Calculation of the Linear-Absorption Spectrum of an Ideal Two-Dimensional System of MoS_2

Vo Chau Duc Phuong [1]

Supervisors
Dr. Huynh Thanh Duc [2]

[1]University of Science, Ho Chi Minh city

[2]Institute of Applied Mechanics and Informatics

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Outline

Transition Metal Dichalcogenides Monolayers

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

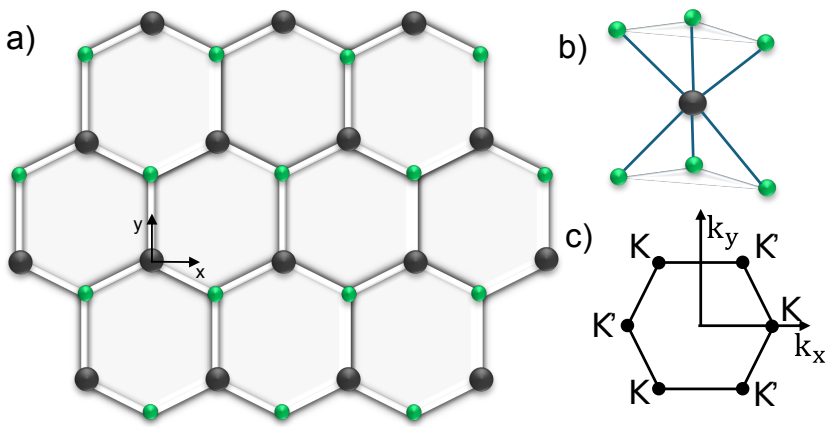


Figure: Structure of TMD and its first Brillouin Zone. M is Transition Metal atom (black dots), X is Dichalcogenide atom (green dots)

Transition Metal Dichalcogenide Monolayers

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

Exciton binding energy can be extracted from the linear absorption spectrum

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 has 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 $\mathbf{r}$

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

Tight-binding Hamiltonian matrix elements:

$$H^{TB}_{\beta\alpha}(\mathbf{k}) = \sum_{\mathbf{R}} \langle\phi_{\beta}(\mathbf{r})| H_{1e} |\phi_{\alpha}(\mathbf{r}-\mathbf{R})\rangle . \tag{3}$$

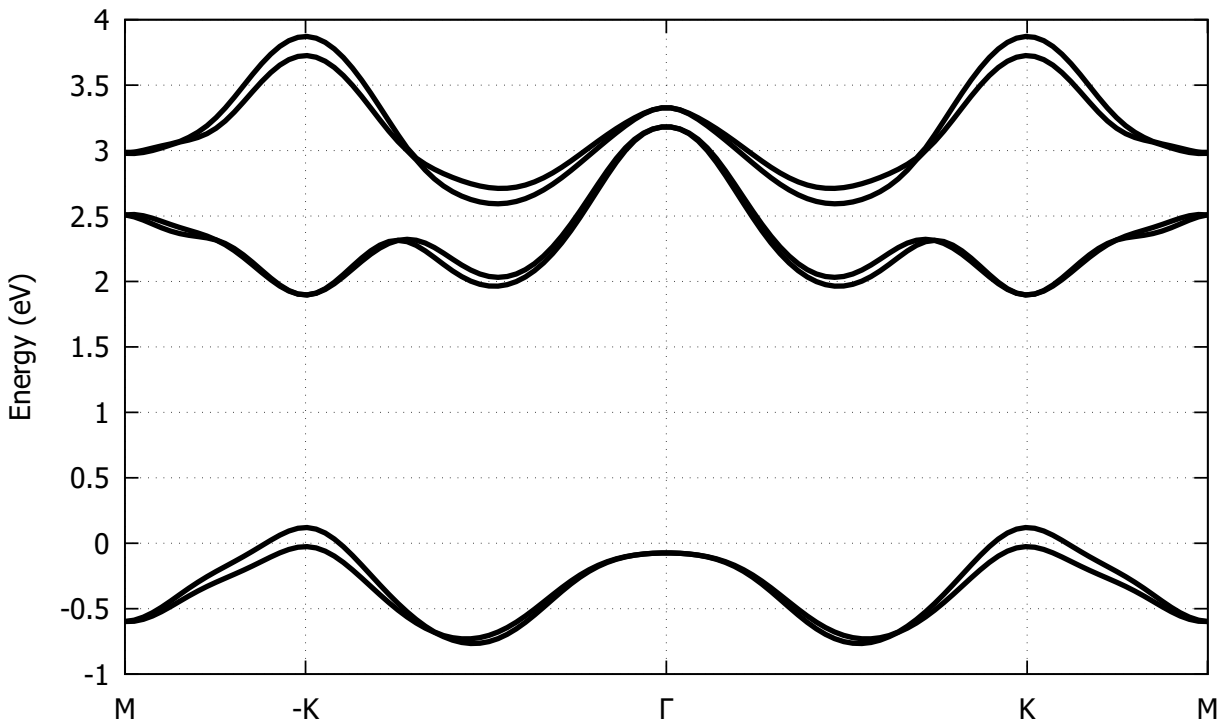
Use basic functions of d-type orbitals:

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

Three-band TB Hamiltonian with SOC has the form:

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

Figure: Band structure of MoS_2 monolayer[1]



[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:

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

where

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

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

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

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:

$$\begin{aligned}\mathbf{P}(t) =& \frac{e}{L^2}\sum_{\mathbf{k}} \mathrm{Tr}\left[\vec{\xi}(\mathbf{k})\rho(\mathbf{k},t)\right] \\ =& \frac{e}{L^2}\sum_{\mathbf{k}\lambda\lambda'} \vec{\xi}_{\lambda\lambda'}(\mathbf{k})\rho_{\lambda'\lambda}(\mathbf{k},t).\end{aligned} \quad (9)$$

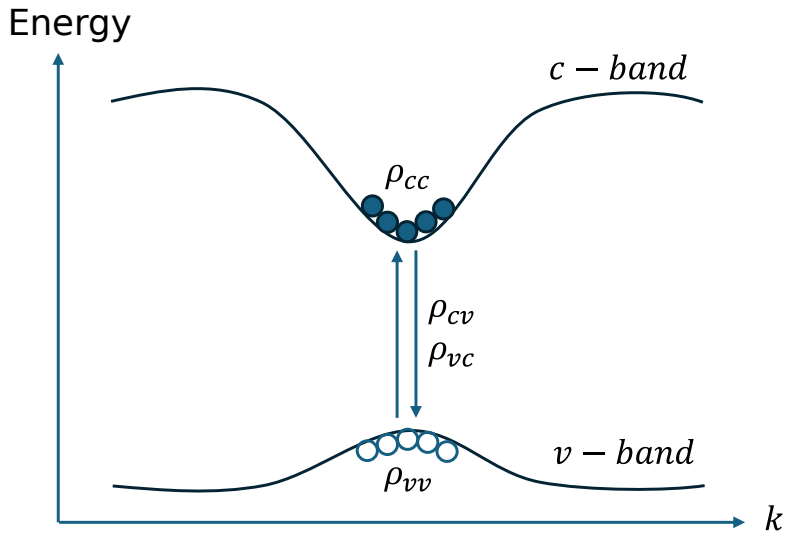


Figure: Density matrix element illustration

Numerical Evaluation of The Sum Over k-space

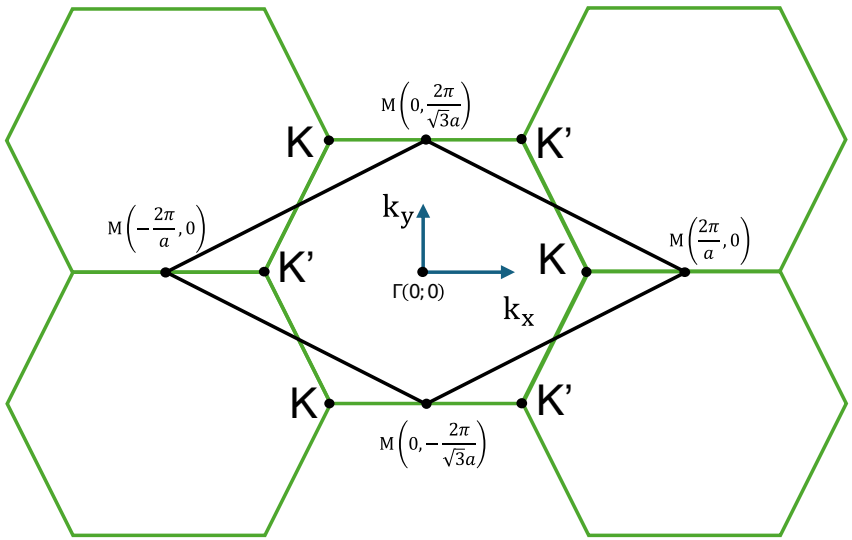
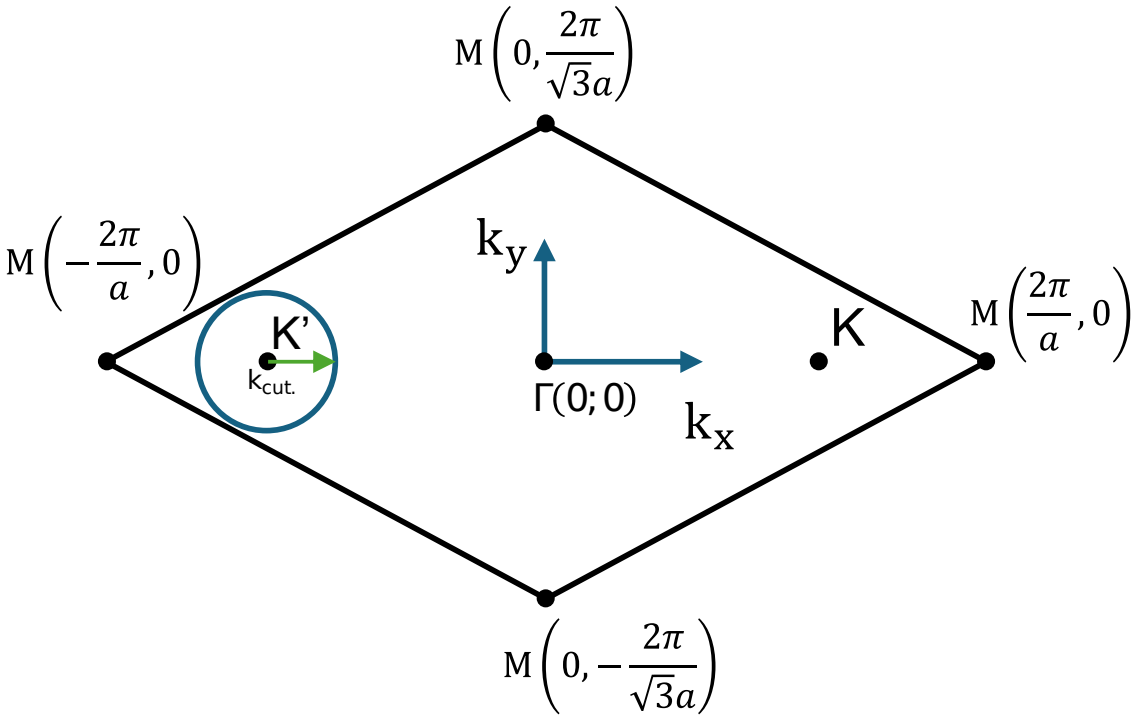


Figure: Rhombus primitive cell

$$\sum_{\mathbf{k}} \ldots \rightarrow \frac{L^2}{4\pi^2} \int \int_{BZ} dk_x dk_y \ldots \tag{10}$$

k-Cutoff



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

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

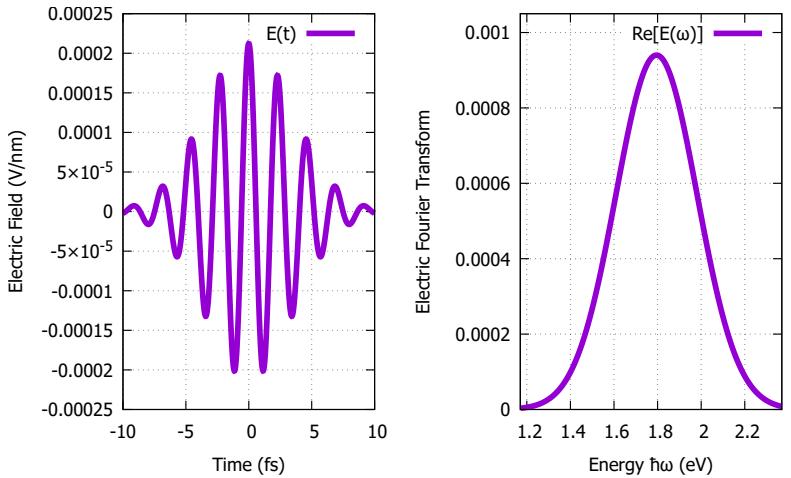
The same for k-points around **K** point

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 coefficient[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:

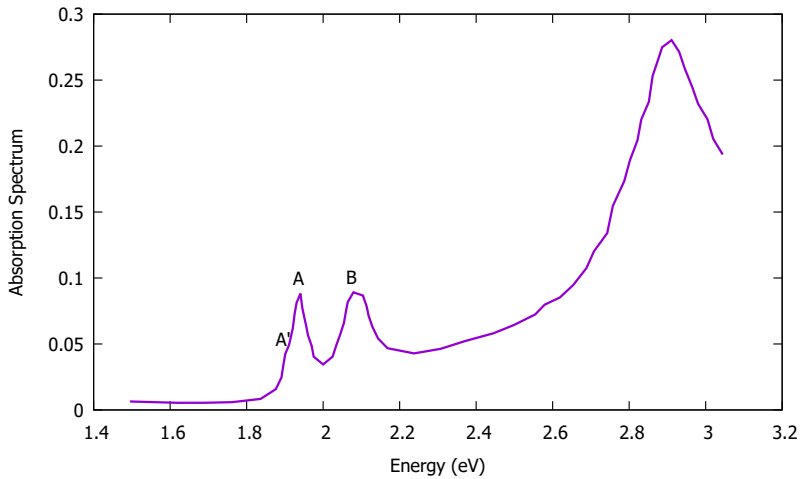


Figure: Measured Absorption Spectrum of MoS_2 at $T = 5K$ extracted from Ref.[3]

$$E_{gap} = 2.15 \pm 0.06\ eV$$

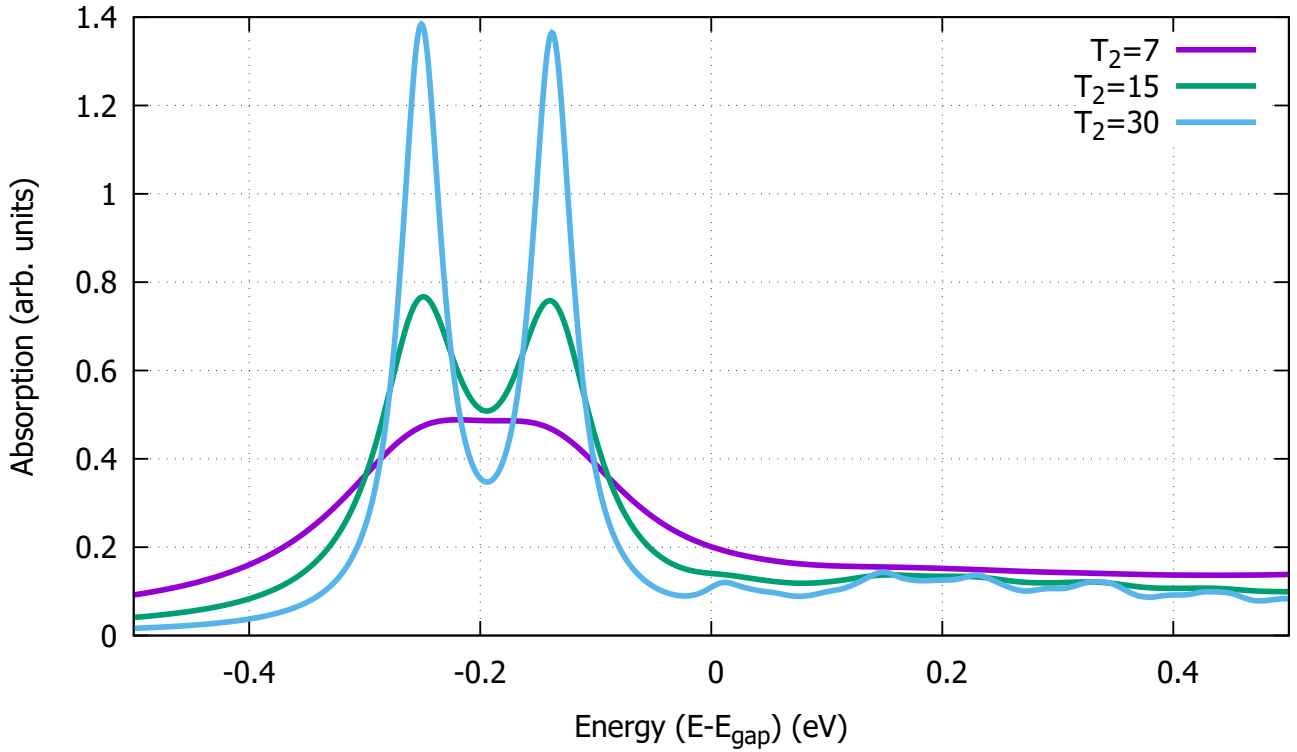
Binding energy:
$E_{bind.} = E_{gap} - E_A = 0.22\ eV$

- Two resonance labeled by A (1.93 eV) and B (2.1 eV) are exciton peaks (band split due to SOC)
- Weak trion peak near A labeled by A' (18 meV)

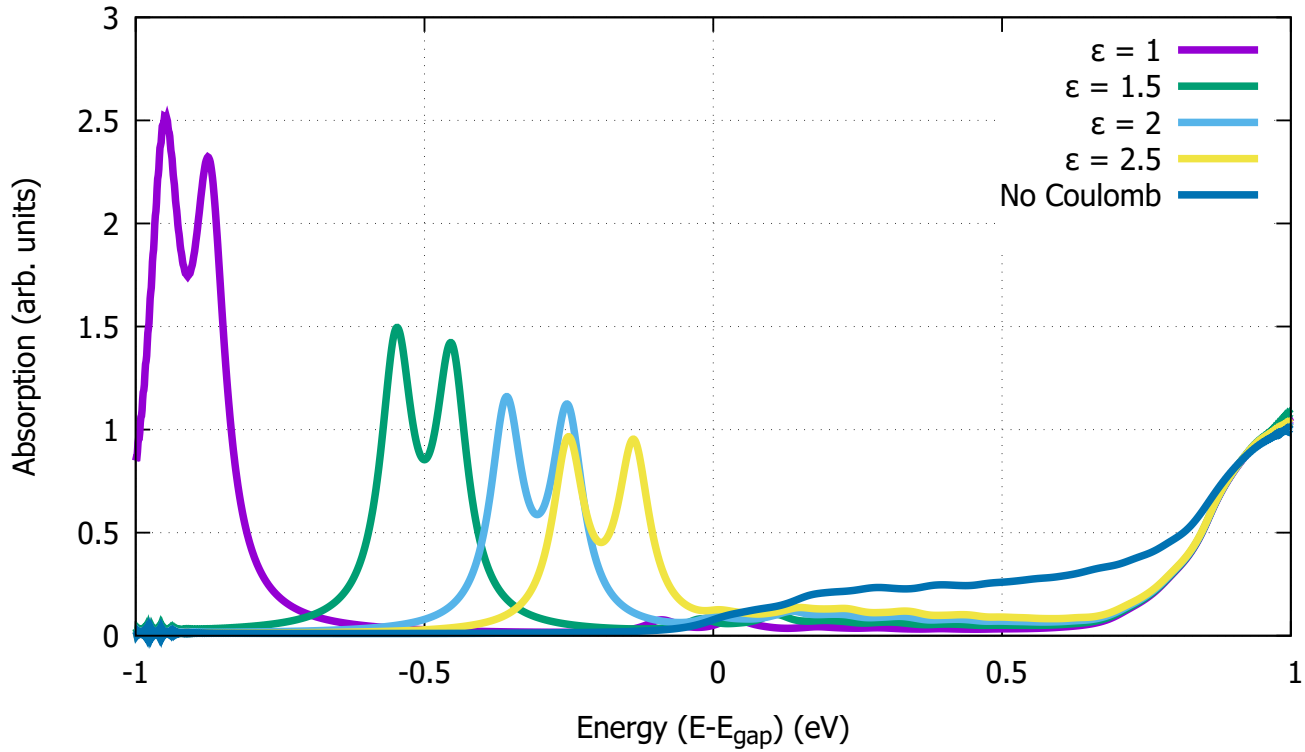
To fit with experiment, we can change:

- Relative permittivity ε
- Dephasing time T_2

[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 $E_{bind.} = 0.2 - 0.5eV$

Summary:

- From three-band TB + SBE $\rightarrow$ Linear Absorption Spectrum
- We confirm the Exciton binding energy in this model is 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.