Columbia University in the City of New York

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Electron Correlation in Nanoscience: Size and Dimensionality

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

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


- $\pi$ band of graphite
- Energy Band Model
  - Zero Gap Semiconductor

Unit cell

\[ a_1 = \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right)a, \quad a_2 = \left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \right)a \]

\[ b_1 = \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right) \frac{4\pi}{\sqrt{3}a}, \quad b_2 = \left( \frac{1}{2}, -\frac{\sqrt{3}}{2} \right) \frac{4\pi}{\sqrt{3}a} \]

\[ E_K = \pm t \sqrt{1 + 4\cos \frac{k_y a}{2} \cos \frac{\sqrt{3}k_x a}{2} + 4\cos^2 \frac{k_y a}{2}} \]
Independent Electron Model: no correlation
Continuous Optical Transitions $\pi$ to $\pi^*$

As expected, continuous visible and IR optical absorption

\[ \delta R_Q = \frac{4}{n_{\text{sub}}^2 - 1} \]

2.6% per layer at 800 nm
Absorption increases in UV at M saddle point

Independent electron model: no correlation

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

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 $\sim 2.6 \text{ fs}$
Fano lineshape at saddle point
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

Exciton binding energy $E_x$

Potential

Radius

in the solid: screened potential

$\sim \frac{1}{\varepsilon r}$

Hydrogen model

quasi-particle continuum

$E_{\text{gap}}$

vac.
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

Remarkable properties all result from strong aromatic pi chemical bonding

Philip Kim

$T = 1.5K, B = 9T$
If electron correlation is strong in graphene, it should be even stronger in semiconducting SWNT:

**Lower dimensionality**

**Less screening**

(7,12) *Chiral Semiconducting Tube*

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


(6,5) nanotube
d_t = 0.76 nm

band gap 1.7 eV

1g

2u

Continuum states

E_{2p} - E_{1s} = 0.31 eV

E_{binding} = 0.43 eV

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.

\[ S_0 + S_1 \iff ME \iff T_1 + T_1 \]
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 by photoexcitation. The excitation mechanism of these states was anal...
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

Quantum Dots compared to Carbon Nanotubes

**4nm CdSe nanocrystal**
- Particle in box orbitals
- Rigid structure
- Hard to collect photocurrent
- Surface States and ligands - terrible

**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: 2.2 eV**
- Kinetic energies 0.4 eV
- Coulomb energy 0.1 eV

**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

De Broglie Electron Momentum
\[ mv = \hbar k = \hbar / \lambda \]

Empty conduction band

Full valence band

\[ \Psi = \phi_{1s}(r_e) \phi_{1s}(r_h) \]

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-polyacetylene optical spectra

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.
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 CH₃NH₃PbI₃

n = 3

2D Perovskite

n = 2

n = 1

d = 2.1 nm

d = 1.4 nm

d = 0.7 nm

(BuNH₃I)₂(CH₃NH₃I)ₙ₋₁(PbI₂)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

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

Crystal Structure of MoS₂

MoS₂ Monolayer Structure

Bulk Unit Cell

S
Mo

Simplified Band Structure of Bulk MoS₂

First Brillouin Zone

Direct Transition:
A, B

Indirect Transition: I
How to measure exciton binding energy

Exciton Rydberg series

2D Hydrogen – model:

\[ E(n) \sim \frac{1}{(n - \frac{1}{2})^2} \]

H. Haug and S.W. Koch “Quantum theory of the optical and electronic properties of semiconductors”
Exciton problem is solved in the effective 2D potential

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

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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?