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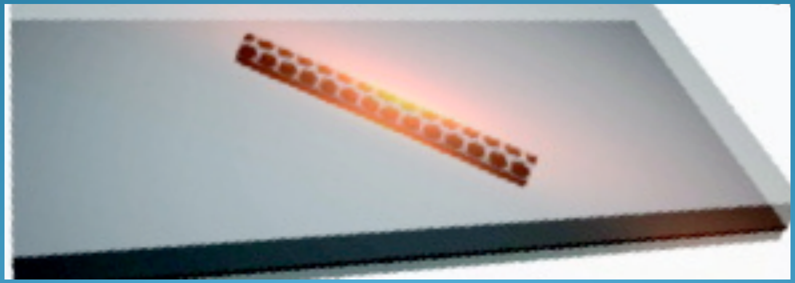
Electronic and Optical Properties of Semiconducting Carbon Nanotubes near Metallic Substrates

Catalin Spataru
Materials Physics Dept.
Sandia National Laboratories



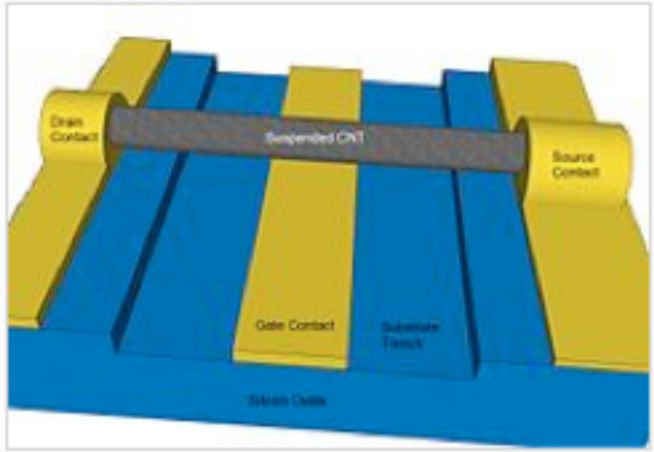
Outline

- Introduction.
- Theoretical approach.
- Quasiparticles and excitons in CNTs near a metal surface.

Introduction

- Understand the changes in properties due to a substrate:

- crucial for potential integration in functional devices.



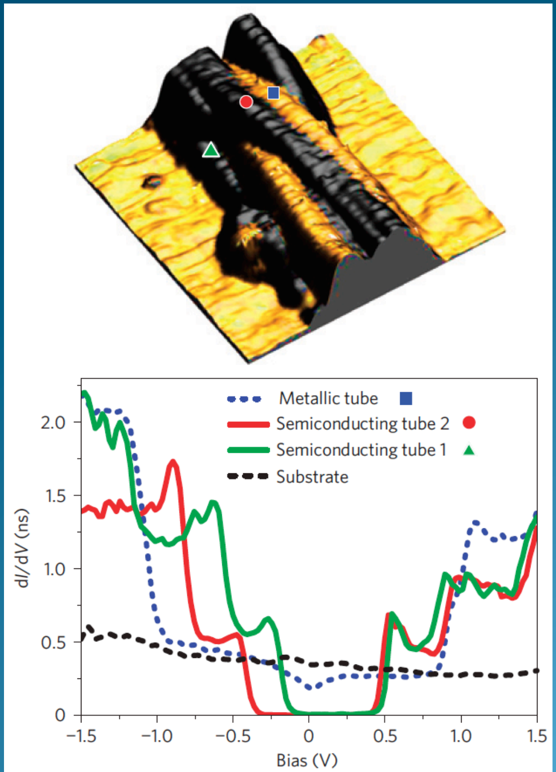
A suspended CNTFET device.

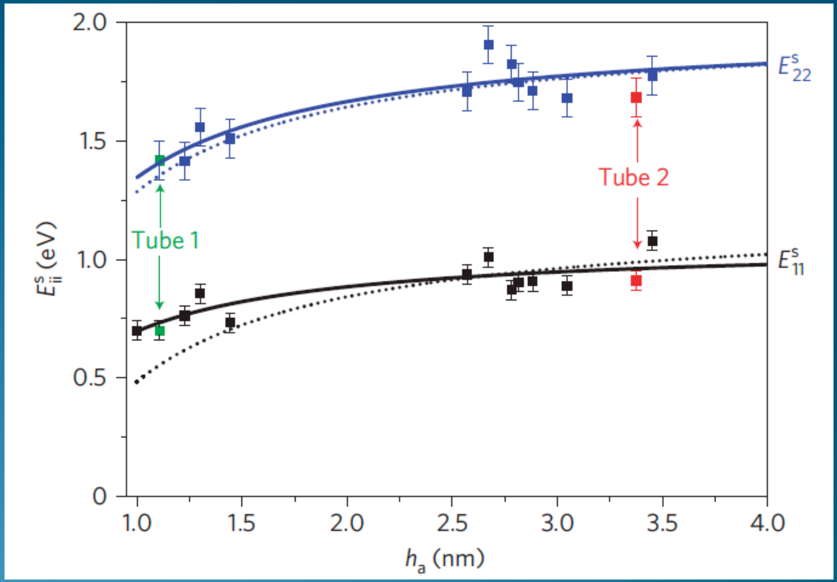
How does the presence of a metallic gate within a few nm from CNT affect the bandgap?

Many-body effects in electronic bandgaps of carbon nanotubes measured by scanning tunnelling spectroscopy

H. Lin[1,2], J. Lagoute[1], V. Repain[1], C. Chacon[1], Y. Girard[1], J.-S. Lauret[3], F. Ducastelle[2], A. Loiseau[2] and S. Rousset[1]*

Nat. Mater. **9**, 235 (2010).





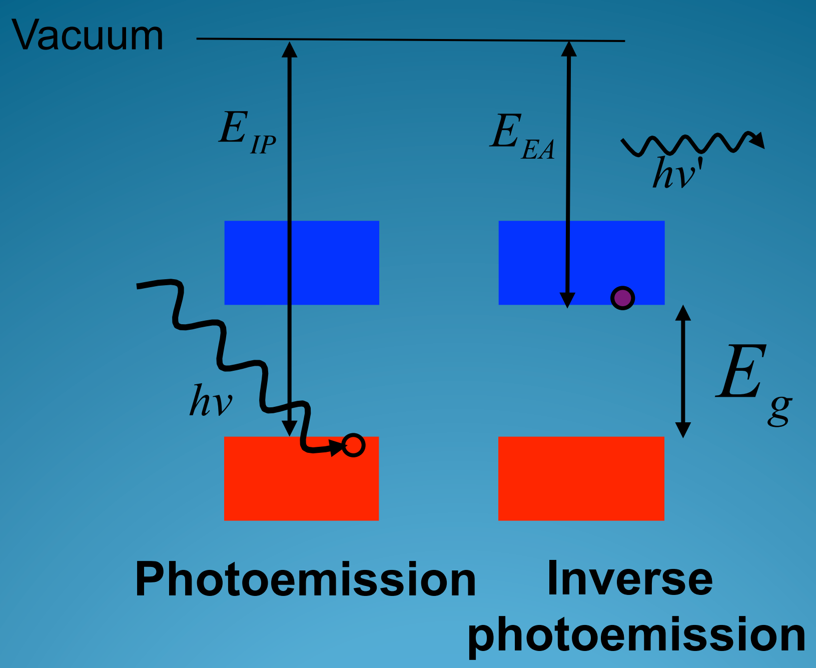
these reasons we provide empirical fits using $E = E_0 - C_1 e^2/(2h_a)$, where $C_1 = 0.52C_0$ for the E_{11} gap and $E = E_0 - C_2 e^2/(2h_a)$ with $C_2 = 0.89C_0$ for the E_{22} separation (solid lines in Fig. 3). Note that

Computational Approach

- Full *ab initio* approach for isolated CNTs.

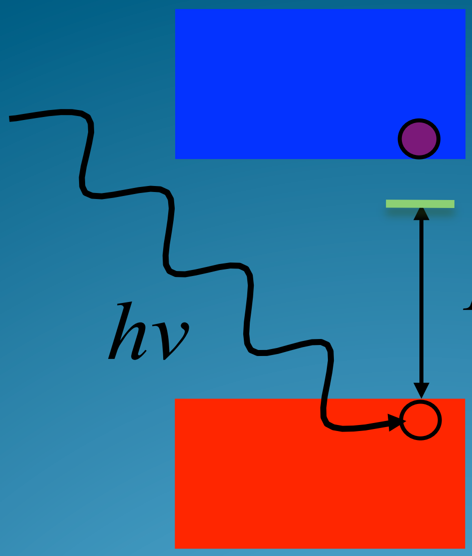
1) **Quasiparticle excitations** (band gaps, electron addition and removal energies)

- ✓ Photoemission & inverse photoemission
- ✓ STM



2) **Electron-hole excitations** (optical gaps, absorption spectra)

- ✓ Optical absorption
- ✓ Fluorescence/photoluminescence
- ✓ Pump-probe experiments

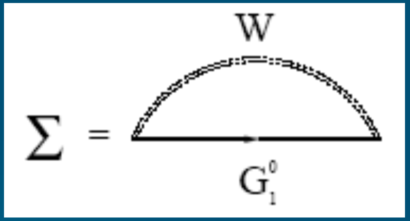


$$E_g^{opt} = E_g - E_{e-h}$$

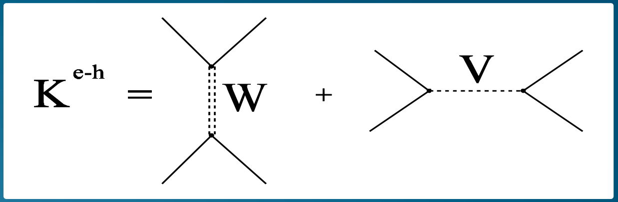
- *Ab initio* calculations done in three stages:

I. Ground state properties: DFT[1].

II. Quasiparticles: GW approximation[2].



III. Excitons: Bethe-Salpeter formalism[3].



- Green's function approach based on first-order perturbation expansion about the screened Coulomb interaction W.

- Perturbation expansion about the bare Coulomb interaction V: partial re-summation of an infinite set of diagrams.

1) Kohn and Sham, *Phys. Rev*. (1965).
2) Hybertsen and Louie, *Phys. Rev. B* (1986).
3) Rohlfing and Louie, *Phys. Rev. B* (2000).

- Embedding approach for CNTs near surfaces.

- Integrate out electron degrees of freedom of surface.

➢ Valid as long as hybridization effects are not important.

➔ Resulting many-body approach is similar to isolated nanostructure case, except:

$$V(\vec{r}-\vec{r}\,') \rightarrow \mathrm{w}(\vec{r},\vec{r}\,',\omega)$$

V=bare Coulomb interaction.
w= screened Coulomb interaction of surface alone.

- Model metallic substrate as planar perfect conductor.

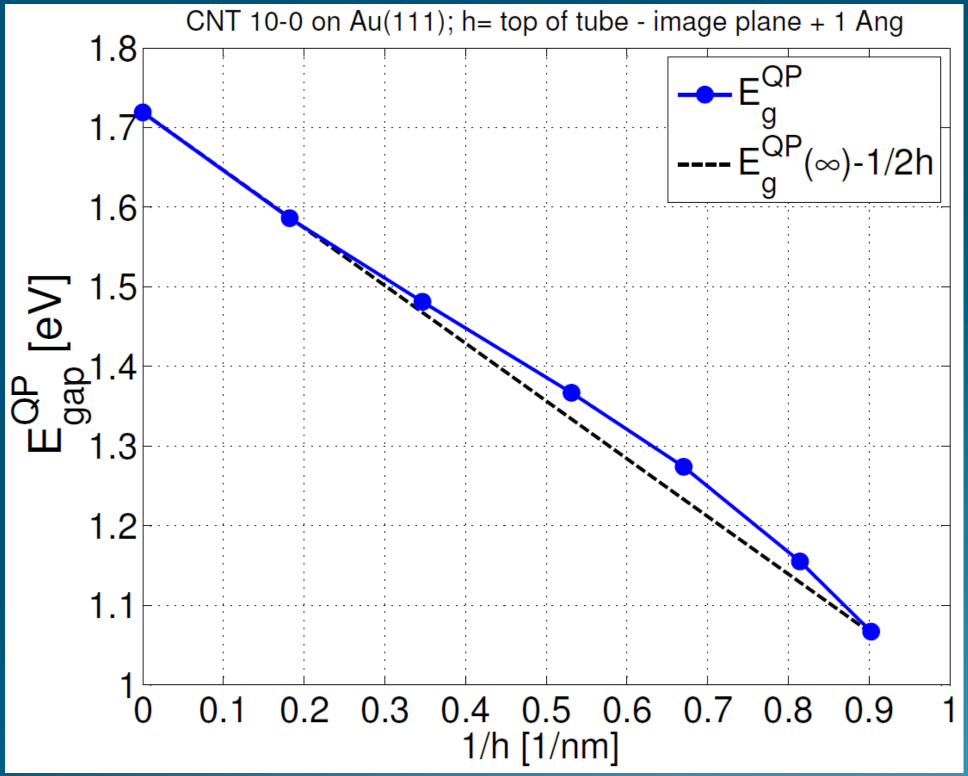
- Metal plasmon energies >> molecular energy levels.

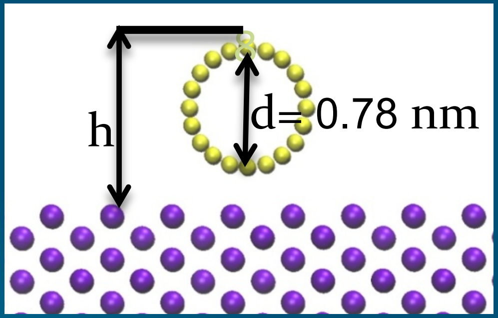
$$w(\vec{r},\vec{r}\,',\omega)=\frac{1}{|\vec{r}-\vec{r}\,'|}-\frac{1}{\sqrt{(x-x')^2+(y-y')^2+(z+z'-2\tilde{z})^2}}$$

$\tilde{z} =$ *image plane position.*

Quasiparticle and exciton renormalization in CNTs near a perfect metal.

10-0 CNT near a perfect metal





$$\delta E_g^{QP} \sim G\epsilon_{CNT}^{-1}\delta w$$

$$\delta w = -\frac{1}{\sqrt{(x-x')^2+(y-y')^2+(z+z'-2\tilde{z})^2}}$$

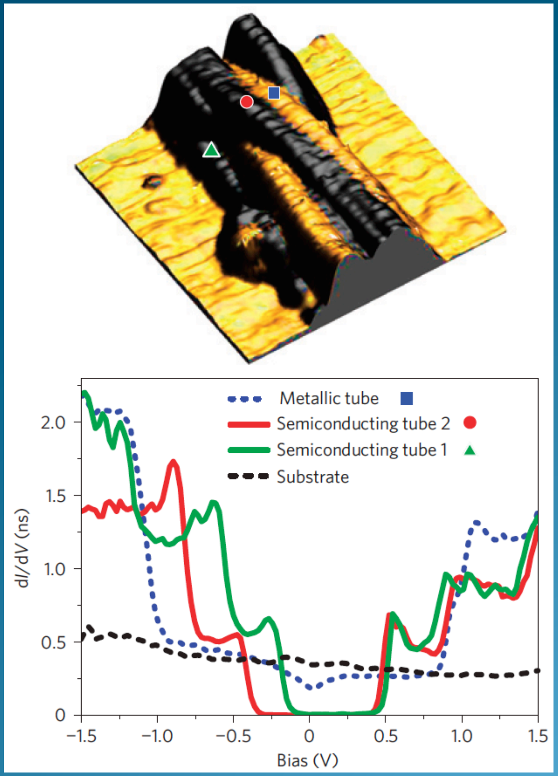
$$\Rightarrow \delta E_g^{QP} \approx -\frac{1}{2h}$$

- QP band gap renormalization as large as 0.65 eV !

- similar apparent height dependence as in experiment.
- for h >> d, intrinsic dielectric properties not important.
- for h < 5 nm, intrinsic dielectric properties play an important role.

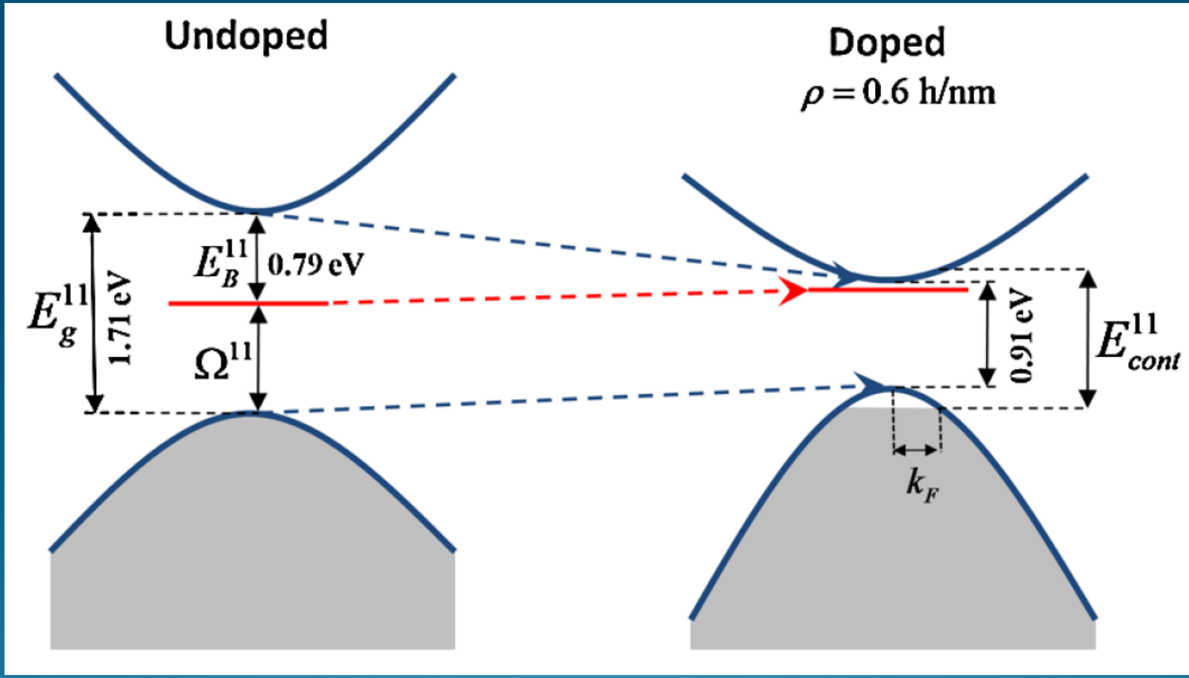
Additional effects may be relevant:

- ✓ charge transfer,
- ✓ hybridization (not important for CNT@Au).



Asymmetric (w.r.t. E_F) peak positions due to tube-substrate charge transfer.

BGR and exciton renormalization in doped 10,0 carbon nanotube

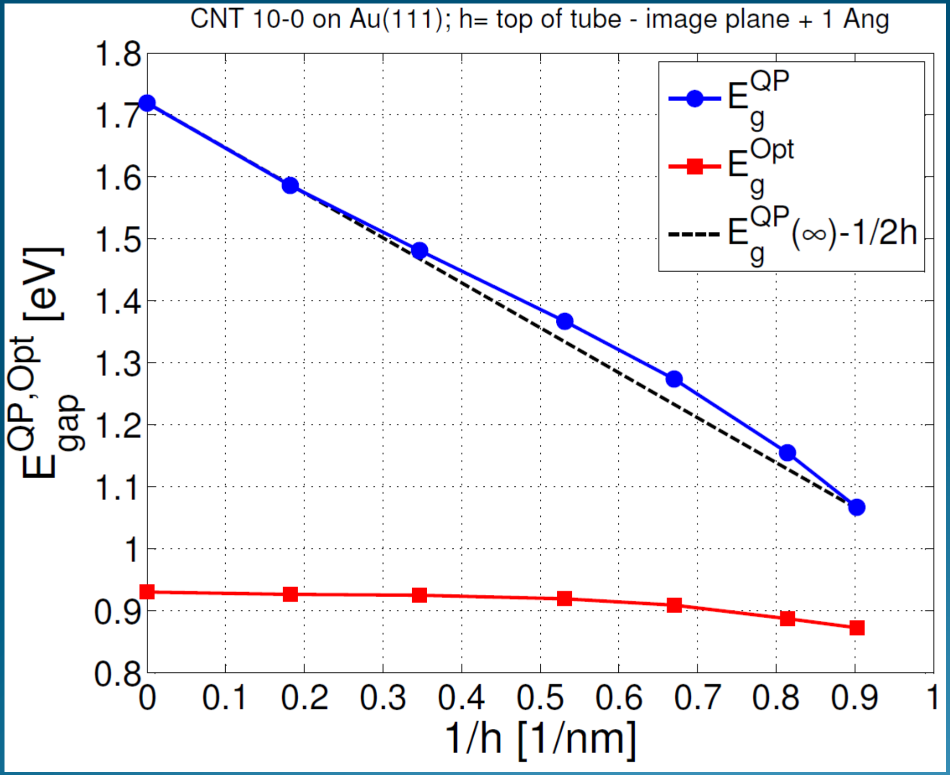


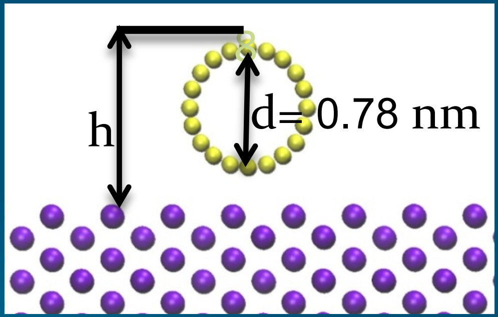
- QP band gap decrease of 800 meV !
- Exciton binding energy decreased by 600 meV !
- Optical absorption edge essentially unchanged!

Spataru and Léonard, *Phys. Rev. Lett.*, **104** 177402 (2010).

Spataru and Léonard, *Chem. Phys.* (2012), http://dx.doi.org/10.1016/j.chemphys.2012.08.021.

10-0 CNT near a perfect metal





$$\delta E_g^{Opt} \ll \delta E_g^{QP}$$

- Optical gap renolmalization is one order of magnitude smaller than QP BGR.
- Transition dipole –image dipole interaction slightly redshifts the optical gap by less than 55 meV.
- Lowest bright exciton not quenched.

Summary

- BGR follows simple height dependence ~1/2h.
- The intrinsic dielectric properties of the CNT play an important role in establishing the image-charge effect at small separations.
- Optical gap suffers order of magnitude smaller renormalization, due to weak transition dipole –image dipole interaction.
- Excitons can still bind; binding energy significantly decreased.

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