Electronic Properties of Atomically Thin Transition Metal Dichalcogenides

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2D Transition Metal Dichalcogenides (TMDC)
Monolayer TMDC

Honeycomb lattice with broken sublattice symmetry/ broken inversion symmetry

K
K'
2D Semiconductors

- Evolution of electronic structure with thickness
- Many-body effects and excitonic interactions
- Accessing individual valleys
Photoluminescence from Atomically Thin MoS$_2$ Layers

Strong enhancement in light emission for monolayer

$>1000 \times$ compared to bulk

Mak et al. PRL (2010)

Atomically Thin MoS$_2$: A New Direct-Gap Semiconductor

Kin Fai Mak,$^1$ Changgu Lee,$^2$ James Hone,$^3$ Jie Shan,$^4$ and Tony F. Heinz$^{1,*}$
Band Gap Variation in MoS$_2$

**Diagram Description:**
- The graph shows the normalized PL (photoluminescence) intensity as a function of photon energy for different number of layers (1lay, 2lay, 3lay, 4lay, 5lay, 6lay).
- Each curve is labeled with its corresponding layer count and magnification factor (X 100, X 300).
- The photon energy range is from 1.4 to 2.2 eV.
- Peak A and B are marked on the graph, indicating areas of quantum confinement.

**References:**
Indirect-Direct Band Gap Transition

Blue: Mo orbitals
Magenta: S orbitals
(Talat Rahman group, UCF)
Variety of TMDC Crystals

MX$_2$ monolayers

MoS$_2$, MoSe$_2$, WSe$_2$, WTe$_2$

1 – 2 eV Direct gaps
CVD Growth of Alloys: $\text{MoS}_{2x} \text{Se}_{2(1-x)}$

Heinz group with Bartels group (UC Riverside) [Adv. Mater. (2014)]
Metal alloys: $\text{Mo}_x \text{W}_{(1-x)}\text{S}$ by Suenaga group [Nat. Commun. (2014)]

Also: Recently demonstrated exfoliated monolayer $\text{MoTe}_2$ with 1.0 eV band gap
Evolution with Layer Thickness
Twisted MoS$_2$ Bilayers

Van der Zande et al. Nano Lett. (2014): with Hone, Muller, Reichman groups
Twisted MoS$_2$ Bilayers

Direct HR-TEM atom imaging – Muller group, Cornell
Twisted MoS$_2$ Bilayers

SHG probe of orientation
Twisted MoS$_2$ Bilayers

PL spectra versus twist angle
Twisted MoS$_2$ Bilayers

PL spectra versus twist angle
Twisted MoS$_2$ Bilayers

PL spectra versus twist angle
Twisted MoS$_2$ Bilayers

Hybridization of electronic states produces new transitions and indirect gap behavior
Twisted MoS$_2$ Bilayers

![Graph showing energy and angle relationship for twisted MoS$_2$ bilayers.](image)

**Figure a:** Illustration of twisted MoS$_2$ bilayers.

**Figure b:** Graph showing the variation of $E_2 - E_1$ and $d - d_0$ with angle.

**Note:** The figure illustrates the energy ($E_2 - E_1$) and separation ($d - d_0$) changes as a function of the angle between the two layers in twisted MoS$_2$ bilayers.
Nonlinear optical properties of single layer MoS$_2$
Giant enhancement of second-harmonic generation from single layer MoS$_2$. 
Second-harmonic generation from MoS$_2$

Direct band gap?
Direct band gap?
Strong second-harmonic again for trilayer MoS$_2$
Strong second-harmonic generation from odd-layer MoS$_2$
Strong second-harmonic generation from odd-layer hexagonal BN
Symmetry criterion for second-harmonic generation

\[ P_i^{(2)} = \sum_{jk} \chi_{ijk}^{(2)} E_j E_k \quad i, j, k = x, y, z \]

SHG is dipole-allowed only in non-centrosymmetric media
Inversion symmetry-breaking in single layer MoS$_2$
Symmetry-breaking in single layer MoS$_2$

MoS$_2$ symmetry group | Second-order polarizability tensor elements
--- | ---
Bulk $D_{6h}^4$ (P63/mmc) | All elements vanish
Even $D_{3d}^3$ (P3m1) | All elements vanish
Odd $D_{3h}^1$ (P6m2) | $x_{yyy} = x_{yxx} = -x_{xxy} = -x_{xyx}$
In-plane dependence of second-harmonic generation

Heinz group, Nano Lett. (2014)
Also: Malard et al (2014)
X. Zhang et al. (2014)
Determination of orientations of crystallographical axes
Piezoelectric Response of MoS$_2$

Heinz group with Hone (Columbia) and Wang (Georgia Tech) Nature 470 (2014).
2D Semiconductors

- Evolution of electronic structure with thickness
- Many-body effects and excitonic interactions
- Accessing individual valleys
Monolayer MoS$_2$ Absorption: Excitonic Transitions

![Diagram of band structure and absorption spectrum showing transitions A and B, with photonic energy range from 1.6 to 2.2 eV.](image)
Exciton Binding Energy?
Excitons in TMDC monolayers

theoretical predictions

$E_X = 500 - 1000 \text{ meV}$ free-standing layers

\[ E_X \sim \frac{\text{effective mass}}{\text{dielectric screening}^2} \]

$\sim 40 \text{ meV} \text{ in bulk}$

- T. Rahman et al., *Phys. Rev. B*, 90, 085419
Higher-Lying Exciton States in WS$_2$
Exciton Rydberg series in 1L WS$_2$

Exciton binding energy $\sim 320$ meV

A. Chernikov et al., *PRL*, 113, 076802 (2014)
Non – Hydrogenic Behavior

Non – uniform dielectric environment

strong screening in the layer

weak screening in the surroundings
Comparison of theory and experiment

Exciton binding energy (supported samples)

\[ E_X = 320 \pm 40 \text{ meV} \]

\[ V_{eh}(r) = -\frac{\pi}{2r_0} \left[ H_0 \left( \frac{r}{r_0} \right) - Y_0 \left( \frac{r}{r_0} \right) \right] \]

see also:

B. Zhu et al., arXiv:1403.5108 (2014)
1s Excitonic Wavefunction in WS$_2$
Exciton wavefunctions

Bohr radius ~ 1 nm

Radial probability

Electron – hole separation (nm)

n = 1

n = 2
Linear Optical Response: Excitons

Heinz group
Phys Rev. B (2014)
Linear Optical Response: Excitons

\( WS_2 \) monolayer
Higher Many-Body States

Exciton

Gate tunable charged exciton

Biexciton: Excitonic molecule

Also: Xiaodong Xu
Charged Excitons

MoSe$_2$

New stable, tunable exciton states

Also: Xiaodong Xu

Biexciton States

Biexciton States: Four Body Correlated State

Observation of Strong Excitonic Interaction in TMDCs

- **Exciton**
- **Trion**
- **Biexciton**
- **e-h Plasma**

**Linear**
- Low excitation density

**Intermediate excitation density**
- Scattering
- Annihilation

**Nonlinear**
- High excitation density
2D Semiconductors

- Evolution of electronic structure with thickness
- Many-body effects and excitonic interactions
- Accessing individual valleys
Valley degree of Freedom

Di Xiao, Wang Yao, Xiaodong Xu, PRL 2012
Valley degree of Freedom
Accessed by Circularly Polarized Light

Di Xiao, Wang Yao, Xiaodong Xu, PRL 2012
Valley dependent optical selection rules

Broken inversion symmetry
Finite \textit{intercellular angular momentum}

Coupled valley-spin excitonic absorption

\begin{itemize}
  \item How exact are the selection rules?
  \item How long can the carriers be retained in one valley?
\end{itemize}

Also: H. Zeng et al., Nature Nanotech
T. Cao et al., Nature Comm.
G. Sallen et al, PR B
Optically induced valley-spin polarization in MoS$_2$ monolayers

$\rho \equiv \frac{I_+ - I_-}{I_+ + I_-}$

Highly selective pumping
Complete retention at one valley

Coupled Valley-Spin in Monolayer MoS$_2$

\[ H_{so} = \frac{1}{2c^2} \tilde{S} \cdot (\tilde{\nabla} V(\tilde{r}) \times \tilde{p}) \]

Zhu et al. PRB 2011
D. Xiao et al. PRL 2012
Open questions

• How to tune and manipulate the individual valley?
Valley Degeneracy

**Break TRS with a magnetic field**

- Valleys are degenerate by *time reversal symmetry*
  - *Electric field*
  - *Strain*
  - *Doping*
Neutral exciton ($X^0$) PL magnetic shift

$\sigma_+$

$K$

Energy (eV)

$0$ $0.5$ $1$

$1.6$ $1.62$ $1.64$ $1.66$ $1.68$

Magnetic field (T)

$-10$ $-5$ $0$ $5$ $10$

PL intensity (arb. unit)

$B = +10 \text{ T}$

$B = -10 \text{ T}$

$\sigma_-$

$K'$

Energy (eV)

$1.6$ $1.62$ $1.64$ $1.66$ $1.68$

Magnetic field (T)

$-10$ $-5$ $0$ $5$ $10$

PL intensity (arb. unit)

$B = +10 \text{ T}$

$B = -10 \text{ T}$
Zeeman shift of the $X^0$ PL peak

<table>
<thead>
<tr>
<th></th>
<th>Experimental slope (0.01 meV/T)</th>
<th>Predicted slope</th>
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<tbody>
<tr>
<td>$X^0$</td>
<td>$+0.12$ meV/T</td>
<td>$+0.12$ meV/T</td>
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</tbody>
</table>

Yilei Li, TFH, ... Jonathan Ludwig, Dmitry Smirnov, Zhiqiang Li (NHMFL), PRL (2014)
Valley polarization by valley splitting

$B$

$E_F$

$K$

$K'$
Variation in Relative Strength of $X^0$ and $X^-$ Emission

$\rightarrow$ Produced valley polarization (population difference)
Valley Control of Transport

Kin Fai Mak, McEuen, Park Cornell

Valley Hall Effect
Science (2014)
Valley Occupation and Excitonic Correlation
Summary: Monolayer TMDs

1. New band structure and light emission for atomically thin layers
   Direct-gap material with strong light emission in monolayer
   New materials, syntheses

2. Strong many-body effects and excitonic interactions
   Excitonic Rydberg series with nonlocal screening
   $\text{WS}_2$ binding energy $\sim 320$ meV
   Tunable charged excitons, biexcitons, ...

3. Accessing the valley degree of freedom
   Selective excitation of valleys by circularly polarized light
   Tuning valleys and creating steady-state population by breaking
   time-reversal symmetry with magnetic field

4. Creating new materials: 2D heterostructures
   Tunable electronic structure as a function of twist angle
   Rapid charge transfer and separation in heterostructures
Collaborators

• Columbia University
  – Heinz group: Burak Aslan, Alexey Chernikov, Heather Hill, Yilei Li, Holger Lange, Kin Fai Mak, Yi Rao, Albert Rigosi, Cyrielle Roquelet, Claudia Ruppert, Dezheng Sun, Yumeng You, Xiaoxiao Zhang, Arend van der Zande
  – Louis Brus group
  – Jim Hone group – Changgu Lee, Gwan Hyoung Lee
  – Philip Kim group
  – David Reichman group: Tim Berkelbach

• Brookhaven National Lab: Mark Hybertsen

• Penn State University: Jie Shan, Kin Fai Mak groups

• Cornell University: David Muller group

• U Central Florida: Talat Rahman group

• UC Riverside: Ludwig Bartels group

• NHMFL, Tallahassee: Dmitry Smirnov and Zhiqiang Li groups
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