Modélisation et étude des propriétés optiques des nanotubes de carbone

Modelling and study of optical properties of carbon nanotubes

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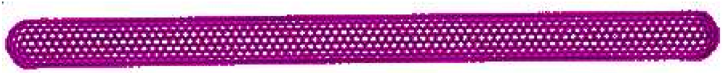
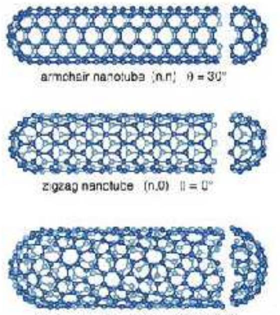
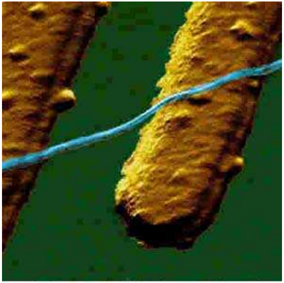
Centre de Physique Théorique, 22 Octobre 2007

Carbon nanotubes

Tubes made of carbon atoms with $\neq$ radiuses, $\neq$ chiralities.





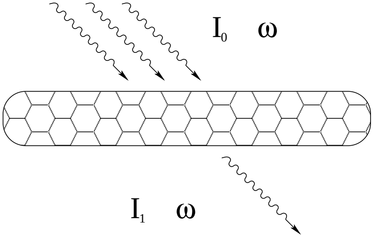


AFM image of an individual carbon nanotube between Pt electrodes spaced by 50 nm. Tans et al., *Nature* **386** (1997) 474.

- Different properties.
- How to sort nanotubes.

Optical spectrum

- A way to sort nanotubes. Monochromatic light sent on CN, low temp.



- Optical absorption spectrum / ω
- Optical absorption spectrum related to radius & chirality.
- explain a part of the optical absorption spectrum (Infrared). (Absorption by e^-)

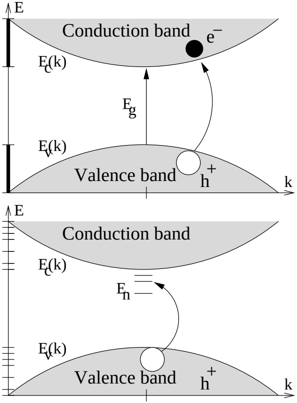
Optical response, physical explanation

Sending light and looking at the absorption of semiconductor CN.

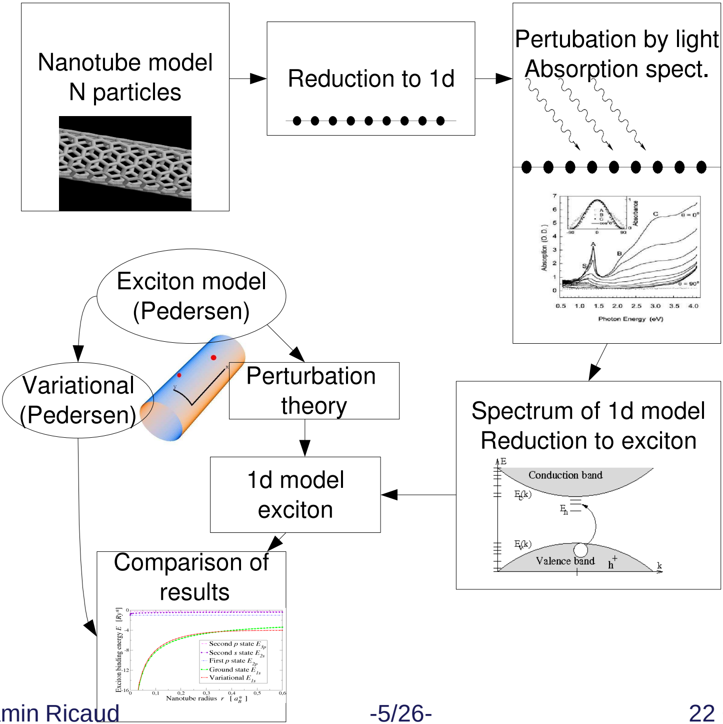
- Without e^--e^- interaction:
  - periodic lattice $\Rightarrow$ bands & gaps
  - Semiconductor: G. state=valence bands full, conduction bands empty.
  - Absorption $\leftrightarrow$ Energy.
- With e^--e^- interaction (weak):
  - "excitons". Wannier (1937), Elliot(1957), Mahan.
  - exciton, coupled e^--h^+: $H_{\text{exc}}\phi_n = E_n\phi_n$
  - Absorption spectrum at 0K with E_g=gap, η=control adiabaticity:

$$\alpha(\omega) \sim \sum_n \frac{|\psi_n(0)|^2}{(E_n + E_g + \hbar\omega)[(E_n + E_g - \hbar\omega)^2 + (\hbar\eta)^2]}$$

[Haug, Koch]



  - **Nanotubes: Exciton eigenstates depend on r.**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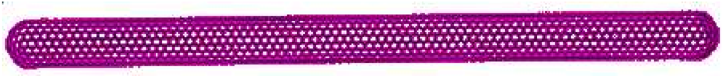
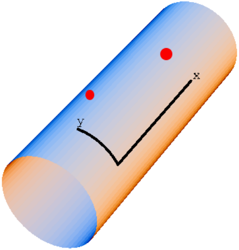
Model for exciton





- Pedersen 2003, Kostov *et al.* 2002
- Exciton: 2 particles on a tube.
- Exciton model Hamiltonian: $H = -\frac{\partial^2}{2m_1 \partial x_1^2} - \frac{\partial^2}{2m_1 \partial y_1^2} - \frac{\partial^2}{2m_2 \partial x_2^2} - \frac{\partial^2}{2m_2 \partial y_2^2} - V^r(x_1 - x_2, y_1 - y_2)$
- Hamiltonian with Coulomb pot. on a cylinder

$$V^r(x, y) = \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}}$$

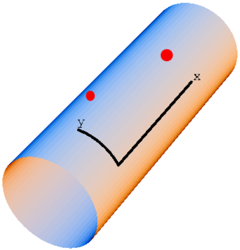
- "center of mass" separation: $X = (m_1 x_1 + m_2 x_2)/(m_1 + m_2)$ $x = x_1 - x_2$, $Y = y_2$, $y = y_1 - y_2$

$$\widetilde{H} = -\frac{\partial^2}{2\mu \partial x^2} - \frac{\partial^2}{2\mu \partial y^2} - \frac{\partial^2}{2m_2 \partial Y^2} - \frac{\partial^2}{m_2 \partial Y \partial y} - V^r(x, y)$$

From H^r to H^r_{eff}, one-dimensional effective Hamiltonian

- $H = -\frac{\partial^2}{2\mu\partial x^2} - \frac{\partial^2}{2\mu\partial y^2} - \frac{\partial^2}{2m_2\partial Y^2} - \frac{\partial^2}{m_2\partial Y\partial y} - V^r(x,y)$
- Projection over modes of $-\frac{\Delta_Y}{2} = \sum_n \frac{n^2}{2r^2}P_n$ (p.b.c.)
- Transverses modes with energy $\frac{n^2}{2r^2}$ and $\chi_n(Y) = \frac{1}{\sqrt{2\pi r}}e^{i\frac{n}{r}Y}$, $P_n = |\chi_n><\chi_n|$
- Only low lying spectrum is interesting.
- Projection on the ground transverse mode $n = 0$:

$$(1\otimes P_0)H^r(1\otimes P_0) = -\frac{\Delta_x}{2\mu} - \frac{\Delta_y}{2\mu} - V^r, \quad \text{in } L^2(\mathbb{R}\times rS^1)$$



- same for y:

$$H^r_{\text{eff}} = -\frac{\Delta_x}{2\mu} - V^r_{\text{eff}} \quad \text{in } L^2(\mathbb{R})$$

$$V^r_{\text{eff}}(x) = \frac{1}{2\pi r}\int_{-\pi r}^{\pi r} \frac{1}{\sqrt{x^2 + 4r^2\sin^2\frac{y}{2r}}}dy$$

From H^r to H^r_{eff}, one-dimensional effective Hamiltonian

$$\widetilde{H^r} = \begin{pmatrix} H^r_{\text{eff}} & & V_{n,m} & \\ & H^r_{\text{eff}} + \frac{1}{2r^2} & & \\ & & H^r_{\text{eff}} + \frac{2}{r^2} & \\ & V_{m,n} & & \ddots \end{pmatrix} = H_{\text{diag}} + H_{\text{offdiag}}, \text{ in}$$

$\ell^2(\mathbb{Z}; L^2(\mathbb{R}))$.

$$V_{m,n}(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{e^{i(m-n)y}}{\sqrt{x^2 + 4r^2 \sin \frac{y}{2}}} dy \qquad x \neq 0$$

- Perturbation theory: comparison $\widetilde{H^r}$ and H_{diag}
- $z \in \rho(H^r_{\text{eff}})$, r small
- $\|(\widetilde{H^r} - z)^{-1} - (H^r_{\text{eff}} - z)^{-1}\| \overset{r \to 0}{\rightarrow} 0$, informations on the spectrum
- H_{offdiag} is H_{diag}-form bounded.
- Difficulty: H^r_{eff} depend on r, choice of z depend on r.

Unperturbed model

$$V_{\text{eff}}^{r}(x) = \frac{1}{2\pi r}\int_{-\pi r}^{\pi r} \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}} dy$$

- Using perturbation theory for small r+ quadratic forms, H_{eff}^{r} approximated by:
- $H_C\psi = \frac{d^2}{dx^2}\psi - \frac{1}{|x|}\psi = E\psi$ with conditions at zero:

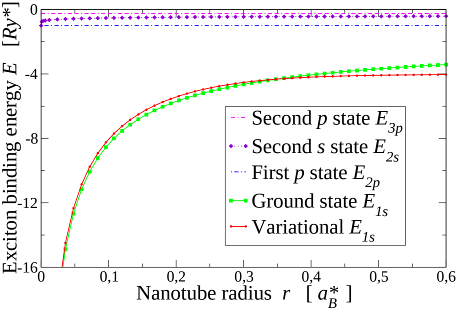
$$\lim_{\varepsilon\to 0}\left[\frac{\psi'(\varepsilon) - \psi'(-\varepsilon)}{2} + 2\ln\frac{r}{2\varepsilon}\psi(0)\right] = 0$$

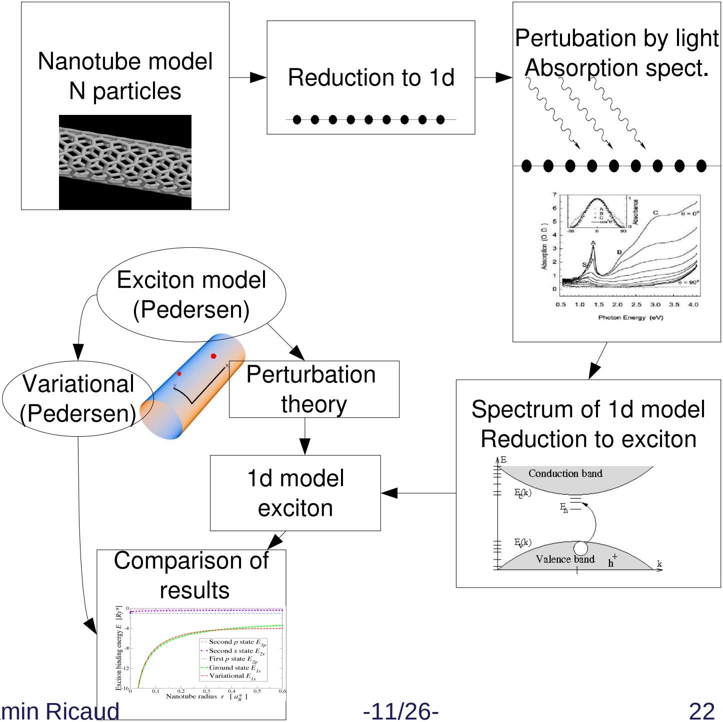
- Odd ψ' not continuous.
- final Hamiltonian depend on r, spectrum is asymptotic.
- Similar to Loudon,1959: $V(x) = \frac{1}{|x|+a}$, $a = r/2$.

results

- even states (S), energies: $E_n = -\frac{1}{\alpha(r,n)^2}$ and functions: Whittaker $\psi_n(x) = W_{\alpha(r,n),\frac{1}{2}}(|x|)$.
- $\alpha(r,n)$ such that $f(\alpha(r,n),r,n) = 0$.
- odd states (P), energies: $E_n = -\frac{1}{n^2}$ and functions (P): Laguerre $\psi_n(x) = e^{-\frac{1}{2}|x|} x L^1_{n-1}(|x|)$.
- fundamental energy: $E_n \sim -4(\ln r)^2$ for small r.

- Stronger bound in 1D.
- excited states: energies & eigenvectors.

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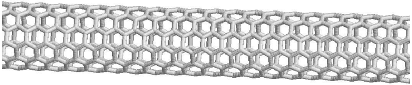
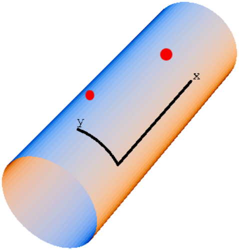
Model for particles on a nanotube





- Nanotube ring: cylinder with P.B.C. $L^2(\mathcal{T}_{L,r}) \approx L^2([-\frac{L}{2}, \frac{L}{2}) \times (-\pi r, \pi r))$
- N fixed atoms (no phonons)
- N delocalized electrons
- Coulomb interaction between e^-

$$H_c := \sum_{j=1}^{N}(-\frac{1}{2}\frac{\partial^2}{\partial x_j^2} - \frac{1}{2}\frac{\partial^2}{\partial y_j^2} + V_{\mathrm{at}}(x_j, y_j)) + \frac{\lambda}{2}\sum_{j\neq k=1}^{N} V_c^{r,L}(x_j - x_k, y_j - y_k)$$

on $\mathcal{H}^N = L^2(\mathcal{T}_{L,r}) \otimes \cdots \otimes L^2(\mathcal{T}_{L,r})$

The potentials

- $V_{\rm at}$ periodic potential /x,y, smooth.
- e^--e^- interaction (for infinite cylinder but not torus):

$$V_c^r(x,y) = \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}}$$

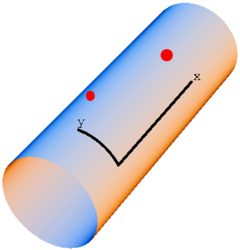
Periodization + tend to Coulomb when $L \to \infty$

$$H_c := \sum_{j=1}^{N} (-\frac{1}{2}\frac{\partial^2}{\partial x_j^2} - \frac{1}{2}\frac{\partial^2}{\partial y_j^2} + V_{\rm at}(x_j, y_j)) + \frac{\lambda}{2} \sum_{j \neq k = 1}^{N} V_c^{r,L}(x_j - x_k, y_j - y_k)$$

From H_c to H_0, one-dimensional effective Hamiltonian for low lying spectrum

$$H_c := \sum_{j=1}^{N}\left(-\frac{1}{2}\frac{\partial^2}{\partial x_j^2} - \frac{1}{2}\frac{\partial^2}{\partial y_j^2} + V_{\rm at}(x_j, y_j)\right) + \frac{\lambda}{2}\sum_{j\neq k=1}^{N} V_c^{r,L}(x_j - x_k, y_j - y_k)$$

- Projection over modes of $-\frac{1}{2}\frac{\partial^2}{\partial y_j^2} = \sum_n \frac{n^2}{2r^2}|\chi_n >< \chi_n|$ (p.b.c.)
- Transverses modes with energy $\frac{n^2}{2r^2}$ and $\chi_n = \frac{1}{\sqrt{2\pi}}e^{i\frac{n}{r}y}$
- Projection on the ground transverse mode $n = 0$:



$$H_0 = \sum_{j=1}^{N}\left(-\frac{1}{2}\frac{\partial^2}{\partial x_j^2} + v_{\rm at}(x_j)\right) + \frac{\lambda}{2}\sum_{j\neq k=1}^{N} v^r(x_j - x_k), \qquad v_{\rm at}(x) = \frac{1}{2\pi r}\int_{-\pi r}^{\pi r} V_{\rm at}(x,y)dy$$

Convergence for small r

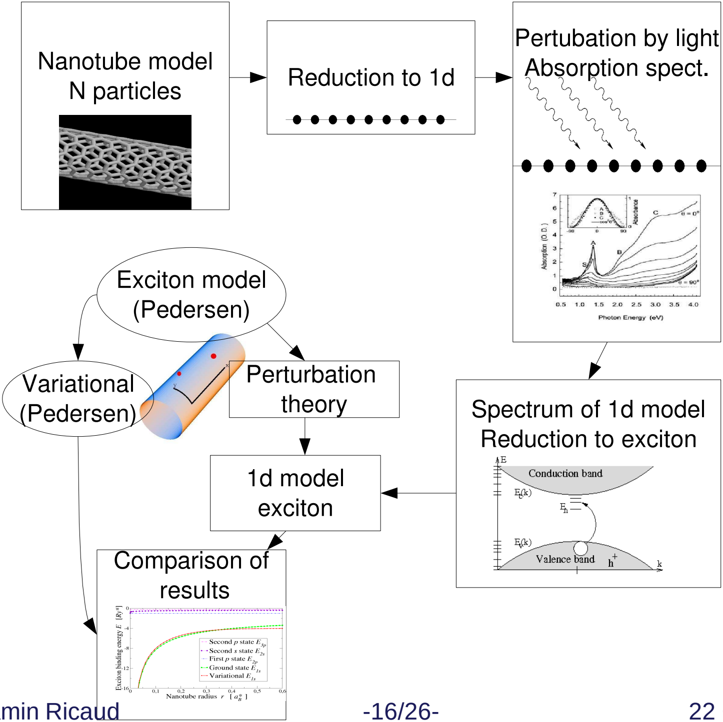
v^r periodization of exciton potential:

$$v_{\text{eff}}^r(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2}}} dy$$

- for $z \in \rho(H_0)$

$$\|R_c^r(z) - R_0^r(z)\| \leq f(r, z) \overset{r \to 0}{\to} 0$$

- But spectrum of H_0 unknown.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Model with external field & linear response

- Absorption spectrum: linear response, Kubo formula
- $\mathrm{Tr}(\rho P)$
- Electromagnetic pertubation:
  $F(t,\omega,\eta) = F_0 \cos(\omega t) e^{\eta t} = F_0 a'(t,\omega,\eta)$
- $\eta > 0$ adiabatic parameter. switched adiabatically from $-\infty$.
- Weyl gauge:

$$H(t) = \frac{1}{2}\sum_{j=1}^{N}\left(\frac{1}{i}\frac{\partial}{\partial x_j} - F_0 a(t,\omega,\eta)\right)^2 + v_{\mathrm{at}}(x_j) + \frac{\lambda}{2}\sum_{j\neq k=1}^{N} v(x_j - x_k).$$

$$= H_0 + F_0 a(t,\omega,\eta)P + \frac{N}{2}(F_0 a(t,\omega,\eta))^2$$

- $a(t,\omega,\eta) \in L^1(-\infty,0)$, a'' continue.
- F_0 small for linear response.
- Perturbation (P) H_0-bounded.

Model with external field & linear response

Absorption spectrum: linear response

$$H(t) = \frac{1}{2}\sum_{j=1}^{N}\left(\frac{1}{i}\frac{\partial}{\partial x_j} - a(t,\omega,\eta)F_0\right)^2 + v_{\mathrm{at}}(x_j) + \frac{\lambda}{2}\sum_{j\neq k=1}^{N} v(x_j - x_k).$$

In the canonical ensemble:

- Liouville Equation: $\frac{\partial\rho}{\partial t} = i[\rho, H(t)]$
- with initial condition $\rho_{eq} = \rho(-\infty) = \frac{e^{-\beta H_0}}{\mathrm{Tr}_{\mathcal{H}^N}(e^{-\beta H_0})}$,
  $\|e^{-\beta H_0}\|_1 = \sum_{\lambda\in\sigma(H_0)} e^{-\beta\lambda} < \infty$
  - Th. X.70 [RS2], existence of a propagator, but initial cond. at $-\infty$.
  - $\rho(t) = \Omega(t,-\infty)\rho_{eq}\Omega^*(t,-\infty)$.
  - Solution exists and is unique. $\rho(t)P$ trace class.

Absorption spectrum

- $\rho(t) = \rho_{eq} + i \int_{-\infty}^{t} [\rho(\sigma), H(\sigma)] d\sigma$
- $\mathrm{Tr}\rho(t)P = \mathrm{Tr}\rho_{eq}P + F_0 \mathrm{Tr}\rho_1(t)P + o(F_0)$. P total momentum.

Absorption: linear response.

$$\alpha(\omega) = \mathrm{Re}[\mathrm{Tr}(\rho_1(0)P)]$$

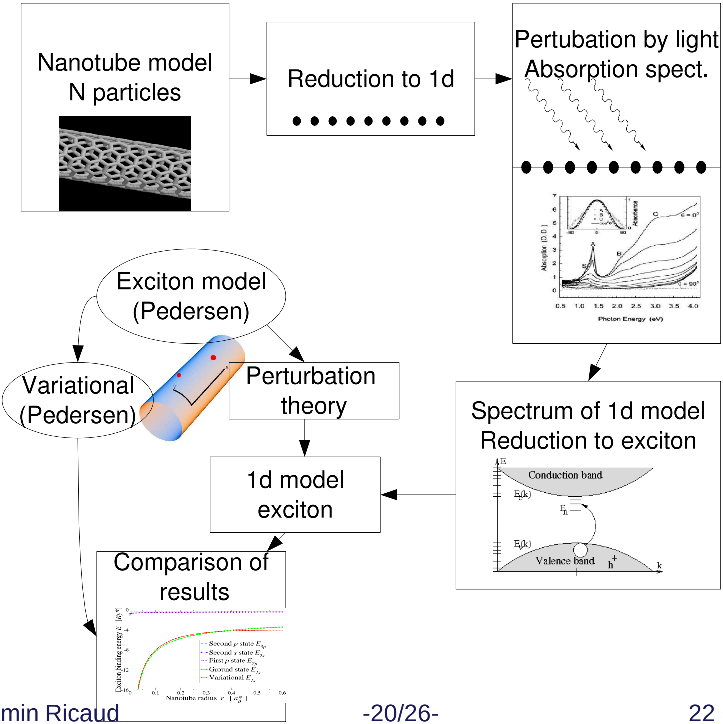
- with:

$$\rho_1(0) := i \int_{-\infty}^{0} a(\sigma, \omega, \eta) e^{i\sigma H_0} [P, \rho_{eq}] e^{-i\sigma H_0} d\sigma.$$

- At temperature 0K:
-

$$\alpha(\omega) = \sum_{k \geq 0} \frac{| < \psi_k, P\psi_0 > |^2}{[E_k - E_0 + \omega)^2 + \eta^2][(E_k - E_0 - \omega)^2 + \eta^2]}$$

- E_k, ψ_k: states of the N particles H_0.



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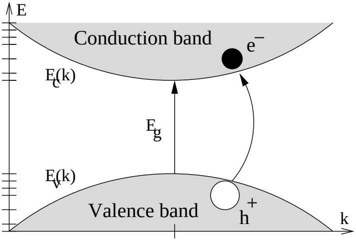
Second s state E_{2s}
First p state E_{2p}
Ground state E_{1s}
Variational E_{1s}

Study of H_0

- Fock subspace of N fermions, statistical physics formalism.
- Basis: eigenvectors of non-interacting e^- problem, antisym.
- Important vectors: $|0>$ (ground state), $a^*_{c,k}a_{v,k}|0>$, ($1h^+$+$1e^-$).

- 2 bands.
- no spin
- same k (justified by physics).
- quadratic behavior around 0.



Study of H_0

Reduction to the subspace: $|0>$, $a^*_{c,k}a_{v,k}|0>$, (ground state+ 1 h^+ in valence band, 1 e^- in conduction band).

- Physicists use it for low T and λ small. But...
- $(N+1 \times N+1)$ matrix on $\ell^2(N+1)$:

$$M = \begin{pmatrix} <0|\hat{H}_0|0> & <0|\hat{H}_0 a^*_{b_c,k} a_{b_v,k}|0> \\ <0|a^*_{b_v,k} a_{b_c,k}\hat{H}_0|0> & <0|a^*_{b_v,k} a_{b_c,k}\hat{H}_0 a^*_{b_c,k} a_{b_v,k}|0> \end{pmatrix}$$

$$= \begin{pmatrix} E_G & \lambda\theta \\ \lambda\theta^* & \delta_{kk'}(E_G + gap) + H_{\mathrm{ex}} \end{pmatrix}, \qquad E_G := E_G(N,\lambda)$$

λ small

- $$M = \begin{pmatrix} E_G & \lambda\theta \\ \lambda\theta^* & E_G + gap + H_{\mathrm{ex}} \end{pmatrix}$$
- Feshbach: $\lambda\theta^*\theta$ rank one perturbation of H_{ex}. Krein: $f(z) = z - \lambda^2(\theta^*, R_{\mathrm{ex}}(z)\theta^*) = 0$, eigenvalues intertwined
- provided we know $\sigma(H_{\mathrm{ex}})$), non degenerated eigenvalues.

approximation:

$$\widetilde{M} = \begin{pmatrix} E_G & 0 \\ 0 & E_G + gap + H_{\mathrm{ex}} \end{pmatrix}$$

H_{ex} to exciton

- H_{ex}: $N \times N$ matrix.
- For $N \to \infty$: negative $\sigma(H_{\mathrm{ex}})$ is close ($\mathcal{O}(\frac{1}{\sqrt{N}})$) to spectrum of:

$$H_{\mathrm{ex}}^c = \mathcal{D} - \lambda \hat{v}_* \qquad \text{on } L^2(-\pi, \pi)$$

- with a scaling $k \to \alpha k$:

$$\alpha^2 \left(\frac{\mathcal{D}(\alpha \cdot)}{\alpha^2} - \frac{\lambda}{\alpha} \hat{v}_*(\alpha \cdot) \right) \qquad \text{on } L^2(-\frac{\pi}{\alpha}, \frac{\pi}{\alpha})$$

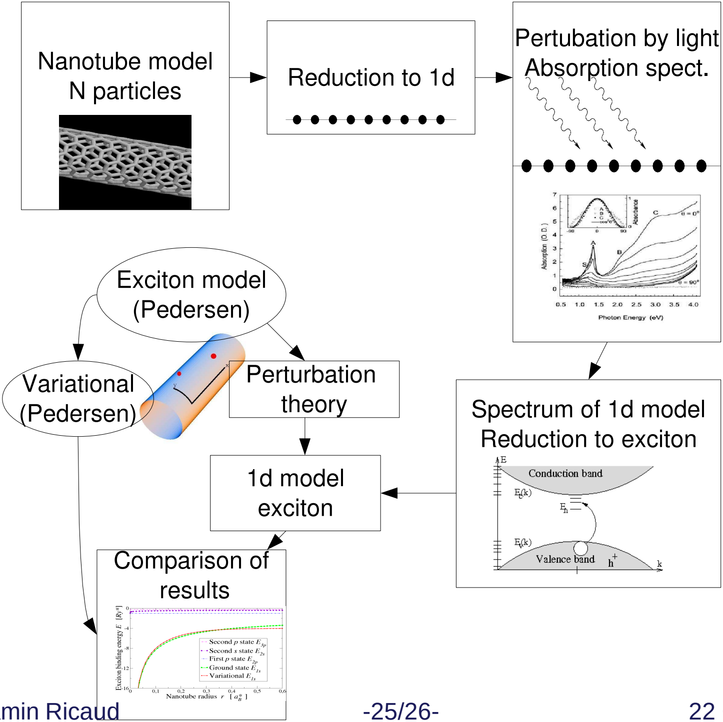
- $\alpha = \lambda$ and λ small: perturbation th. with unperturbed op. ($\mathcal{O}(\lambda^{2/9} |\ln \lambda|)$):

$$h = \lambda^2 \left(\mathcal{D}''(0) \frac{k^2}{2} - \hat{v}_*(\lambda \cdot) \right) \quad \text{on} \quad L^2(\mathbb{R}).$$

- Fourier:

$$-\frac{\partial^2}{2m\partial x^2} - \frac{1}{\lambda} v(\frac{1}{\lambda} \cdot), \qquad v(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{\sqrt{x^2 + 4\sin^2 \frac{y}{2}}} dy$$

- This is the Hamiltonian of the exciton (with CM removed).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Conclusions

Summary

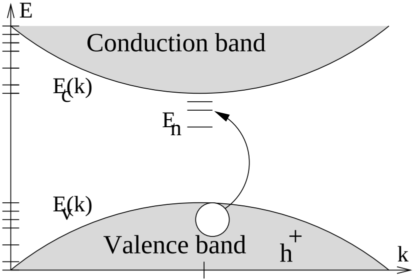
- relation between radius and absorption peaks + quasi analytic results.
- “Rigourous approach” for the absorption coefficient
- justification of “Pedersen” exciton
- New physical results for excitons in nanotubes

Suggestions

- Matrix M, Biexcitons,...
- reduction to one dimension, spectrum of the unperturbed model

Absorption coefficient

$$\alpha(\omega) = \sum_{n\geq 0} \frac{CN\omega\eta \cdot |\phi_n(0)|^2}{[(E_n + E_g + \hbar\omega)^2 + \eta^2))][((E_n + E_g - \hbar\omega)^2 + \eta^2)]} \times$$
$$\times \left(1 + \mathcal{O}(\frac{1}{\sqrt{N}}) + \mathcal{O}(\lambda^{2/9}|\ln \lambda|)\right) + o_{1/\beta}(1)$$



The interaction potential

- e^--e^- interaction (for infinite cylinder but not torus):

$$V_c^r(x,y) = \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}}$$

Periodization: ($y \neq 0$, $p \neq 0$)

$$\widehat{V}_c^r(p,y) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} e^{-ipx} V_c^r(x,y)dx = \sqrt{\frac{2}{\pi}} K_0(|2pr \sin(y/2)|)$$

$$V_c^{r,L}(x,y) = \frac{1}{\sqrt{2\pi}} \sum_{m \in \mathbb{Z}^*} e^{i\frac{2m\pi x}{L}} \widehat{V}_c^r(p,y) \cdot \frac{2\pi}{L} + \int_{-\frac{L}{2}}^{\frac{L}{2}} V_c^r(x',y)dx' \frac{1}{L}$$

- tend to Coulomb when $L \to \infty$

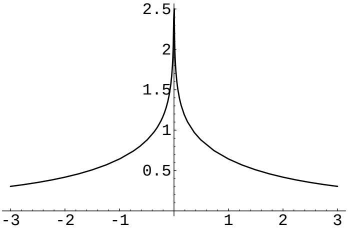
$$H_c := \sum_{j=1}^{N} \left(-\frac{1}{2}\frac{\partial^2}{\partial x_j^2} - \frac{1}{2}\frac{\partial^2}{\partial y_j^2} + V_{\mathrm{at}}(x_j, y_j)\right) + \frac{\lambda}{2} \sum_{j \neq k = 1}^{N} V_c^{r,L}(x_j - x_k, y_j - y_k)$$

The interaction potiential

v^r periodization of exciton potential:

$$v^r_{\mathrm{eff}}(x) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2}}} dy$$

- $v^r(x) \overset{x \to 0}{\sim} |\ln |x||$.
- More regular than the Coulomb potential. $v^r \in L^2$.
- Δ-bounded with bound 0 on the line.



$$H_0 = \sum_{j=1}^{N}(-\frac{1}{2}\frac{\partial^2}{\partial x_j^2} + v_{\mathrm{at}}(x_j)) + \frac{\lambda}{2}\sum_{j \neq k=1}^{N} v^r(x_j - x_k)$$

- with domain: $D(\Delta)$.