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]

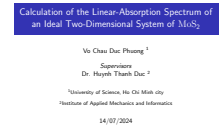
[1]University of Science, Ho Chi Minh city

[2]Institute of Applied Mechanics and Informatics

14/07/2024

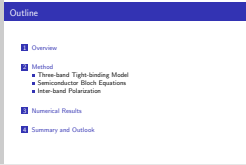
2024-07-08

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



Good day, teachers and fellow students. Now is my turn to present my work, on the "Calculation of the linear absorption spectrum of MoS2".

Outline



First, let's go through the overview of this presentation. I will go through the overview of the compound, its properties, and why we choose this path

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

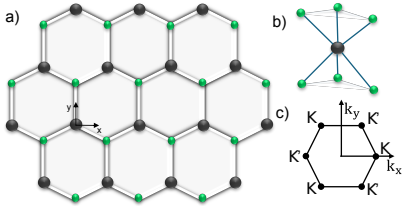


Figure: Structure of TMD and its first Brillouin Zone. M is Transition Metal atom (black dots), X is Dichalcogenide atom (green dots)

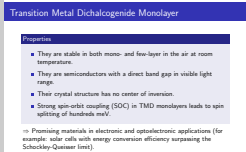
Transition metal dichalcogenides, which I will refer to as TMD, are compounds of the type MX2. The monolayer structure is like a sandwich, with chalcogenide layers above and below and the transition metal layer in between. The first Brillouin zone, which I will abbreviate as BZ, has a hexagonal shape. TMD has a layered structure, so it's easy to create a monolayer by extracting the layers like a Lego structure.

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.

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



The monolayer of TMD has some interesting properties, such as: "Stable in the air at the room's temperature", direct band-gap in the visible light range, "no center of inversion" and strong spin-orbit coupling. These properties of TMD promise it will become a gift material in electronic and optoelectronic. For example: making solar cells with aiming to surpass the Schockley-Queisser limit.

Exciton Binding Energy In TMD

What is the purpose of calculating the linear absorption spectrum?
→ Exicton binding energy

Overview

- TMD is a low-dimensional material → huge exciton binding energy in compared with bulk semiconductors → 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) ⇒ more precise calculations to match with the experiments.
- Theories only fit bandstructure around highly symmetry points such as K/K', not on entire BZ ⇒ a models for fitting in the entire BZ.

Exciton Binding Energy In TMD
What is the purpose of calculating the linear absorption spectrum?
→ Exicton binding energy
Overview
- TMD is a low-dimensional material → huge exciton binding energy in compared with bulk semiconductors → 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) ⇒ more precise calculations to match with the experiments.
- Theories only fit bandstructure around highly symmetry points such as K/K', not on entire BZ ⇒ a models for fitting in the entire BZ.

In this work, we calculate the linear absorption spectrum to obtain the exciton binding energy. Since TMD is a low-dimensional material, it results in a huge exciton binding energy (two magnitude orders compared with other bulk semiconductors). Early theories predict binding energy is too large compared with the experiment, so we need to calculate it to match with the experiment. In this work, we choose a tight-binding model, which is developed to fit 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:

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

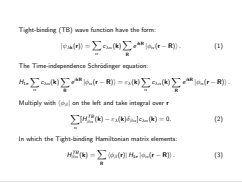
Multiply with $\langle\phi_{\beta}|$ on the left and take integral over $\mathbf{r}$

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

In which the Tight-binding Hamiltonian matrix elements:

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

2024-07-08
Calculation of the Linear-Absorption Spectrum of an Ideal Two-Dimensional System of MoS_2
Method
Three-band Tight-binding Model



The tight-binding wave function has the form of Eq. (1). Including it into the time-independence Schrödinger to get Eq. (2) and Eq. (3).

Use basic functions of d-type orbitals:

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

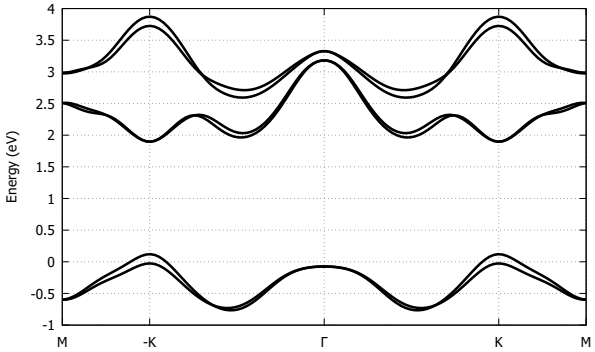
Three-band TB Hamiltonian with SOC has the form:

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

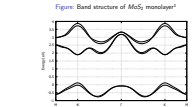
Use basic functions of d-type orbitals:
$|\phi_1\rangle = d_{z^2}, |\phi_2\rangle = d_{xy}, |\phi_3\rangle = d_{x^2-y^2}.$
Three-band TB Hamiltonian with SOC has the form:
$H^{TB}_{6\times6}(\mathbf{k}) = \begin{bmatrix} H^{TB}_{3\times3}(\mathbf{k}) + \gamma L_z & 0 \\ 0 & H^{TB}_{3\times3}(\mathbf{k}) - \gamma L_z \end{bmatrix}, \quad L_z = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{bmatrix}.$

The model we use in this work is called the three-band tight-binding models, It using basic function of 3 d-type orbitals as shown. The full Hamiltonian at a k-point is a 6 by 6 matrix when take spin orbit coupling into account.

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".



The BS of this model is shown here, which huge band split (about 144 meV) at K and K' points. In this work, we will focus on the transition between the valence bands and the first pair of conduction bands.

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

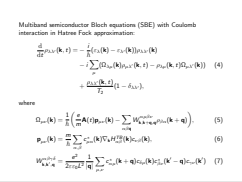
$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{\lambda\lambda'}(\mathbf{k},t) = -\frac{i}{\hbar}(\varepsilon_\lambda(\mathbf{k}) - \varepsilon_{\lambda'}(\mathbf{k}))\rho_{\lambda\lambda'}(\mathbf{k}) - i\sum_\mu(\Omega_{\lambda\mu}(\mathbf{k})\rho_{\mu\lambda'}(\mathbf{k},t) - \rho_{\lambda\mu}(\mathbf{k},t)\Omega_{\mu\lambda'}(\mathbf{k}))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

where

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

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

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



Using the semiconductor Bloch equation (SBE), we solve it in the form of Eq. (4) to obtain the time-dependent evolution of density matrix elements.

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:

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

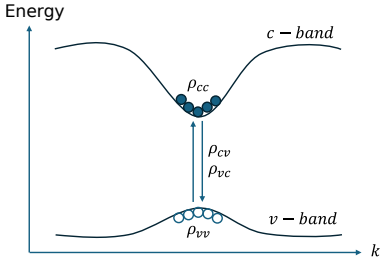
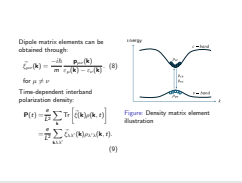


Figure: Density matrix element illustration



Along with the dipole matrix element, we can obtain the interband polarization through Eq. (9).

Evaluate Numerically Sum Over k-Space

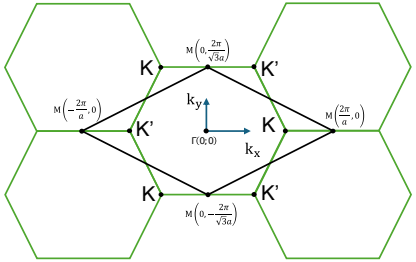


Figure: Rhombus primitive cell

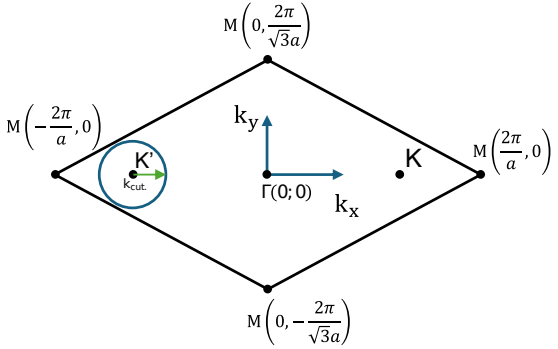
Numerical evaluate

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

2024-07-08
Calculation of the Linear-Absorption Spectrum of an Ideal Two-Dimensional System of MoS_2
Numerical Results
Evaluate Numerically Sum Over k-Space

1. However, the hexagon BZ of TMD is inconvenient for us when sampling the k-grid, so we will use the rhombus primitive cell with the same area as the hexagon.
2. In order to numerically evaluate results across the entire BZ, we approximate the sum by the integral.

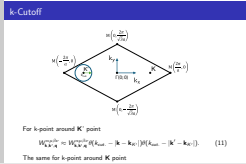
k-Cutoff



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



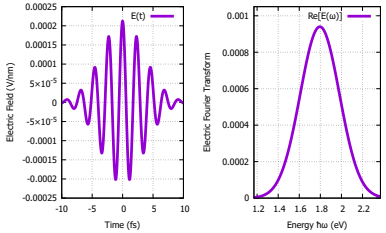
1. When considering the Coulomb interaction, it's essential to account for every k-point in the Rhombus. However, including every k-point may result in an overwhelming workload for achieving convergence. For this reason, we employ a technique that focuses specifically on k-points around K and K'.
2. For instance, with the K' point, we draw a circle and calculate the Coulomb interaction only if both points fall within this circle. The same process applies to the K point.

Electromagnetic Field

The electric field has a Gaussian envelope form:

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

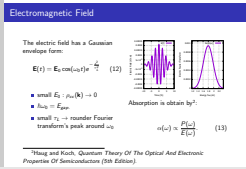
- small $E_0 : \rho_{cc}(\mathbf{k}) \to 0$
- $\hbar\omega_0 = E_{gap}$.
- small $\tau_L \to$ rounder Fourier transform's peak around ω_0



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)*.



The polarized external field has a Gaussian envelope form with these properties to obtain the weak excitation limit for the linear absorption calculation.

Experiment measure:

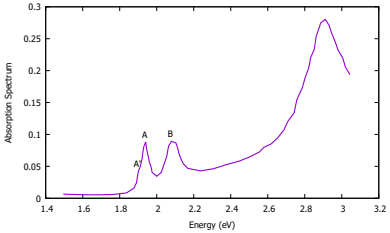


Figure: Measured Absorption Spectrum of MoS_2 at $T = 5K$ extracted from Ref.[3]

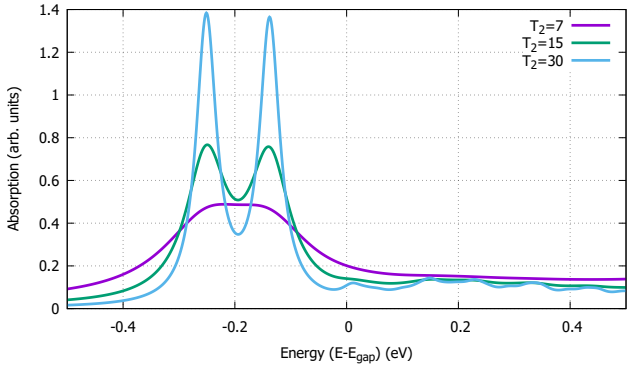
- Two resonance labeled by A and B are Exciton peaks (band split due to SOC).
- Weak trion peak near A labeled by A'

To fit with experiment, we can change:

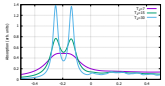
- Relative permittivity ε
- Dephasing time T_2

[3] Zhang et al., "Absorption of light by excitons and trions in monolayers of metal dichalcogenide MoS_2".

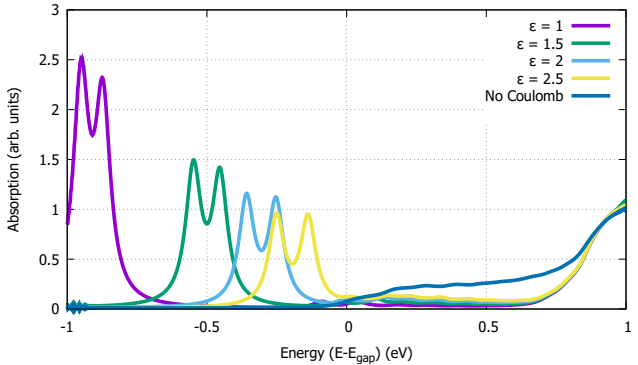
1. The experiment measurement gives us two peaks, labeled as A and B,
2. they also have a weak trion peak in here.
3. To fit with the measurement, we will investigate the relationship between relative permittivity and dephasing time T2 with linear absorption spectrum.



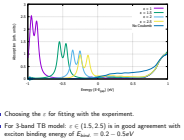
- Choosing the T_2 for clearer Exciton peak.
- The bigger T_2, the clearer main Exciton peaks $\rightarrow$ confirm two peak.
- At $T_2 = 30$ *fs* show other smaller peaks $\rightarrow$ predict other peaks.



1. As we vary T2, two peaks become clearer at bigger T2, which agrees with the measurement.
2. We can also see smaller peaks, which are other exciton peaks but too small to appear in the measurement.



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



1. The binding energy is affected through the relative permittivity, as we increase the epsilon, two peaks move to the right of the spectrum.
2. With the same epsilon equal to 2.5, we obtain the same results as the experiment, approximately 0.24 eV for the exciton binding energy.

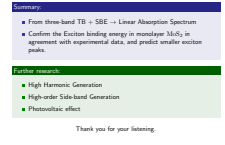
Summary:

- From three-band TB + SBE → 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.



1. So far, we have used the three-band tight-binding model and semiconductor Bloch equations to calculate the linear absorption spectrum. We confirm that this model matches the results with the experiment data and also predicts smaller exciton peaks.
2. For further results, we can include the many-body interaction in the calculation of other phenomena for a realistic picture of TMD's properties.