Columbia University in the City of New York

Louis Brus, Chemistry Department

POSTECH Symposium, Korea, August 2015

Electron Correlation in Nanoscience: Size and Dimensionality

Small molecules, short polymers, quantum dots, carbon nanotubes, graphene, 2D lead perovskites, molybdenum disulfide, etc.

Accounts of Chemical Research (**2014**), 47, 2951-2929.

What are the electrons doing?

Special aspects of Electronic Structure in Nanoscience

1. Quantum Size Effect (single electron property) -- Quantum Dots

2. Strong electron correlation in 1D and 2D systems, and relation to dielectric screening -- Carbon Nanotubes

3. Coherent Photon Scattering (balance between photon absorption and scattering) -- plasmons in Ag nanocrystals.

This talk will mainly focus on strong electron correlation

Background: Independent Electron Model

Normally in theory (Hartree-Fock) an electron's interaction with other electrons is included only in an average or mean field way.

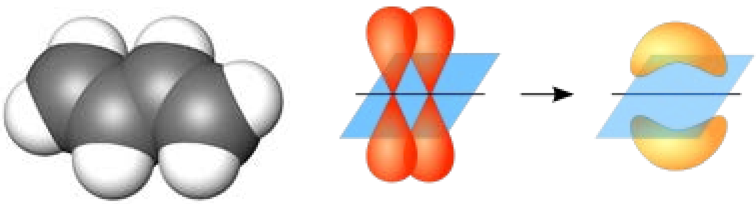
This idea works well in regular Molecular Orbital theory, and in the band structure of 3D semiconductors.

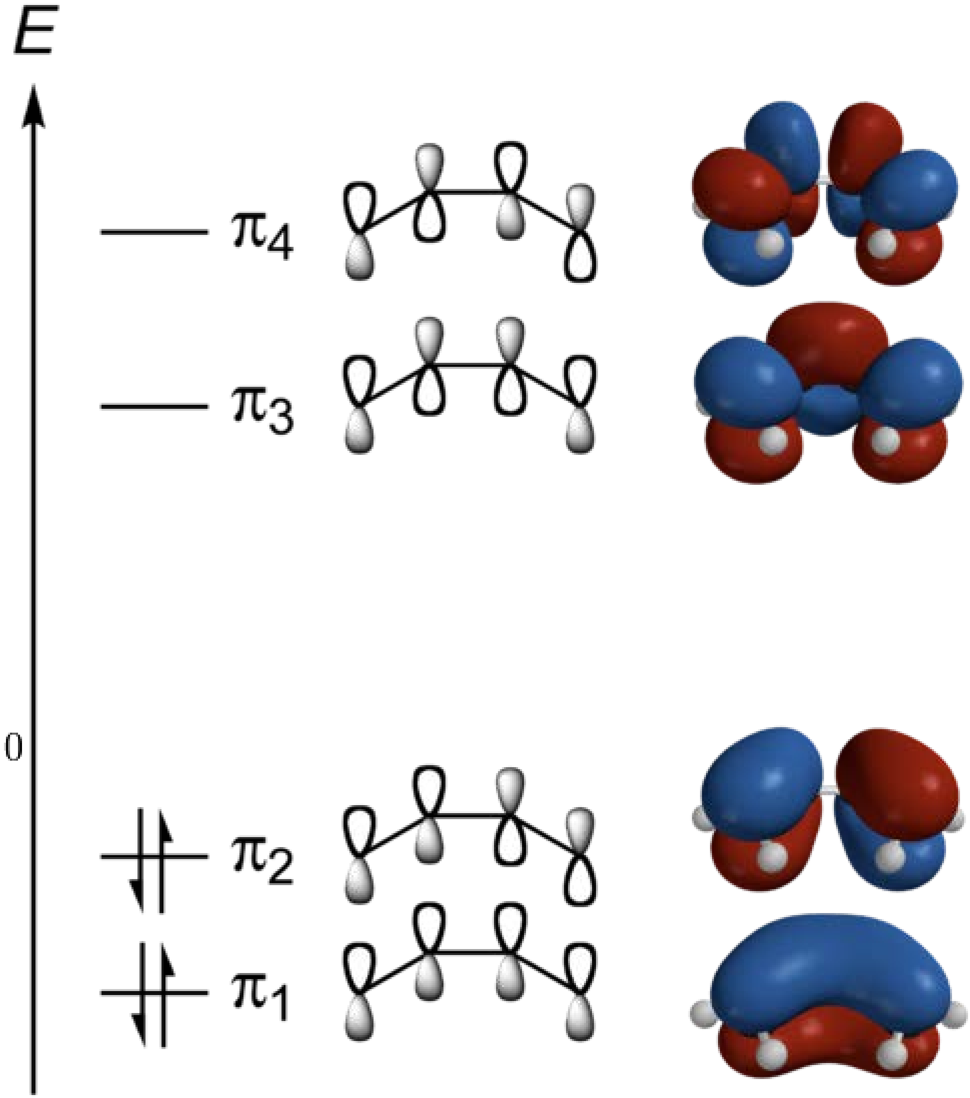
However, explicit electron correlation, going beyond this model, is essential in 1D and 2D nanoscience.

Small molecules:

Hückel molecular orbitals for P electrons

Butadiene





$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = 0$$

$$(\alpha - E)(\alpha + \beta - E) - \beta^2 = 0$$

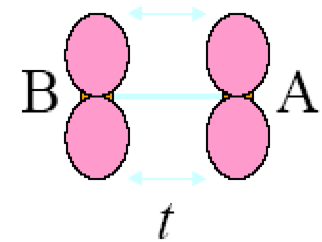
$$E\pm = \alpha + \frac{1 \pm \sqrt{5}}{2}\beta$$

No Correlation

Graphene: high symmetry, translational symmetry and infinite size

Energy bands of Graphite

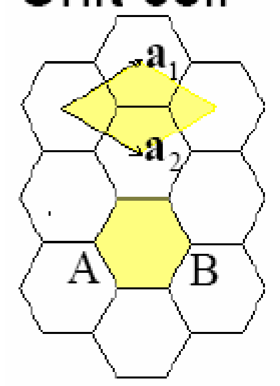
P. R. Wallace, *Phys. Rev*, **71** 622 (1947).



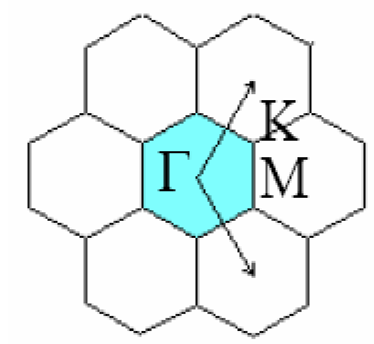
- π band of graphite

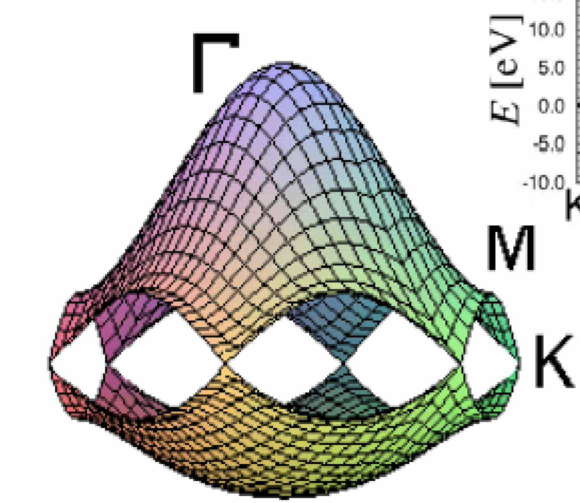
- Energy Band Model
  - Zero Gap Semiconductor

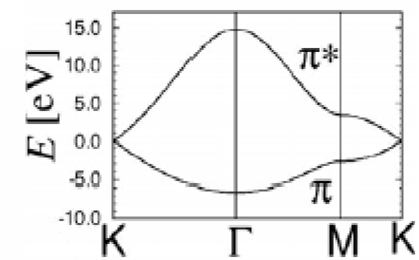
Unit cell



B.Z.







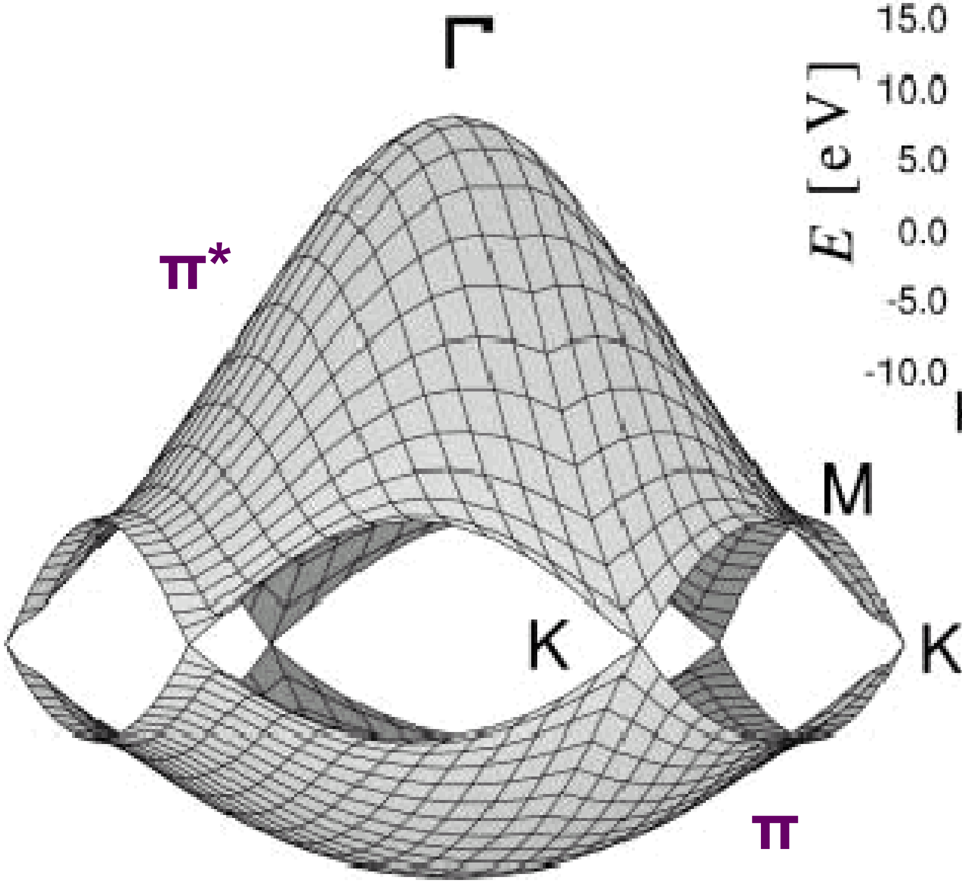
$$\mathbf{a}_1 = (\frac{\sqrt{3}}{2}, \frac{1}{2})a,\ \mathbf{a}_2 = (\frac{\sqrt{3}}{2}, -\frac{1}{2})a$$

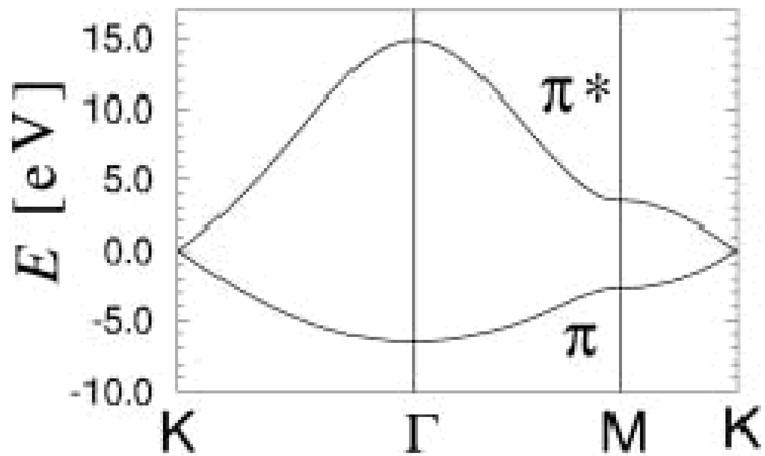
$$\mathbf{b}_1 = (\frac{1}{2}, \frac{\sqrt{3}}{2})\frac{4\pi}{\sqrt{3}a},\ \mathbf{b}_2 = (\frac{1}{2}, -\frac{\sqrt{3}}{2})\frac{4\pi}{\sqrt{3}a}$$

$$E_k = \pm t\sqrt{1 \pm 4\cos\frac{k_y a}{2}\cos\frac{\sqrt{3}k_x a}{2} + 4\cos^2\frac{k_y a}{2}}$$

M. Dresselhaus

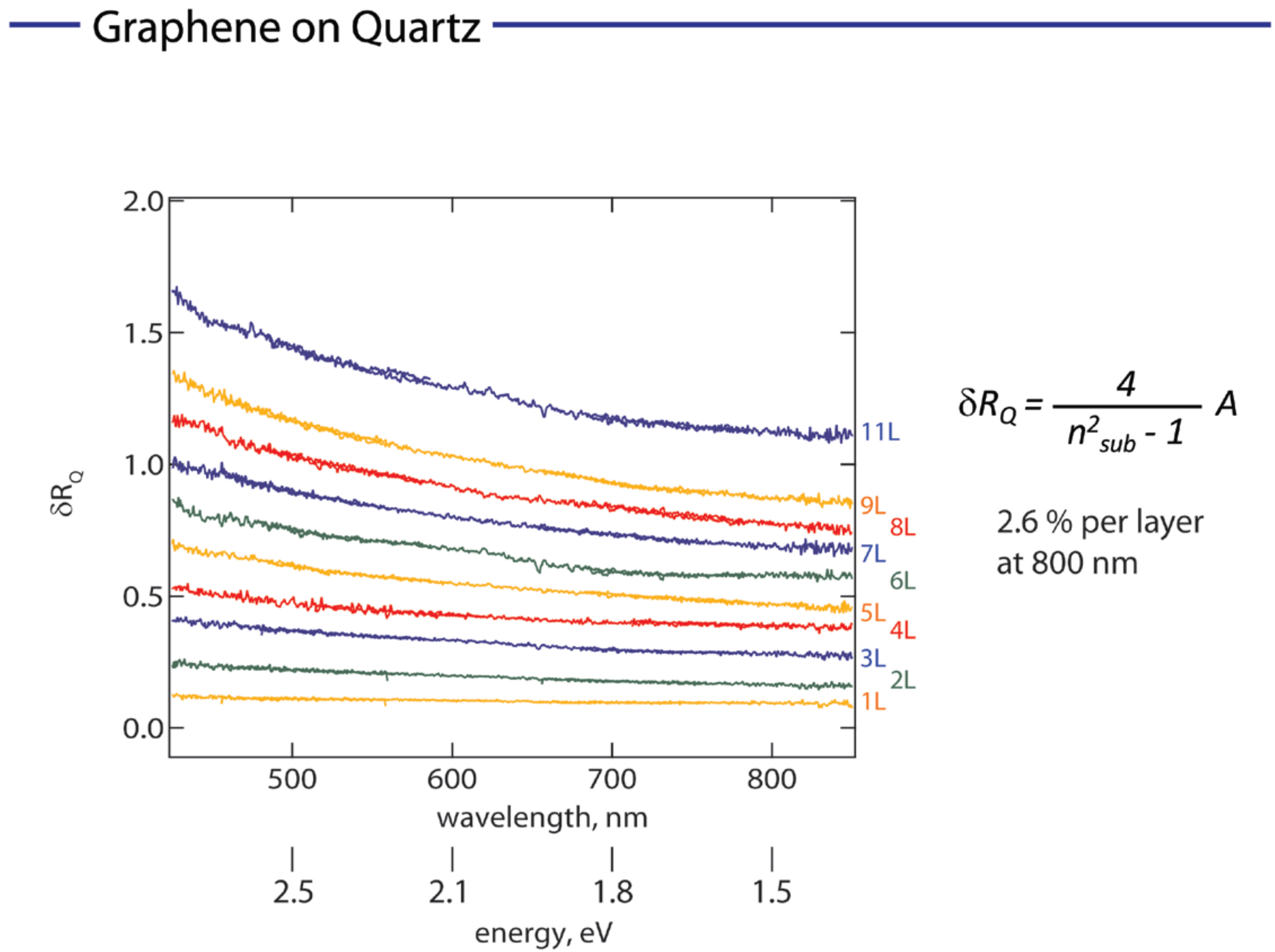
Independent Electron Model: no correlation
Continuous Optical Transitions π to π*





Saito and Kataura, *Topics Appl. Phys.* **2001**, *80*, 213

As expected, continuous visible and IR optical absorption

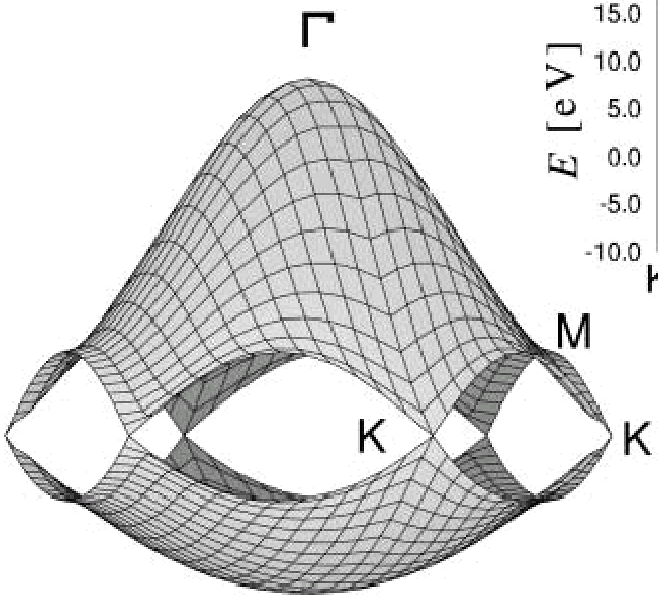


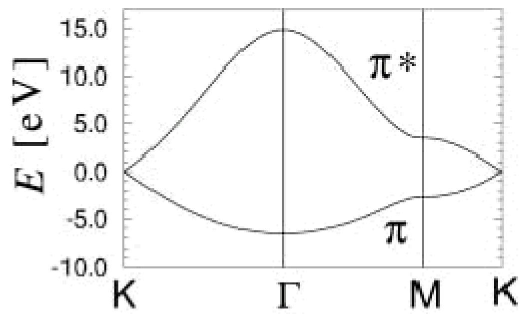
$$\delta R_Q = \frac{4}{n^2_{sub} - 1} A$$

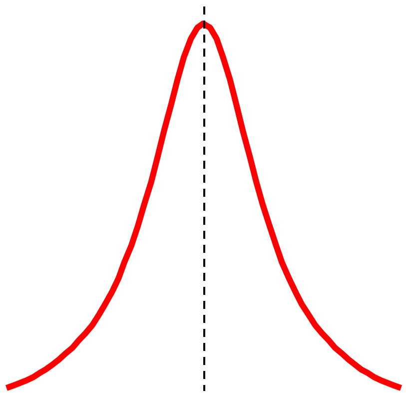
2.6 % per layer
at 800 nm

Absorption increases in UV at M saddle point

Independent electron model: no correlation







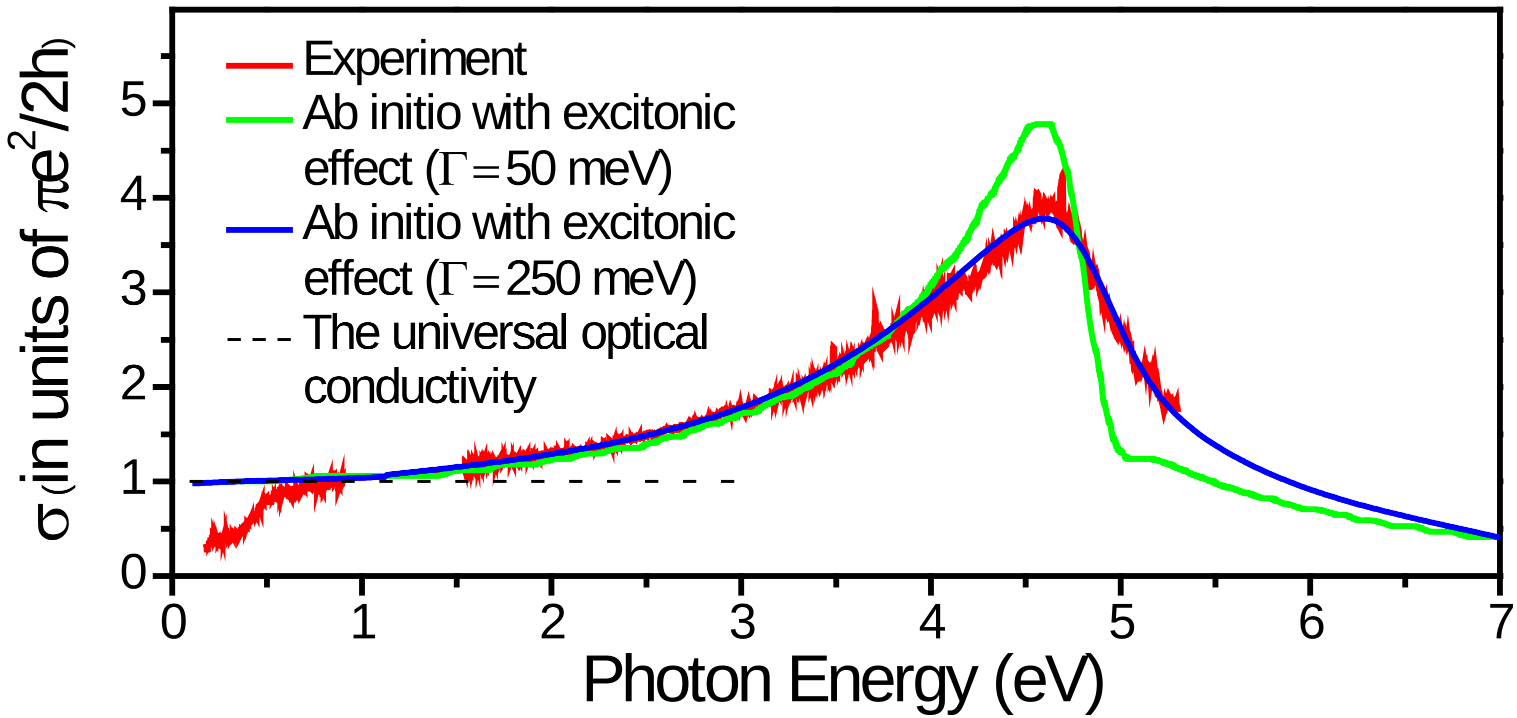
E_0

$$DOS_{SP}^{2D}(\omega) \propto -\ln\left|1-\frac{\omega}{E_0}\right|$$

Symmetric line shape
near the saddle point, **assuming no electron correlation**

Mak and Heinz

Correlation: An Exciton (electron-hole bound state) with 0.25eV Binding Energy forms at the M saddle point, even though the system is metallic



Existence of strong e-h interactions at the graphene saddle point

Quasiparticles' lifetime near the M-point ~ 2.6 fs

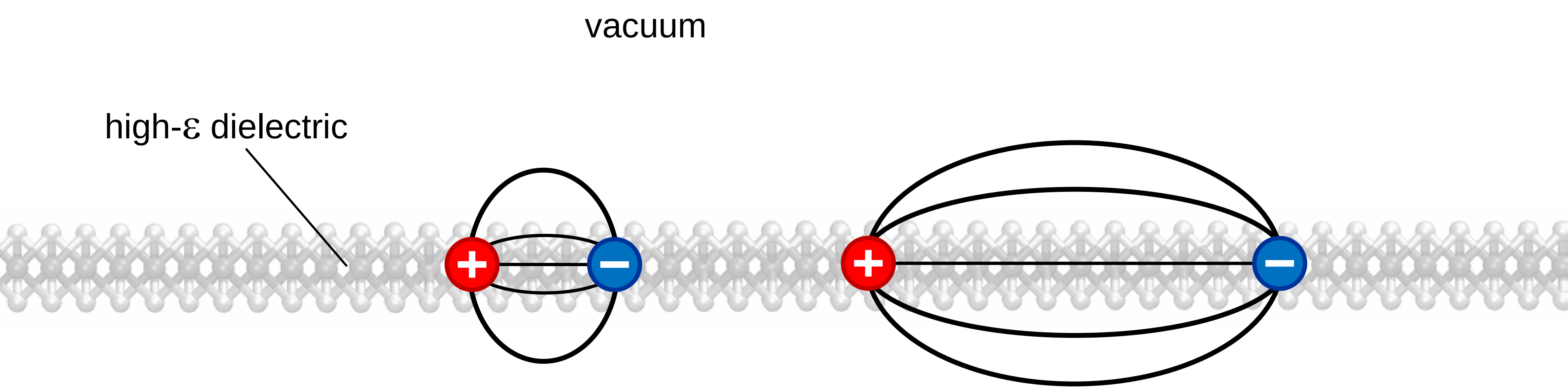
Also Chae etal, (von Klintzing group) Nano Lett. (2011) 11, 1379.

Fano lineshape at saddle point

Mak - Heinz

Yang et al. PRL 103, 186802 (2009)

Exciton: Bound Excited Electronic State of electron and hole orbiting each other

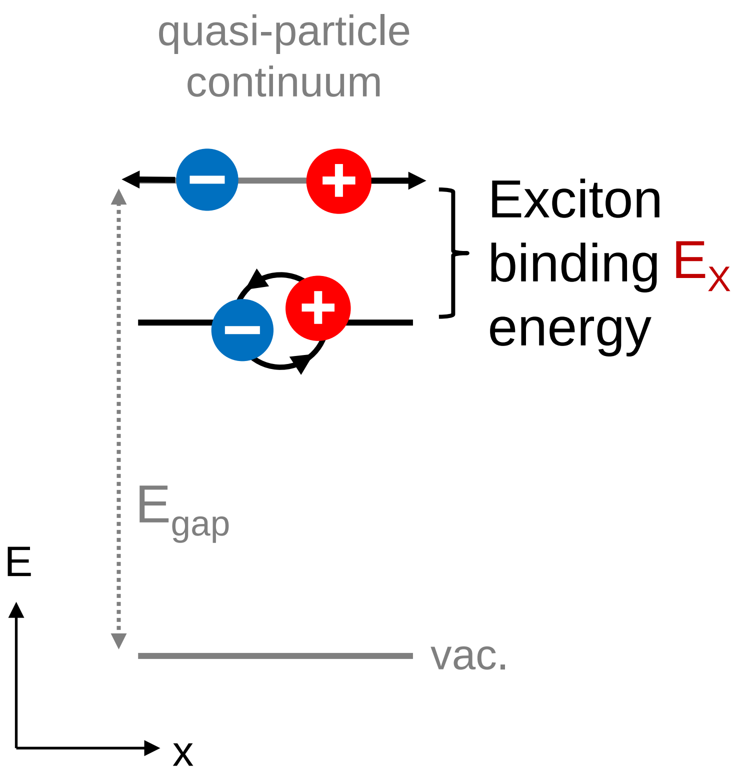


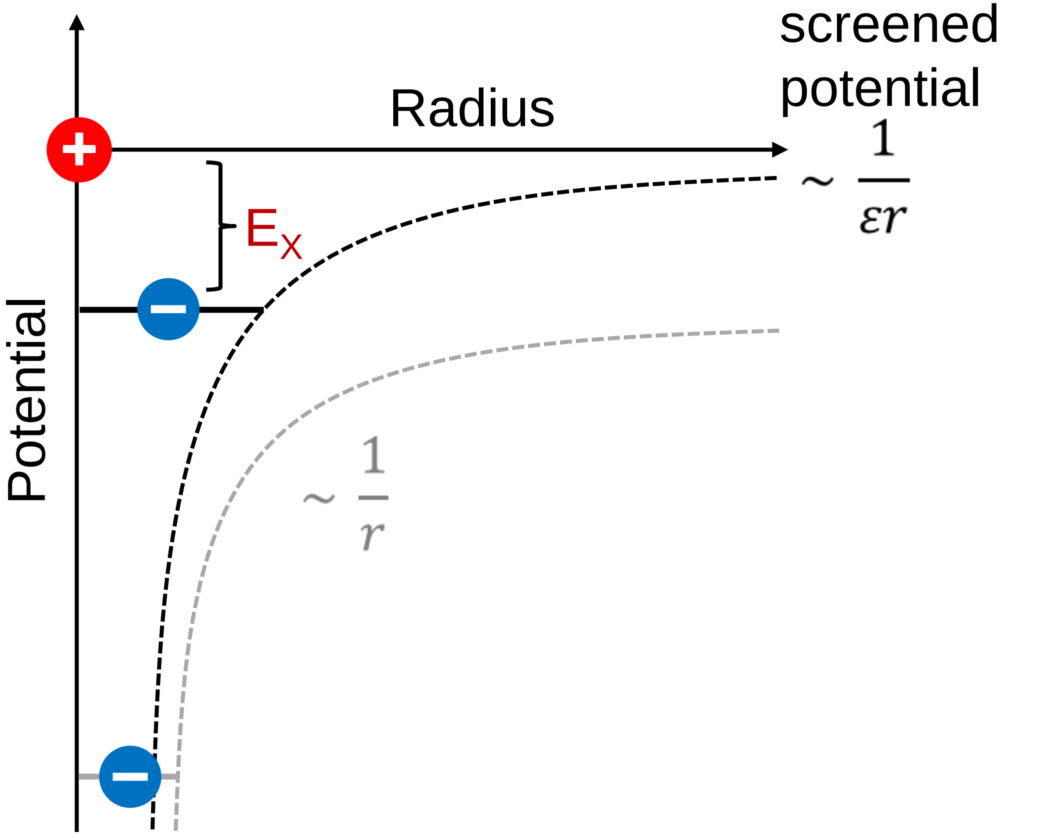
Short range: **strong** screening

Long range: **weak** screening

Electric field fringes out of 2D graphene into vacuum

Exciton binding energy





Strong Correlation in ground electronic state: Fractional quantum Hall effect in high magnetic field

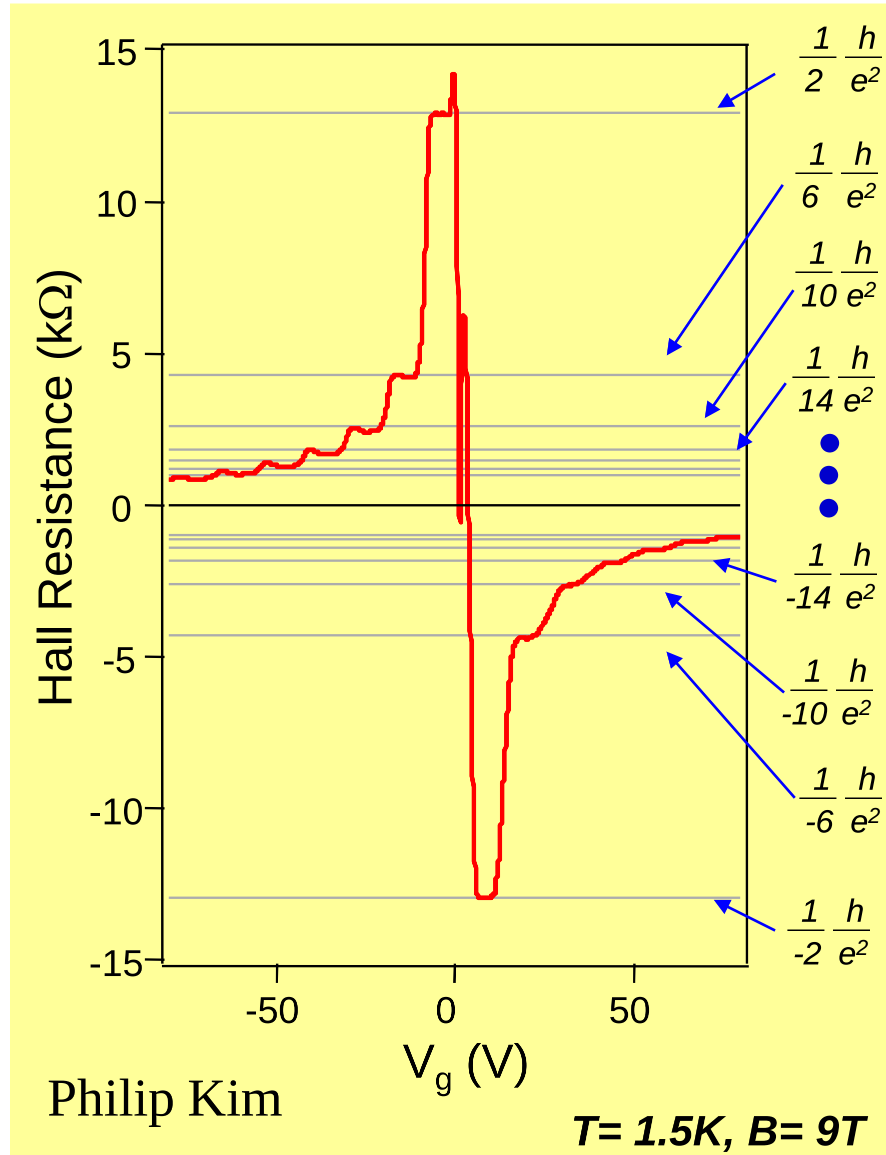
Classic signature of Correlated Electron Motion at low temperature

Robust effect implies that electron-electron interactions are essentially unscreened.

Bolton et al, Nature 2009, 462, 192
Du et al, Nature 2009, 462, 192.

Remarkable properties all result from strong aromatic pi chemical bonding

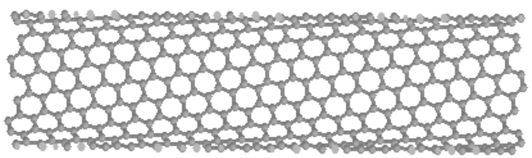
Fractional Quantum Hall Effect



If electron correlation is strong in graphene, it should be even stronger in semiconducting SWNT:

Lower dimensionality

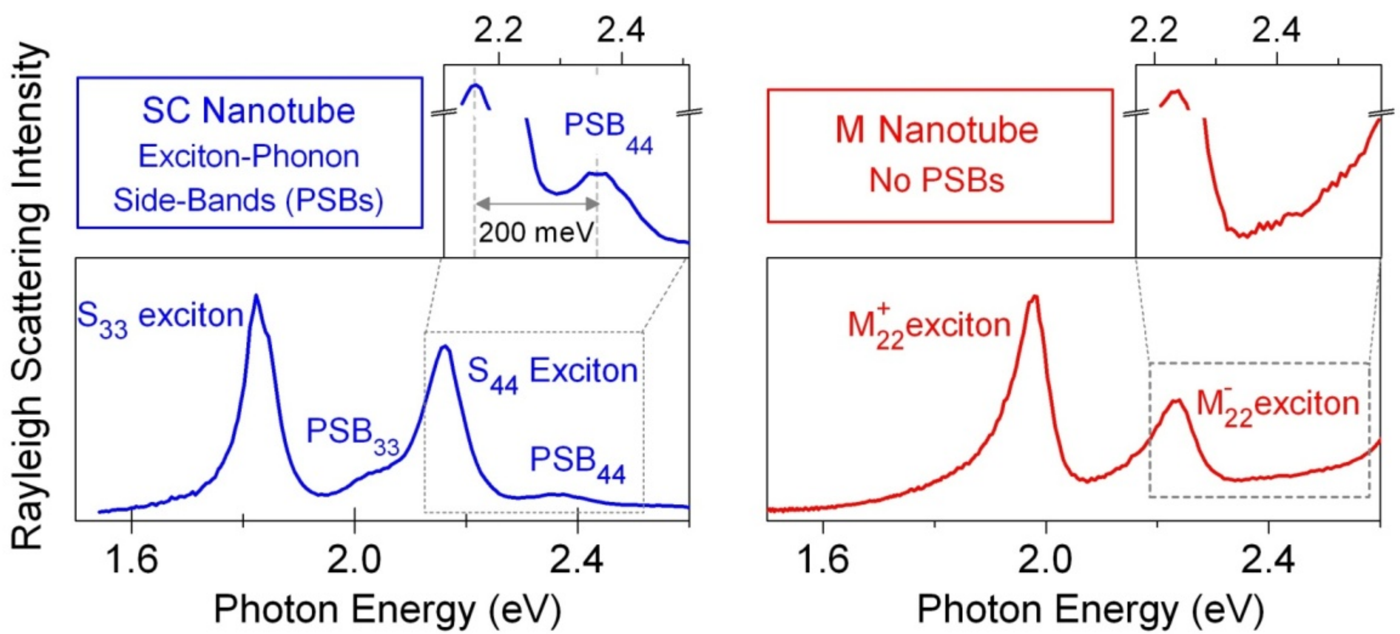
Less screening



(7,12) Chiral Semiconducting Tube

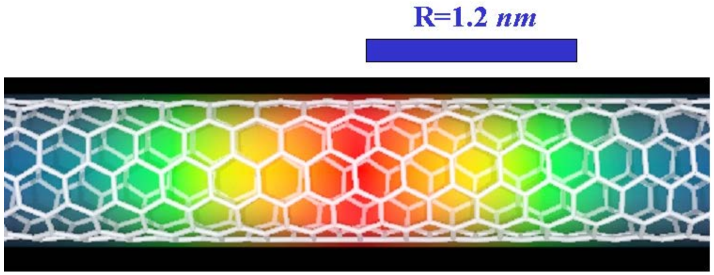
Rayleigh Scattering of Single Carbon Nanotubes shows very strong exciton electron correlation, as predicted by Ando. J. *Phys. Soc. Jpn*. **1997** 66, 1066-1073.

Optical spectra of both metallic and semiconducting tubes show excitons instead of continuous bands; band gap not apparent



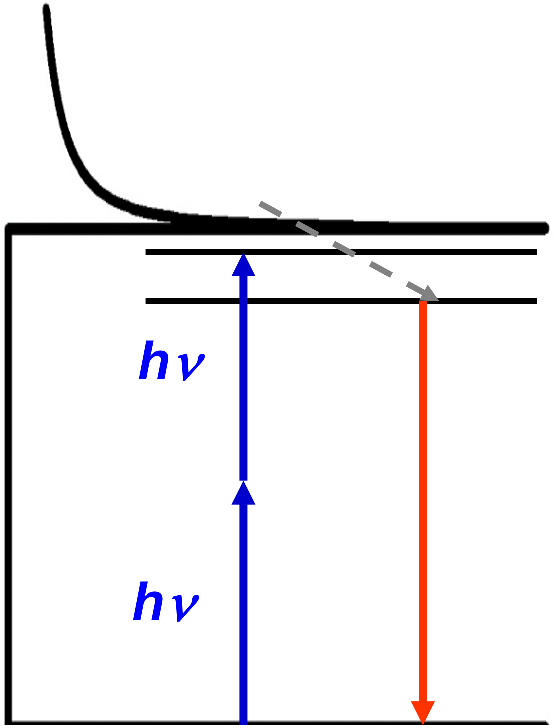
Feng Wang, Matt Sfeir, Tony Heinz, Jim Hone, Lou Brus

Neutral Bound Excitons Due to electron-hole attraction



Exciton envelope wavefunction:

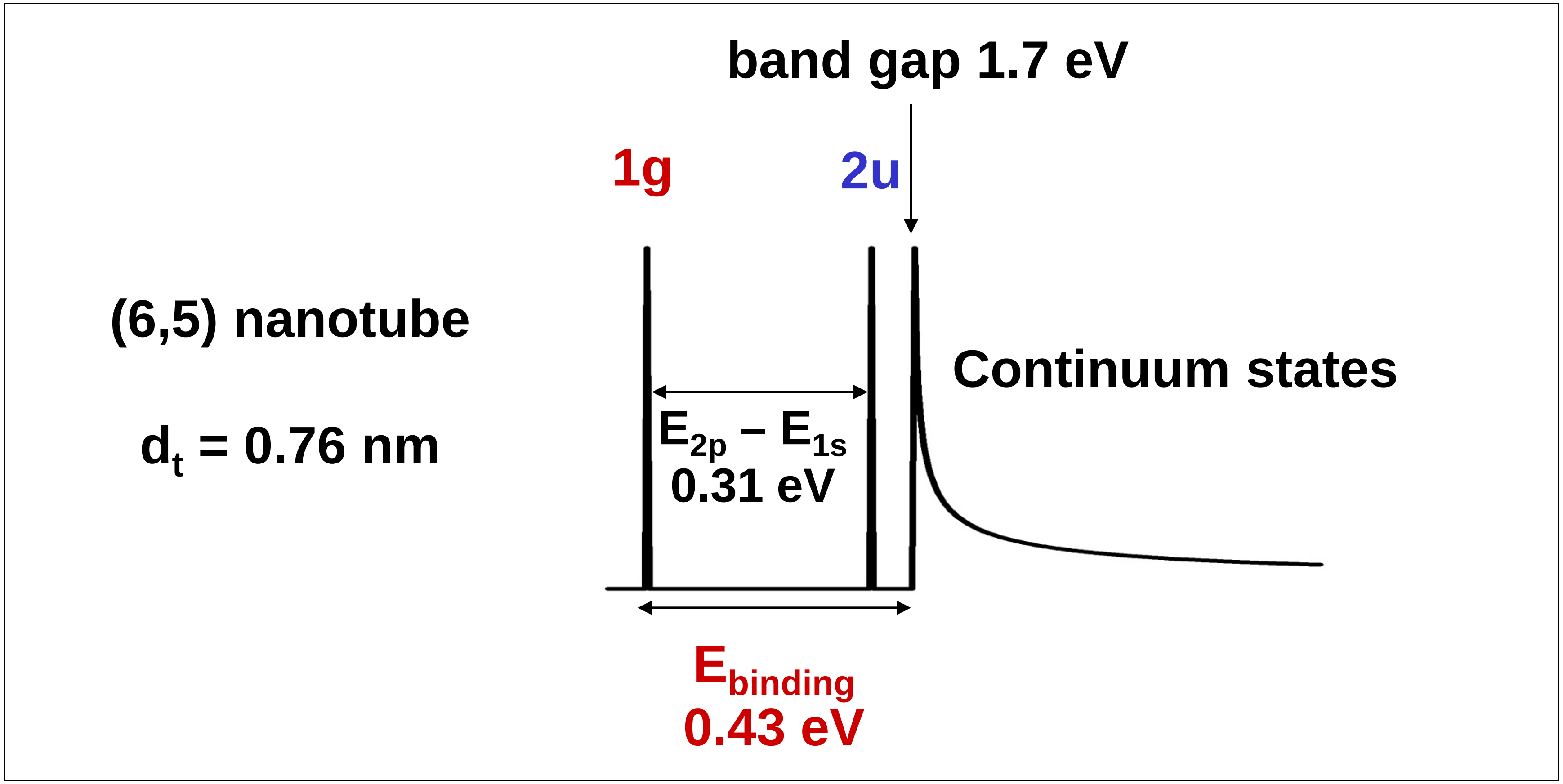
Neutral excited state moves as a unit along the SWNT



Exciton Bound states below the van Hove Band Edge

Two photon luminescence excitation spectra reveals exciton binding strength

F. Wang *etal*, Science <u>308</u>, 838(2005)

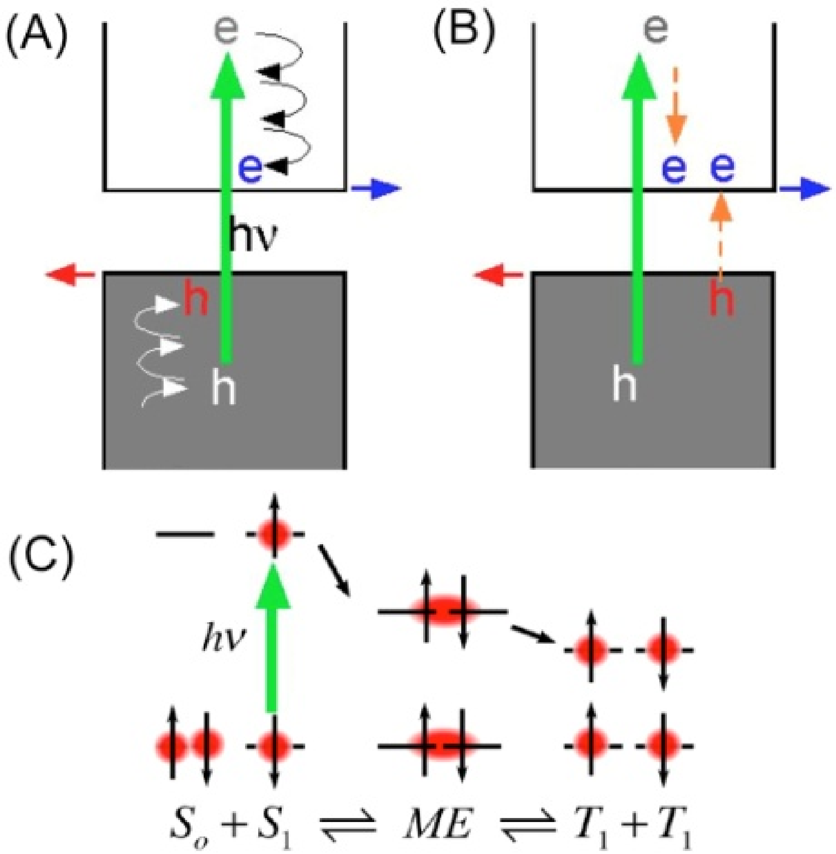


For comparison:

Poly(phenylene vinylene) ~ 0.35 eV

Semiconductor nanowires ~ tens of meV

Strong correlation in carbon nanotubes also creates femtosecond multiple exciton generation by hot electrons



Strong Correlation: Enhanced impact ionization in semiconducting carbon nanotubes

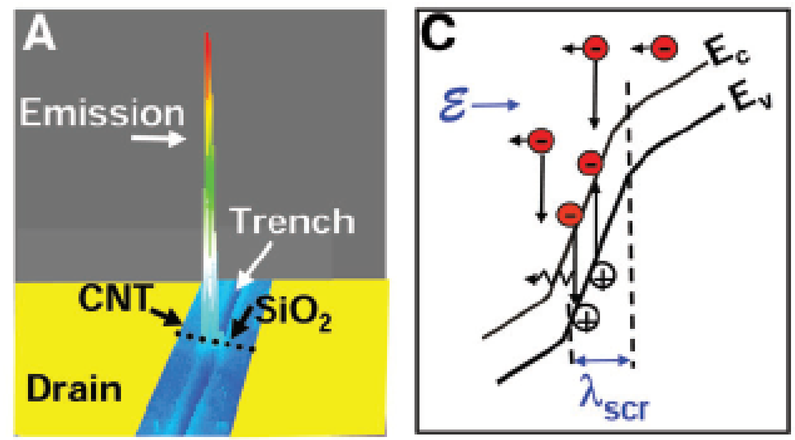
Decay of accelerated "hot" electrons by exciton creation rather than phonon creation

Bright Infrared Emission from Electrically Induced Excitons in Carbon Nanotubes

Jia Chen,[1*] Vasili Perebeinos,[1] Marcus Freitag,[1] James Tsang,[1] Qiang Fu,[2] Jie Liu,[2] Phaedon Avouris[1*]

We used the high local electric fields at the junction between the suspended and supported parts of a single carbon nanotube molecule to produce unusually bright infrared emission under unipolar operation. Carriers were accelerated by band-bending at the suspension interface, and they created excitons that radiatively recombined. This excitation mechanism is ~1000 times more efficient than recombination of independently injected electrons and holes, and it results from weak electron-phonon scattering and strong electron-hole binding caused by one-dimensional confinement. The ensuing high excitation density allows us to observe emission from higher excited states not seen bv photoexcitation. The excitation mechanism of these states was anal

18 NOVEMBER 2005 VOL 310 SCIENCE



Hot Carrier Impact Exciton generation rate 10^{+15} s^{-1}

Why? Increased electron-electron interaction in Nanostructures

Two independent factors: dimensionality and screening

1. Dimensionality with no change in screening:

3D bulk semiconductor: weak Coulomb, excitons not important
2D confinement in plane: Coulomb interaction up by 4x
1D confinement on line: Coulomb interaction diverges!
Low Dimensionality implies increased electron-electron correlation

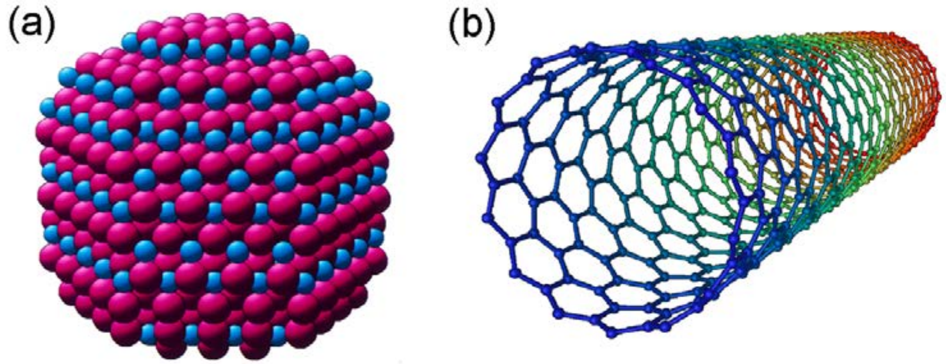
0D quantum dot is a different case: no dissociation, less correlated motion,
Finite Coulomb interaction, kinetic energies larger

2. Screening of Coulomb interaction:

reduced screening in 1D,
almost full screening in 0D
Reduced screening implies increased electron-electron correlation

Schmitt-Rink et al. Adv. Phys. 1989 38, 89-188 Brus, Nano Letters 10, 363 (2010)

Quantum Dots compared to Carbon Nanotubes



4nm CdSe nanocrystal

Particle in box orbitals
Rigid structure
Hard to collect photocurrent
Surface States and ligands - terrible

Band gap: 2. 2 eV
Kinetic energies 0.4 eV
Coulomb energy 0.1 eV

1nm Carbon Nanotube

Plane wave basis orbitals
Rigid structure: minor Franck-condon shift
Easy to collect photocurrent
No Surface States or ligands - excellent

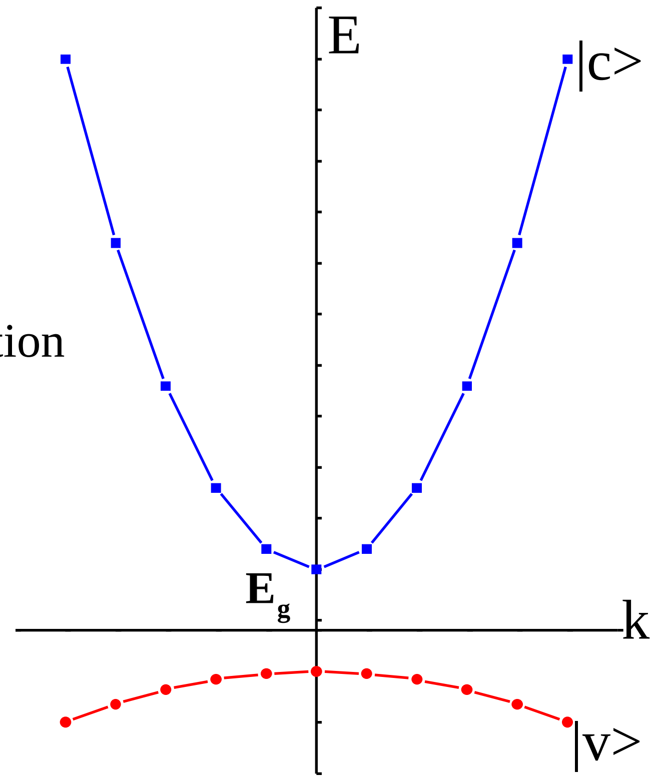
Band Gap: 1.7 eV
Kinetic Energies 0.4 ev
Coulomb Energy: 0.8 eV

Carbon Nanotubes and Graphene have very high electron correlation

Expect MEG, and Impact Ionization.

Quantum confinement of electron and hole in Qdot
Weak correlation

Empty conduction band



Full valence band

De Broglie Electron Momentum
mv=hk=h/λ

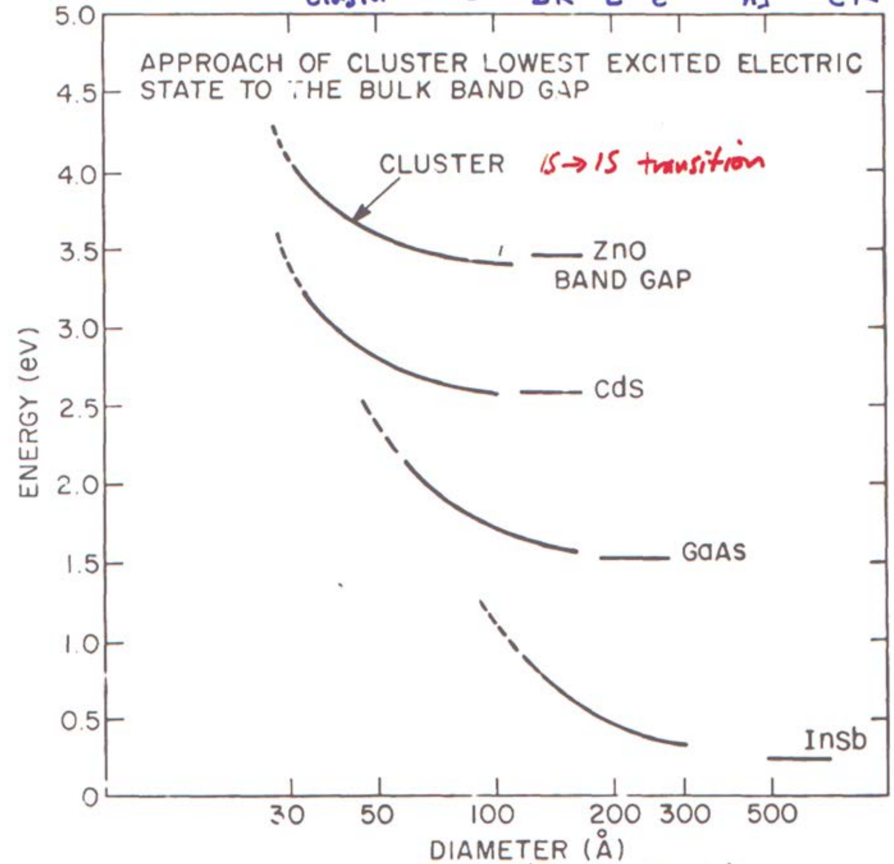
electron wavelength λ quantized in particle:

L. Brus, J. Chem. Phys. 79, 5566 (1983); 80, 4403 (1984)

Electron Correlation — Coulomb attraction between e^- and h^+

$\Psi \simeq \phi_{1s}(r_e)\,\phi_{1s}(r_h)$ zero order

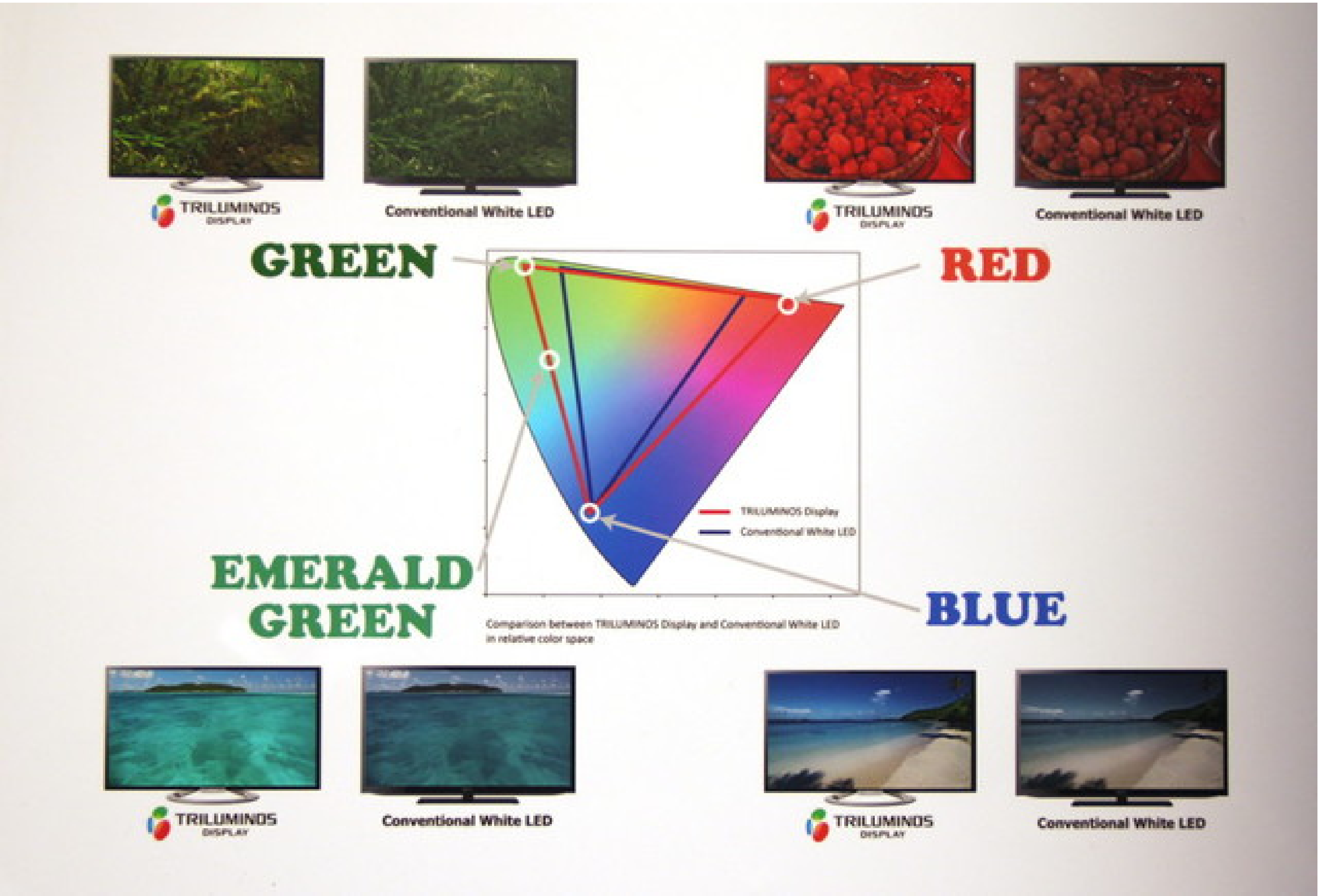
$$E^*_{cluster} = E_g + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right] - \frac{1.8e^2}{\epsilon R} + $$



No adjustable parameters!

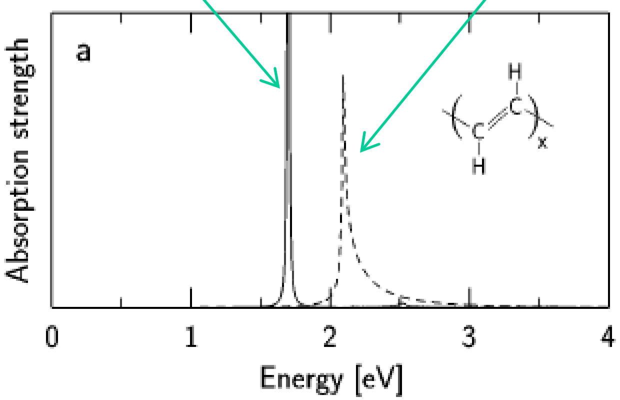
Luminescent Core/Shell Qdots are used in Televisions, Smart Phones, and Tablets.

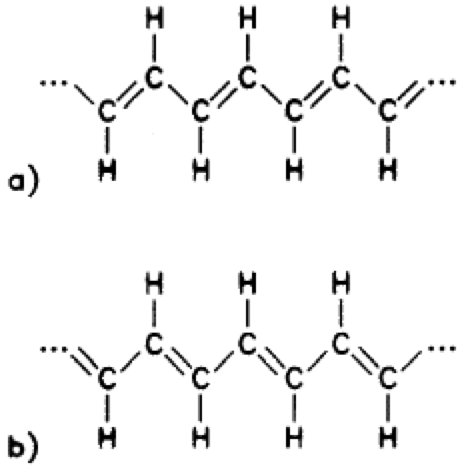
Qdots absorb **blue** GaN LED light and emit pure **red** and **green** light to make a vivid 3 color LCD Display



Extreme Correlation in purely 1D pi electron system: Linear trans-polyacteylene optical spectra

exciton 1D jdos



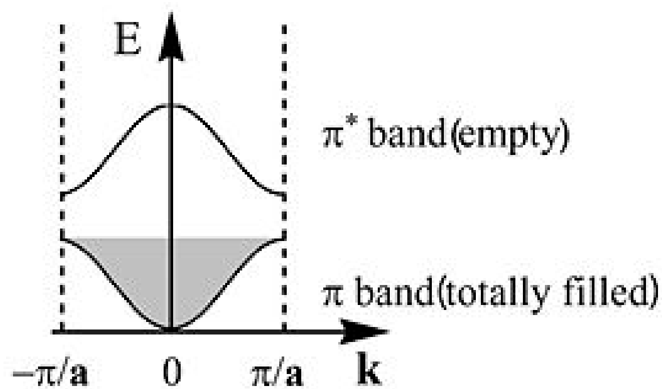


Strict 1D system

Bethe-Saltpeter equation

Exciton binding energy 0.4 eV

Rohlfing and Louie, PRL 82, 1959 (1999)



However, polyacetylene **exciton** decay into **solitons** which lie inside the band gap.

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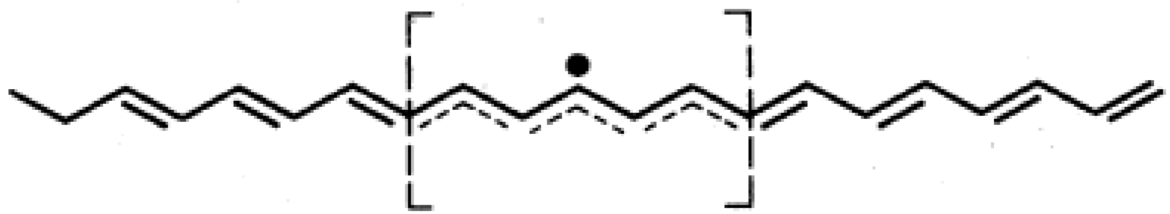
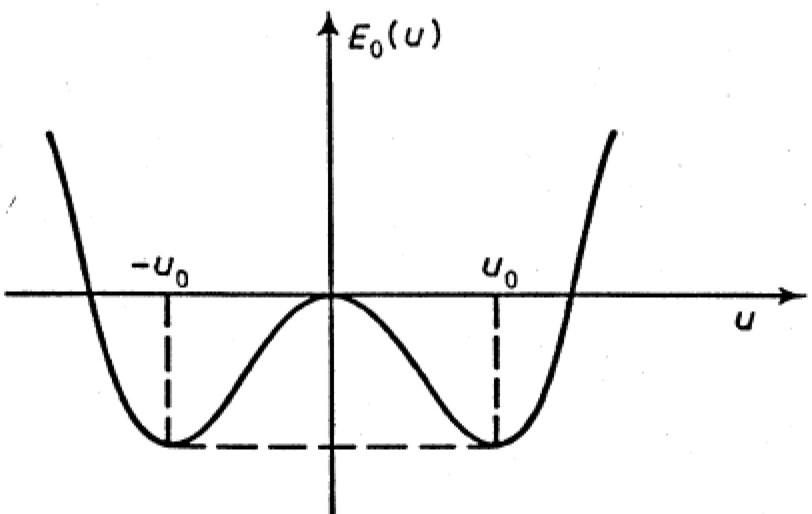
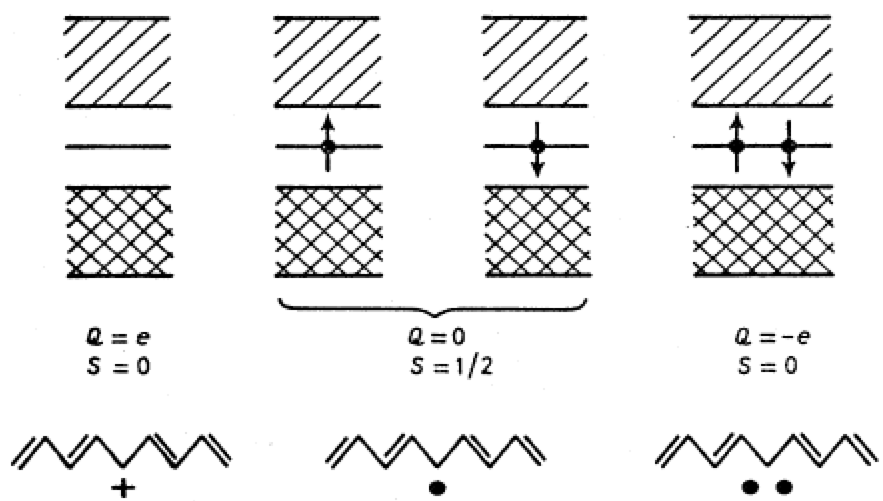
Strongly correlated solitons in 1D polyacetylene



A valence bond type structure in organic chemistry



Bond displacement



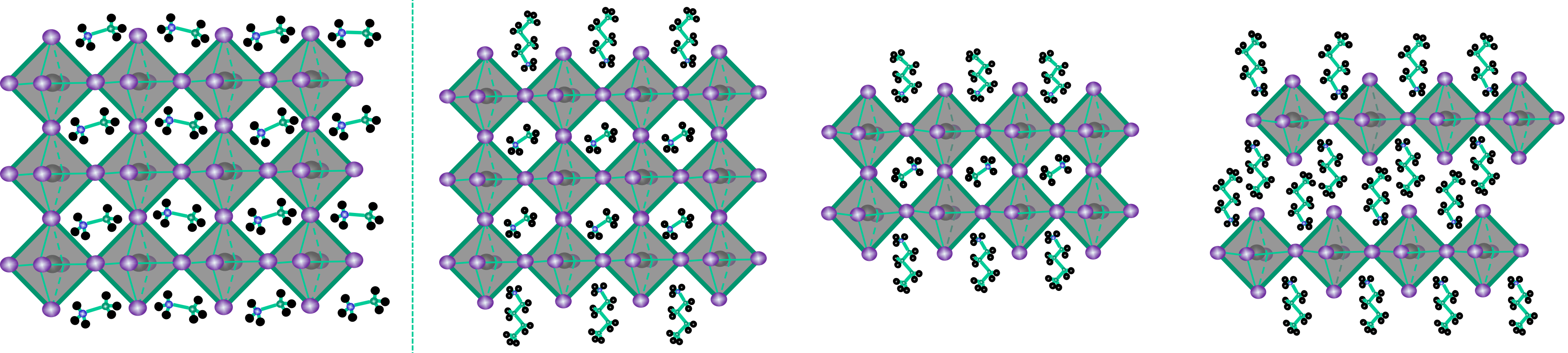
Heeger et al, Rev Mod Phys 60 (1988)

Strong correlation in 2D Pb-halide Perovskites

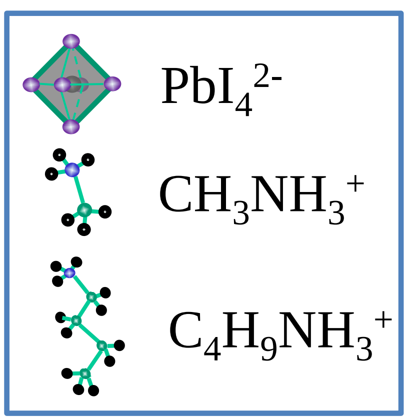
3D $CH_3NH_3PbI_3$

2D Perovskite

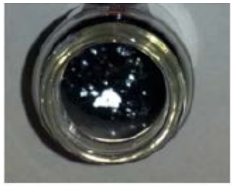
n = 3 | n = 2 | n =1



d = 2.1 nm | d = 1.4 nm | d = 0.7 nm

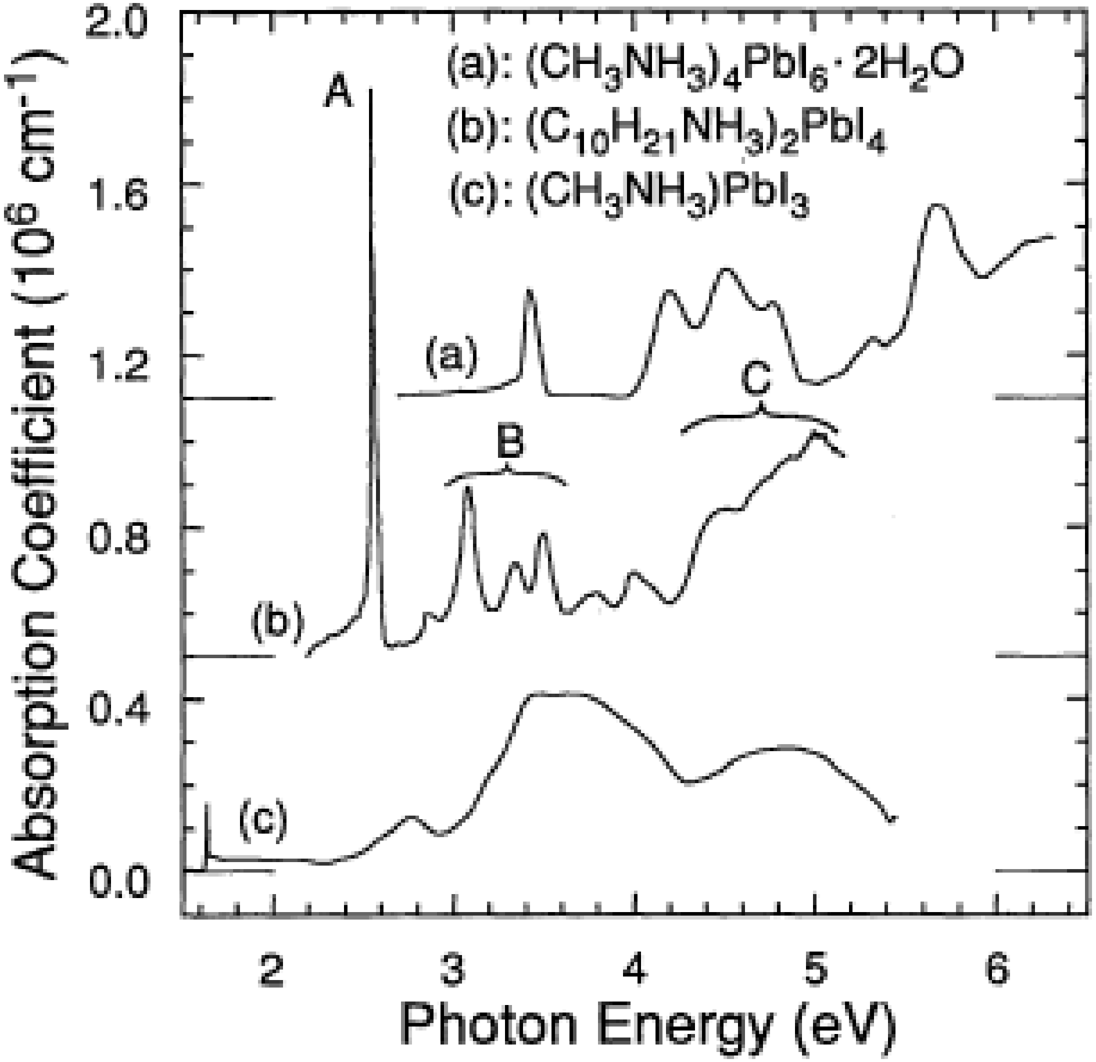


$(BuNH_3I)_2(CH_3NH_3I)_{n-1}(PbI_2)_n$



- **N is the number of inorganic layers.**

Dramatic Change in Optical spectra of 2D and 3D perovskites



Exciton binding energy:

3D 37 mev

2D 320 mev

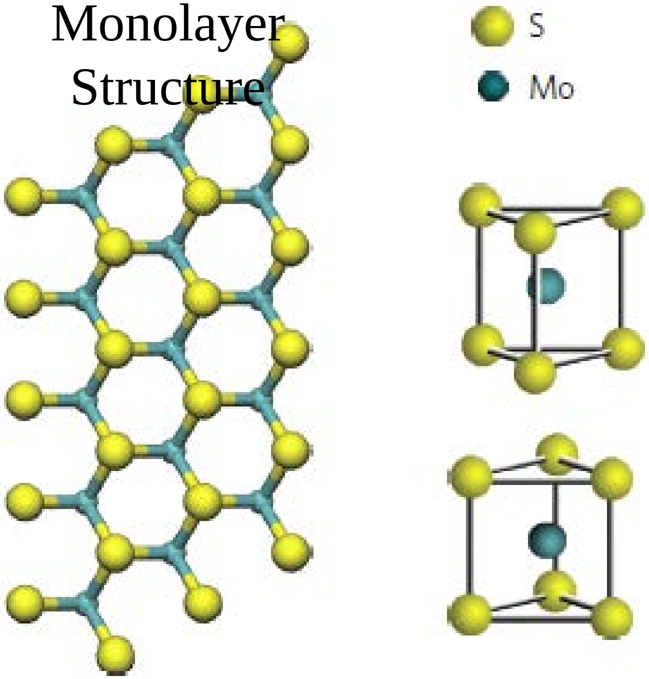
Hirasawa, M.; Ishihara, T., Goto, T. *J. Phys. Soc. Jpn.* **1994**, 63, 3870-3879.

MoS2 becomes direct gap in single layers and emits strongly valence and conduction bands made from Mo d states

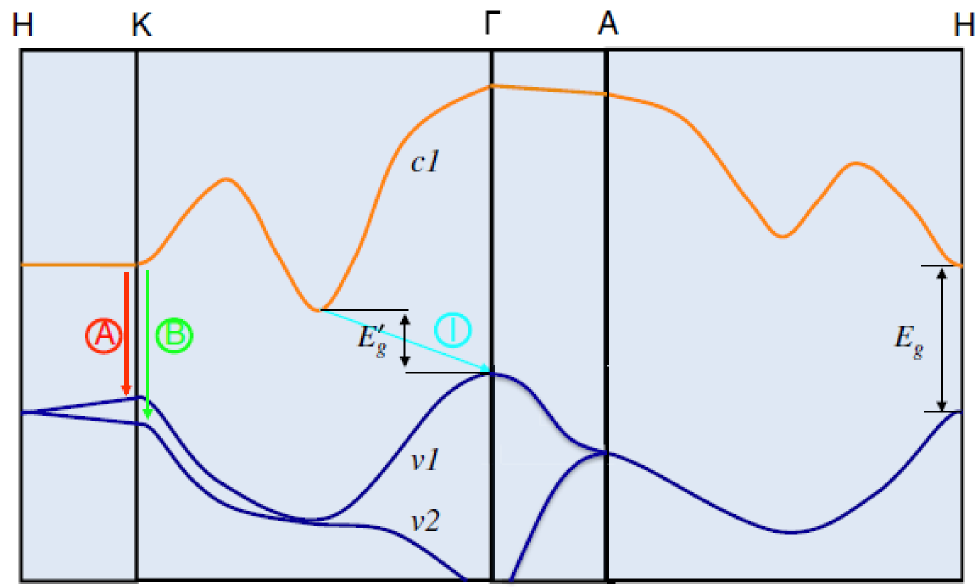
Crystal Structure of MoS_2

MoS2 Monolayer Structure

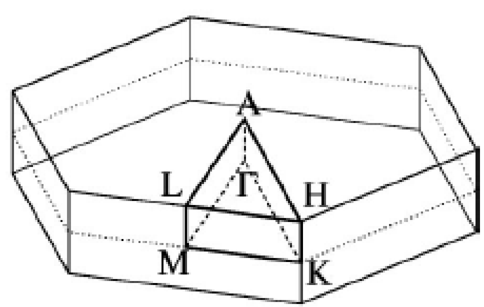
Bulk Unit Cell



Simplified Band Structure of Bulk MoS_2



First Brillouin Zone

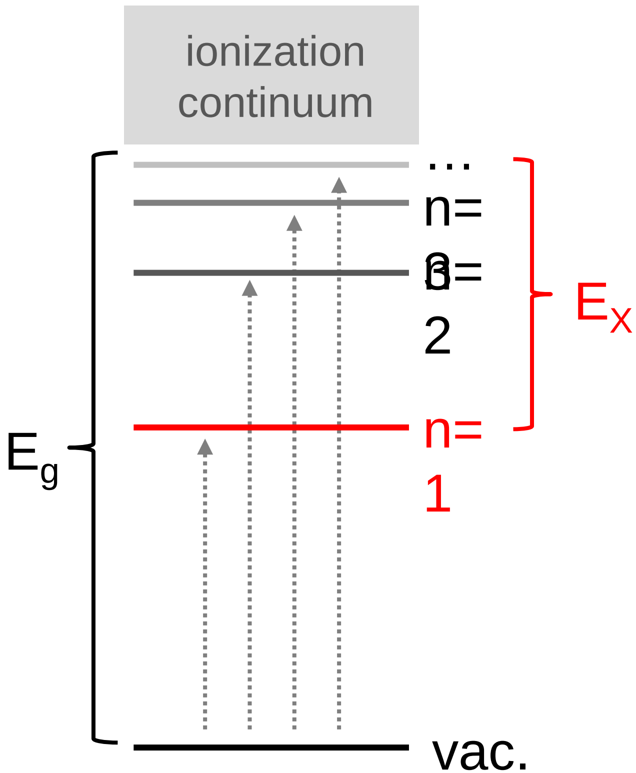


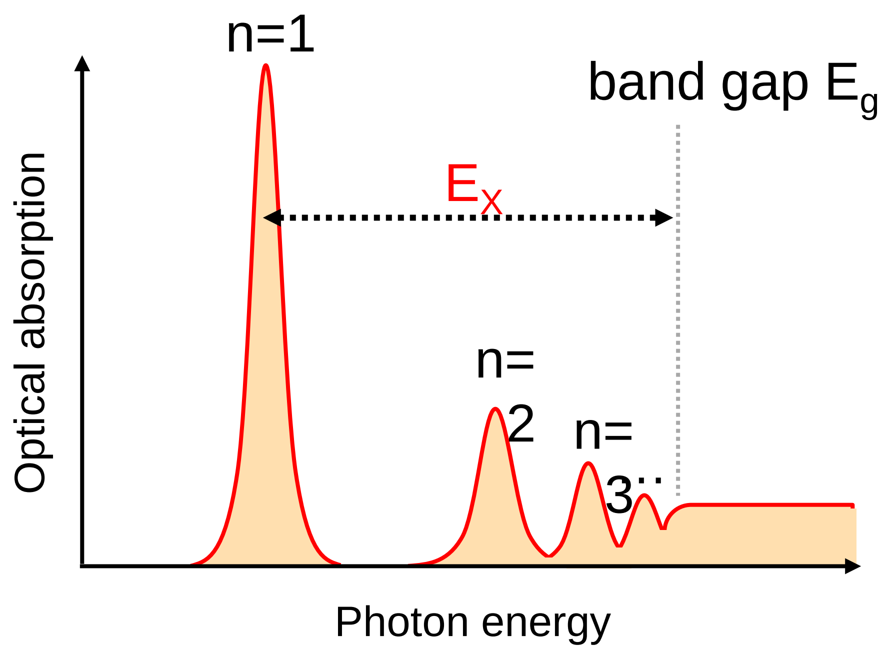
Direct Transition: A, B

Indirect Transition: I

How to measure exciton binding energy

Exciton Rydberg series



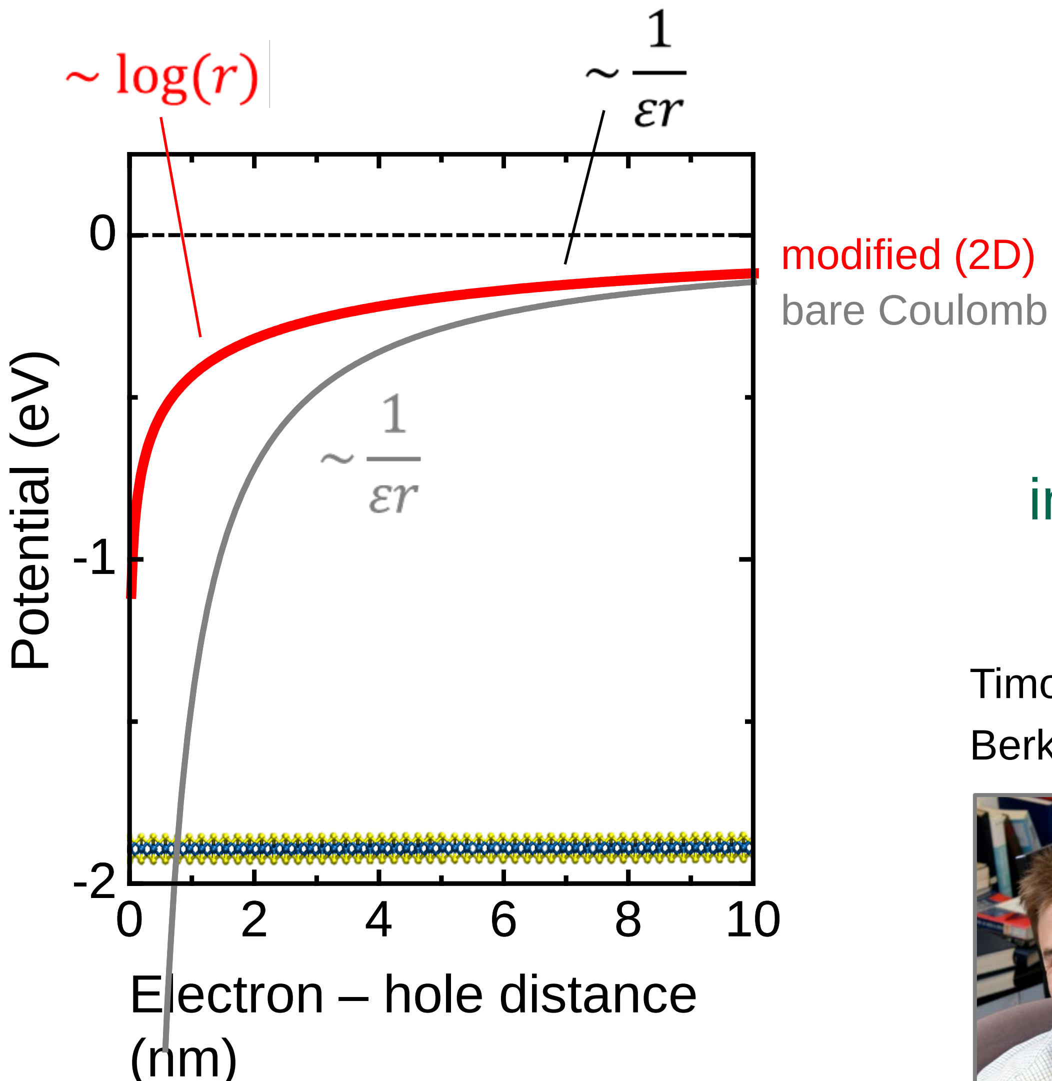


2D Hydrogen – model: $E(n) \sim \frac{1}{(n - ½)^2}$

H. Haug and S.W. Koch *"Quantum theory of the optical and electronic properties of semiconductors"*

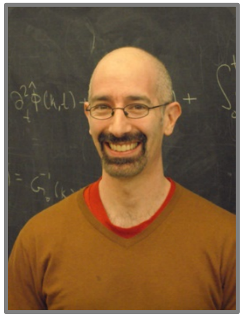
Chernikov - Heinz

2D screening potential



Exciton problem is solved in the effective 2D potential

Theory:

Timothy C. Berkelbach	Mark S. Hybertsen	David R. Reichmann
		

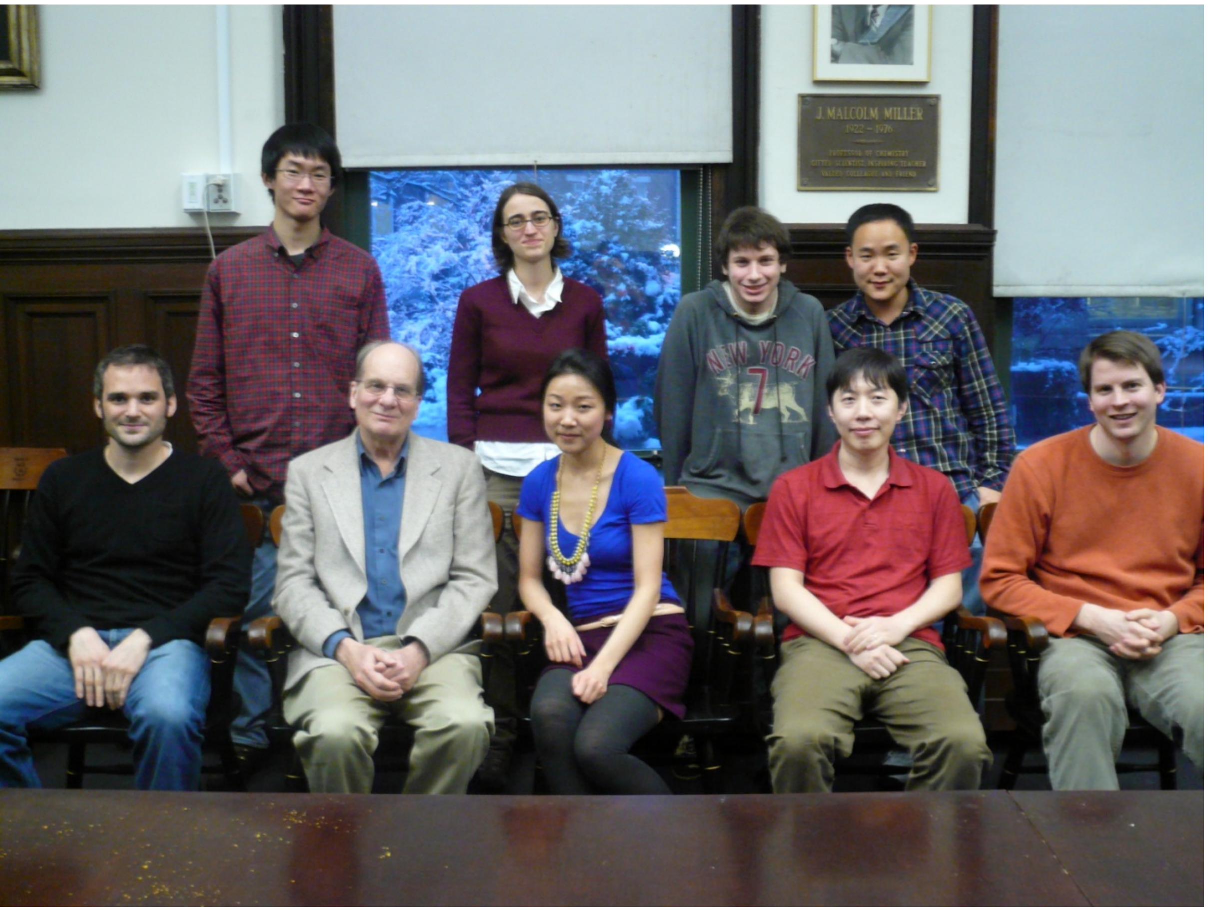
Columbia University

Brookhaven National Laboratory

P. Cudazzo et al. *Phys. Rev. B*. (2011)

T.C. Berkelbach et al. *Phys. Rev. B.* (2013)

Thanks to NSF, DOE, Keck Foundation, AFOSR MURI, MIRT collaborators and especially students!



Graphene students and postdocs:

Sunmin Ryu, Stephane Berciaud, Haitao Liu, Andrew Crowther, Naeyoung Jung, Li Liu, Zheyuan Chen, Yinsheng Guo, Elizabeth Thrall

Conclusion

1) Sp3 hybridized Qdot Size Dependent Electrical and Optical Properties result from Simple Quantum Confinement. Surface States are a problem. Electron-Hole Coulomb interaction is minor.

2) Qdots are new classes of large molecules and are excellent chromophores.

3) Sp2 hybridized SWNT and graphene are unique systems: they show ballistic transport and have huge physical strength. **No localized surface States**. Electron-Hole Coulomb interaction is very strong.

4) In 1D and 2D, simple band structure is misleading. Explicit Correlation is necessary.

5) In nanoscience the most creative and essential aspect is synthesis and materials technology– can we make the exact structure we want at exactly the right place?