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

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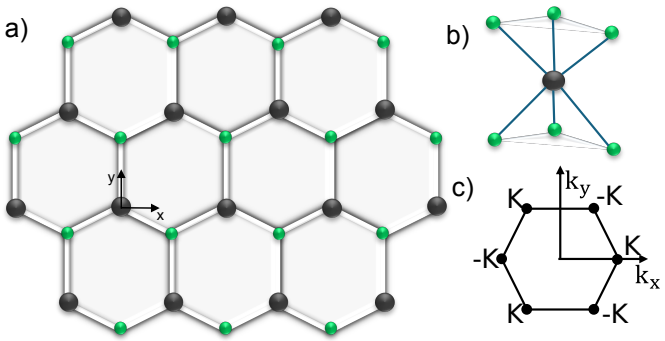
Outline

Transition Metal Dichalcogenides Monolayer

Transition Metal Dichalcogenides (TMD) are compound of the type MX_2. In these groups, we focus on the group-VIB TMD:



- TMD stable in both mono- and few-layer in the air at room temperature.
- TMD group-VIB monolayer are semiconductor with a direct band gap.
- Strong spin-orbit Coupling (SOC) in TMD monolayer leads to spin splitting of hundreds meV.

Tight-Binding (TB) wave function have the form of Linear combination of Atomic Orbital (LCAO):

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

Basic functions of d-type Orbitals: $|\phi_1\rangle = d_{z^2}, |\phi_2\rangle = d_{xy}, |\phi_3\rangle = d_{x^2-y^2}$
Time-independence independence-electron approximation 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:

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

Three-band TB Hamiltonian with SOC has the form:

$$H^{TB}_{6\times6}(\mathbf{k}) = \begin{bmatrix} H^{TB}_{3\times3}(\mathbf{k}) + \gamma L_z & 0 \\ 0 & H^{TB}_{3\times3}(\mathbf{k}) - \gamma L_z \end{bmatrix}, \quad L_z = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{bmatrix} \tag{4}$$

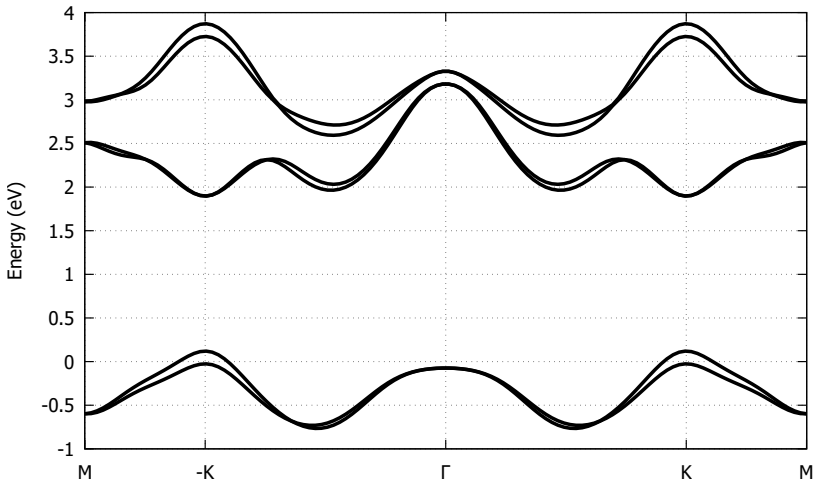


Figure: Bandstructer calculated from 3-band TB models[1]

Inter-band Polarization

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

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\rho_{\lambda\lambda'}(\mathbf{k},t) = &-\frac{i}{\hbar}(\varepsilon_{\lambda}(\mathbf{k})-\varepsilon_{\lambda'}(\mathbf{k}))\rho_{\lambda\lambda'}(\mathbf{k}) \\ &- i\sum_{\mu}(\Omega_{\lambda\mu}(\mathbf{k})\rho_{\mu\lambda'}(\mathbf{k},t)-\rho_{\lambda\mu}(\mathbf{k},t)\Omega_{\mu\lambda'}(\mathbf{k})) \\ &+ \frac{\rho_{\lambda\lambda'}(\mathbf{k},t)}{T_2}(1-\delta_{\lambda\lambda'}),\end{aligned} \tag{5}$$

where

$$\Omega_{\mu\nu}(\mathbf{k}) = \frac{1}{\hbar}\left(\frac{e}{m}\mathbf{A}(t)\mathbf{p}_{\mu\nu}(\mathbf{k}) - \sum_{\alpha\beta\mathbf{q}} W^{\alpha\mu\beta\nu}_{\mathbf{k},\mathbf{k}+\mathbf{q},\mathbf{q}}\rho_{\beta\alpha}(\mathbf{k}+\mathbf{q})\right), \tag{6}$$

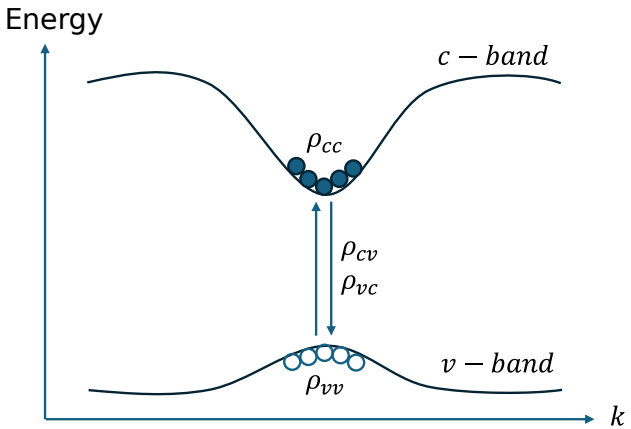
$$\mathbf{p}_{\mu\nu}(\mathbf{k}) = \frac{m}{\hbar}\sum_{\alpha,\beta} c^{*}_{\mu\alpha}\nabla_{\mathbf{k}}H^{TB}_{\alpha\beta}(\mathbf{k})c_{\nu\beta}(\mathbf{k}) \tag{7}$$

For $\mu \neq \nu$:

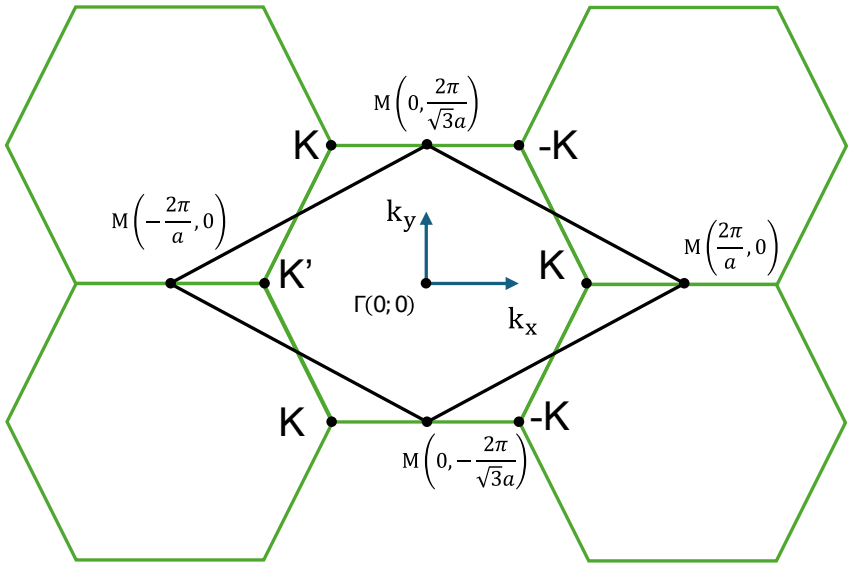
$$\vec{\xi}_{\mu\nu}(\mathbf{k}) = \frac{-i\hbar}{m} \frac{\mathbf{p}_{\mu\nu}(\mathbf{k})}{\varepsilon_{\mu}(\mathbf{k}) - \varepsilon_{\nu}(\mathbf{k})} \quad (8)$$

Time-dependence interband polarization density:

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

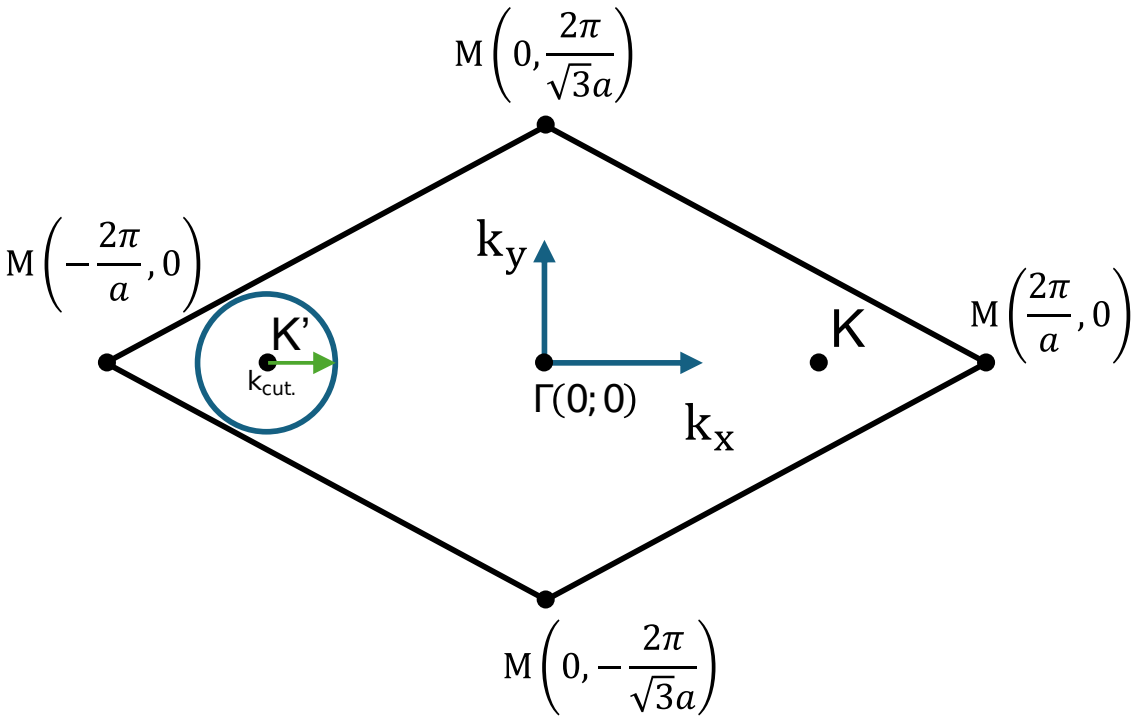


Numerical Sum Over k-Space



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

k-Cutoff

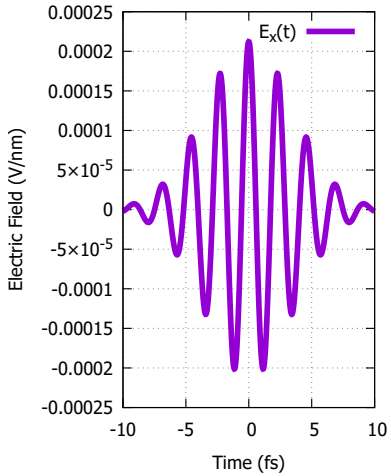


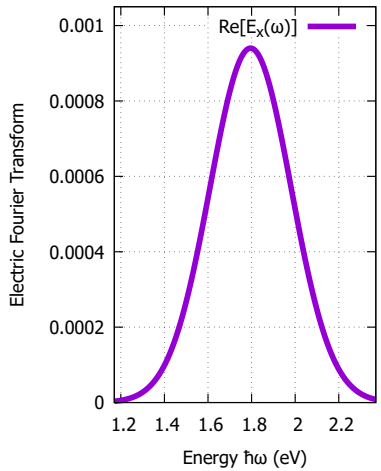
$$W^{\alpha\mu\beta\nu}_{\mathbf{k},\mathbf{k}',\mathbf{q}} \approx W^{\alpha\mu\beta\nu}_{\mathbf{k},\mathbf{k}',\mathbf{q}} \theta(k_{cut.} - |\mathbf{k} - \mathbf{k}_{K'}|)\theta(k_{cut.} - |\mathbf{k}' - \mathbf{k}_{K'}|). \qquad (11)$$

Electromagnetic has Gaussian form:

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

- small E_0
- $\hbar\omega = E_{gapp.} \rightarrow$ linear absorption
- small τ_L for better range around ω





Absorption obtain by:

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

Experiment measure:

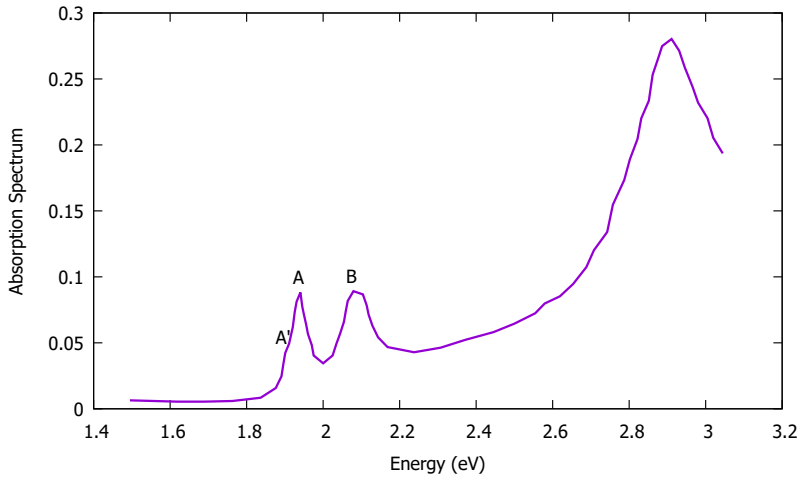
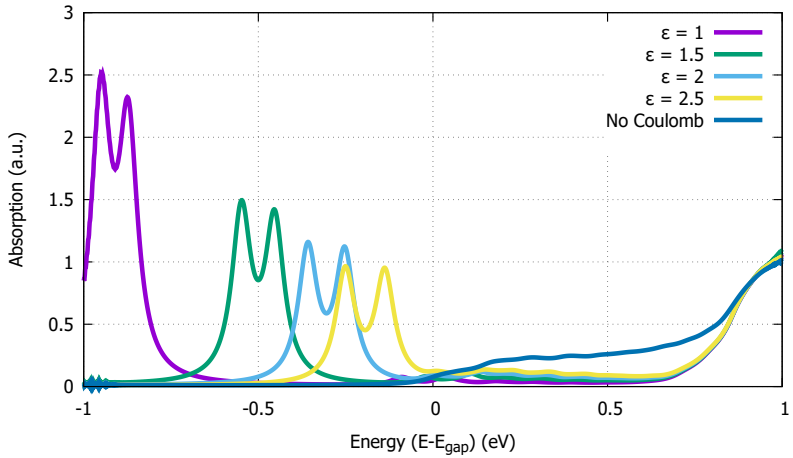
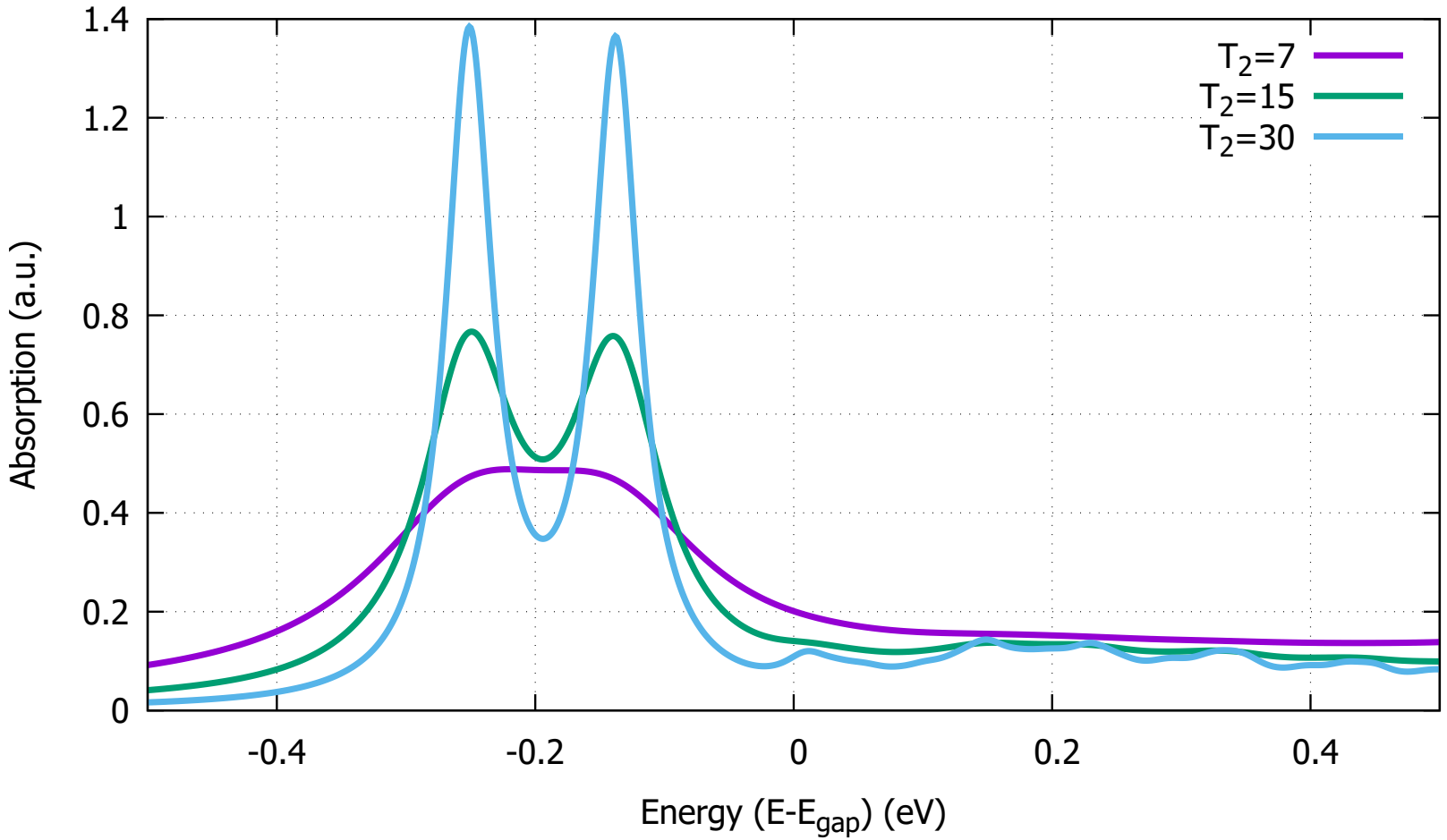


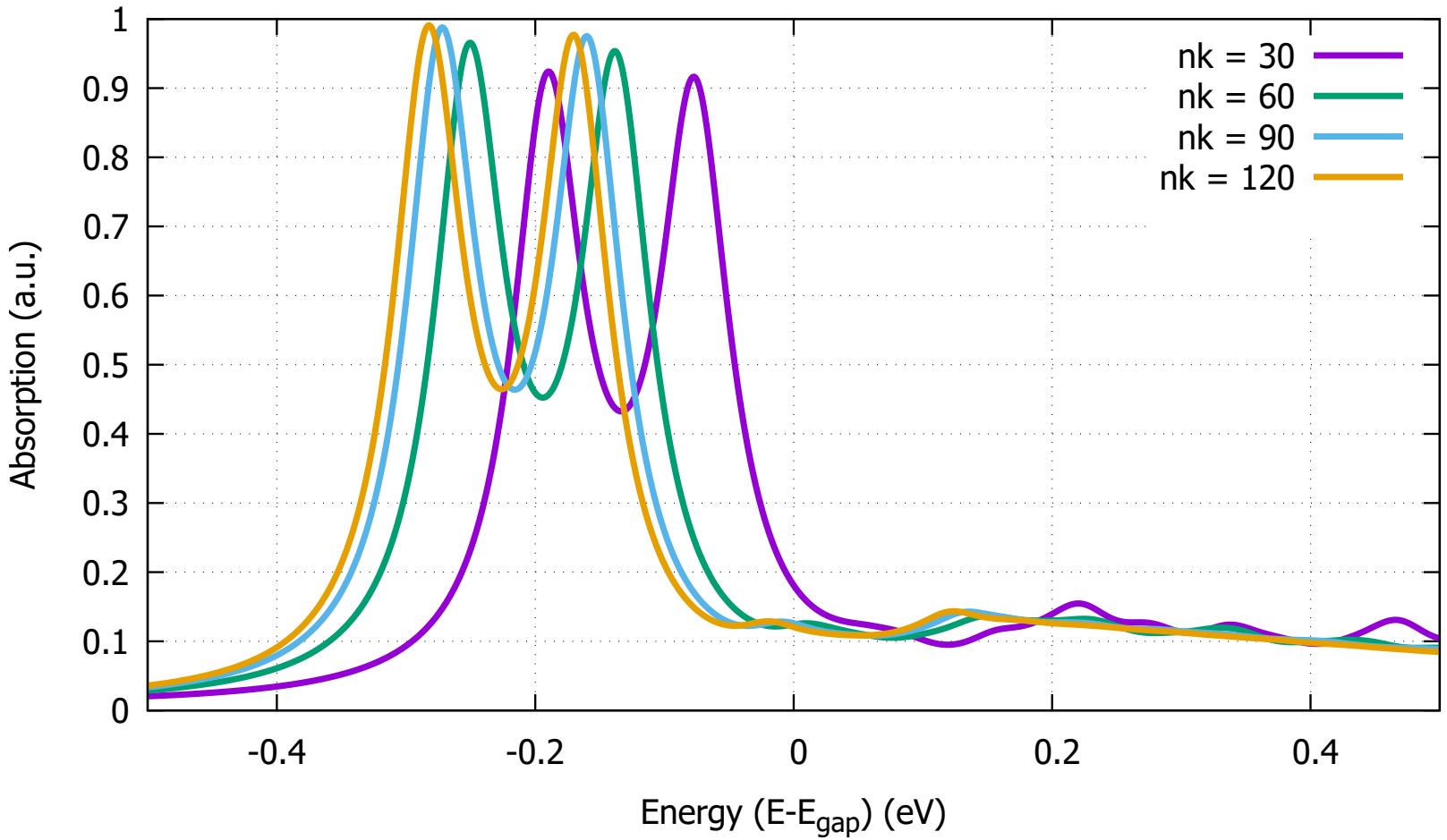
Figure: Measure Absorption Spectrum of MoS_2 at $T = 5K$ extracted from [2]

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



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


1.4
1.2
1
0.8
0.6
0.4
0.2
0
Absorption (a.u.)
-0.4
-0.2
0
0.2
0.4
Energy (E-E$_{gap}$) (eV)
T$_2$=7
T$_2$=15
T$_2$=30


Absorption (a.u.)
Energy (E-E$_{gap}$) (eV)
nk = 30
nk = 60
nk = 90
nk = 120
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.4
-0.2
0
0.2
0.4

Summary:

- From three-band TB + SBE $\rightarrow$ Linear Absorption Spectrum
- Confirm on Exciton binding energy in monolayer $\mathrm{MoS_2}$ in contract with experiment.

Further calculation:

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

[1] G.-B. Liu, W.-Y. Shan, Y. Yao, W. Yao, and D. Xiao, "Three-band tight-binding model for monolayers of group-VIB transition metal dichalcogenides," *Physical Review B*, vol. 88, p. 085433, Aug. 2013. Publisher: American Physical Society.

[2] C. Zhang, H. Wang, W. Chan, C. Manolatou, and F. Rana, "Absorption of light by excitons and trions in monolayers of metal dichalcogenide $\mathrm{Mo}{\mathrm{S}}_{2}$: Experiments and theory," *Physical Review B*, vol. 89, p. 205436, May 2014. Publisher: American Physical Society.