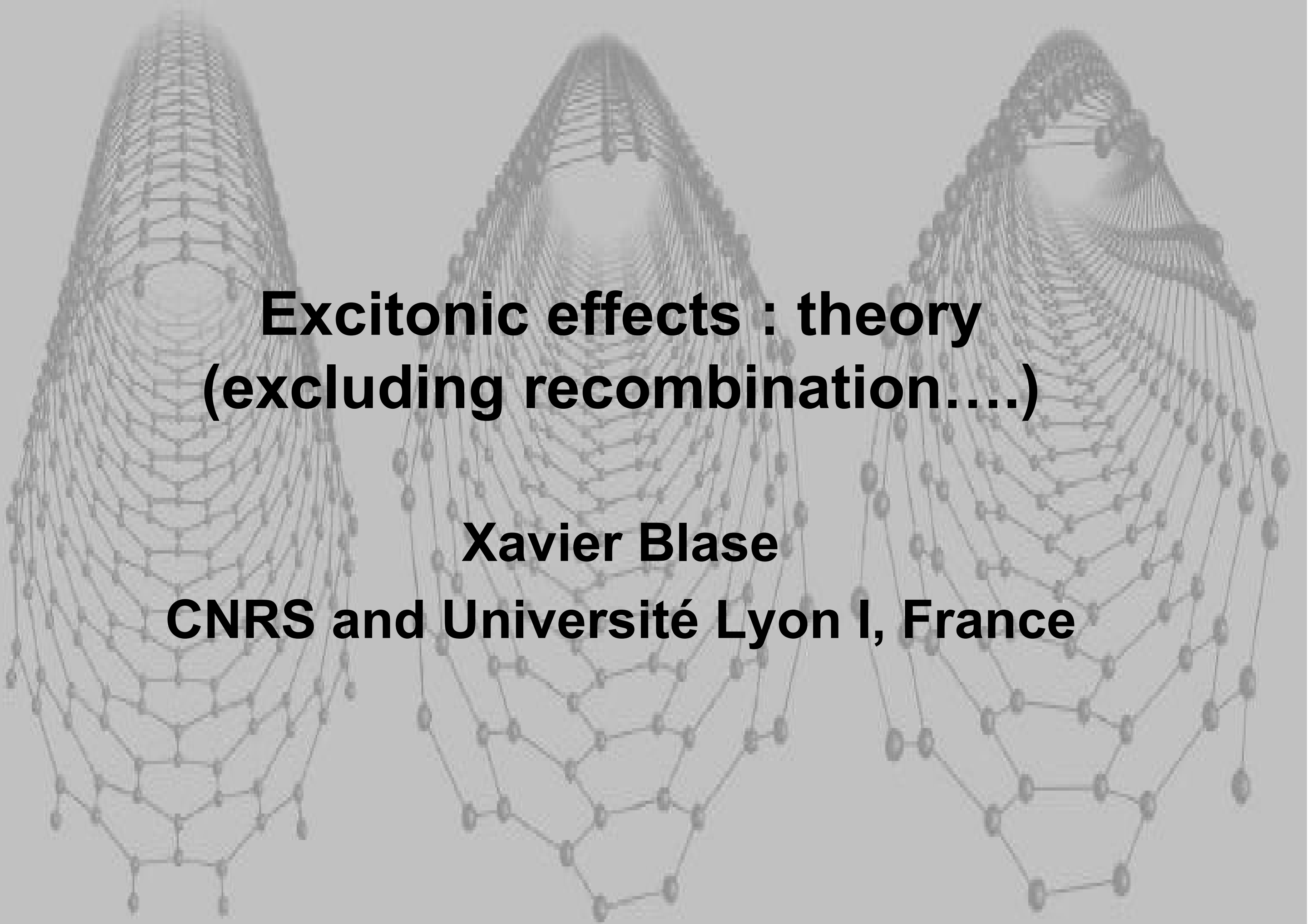
Réunion thématique Nanotubes GDR-E Paris Vendredi 25 Mai 2007



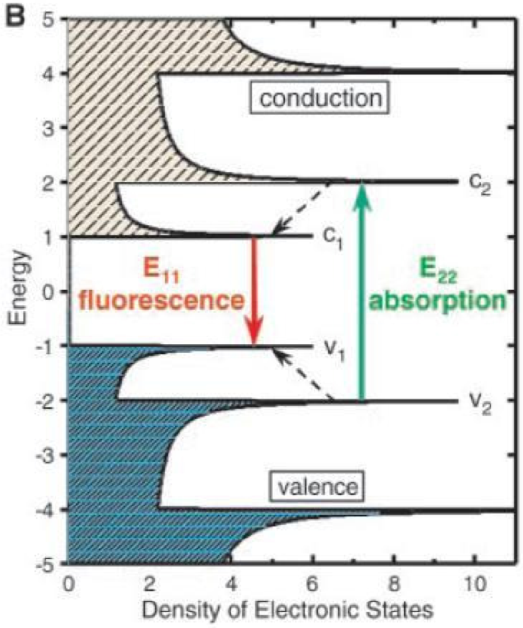
Excitonic effects : theory (excluding recombination….)

Xavier Blase

CNRS and Université Lyon I, France

Optical properties in the independent electron approximation

Early interpretation of optical data identified the absorption peaks with the energy difference E_{ii} between vHs in the unoccupied and occupied bands.



Independent electron approximation: the electronic eigenstates are assumed not to be modified upon electronic excitation

$$\alpha(\omega) = \frac{\epsilon_2(\omega)\omega}{n(\omega)c} \quad \text{with:} \quad \epsilon_2 = \mathrm{Im}(\epsilon)$$

$$\epsilon_2(\omega) = \frac{2\pi e}{m_e\omega}\sum_{c,v}\sum_{\mathbf{k}} |M(cv\mathbf{k})|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \omega)$$

$\boxed{\times\ n_v(1-n_c)}$

Selection rules and strength

Convoluted DOS

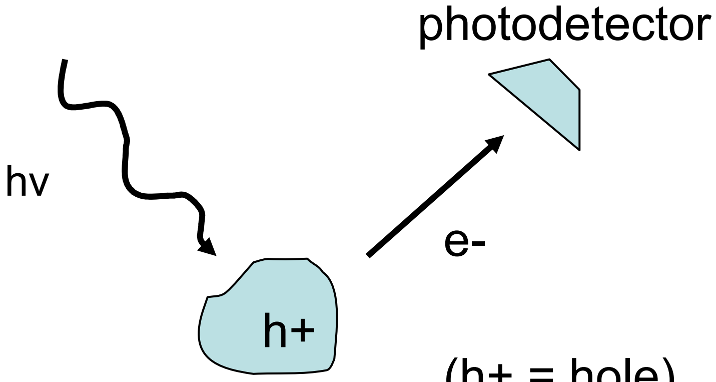
Population

Neglects depolarization fields (local fields) and excitonic effects

The selection rules and oscillator strength are imposed by the dipole matrix elements.

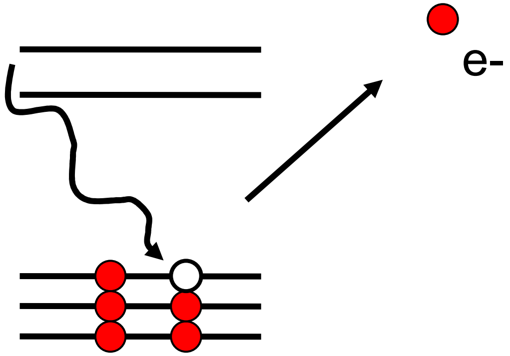
$\Gamma_v{}^*\Gamma_c = \Sigma_i\, \Gamma_i$ The dipolar operator representation (which depends on polarization) must belong to one of the product Γ_i representations for allowed transition.

Photoemission and optical gaps



(h+ = hole)

Photo-emission experiment: the electron (hole) goes to infinity => the system is in its ground-state with N-1 (N+1) electron.

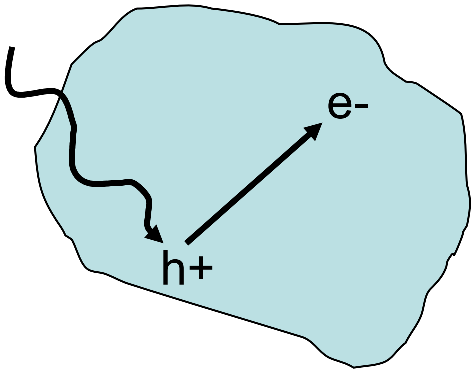


○ = hole

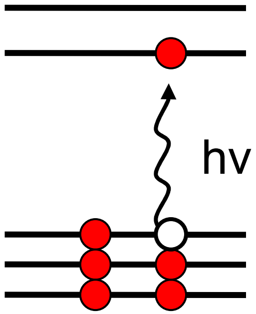
$IE=E^0(N-1)-E^0(N) = -T(e-) + h\nu$

$EA=E^{\circ}(N+1)-E^0(N)$

$E_g^{QP} = EA-IE = 2E^0(N) - E^0(N+1) - E^0(N-1)$



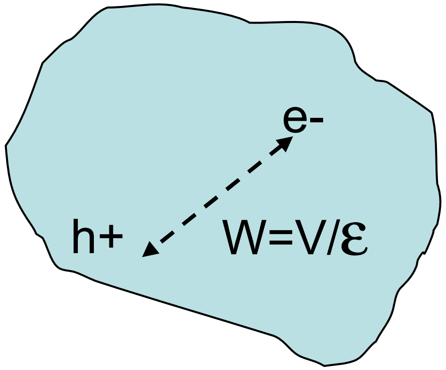
Optical experiment: neutral excitation where hole and electron remain in the system and interact!!



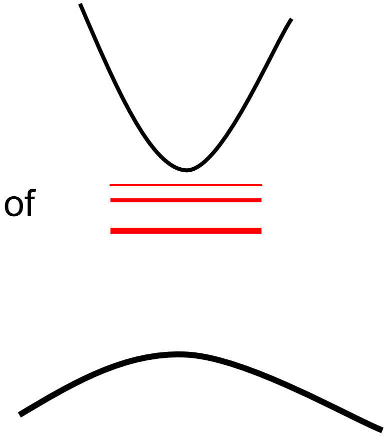
$E_g^{optical} = \min\,[E(e-;h+) – E^0(N)]$
(threshold of absorption)

Electron-hole interactions and Mott-Wannier excitons

The optical gap $E_g^{optical}$ is smaller than the photoemission gap E_g^{QP}. The difference stems from the binding energy E^{eh} of the interacting electron-hole pair (=exciton)



Electron and hole interacting via the Coulomb potential V screened by the dielectric constant ε



$$\mathbf{x} = \mathbf{x_e} - \mathbf{x_h} \text{ and } \mathbf{X} = \frac{m_e \mathbf{x_e} + m_h \mathbf{x_h}}{m_e + m_h}$$

$$H = \frac{p_e^2}{2m_e} + \frac{p_h^2}{2m_h} - \frac{e^2}{\epsilon|\mathbf{x}|} = \frac{P^2}{m_e + m_h} + \frac{p^2}{2\mu} - \frac{e^2}{\epsilon|\mathbf{x}|}$$

$$1/\mu = 1/m_e + 1/m_h$$

$$\psi_{\mathbf{K},n} = e^{i\mathbf{K}\cdot\mathbf{X}} F_n(\mathbf{x})\phi_e(\mathbf{x_e})\phi_h(\mathbf{x_h})$$

$$E_{\mathbf{K},n} = E_n + \frac{K^2}{2(m_e + m_h)} \text{ with: } E_n = -\frac{1}{n^2}\left(\frac{\mu}{\epsilon^2 m_e}\right)\left(\frac{m_e e^4}{2\hbar^2}\right)$$

The smaller ε (the larger the gap), the larger the binding energy

This model assumes delocalized (weakly bound) e-h pair (to justify the use of the effective mass approach and long-range macroscopic dielectric constant) => Mott-Wannier excitons (Elliott, Phys. Rev. 108, 1384 (1957)). Also predicts a $1/n^3$ dependence of the oscillator strength.

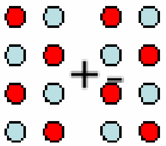
(Quantum theory of solids, Kittel)

Localized or Frenkel excitons. Which model for nanotubes ?

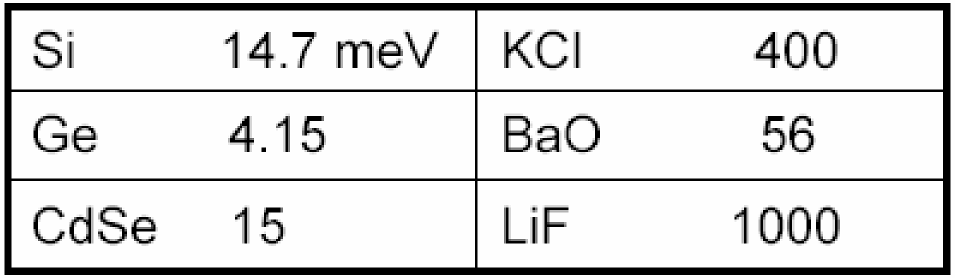
In ionic crystals (alkali halides, molecular crystals, etc.), electron and hole are localized on « one atom/molecule » => Mott-Wannier model fails.

The exciton can be roughly described as the excited state of a single atom/molecule in the crystal field of the neighbours

The exciton can propagate by hopping from one site to another but e-h remains tightly bound.



Frenkel exciton



Si	14.7 meV	KCl	400
Ge	4.15	BaO	56
CdSe	15	LiF	1000

Bound excitons binding energies (Kittel)

What model should we use for nanotubes ?? Wannier or Frenkel ??
Which dielectric constant (Kane and Mele, PRL **90**, 207401 (2003))??

=> Use quantum mechanics « microscopic » approaches instead.

A few results/considerations for strictly 1D systems

In strictly 1D systems, Coulomb integrals give rise to singularities ..

3D $\int d^3\vec{r}\,/\,r = \int r^2 dr d\Omega\,/\,r = \int r dr d\Omega$

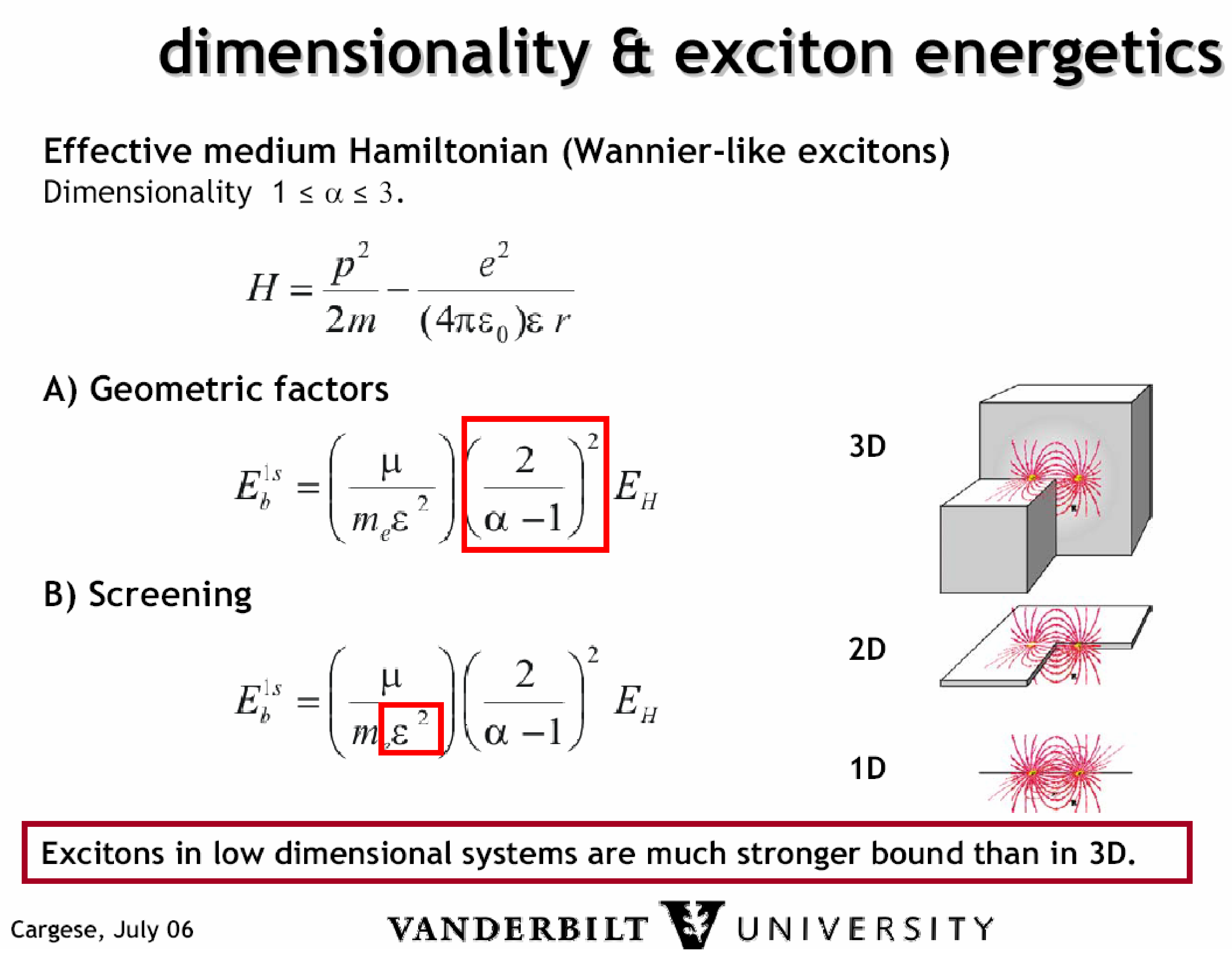
1D $\int dr\,/\,r \approx \ln(r)$

A few exact results (Hydrogen atom « on a line », Wannier excitonic problem, etc.) have been worked out in the literature for strictly 1D world.

Concentration of oscillator strength f_i on the low lying excitons
(Note: Thomas-Reiche-Kuhn sum rule: $\Sigma_i\ f_i=1$)

This should somehow apply to nanotubes ….

(R. Loudon, 1959, Am. J. Phys. 27, 649; Ogawa, Takagahara, PRB 43 (1991) 14325; ibid. PRB 44, 8138)



dimensionality & exciton energetics

Effective medium Hamiltonian (Wannier-like excitons)

Dimensionality $1 \leq \alpha \leq 3$.

$$H = \frac{p^2}{2m} - \frac{e^2}{(4\pi\varepsilon_0)\varepsilon\, r}$$

A) Geometric factors

$$E_b^{1s} = \left(\frac{\mu}{m_e \varepsilon^2}\right) \boxed{\left(\frac{2}{\alpha - 1}\right)^2} E_H$$

B) Screening

$$E_b^{1s} = \left(\frac{\mu}{m_e \boxed{\varepsilon^2}}\right) \left(\frac{2}{\alpha - 1}\right)^2 E_H$$

Excitons in low dimensional systems are much stronger bound than in 3D.

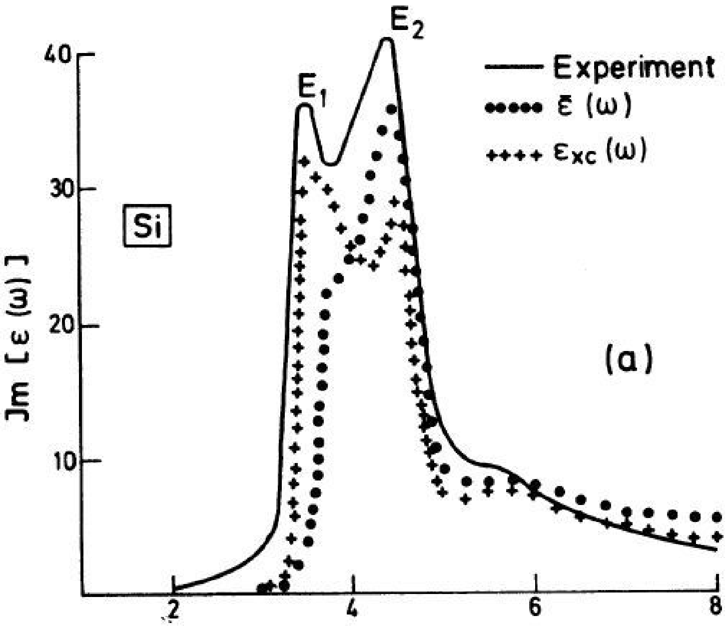
Cargese, July 06

VANDERBILT UNIVERSITY

(courtesy Tobias Hertel, Vanderbilt University, from his lecture in Cargese, July 2006)

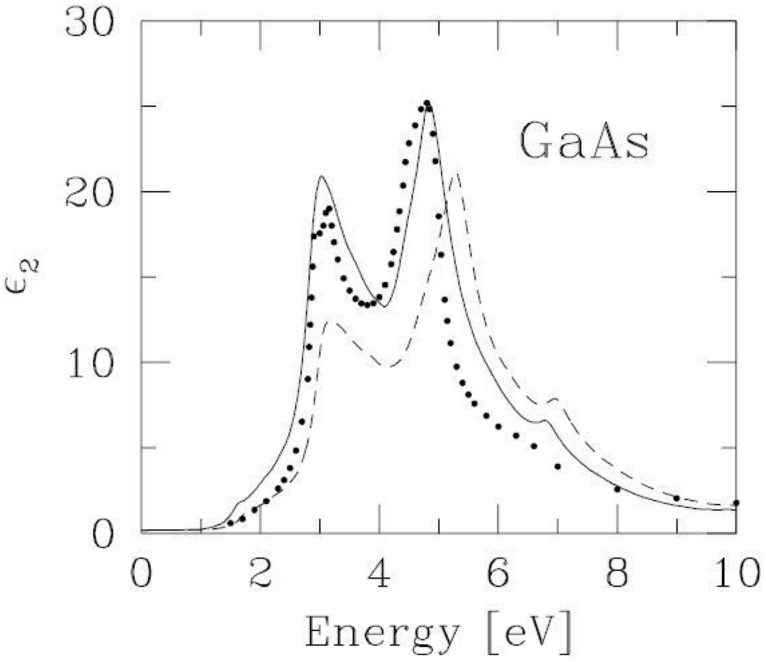
Excitonic effects in the continuum

The Mott-Wannier or Frenkel models aim at obtaining the energy spectrum of bound excitons (transitions below the band gap). Actually excitonic effects have also an important role in the continuum (above the absorption threshold) with a large spectral shift to lower energies (red shift) of the absorption peaks intensity



xc = with excitonic effects (BSE)

Hanke+Sham, PRL **21**, 4656 (1980)



Dots: experiment
Dashed : no excitonic effects
Full line: theory with excitons

Rohlfing, Louie, PRL 81, 2312 (1998)

Beyond the independent electron approximation

An exciton is an excited state of the many-electron system. All techniques allowing to calculate many-body excited states can deal with excitons:

Many-body variational approaches: Quantum Monte Carlo, Coupled Clusters, etc.
(extremely expensive in terms of computer time: can deal with very few atoms)

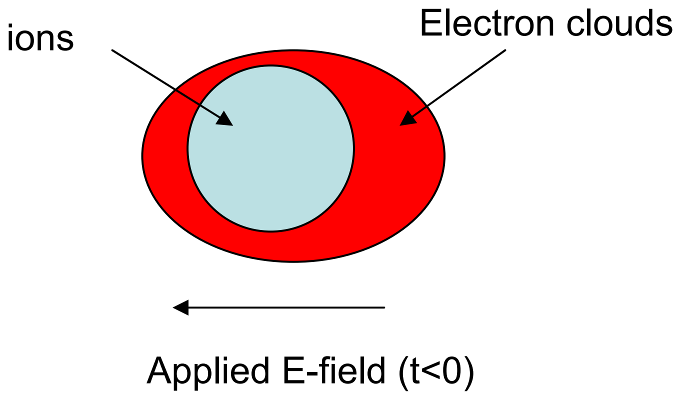
Exemple: comparison of LDA,HF,BSE and QMC on small molecules:
Grossmann et al., PRL 86, 472 (2001)

Perturbative approaches: Bethe-Salpeter, Möller-Plesset, etc.
(expensive but less than above: up to a few tens of atoms with *ab initio* techniques, up to a few hundred with tight-binding implementations)
Onida et al., Rev. Mod. Phys. 74, 601 (2002)

Extension of mean-field approaches (single-electron in an effective field) to time-dependent perturbation: TDDFT, etc.
(cheap, can afford a few hundred atoms ab initio, but several approximations known to fail badly in particular for extended systems.)
Onida et al., Rev. Mod. Phys. 74, 601 (2002)

Time dependent density functional theory (TDDFT)

Several implementations: a conceptualy easy one is to solve the time dependent Schrodinger equation in the presence of an applied electric field



Look at the evolution of charge density n(t) (oscillations) after switching off the field:

$i\hbar\, \delta\phi(\mathbf{r},t)/\delta t = \hat{H}(t)\, \phi(\mathbf{r},t)$
$\hat{H}(t) = -\frac{1}{2}\nabla^2 + V^{ion}(\mathbf{r}) + V^{xc}[n,t] + V^{field}(\mathbf{r},t)$

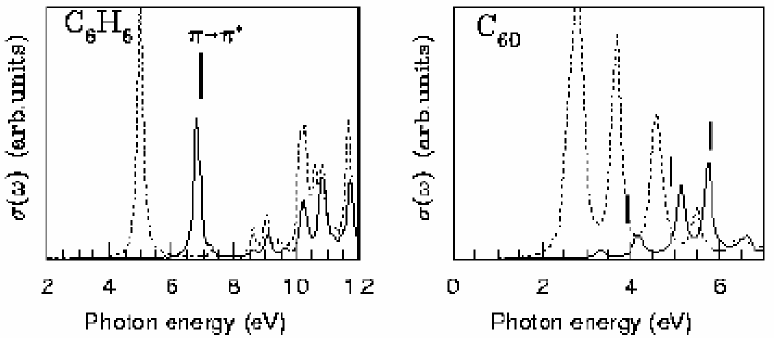
$V^{xc}[n,t] \approx V^{xc}_{adiab}(n(\mathbf{r},t))$
Adiabatic approximation

Runge+Gross, PRL **52**, 997 (1984)
Yabana+Bertsch, PRB **54**, 4484 (1996)
Onida et al., RMP **74**, 601 (2002)

$\delta n(t) \Rightarrow \delta n(\omega) \Rightarrow \kappa(\omega) = \delta n(\omega)/V^{field}(\omega)$
$\varepsilon^{-1}(\omega) = 1 + V^{C}\, \kappa(\omega)$

The exchange-correlation V^{xc} functional (electron interactions beyond Hartree) is usually chosen to be adiabatic and local => for weakly-bound excitons (Mott-Wannier), the long range e-h interaction is missing **:** this approach fails for extended systems, but seems to work well for small molecules.

TDDFT: a few exemples



Dotted: free electron model; Full line: TDDFT
Vertical lines: exp. (Blase, Ordejón, PRB 2004)

Green fluorescent chromophore protein,
Marques *et al.*, PRL 90, 258101 (2003)

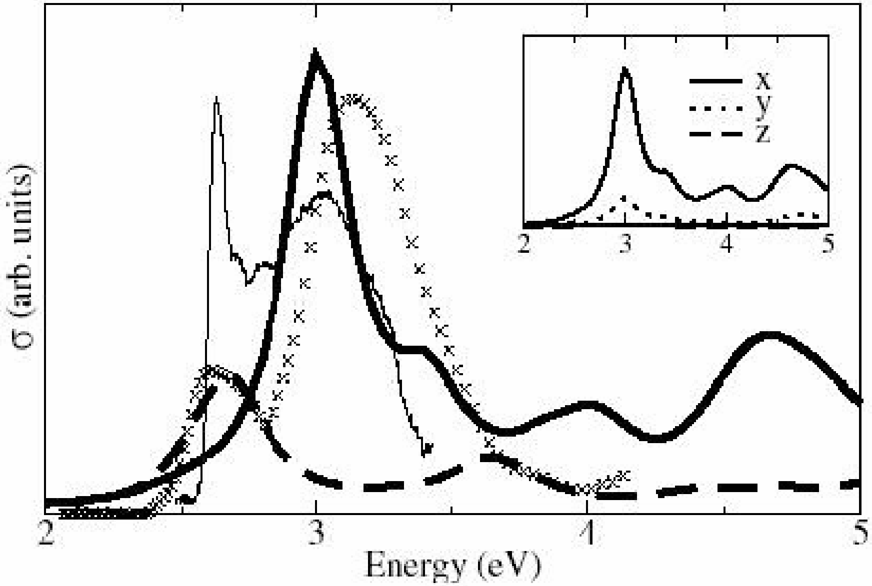
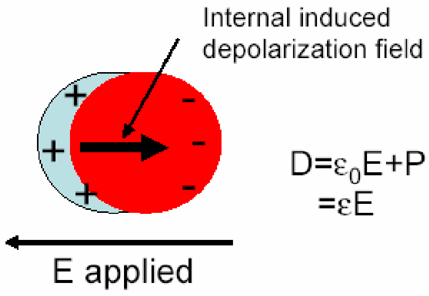


FIG. 2. Computed photoabsorption cross section of the neutral (thick solid line) and anionic (thick dashed line) chromophores, along with experimental results taken from Refs. [4,8] (thin solid line and crosses, respectively). For comparative purposes, we divided the anionic results by 4 with respect to the neutral results. Inset: decomposition of the computed spectra of the neutral chromophore in the three directions, showing the inherent anisotropy of the GFP molecule.

Note: depolarization field
(huge in finite size systems)



$D=\varepsilon_0 E+P$
$=\varepsilon E$

In finite size systems, where e-h are necessarily localized, TDDFT gives rather good results.

Bethe-Salpeter pertubative approach

Include electron-hole interactions to lower order as a function of the (screened) Coulomb potential. The two « lowest diagrams » are the direct screened Coulomb e-h interaction and the exchange term:

Solve the two body (e,h) Schrödinger equation on the independent electron-hole pair basis |vck> ≡ $\phi_{vk}(r)\phi_{ck}(r')$ (solution = linear combination of the |vck>):

$$\sum_{v'c'\mathbf{k}'} H^{BSE}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E^{\lambda} \boxed{A^{\lambda}_{vc\mathbf{k}}}$$

Coefficients of solutions on |vck> basis

$$H^{BSE} = H^{diag} + H^{direct} + H^{x}$$

$$H^{diag}_{vc\mathbf{k},v'c'\mathbf{k}'} = (\epsilon_{v\mathbf{k}} - \epsilon_{c\mathbf{k}})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'}$$

$$H^{direct}_{vc\mathbf{k},v'c'\mathbf{k}'} = -\int d^3\mathbf{r}\,d^3\mathbf{r}'\,\phi_{v\mathbf{k}}(\mathbf{r})\phi^*_{c\mathbf{k}}(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\phi^*_{v'\mathbf{k}'}(\mathbf{r})\phi^*_{c'\mathbf{k}'}(\mathbf{r}')$$

$$H^{x}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int d^3\mathbf{r}\,d^3\mathbf{r}'\,\phi_{v\mathbf{k}}(\mathbf{r})\phi^*_{c\mathbf{k}}(\mathbf{r})\bar{v}(\mathbf{r},\mathbf{r}')\phi^*_{v'\mathbf{k}'}(\mathbf{r}')\phi^*_{c'\mathbf{k}'}(\mathbf{r}')$$

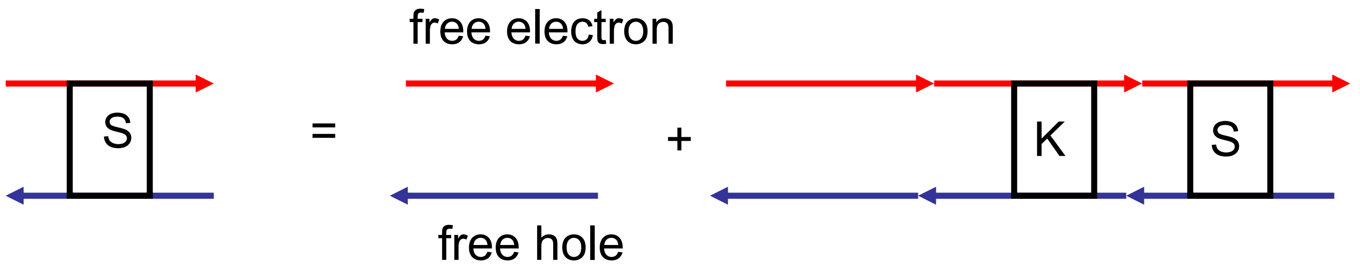
$W(r,r',\omega)= \int dr'\, V^C(r')\, \varepsilon^{-1}(r,r',\omega)$

Independent electron part

Screened Coulomb interaction (usually chosen static).
A sophisticated version of the Elliott model.

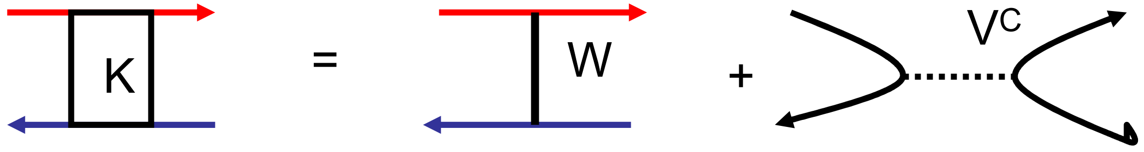
Exchange term: important as it acts on spin-space: it stabilizes the triplet states (=> Hund's rule).
Unscreened since instantaneous.

Bethe-Salpeter: perturbation theory at a glance



Dyson equation
$S=S^0 + S^0KS$

Avec:



Direct term
(screened)

Exchange
(unscreened)

W, screened Coulomb potential => empirical approach that goes beyond strictly first-order perturbation theory.

Note:

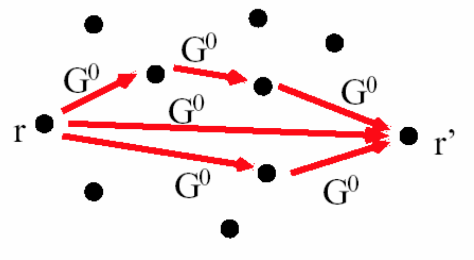
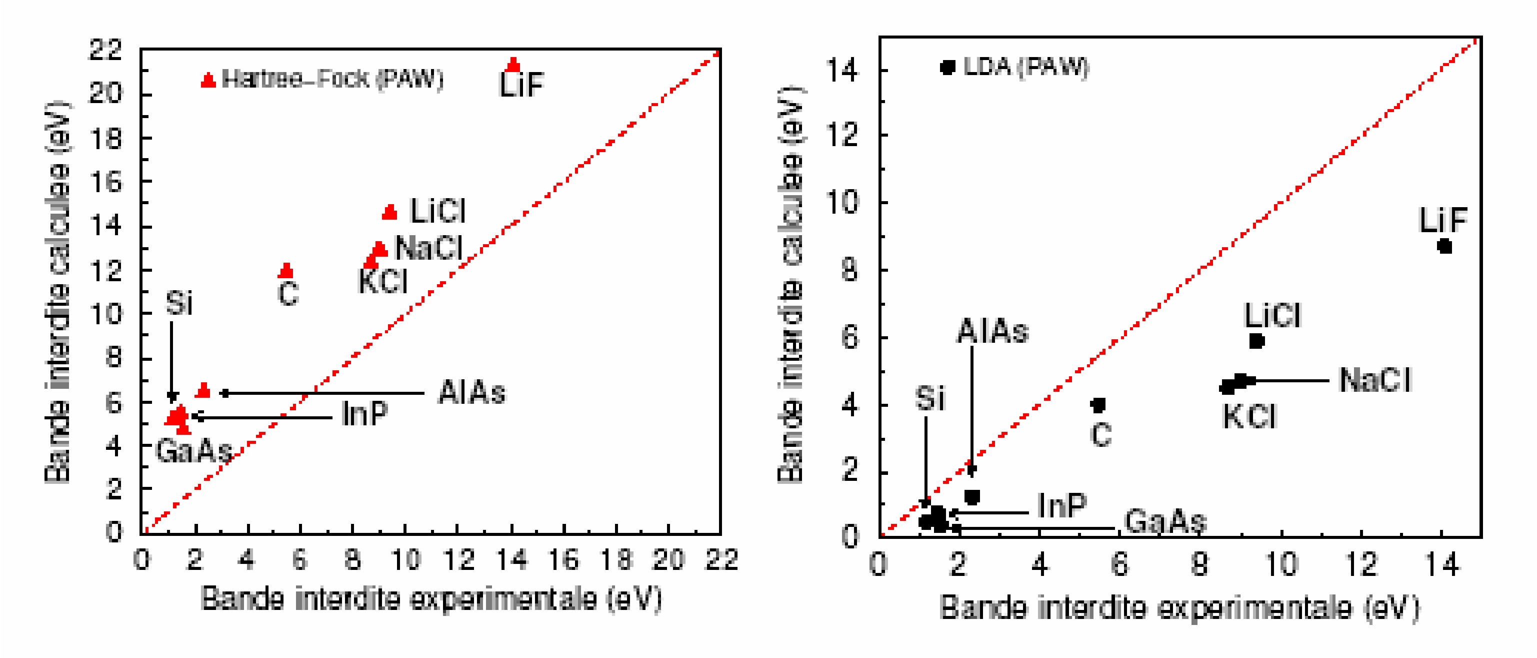


Figure 1 - *Le billard quantique illustré.*

$G=G^0 + G^0\,V\,G^0 + G^0VG^0VG^0 + G^0VG^0VG^0VG^0 \ldots$
$= G^0 + G^0VG$ (Dyson)

Before Bethe-Salpeter: GW calculations to get the correct band gap

DFT underestimates severely the band gap (Hartree-Fock severely overestimates)



(courtesy Brice Arnaud, Rennes)

⇒ First get the correct band gap to be able to compare with experiment
⇒ perform accurate many-body perturbation theory: GW calculations

(and then compute exciton binding energies with Bethe-Salpeter).

Bethe-Salpeter: a few results

Excitons in bulk SiO_2

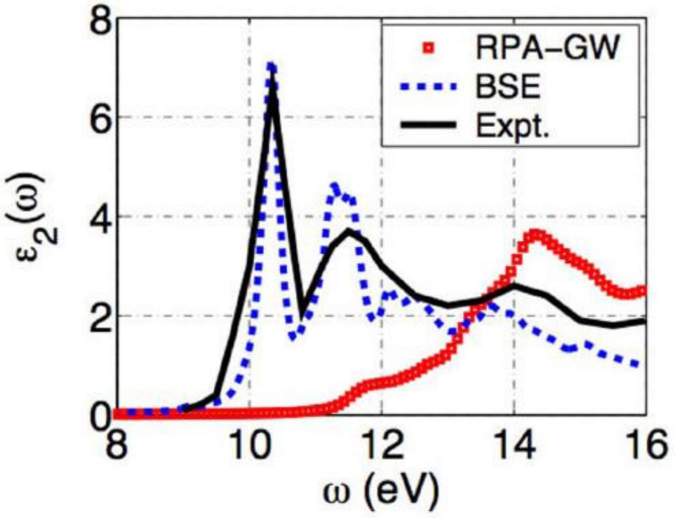


FIG. 1 (color online). Imaginary part of the frequency-dependent macroscopic dielectric function for α-quartz. Red squares are calculated results neglecting electron-hole interactions, blue dashes are calculated including electron-hole interactions, and the solid black is experimental data [32].

(Ismael-Beigi+Louie, PRL 95 (2005)

Transpolyacethylene and PPV

Rohlfing, Louie, PRL 82, 1959 (1999)

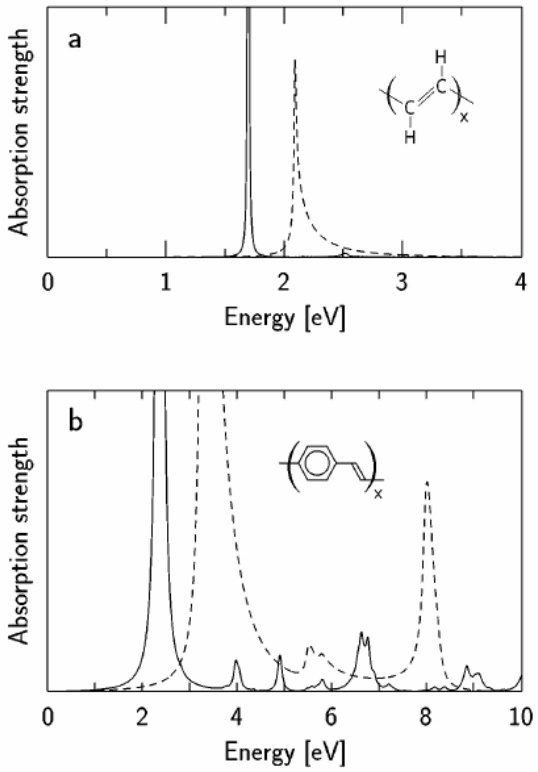
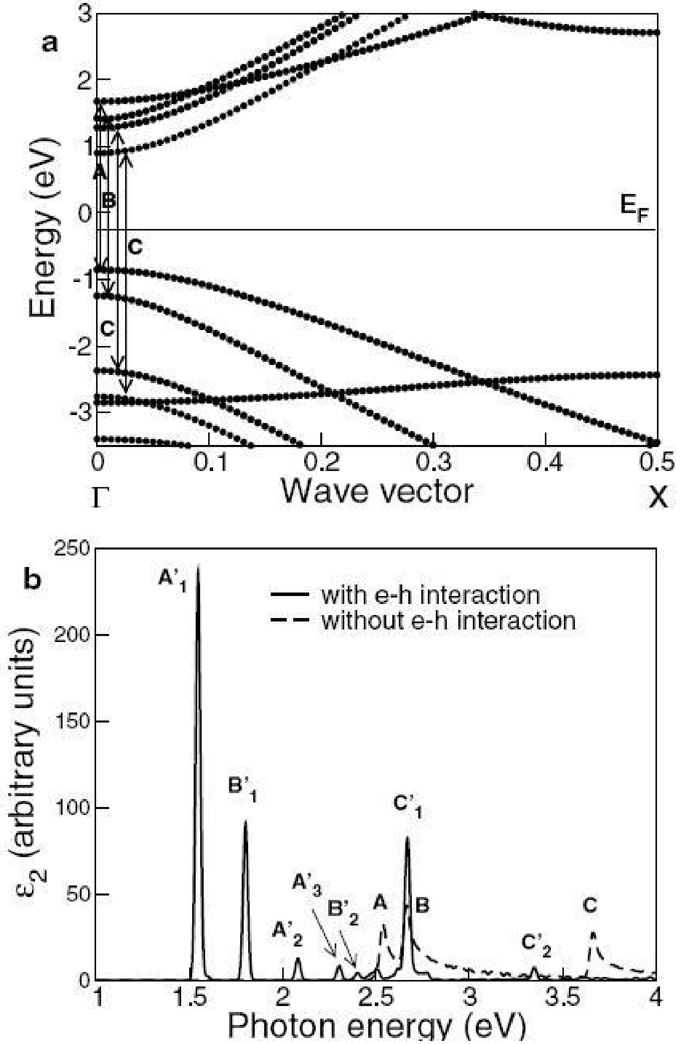


FIG. 2. Calculated optical absorption spectrum of trans-polyacetylene (a) and PPV (b) in arbitrary units. The solid (dashed) lines denote spectra including (neglecting) electron-hole interaction. The polarization vector of the electric field is along the polymer chain. The figure includes an artificial broadening of 0.005 eV (0.05 eV) for trans-polyacetylene (PPV).

Note: forces within the BSE framework are starting to be available =>relaxation in the excited state, excitonic self-trapping, etc. (e.g.: Ismael-Beigi+Louie, PRL 95, (2005); Artacho et al., PRL 93, 116401 (2004); etc).

Excitonic effects on small semiconducting tubes (calculations)



Spataru et al., PRL 2004

Semi-empirical studies:
Ando, J.Phys.Soc.Jpn. **66**, 1066 (1997);
Perebeinos *et al.*, PRL **92**, 257402 (2004)

Ab initio BSE studies:
Spataru *et al.*, Phys. Rev. Lett. **92**, 077402 (2004)
Chang *et al.*, Phys. Rev. Lett. **92**, 196401 (2004)

In a small semiconducting (8,0) tube, exciton binding energy as large as 1 eV !!

Inversion of intensity between 1st and 2nd transition !!

The strength of the direct and X terms enhanced in large gap semiconducting tubes (small dielectric constant) and small tubes (confinement effects + screening reduced) => larger excitonic effects in small and “large gap” CNTs.

Back to the Wannier picture for nanotubes (PRB 74, 121401 (2006))

Fit the parameters (on-site Coulomb U_0, dielectric constant ε) of a Wannier like model Hamiltonian to reproduce the (Bethe-Salpeter) ab initio results:

$$U^{scr}_{Ohno}(R) = \frac{U_0}{\epsilon\sqrt{\left(\frac{4\pi\epsilon_0}{e^2}U_0 R\right)^2 + 1}}.$$

Potentiel Coulombien

écranté par ε

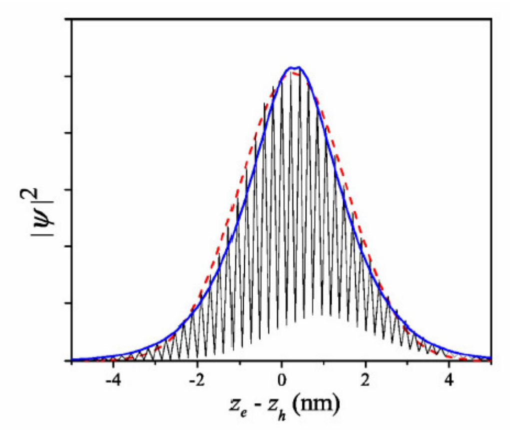
$$\langle T\rangle = \frac{\hbar^2}{4m^*\sigma^2},$$

Energie cinétique
($1/m^*=1/m^h+1/m^e$)

Fonction enveloppe
(v,c=4 bandes)

$$\psi(\vec{r}_e,\vec{r}_h) = C\sum_{v,c} \underline{A_{vc}}\,\phi_c(\vec{r}_e)\phi^*_v(\vec{r}_h)e^{-(z_e - z_h)^2/2\underline{\sigma}^2},$$

Parametre variationnels



Fonction enveloppe

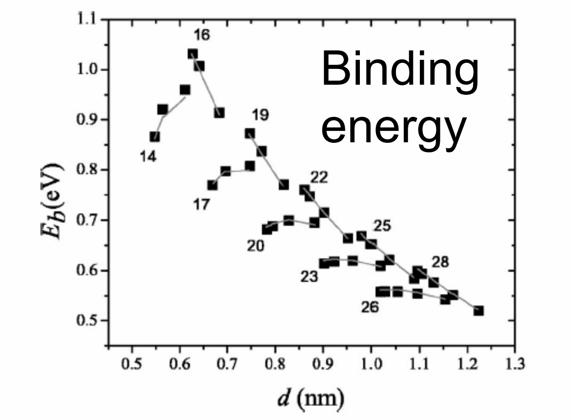


FIG. 2. Binding energies for the lowest-energy bright excitons in 38 SWNTs with varying diameter and chirality. The dots are our model results and the lines represent the analytical fit using Eq. (7). The labels indicate the $(2n+m)$ families.

Binding energy: en 1/d

Chirality effect: $\cos 3\theta/d^2$

Exchange energy: en $1/d^2$

Excitons in insulating *h*-BN systems

h-BN is a wide gap insulator => expect large excitonic effects (bound excitons)

Experiments:
Watanabe et al., *Nature Mat.* **3**, 404 (2004)
Lauret et al., PRL **94**, 037405 (2005)
Arenal et al., PRL **95**, 127601 (2005)

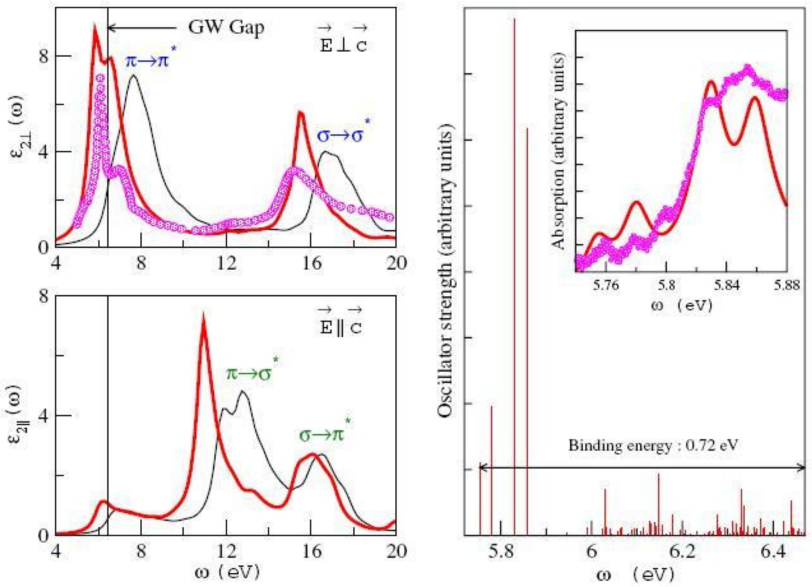


FIG. 2 (color online). Left panel: Calculated imaginary part of the dielectric function of bulk hexagonal boron nitride with (thick solid line) and without (thin solid line) excitonic effects for light polarized perpendicular (in-plane polarization) and parallel to the **c** axis versus photon energy compared with the experimental data (empty circles) of Ref. [10]. Right panel: Oscillator strength of excitonic states inside the *GW* gap. Inset: Calculated absorption spectrum versus photon energy (thick solid line) compared with the experimental data (empty circles) of Ref. [6]. Note that the experimental data have been shifted towards higher energy by 0.03 eV to facilitate the comparison and that we used 1152 **k** points (12 × 12 × 8 mesh grid) to converge our results.

Theory:
Layered « bulk » BN: binding 0.7 eV
Isolated sheet: up to 2 eV
Small tubes: up to 3 eV

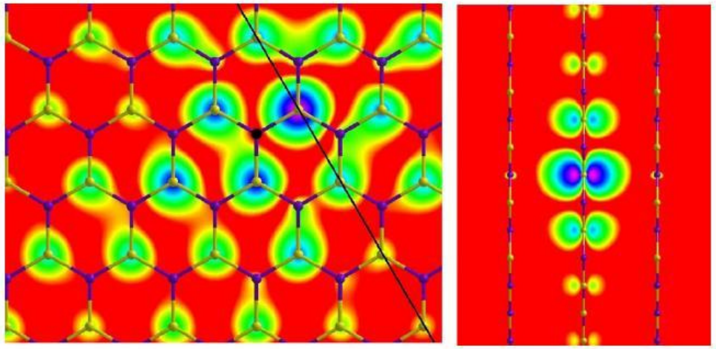


FIG. 3 (color online). Two dimensional projections of the probability density $|\Psi^{\lambda}(\mathbf{r}_h, \mathbf{r}_e)|^2$ for the exciton state at 5.780 eV. The left panel shows the distribution of the electron relative to the hole located slightly above a nitrogen atom (black circle) in a plane containing the hole and perpendicular to the **c** axis. The right panel shows the distribution of the electron relative to the hole in a plane parallel to the **c** axis passing through the line shown in the left panel.

Theory:
Arnaud et al., PRL **96**, 026402 (2006)
Park et al., PRL **96**, 126105 (2006)
Wirtz et al., PRL **96**, 126104 (2006)

Photoluminescent *h*-BC_2N materials

Experimental evidence of visible range photoluminescent character.

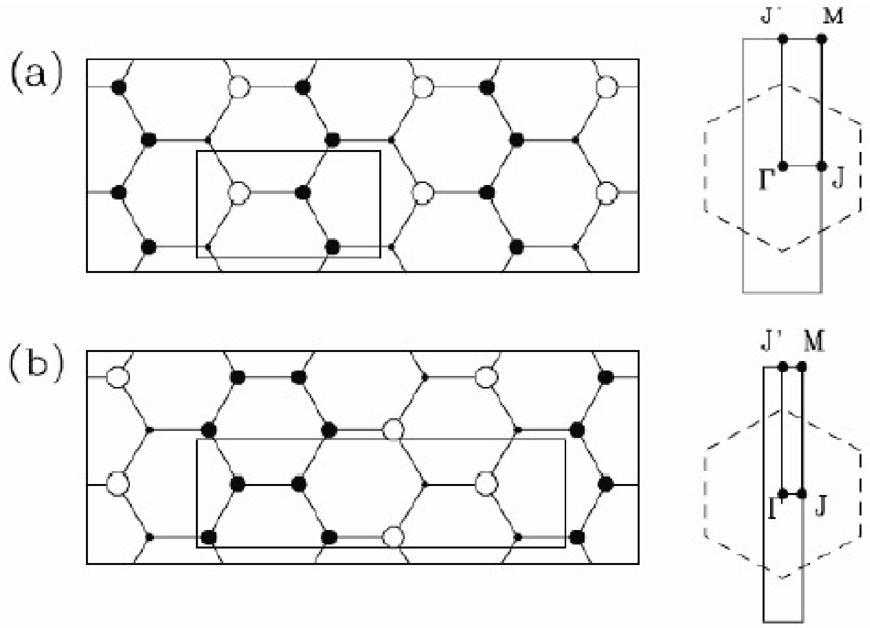
Watanabe et al., PRL **77**, 187 (1996)
Chen et al., PRL **83**, 2406 (1999)

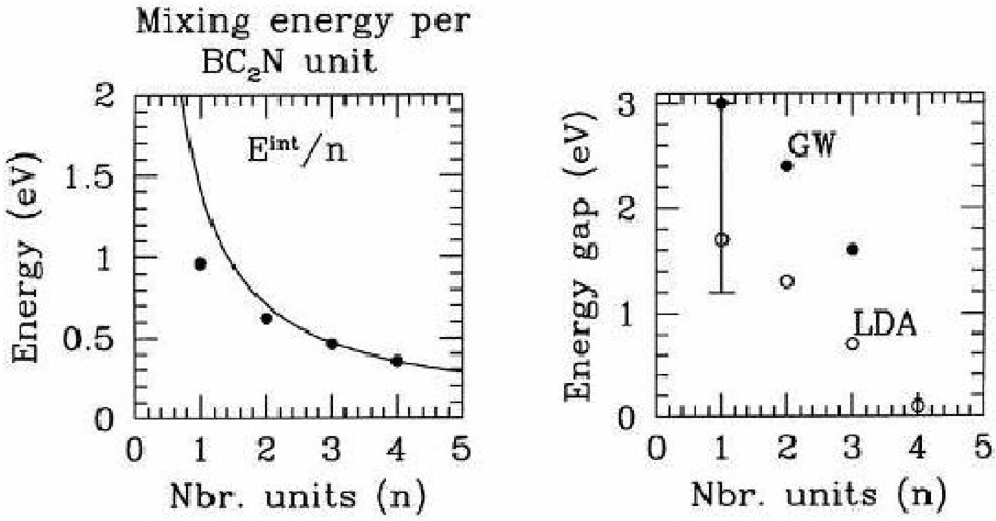
Theory: tendency towards segregation in large pure C or BN domains.

Liu, *et al*., PRB **39**, 1760 (1988).
Blase et al., APL **70**, 197 (1997)
Blase et al., Appl. Phys. A **68**, 293 (1999)
Mazzoni et al., PRB **73**, 073108 (2006)

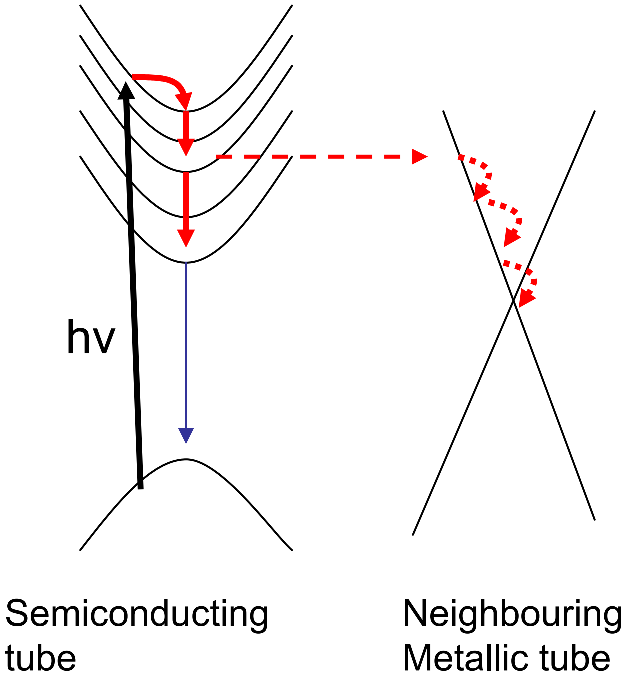
Upon segregation, band gap goes from zero to 3 eV (visible range 1.8-3 eV)

Blase et al., Appl. Phys. A **68**, 293 (1999)
Mazzoni et al., PRB **73**, 073108 (2006)





Radiative and non-radiative recombination; radiative lifetime



Radiative recombination: the electron falls back into the valence bands (e-h recombination) by emitting a photon. The lifetime with respect to e-h recombination is related to the square of the dipole matrix elements between excited and ground state (Fermi golden rule)

Black arrow: absorption in the conduction bands
Red arrows: fast thermalisation to the bottom of the conduction bands
Blue arrow: recombination with photon emission

Dotted arrows: jump onto a neighboring metallic tubes and emission-less thermalization

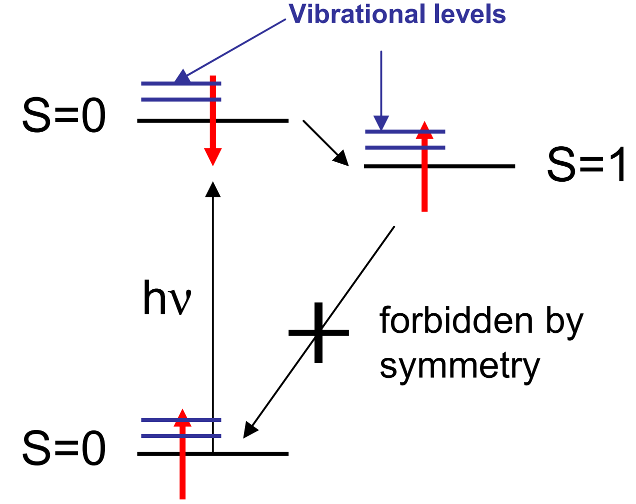
Various phenomena, such as trapping of hot carriers by defects, jump onto metallic objects, etc. cause that electrons do not emit a photon => non-radiative processes

PL efficiency: Ratio of adsorbed photons to emitted photons ..
Fluorescence: short lifetimes (down to picoseconds)
Phosphorescence: very long (up to days) lifetimes (« glow in the dark » objects)

« Black » excitons

The lowest excited state can have zero dipole matrix element with the ground state
=> the exciton cannot recombine by emitting a photon
=> black exciton and low PL efficiency

The excited state can be orthogonal to the ground state by its real space component (look at real-space group representations) or spin component (look at total S value)



(Jablonski diagram)

Singlet and triplet state

The triplet state |++> (S=1) can be at lower an energy than the singlet states |+-> (S=0) due to the exchange term.

The exchange term scales as $1/d^2$ (d tube diameter)
See: Capaz et al. PRB 74, 121401(R) (2006)

SO or applied magnetic field can mix the singlet and triplet states and make the dipole matrix elements non-zero. SO is weak in tubes (light elements)

Note: at finite T, singlets close to triplets are also populated => lifetime should average over all excited states with proper thermal population statistics.
(See: Spataru et al., PRL **95**, 247402 (2005))