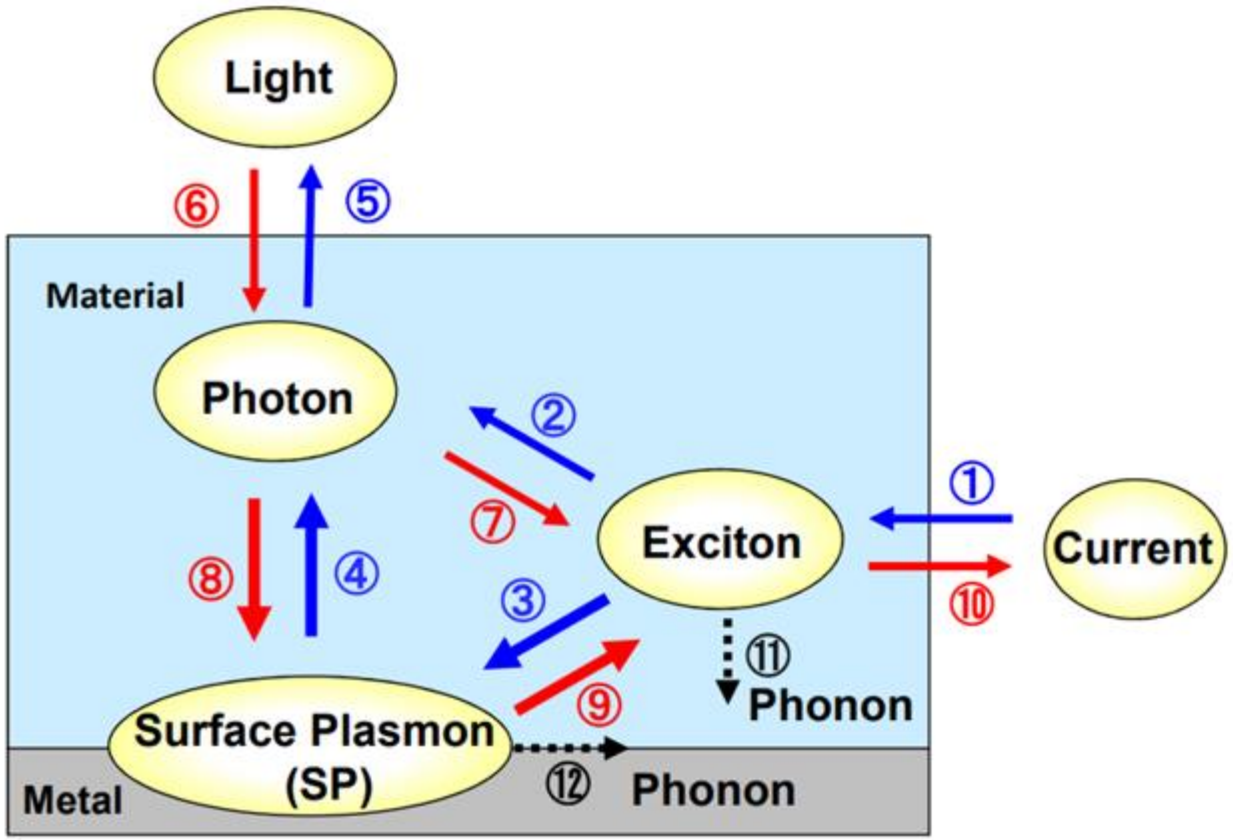
Excitons: Bound electron-hole pairs

Frenkel exciton

Wannier-Mott exciton







Journal of Photochemistry and Photobiology C: Photochemistry Reviews

Bose-Einstein Condensation of Excitons

PHYSICAL REVIEW VOLUME 126, NUMBER 5 JUNE 1, 1962

Bose-Einstein Condensation of Excitons

JOHN M. BLATT
Courant Institute of Mathematical Sciences, New York University, New York, New York and Applied Mathematics Department, University of New South Wales, New South Wales, Australia

AND

K. W. BÖER AND WERNER BRANDT
Department of Physics, Radiation and Solid-State Laboratory, New York University, New York, New York

(Received January 8, 1962)

Exciton = electron + hole = Boson

$$T_C \cong \frac{h^2}{2\pi m k_B}\left[\frac{n}{2.612(2s+1)}\right]^{2/3}$$

Lighter *m* for higher *Tc*

Bose–Einstein condensation of exciton polaritons

Nature **443**, 409–414 (28 September 2006)

J. Kasprzak[1], M. Richard[2], S. Kundermann[2], A. Baas[2], P. Jeambrun[2], J. M. J. Keeling[3], F. M. Marchetti[4], M. H. Szymańska[5], R. André[1], J. L. Staehli[2], V. Savona[2], P. B. Littlewood[4], B. Deveaud[2] & Le Si Dang[1]

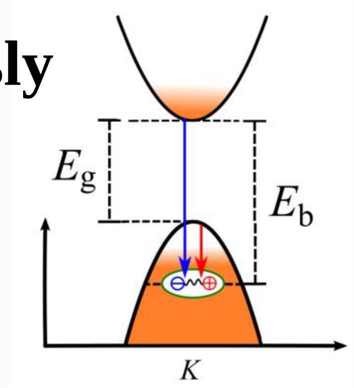
Phase transitions to quantum condensed phases—such as Bose–Einstein condensation (BEC), superfluidity, and superconductivity—have long fascinated scientists, as they bring pure quantum effects to a macroscopic scale. BEC has, for example, famously been demonstrated in dilute atom gas of rubidium atoms at temperatures below 200 nanokelvin. Much effort has been devoted to finding a solid-state system in which BEC can take place. Promising candidate systems are semiconductor microcavities, in which photons are confined and strongly coupled to electronic excitations, leading to the creation of exciton polaritons. These bosonic quasi-particles are 10^9 times lighter than rubidium atoms, thus theoretically permitting BEC to occur at standard cryogenic temperatures. Here we detail a comprehensive set of experiments giving compelling evidence for BEC of polaritons. Above a critical density, we observe massive occupation of the ground state developing from a polariton gas at thermal equilibrium at 19 K, an increase of temporal coherence, and the build-up of long-range spatial coherence and linear polarization, all of which indicate the spontaneous onset of a macroscopic quantum phase.

Excitonic Insulators

Can exciton BEC be the ground state?

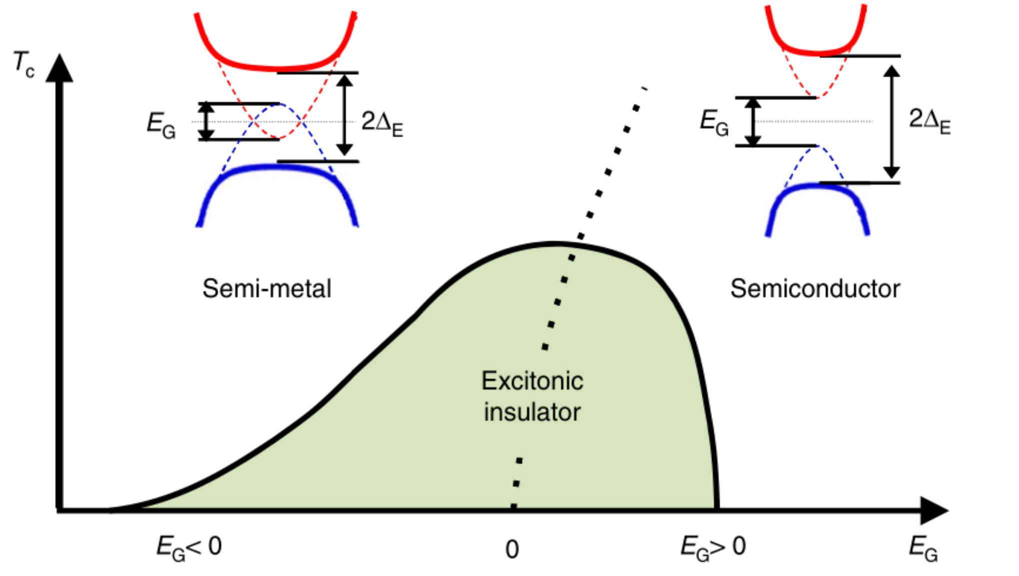
It involves two aspects

- Excitons spontaneously form when $E_b > E_g$
- Excitons undergo a Bose condensation



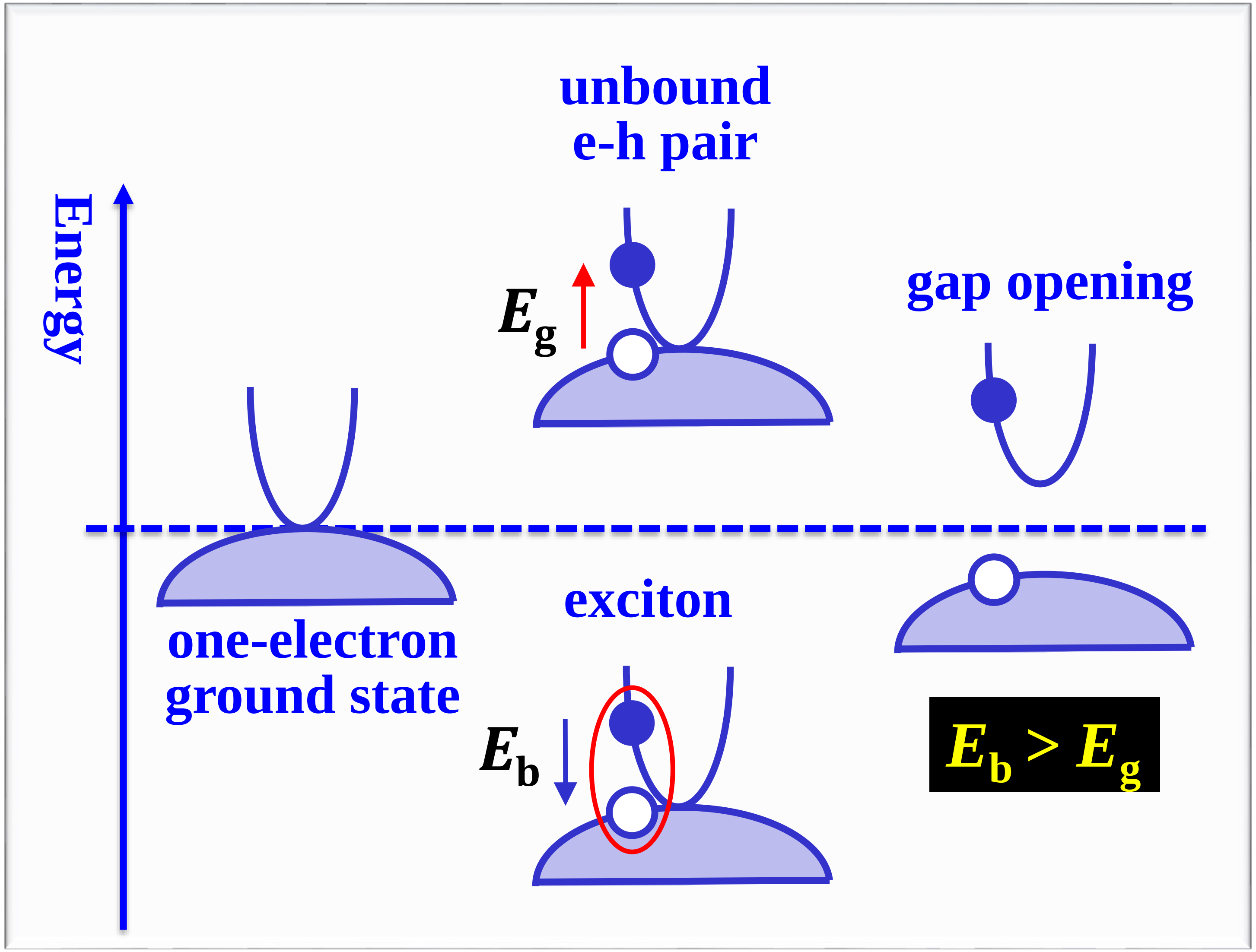
Mott, Phil. Mag, 1961;
Knox, 1963;
Keldysh, Kopaev, Sov. Phys .-Solid State 1965;
DesCloizeaux, J. Phys. Chem. Solids 1965;
Jérome, Rice, Kohn, Phys. Rev. 1967;
Halperin, Rice, Rev. Mod. Phys. 1968;
Kohn, Sherrington Rev. Mod. Phys. 1970

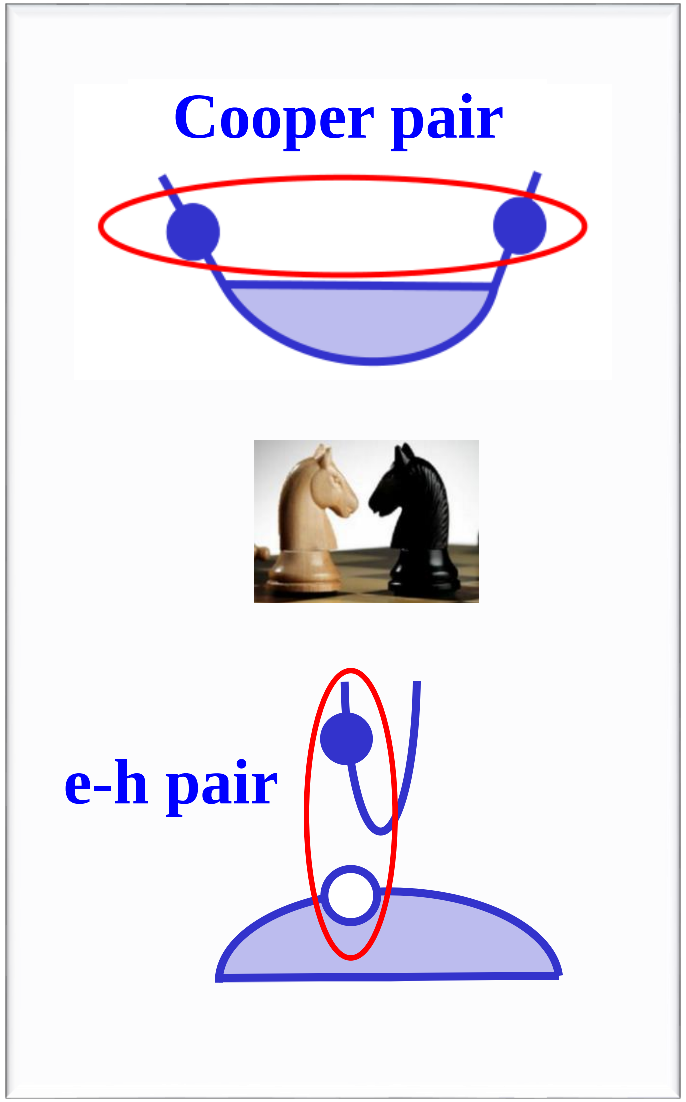
Excitonic insulator scenario



Novel Physics
- BCS-BEC crossover
- Spontaneous symmetry breaking
- Off-diagonal long-range order
- Many-body ground state

Excitonic Instability





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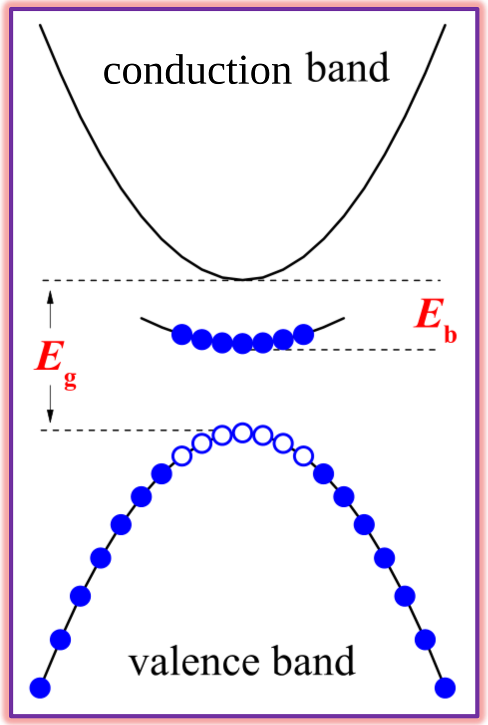
Materialization

Limited material candidates **No representative excitonic insulator**

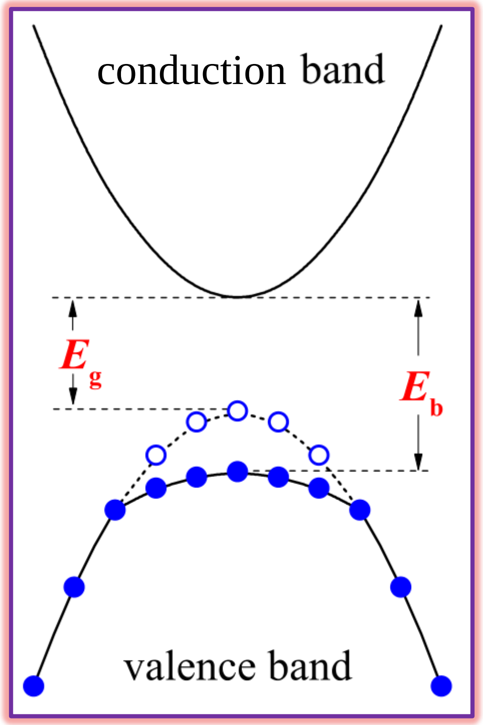


Band insulator

material

Reality: $E_b < E_g$

Ideal: $E_b > E_g$



Excitonic insulator

ZnO: E_g 3.4 eV vs. E_b 60 meV

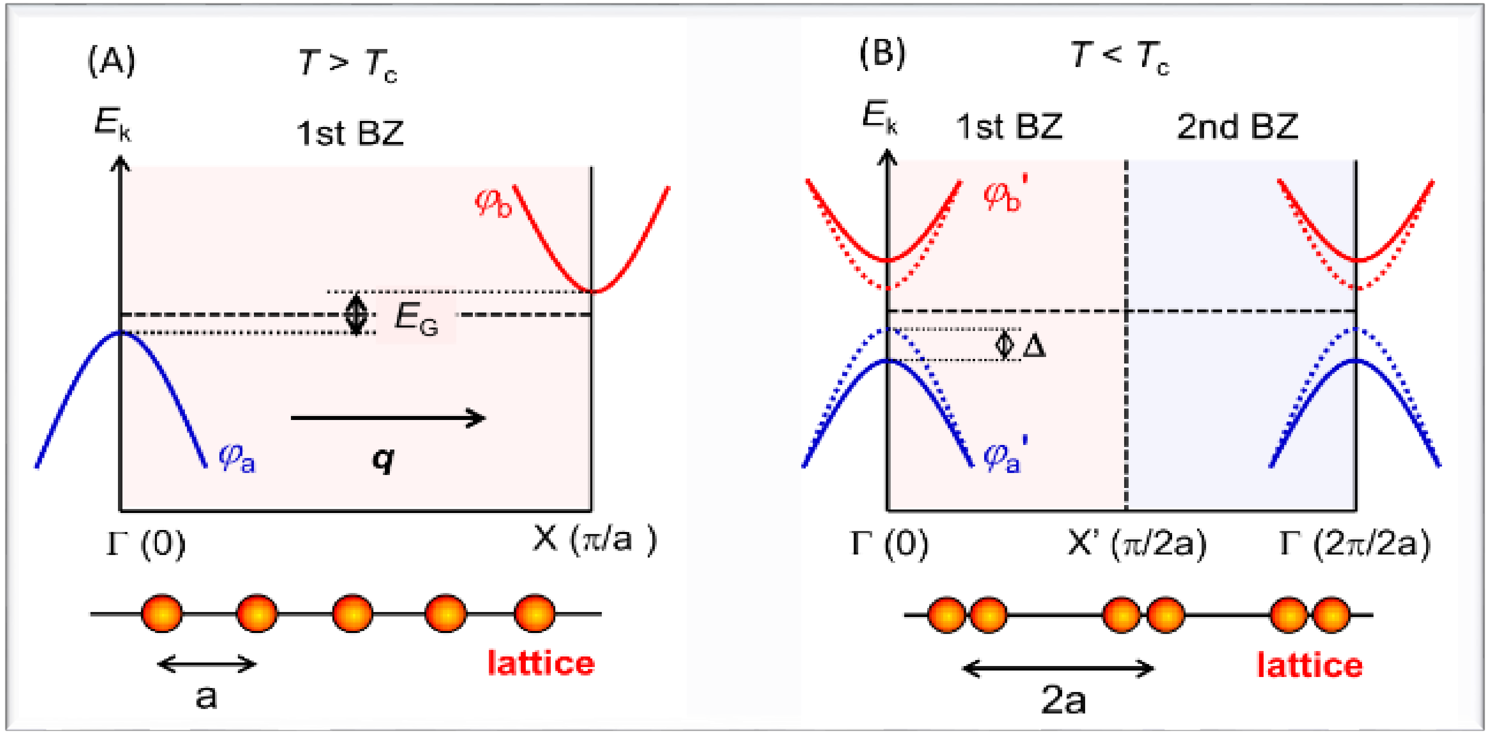
Materialization

1st type:

Indirect gap, e.g., $TiSe_2$

√
Suppressed screening

×
Coupling with phonons
Confuse with Jahn-Teller



Yangfan LU, Thesis (No. 47-127015)

Materialization

2^{nd} type: (TNS)

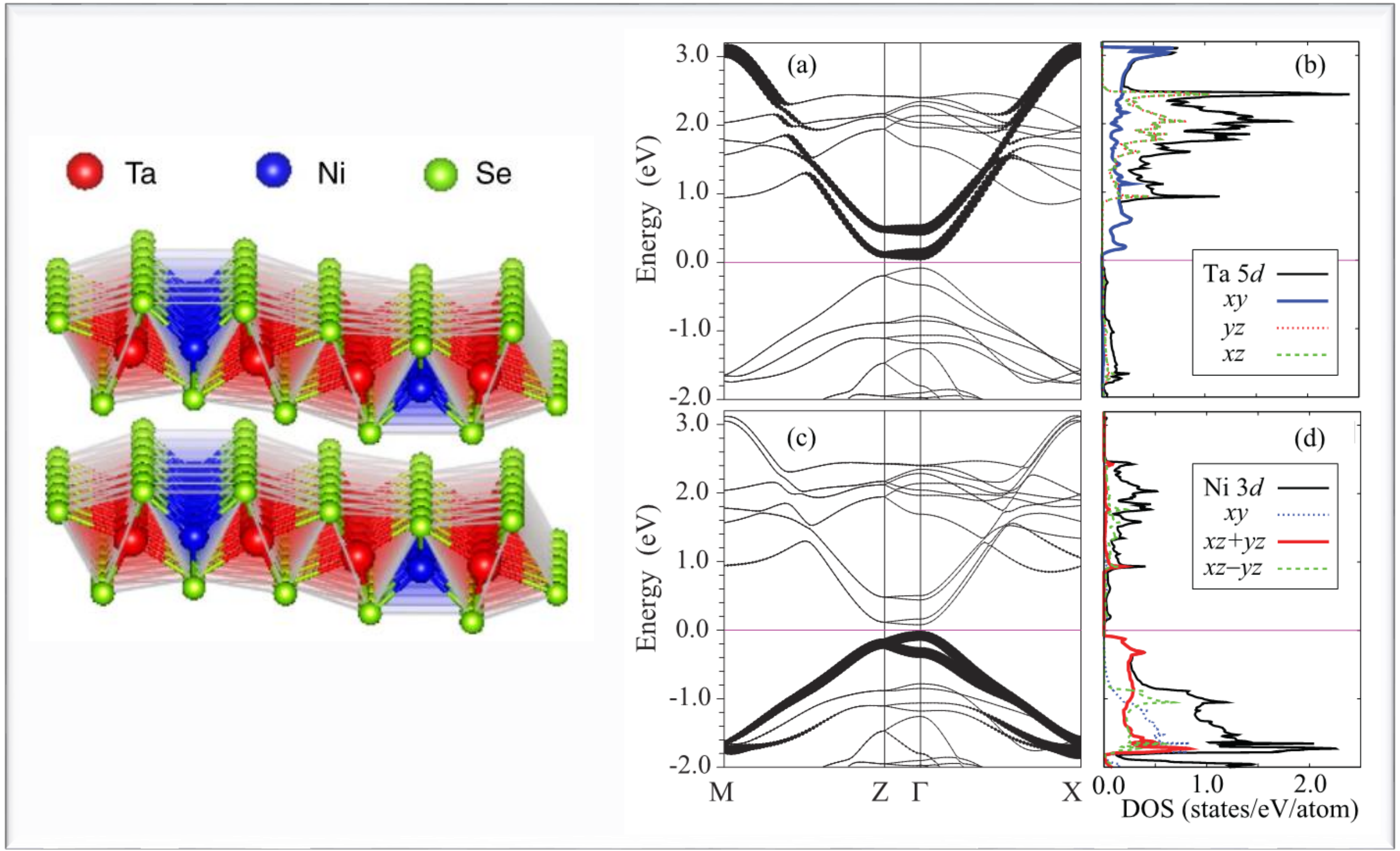
~Zero gap, e.g., Ta_2NiSe_5

√

Phase transition T_c ~ 327 K

×

- **Complex structure**
- **Structural distortion**
- **E_b up to 0.16 eV**
- **Symmetry breaking**
  Discrete vs. Continuous



Mazza et al., PRL 124, 197601 (2020); Lu et al. Nat. Commun. 8, 14408 (2017); Kaneko et al., PRB 87, 035121 (2013)

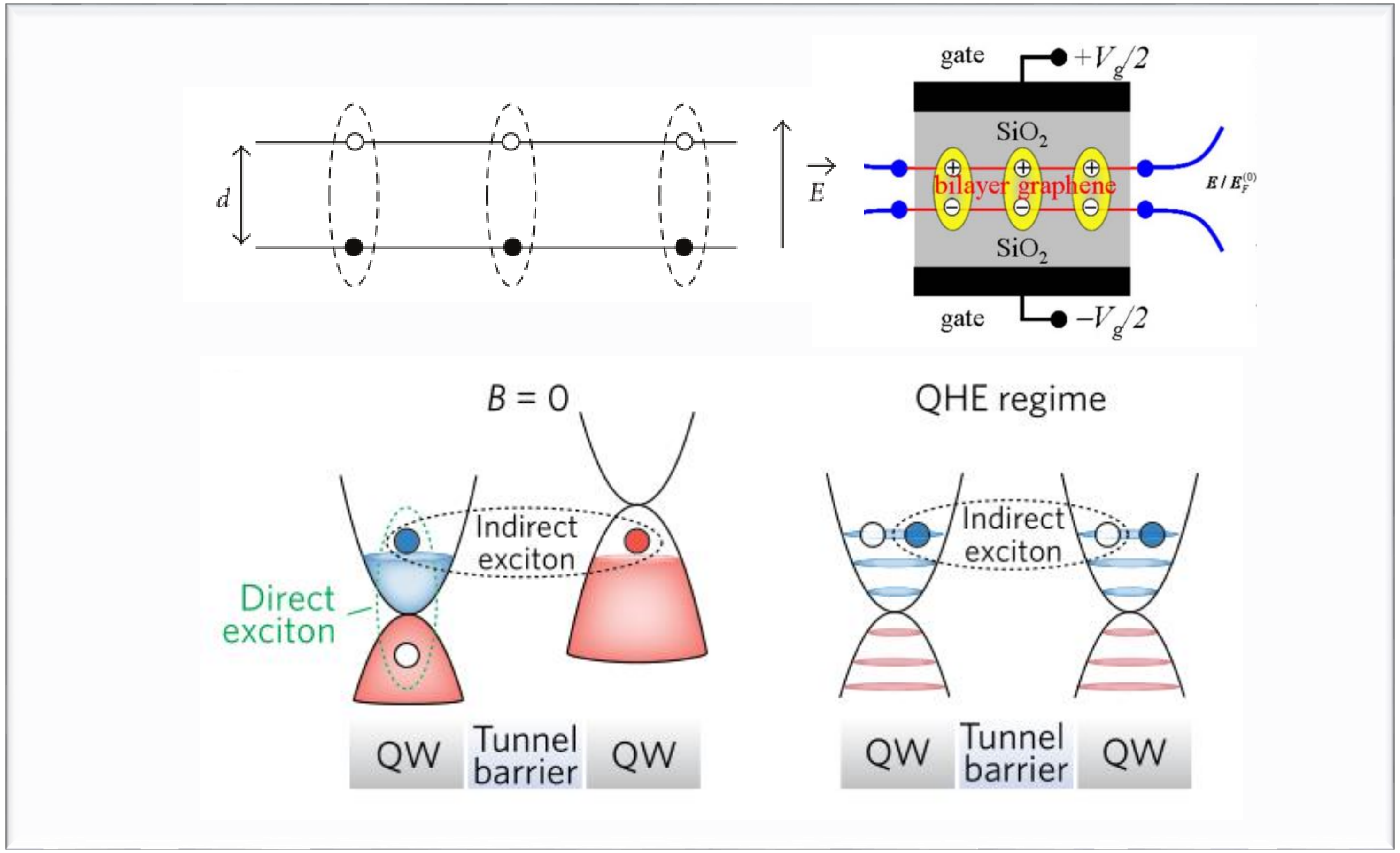
Materialization

3rd type:

~Interface, e.g., e-h bilayer

√
- Spatial separation
- Longer lifetime

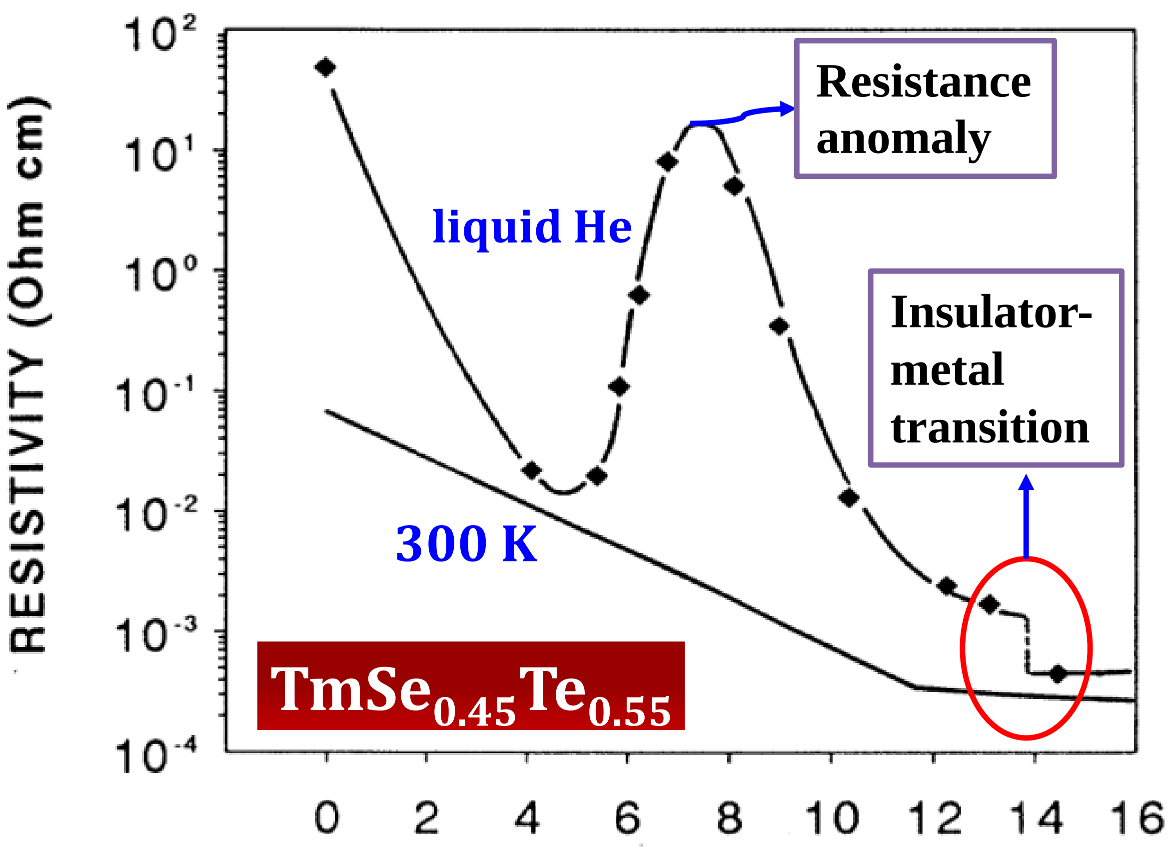
×
- May not thermodynamic ground state
- e-h pair ≠ exciton

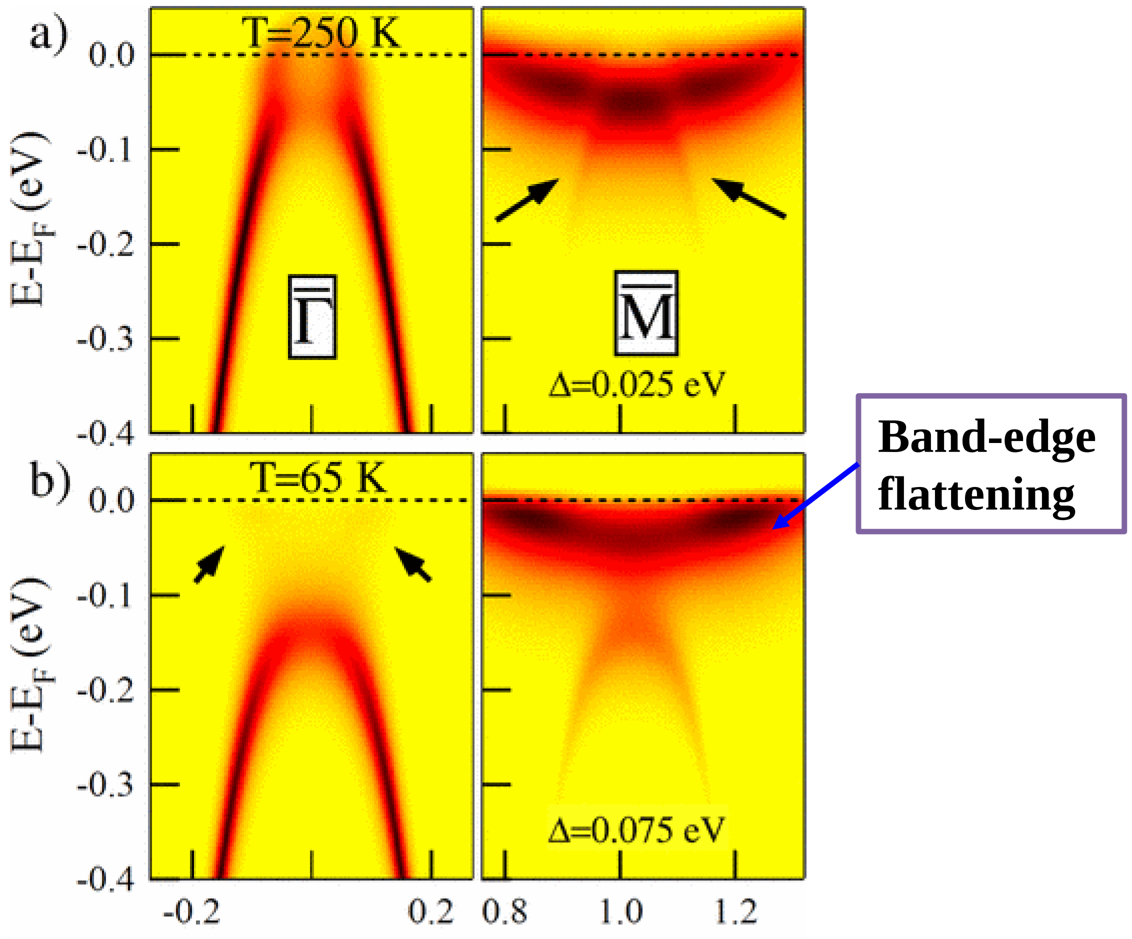


Eisenstein et al, Nature 432, 691 (2004); Min et al., PRB 78, 121401 (2008); Snoke, Adv. Condens. Matter Phys. 2011, 938609 (2011); Li et al., Nat. Phys. 13, 751 (2017); Liu et al., Science 375, 205 (2022)

Experimental Identification

Hard to confirm Confused by competing mechanisms like Jahn-Teller





Bucher et al., PRL 67, 2717 (1991); Cercellier et al., PRL 99, 146403 (2007)

Omission

(1) Direct-gap systems

- Why always small gap semiconductors or semimetals?
- Naturally avoid intervention of Jahn-Teller mechanism

(2) Band engineering

- More opportunities from extrinsically tuning E_g and/or E_b
- More space for devices based on excitonic insulators

(3) Spin and other order

- Novel quantum state from spin-polarization
- Multifunctionality due to the combination

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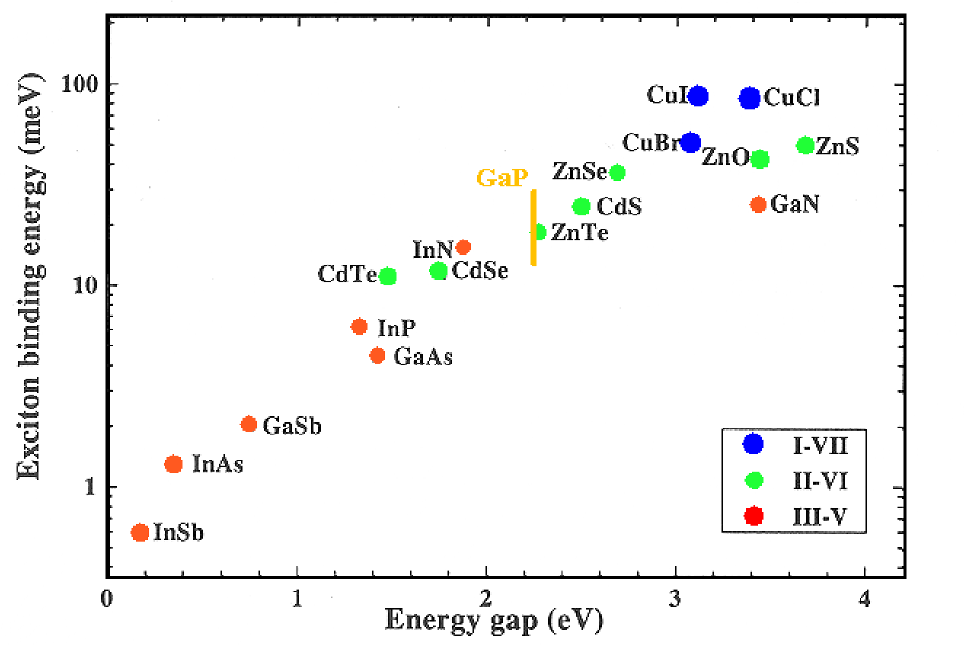
The key for EIs: Screening interaction

(1) Small E_b

$$E_b \propto \frac{\mu}{\varepsilon^2}$$



https://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_5/advanced/t5_1_3.html

(2) E_b and E_g are coupled

If $E_b \neq 0$ at $E_g = 0$, it is an EI.

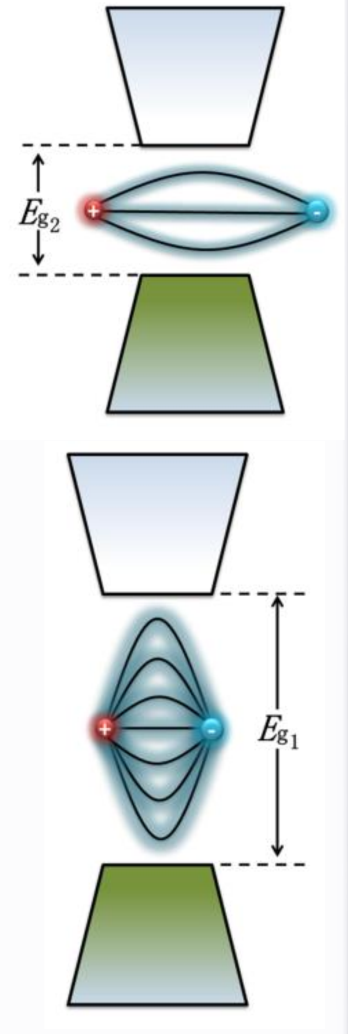
System screening is evaluated by

$$\varepsilon = A \sum_{c,v} \int_{\mathbf{k}} \frac{|\langle u_{c,\mathbf{k}}|\nabla_{\mathbf{k}}|u_{v,\mathbf{k}}\rangle|^2}{E_{c,\mathbf{k}} - E_{v,\mathbf{k}}} d\mathbf{k},$$

min: E_g

which tells that $E_g \to 0$, ε diverse.

So, $E_b \to 0$ at $E_g \to 0$.



The key for EIs: Screening interaction

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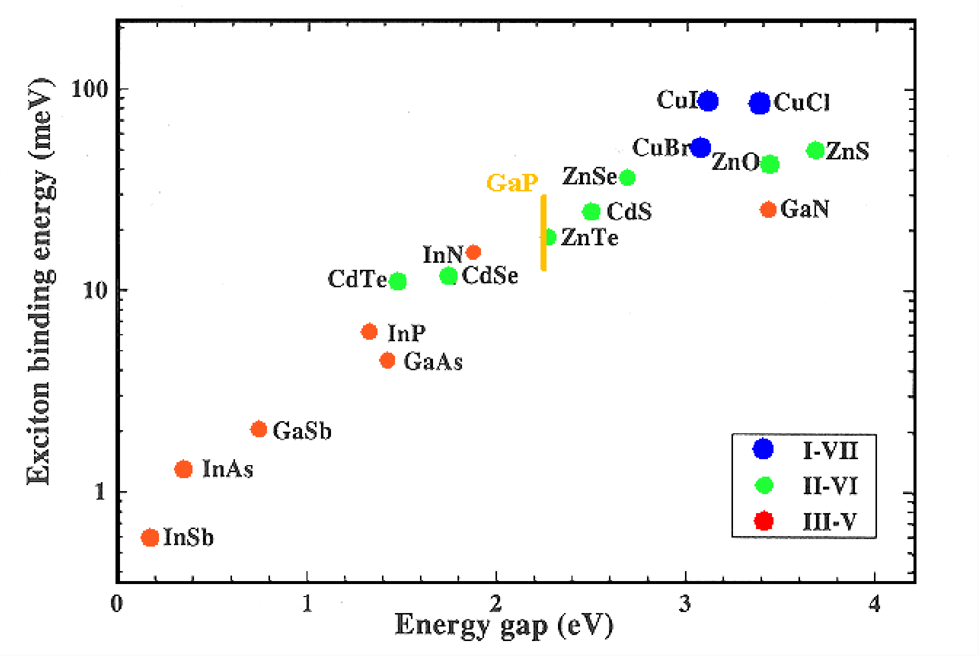
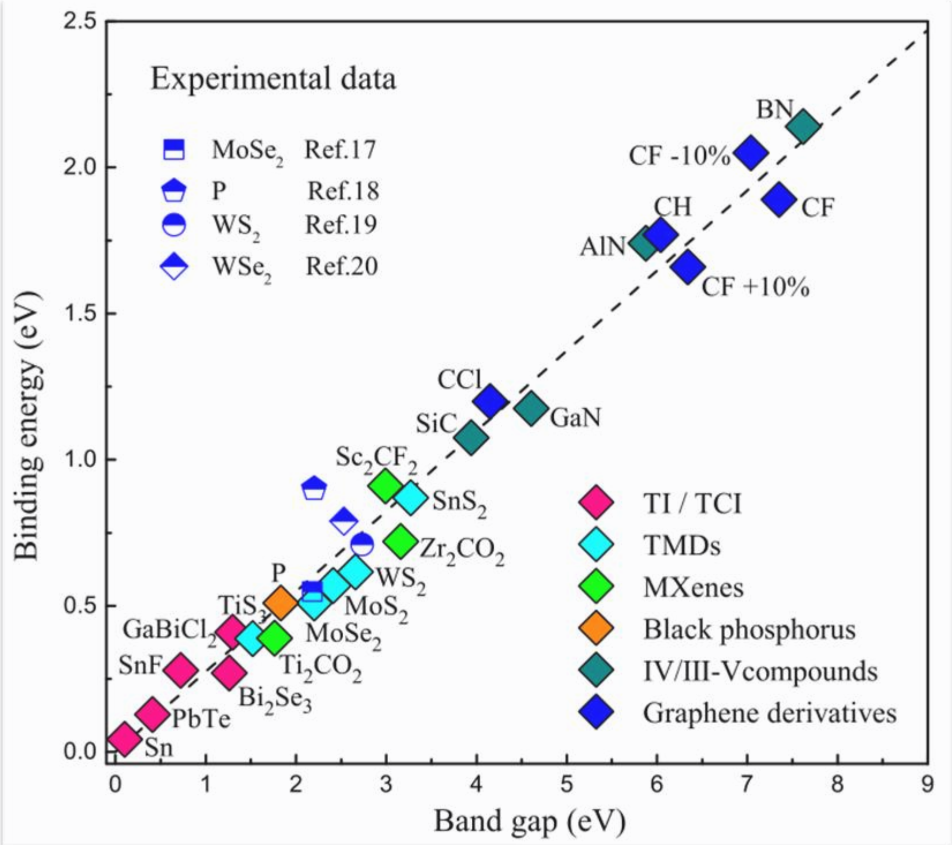
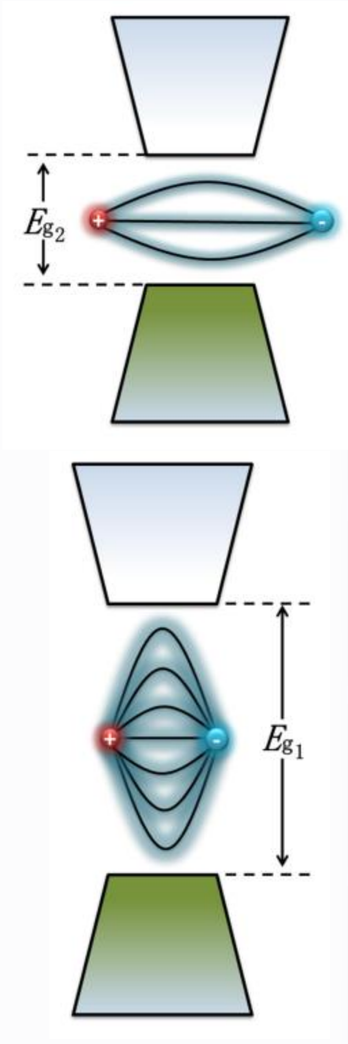


https://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_5/advanced/t5_1_3.html

(2) Linear scaling $E_b \approx E_g/4$





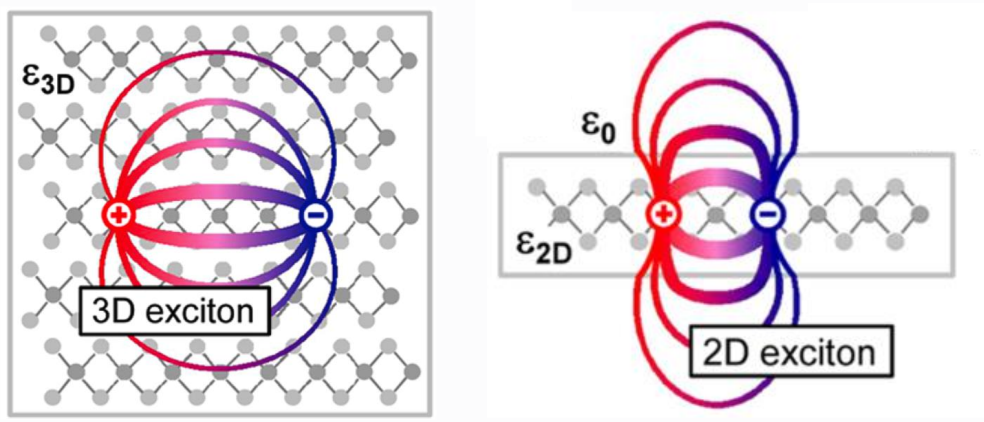
PRL 118, 266401 (2017)

Bright excitons

Dark excitonic insulators

Ideal hydrogen model

- 3D E_b = Ry*
- 2D E_b = 4 Ry*
- 1D $E_b \to \infty$



Cudazzo et al., PRB 84, 085406 (2011);
Chernikov et al., PRL 113, 076802 (2014)

⊕

System screening

$$\varepsilon = A \sum_{c,v} \int_{\mathbf{k}} \frac{|\langle u_{c,\mathbf{k}} | \nabla_{\mathbf{k}} | u_{v,\mathbf{k}} \rangle|^2}{E_{c,\mathbf{k}} - E_{v,\mathbf{k}}} d\mathbf{k},$$

min: E_g

When

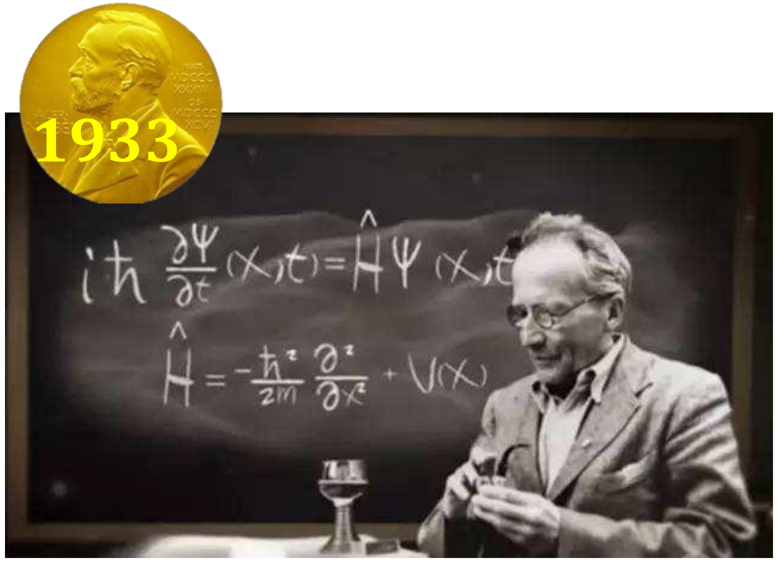
$$|\langle u_{c,k} | \nabla_k | u_{v,k} \rangle|_{E_g} = 0$$ **inactive**

ε do not diverse if $E_g \to 0$.

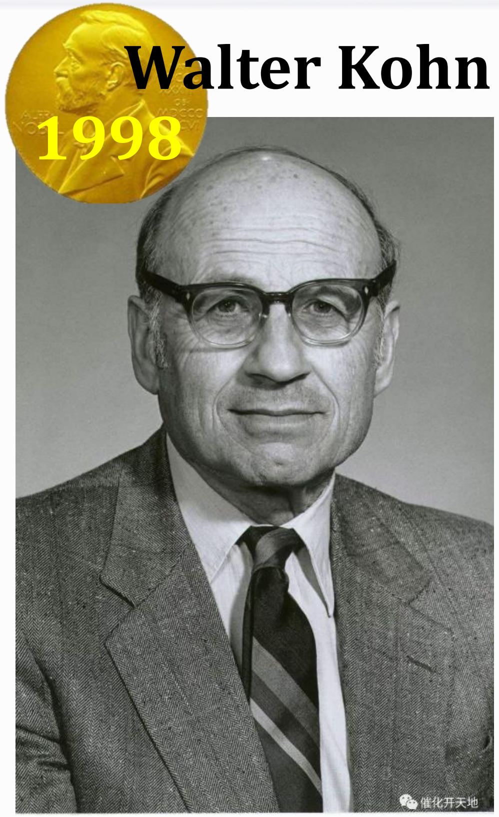
- ✓ Decrease screening
- ✓ Decouple E_g and E_b

PRB 98, 081408(R) (2018)

Methods: Density functional theory



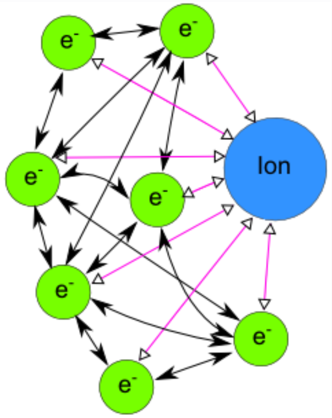
exponential-wall



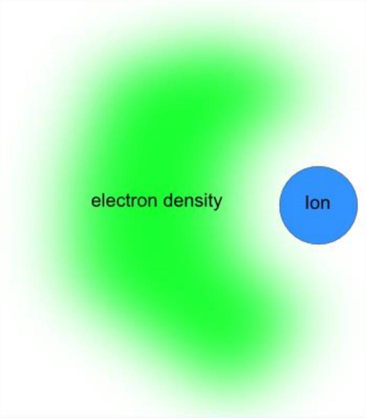
HK theorem:

1) $\boldsymbol{\rho(r) \leftrightarrow v(r)}$

2) $\boldsymbol{E_0 = \min_{\rho}\{E(\rho)\}}$



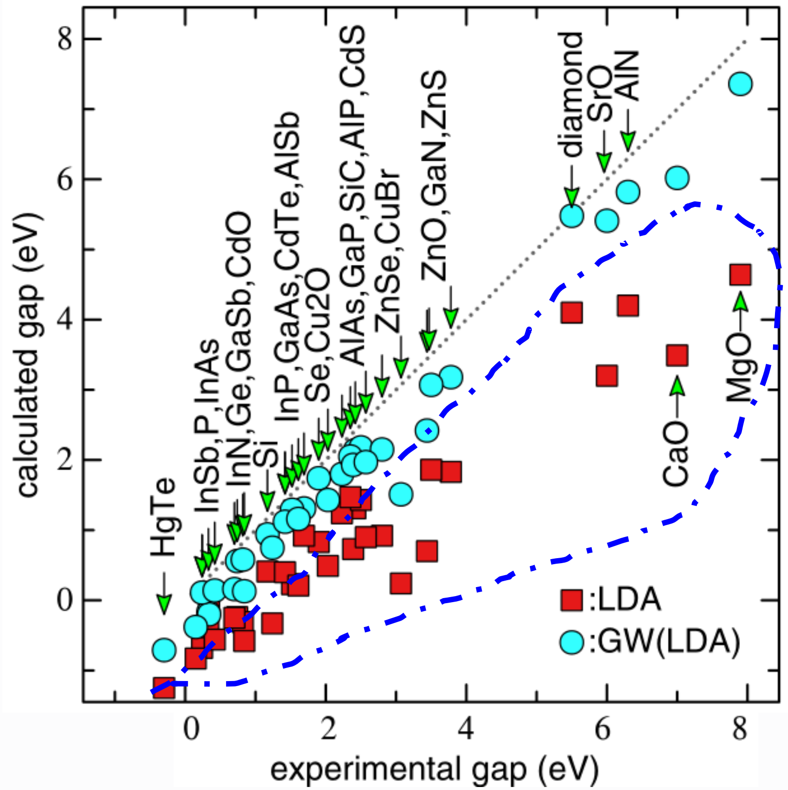
3N → 3



$$
\begin{aligned}
\hat{H}_{KS} &= \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext} \\
&= -\frac{\hbar^2}{2m_e}\vec{\nabla}_i^2 + \frac{e^2}{4\pi\epsilon_0}\int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}' + \boxed{V_{xc}} + V_{ext}
\end{aligned}
$$

Methods: Exchange-Correlation functionals

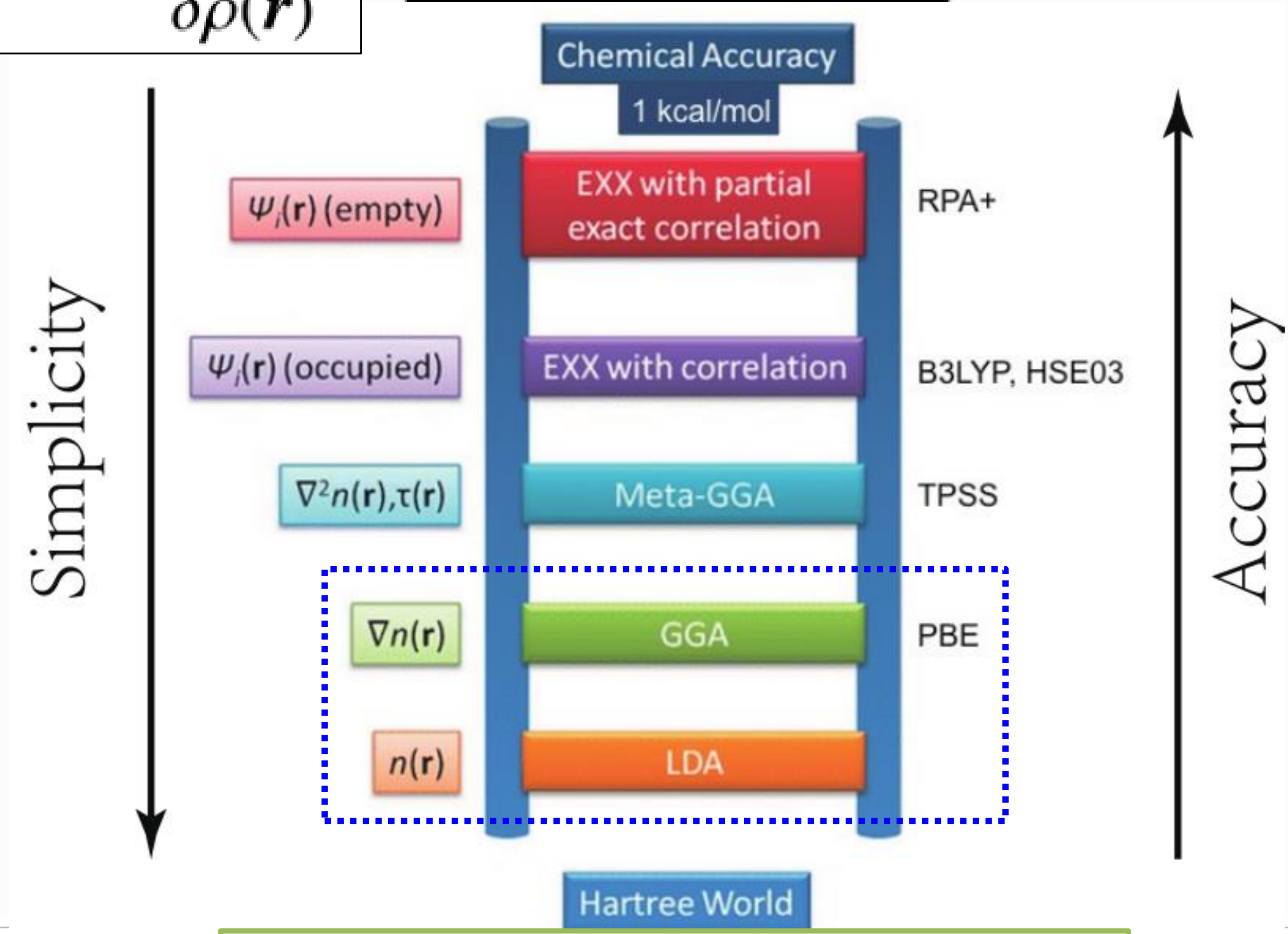
Bandgap underestimation



Schilfgaarde et al., PRL 96, 226402 (2006)

$$V_{xc}(\boldsymbol{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\boldsymbol{r})}$$

Jacob ladder



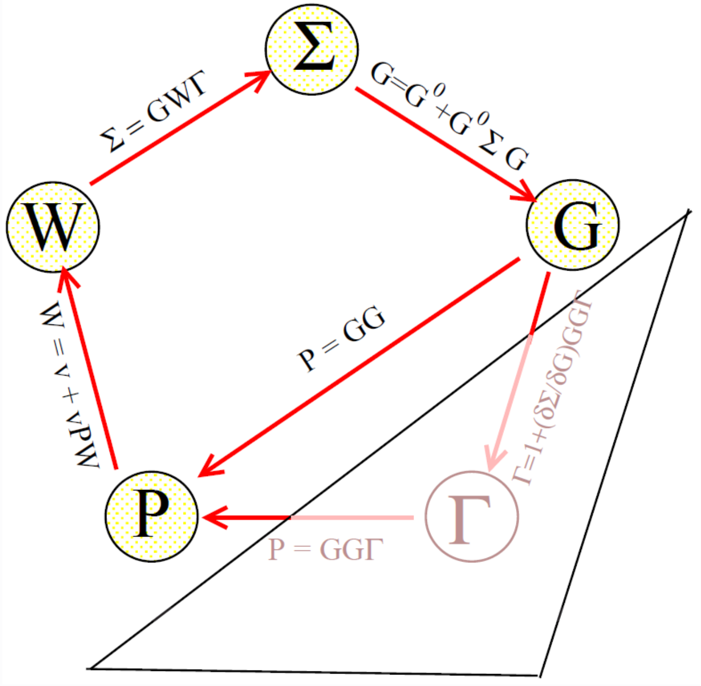
https://www.sas.upenn.edu/ jianmint/Research/

Methods: GW-BSE formula

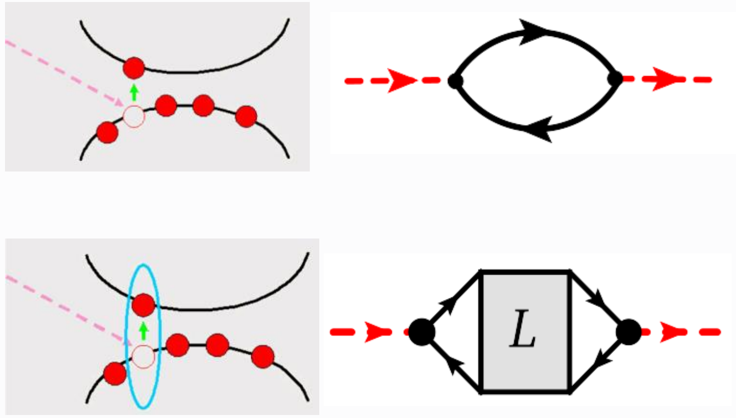
Propagator: Green's function

self-energy Σ

$$G = G^0 + G^0 \Sigma G$$



two-body problem



Bethe-Salpeter Eq. by Green's function

$$H^{eff} = H^{diag} + 2\gamma_x H^x + \gamma_c H^{dir}$$

$$H^{diag}_{vck,v'c'k'} = (E_{ck} - E_{vk})\delta_{vv'}\delta_{cc'}\delta_{kk'}$$

$$H^{dir}_{vck,v'c'k'} = -\int d^3r\, d^3r'\, \psi_{vk}(r)\psi^*_{ck}(r') W(r,r') \psi^*_{v'k'}(r)\psi_{c'k'}(r')$$

$$H^{x}_{vck,v'c'k'} = \int d^3r\, d^3r'\, \psi_{vk}(r)\psi^*_{ck}(r) \bar{v}(r,r') \psi^*_{v'k'}(r')\psi_{c'k'}(r')$$

DFT-GW-BSE calculations for materials

- DFT/HSE/G_0W_0 for E_g
- E_g is converged to within 0.01 eV
- Bethe-Salpeter equation for E_b
- Singlet/Triplet/Spin-orbit coupling

When: $E_t = E_g - E_b$ < 0,
Excitons spontaneously form, as an EI candidate.

Large- and Direct-gap EIs

2D limit of III-V semiconductors

"Dark" from parity forbidden

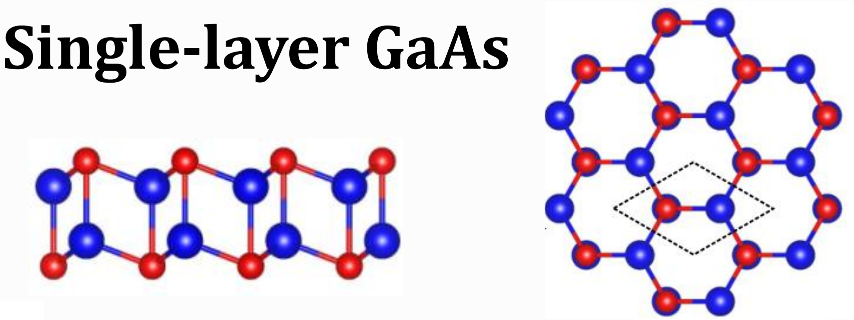
same parity

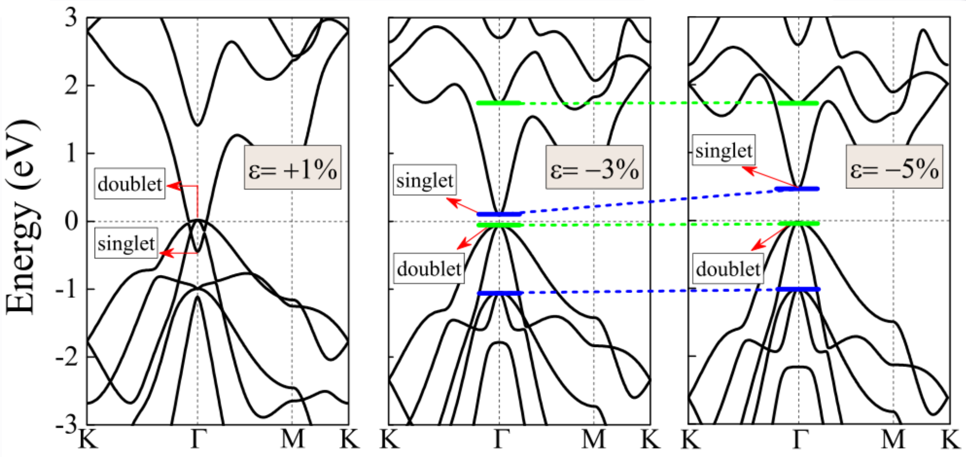
$$|\langle u_{c,\boldsymbol{k}}|\nabla_{\boldsymbol{k}}|u_{v,\boldsymbol{k}}\rangle|_{E_g} = 0$$

$q \cdot \vec{r}$ **odd**

Centrosymmetric

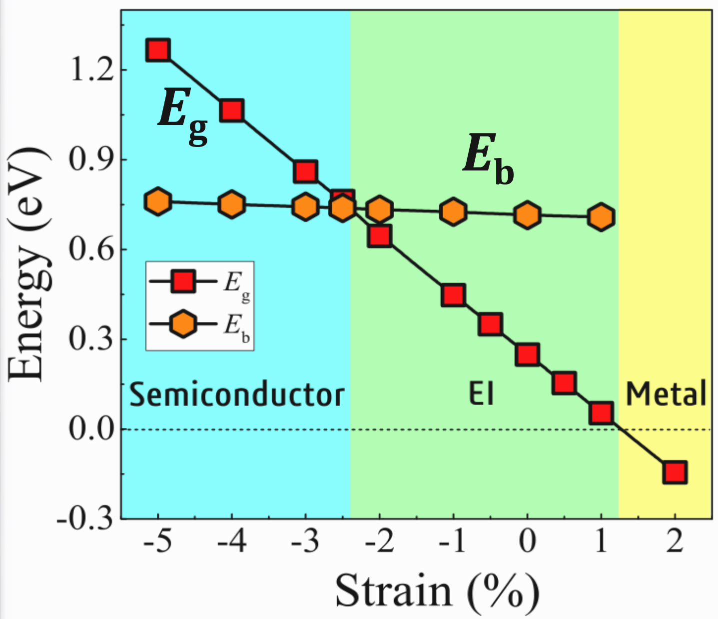
Single-layer GaAs





Band engineering by strain

HSE06

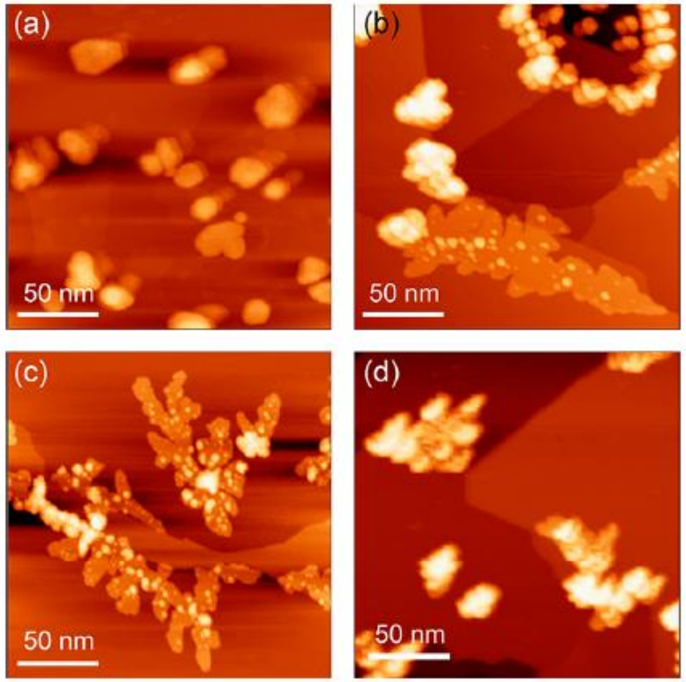


Different dependence

PRB 98, 081408(R) (2018)

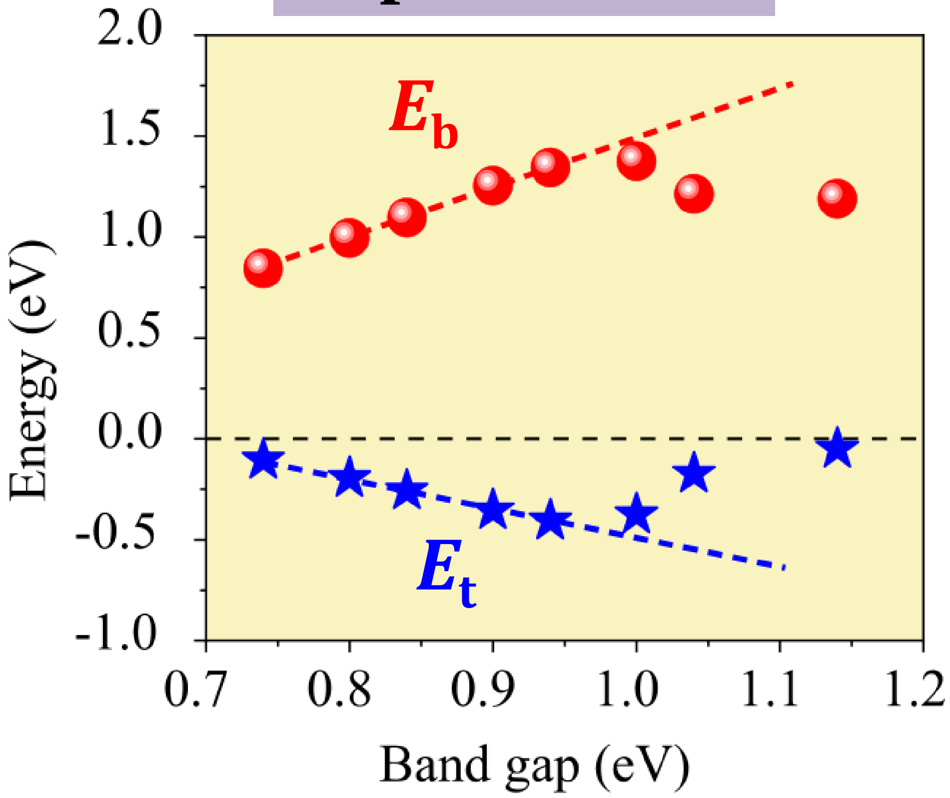
Large- and Direct-gap EIs

2D limit of III-V semiconductors **AlSb: Intrinsic excitonic insulator**



Qin et al.,
ACS nano 15, 8184 (2021)

Exp： 0.93 eV



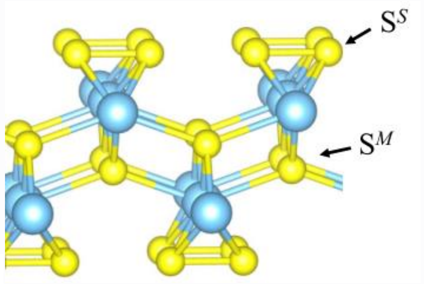
PRB 104, 085133 (2021)

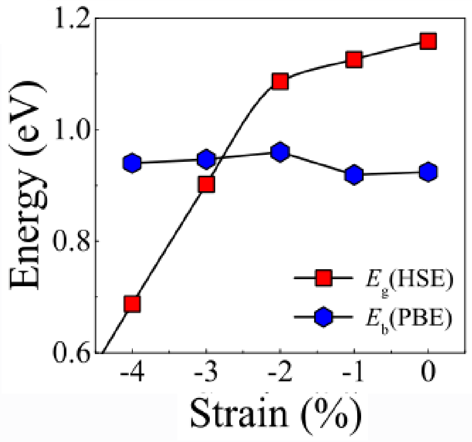
Large- and Direct-gap EIs

Monolayer $TiS_{3-x}Se_x$ alloy

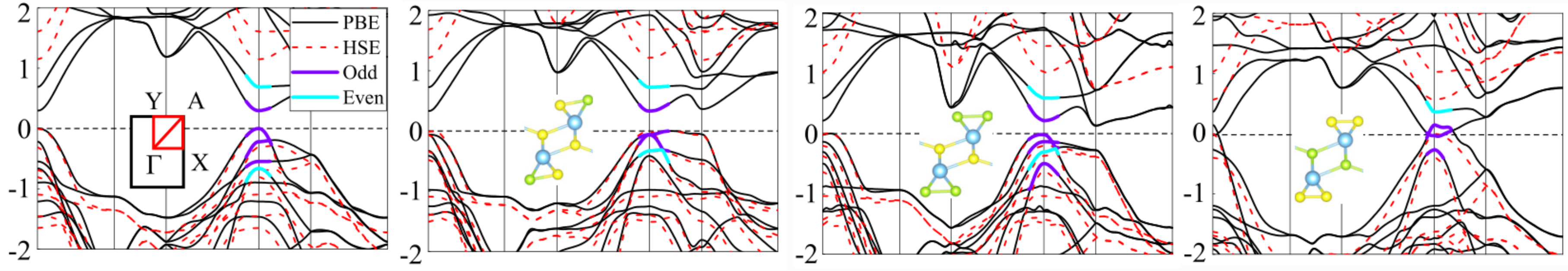
Asymmetric modulation of E_g and E_b

TiS_3: Existence





Strain leads to EI

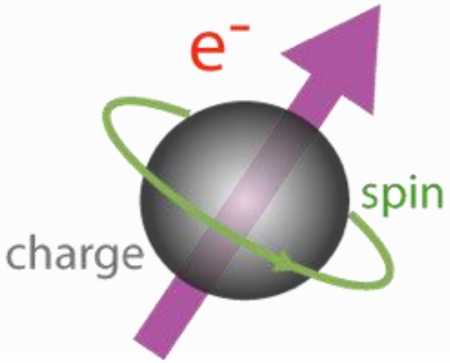


	Minimum gap (eV)		Direct gap (eV)			
	PBE	HSE06	PBE	HSE06	E_t (eV)	E_b (eV)
TiS_3	0.30	1.15	0.30	1.15	0.40	0.75
TiS_2Se^S	0.33	1.18	0.39	1.21	0.48	0.73
$TiSSe_2$	0.13	0.76	0.21	1.01	0.20	0.81
TiS_2Se^M	Metal	0.58	Metal	0.58	−0.13	0.71

Asymmetric dependence of E_g and E_b on Se→S position

PRB 102, 155119 (2020)

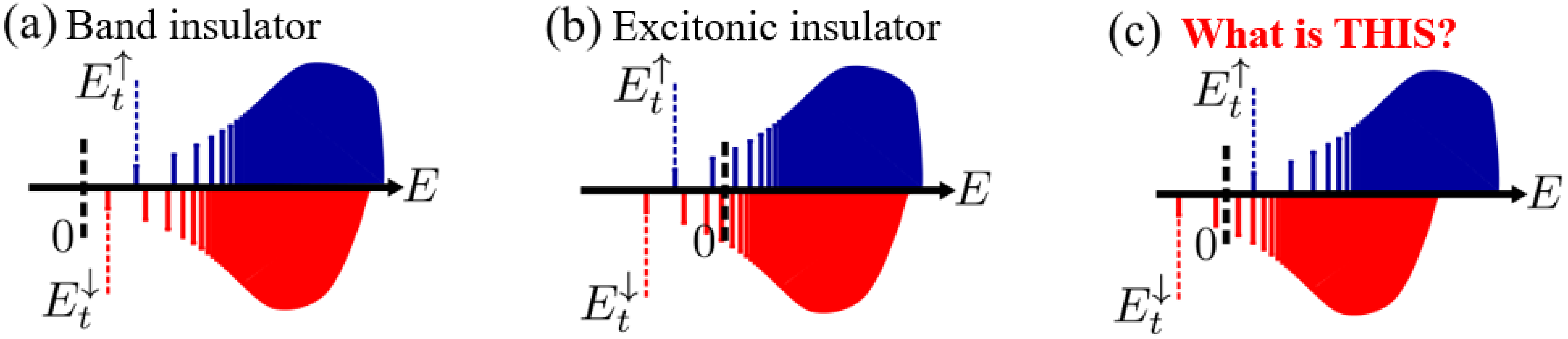
Magnetic EIs：Half excitonic insulators



What would happen if an excitonic instability

in a spin-polarized insulator?

- **One should have three scenarios:**



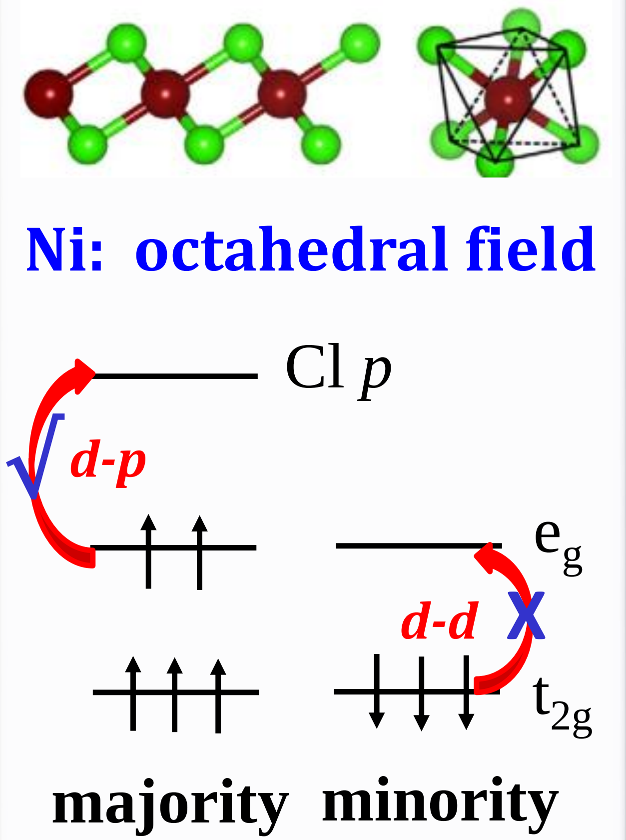
Gap by fermions

Gap by bosons

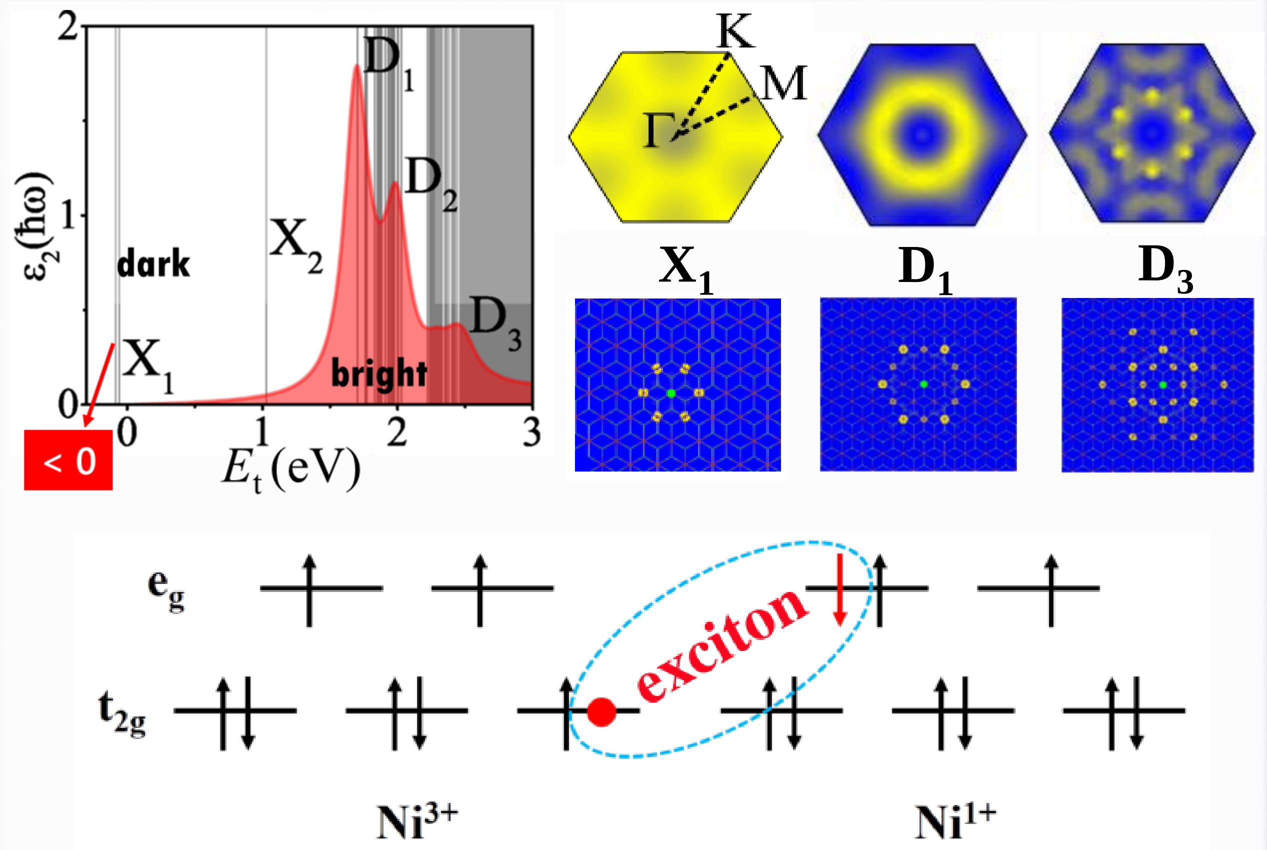
Single-spin exciton BEC

Magnetic EIs： Half excitonic insulators

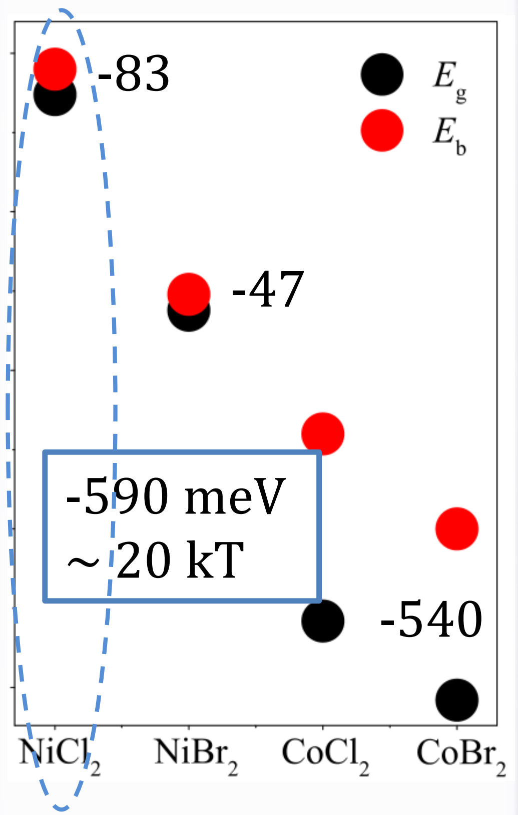
Monolayer $NiCl_2$; $NiBr_2$; $CoCl_2$; $CoBr_2$ "Dark" from orbital forbidden



Electronic band



X_1 formation affects magnetic exchange



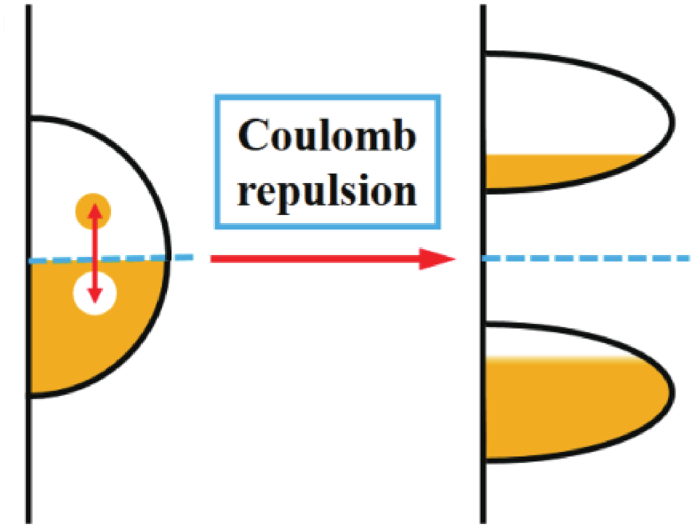
Similar physics

PRL 122, 236402 (2019)

one-electron gap up to 3.4 eV

Magnetic EIs： Spin-triplet excitonic insulators

- **Singlet S = 0**



Under Tamm-Dancoff approximation

$$(E_c - E_v)A^S_{vc} + \sum_{v'c'} K^{AA}_{vc,v'c'}(\Omega_S)A^S_{v'c'} = \Omega_S A^S_{vc}$$

$$K^{AA}_{vc,v'c'}(\Omega_S) = -W + V$$

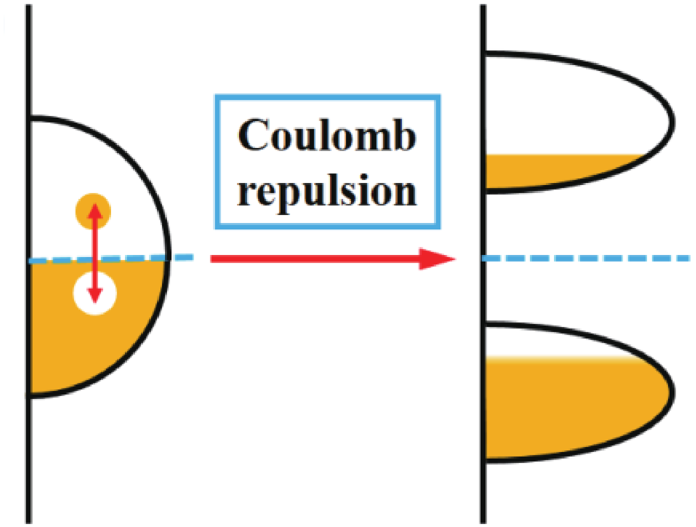
V → **Exciton splitting**

W → **Exciton binding**

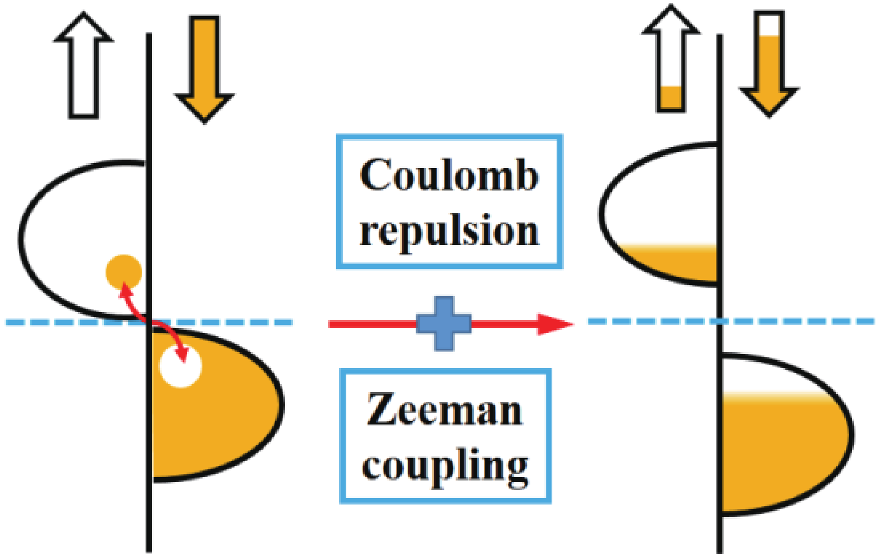
Triplet: Energetically more favorable

Magnetic EIs: Spin-triplet excitonic insulators

- **Singlet $S = 0$**



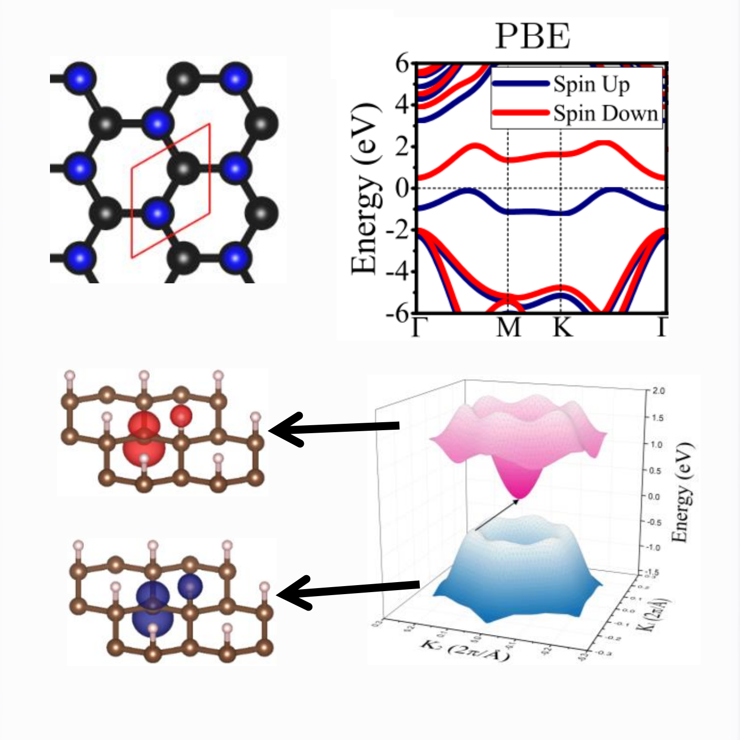
- **Triplet $S = 1$**



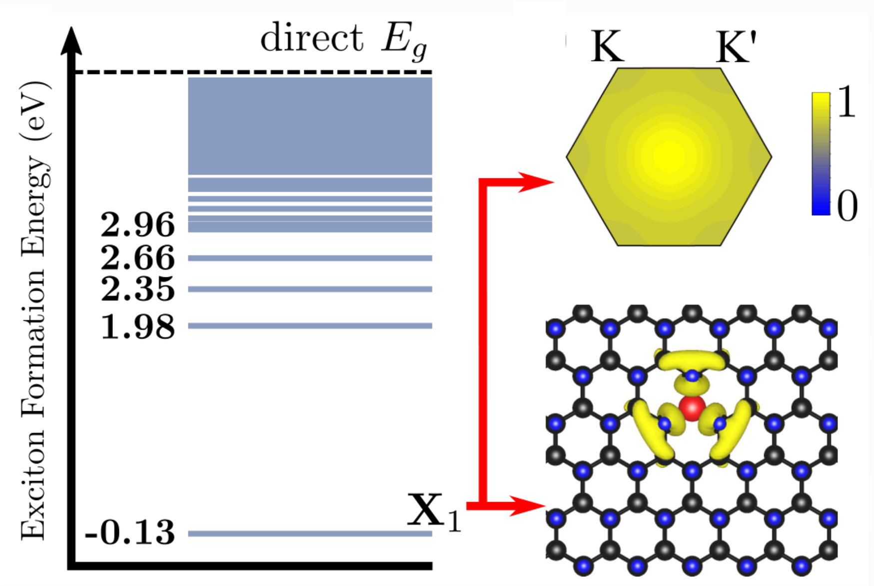
✓ Carry spin ⟶ spin superfluidity

Magnetic EIs： Spin-triplet excitonic insulators

Ferromagnetic graphone “Dark” from spin forbidden

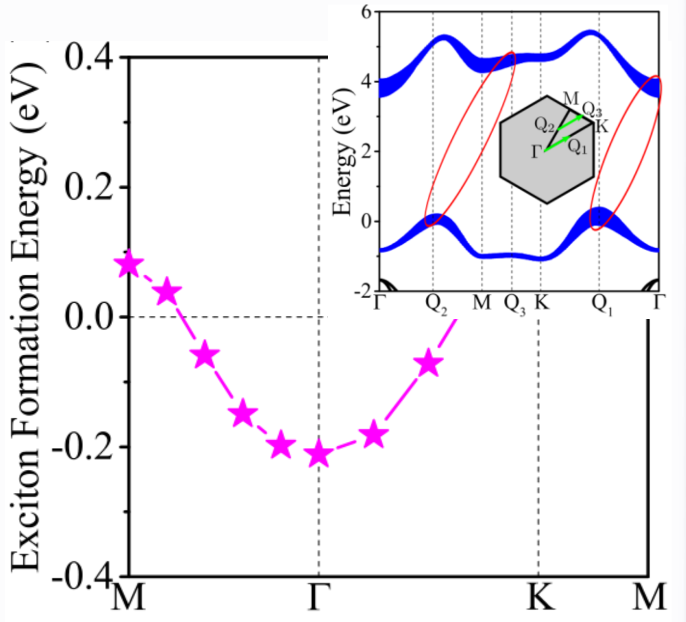


In-situ spin-flip



Low-energy excitation

Indirect-direct transition



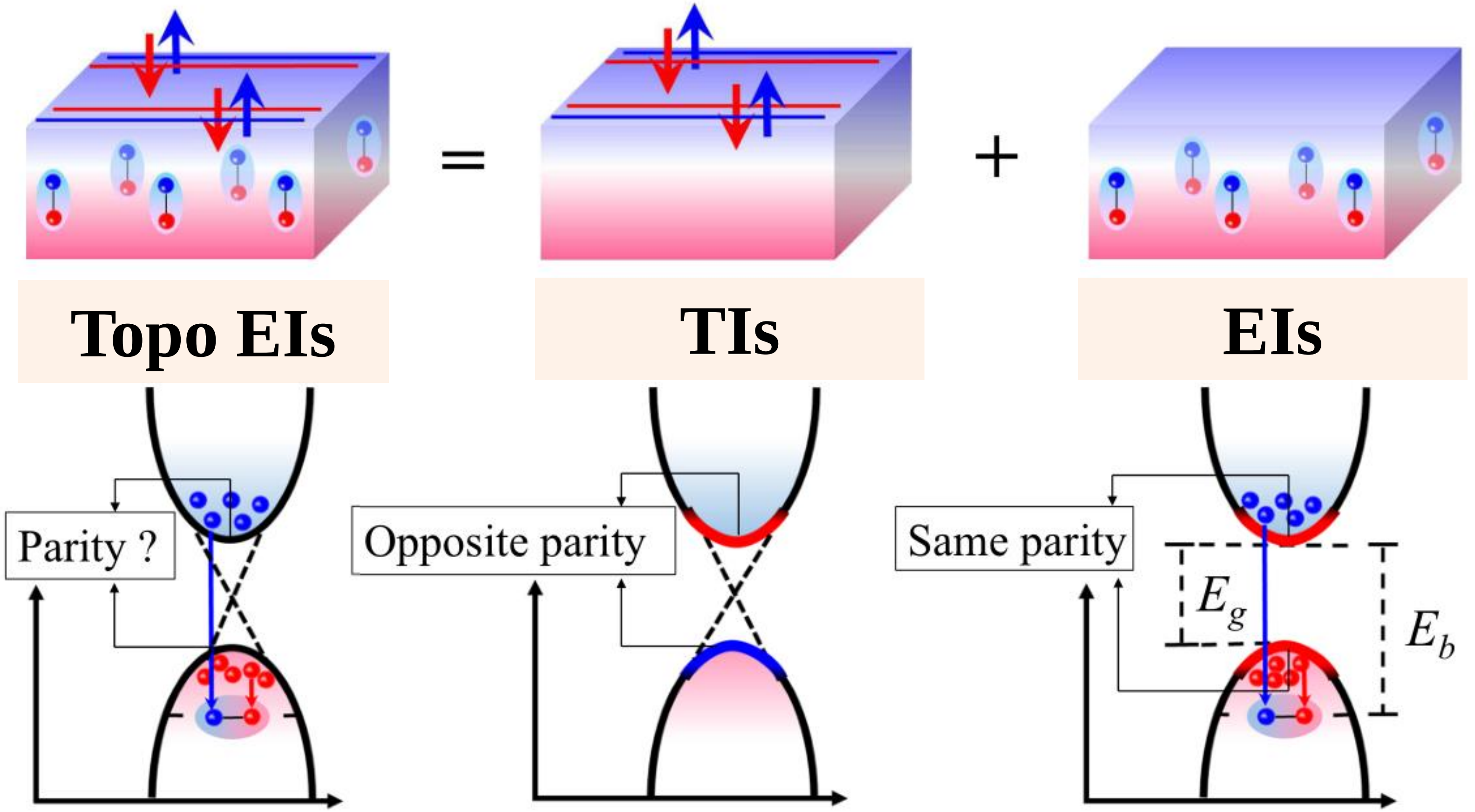
Nonlocal screening

PRL 124, 166401 (2020)

Topological EIs： Parity frustration

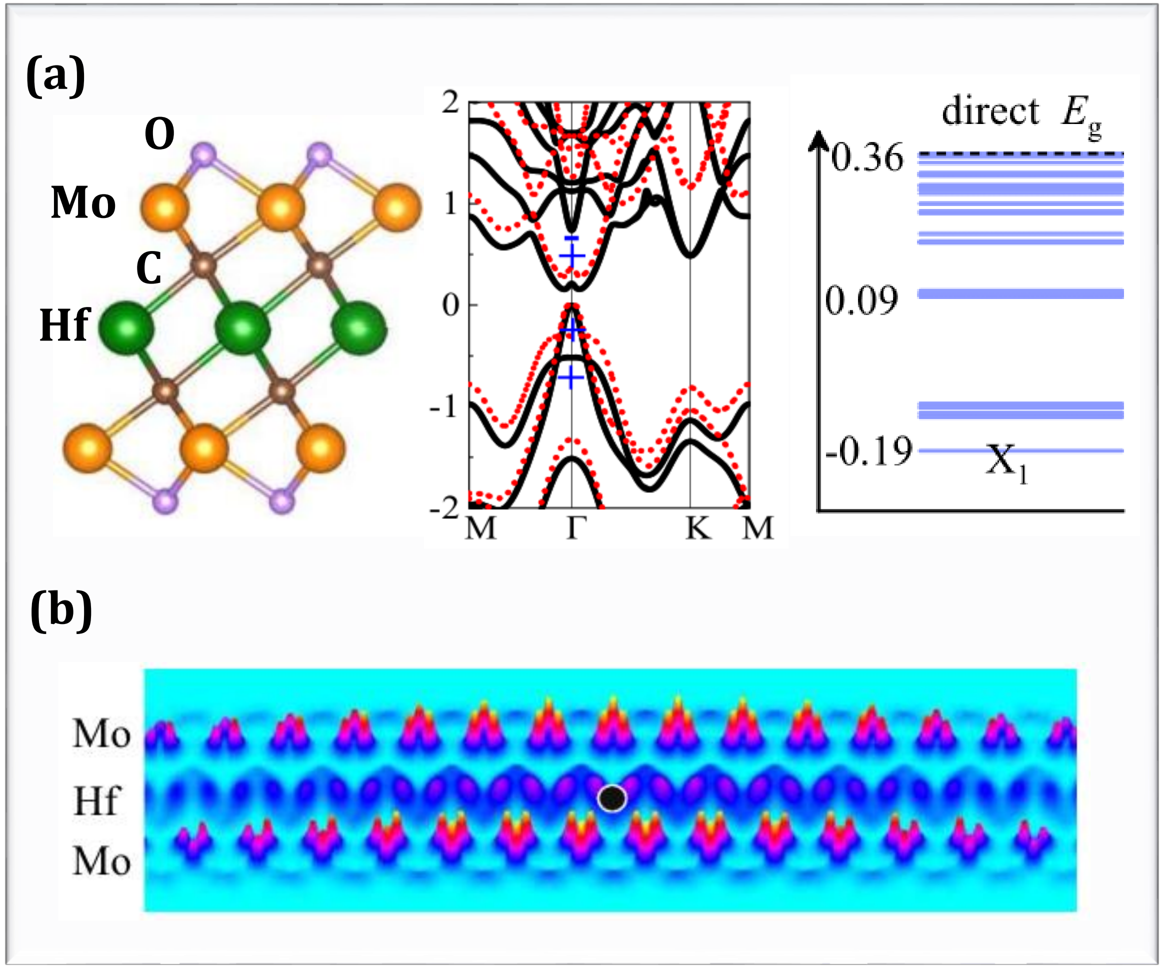
Topo EIs combine topo edge states and spontaneous exciton BEC

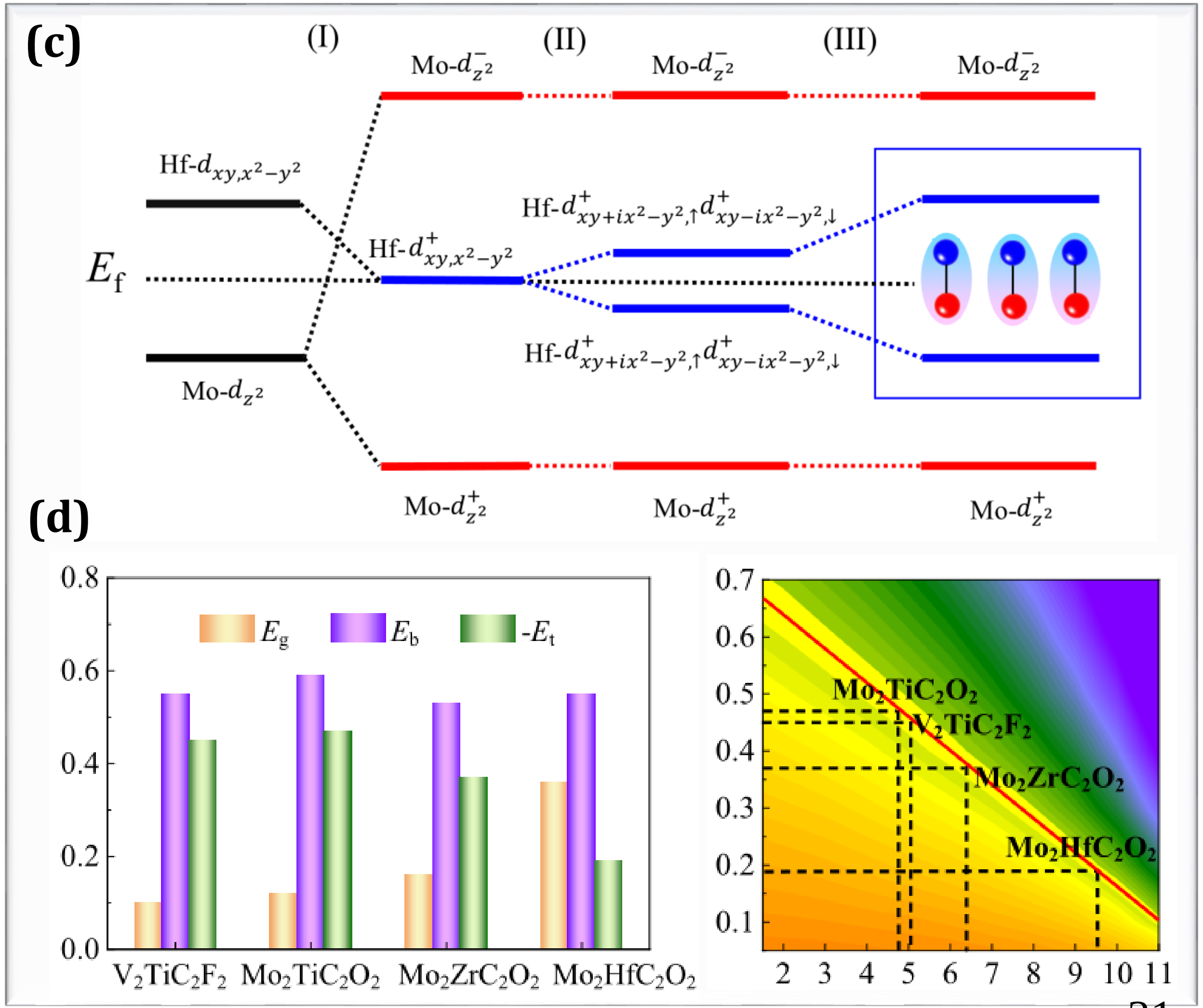
- ✓ Enlarged gap
- ✓ SOC-independent, light elements
- ✓ Defect immune
- ✓ Superfluid bulk + dissipationless edge



Topological EIs：functional segregation

MXenes $M_2M'C_2O_2$ **SOC-independent band inversion**





PRB 107, 235147 (2023)

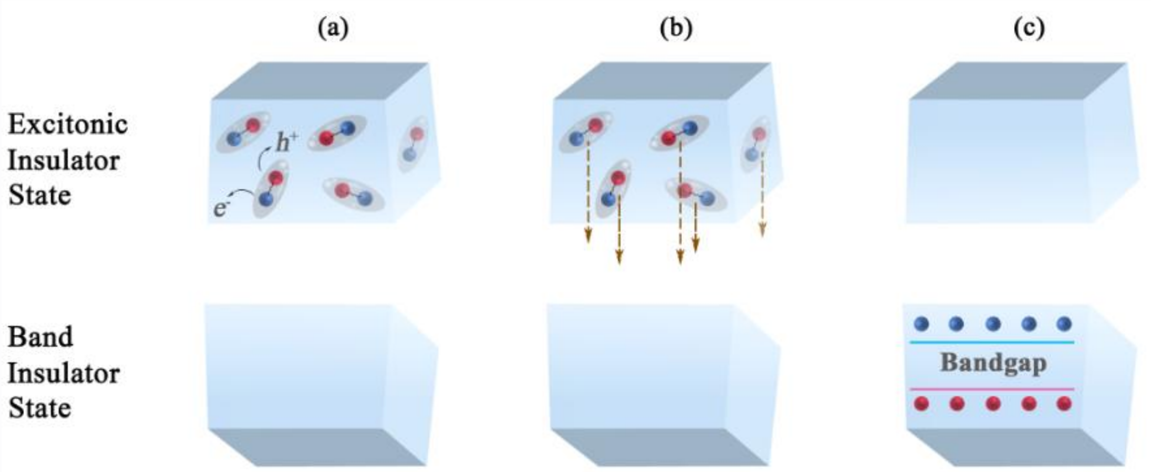
Application potential: (1) Coherent source

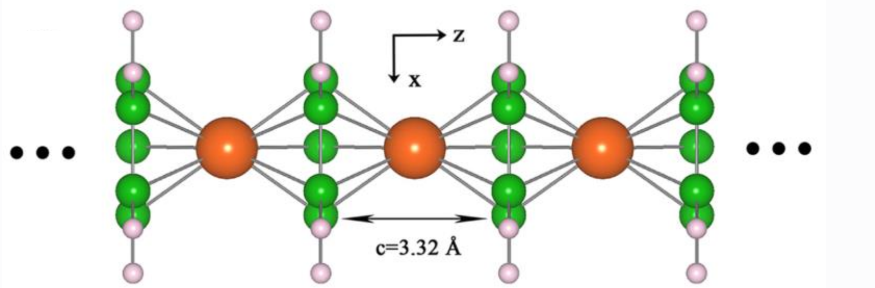
MnCp molecular wire **Electric-field-driven "bright-exciton" instability**

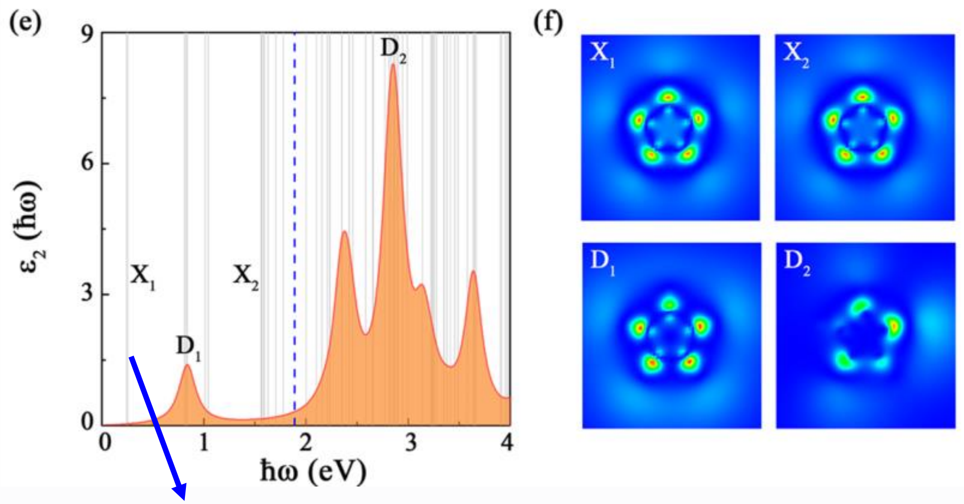
EIs— quantum state— coherent light

① e-h radiative combination

② controlled phase transition





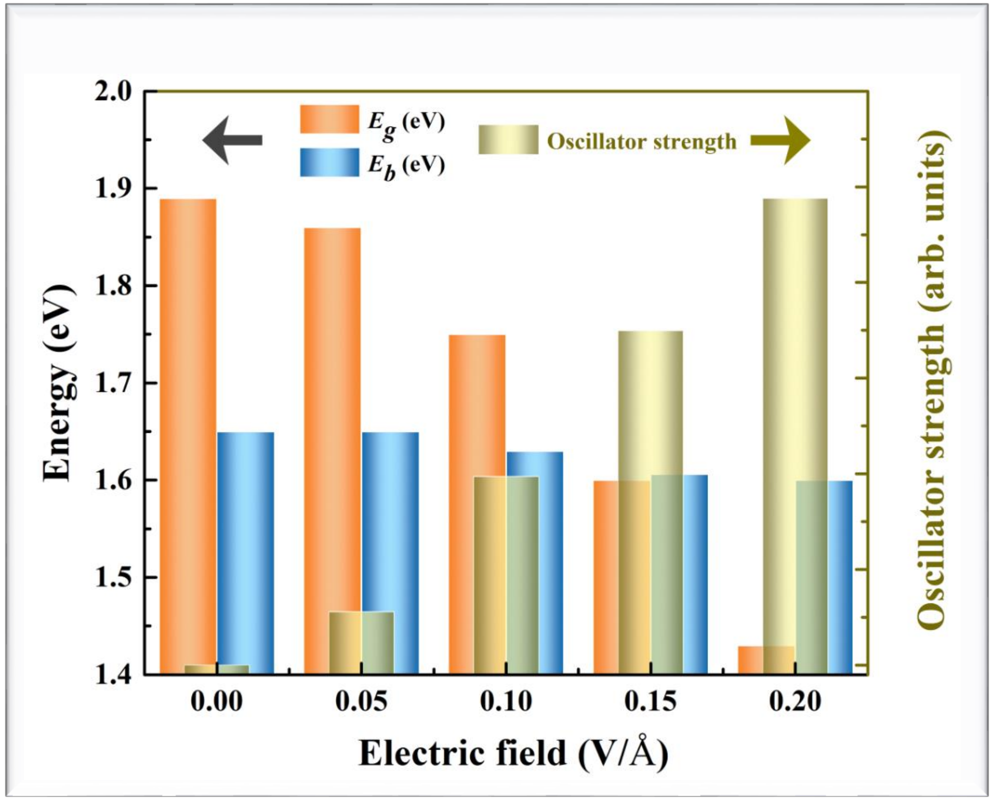


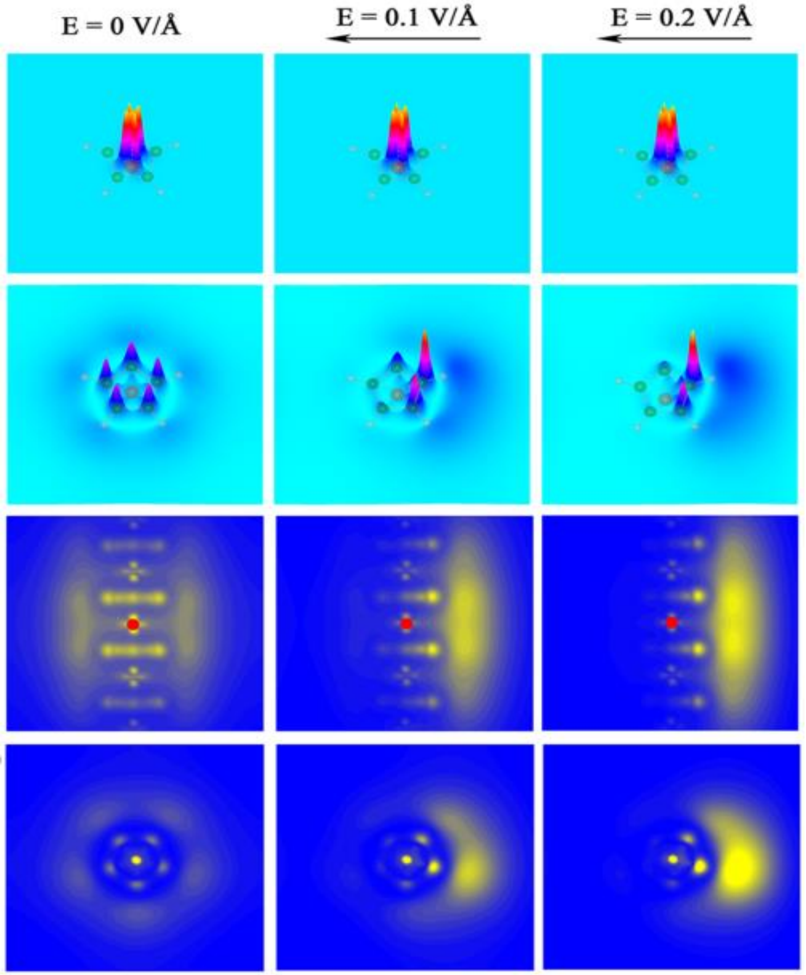
D_{5h} Mn_e_2 ⟶✕ Cp π

PRB 104, 085150 (2021)

Application potential: (1) Coherent source

MnCp molecular wire **Electric-field-driven "bright-exciton" instability**





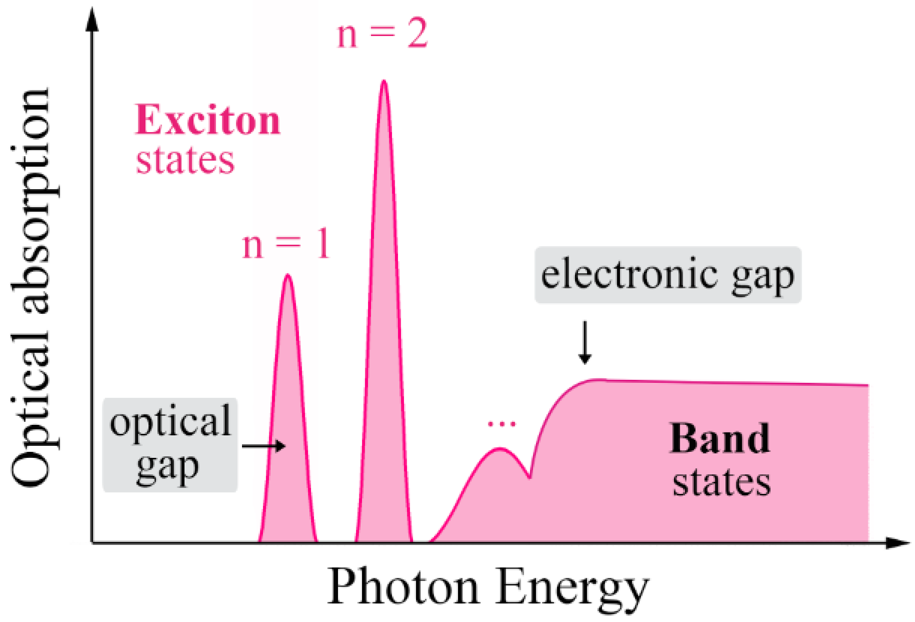
giant Stark effect

symmetry breaking

PRB 104, 085150 (2021)

Application potential: (2) Photodetectors

CrBz molecular wire **Full-spectrum photodetectors by doping an EI**

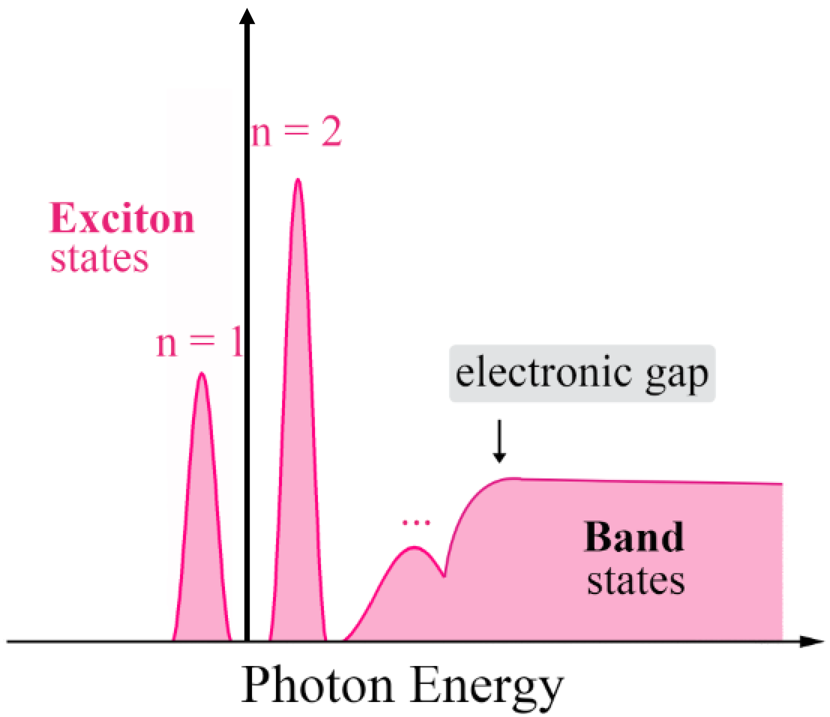


Conventional semiconductors

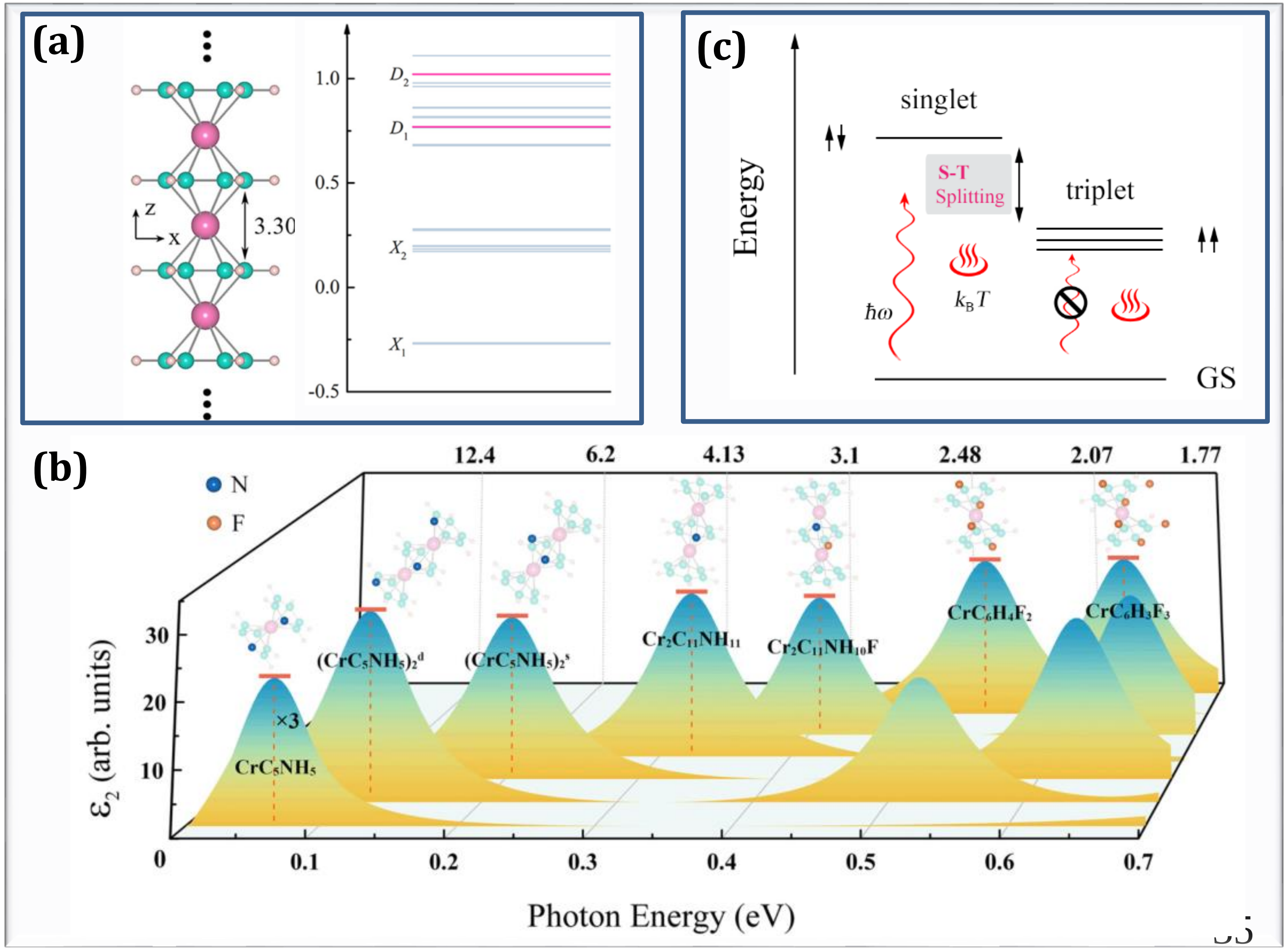
PRB 106, 035135 (2022)

Application potential: (2) Photodetectors

CrBz molecular wire **Full-spectrum photodetectors by doping an EI**



Excitonic insulators



PRB 106, 035135 (2022)

Outline

- What is the excitonic insulator?
- Development status and bottlenecks
- Our research: Dark exciton strategy and Materialization
- Conclusion, Perspective and Acknowledgements

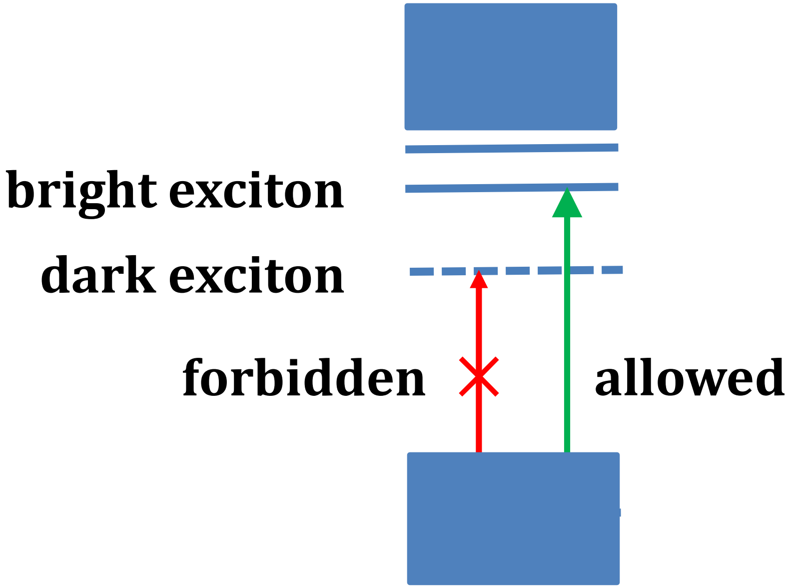
Conclusion

1. **Dark-excion-clue for excitonic instability**
2. **Benefits from combination with spin and topology**

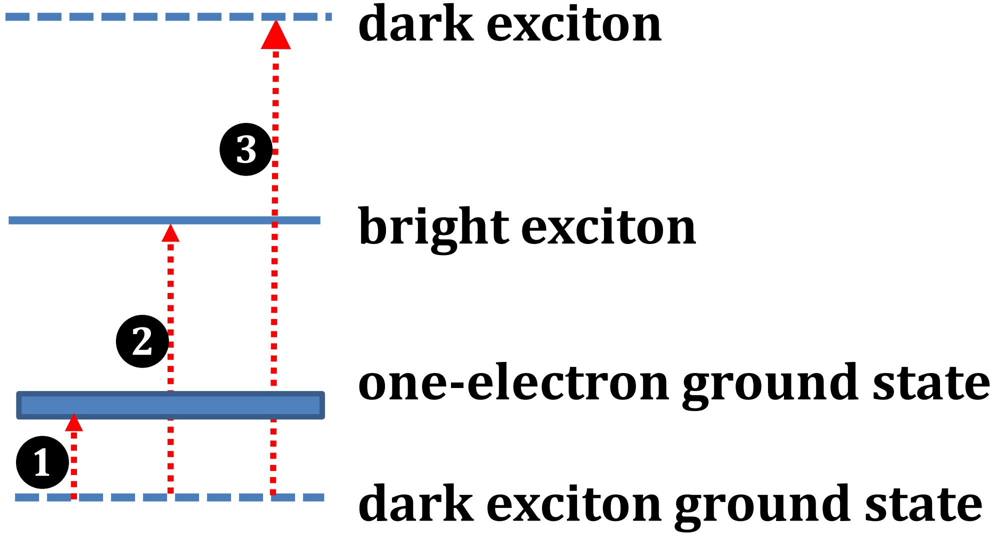
	Weak interaction limit	Strong interaction limit
Singlet (S=0)	BCS superconductors [RMP 75, 657 (2003)]	^4He [RMP 47, 331 (1975)]
Triplet (S=1)	Ferromagnetic superconductors [RMP 75, 657 (2003)]	^3He [RMP 47, 331 (1975)]

Open questions

Band insulator (BI)



Excitonic insulator (EI)

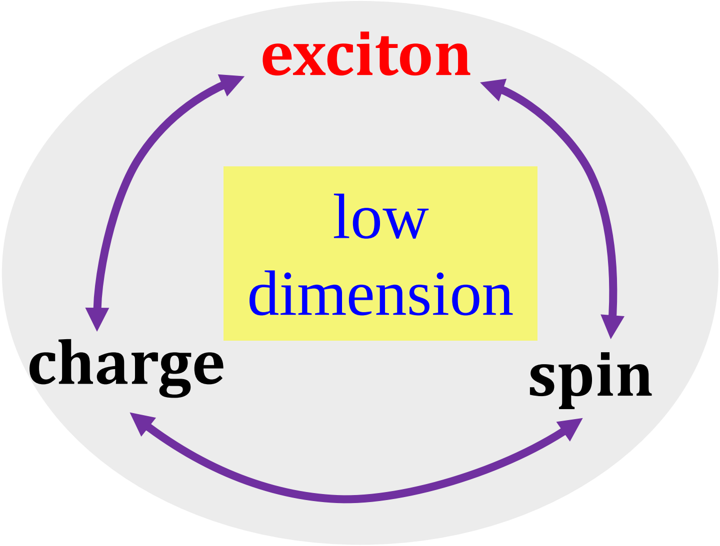


When EI forms, what happens to optical absorption?

Among ❶, ❷, and ❸, which one(s) are optically allowed?

Perspective

- How to definitely identify an excitonic insulator?
- Any unique phenomenon as fingerprints?



Thank You for Attention!