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.

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

\[
\epsilon_2(\omega) = \frac{2\pi e}{m_e \omega} \sum_{c,v} \sum_k |M(cvk)|^2 \delta(E_c(k) - E_v(k) - \omega) \times n_v(1-n_c)
\]

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.

$\Gamma_v \Gamma_c = \sum_i \Gamma_i$ \quad The dipolar operator representation (which depends on polarization) must belong to one of the product $\Gamma_i$ representations for allowed transition.
Photoemission and optical gaps

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

\[ IE = E^0(N-1) - E^0(N) = -T(e^-) + hv \]
\[ EA = E^o(N+1) - E^0(N) \]

\[ E_{g\,QP} = EA - IE = 2E^0(N) - E^0(N+1) - E^0(N-1) \]

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

Conduction Bands

Hydrogenic serie of exciton levels

Valence bands

Electron and hole interacting via the Coulomb potential $V$ screened by the dielectric constant $\varepsilon$

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

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

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

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

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

This model assumes delocalized (weakly bound) e-h pair (to justify the use of the effective mass approach and long-range macroscopic dielectric constant)

$\Rightarrow$ 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.

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 ..

\[
\int d^3 \vec{r} / r = \int r^2 dr d\Omega / r = \int rdr d\Omega
\]

\[
\int dr / r \approx \ln(r)
\]

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, Takahara, PRB 43 (1991) 14325; ibid. PRB 44, 8138)
dimensionality & exciton energetics

Effective medium Hamiltonian (Wannier-like excitons)
Dimensionality $1 \leq \alpha \leq 3$.

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

A) Geometric factors

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

B) Screening

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

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

Cargese, July 06

(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.

\[ xc = \text{with excitonic effects (BSE)} \]

Hanke+Sham, PRL 21, 4656 (1980)

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

Rohlfing, Louie, PRL 81, 2312 (1998)
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)

*Example:* 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 conceptually easy one is to solve the time dependent Schrödinger equation in the presence of an applied electric field.

![Diagram showing ions and electron clouds with an applied E-field (t<0)]

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

$$i\hbar \frac{\delta \phi(r,t)}{\delta t} = \hat{H}(t) \phi(r,t)$$

$$\hat{H}(t) = -\frac{1}{2} \nabla^2 + V_{\text{ion}}(r) + V_{\text{xc}}[n,t] + V_{\text{field}}(r,t)$$

$$V_{\text{xc}}[n,t] \approx V_{\text{xc}}^{\text{adiab}}(n(r,t))$$

**Adiabatic approximation**

$$\delta n(t) \Rightarrow \delta n(\omega) \Rightarrow \kappa(\omega) = \frac{\delta n(\omega)}{V_{\text{field}}(\omega)}$$

$$\varepsilon^{-1}(\omega) = 1 + V_C \kappa(\omega)$$

The exchange-correlation $V_{\text{xc}}$ functional (electron interactions beyond Hartree) is usually chosen to be adiabatic and local $\Rightarrow$ 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.

Yabana+Bertsch, PRB 54, 4484 (1996)
Onida et al., RMP 74, 601 (2002)
TDDFT: a few examples

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

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.

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 \(|vck> \equiv \phi_{vk}(r)\phi_{ck}(r')\) (solution = linear combination of the \(|vck>\)

\[
\sum_{v'c'k'} H_{vck,v'c'k'}^{BSE} A_{v'c'k'}^\lambda = E_{vck}^\lambda A_{vck}^\lambda \\
H_{vck,v'c'k'}^{BSE} = H_{vck,v'c'k'}^{diag} + H_{vck,v'c'k'}^{direct} + H_{vck,v'c'k'}^{x} \\
H_{vck,v'c'k'}^{diag} = (\epsilon_{vk} - \epsilon_{ck})\delta_{vv'}\delta_{cc'}\delta_{kk'} \\
H_{vck,v'c'k'}^{direct} = -\int d^3rd^3r' \phi_{vk}(r)\phi_{ck}^*(r')W(r,r')\phi_{v'k'}^*(r')\phi_{c'k'}(r') \\
H_{vck,v'c'k'}^{x} = \int d^3rd^3r' \phi_{vk}(r)\phi_{ck}^*(r)\bar{V}(r,r')\phi_{v'k'}(r')\phi_{c'k'}^*(r')
\]

Coefficients of solutions on \(|vck>\) basis

\[W(r,r',\omega) = \int dr' V^c(r') \mathcal{E}^{-1}(r,r',\omega)\]

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

\[ S = S^0 + S^0KS \]

Avec:

\[ K = W + V^C \]

Free electron

Direct term (screened)

Exchange (unscreened)

W, screened Coulomb potential \( \Rightarrow \) empirical approach that goes beyond strictly first-order perturbation theory.

Note:

\[ G = G^0 + G^0V + G^0VG^0VG^0 + G^0VG^0VG^0VG^0 \ldots = G^0 + G^0VG \text{ (Dyson)} \]
Before Bethe-Salpeter: GW calculations to get the correct band gap

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

⇒ 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$_2$

![Graph showing 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].](image)

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

Transpolyacetylene and PPV
Rohlfing, Louie, PRL 82, 1959 (1999)

![Graph showing 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).](image)

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)

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

Ab initio BSE studies:

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

$$U_{O\text{hno}}^{\text{scr}}(R) = \frac{U_0}{\varepsilon \sqrt{\left(\frac{4\pi \varepsilon_0}{e^2} U_0 R\right)^2 + 1}}.$$

**Fonction enveloppe (v,c=4 bandes)**

Potential Coulombien écranté par $\varepsilon$

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

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

**binding energy: en 1/d**

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

Exchange energy: $\text{en } 1/d^2$

**Paramètre variationnels**

**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.
Excitons in insulating $h$-BN systems

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

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

**Experiments:**
- Lauret et al., PRL 94, 037405 (2005)
- Arenal et al., PRL 95, 127601 (2005)

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**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 ($12 \times 12 \times 8$ mesh grid) to converge our results.

**FIG. 3 (color online).** Two dimensional projections of the probability density $|\Psi^A(r_h, r_e)|^2$ 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.

Blase et al., APL 70, 197 (1997).
Mazzoni et al., PRB 73, 073108 (2006).

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

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)
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)

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))