Exciton Binding Energy and Nonhydrogenic Rydberg Series in Monolayer WS_2

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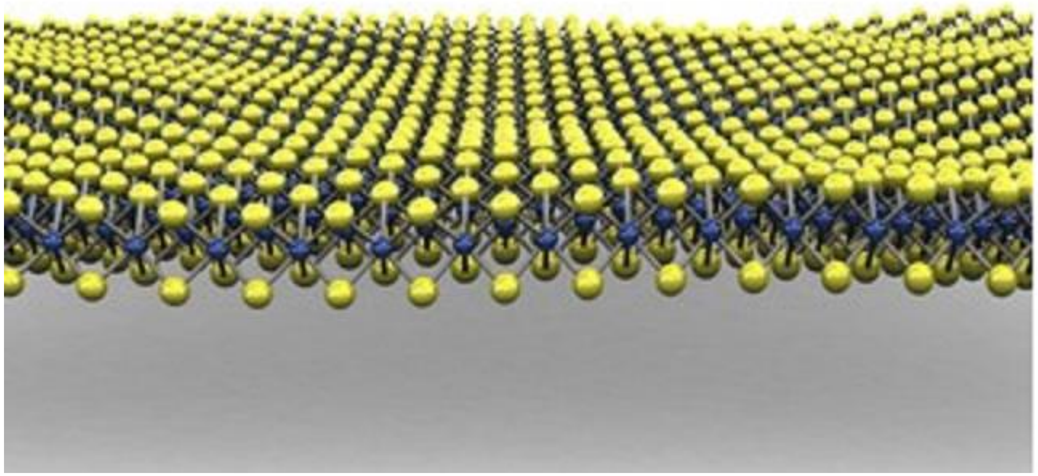
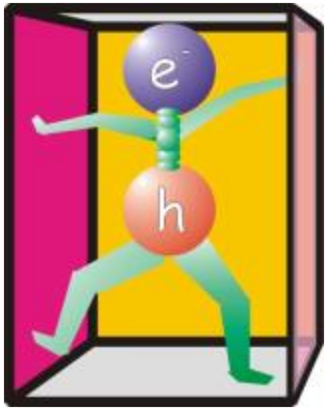


Why Study Monolayer WS_2?

- Model transition-metal dichalcogenide (TMD)
  - Large splitting between A and B excitons means no overlap between them
- 2D properties of TMDs show promise
  - Carrier concentration easily controllable with light
    - Possible because of direct bandgap

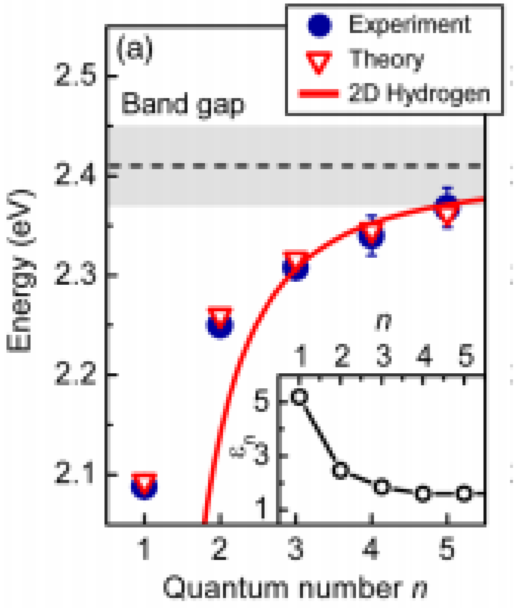
Measuring the exciton binding energies

- Researchers shined linearly polarized light on monolayer WS_2
- Measured the reflectance of light at various energies in order to measure the energy level of excited excitons



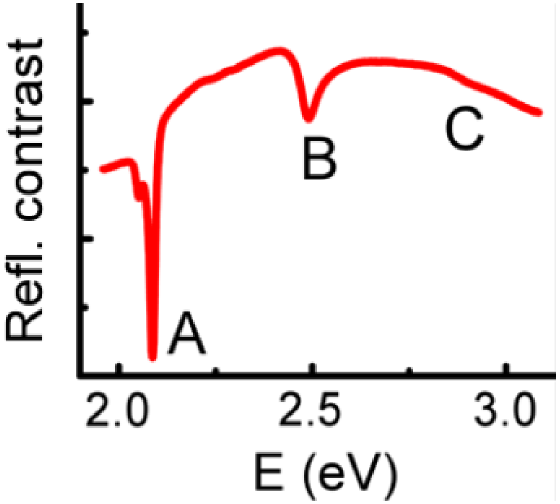
Excitonic energies don’t show hydrogenic behavior

- Plotted observed exciton energy levels
  - Did not observe the expected hydrogenic energy spectrum
- Calculated a band gap of 0.32 eV



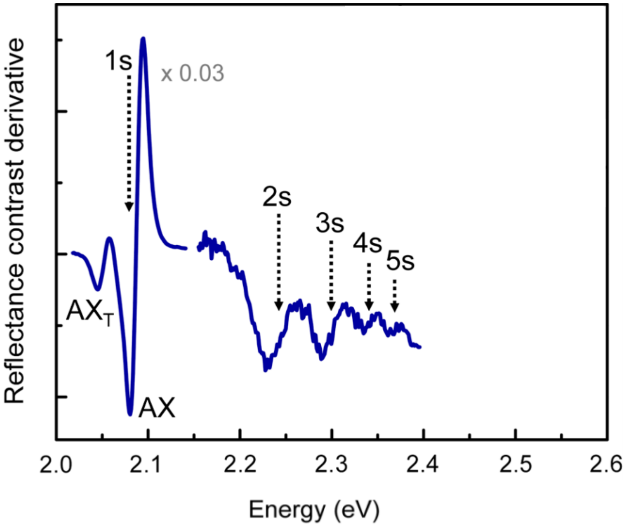
Measurements of Reflectivity Contrast Peaks

Reflectance contrast of monolayer WS_2 measured



Calculated derivative

- Shows peaks more clearly



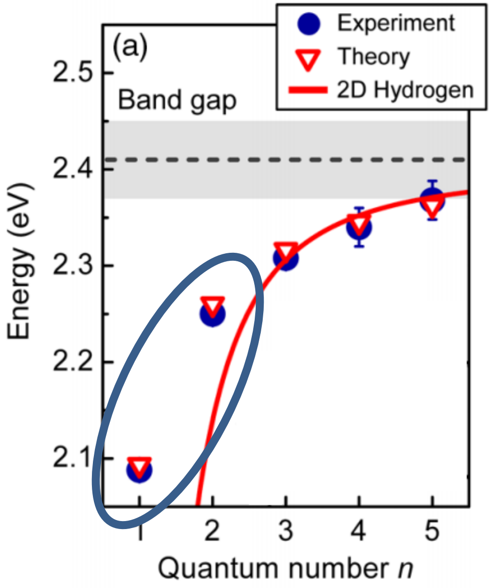
Fitting Binding Energies to Hydrogenic Hamilton

Fit energies of Rydberg excitons to hydrogenic Hamiltonian

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{\varepsilon r}$$

$$E = E_g - E_b^n$$

$$E_b^n = \frac{\mu e^4}{2\hbar^2\varepsilon^2\left(n - \frac{1}{2}\right)^2}$$

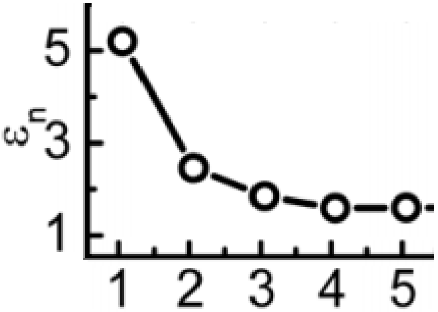


Fitted value of E_g is 2.41eV
Gives value for E_b as 0.32eV

Energy Levels Don’t Match Hydrogenic Hamiltonian

Recalculate ε as function of n

$$\varepsilon_n = \left[\frac{2\hbar^2 E_{b,expt}^{n}\left(n-\frac{1}{2}\right)^2}{\mu e^4}\right]^{\frac{1}{2}}$$

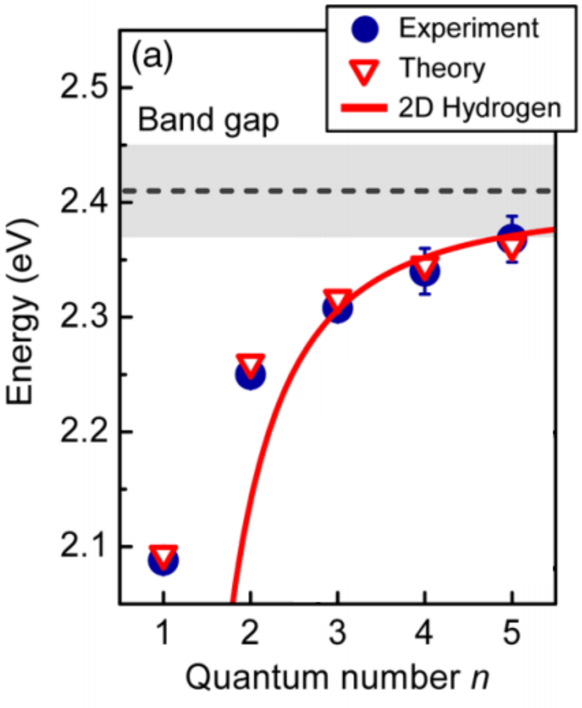


Use a different potential form to account for antiscreening in monolayer

$$V(r) = -\frac{\pi e^2}{2r_0}\left[H_0\left(\frac{r}{r_0}\right) - Y_0\left(\frac{r}{r_0}\right)\right]$$

Provides the necessary long range 1/r behavior, but alters the short range potential primarily

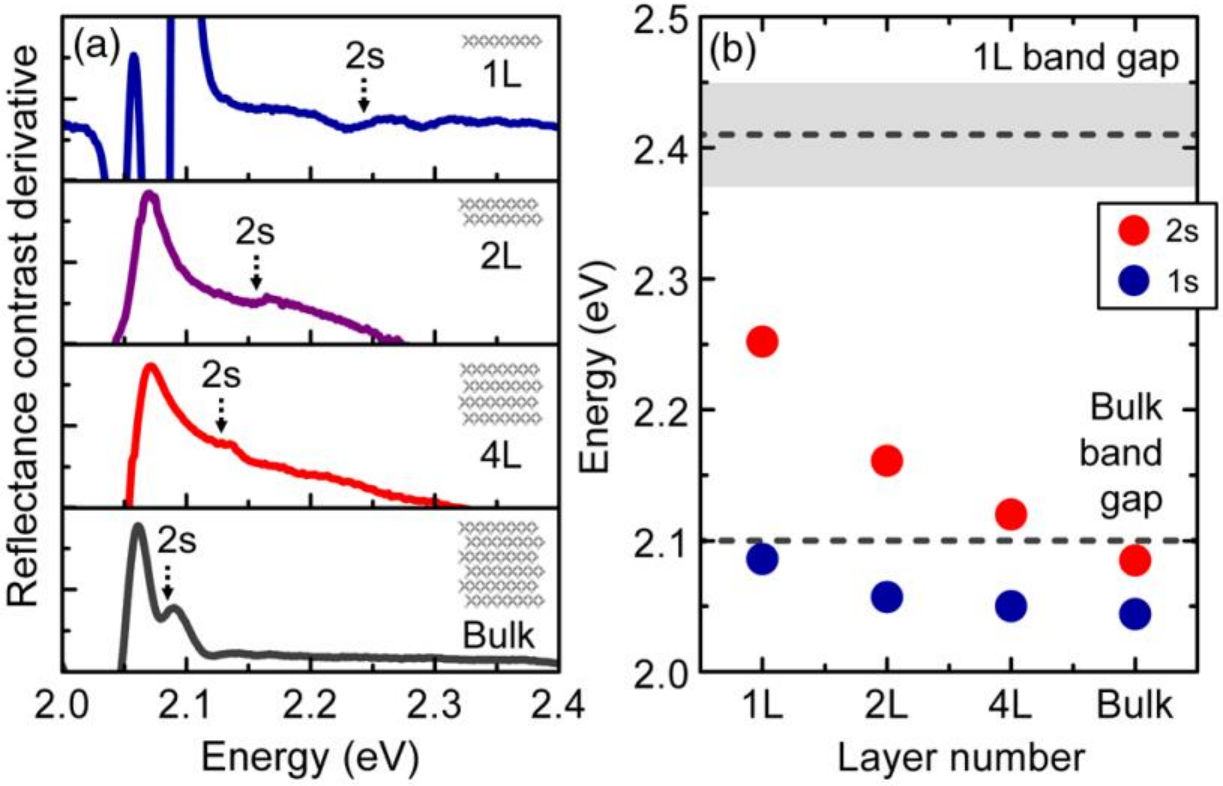
Fitting the Experimental Data with New Hamiltonian



Fitting parameters r_0 and E_g are calculated to be 75Å and 2.41eV

Gives 1s exciton binding energy of 0.32eV – accurate with experiment

Number of Layers Changes the Energy and Number of Exciton Excitations



Primarily a monolayer effect, very quickly drops off with increasing thickness

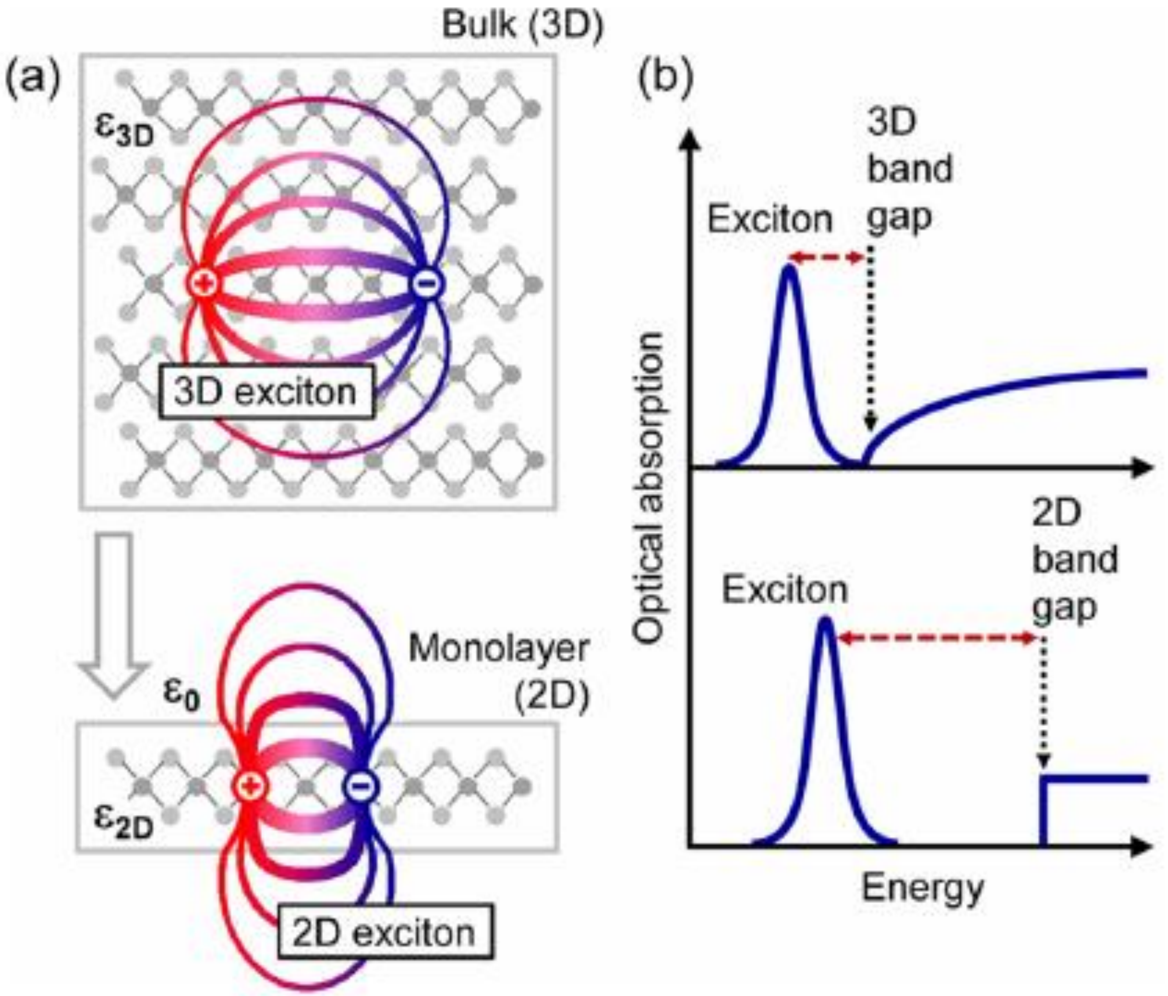
Review of Important Ideas

- Authors used reflectance to determine exciton binding energy in WS_2
- Energy levels for $n > 2$ resemble Hydrogen energy levels (Rydberg series)
- Deviations well-explained by screening effects

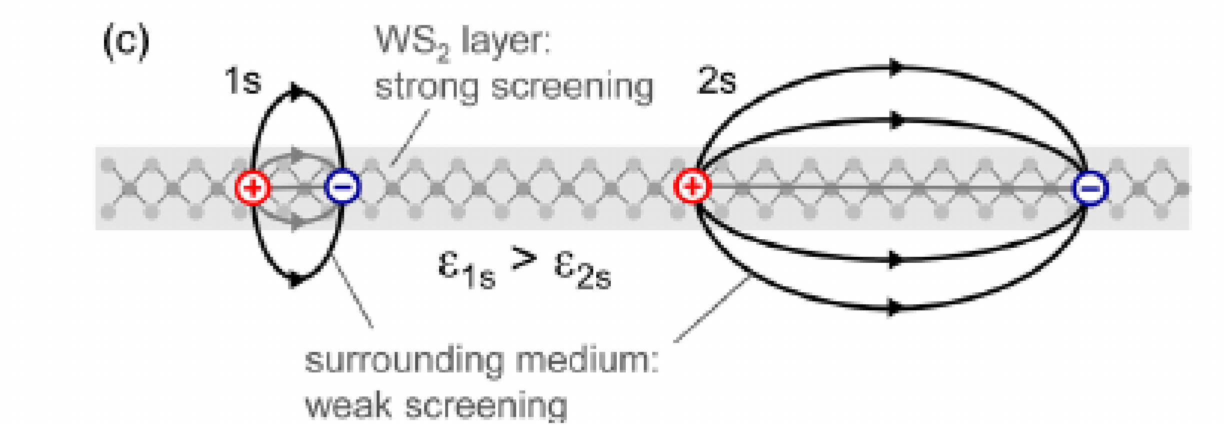
Are these properties universal?

- Authors want to understand properties of TMDs
- Do their results extend to other such materials?
  - Nonhydrogenic model derived based on geometry of system
  - Should be universally applicable to similar monolayers

Why results might apply to other 2D materials



Screening Depends on the Size of the Exciton



- Larger excitons/higher n values, the electric field exists significantly outside the monolayer
  - Lowers the screening

High Binding Energy

- Non-hydrogenic behavior and high binding energy (0.32 eV) common in 2D TMDs
- Implies high thermal stability
- Potential applications in optoelectronics in visible range
- Higher order effects likely to be important (trion and biexiton formation)

Critiques of the Paper

- Well-written paper gives especially good introduction and qualitative descriptions
- Much supplementary material (including setup)
- Measured relative reflectance, reported its energy derivative
- Not specified how to obtain energy levels from this measurement
- Errors given without explanation

Citation Analysis: Basic Facts

- “Birthday” : August 13, 2014

- 87 Citations so far (via SCOPUS)
  - 78 in 2015

Citation Context Within Field

- Out of 87 citations, 75 are independent of the Columbia/ Brookhaven group
- Cited 6 times each by Berkeley
- Citations of Citations
  - Exciting field
- References
  - 27 of 35 references are from 2009+

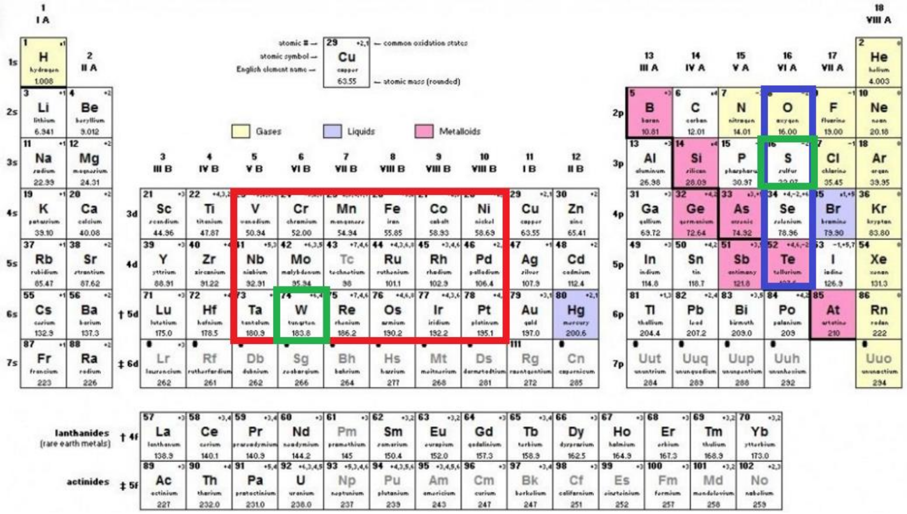
Xia, F., Wang, H., Xiao, D., Dubey, M., Ramasubramaniam, A.	2014	Nature Photonics	57
Aivazian, G., Gong, Z., Jones, A.M., (...), Yao, W., Xu, X.	2015	Nature Physics	24
Wang, X., Jones, A.M., Seyler, K.L., (...), Xu, X., Xia, F.	2015	Nature Nanotechnology	20
Zhu, B., Chen, X., Cui, X.	2015	Scientific Reports	18
Srivastava, A., Sidler, M., Allain, A.V., (...), Kis, A., Imamołlu, A.	2015	Nature Physics	18
Wang, G., Marie, X., Gerber, I., (...), Balocchi, A., Urbaszek, B.	2015	Physical Review Letters	17
Li, Y., Chernikov, A., Zhang, X., (...), Hone, J., Heinz, T.F.	2014	Physical Review B - Condensed Matter and Materials Physics	16
Li, Y., Ludwig, J., Low, T., (...), Smirnov, D., Heinz, T.F.	2014	Physical Review Letters	12
Wu, F., Qu, F., Macdonald, A.H.	2015	Physical Review B - Condensed Matter and Materials Physics	11

Evolution of the Field

- Two Main Paths

  -2D layers in general

  - Excitons in very similar materials (MoS2,ReS2,WSe2)



Similar Subsequent Studies

- Exciton Binding Energy of Monolayer WS2(Keliang He, Nardeep Kumar,et al.)
  - studies trion binding energy, exciton-exciton annihilation
- Probing Excitonic Dark States in Single-layer Tungsten Disulfide(Ziliang Ye, Ting Cao,et al.)
  - studies dark states that do not absorb/transmit photons
- Non-linear Optical Spectroscopy of Excited Exciton States for Efficient Valley Coherence Generation in WSe2 Monolayers(G. Wang, X. Marie,et al.)
  - studies valley coherence (electron states at band edges)

Similar Studies

- Optically bright *p*-excitons indicating strong Coulomb coupling in transition-metal dichalcogenides(Tineke Stroucken, Stephan W. Koch)
  - experimentally compares resonance energies with computed values
  - optically bright excitonic transitions have *p*-like symmetry

- Tightly Bound Excitons in Monolayer WSe2 (Keliang He, Nardeep Kumar, et al.)
  - excited exciton states even at room temperature

Authors’ Continued Interest

- Recent Paper Titles

-Binding energies and spatial structures of small carrier complexes in monolayer transition-metal dichalcogenides via diffusion Monte Carlo

-Electrical Tuning of Exciton Binding Energies in Monolayer WS2

-Observation of excitonic Rydberg states in monolayer MoS2 and WS2 by photoluminescence excitation spectroscopy

-Observation of biexcitons in monolayer WSe 2

Future of the Field

- 2D materials are in high demand
  - relatively young field (c. 2004)
  - Graphene studies win 2010 Nobel Prize (Andre Geim, Konstantin Novoselov)
- Applications to technology
  - WS2 offers large binding energy, band gap
  - 2D features:
    - Coulomb interaction enhancement
    - many-body physics
    - high performance field effect transistors