Calculation of the Linear-Absorption Spectrum of an Ideal Two-Dimensional System of $\mathrm{MoS_2}$

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Supervisors
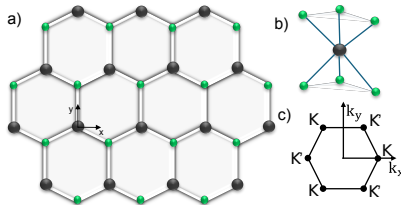Dr. Huynh Thanh Duc [2]

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Outline

Group VI-B Transition Metal Dichalcogenides (TMD) are compound semiconductors of the type MX_2. :

Figure: Structure of TMD and its first Brillouin Zone. M is Transition Metal atom (black dots), X is Dichalcogenide atom (green dots)

Transition Metal Dichalcogenide Monolayer

Properties

- They are stable in both mono- and few-layer in the air at room temperature.

- They are semiconductors with a direct band gap in visible light range.

- Their crystal structure has no center of inversion.

- Strong spin-orbit coupling (SOC) in TMD monolayers leads to spin splitting of hundreds meV.

$\Rightarrow$ Promising materials in electronic and optoelectronic applications (for example: solar cells with energy conversion efficiency surpassing the Schockley-Queisser limit).

Exciton Binding Energy In TMD

What is the purpose of calculating the linear absorption spectrum?
$\rightarrow$ Exiton binding energy

Overview

- TMD is a low-dimensional material $\rightarrow$ huge exciton binding energy in compared with bulk semiconductors $\rightarrow$ electron-hole Coulomb interaction need to be calculated and taken into account.

- Early theories predict large binding energy ($0.5 - 1$ eV) in compare with experiment ($0.2 - 0.5$ eV) $\Rightarrow$ more precise calculations to match with the experiments.

- Theories only fit bandstructure around highly symmetry points such as K/K', not on entire BZ $\Rightarrow$ a models for fitting in the entire BZ.

Tight-binding (TB) wave function have the form:

$$|\psi_{\lambda\mathbf{k}}(\mathbf{r})\rangle = \sum_{\alpha} c_{\lambda\alpha}(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} |\phi_{\alpha}(\mathbf{r} - \mathbf{R})\rangle. \tag{1}$$

The Time-independence Schrödinger equation:

$$H_{1e} \sum_{\alpha} c_{\lambda\alpha}(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} |\phi_{\alpha}(\mathbf{r} - \mathbf{R})\rangle = \varepsilon_{\lambda}(\mathbf{k}) \sum_{\alpha} c_{\lambda\alpha}(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} |\phi_{\alpha}(\mathbf{r} - \mathbf{R})\rangle.$$

Multiply with $\langle\phi_{\beta}|$ on the left and take integral over $\mathbf{r}$

$$\sum_{\alpha} [H_{\beta\alpha}^{TB}(\mathbf{k}) - \varepsilon_{\lambda}(\mathbf{k})\delta_{\beta\alpha}] c_{\lambda\alpha}(\mathbf{k}) = 0. \tag{2}$$

In which the Tight-binding Hamiltonian matrix elements:

$$H_{\beta\alpha}^{TB}(\mathbf{k}) = \sum_{\mathbf{R}} \langle\phi_{\beta}(\mathbf{r})| H_{1e} |\phi_{\alpha}(\mathbf{r} - \mathbf{R})\rangle. \tag{3}$$
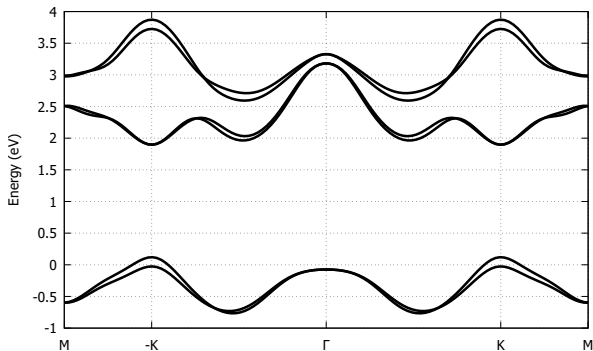
Use basic functions of d-type orbitals:

$$|\phi_1\rangle = d_{z^2}, |\phi_2\rangle = d_{xy}, |\phi_3\rangle = d_{x^2-y^2}.$$

Three-band TB Hamiltonian with SOC has the form:

$$H_{6\times6}^{TB}(\mathbf{k}) = \begin{bmatrix} H_{3\times3}^{TB}(\mathbf{k}) + \gamma L_z & 0 \\ 0 & H_{3\times3}^{TB}(\mathbf{k}) - \gamma L_z \end{bmatrix}, \quad L_z = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{bmatrix}.$$

Figure: Band structure of MoS_2 monolayer[1]

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[1]Liu et al., "Three-band tight-binding model for monolayers of group-VIB transition metal dichalcogenides".

Multiband semiconductor Bloch equations (SBE) with Coulomb interaction in Hatree Fock approximation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{\lambda\lambda'}(\mathbf{k}, t) = -\frac{i}{\hbar}(\varepsilon_\lambda(\mathbf{k}) - \varepsilon_{\lambda'}(\mathbf{k}))\rho_{\lambda\lambda'}(\mathbf{k})$$
$$- i\sum_\mu (\Omega_{\lambda\mu}(\mathbf{k})\rho_{\mu\lambda'}(\mathbf{k}, t) - \rho_{\lambda\mu}(\mathbf{k}, t)\Omega_{\mu\lambda'}(\mathbf{k})) \quad (4)$$
$$+ \frac{\rho_{\lambda\lambda'}(\mathbf{k}, t)}{T_2}(1 - \delta_{\lambda\lambda'}),$$

where

$$\Omega_{\mu\nu}(\mathbf{k}) = \frac{1}{\hbar}\left(\frac{e}{m}\mathbf{A}(t)\mathbf{p}_{\mu\nu}(\mathbf{k}) - \sum_{\alpha\beta\mathbf{q}} W_{\mathbf{k},\mathbf{k}+\mathbf{q},\mathbf{q}}^{\alpha\mu\beta\nu}\rho_{\beta\alpha}(\mathbf{k} + \mathbf{q})\right), \quad (5)$$

$$\mathbf{p}_{\mu\nu}(\mathbf{k}) = \frac{m}{\hbar}\sum_{\alpha,\beta} c_{\mu\alpha}^*(\mathbf{k})\nabla_\mathbf{k} H_{\alpha\beta}^{TB}(\mathbf{k})c_{\nu\beta}(\mathbf{k}), \quad (6)$$

$$W_{\mathbf{k},\mathbf{k}',\mathbf{q}}^{\alpha\beta\gamma\delta} = \frac{e^2}{2\varepsilon\varepsilon_0 L^2}\frac{1}{|\mathbf{q}|}\sum_{\mu,\nu} c_{\alpha\mu}^*(\mathbf{k} + \mathbf{q})c_{\delta\mu}(\mathbf{k})c_{\beta\nu}^*(\mathbf{k}' - \mathbf{q})c_{\gamma\nu}(\mathbf{k}') \quad (7)$$

Dipole matrix elements can be obtained through:

$$\vec{\xi}_{\mu\nu}(\mathbf{k}) = \frac{-i\hbar}{m} \frac{\mathbf{p}_{\mu\nu}(\mathbf{k})}{\varepsilon_\mu(\mathbf{k}) - \varepsilon_\nu(\mathbf{k})}. \quad (8)$$

for $\mu \neq \nu$

Time-dependent interband polarization density:

$$\begin{aligned}
\mathbf{P}(t) &= \frac{e}{L^2} \sum_{\mathbf{k}} \mathrm{Tr} \left[\vec{\xi}(\mathbf{k}) \rho(\mathbf{k}, t) \right] \\
&= \frac{e}{L^2} \sum_{\mathbf{k}\lambda\lambda'} \vec{\xi}_{\lambda\lambda'}(\mathbf{k}) \rho_{\lambda'\lambda}(\mathbf{k}, t).
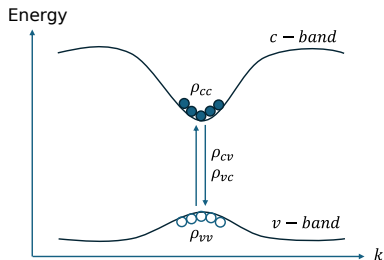\end{aligned}$$

$$(9)$$

Figure: Density matrix element illustration
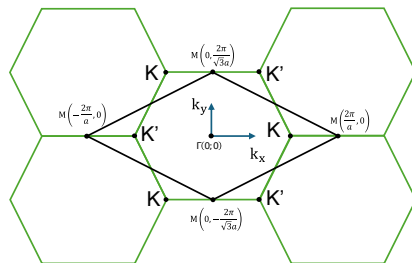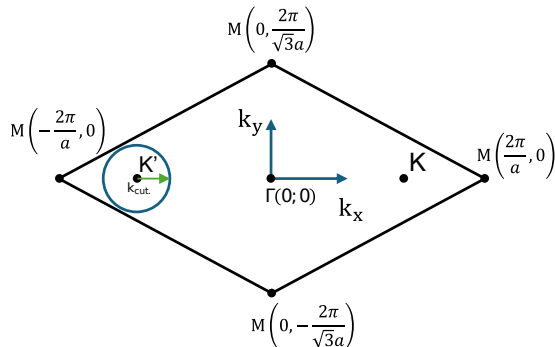
Evaluate Numerically Sum Over k-Space

Figure: Rhombus primitive cell

Numerical evaluate

$$\sum_{\mathbf{k}} ... \rightarrow \frac{L^2}{4\pi^2} \int\int_{BZ} dk_x dk_y ... \qquad (10)$$

k-Cutoff

For k-point around **K**' point

$$W_{\mathbf{k},\mathbf{k'},\mathbf{q}}^{\alpha\mu\beta\nu} \approx W_{\mathbf{k},\mathbf{k'},\mathbf{q}}^{\alpha\mu\beta\nu} \theta(k_{cut.} - |\mathbf{k} - \mathbf{k}_{K'}|)\theta(k_{cut.} - |\mathbf{k'} - \mathbf{k}_{K'}|). \qquad (11)$$

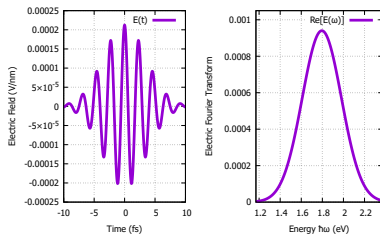The same for k-point around **K** point

Electromagnetic Field

The electric field has a Gaussian envelope form:

$$\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega_0 t) e^{-\frac{t^2}{\tau_L^2}} \qquad (12)$$

- small E_0 : $\rho_{cc}(\mathbf{k}) \to 0$

- $\hbar\omega_0 = E_{gap.}$

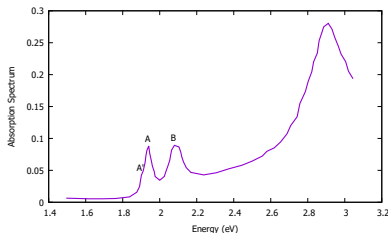- small $\tau_L \to$ rounder Fourier transform's peak around ω_0

Absorption is obtain by[2]:

$$\alpha(\omega) \propto \frac{P(\omega)}{E(\omega)}. \qquad (13)$$

[2]Haug and Koch, *Quantum Theory Of The Optical And Electronic Properties Of Semiconductors (5th Edition)*.

Experiment measure:

Figure: Measured Absorption Spectrum of MoS_2 at $T = 5K$ extracted from Ref.[3]

- Two resonance labeled by A and B are Exciton peaks (band split due to SOC).

- Weak trion peak near A labeled by A'

To fit with experiment, we can change:

- Relative permittivity ε

- Dephasing time T_2

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[3]Zhang et al., "Absorption of light by excitons and trions in monolayers of metal dichalcogenide MoS_2".
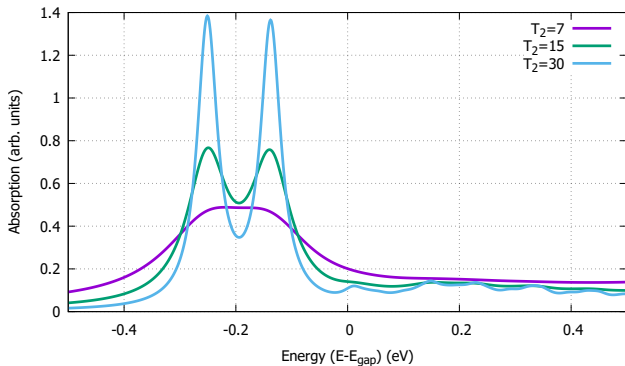
- Choosing the T_2 for clearer Exciton peak.

- The bigger T_2, the clearer main Exciton peaks $\rightarrow$ confirm two peak.

- At $T_2 = 30$ *fs* show other smaller peaks $\rightarrow$ predict other peaks.
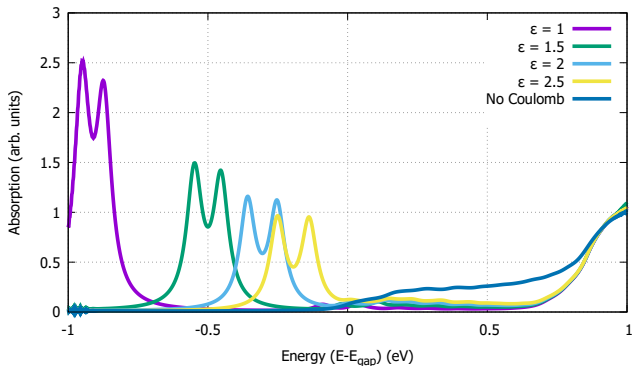
- Choosing the ε for fitting with the experiment.

- For 3-band TB model: $\varepsilon \in (1.5, 2.5)$ is in good agreement with exciton binding energy of $E_{bind.} = 0.2 - 0.5 eV$

Summary:

- From three-band TB + SBE $\rightarrow$ Linear Absorption Spectrum

- Confirm the Exciton binding energy in monolayer MoS_2 in agreement with experimental data, and predict smaller exciton peaks.

Further research:

- High Harmonic Generation

- High-order Side-band Generation

- Photovoltaic effect

Thank you for your listening.