

Экситоны в двумерных материалах

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ФТИ им. А.Ф. Иоффе, Санкт-Петербург

Лекция 1: энергетический спектр и оптические свойства экситонов

- 1 Двумерные диалкогениды переходных металлов
- 2 Теория экситонов Ванье-Мотта
- 3 Особенности кулоновского взаимодействия и экситонной серии в 2D
- 4 Тонкая структура экситонных состояний
- 5 Взаимодействие экситонов и электронов: трионы и ферми-поляроны
- 6 Пара слов о том, как экситоны взаимодействуют друг с другом
- 7 Экситоны, фононы и упругие деформации

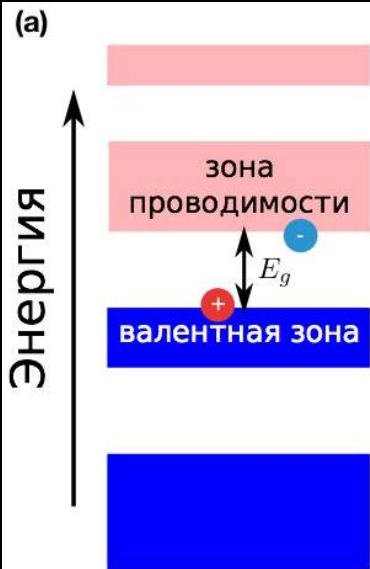
**ЛЕТНЯЯ ШКОЛА
ФОНДА «БАЗИС»**

БАЗИС



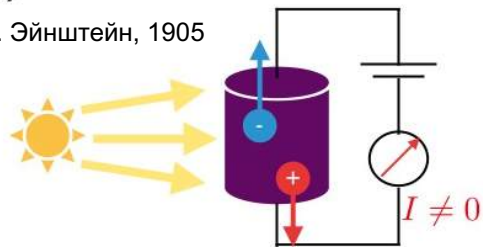
Фондальный фонд
ФТИ им. А.Ф. Иоффе

Современные проблемы физики конденсированного состояния



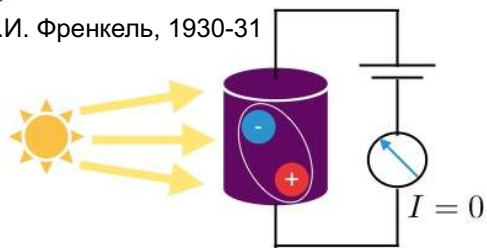
(б)

А. Эйнштейн, 1905



(в)

Я.И. Френкель, 1930-31



JANUARY 1, 1931

PHYSICAL REVIEW

VOLUME 37

ON THE TRANSFORMATION OF LIGHT INTO HEAT IN SOLIDS. I

By J. FRENKEL

DEPARTMENT OF PHYSICS, UNIVERSITY OF MINNESOTA

(Received November 25, 1930)

ABSTRACT

Starting from the analogy between a crystal and molecule, it is shown that electronic excitation, forming the first step in the process of light absorption, is not confined to a particular atom, but is diluted between all of them in the form of "excitation waves," similar to sound waves which are used to describe the heat motion in the same crystal. Owing to the interaction between the atoms the excitation state is split



AUGUST 1, 1937

PHYSICAL REVIEW

VOLUME 5

The Structure of Electronic Excitation Levels in Insulating Crystals

GEORGE H. WANNINK
Princeton University, Princeton, New Jersey

(Received May 13, 1937)

In this article, a method is given to calculate the energy spectrum for an excited electron configuration in an insulating crystal. The configuration considered consists of a single excited electron (taken out of a full band) of N electrons. The multiplicity of the states is $2N$. It is shown that because of the Coulomb attraction between the electron and the hole N^2 states are split off from the bottom of the excited band, so that in these states the electron and hole escape, or hole recombine. The analogy of these states to the spectrum of a diatomic molecule is established quantitatively. The indices of the Bloch band appear as "effective potential" and the Bloch band itself as the continuum of ionization threshold energy.



On the absorption of light by crystals

By N. F. MOTT, F.R.S., H. H. WILK, *Physical Laboratory, University of Bristol*

(Received 14 June 1938)

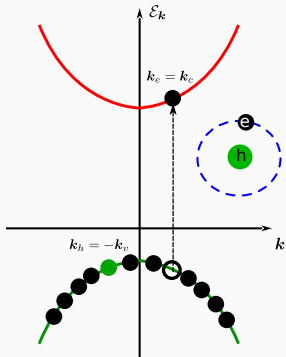
1. THEORY OF THE ABSORPTION OF LIGHT

The purpose of this paper is to discuss the absorption of light in metallic solids, and in particular the mechanism by which the energy of the light absorbed is converted into heat.



Wannier-Mott excitons are the analogues of hydrogen atoms

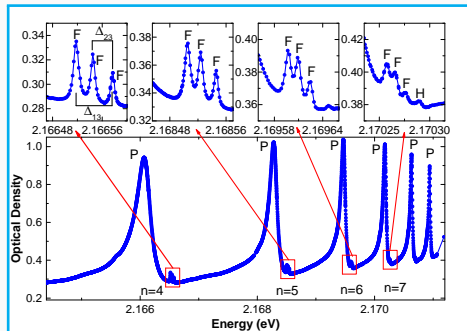
Energy bands



Exciton

First observation in Cu_2O

E.F. Gross, N.A. Karyew (1952)



Kazimierzczuk et al. (2014)

Energy scales

Exciton Rydberg energy

$$\mathcal{R} \sim (1 \dots 500) \text{ meV}$$

Bohr radius

$$a_B^* \sim (10 \dots 100) \text{ \AA}$$

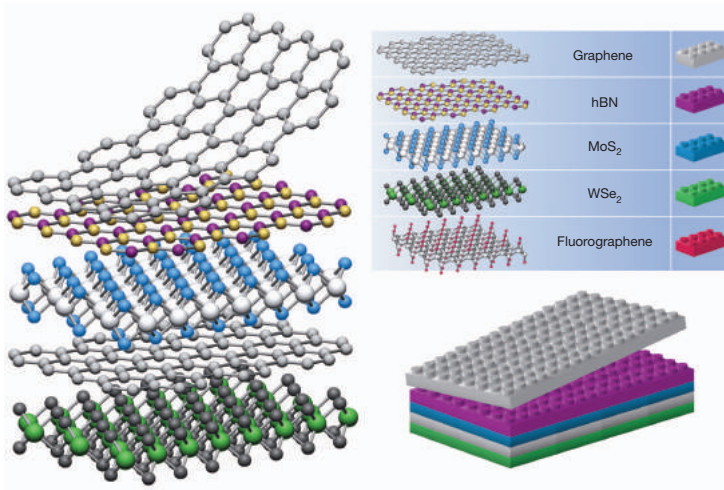
Rydberg excitons up to $1 \mu\text{m}$
can be observed in Cu_2O

$$n \leq 25 \dots 28$$

Excitons govern optical properties in most of semiconductors
and semiconductor low-dimensional systems

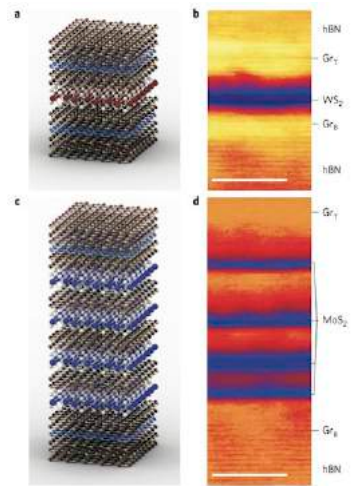
Two-dimensional materials

are the platform for van der Waals heterostructures



Geim, Grigorieva (2013)

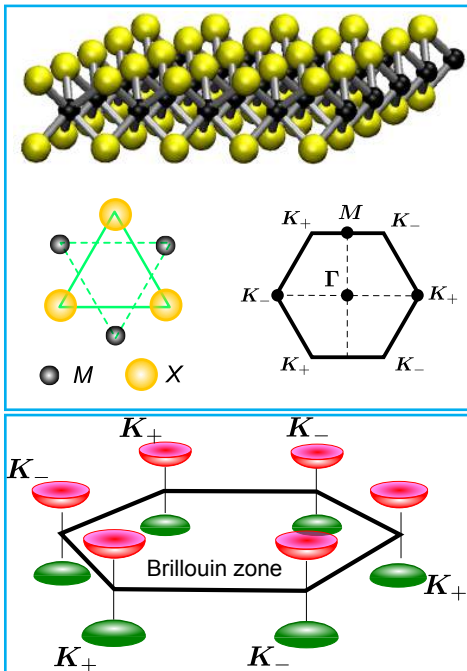
Lattice matching is not required



Withers et al. (2015)

New degree of freedom: twist angle

Direct and inverse lattices of MX_2 monolayers



MoS_2 , MoSe_2 , WS_2 , WSe_2 , etc.

D_{3h} point symmetry: horizontal reflection plane (σ_h), three-fold rotation axes (C_3 , S_3), $3C_2$, $2\sigma_v$

no space inversion: SO-splitting, second harmonic generation

Hexagonal Brillouin zone, direct band gaps are formed at the K_+ and K_- edges

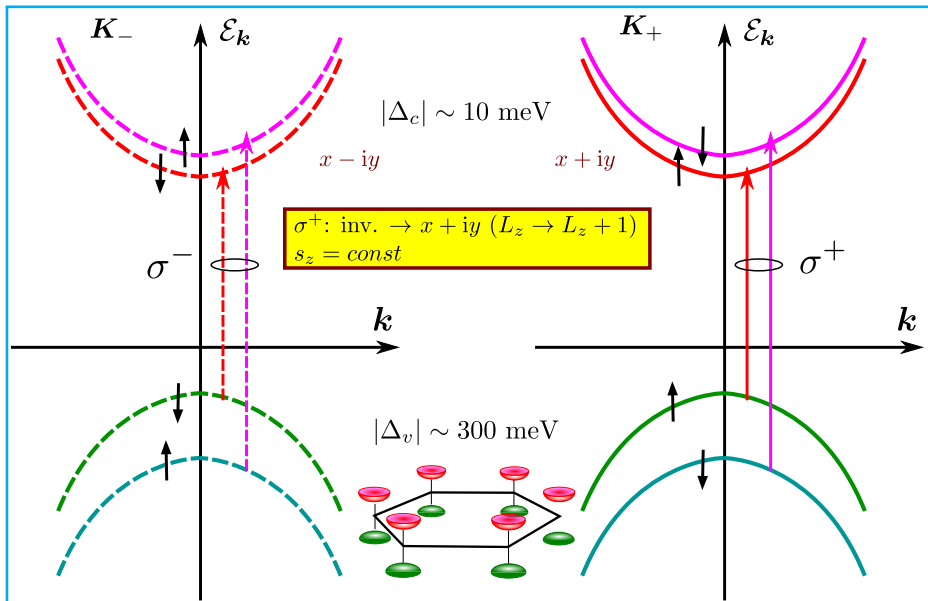
Valley symmetry is C_{3h}

K_+ and K_- valleys are related by the time reversal symmetry

$$\mathcal{H}_{\text{eff}} = \hbar v(\boldsymbol{\sigma} \cdot \mathbf{k}) + \frac{E_g}{2}\sigma_z$$

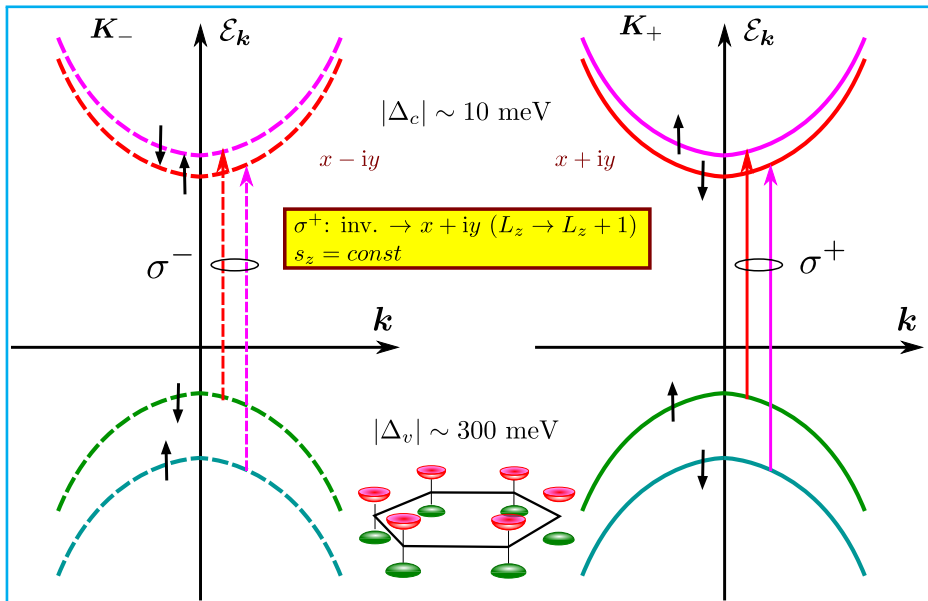
Band structure and optical selection rules

Mo-based

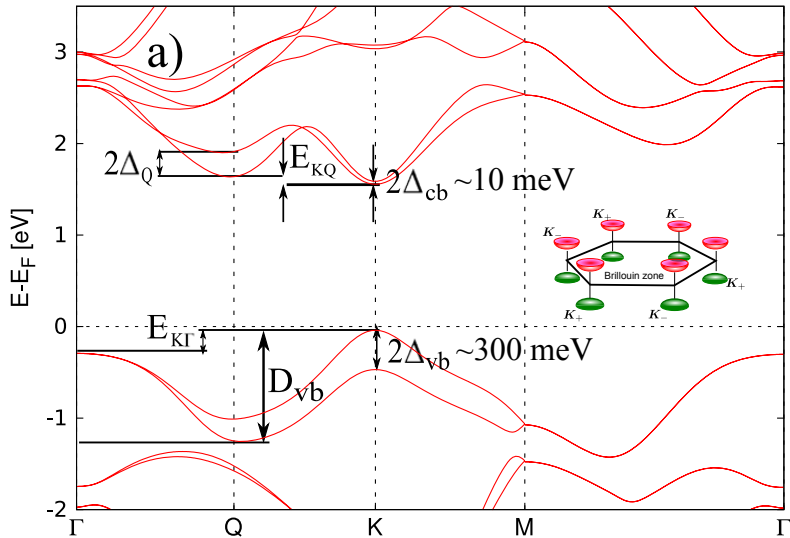


Band structure and optical selection rules

W-based



DFT-based energy spectrum of MoS₂ monolayer



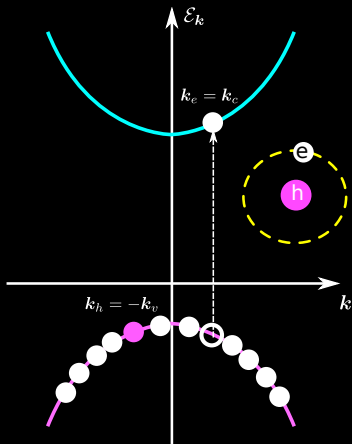
Kormanyos et al. (2015)

Модель Ванье-Мотта

Электрон и дырка связываются в экситон

$$\Psi_{\text{exc}} = \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h} |\mathbf{k}_e, n_e; \mathbf{k}_h, n_h\rangle = \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h} \mathcal{U}_\mu(\mathbf{k}_e, \mathbf{k}_h)$$

$|\mathbf{k}_e, n_e; \mathbf{k}_h, n_h\rangle$ волновая функция с заполненным состоянием $|\mathbf{k}_e, n_e\rangle$ зоны проводимости и пустым состоянием $\mathcal{K}|\mathbf{k}_h, n_h\rangle$ валентной зоны (\mathcal{K} – инверсия времени: $\mathbf{k} \rightarrow -\mathbf{k}$, $s \rightarrow -s$)



Волновая функция в модели Ванье-Мотта

$$\Psi_{\mathbf{K}; \nu, \mu}(\mathbf{r}_e, \mathbf{r}_h) = \frac{\exp(i\mathbf{K}\mathbf{R})}{\sqrt{V}} \Phi_\nu(\boldsymbol{\rho}) \mathcal{U}_\mu(\mathbf{r}_e, \mathbf{r}_h)$$

$\Phi_\nu(\boldsymbol{\rho})$ – “водородоподобная” огибающая

$$\nu = 1s, 2s, 2p, \dots$$

Электрон-дырочное представление – 1

Коммутационные соотношения для фермионов:

$$\hat{a}_{m,\mathbf{k}}^\dagger \hat{a}_{m',\mathbf{k}'} + \hat{a}_{m',\mathbf{k}'} \hat{a}_{m,\mathbf{k}}^\dagger = \delta_{m,m'} \delta_{\mathbf{k},\mathbf{k}'}$$

Переход от электронов к дыркам:

$$\hat{c}_{m,\mathbf{k}} = \hat{a}_{m,-\mathbf{k}}^\dagger \quad \hat{c}_{m,\mathbf{k}}^\dagger = a_{m,-\mathbf{k}}$$

(коммутационное соотношение не меняется)

Заселенности состояний:

$$\bar{f}_{m,\mathbf{k}} = \langle c_{m,\mathbf{k}}^\dagger c_{m,\mathbf{k}} \rangle = \langle a_{m,-\mathbf{k}} a_{m,-\mathbf{k}}^\dagger \rangle = 1 - \langle a_{m,-\mathbf{k}}^\dagger a_{m,-\mathbf{k}} \rangle = 1 - f_{m,-\mathbf{k}}$$

дырка соответствует инвертированному по времени ($\mathbf{k} \rightarrow -\mathbf{k}$) незанятому состоянию в валентной зоне

Переход от электронов к дыркам:

$$\hat{c}_{m,\mathbf{k}} = \hat{a}_{m,-\mathbf{k}}^{\dagger} \quad \hat{c}_{m,\mathbf{k}}^{\dagger} = a_{m,-\mathbf{k}}$$

(коммутационное соотношение не меняется)

Энергия дырки:

$$E_{m,\mathbf{k}} \hat{a}_{m,\mathbf{k}}^{\dagger} \hat{a}_{m',\mathbf{k}'} = E_{m,\mathbf{k}} c_{m,-\mathbf{k}} c_{m,-\mathbf{k}}^{\dagger} = E_{m,\mathbf{k}} - E_{m,\mathbf{k}} c_{m,-\mathbf{k}}^{\dagger} c_{m,-\mathbf{k}}$$

В простой зоне $E_{m,\mathbf{k}} = E_{m,-\mathbf{k}}$.

Энергия дырки противоположна энергии электрона в валентной зоне

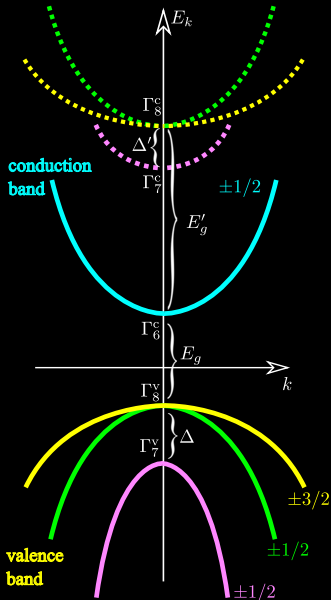
Энергия кулоновского взаимодействия:

$$U = \int d\mathbf{r}_1 d\mathbf{r}_2 V(\mathbf{r}_1 - \mathbf{r}_2) a_c^\dagger(\mathbf{r}_1) a_v^\dagger(\mathbf{r}_2) a_v(\mathbf{r}_2) a_c(\mathbf{r}_1),$$

$$\begin{aligned} a_c^\dagger(\mathbf{r}_1) a_v^\dagger(\mathbf{r}_2) a_v(\mathbf{r}_2) a_c(\mathbf{r}_1) &\rightarrow a_c^\dagger(\mathbf{r}_1) c_v(\mathbf{r}_2) c_v^\dagger(\mathbf{r}_2) a_c(\mathbf{r}_1) \\ &\rightarrow -a_c^\dagger(\mathbf{r}_1) c_v^\dagger(\mathbf{r}_2) c_v(\mathbf{r}_2) a_c(\mathbf{r}_1), \end{aligned}$$

$$U = - \int d\mathbf{r}_1 d\mathbf{r}_2 V(\mathbf{r}_1 - \mathbf{r}_2) a_c^\dagger(\mathbf{r}_1) c_v^\dagger(\mathbf{r}_2) c_v(\mathbf{r}_2) a_c(\mathbf{r}_1).$$

Электрон притягивается к дырке!



Базисные блоховские функции

$$\mathcal{U}_{n_e n_h}(\mathbf{r}_e, \mathbf{r}_h) = u_{n_e, \mathbf{0}}(\mathbf{r}_e) \tilde{u}_{n_h, \mathbf{0}}(\mathbf{r}_h) \quad (N_e \times N_h)$$

Волновая функция пары

$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{n_e, n_h} C_{n_e k_e, n_h k_h} e^{i\mathbf{k}_e \mathbf{r}_e + i\mathbf{k}_h \mathbf{r}_h} \mathcal{U}_{n_e n_h}(\mathbf{r}_e, \mathbf{r}_h)$$

Эффективный гамильтониан ($V_C(\rho) = -\frac{e^2}{\epsilon\rho}$)

$$\mathcal{H}_{n_e n'_e}^e(\hat{\mathbf{k}}_e) \delta_{n_h n'_h} + \mathcal{H}_{n_h n'_h}^h(\hat{\mathbf{k}}_h) \delta_{n_e n'_e} + V_C(\rho) \delta_{n_e n'_e} \delta_{n_h n'_h} + \delta \hat{V} \quad (\text{поправки, обменное взаимодействие, ...})$$

Экситон в заиси меди: от 1950х

Уравнение Шредингера для относительного движения e и h

$$-\frac{\hbar^2}{2\mu}\Delta_{\rho}\Phi(\rho) - \frac{e^2}{\epsilon\rho}\Phi(\rho) = E\Phi(\rho), \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

Е.Ф. Гросс и Н.А. Карьев, ДАН СССР **84**, 471 (1952)

энергия связи

$$E_b = \frac{\mathcal{R}}{n^2}$$

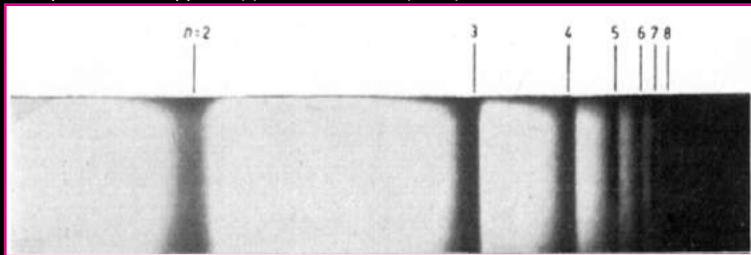
энергия возбуждения

$$E_{exc} = E_g - \frac{\mathcal{R}}{n^2}$$

параметры:

$$\mathcal{R} \approx 90 \text{ meV}, \quad a_B \approx 11 \text{ \AA}$$

$$\mathcal{R} = \frac{\mu e^4}{2\epsilon^2 \hbar^4}, \quad a_B = \frac{\hbar^2 \epsilon}{\mu e^2}$$



E.F. Gross, Nuovo Cimento Suppl. 3, 672-701 (1956)

Классификация состояний

$S (l = 0), P (l = 1), D (l = 2), F (l = 3) \dots$

Экситон в записи меди: от 1950х

Уравнение Шредингера для относительного движения e и h

$$-\frac{\hbar^2}{2\mu} \Delta$$

$$+ \frac{1}{m_h}$$

энергия связи

$$E_b = \frac{\mathcal{R}}{n^2}$$

энергия возбуждения

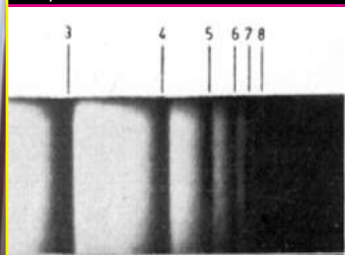
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(1952)



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$$a_B \approx 11 \text{ \AA}$$

= 3) ...

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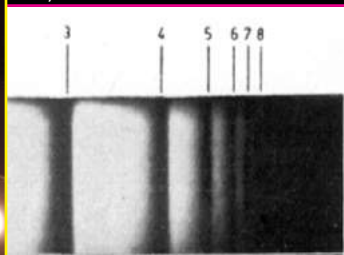
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(1952)



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СПбГУ, музей Е.Ф. Гросса

Экситон в записи меди: от 1950х

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$$-\frac{\hbar^2}{2\mu}\Delta\rho\Phi(\rho) - \frac{e^2}{\epsilon\rho}\Phi(\rho) = E\Phi(\rho), \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

Е. Ф. Гросс и Н. А. Карачев, ДАН СССР 84, 471 (1952)

энергия связи

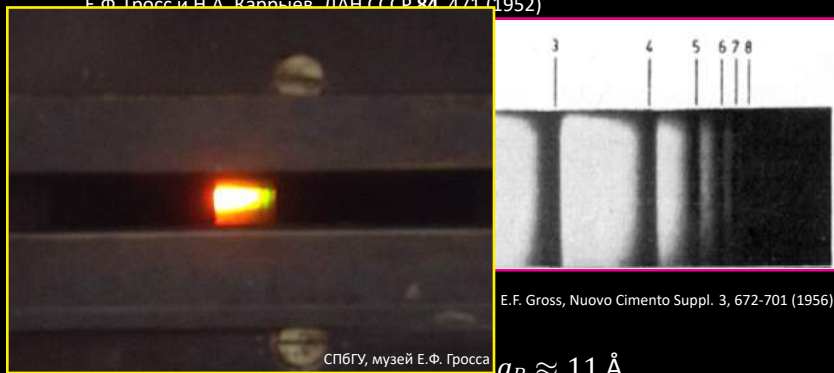
$$E_b = \frac{\mathcal{R}}{n^2}$$

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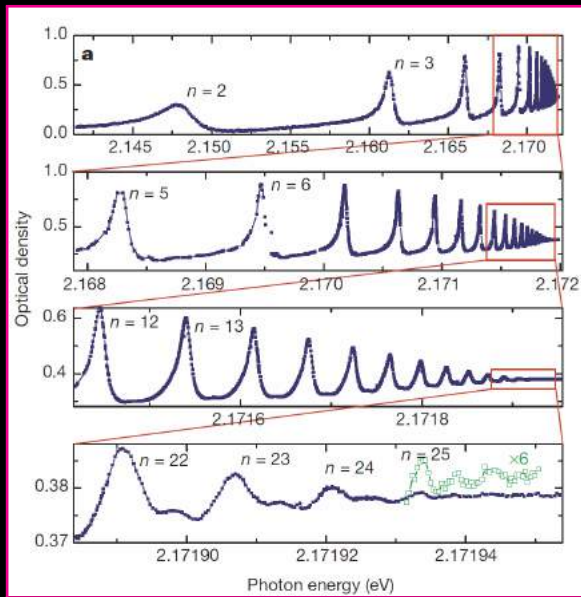
СПбГУ, музей Е.Ф. Гросса

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Классификация состояний

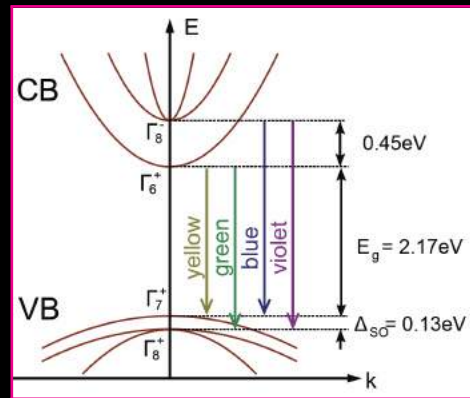
$S (l = 0), P (l = 1), D (l = 2), F (l = 3) \dots$

Экситон в закиси меди: от 1950х до 2010х



Отклонения от водородоподобной модели

$$E_n \approx \frac{\mathcal{R}}{(n - \delta_{nl})^2}$$



T. Kazimierczuk, D. Fröhlich, S. Scheel, H. Stolz, M. Bayer, Nature **514**, 343 (2014)

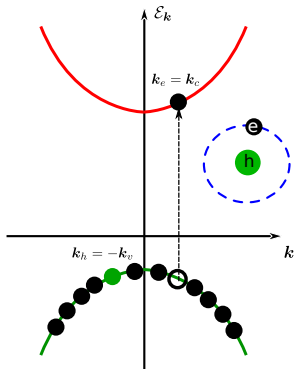
$$\Delta_{SO} \sim \mathcal{R}$$

Excitons in 2D semiconductors

Optically created electron-hole pairs form excitons

$$\Psi_{\text{exc}} = \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h} |\mathbf{k}_e; \mathbf{k}_h\rangle = \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h} \mathcal{U}_\mu(\mathbf{k}_e, \mathbf{k}_h)$$

$|\mathbf{k}_e; \mathbf{k}_h\rangle$ is the wavefunction of the state where the $|\mathbf{k}_e\rangle$ conduction band state is occupied and the $|\mathbf{k}_h\rangle$ valence band state is empty



Exciton wavefunction

$$\Psi_{\mathbf{K}; \nu, \mu}(\rho_e, \rho_h) = \frac{\exp(i\mathbf{K}\mathbf{R})}{\sqrt{S}} \Phi_\nu(\rho) \mathcal{U}_\mu(\rho_e, \rho_h)$$

Envelope function (1s, 2p, ...)

$$-\frac{\hbar^2}{2\mu} \Delta_\rho \Phi(\rho) + V(\rho) \Phi(\rho) = E \Phi(\rho) \quad \mu = \frac{m_e m_h}{m_e + m_h}$$

*non-parabolicity & SO-coupling: Trushin, Goerbig, Belzig (2018)
Leppenen, Golub, Ivchenko (2020)*

Multiband description

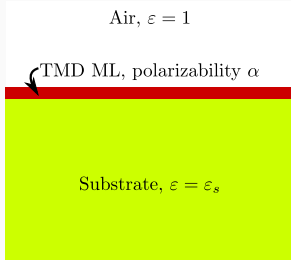
$$\Psi_{\text{exc}} = \sum_{\mathbf{k}_e, n_e, \mathbf{k}_h, n_h} C_{\mathbf{k}_e, n_e, \mathbf{k}_h, n_h} |\mathbf{k}_e, n_e; \mathbf{k}_h, n_h\rangle$$

Coulomb interaction in 2D semiconductors

Thin films: Rytova (1967), Chaplik, Entin (1972), Keldysh (1979)

2D crystals: Cudazzo et al. (2011); Berkelbach et al. (2013)

Effective Coulomb potential $V(\rho)$



Large distances

$$V(\rho) \approx -\frac{2e^2}{1 + \epsilon_s} \frac{1}{\rho}$$

Small distances

$$V(\rho) \approx \frac{e^2}{r_0} \ln\left(\frac{\rho}{r_0}\right)$$

$$r_0 = 2\pi\alpha \quad (\sim \epsilon_{\text{TMD}} d)$$

$$\propto \frac{1}{q}, \quad q \ll \frac{1}{r_0} \text{ (2D)}$$

$$V_q = -\frac{2\pi e^2}{\epsilon_* q} \frac{1}{(1 + qr_0)}$$

$$\propto \frac{1}{q^2}, \quad q \gg \frac{1}{r_0} \text{ (3D)}$$

Technical details

Additional (open) issue: role of retardation – frequency dependent screening (?)

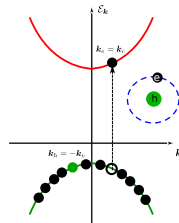
Wannier-Mott excitons in 2D materials

Excitons control optical properties of MX_2 :

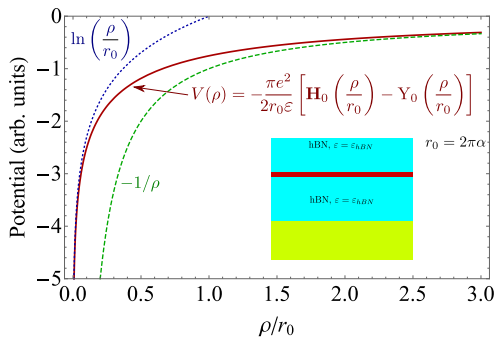
$$E_{2B} \approx 200 \dots 500 \text{ meV}, \quad a_{2B} \approx 10 \dots 30 \text{ \AA}$$

DFT+BSE: Diana Y. Qiu, Felipe H. da Jornada, Steven G. Louie (2013)

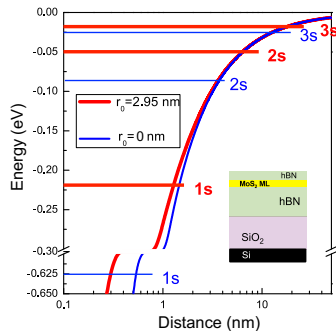
radiative lifetime: $\tau_X = 1/(2\Gamma_0) \sim 1 \text{ ps}$



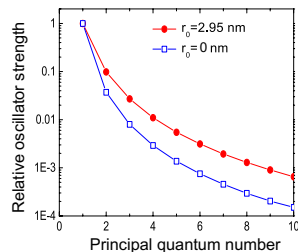
Coulomb potential with **dielectric contrast** N.S. Rytova (1967)
L.V. Keldysh (1979)



Excitonic series



Relative oscillator strengths



Review: *Phys.-Usp.* **61**, 825 (2018); *Rev. Mod. Phys.* **90**, 021001 (2018); *JETP Letters* **113**, 7 (2021)

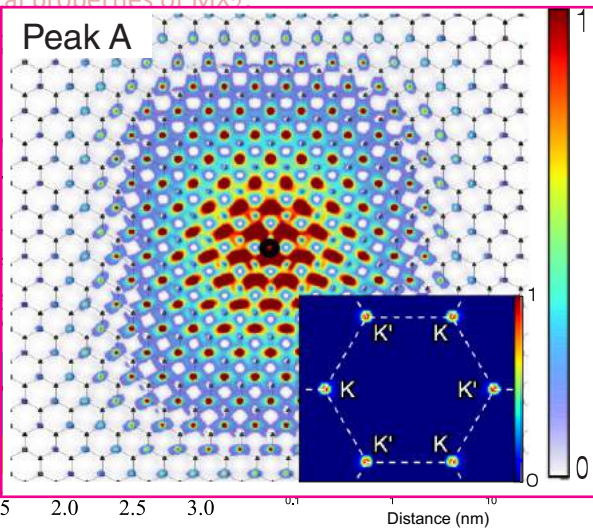
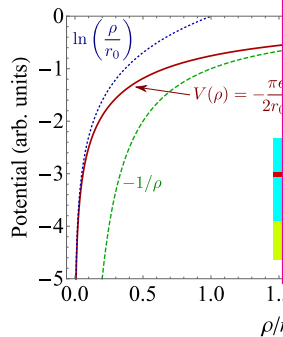
Wannier-Mott excitons in 2D materials

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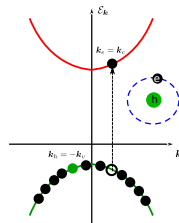
$$E_{2B} \approx$$

radiative lifetime: τ_X

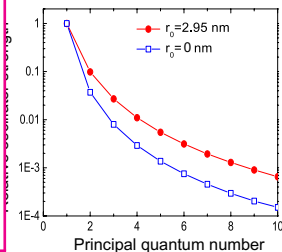
Coulomb potential with dielectr



(3)

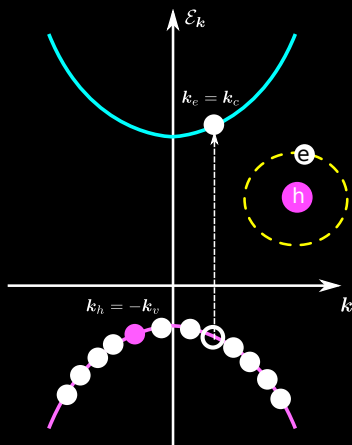


Relative oscillator strengths



Review: *Phys.-Usp.* **61**, 825 (2018); *Rev. Mod. Phys.* **90**, 021001 (2018); *JETP Letters* **113**, 7 (2021)

Междузонный оптический переход



Оператор возмущения

$$H_0 = \frac{\hat{p}^2}{2m_0} + V_0(\mathbf{r}), \quad \hat{p} \rightarrow \hat{p} - \frac{e}{c}\mathbf{A}, \quad \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$$

$$\text{В первом порядке по } \mathbf{A}: \quad \hat{V}_{dip} = -\frac{e}{m_0 c} \mathbf{A} \cdot \hat{p}$$

Междузонный матричный элемент импульса

$$p_{cv,\alpha} = -i\hbar \int d\mathbf{r} u_{c,0}^*(\mathbf{r}) \frac{\partial}{\partial x_\alpha} u_{v,0}(\mathbf{r})$$

Разрешенный переход

$$p_{cv,\alpha} \neq 0$$

Запрещенный переход

$$p_{cv,\alpha} = 0$$

Разрешенные переходы

Междузонный матричный элемент импульса

$$\hat{V}_{dip} = -\frac{e}{m_0 c} \mathbf{A} \cdot \hat{\mathbf{p}}, \quad p_{cv,\alpha} = -i\hbar \int d\mathbf{r} u_{c,0}^*(\mathbf{r}) \frac{\partial}{\partial x_\alpha} u_{v,0}(\mathbf{r}) \neq 0$$

Волновая функция экситона

$$\Psi_{exc} = \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h} e^{i\mathbf{k}_e \mathbf{r}_e + i\mathbf{k}_h \mathbf{r}_h} u_{c,0}(\mathbf{r}_e) \tilde{u}_{v,0}(\mathbf{r}_h)$$

Возбуждение экситона

$$\langle exc | \hat{V}_{dip} | 0 \rangle = -\frac{e}{m_0 c} \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h}^* e^{-i\mathbf{k}_e \mathbf{r}_e - i\mathbf{k}_h \mathbf{r}_h} p_{cv,\alpha} \delta_{\mathbf{k}_e, -\mathbf{k}_h} \propto \Phi^*(0)$$

Активны S-экситоны, у которых $\Phi(0) \neq 0$, например, в GaAs или в TMDC.

Симметрия экситонных состояний

$$\text{представление} \quad \mathcal{D}_{exc} = \mathcal{D}_e \otimes \mathcal{D}_h \otimes \mathcal{D}_{env}$$

Запрещенные переходы

Междузонный матричный элемент импульса

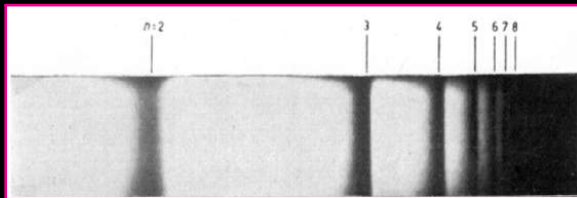
$$\hat{V}_{dip} = -\frac{e}{m_0 c} \mathbf{A} \cdot \hat{\mathbf{p}}, \quad p_{cv,\alpha} = -i\hbar \int d\mathbf{r} u_{c,k}^*(\mathbf{r}) \frac{\partial}{\partial x_\alpha} u_{v,k}(\mathbf{r}) \neq 0 \propto k_\beta$$

(за счет подмешивания далеких зон)

Возбуждение экситона

$$\langle exc | \hat{V}_{dip} | 0 \rangle \propto \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h}^* e^{-i\mathbf{k}_e \mathbf{r}_e - i\mathbf{k}_h \mathbf{r}_h} k_\beta \delta_{\mathbf{k}_e, -\mathbf{k}_h} \propto \left. \frac{\partial \Phi^*}{\partial r_\beta} \right|_{r \rightarrow 0}$$

Активны P -экситоны, у которых $\Phi'(0) \neq 0$ (пример: P -экситоны в Cu_2O).



Экситонные поляритоны

фотон \rightarrow экситон \rightarrow фотон \rightarrow экситон \rightarrow фотон \rightarrow ...

Волновая функция системы

$$\Psi = |0\rangle + \sum_{\alpha} C_{\alpha} |\text{exc}, \alpha\rangle, \quad \alpha = x, y, \text{ или } z$$

Поляризация, наведенная экситоном

$$\mathbf{P} = (P_x, P_y, P_z), \quad P_{\alpha} = dC_{\alpha} + \text{c.c.},$$

d – микроскопический дипольный момент экситона

$$\left(\mathcal{E}_{\text{exc}} + \frac{\hbar^2 Q^2}{2M} - \hbar\Omega \right) C_{\alpha} = dE_{\alpha, \Omega}^+$$
$$\left[\left(\frac{\Omega}{c} \right)^2 \varkappa_b(\Omega) - Q^2 \right] E_{\alpha, \Omega}^+ = -4\pi \left(\frac{\Omega}{c} \right)^2 (dC_{\alpha} + \text{c.c.})$$

Экситонные поляритоны – смешанные квазичастицы света и вещества

Экситонные поляритоны

ФОТОН → ЭКСИТОН → ФОТОН → ЭКСИТОН → ФОТОН → ...

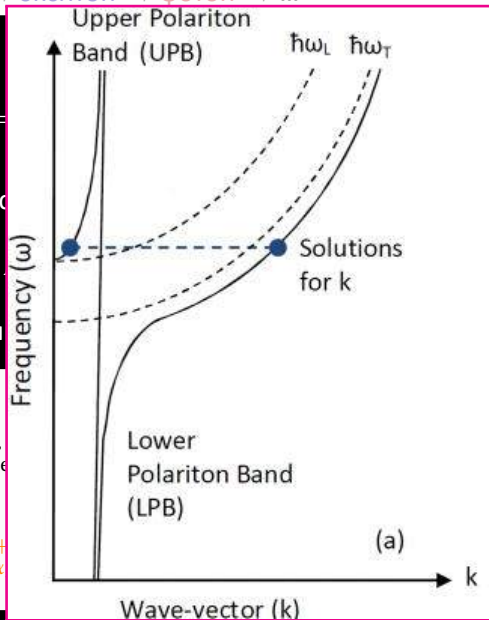
Волновая функция системы

$\Psi =$

Поляризация, наведенная эк

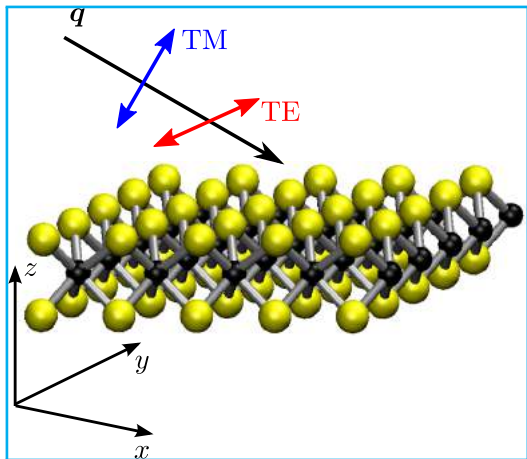
d – микроскопический дипол

$$\left[\left(\frac{\Omega}{c} \right)^2 \chi_b(\Omega) - Q^2 \right] E_{\alpha}^{+}$$



Экситонные поляритоны –
решенные квазичастицы
фотона и вещества

2D systems: radiative decay of excitons



Maxwell equations:

$$\text{rot rot } \mathbf{E} = \left(\frac{\omega}{c}\right)^2 [\mathbf{E} + 4\pi\mathbf{P}(z)]$$

Exciton-induced polarization:

$$\mathbf{P}(z) = \delta(z)\mathbf{E}_{\parallel}(z) \frac{|\varphi(0)|^2}{\omega_0 - \omega + i\Gamma} \frac{e^2|p_{cv}|^2}{\hbar\omega_0^2 m_0^2}$$

Reflection coefficient poles determine eigenfrequencies (polariton modes)

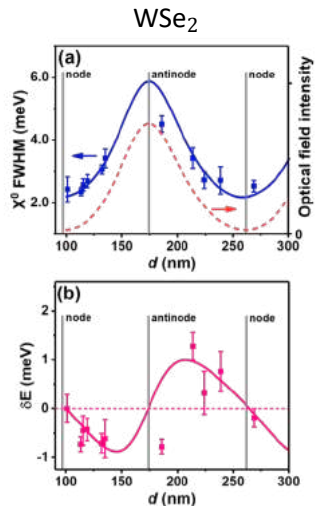
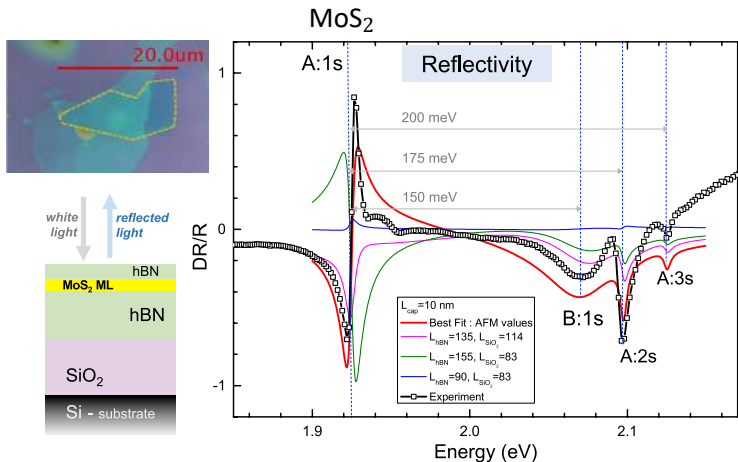
Normal incidence $r(\omega) = \frac{i\Gamma_0}{\omega_0 - \omega - i(\Gamma_0 + \Gamma)}$

$$\hbar\Gamma_0 = 2\pi \frac{\omega}{c} \frac{e^2|p_{cv}|^2}{\omega_0^2 m_0^2} |\varphi(0)|^2 \sim \mathcal{R} \frac{a_0^3}{a_B^2 \lambda} \sim \alpha \left(\frac{a_0}{a_B}\right)^2 \mathcal{R},$$

$$\frac{\Gamma_0}{\Gamma_{at}} \sim \underbrace{\left(\frac{\lambda}{a_0}\right)^2}_{\text{collective} \propto N_{at}} \left(\frac{a_0}{a_B}\right)^2, \quad \lambda \sim \frac{c}{\omega_0}$$

equivalent to $\hbar\Gamma_0 = 2\pi \sum_{k\lambda} |V_{k\lambda}|^2 \delta(\hbar\omega_0 - \hbar\omega_k)$

Excitons in optical response: role of heterostructure



Multiple light reflections are important in van der Waals heterostructures

Phys. Rev. Materials **2**, 011001(R) (2018); *Phys. Rev. Lett.* **123**, 067401 (2019); *Comptes Rendus Physique* **22**, 43 (2021); *Phys. Rev. Lett.* **131**, 116901 (2023)

Экситоны в двумерных материалах

М.М. Глазов

ФТИ им. А.Ф. Иоффе, Санкт-Петербург

Лекция 1

- 1 Двумерные диалькогениды переходных металлов
- 2 Теория экситонов Ванье-Мотта
- 3 Особенности кулоновского взаимодействия и экситонной серии в 2D
- 4 **Тонкая структура экситонных состояний**
- 5 Взаимодействие экситонов и электронов: трионы и ферми-поляроны
- 6 Пара слов о том, как экситоны взаимодействуют друг с другом
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**ЛЕТНЯЯ ШКОЛА
ФОНДА «БАЗИС»**

БАЗИС



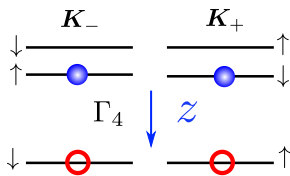
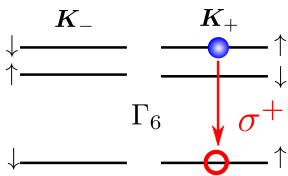
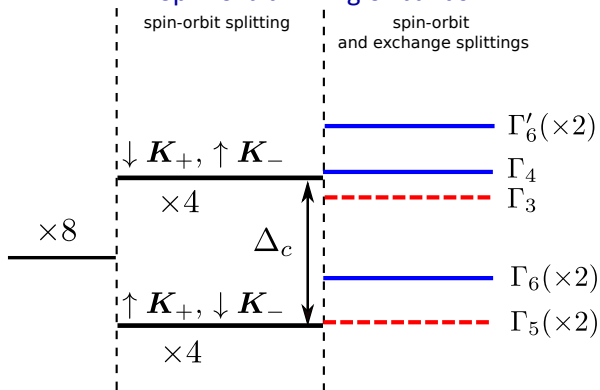
Международный фонд
ИТ имени А.Ф. Иоффе

Bright and dark excitons in MX_2

Spin-orbit mixing of bands

spin-orbit splitting

spin-orbit and exchange splittings

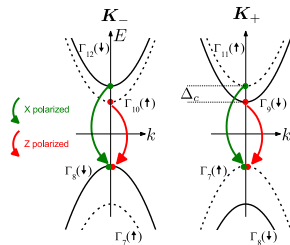
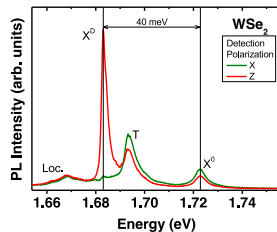
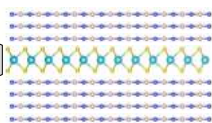


prediction: *PRB* **89**, 201302(R) (2014);

Polarization basis

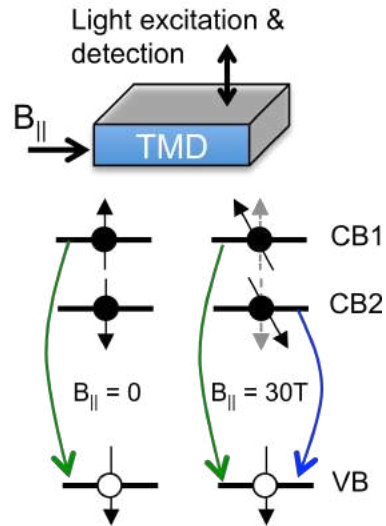
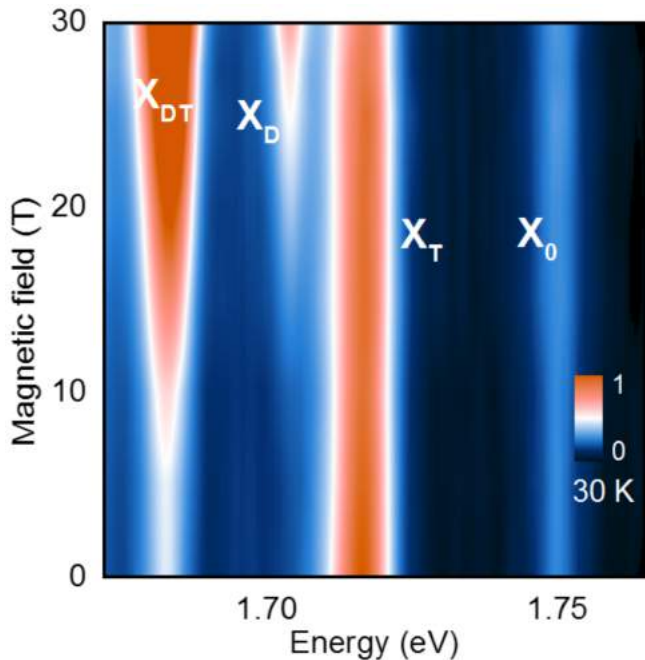


Y Light propagation vector



experiment&model: *PRL* **119**, 047401 (2017)

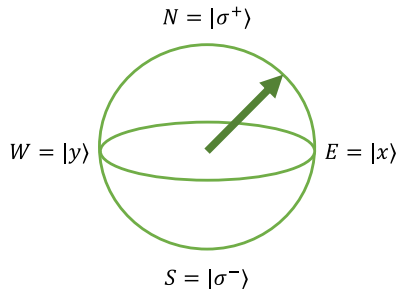
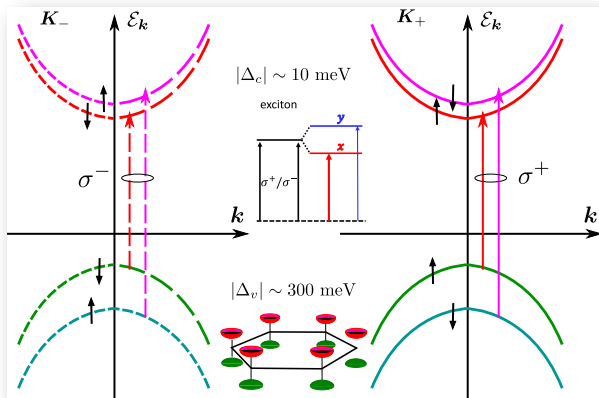
Spin-dark excitons are activated in B -field



X.-X. Zhang et al. (2017)

Optical transitions are active in circular polarizations

Bright exciton doublet: pseudospin 1/2



Density matrix $\hat{\rho} = N\hat{I} + S \cdot \hat{\sigma}$
 Hamiltonian $\hat{\mathcal{H}} = \frac{\hbar}{2}(\hat{\sigma} \cdot \Omega)$

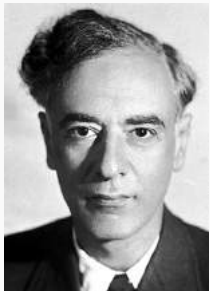
Обменное взаимодействие: история

- Л.Д. Ландау и В.Б. Берестецкий разработали теорию позитрония с учетом обменного взаимодействия электрона и позитрона (1949)
- Теория обменного взаимодействия между электроном и дыркой развивалась Дрессельхаузом, Эллиотом и Рашбой (1950s-60s)

Последовательная теория обменного взаимодействия e и h

разработана Г.Л. Биром и Г.Е. Пикусом (ФТИ) и М.М. Денисовым и В.П. Макаровым (ФИАН) в начале 1970-х.

Ландау



Берестецкий



Бир



Пикус



Два электрона. Принцип Паули

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = -\Psi(\mathbf{r}_2, s_2; \mathbf{r}_1, s_1)$$

– полная волновая функция должна быть антисимметричной

Пренебрегая кулоновским и спин-орбитальным взаимодействиями

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) \propto [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)]\chi_{s_1, s_2}$$

Спиновая функция

$$\chi_{s_1, s_2} = \begin{cases} \uparrow\uparrow \\ \frac{\uparrow\downarrow + \downarrow\uparrow}{\sqrt{2}} \\ \downarrow\downarrow \\ \frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}} \end{cases}$$

$$E_d = 2\mathcal{N}^2 \frac{e^2}{\kappa} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\psi_1^2(\mathbf{r}_1)\psi_2^2(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

$$E_x = 2\mathcal{N}^2 \frac{e^2}{\kappa} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

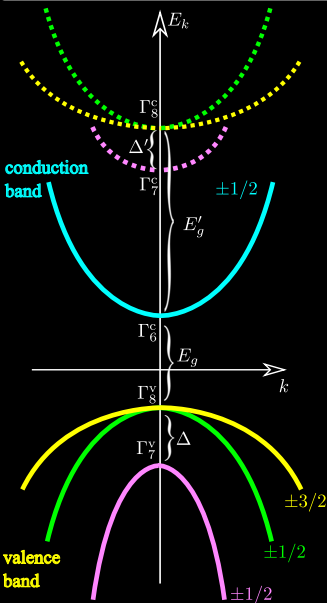
$$E_s = E_d + E_x$$

Многозонная модель

Электроны и дырки – возбуждения одной системы

– волновая функция пары должна быть антисимметрична

см. Г.Л. Бир, Г.Е. Пикус, Симметрия и деформационные эффекты в полупроводниках



Базисные блоховские функции

$$\mathcal{U}_{n_e n_h}(\mathbf{r}_e, \mathbf{r}_h) = u_{n_e, 0}(\mathbf{r}_e) \tilde{u}_{n_h, 0}(\mathbf{r}_h) \quad (N_e \times N_h)$$

Волновая функция пары

$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{n_e, n_h} C_{n_e k_e, n_h k_h} e^{i\mathbf{k}_e \mathbf{r}_e + i\mathbf{k}_h \mathbf{r}_h} \mathcal{U}_{n_e n_h}(\mathbf{r}_e, \mathbf{r}_h)$$

Эффективный гамильтониан

$$\mathcal{H}_{n_e n'_e}^e(\hat{\mathbf{k}}_e) \delta_{n_h n'_h} + \mathcal{H}_{n_h n'_h}^h(\hat{\mathbf{k}}_h) \delta_{n_e n'_e} + V(\rho) \delta_{n_e n'_e} \delta_{n_h n'_h} + \delta \hat{V} \quad (\text{обменное взаимодействие})$$

Коротко- и дальнедействующие вклады

$$\mathcal{V}_{\text{exch}} \equiv \mathcal{V}(n_e, n_h; n'_e, n'_h)$$

$$\Psi_{\text{exc}} = \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h} |\mathbf{k}_e, n_e; \mathbf{k}_h, n_h\rangle; \quad \Psi'_{\text{exc}} = \sum_{\mathbf{k}_e, \mathbf{k}_h} C_{\mathbf{k}_e, \mathbf{k}_h} |\mathbf{k}_e, n'_e; \mathbf{k}_h, n'_h\rangle$$

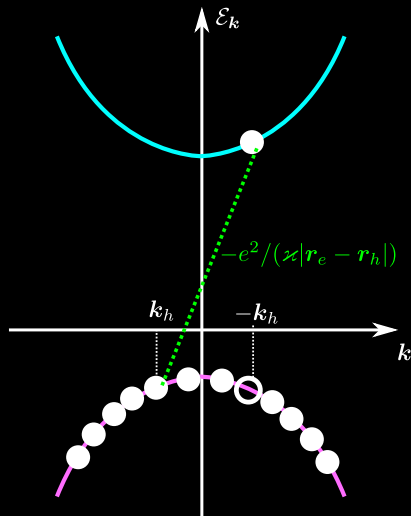
Кулоновское взаимодействие:

$$\langle \mathbf{k}_e, n_e; \mathbf{k}_h, n_h | \frac{e^2}{\varkappa |\mathbf{r}_e - \mathbf{r}_h|} | \mathbf{k}'_e, n'_e; \mathbf{k}'_h, n'_h \rangle \Rightarrow$$

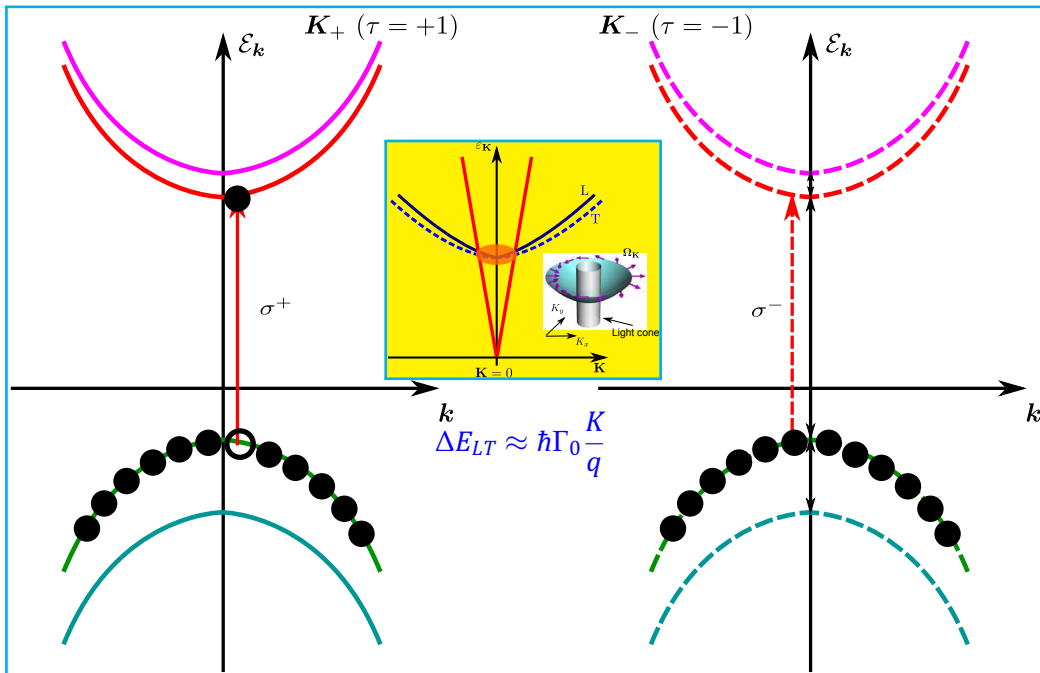
с учетом периодичности блоховских амплитуд выполняем суммирование по векторам обратной решетки $\mathbf{G}, \mathbf{G}' \Rightarrow$

члены с $\mathbf{G} = \mathbf{G}'$ – дальнедействующий вклад

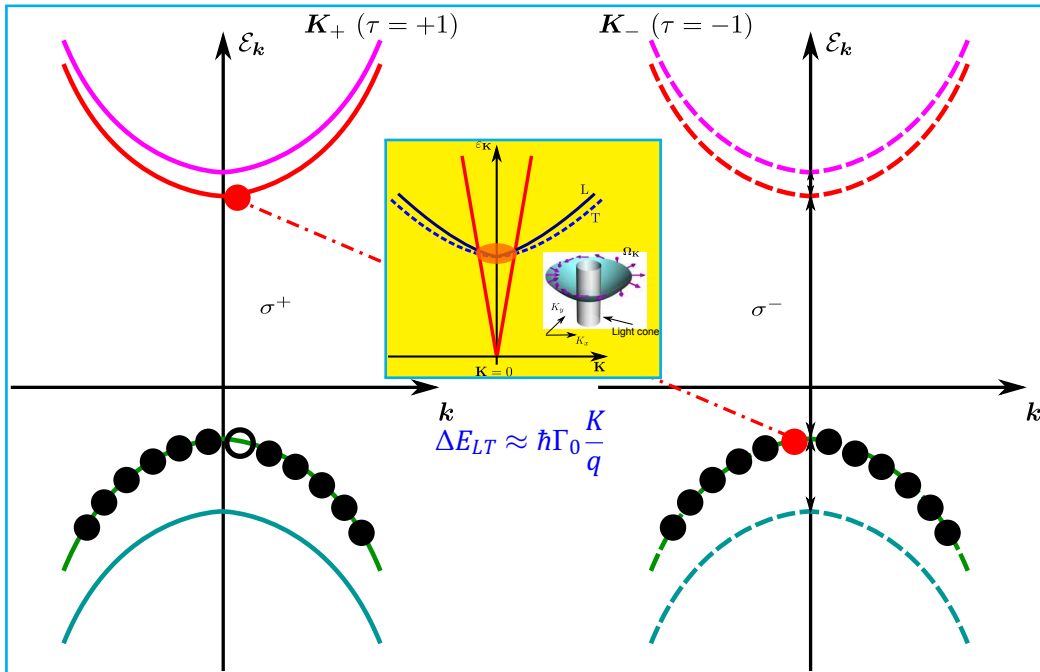
члены с $\mathbf{G} \neq \mathbf{G}'$ – короткодействующий вклад



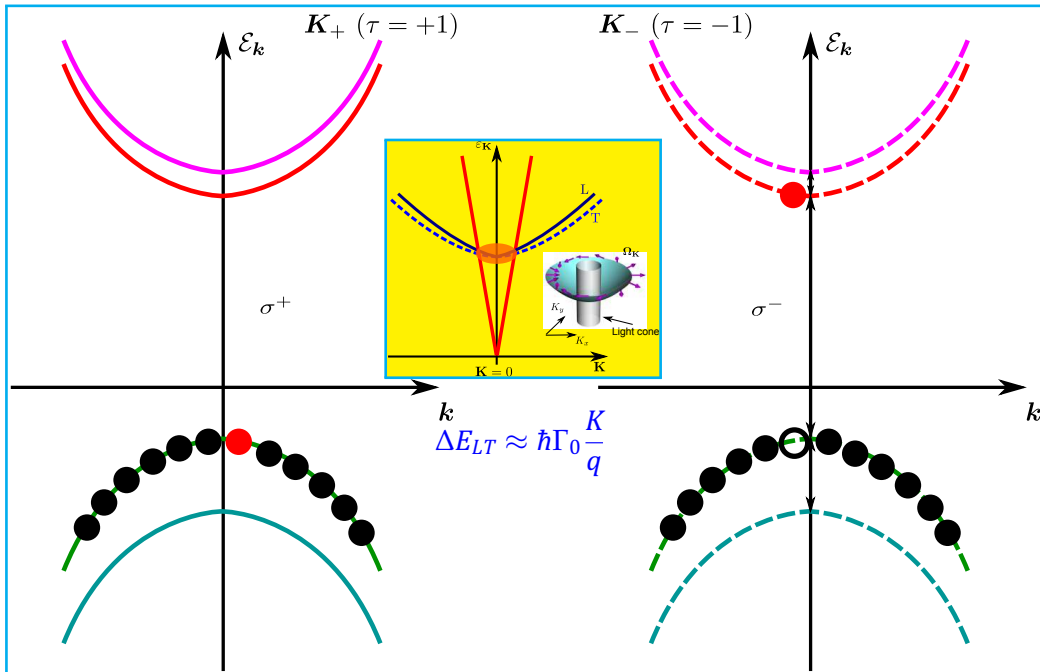
Long-range exchange: spin flip of exciton



Long-range exchange: spin flip of exciton



Long-range exchange: spin flip of exciton

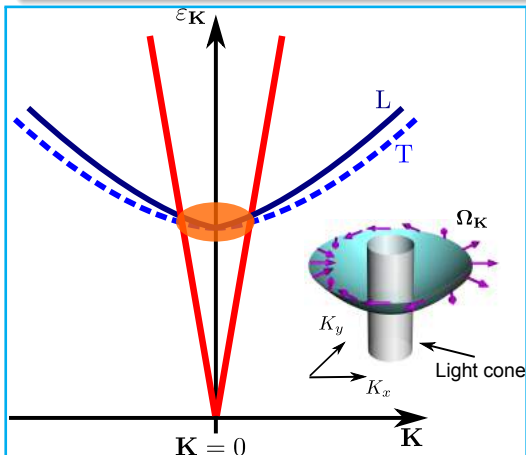


Fine structure of radiative doublet (suspended ML)

Exciton effective Hamiltonian in the basis of σ^+ and σ^- states:

Exciton with the wavevector \mathbf{K} in the monolayer plane:

$$\mathcal{H}_X = \mathcal{A}(K) \begin{pmatrix} 0 & (K_x - iK_y)^2 \\ (K_x + iK_y)^2 & 0 \end{pmatrix} = \frac{\hbar}{2} (\boldsymbol{\Omega}_K \cdot \boldsymbol{\sigma}), \quad \mathcal{A}(K) = \frac{\hbar^2 c \Gamma_0}{KE_g}$$

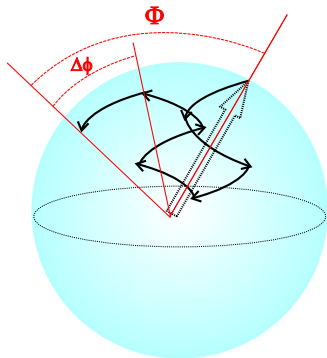


- Moving exciton states are split into TE & TM (T & L) modes
- \mathcal{H}_X is the driving force for exciton spin-valley dynamics
- Effect results from the interaction of exciton with the induced electromagnetic field

$$\Delta E = \hbar \Gamma_0 \frac{K^2}{q \sqrt{K^2 - q^2}} \approx \hbar \Gamma_0 \frac{K}{q}, \quad q = \frac{E_g}{\hbar c}$$

Theory for QWs: *Maialle, de Andrada e Silva, Sham (1993); Goupalov, Ivchenko, Kavokin (1998)*
Theory for TMDCs: *MMG et al. PRB 89, 201302(R) (2014); Yu et al. Nat. Commun. (2014); Yu, Wu, PRB (2014)*

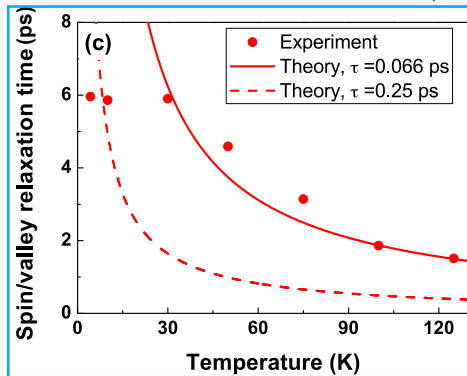
$$\frac{\partial \mathbf{S}_K}{\partial t} + \mathbf{S}_K \times \boldsymbol{\Omega}_K = \mathbf{Q}\{\mathbf{S}\}$$



$$\Delta\phi \sim \Omega_K \tau_2 \ll 1$$

Redfield (1957); Dyakonov, Perel' (1971)

Maijle et al. (1993)



Exciton optical orientation and relaxation is observed up to $T \sim 100$ K

Thermalized excitons

$$\frac{1}{\tau_{zz}} = \langle \Omega_K^2 \tau \rangle = \frac{2\alpha^2 \tau M k_B T}{\hbar^2}, \quad \alpha = \frac{c\hbar\Gamma_0}{E_g} \frac{n+1}{n^2+1}, \quad \tau_R = \frac{1}{2\Gamma_0} = 3 \text{ ps}$$

Экситоны в двумерных материалах

М.М. Глазов

ФТИ им. А.Ф. Иоффе, Санкт-Петербург

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**ЛЕТНЯЯ ШКОЛА
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Фондальный фонд
ИТ-инноваций

Coulomb-correlated complexes in semiconductors

Physical Review Letters

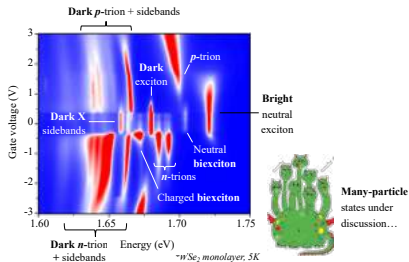
MOBILE AND IMMOBILE EFFECTIVE-
MASS-PARTICLE COMPLEXES IN
NONMETALLIC SOLIDS

Murray A. Lampert

RCA Laboratories,
Princeton, New Jersey

(Received November 14, 1958)

Quite recently the study of excitons has taken a front-rank position among the techniques for the study of nonmetallic solids.¹ It is the pur-

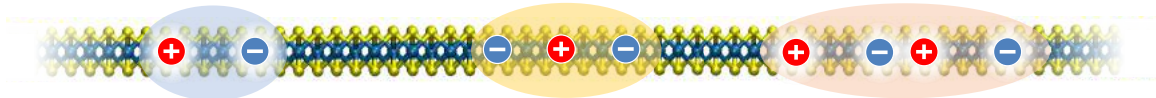


Courtesy A. Chernikov

Exciton

Trion

Biexciton



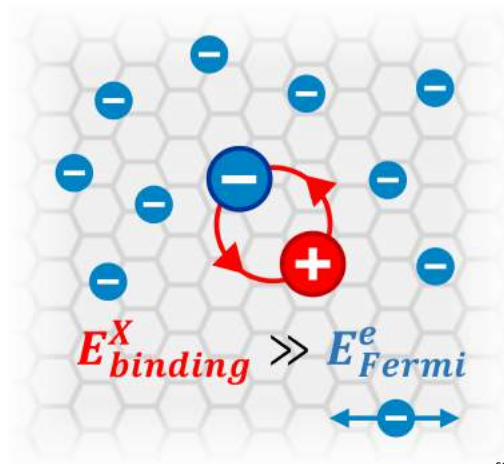
Coulomb-bound
electron-hole pair
cf. *hydrogen atom*
or *positronium*

Bound state of exciton
and electron or hole
cf. *ion*

Bound state
of two excitons
cf. *molecule*

Excitonic ions: Trions

In 2D TMDCs excitons are extremely stable to the doping since $E_B \gg E_F$



see, e.g., *physica status solidi B* **255**, 1800216 (2018)

Exciton can attract an electron and form a three-particle bound state: **trion**

Lampert (1958); Stébé, A. Ainane (1989); Sergeev, Suris (2001)

Excitonic ions: Trions

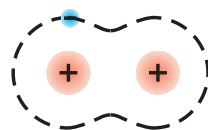
In 2D TMDCs excitons are extremely stable to the doping since $E_B \gg E_F$

- X^+ and X^- trions are the analogues of H_2^+ and H^- ions, but, typically, no adiabaticity $m_e \approx m_h$

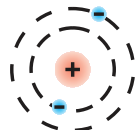
prediction: M. A. Lampert (1958)

observation II-VI QWs: K. Kheng, R. T. Cox, Merle Y. d' Aubigné et al. (1993)

observation in TMDC MLs: Kin Fai Mak et al. (2013)



X^+ - trion



X^- - trion

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \left(\Delta_1 + \Delta_2 + \frac{2\sigma}{1+\sigma} \nabla_1 \cdot \nabla_2 \right) + V(\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2) - V(\boldsymbol{\rho}_1) - V(\boldsymbol{\rho}_2); \quad \sigma = \frac{m_2}{m_1}$$

$V(\boldsymbol{\rho})$ is the screened Coulomb potential Rytova-Keldysh potential

Variational approach:

simplest trial fun. $\varphi(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2) \propto e^{-\rho_1/a_x - \rho_2/a_{tr}} + e^{-\rho_2/a_x - \rho_1/a_{tr}}$, $\boldsymbol{\rho}_1 = \mathbf{r}_{e,1} - \mathbf{r}_h$, $\boldsymbol{\rho}_2 = \mathbf{r}_{e,2} - \mathbf{r}_h$

+ more sophisticated functions

Berkelbach et al. (2013); Courtade, Semina, et al. (2017)

Other approaches include quantum Monte-Carlo, semi-analytical approximations, direct numerical diagonalization of the Hamiltonian, etc.

Ganchev et al. (2015); Kezerashvili, Tsiklauri (2017); Tempelaar, Berkelbach (2019); ...

review: M.A. Semina and R.A. Suris, Localized excitons and trions in semiconductor nanosystems, Physics-Uspekhi (2022)

Excitonic ions: Trions

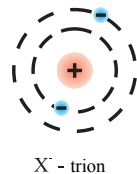
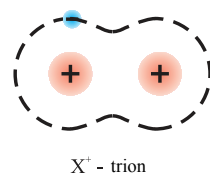
In 2D TMDCs excitons are extremely stable to the doping since $E_B \gg E_F$

- X^+ and X^- trions are the analogues of H_2^+ and H^- ions, but, typically, no adiabaticity $m_e \approx m_h$

prediction: M. A. Lampert (1958)

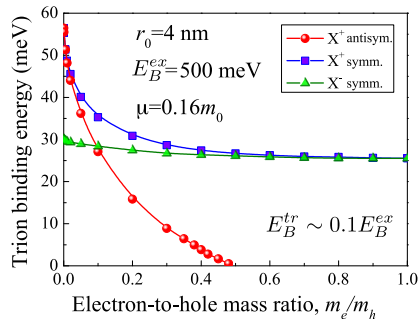
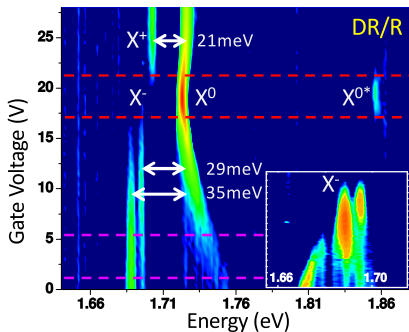
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$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \left(\Delta_1 + \Delta_2 + \frac{2\sigma}{1+\sigma} \nabla_1 \cdot \nabla_2 \right) + V(\rho_1 - \rho_2) - V(\rho_1) - V(\rho_2); \quad \sigma = \frac{m_2}{m_1}$$

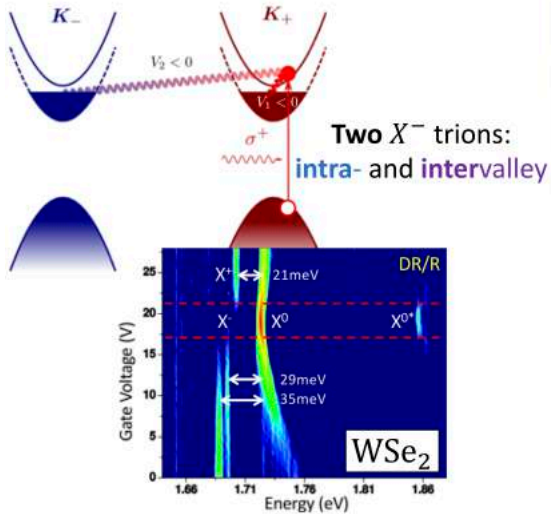
$V(\rho)$ is the screened Coulomb potential Rytova-Keldysh potential



see e.g., PRB 96, 085302 (2017)

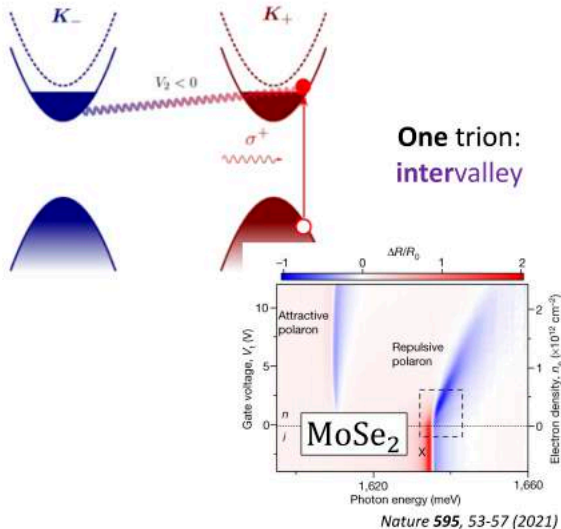
Basics of trion fine structure: interplay of two spin and valley states

Tungsten (W) dichalcogenides



Phys. Rev. B **96**, 085302 (2017)

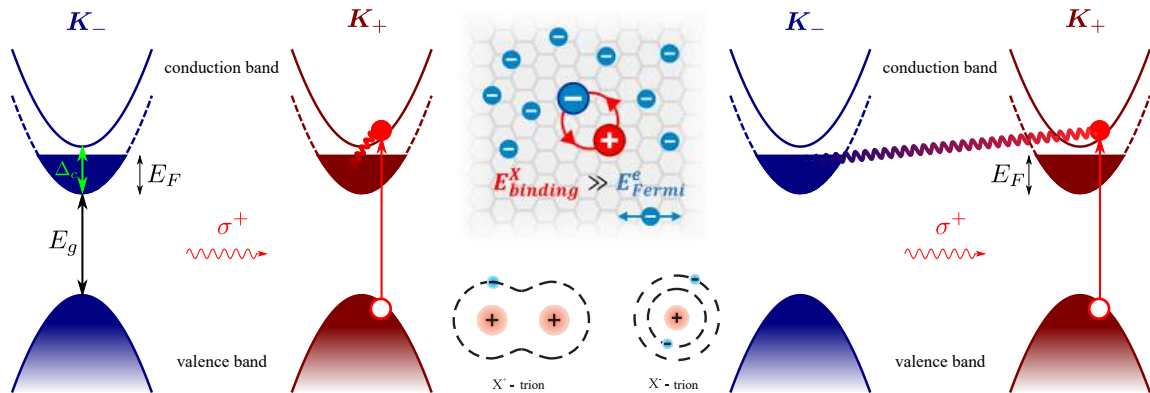
Molybdenum (Mo) dichalcogenides



Nature **595**, 53-57 (2021)

Bose-Fermi mixtures of excitons and carriers: Trions & Fermi polarons

Exciton interacts with resident charge carriers



Exciton can attract an electron and form a three-particle bound state: **trion**

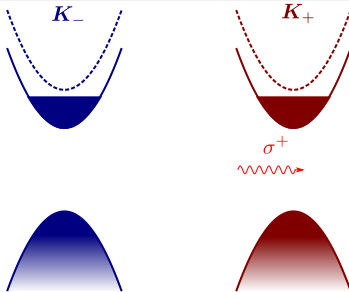
Lampert (1958); Stébé, A. Ainane (1989); Sergeev, Suris (2001)

Any electron can be picked up: “attractive impurity” in Fermi sea, i.e., **Suris tetron/Fermi polaron**

Suris (2001,2003); Schmidt et al. (2012); Sidler et al. (2016); Efimkin & MacDonald (2017)

Exciton in a Fermi sea

Photogeneration of an exciton and a trion formation: **an electron is picked out of the Fermi sea to form a trion and a Fermi-sea hole is left behind.** Trion+FS-hole state (Suris tetron)



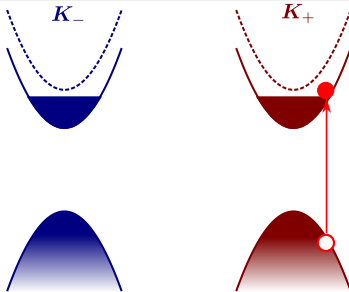
Ansatz manybody wavefunction $E_F \ll E_{b,T} \ll E_{b,X}$

$$\Psi_{\mathbf{k}} = \varphi(\mathbf{k}) X_{\mathbf{k}}^{\dagger} |0\rangle + \sum_{\mathbf{p}, \mathbf{q}} \underbrace{F_{\mathbf{p}, \mathbf{q}}(\mathbf{k}) X_{\mathbf{k}+\mathbf{q}-\mathbf{p}}^{\dagger} e_{\mathbf{p}}^{\dagger}}_{\text{trion}} \underbrace{e_{\mathbf{q}}}_{\text{FS-hole}} |0\rangle$$

Suris (2003), Chevy (2006)

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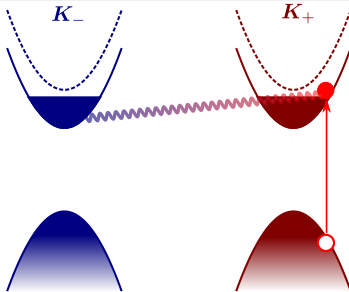
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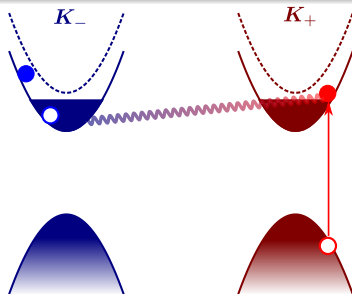
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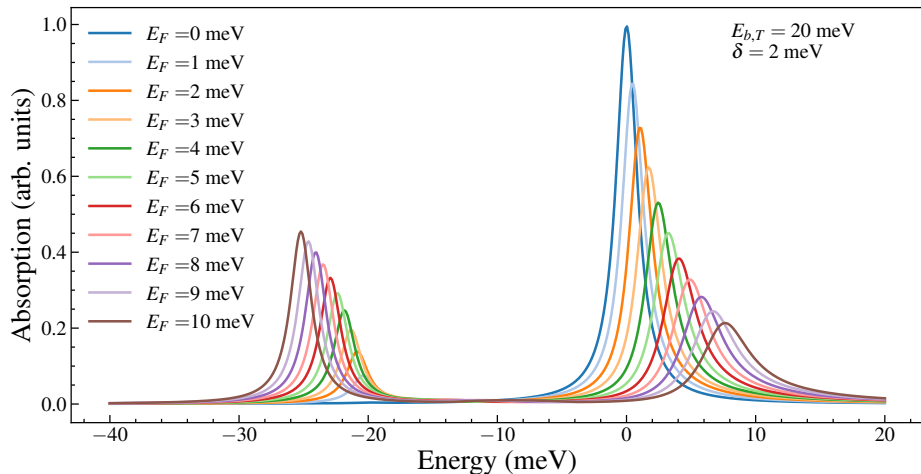
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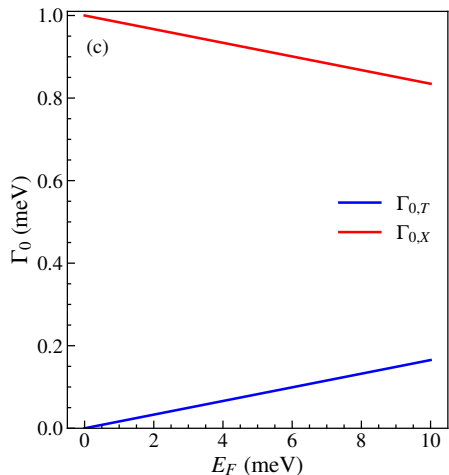
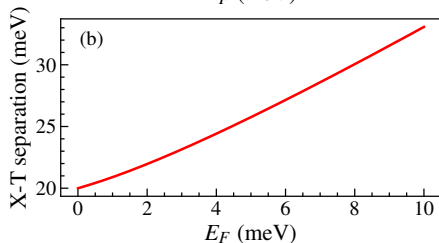
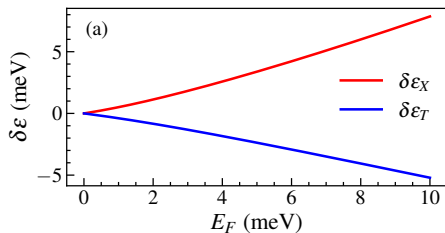
Optical absorption spectra: Theory

$$\varepsilon_T = -E_{b,T} + E_F \left\{ \frac{M_T}{M_X} - \frac{M_X}{M_T} \left[1 - \exp \left(-\frac{M_X^2}{M_T^2} \right) \right]^{-1} \right\}, \quad \mathcal{G}_X(\varepsilon, 0) \approx \frac{E_F/E_{b,T}}{4 \left(\frac{M_T}{M_X} \right)^3 \sinh^2 \left[\frac{1}{2} \left(\frac{M_X}{M_T} \right)^2 \right] (\varepsilon + \varepsilon_T + i\delta/2)}$$

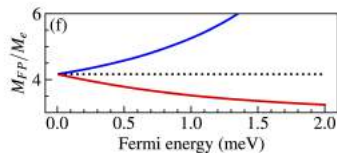
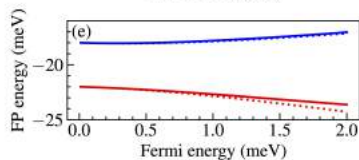
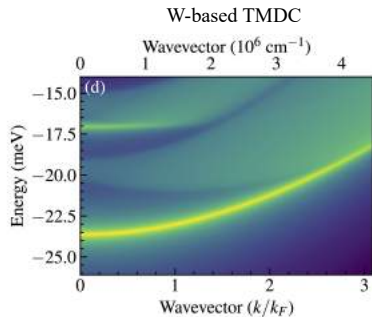
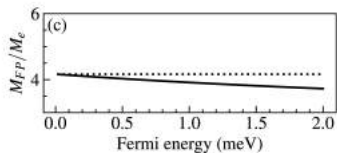
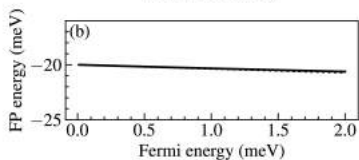
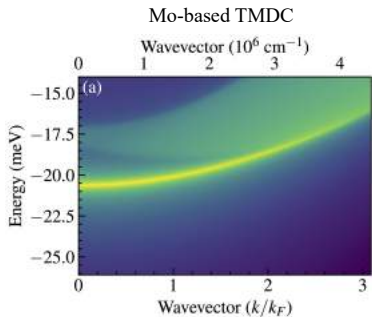


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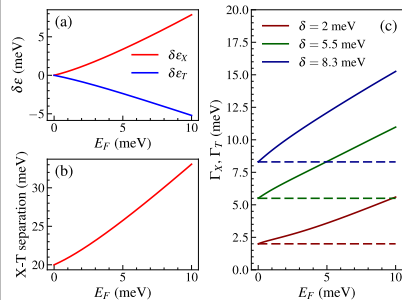
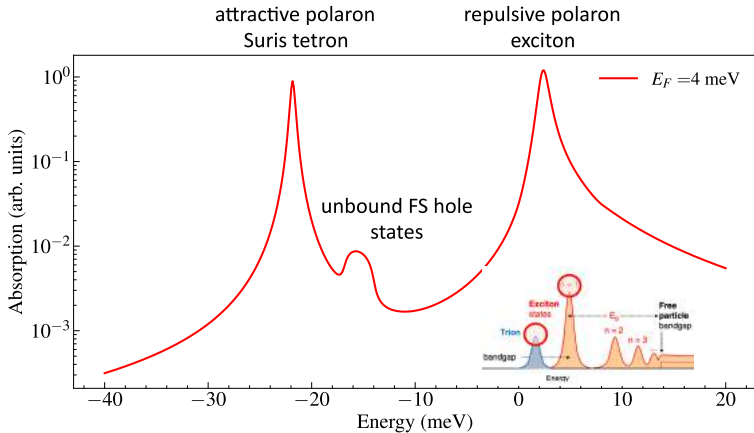


Dispersion



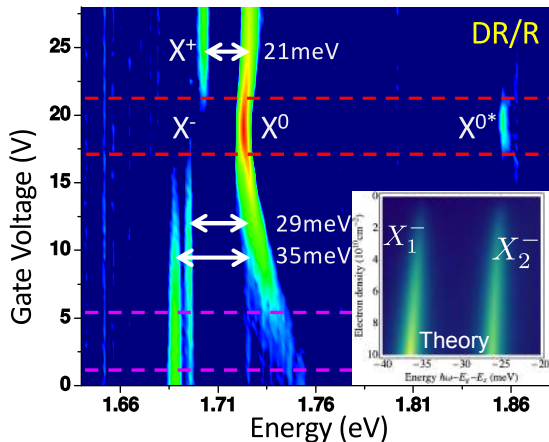
Optical spectra of doped 2D semiconductors

Suris (2001,2003); Klawunn, Recati (2011); Koschorreck et al. (2012); Schmidt et al. (2012); Sidler et al. (2016); Efimkin & MacDonald (2017)



Nano Lett. **23**, 4708 (2023)

Optical absorption spectra: Experiment and theory



PRB **96**, 085302 (2017)

J. Chem. Phys. **153**, 034703 (2020)

In many cases, the trion and Fermi polaron approaches give same or similar results

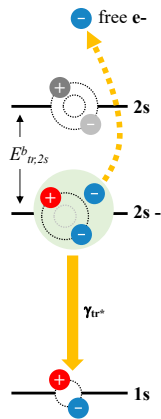
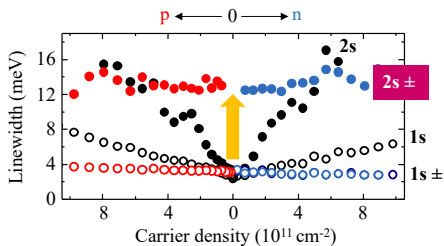
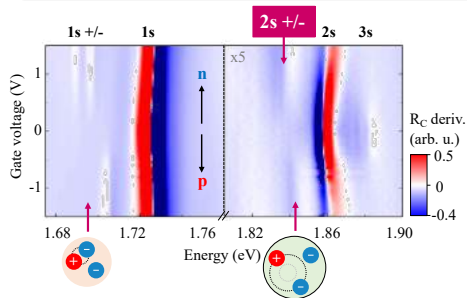
J. Chem. Phys. **153**, 034703 (2020); Phys. Rev. B **105**, 075311 (2022); Nano Lett. **23**, 4708 (2023)

The fine structure in these approaches is different because of their different statistics

2D Mater. **10**, 035034 (2023); J. Lum. **273**, 120700 (2024)

Excited trion states

In MX_2 monolayers the Coulomb interaction is strong and **excited state trions** are observed where electron **interacts with 2s exciton**; $E_{tr,2s}^b \approx 20$ meV

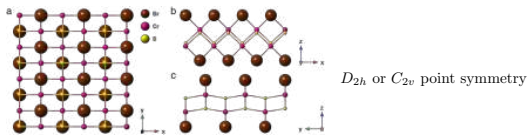


Excited trions can autoionize: $2s^- \rightarrow 1s + e^-$

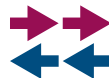
$$E_{tr,2s}^b \approx E_{2s}^b \exp\left(\frac{1}{DV_{22}}\right), \quad \gamma_{tr,2s} \approx E_{tr,2s}^b \pi \frac{|V_{12}|^2}{|V_{22}|^2}$$

V_{ij} are the coupling matrix elements between is and js states

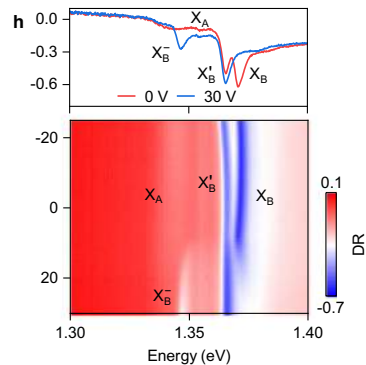
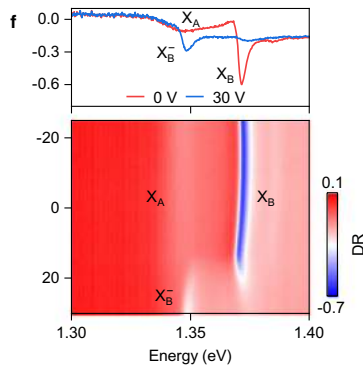
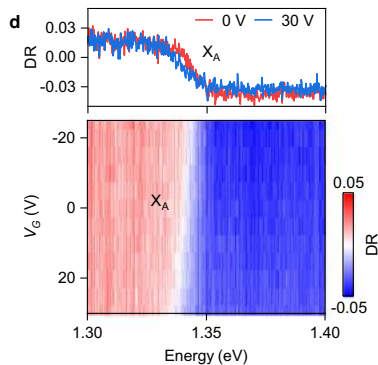
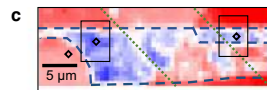
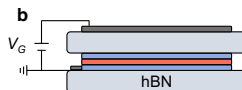
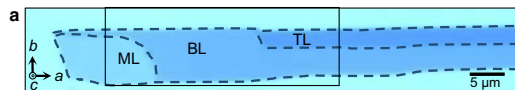
Trions in van der Waals magnet CrSBr



Antiferromagnetic interlayer interaction



Ferromagnetic coupling of spins within the layers



Экситоны в двумерных материалах

М.М. Глазов

ФТИ им. А.Ф. Иоффе, Санкт-Петербург

Лекция 1

- 1 Двумерные диалкогениды переходных металлов
- 2 Теория экситонов Ванье-Мотта
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**ЛЕТНЯЯ ШКОЛА
ФОНДА «БАЗИС»**

БАЗИС

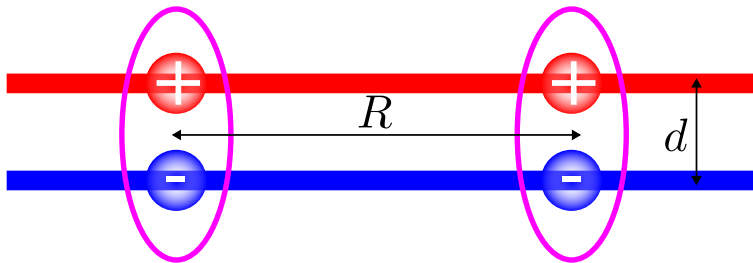


Фондальный фонд
ИТ имени А.Ф. Иоффе

Dipolar repulsion of excitons in bilayers

Direct Coulomb interaction

$$U(R) \approx \frac{2e^2}{\epsilon} \left(\frac{1}{R} - \frac{1}{\sqrt{R^2 + d^2}} \right), \quad V = \int U(R) d^2R = \frac{4\pi e^2 d}{\epsilon}$$



Interaction-induced blueshift $\Delta E(n) = Vn$ “plate capacitor model”

Butov, Shashkin, Dolgoplov, Campman, Gossard (1999)

Exciton-exciton correlations: $V \rightarrow \mathcal{K}(T)V$, $\mathcal{K}(T) \approx 0.1 \dots 1$

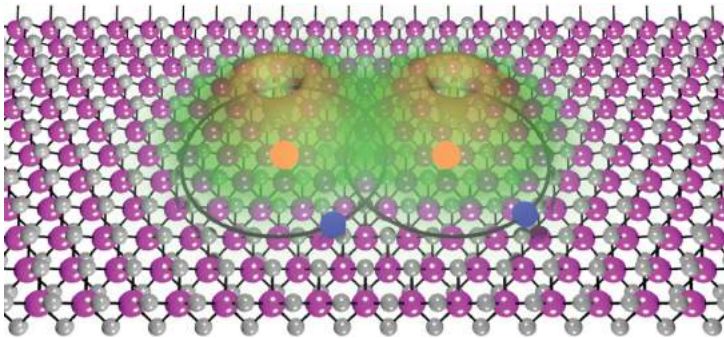
Zimmermann, Schindler (2007,2008); Laikhtman, Rapaport (2009)

+ band gap renormalization and screening ...

2D semiconductors: *Erkensten, Brem, Perea-Causin, Malic (2022); Steinhoff, et al. (2023)*

Exchange interaction of excitons in monolayers

In monolayers direct Coulomb interaction is suppressed due to the charge neutrality



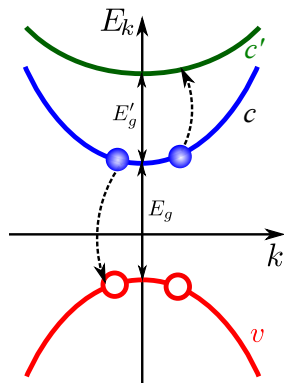
Exchange contribution \Rightarrow overlap of the wavefunctions:

$$V_{\uparrow\uparrow} \sim E_B a_B^2, \quad V_{\uparrow\downarrow} \sim \frac{\hbar^2}{M} \ln \left(-\frac{E}{E_{bi}} \right)$$

Quantum wells: Ciuti, Savona, Piermarocchi, Quattropani, Schwendimann (1998); Combescot, Betbeder-Matibet, Dubin (2008);
Microcavities: Tassone, Yamamoto (1999); MMG, Ouerdane, Pillozzi, Malpuech, Kavokin, D'Andrea (2009);
2D semiconductors: Shahnazaryan, Iorsh, Shelykh, Kyriienko (2017)

Exciton-exciton annihilation: Auger-like process

Resonant interaction of excitons



Conservation laws:

$$E_1 + E_2 = E_f, \quad \mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_f$$

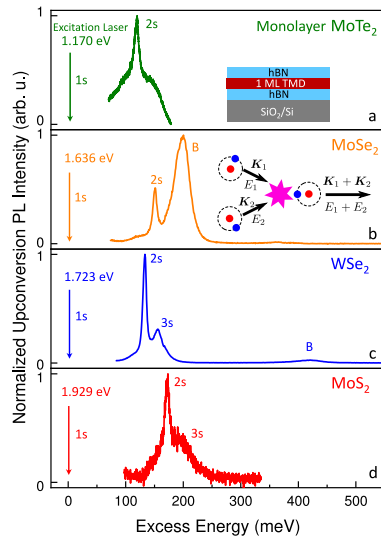
$$\text{Resonance: } E'_g \approx E_g - E_B$$

$$\frac{dn_{cv}}{dt} = -R_A n_{cv}^2 = -\frac{dn_{c'v}}{dt}$$

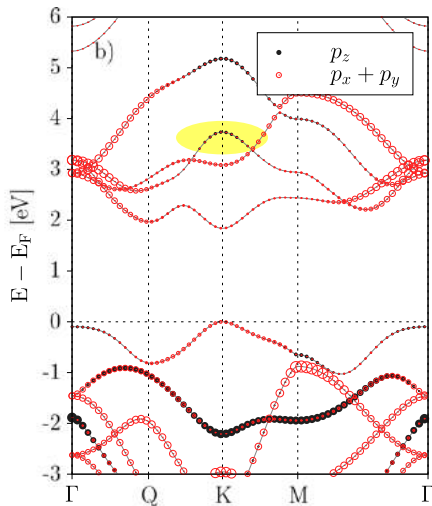
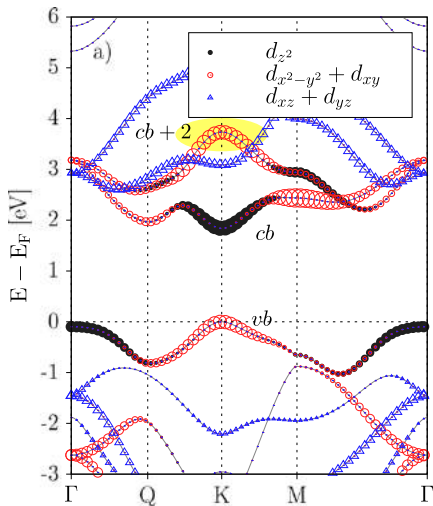
$$R_A \propto \frac{E_B^2}{k_B T} \left| \frac{p_{cv} p_{c'v}}{E_g E_{g'}} \right|^2 e^{-|\delta|/k_B T}$$

Resonant Auger process populates excited states
(photoluminescence upconversion)

(eV)	MoS ₂	MoSe ₂	WSe ₂	MoTe ₂
E_g	1.8	1.6	1.7	1.7
E'_g	1.2	1	1.4	1.3
E_B	0.2	0.18	0.16	0.16

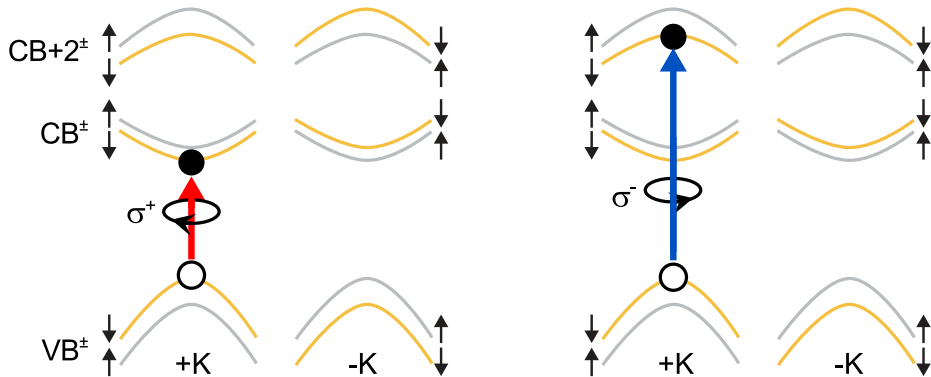


“High-lying” conduction band $cb + 2$ in MX_2 has $m_e < 0$



Kormanyos et al. (2015)

Optical selection rules to the high-lying band are inverted

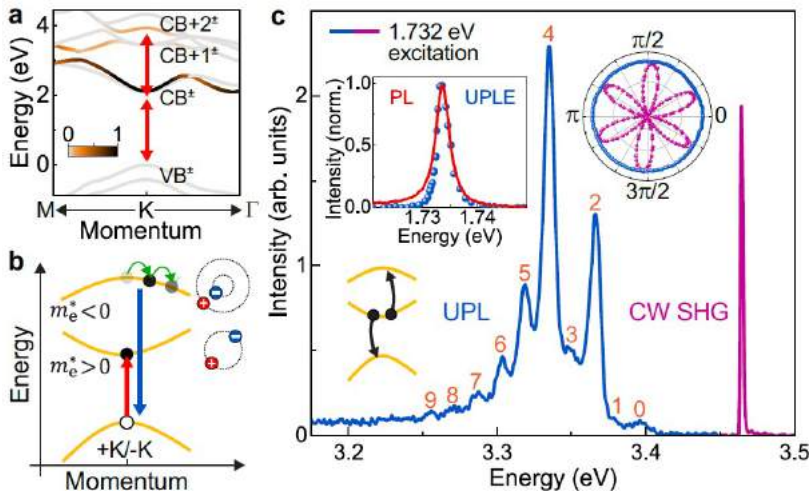


Transition	+K valley		-K valley	
	Irrep	Helicity	Irrep	Helicity
VB ↔ CB+2	$A' \leftrightarrow E_2'$	σ^-	$A' \leftrightarrow E_1'$	σ^+
VB ↔ CB	$A' \leftrightarrow E_1'$	σ^+	$A' \leftrightarrow E_2'$	σ^-

High-lying $vb \leftrightarrow cb + 2$ excitons in WSe_2 monolayers are formed as a result of a resonant Auger process $E'_g \approx E_g - E_b$

Nat. Commun. 8, 14927 (2017); Phys. Rev. X 8, 031073 (2018)

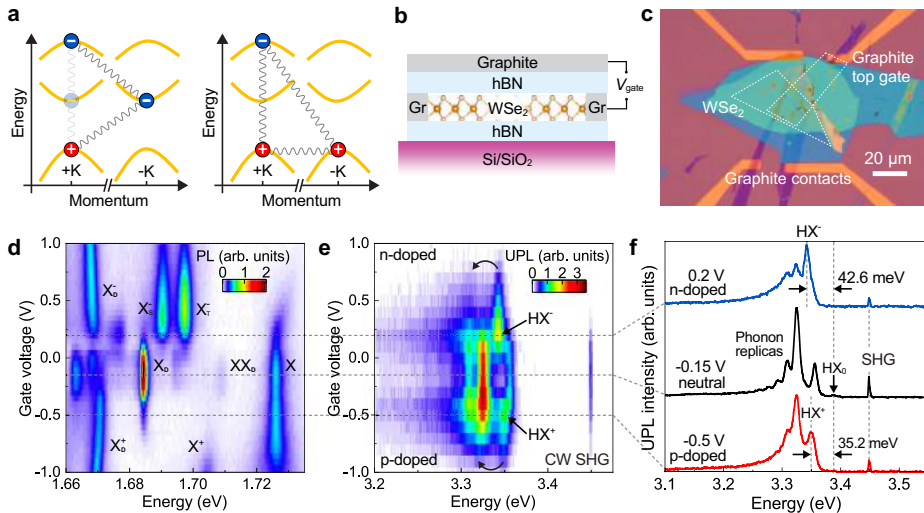
high-lying (HX) excitons



strong exciton-phonon coupling results in replicas (1 – 9)

observation of HXs: Kaiqiang Lin et al. (2021)

High-lying triions with 20 ... 40 meV binding energies



High-lying triions	WSe ₂		MoSe ₂	
	HX ⁻	HX ⁺	HX ⁻	HX ⁺
Binding energy (meV)	43	35	21	21
Band-edge triions	X _s ⁻	X _r ⁻	X ⁻	X ⁺
Binding energy (meV)	36	29	21	26

Nat. Commun. **13**, 6980 (2022);
Oxford Open Mat. Sci. **3**, itad004 (2023)

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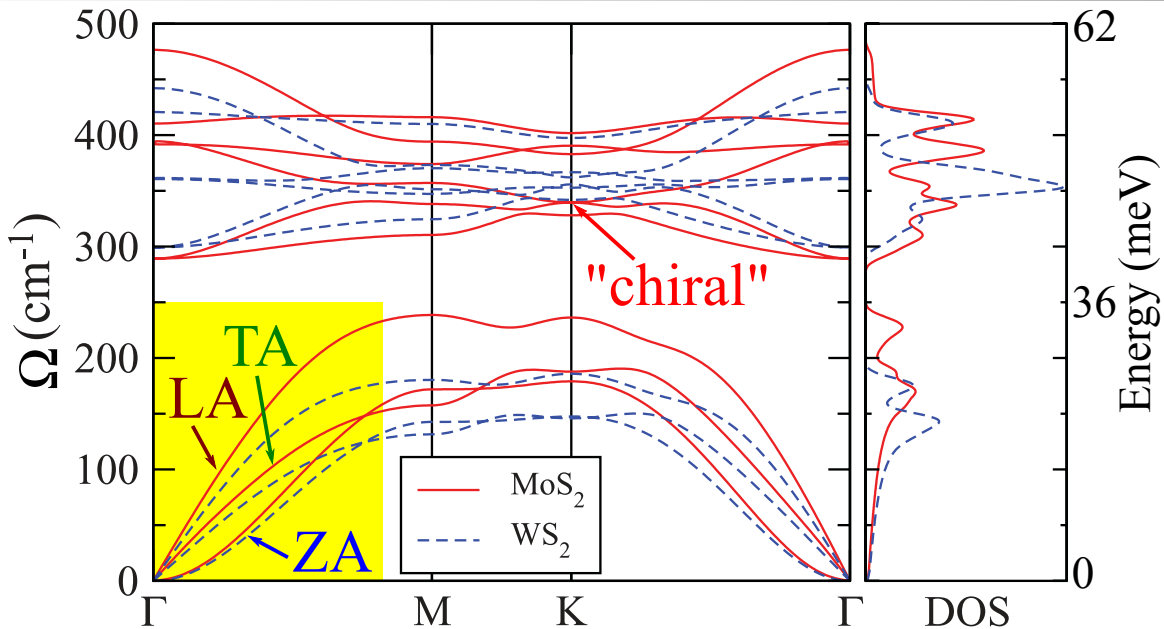
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ФОНДА «БАЗИС»**

БАЗИС

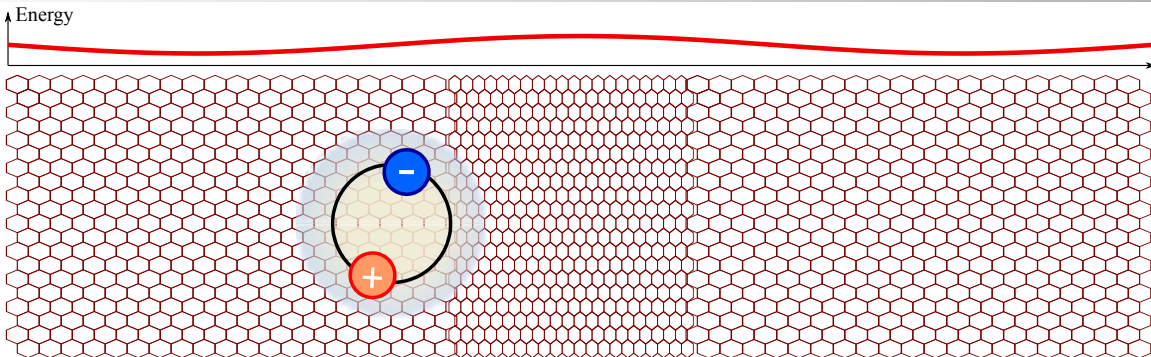


Фондальный фонд
ИТ-инноваций

Vibration spectrum



Deformation potential



Lattice deformation \Rightarrow shift of the electron and hole energies \Rightarrow variation of exciton energy

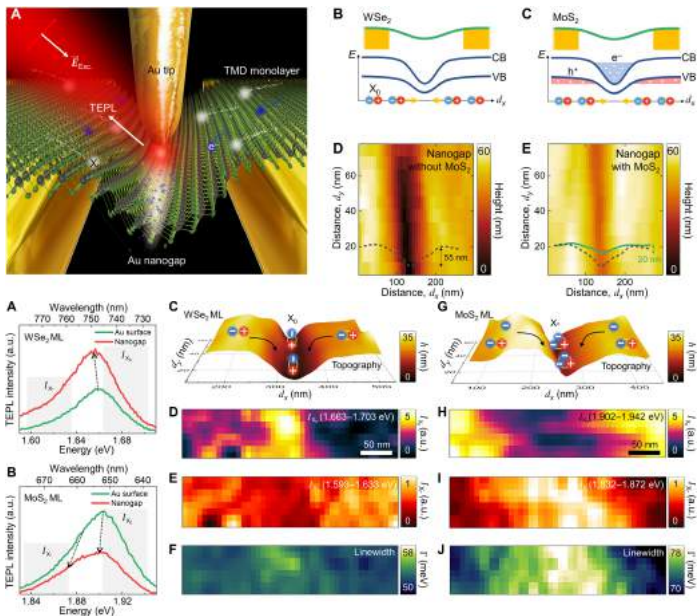
$$\Delta E_x = (D_c - D_v)(\epsilon_{xx} + \epsilon_{yy}) \propto (\mathbf{q} \cdot \mathbf{u}_q)$$

Matrix element:

$$M_{k'k}^q = \sqrt{\frac{\hbar}{2\rho\Omega_q S}} q(D_c - D_v) \mathcal{F}(q), \quad \mathcal{F}(q) \approx \frac{1}{[1 + (qa_B/4)^2]^{3/2}} \approx 1$$

effective for LA mode; piezo interaction [$\propto \sqrt{q}/(1 + r_0q)$ in 2D] is weak

Exciton-phonon scattering rates



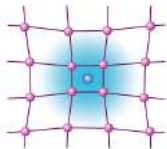
Benimetskiy et al. (2019); Rosati et al. (2020); Moon et al. (2020); Dirnberger et al. (2021); Hyeonwoo Lee et al. (2021)

Polarens: combining electronic and vibrational excitations

Electrons “drag” crystal lattice

⇒ energy and mass renormalization.

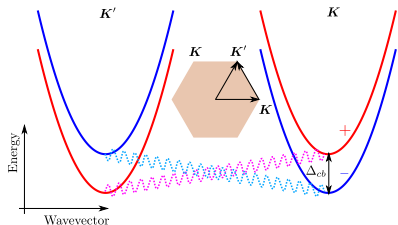
Electrons are “dressed” by phonons (usually, long-wavelength optical).



Landau (1933); Pekar (1946); Landau, Pekar (1948); Fröhlich (1954)

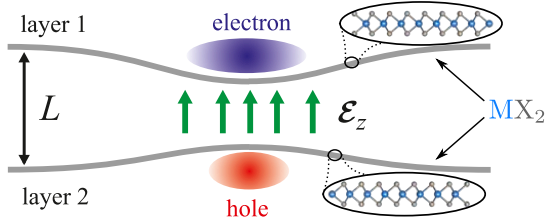
Fröhlich polaron in 2D MX₂: *P.-F. Li, Z.-W. Wang, JAP 123, 204308 (2018); Q. Chen, W. Wang, F. M. Peeters, JAP 123, 214303 (2018)*

Two valleys: Intervalley polaron



Glazov, Semina, Robert, Urbaszek, Amand, Marie, PRB 100, 041301(R) (2019)

Flexural vibrations: flexuron and interlayer polaron



*Katsnelson, PRB 82, 205433 (2010); Semina, Glazov, Sherman, Ann. Phys. (Berlin), 2000339 (2020)
Iakovlev, Semina, Glazov, Sherman, PRB 105, 205305 (2022)*

Strain-induced effective Hamiltonian

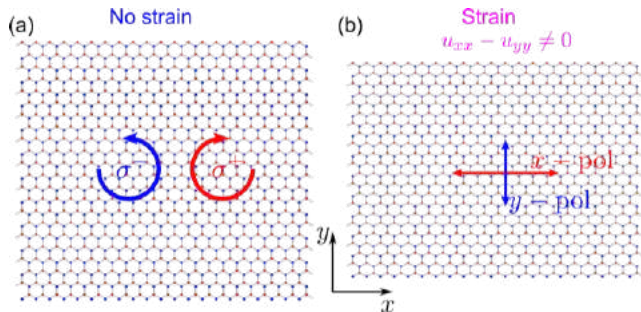
Deformation tensor $u_{ij} \equiv \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) = u_{ji}$

Pseudospin Hamiltonian $\mathcal{H} = \frac{\hbar}{2} (\hat{\sigma} \cdot \mathbf{\Omega})$

$$\Omega_x = \mathcal{A}(K)(K_x^2 - K_y^2) + \mathcal{B}(u_{xx} - u_{yy})$$

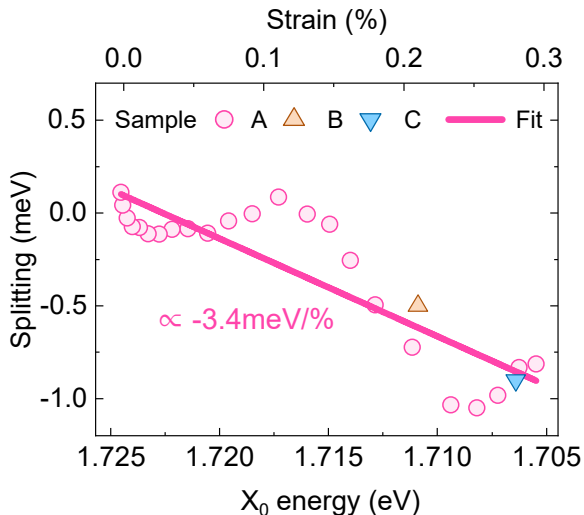
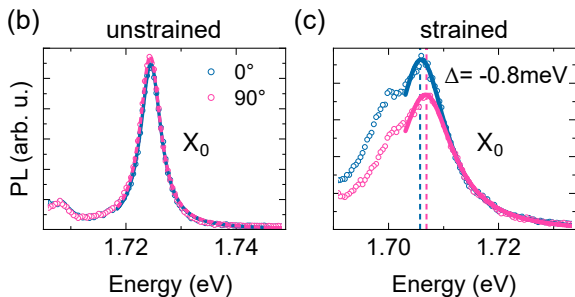
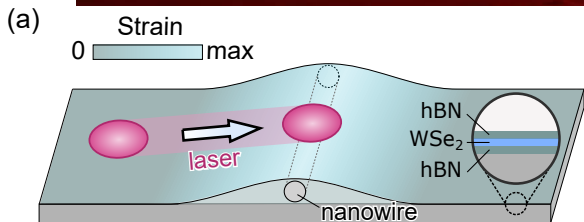
$$\Omega_y = 2\mathcal{A}(K)K_x K_y + 2\mathcal{B}u_{xy}$$

$$\Omega_z = \mathcal{C}[(u_{xx} - u_{yy})K_x - 2u_{xy}K_y]$$



Strain breaks three-fold rotational symmetry of the ML \Rightarrow linear polarization, splitting of states

Experiment and theory



Экситоны в двумерных материалах

М.М. Глазов

ФТИ им. А.Ф. Иоффе, Санкт-Петербург

Лекция 1: энергетический спектр и оптические свойства экситонов

- 1 Двумерные дихалькогениды переходных металлов
- 2 Теория экситонов Ванье-Мотта
- 3 Особенности кулоновского взаимодействия и экситонной серии в 2D
- 4 Тонкая структура экситонных состояний
- 5 Взаимодействие экситонов и электронов: трионы и ферми-поляроны
- 6 Пара слов о том, как экситоны взаимодействуют друг с другом
- 7 Экситоны, фононы и упругие деформации

Лекция 2. Экситонный транспорт: классические и квантовые эффекты

**ЛЕТНЯЯ ШКОЛА
ФОНДА «БАЗИС»**

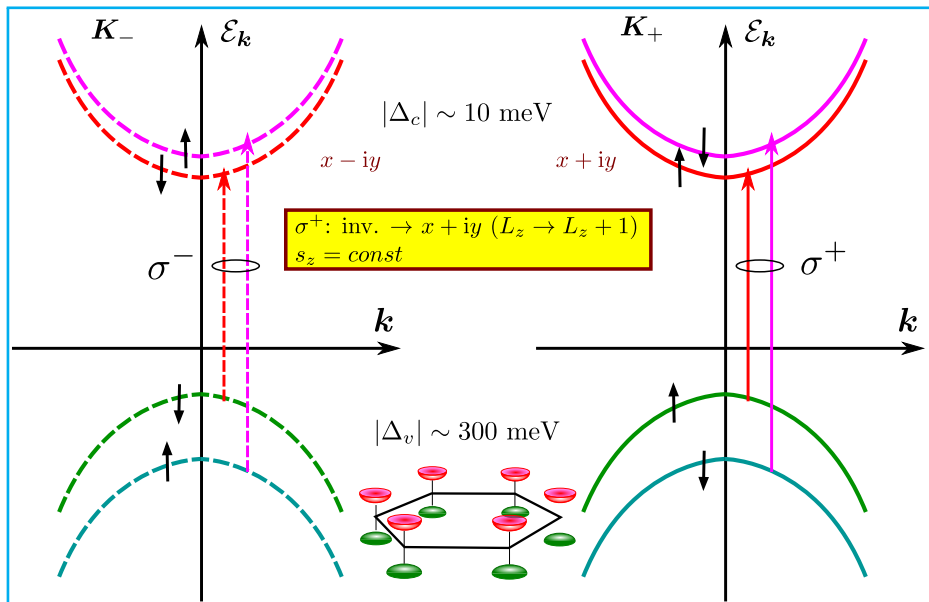
БАЗИС



Фондальный фонд
ИТ имени А.Ф. Иоффе

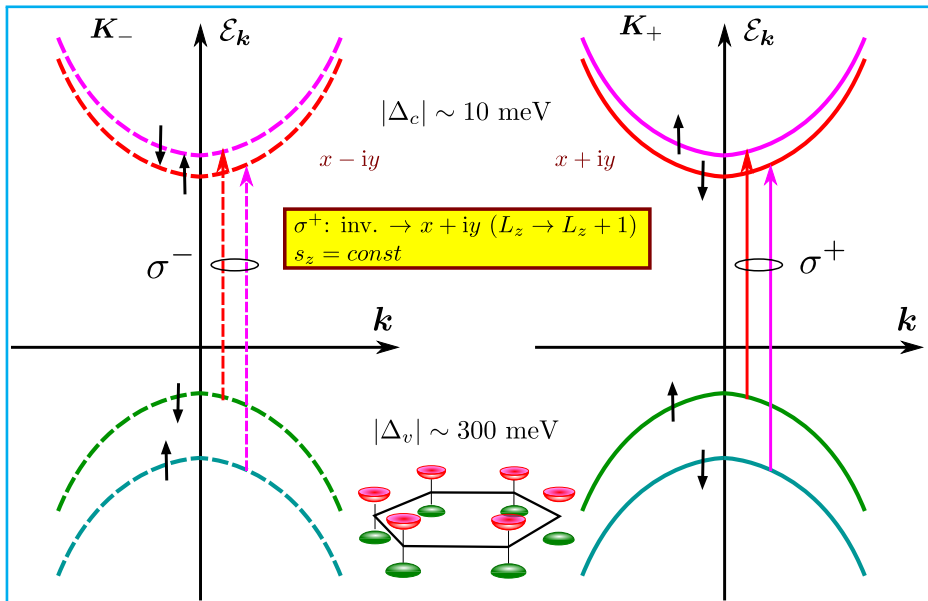
Band structure and optical selection rules

Mo-based



Band structure and optical selection rules

W-based



Technical details

2D layer in vacuum, polarizability $\alpha \approx \frac{\epsilon_{\text{TMD}} - 1}{4\pi} a_0$:

$$\mathbf{P}(\rho, z) = \delta(z) \alpha \mathbf{E}_{\parallel}(\rho, z=0), \quad \mathbf{E}_{\parallel} = -\frac{\partial \phi(\mathbf{r})}{\partial \rho}.$$

Induced charge density

$$e\delta n = -\frac{\partial P_x}{\partial x} - \frac{\partial P_y}{\partial y} = \delta(z) \alpha \frac{\partial^2 \phi}{\partial \rho^2}.$$

Maxwell's equation

$$\text{div } \mathbf{E} = -\frac{\partial^2 \phi}{\partial \mathbf{r}^2} = 4\pi e[\delta(\mathbf{0}) + \delta n].$$

In the \mathbf{k} -space

$$(k_{\parallel}^2 + k_z^2) \phi_{\mathbf{k}_{\parallel}, k_z} = 4\pi e - 4\pi \alpha k_{\parallel}^2 \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \phi_{\mathbf{k}_{\parallel}, k_z},$$
$$V_{k_{\parallel}} = -e \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \phi_{\mathbf{k}_{\parallel}, k_z} = -\frac{2\pi e^2}{k_{\parallel}(1 + 2\pi \alpha k_{\parallel})} \Rightarrow V(\rho) = \sum_{k_{\parallel}} V_{k_{\parallel}} e^{i\mathbf{k}_{\parallel} \cdot \rho}$$

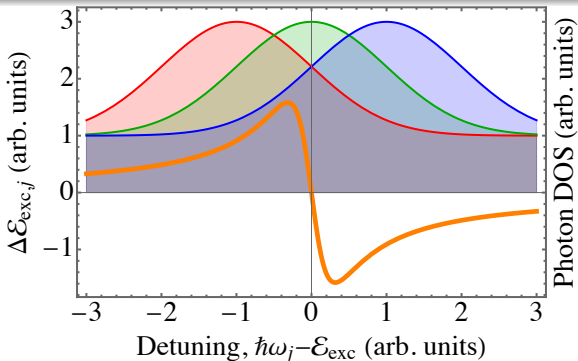
Light-matter coupling: Quantum electrodynamics

Shifts of the **excited** and **ground** states due to the virtual photon emission-absorption processes:

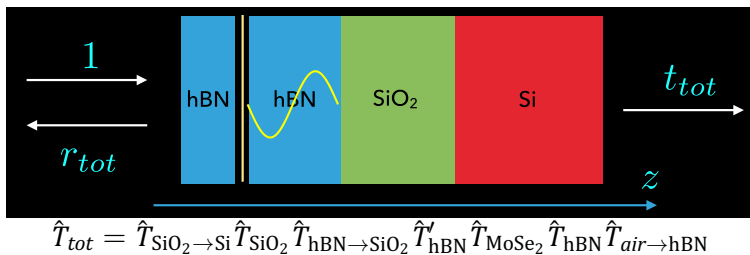
$$\Delta\mathcal{E}_{\text{exc}} = \sum_j \frac{|V_j|^2}{\mathcal{E}_{\text{exc}} - \hbar\omega_j + i0}, \quad \Delta\mathcal{E}_0 = \sum_j \frac{|V_j|^2}{-\mathcal{E}_{\text{exc}} - \hbar\omega_j + i0}$$

$$\Delta\mathcal{E} = \Delta\mathcal{E}_{\text{exc}} - \Delta\mathcal{E}_0 = 2\mathcal{E}_{\text{exc}} \sum_j \frac{|V_j|^2}{\mathcal{E}_{\text{exc}}^2 - (\hbar\omega_j)^2 + i0} \Rightarrow 4\pi \left| \frac{\mathcal{E}_{\text{exc}} D_{\text{exc}}}{\hbar c} \right|^2 G_{\mathcal{E}_{\text{exc}}/\hbar}(z_{ML}, z_{ML})$$

Lamb shift = $\text{Re}\{\Delta\mathcal{E}\}$, radiative decay = $\text{Im}\{\Delta\mathcal{E}\}$



Light-matter coupling: Transfer matrix method



$$(\mathcal{E}_{\text{exc}} - \hbar\omega)P_{\text{exc}}(z) = |D_{\text{exc}}|^2 E(z_{ML}) \delta(z - z_{ML})$$

$$E(z) = -4\pi \left(\frac{\omega}{c}\right)^2 \frac{|D_{\text{exc}}|^2}{\mathcal{E}_{\text{exc}} - \hbar\omega} E(z_{ML}) G_{\omega}(z, z_{ML})$$

$$\hbar\delta\omega_0^{\text{eff}} - i\hbar\Gamma_0^{\text{eff}} = 4\pi \left| \frac{\mathcal{E}_{\text{exc}} D_{\text{exc}}}{\hbar c} \right|^2 G_{\mathcal{E}_{\text{exc}}/\hbar}(z_{ML}, z_{ML})$$

General case: linear response theory

eigenmodes are the poles of the reflectivity

$$r_{\text{tot}}(\omega) = \frac{Z_r}{\omega_0^{\text{eff}} - \omega - i(\Gamma_0^{\text{eff}} + \Gamma)} + \dots$$

Monolayer on a substrate with reflectivity $r_s \approx re^{2iqd} \Rightarrow$ oscillatory dependence on d

$$\Gamma_0^{\text{eff}} \approx \Gamma_0^{\text{vac}} \underbrace{(1 + \text{Re}\{r_s\})}_{\text{Purcell effect}}, \quad \omega_0^{\text{eff}} \approx \omega_0 + \Gamma_0^{\text{vac}} \underbrace{\text{Im}\{r_s\}}_{\text{Lamb shift}}$$

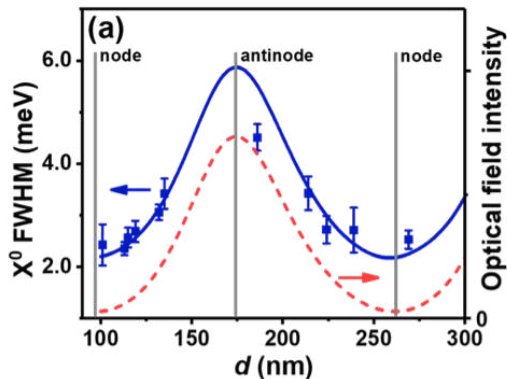
“Polariton” effect in 2D: experiment and theory

Phys. Rev. Lett. **131**, 116901 (2023)

$$r_s \approx r \exp(2iqd)$$

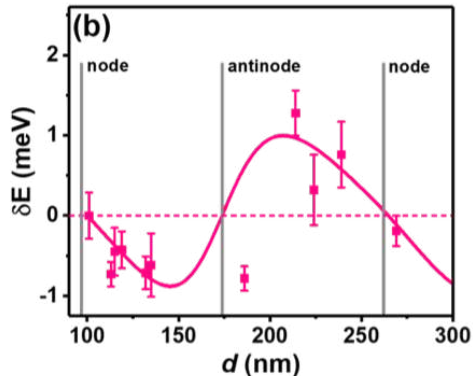
Purcell effect $\Gamma_0 = \Gamma_0^{\text{vac}}(1 + \text{Re}\{r_s\})$

Lamb shift $\Delta\mathcal{E} = \hbar\Gamma_0^{\text{vac}} \text{Im}\{r_s\}$



variation of exciton radiative lifetime

also confirmed on MoSe₂: Phys. Rev. Lett. **123**, 067401 (2019)



variation of exciton transition energy

see also:

Hong et al., Optica **6**, 1443 (2019); Zhou et al., Phys. Rev. Lett. **124**, 027401 (2020); Rogers et al., Phys. Rev. Research **2**, 012029 (2020); Groep et al., Nat. Photonics **14**, 426 (2020)

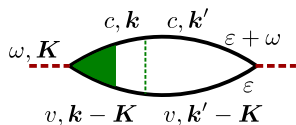
Environment also affects spin/valley dynamics of excitons: PRB **103**, 085302 (2021)

Electron-hole exchange interaction: microscopics

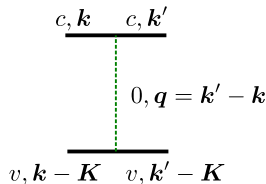
Long-range exchange interaction results from the interaction of exciton with the induced electromagnetic field

Bir, Aronov, Pikus (1971); Denisov, Makarov (1973)

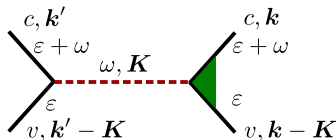
(a) Exciton



(b) Direct interaction



(c) Exchange interaction



$$V_{\alpha\beta, \mathbf{K}}^{\text{exch}} = -\frac{2\hbar\omega}{c} \Gamma_0 \mathcal{G}_{\alpha\beta}(\omega, \mathbf{K}, z=0, z'=0)$$

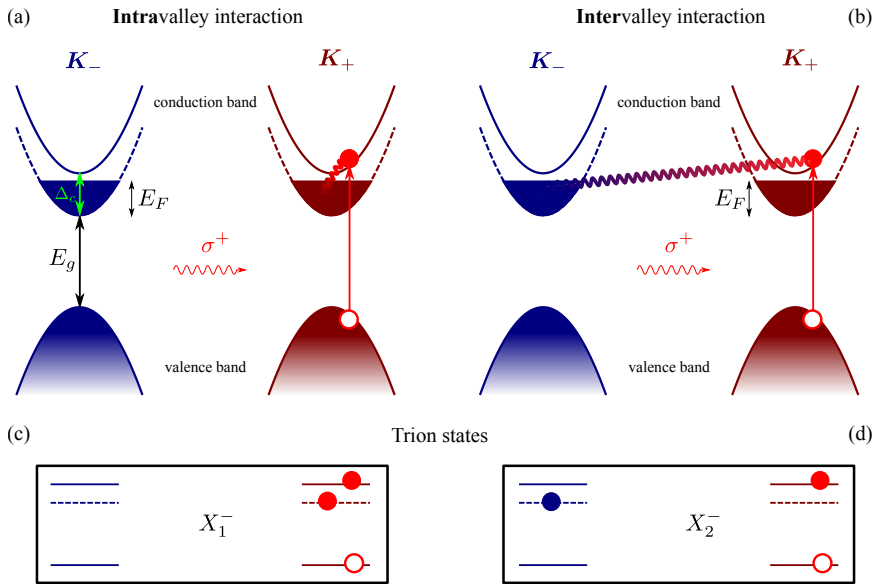
$$\Delta \mathbf{E} - \nabla(\nabla \cdot \mathbf{E}) + \left(\frac{\omega}{c}\right)^2 \varepsilon(z) \mathbf{E} = -i \frac{4\pi\omega}{c^2} \mathbf{j}(z)$$

$$E_\alpha(z) = i \frac{4\pi\omega}{c^2} \int \mathcal{G}_{\alpha\beta}(\omega; \mathbf{K}; z, z') j_\beta(z') dz'$$

$$\det \left\{ \delta_{\alpha\beta} - \frac{2i\omega_0}{c} \frac{i\Gamma_0}{\omega - \omega_0 + i\Gamma} \mathcal{G}_{\alpha\beta}(\omega_0, \mathbf{K}; 0, 0) \right\} = 0$$

Fermi-polaron concept (pedestrian approach) — I

J. Chem. Phys. **153**, 034703 (2020)



Attractive “impurity” in a Fermi-sea: $E_{b,X} \sim 300 \text{ meV} \gg E_{b,T} \sim 30 \text{ meV}$

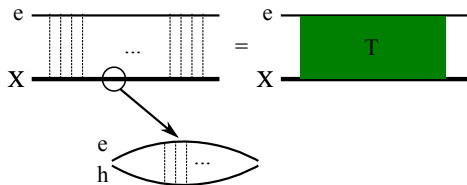
Fermi-polaron concept (pedestrian approach)

Exciton-electron scattering matrix

$$G(\varepsilon, \mathbf{k}) = \frac{1}{\varepsilon - E - \frac{\hbar^2 k^2}{2m_x} + i0}$$

$$T(\varepsilon, \mathbf{k}) = V + V \sum_{\mathbf{p}} (1 - n_{\mathbf{p}}) G \left(\varepsilon - \frac{\hbar^2 p^2}{2m_e}, \mathbf{k} - \mathbf{p} \right) T(\varepsilon, \mathbf{k})$$

$$E_{b,T} \approx E_{b,X} \exp \left(\frac{1}{DV} \right)$$



Bound state wavefunction

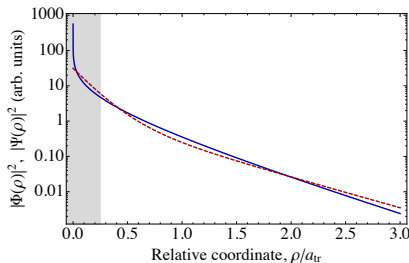
trion (var.): $\varphi(\rho_1, \rho_2) \propto e^{-\rho_1/a_x - \rho_2/a_{tr}} + e^{-\rho_2/a_x - \rho_1/a_{tr}}$

$$\rho_1 = \mathbf{r}_{e,1} - \mathbf{r}_h, \rho_2 = \mathbf{r}_{e,2} - \mathbf{r}_h$$

FP (short-range): $\Phi(\rho) \propto K_0(\rho/a_{tr}), \quad a_{tr} = \sqrt{\frac{\hbar^2}{2mE_{b,T}}}$

$$\rho = \mathbf{r}_e - \mathbf{r}_x$$

beyond short-range: Fey et al. (2020); Efimkin et al. (2021)



Fermi-polaron concept (pedestrian approach)

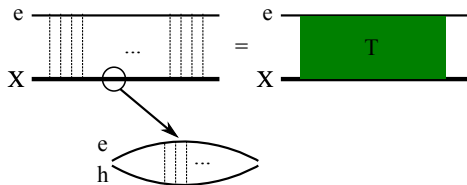
J. Chem. Phys. **153**, 034703 (2020)

Exciton-electron scattering matrix

$$G(\varepsilon, \mathbf{k}) = \frac{1}{\varepsilon - E - \frac{\hbar^2 k^2}{2m_x} + i0}$$

$$T(\varepsilon, \mathbf{k}) = V + V \sum_{\mathbf{p}} (1 - n_{\mathbf{p}}) G \left(\varepsilon - \frac{\hbar^2 p^2}{2m_e}, \mathbf{k} - \mathbf{p} \right) T(\varepsilon, \mathbf{k})$$

$$E_{b,T} \approx E_{b,X} \exp \left(\frac{1}{DV} \right)$$



Fermi-polarons

$$\Sigma = \sum_{\mathbf{k}} n_{\mathbf{k}} T \approx N_e T$$

$$\hbar\omega = E_X - E_{b,T}^b - \frac{E_F}{E_{b,T}}$$

$$f = \frac{E_F}{E_{b,T}} f_X$$

$$\mathcal{G}_x(\varepsilon, \mathbf{k}) = \text{---} = \text{---} + \text{---}$$

Suris (2001, 2003); Schmidt et al. (2012); Efimkin & MacDonald (2017)

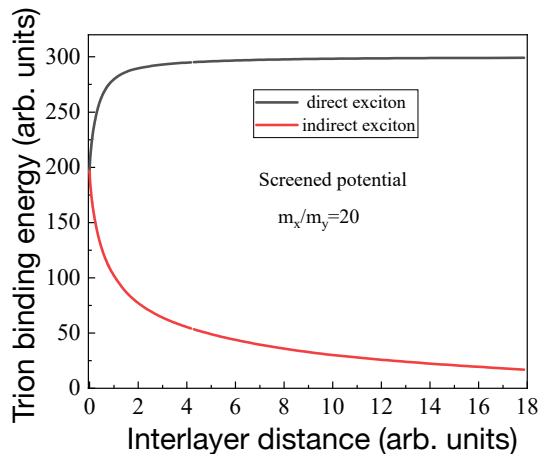
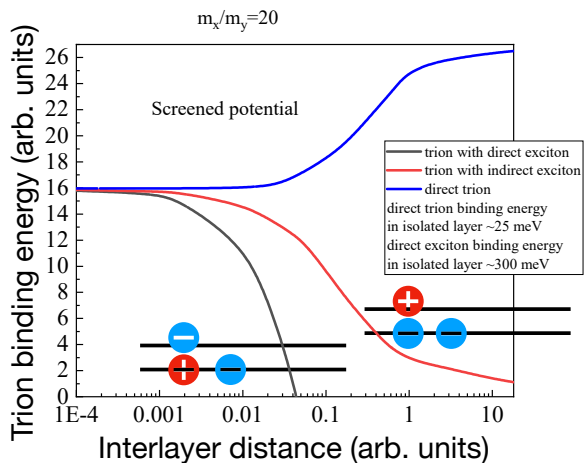
Ansatz manybody wavefunction

$$\Psi_{\mathbf{k}} = \varphi(\mathbf{k}) X_{\mathbf{k}}^{\dagger} |0\rangle + \sum_{\mathbf{p}, \mathbf{q}} \underbrace{F_{\mathbf{p}, \mathbf{q}}(\mathbf{k}) X_{\mathbf{k}+\mathbf{q}-\mathbf{p}}^{\dagger} e_{\mathbf{p}}^{\dagger}}_{\text{trion}} \underbrace{e_{\mathbf{q}}}_{\text{FS-hole}} |0\rangle$$

Suris (2003), Chevy (2006)

Trions in van der Waals antiferromagnet CrSBr: theory

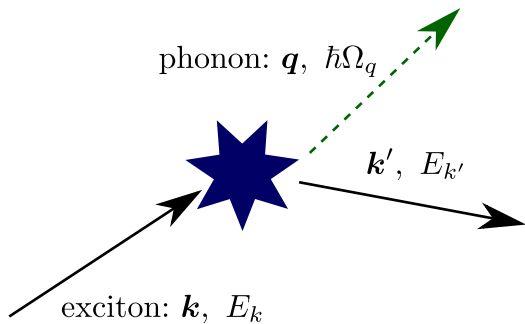
Strongly anisotropic spectrum + spin-layer locking



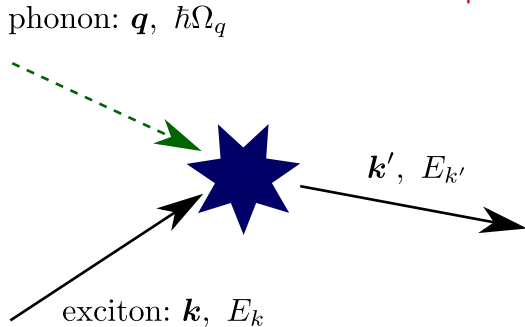
by courtesy of Marina Semina

Scattering rates

Emission



Absorption



Quasi-elastic scattering

at $k_B T \gg Ms^2 \sim 100 \mu\text{eV}$ the involved phonon energy $\hbar\Omega_q \ll k_B T$
(M is the exciton mass, s is the speed of sound)

$$\frac{1}{\tau_p} = \frac{2\pi}{\hbar} \sum_{\mathbf{q}} |M_{\mathbf{k}'\mathbf{k}}^{\mathbf{q}}|^2 (1 - \cos\theta) (1 + 2n_q) \delta(E_k - E_{k'}) = c \frac{k_B T}{\hbar} \quad (c \sim 1)$$

Energy relaxation rate:
$$\frac{1}{\tau_e} = \frac{2M^2(D_c - D_v)^2}{\hbar^3 \rho} \sim \frac{1}{10 \text{ ps}} \ll \frac{1}{\tau_p} \quad @ T \gtrsim 2 \text{ K}$$

Time scales

Quasielasticity:

$$\Delta\epsilon \sim \sqrt{k_B T M s^2} \ll k_B T \Rightarrow \delta\epsilon^2(t) \sim (\Delta\epsilon)^2 \frac{t}{\tau}$$

Momentum relaxation time

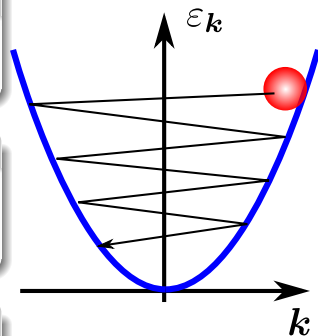
$$\tau = \frac{M s^2}{k_B T} \tau_0, \quad \tau_0^{-1} = \frac{M^2 (\Xi_c - \Xi_v)^2}{\rho \hbar^3}$$

Energy relaxation time

$$\delta\epsilon(\tau_\epsilon) \sim k_B T \Rightarrow \tau_\epsilon = \frac{\tau_0}{2} \gg \tau$$

Phase relaxation time

$$\delta\epsilon(\tau_\phi) \sim \frac{\hbar}{\tau_\phi} \Rightarrow \tau_\phi \sim \left[\frac{\hbar^2 \tau_0}{(k_B T)^2} \right]^{1/3} \Rightarrow \frac{\tau_\phi}{\tau} \propto T^{1/3}$$



$$\tau_\epsilon \gg \tau_\phi \gg \tau$$

Altshuler, Aronov, Khmel'nitsky (1981)

Acoustic phonon scattering: quantum effects get stronger with the temperature increase

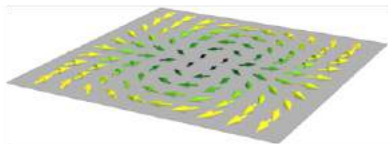
Various scattering mechanisms

Scattering mechanism	$D_{cl}(T)$	τ_ϕ/τ	$\delta D(T) < 0$
LA	T^0	$T^{1/3}$	↓
LA + disorder	T	$T^{-2/3}$	↑
flexural, 1ML	T^0	T^0	const
flexural, 2ML, $T < T_0$	T^0	$T^{2/3}$	↓
flexural, 2ML, $T > T_0$	$T^{3/2}$	$T^{-5/6}$	↑
LA, overdamped	T^0	$T^{1/2}$	↓
LA + free e/h	T^0	T/n	↓

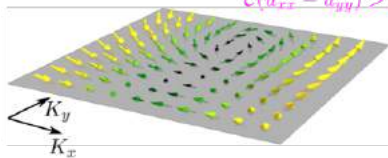
APL 121, 192106 (2022)

Effective magnetic field: details

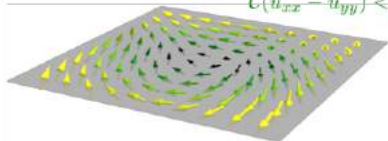
(a) No strain



(b) Strain $B(u_{xx} - u_{yy}) > 0$
 $C(u_{xx} - u_{yy}) > 0$



(c) Strain $B(u_{xx} - u_{yy}) < 0$
 $C(u_{xx} - u_{yy}) < 0$



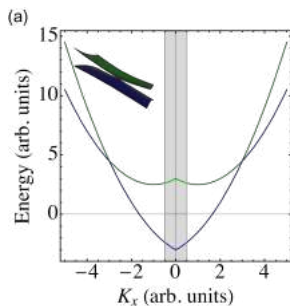
Pseudospin Hamiltonian $\mathcal{H} = \frac{\hbar}{2}(\hat{\sigma} \cdot \mathbf{\Omega})$

$$\Omega_x = \mathcal{A}(K)(K_x^2 - K_y^2) + \mathcal{B}(u_{xx} - u_{yy})$$

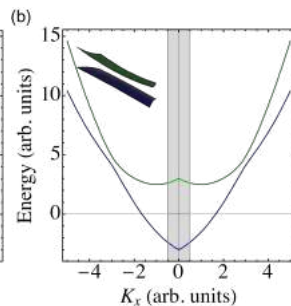
$$\Omega_y = 2\mathcal{A}(K)K_xK_y + 2\mathcal{B}u_{xy}$$

$$\Omega_z = \mathcal{C}[(u_{xx} - u_{yy})K_x - 2u_{xy}K_y]$$

$\mathcal{C} = 0$



$\mathcal{C} \neq 0$



Splitting at $\mathbf{K} = 0$, formation of Dirac points at $\mathbf{K} \neq 0$