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

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

First, let's go through the overview of this presentation. I will go through:

1. the overview of the compound, its properties, and why we choose this path.
2. Then, introducing the model we are using, the equations and the outcome we need to calculate.
3. after that, talk and discussion about the results
4. finally, I will summary and talk about further research

Transition Metal Dichalcogenides Monolayers

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

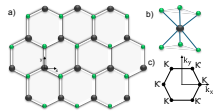

Figure: Structure of TMD and its first Brillouin Zone. *M* is Transition Metal atom (black dots), *X* is Dichalcogenide atom (green dots)

1. Transition metal dichalcogenides, which I will refer to as TMD, are compounds of the type MX2.
2. TMD has a layered structure, so it's easy to create a monolayer by extracting the layers like a Lego structure. The monolayer structure is like a sandwich, with chalcogenide layers above and below and the transition metal layer in between, you can see in figure a from top and b from side in here.
3. The first Brillouin zone, which I will abbreviate as BZ, has a hexagonal shape, show in figure c.

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.

⇒ 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:

1. Stable in the air at the room's temperature
2. direct band-gap in the visible light range
3. "no center of inversion"
4. 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

Exciton binding energy can be extracted from the linear absorption spectrum

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.

1. 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 (about two magnitude orders compared with other bulk semiconductors).
2. Early theories predict binding energy is too large compared with the experiment, so we need to calculate it to match with the experiment.
3. In this work, we choose a tight-binding model, which is developed to fit in the entire BZ.

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

Method

Three-band Tight-binding Model

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:

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

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).

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

Method

Three-band Tight-binding Model

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.

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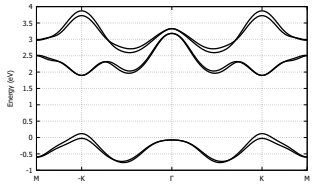
Method

Three-band Tight-binding Model

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.

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

Method

Semiconductor Bloch Equations

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

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

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

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

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.

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

Method

Inter-band Polarization

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:

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

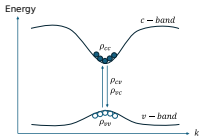


Figure: Density matrix element illustration

Using the density and dipole matrix elements, we can obtain the time dependence interband polarization through Eq.(9)

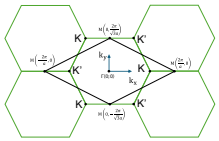


Figure: Rhombus primitive cell

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

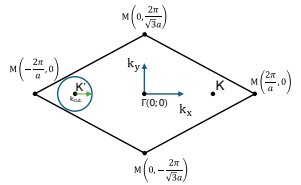
1. As I have mentioned above, The first Brillouin Zone of monolayer TMD have the shape of Hexagon. However, the hexagon is inconvenient for us when sampling the k-grid, so we will use the rhombus primitive cell with the same area as the hexagon.
2. In order to evaluate the numerical results in the entire BZ, we approximate the sum by this integral.

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

Numerical Results

k-Cutoff

k-Cutoff



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

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

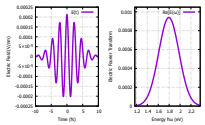
The same for k-points around **K** point

1. When considering the Coulomb interaction, it's essential to account for every k-point in the Rhombus primitive cell. 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:

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



- 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]:

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

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

1. The polarized external field has a Gaussian envelope form with these properties to obtain the weak excitation limit for the linear absorption calculation.
2. The absorption coefficient will be obtained by Eq. (13)
3. P and E is Fourier transformation of polarization density and external field, respectively

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

Numerical Results

Experiment measure:

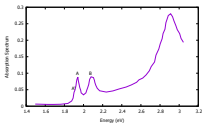


Figure: Measured Absorption Spectrum of MoS_2 at $T = 5K$ extracted from Ref.[3]

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

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:

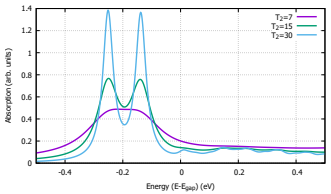
- Relative permittivity ε
- Dephasing time T_2

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

1. The experiment measurement gives us two peaks, labeled as A (1.93 eV) and B (2.1 eV), the binding energy will be obtain by extract the exciton peak from the bandgap energy
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.

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

Numerical Results



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

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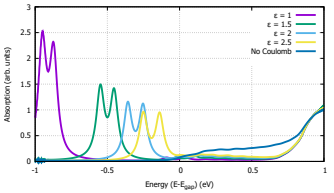
Numerical Results



- 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
- 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.

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 calculating other phenomena for a realistic picture of TMD's properties.