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

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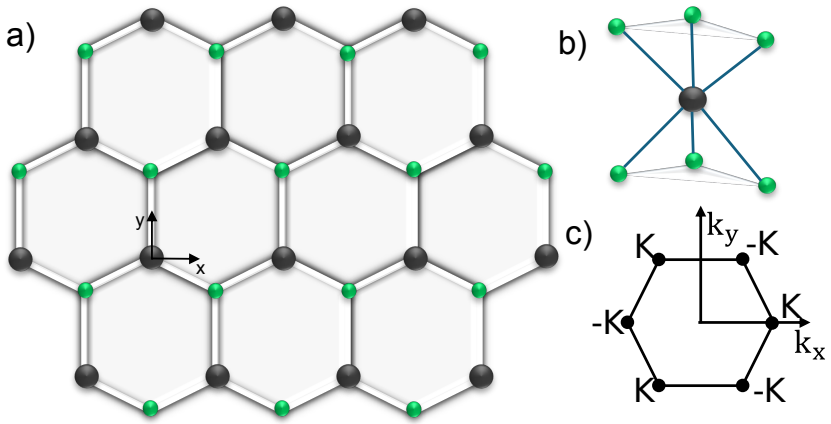
Outline

Group VI-B Transition Metal Dichalcogenide (TMD) are compound semiconductors of the type MX_2. M is Transition Metal atom (black dots), X is Dichalcogenide atom (green dots):



Transition Metal Dichalcogenide Monolayer

- 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 range.
- Its monolayer form has no center of inversion.
- Strong spin-orbit Coupling (SOC) in TMD monolayers leads to spin splitting of hundreds meV.

$\Rightarrow$ Promise material in electronic and optoelectronic applications (for example: solar cell).

Exciton Binding Energy In TMD

Why calculate the linear absorption spectrum?
$\rightarrow$ Exicton binding energy

- TMD is a low-dimensional material $\rightarrow$ huge binding energy in compare with bulk semiconductor $\rightarrow$ many-body interaction play key role $\Rightarrow$ need to be calculated and taken into account in any further many-body calculation.
- Early theories predict binding energy too large $(0.5 - 1$ eV) in compare with experiment $(0.2 - 0.5$ eV) $\Rightarrow$ need precise calculation in agreement with the experiment.
- Other theories only fit bandstructure around highly symmetry points such as K/K', not on entire BZ $\Rightarrow$ Tight-binding method for fitting on entire BZ.

Tight-binding (TB) wave function have the form of linear combination of atomic orbital (LCAO):

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

The Time-independence Schrödinger equation with LCAO included:

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

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

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

In which the Tight-binding Hamiltonian matrix elements:

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

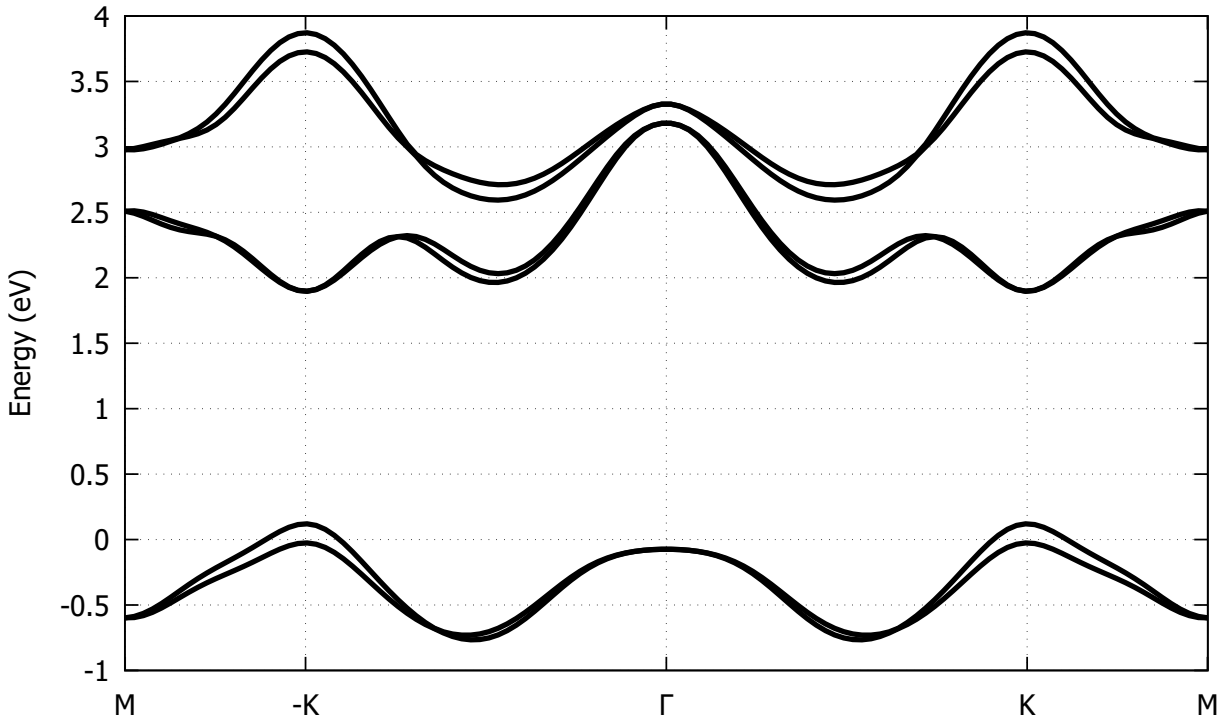
Use basic functions of d-type orbitals:

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

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



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

Multiband velocity gauge 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

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

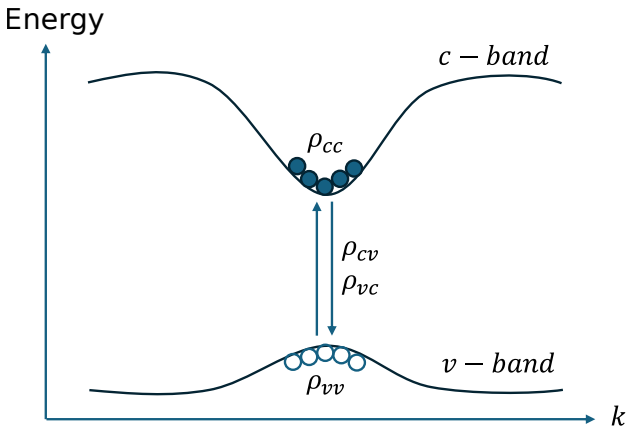
$$\mathbf{p}_{\mu\nu}(\mathbf{k}) = \frac{m}{\hbar}\sum_{\alpha,\beta} c^*_{\mu\alpha}\nabla_{\mathbf{k}}H^{TB}_{\alpha\beta}(\mathbf{k})c_{\nu\beta}(\mathbf{k}). \tag{6}$$

For $\mu \neq \nu$:

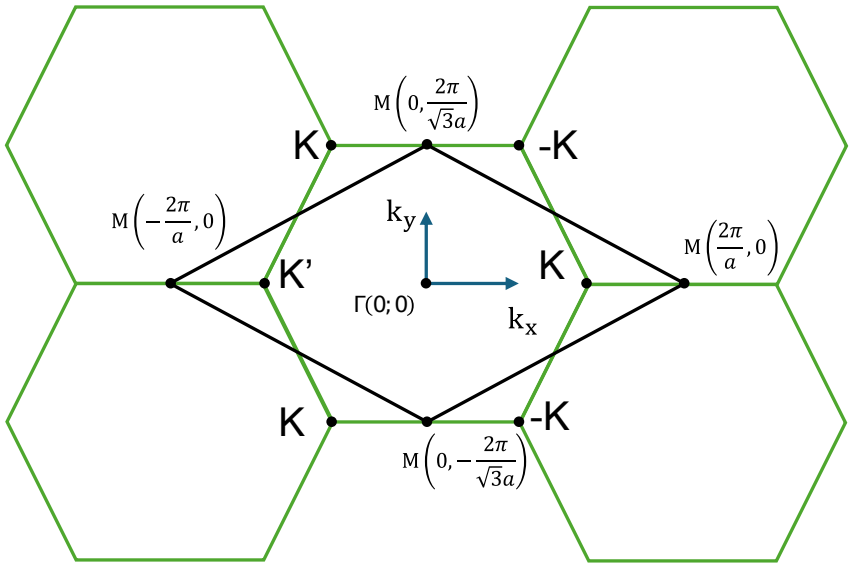
$$\vec{\xi}_{\mu\nu}(\mathbf{k}) = \frac{-i\hbar}{m} \frac{\mathbf{p}_{\mu\nu}(\mathbf{k})}{\varepsilon_\mu(\mathbf{k}) - \varepsilon_\nu(\mathbf{k})}. \quad (7)$$

Time-dependent interband polarization density:

$$\begin{aligned}\mathbf{P}(t) =& \frac{e}{L^2} \sum_{\mathbf{k}} \mathrm{Tr}\left[\vec{\xi}(\mathbf{k})\rho(\mathbf{k}, t)\right] \\ =& \frac{e}{L^2} \sum_{\mathbf{k}\lambda\lambda'} \vec{\xi}_{\lambda\lambda'}(\mathbf{k})\rho_{\lambda'\lambda}(\mathbf{k}, t).\end{aligned} \quad (8)$$

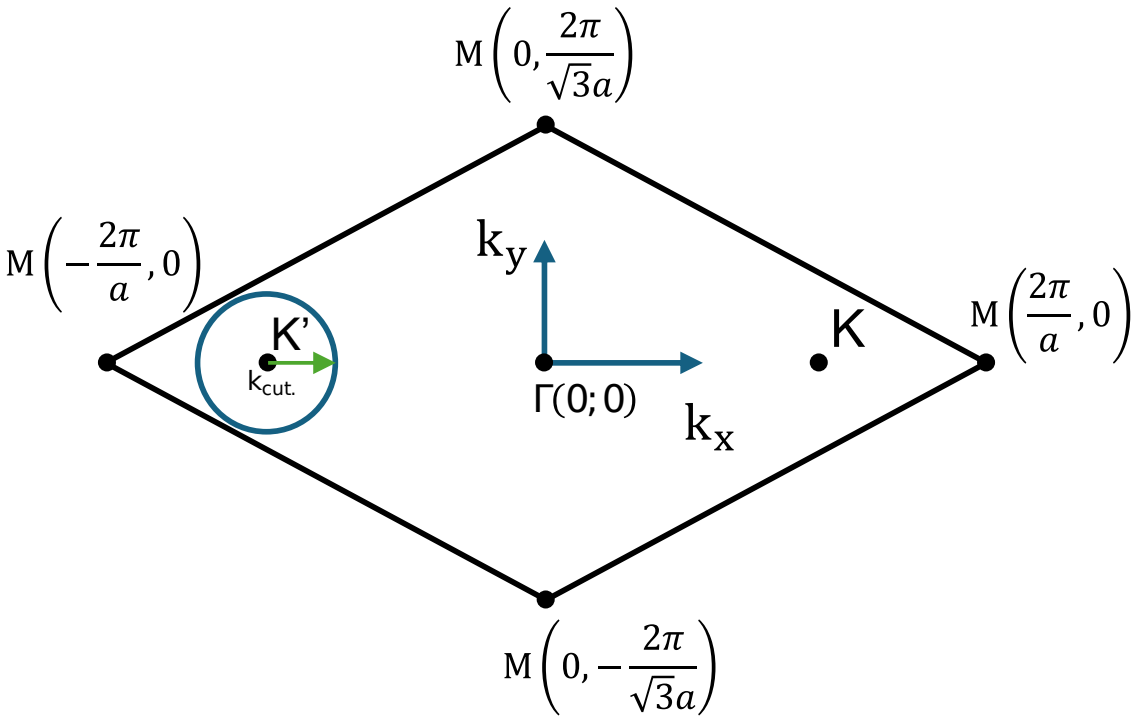


Numerical Sum Over k-Space



$$\sum_{\mathbf{k}} \ldots \rightarrow \frac{L^2}{4\pi^2} \int \int_{BZ} dk_x dk_y \ldots \tag{9}$$

k-Cutoff



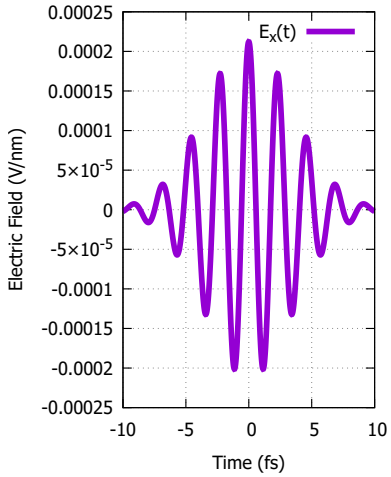
$$W^{\alpha\mu\beta\nu}_{\mathbf{k},\mathbf{k}',\mathbf{q}} \approx W^{\alpha\mu\beta\nu}_{\mathbf{k},\mathbf{k}',\mathbf{q}} \theta(k_{cut.} - |\mathbf{k} - \mathbf{k}_{K'}|)\theta(k_{cut.} - |\mathbf{k}' - \mathbf{k}_{K'}|). \qquad (10)$$

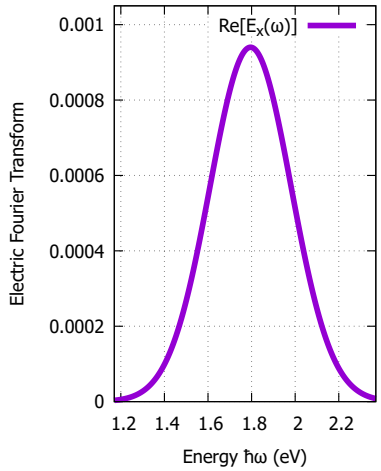
Electromagnetic Field

Electric field has Gaussian envelope form:

$$\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega_0 t) e^{-\frac{t^2}{\tau_L^2}} \qquad (11)$$

- small E_0 : $\rho_{cc}(\mathbf{k}) \to 0$
- $\hbar\omega = E_{gap.} \to$ linear absorption
- small τ_L for better range around ω_0





Absorption is obtain by[1]:

$$\alpha(\omega) \propto \frac{P(\omega)}{E(\omega)}. \qquad (12)$$

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

Experiment measure:

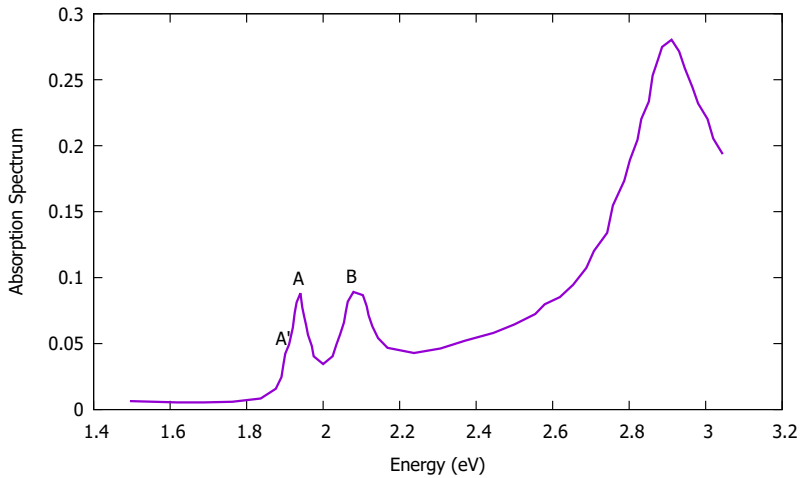
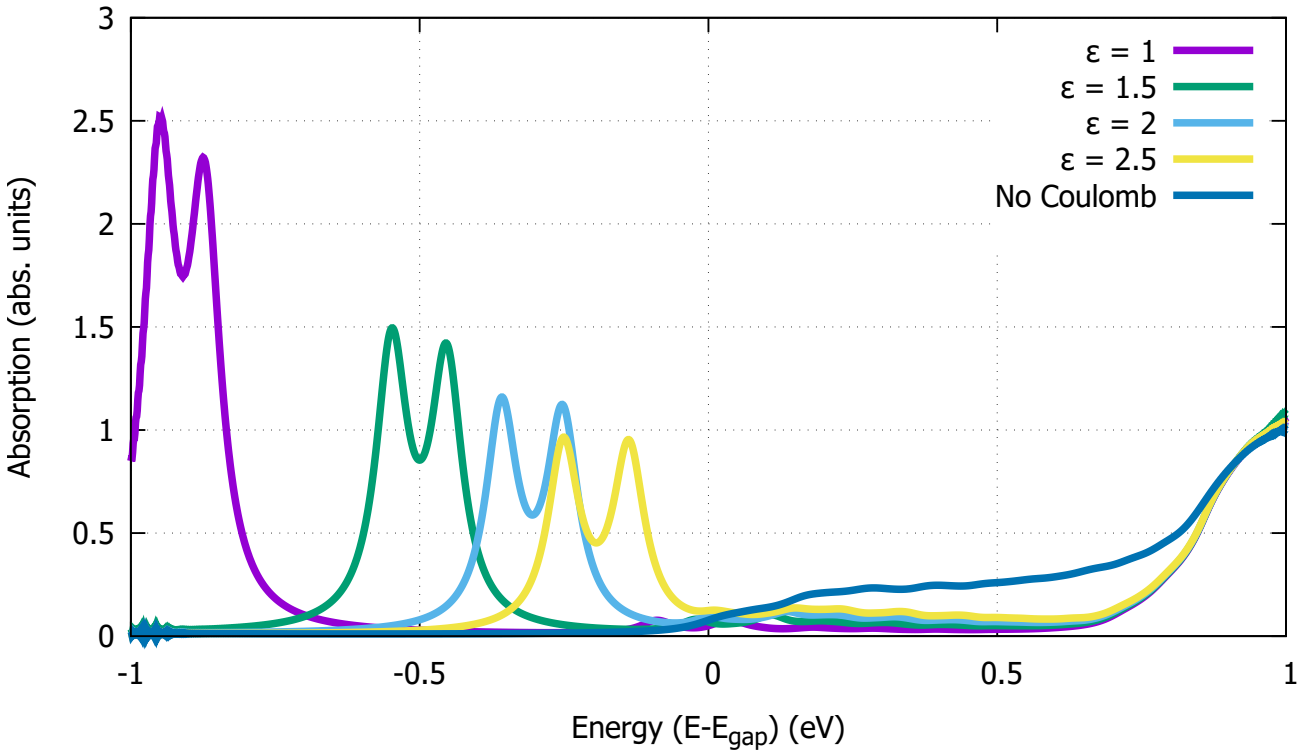


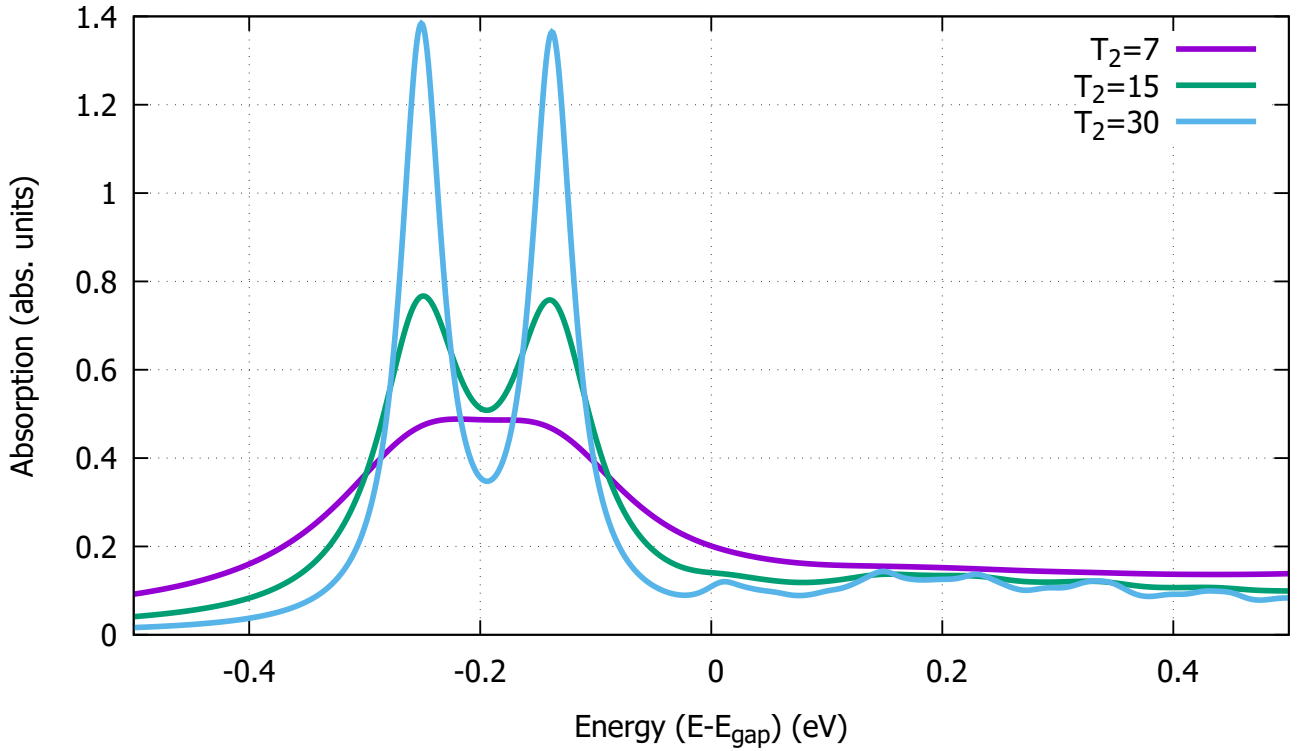
Figure: Measure Absorption Spectrum of MoS_2 at $T = 5K$ extracted from[2]

- Two resonance labeled by A and B are Exciton peaks. Show band split by SOC
- Small trion peak near A label by A'

[2] Zhang et al., "Absorption of light by excitons and trions in monolayers of metal dichalcogenide $\mathrm{Mo}{\mathrm{S}}_{2}$".



- Choosing the ε for fitting with the experiment.
- For 3-band TB model: $\varepsilon \in (1.5, 2.5)$ is good agreement with Exciton binding energy $E_{bind.} = 0.2 - 0.5eV$



- Choosing the T_2 for clearer Exciton peak.
- The bigger T_2, the clearer main Exciton peaks $\rightarrow$ confirm.
- At $T_2 = 30fs$ show other smaller exciton peaks $\rightarrow$ predict.

Summary:

- From three-band TB + SBE $\rightarrow$ Linear Absorption Spectrum
- Confirm the Exciton binding energy in monolayer $\mathrm{MoS_2}$ in contract with the experiment, predict smaller exciton peaks.

Further research:

- High Harmonic Generation
- High-order Side-band Generation
- Photovoltaic effect