NEAR-FIELD ELECTRODYNAMICS
OF ATOMICALLY DOPED
CARBON NANOTUBES

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Basic physical properties of single-walled carbon nanotubes (CNs)

Motivation

Near-field electrodynamics. The model

Atomic spontaneous decay dynamics near a carbon nanotube

van der Waals energy of an atom near a carbon nanotube

Conclusions
BASIC PHYSICAL PROPERTIES
OF SINGLE-WALLED CNs
(1) classification of single-walled CNs

Graphene single sheet

Single-walled carbon nanotube of \((m,n)\) type
BASIC PHYSICAL PROPERTIES
OF SINGLE-WALLED CNs
(2) Brillouin zone structure of achiral CNs

Brillouin zone structure of achiral CNs

0,0 0,5 1,0 1,5 2,0 2,5
-10
-8
-6
-4
-2
0
2
4
6
8
10

Conductivity normalized

Zigzag: \((m,0)\)
m = 3q – metallic \((q =1,2,3,\ldots)\)

\[
p_{\phi} = \frac{\hbar s}{R_{cn}}, \quad s = 1,2,\ldots,m
\]

Armchair: \((m,m)\)
m metallic for all \(m\)

Typical frequency dependence of the conductivity

Zigzag \((9,0)\)
- \(\text{Re } \sigma_{zz}\)
- \(\text{Im } \sigma_{zz}\)

\[
x = \frac{\hbar \omega}{2\gamma_0}, \quad \gamma_0 = 2.7 \text{ eV}
\]
TEM image of a sample partially filled by Cs atoms. The inset sets off the encapsulated atoms by dotting with black circles [after J.-H.Jeong et al. PRB68,075410(2003)].

- Nanotube/atomic physical properties are substantially modified in a controllable way when doping nanotubes with impurity atoms.

New challenging nanophotonics applications of atomically doped carbon nanotube systems as various sources of coherent light emitted by dopant atoms.
NEAR-FIELD ELECTRODYNAMICS.
THE MODEL
(1) the geometry of the problem

- I.V. Bondarev & Ph. Lambin, Phys. Lett. A, to be published
- I.V. Bondarev & Ph. Lambin, cond-mat/0401332
- I.V. Bondarev & Ph. Lambin, cond-mat/0404211 [submitted to SSC]
- I.V. Bondarev et al., PRL 89, 115504 (2002)
THE MODEL

(2) Hamiltonian

Field quantization in the presence of dispersing and absorbing bodies:

Hamiltonian:
\[ \hat{H} = \hat{H}_F + \hat{H}_A + \hat{H}_{AF}^{(1)} + \hat{H}_{AF}^{(2)} \]

Field:
\[ \hat{H}_F = \int_0^\infty d\omega \hbar \omega \int d\mathbf{R} \hat{f}^+ (\mathbf{R}, \omega) \hat{f} (\mathbf{R}, \omega) \]

Atom:
\[ \hat{H}_A = \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i,j} q_i q_j | \mathbf{r}_i - \mathbf{r}_j | \]

Interaction I: (electric dipole)
\[ \hat{H}_{AF}^{(1)} = - \sum_i \frac{q_i}{m_i c} \hat{p}_i \cdot \hat{A}(\mathbf{r}_A) + \hat{d}_A \cdot \nabla \phi(\mathbf{r}_A) \]

Interaction II: (diamagnetic)
\[ \hat{H}_{AF}^{(2)} = \sum_i \frac{q_i^2}{2m_i c^2} \hat{A}^2 (\mathbf{r}_A) \]

\[ \hat{A}(\mathbf{r}) = \int_0^\infty d\omega (i\omega)^{-1} \hat{E}^\perp (\mathbf{r}, \omega) + h.c., \quad -\nabla \phi(\mathbf{r}) = \int_0^\infty d\omega \hat{E}^\parallel (\mathbf{r}, \omega) + h.c. \]

\[ \hat{E}^{\perp (0)}(\mathbf{r}, \omega) = \int d\mathbf{r}' \delta^{\perp (0)} (\mathbf{r} - \mathbf{r}') \cdot \hat{E}(\mathbf{r}', \omega), \quad \mathbf{r} = \{r, \varphi, z\} \]

Maxwell equations with an external source (CN)
\[ \nabla \times \hat{E}(\mathbf{r}, \omega) = i \frac{\omega}{c} \hat{H}(\mathbf{r}, \omega), \quad \nabla \times \hat{H}(\mathbf{r}, \omega) = -i \frac{\omega}{c} \hat{E}(\mathbf{r}, \omega) + \frac{4\pi}{c} \hat{I}(\mathbf{r}, \omega) \]
\[ \hat{I}(\mathbf{r}, \omega) = \int d\mathbf{R} \delta(\mathbf{r} - \mathbf{R}) \hat{J}(\mathbf{R}, \omega) = 2 \hat{J}(\mathbf{R}_{en}, \varphi, z, \omega) \delta(\mathbf{r} - \mathbf{R}_{en}) \]
\[ \hat{J}(\mathbf{R}, \omega) = \sqrt{\hbar \omega \text{Re} \sigma_{zz}(\mathbf{R}_{en}, \omega)} / \pi \hat{f}(\mathbf{R}, \omega) \mathbf{e}_z, \quad \mathbf{R} = \{R_{en}, \varphi, Z\} \]

\[ \hat{E}(\mathbf{r}, \omega) = i \frac{4\pi \omega}{c^2} \int d\mathbf{R} \mathbf{G}(\mathbf{r}, \mathbf{R}, \omega) \cdot \hat{J}(\mathbf{R}, \omega), \quad \hat{H} = i(\omega / c)^{-1} \nabla \times \hat{E} \]

\[ \mathbf{G}(\mathbf{r}, \mathbf{R}, \omega) \] is the classical field Green tensor
THE MODEL

(3) two-level approximation

\[ \hat{H} = \int_0^\infty d\omega \hbar \omega \int d\mathbf{R} \hat{f}^+(\mathbf{R}, \omega) \hat{f}(\mathbf{R}, \omega) + \frac{\hbar \tilde{\omega}_A}{2} \hat{\sigma}_z + \int_0^\infty d\omega \int d\mathbf{R} \left[ g^{(+)}(r_A, \mathbf{R}, \omega) \hat{\sigma}^+ - g^{(-)}(r_A, \mathbf{R}, \omega) \hat{\sigma}^- \right] \hat{f}(\mathbf{R}, \omega) + h.c. \]

Renormalized atomic frequency (due to diamagnetic interaction)

\[ \tilde{\omega}_A(r_A) = \omega_A \left( 1 - \frac{2}{(\hbar \omega_A)^2} \int_0^\infty d\omega \hbar \omega \int d\mathbf{R} \left| g^{\pm}(r_A, \mathbf{R}, \omega) \right|^2 \right) \]

Electric dipole coupling (electric dipole interaction)

\[ g^{(+)}(r_A, \mathbf{R}, \omega) = g^{\pm}(r_A, \mathbf{R}, \omega) \pm \frac{\omega}{\omega_A} g^\|(r_A, \mathbf{R}, \omega) \]

\[ g^{\perp\perp}(r_A, \mathbf{R}, \omega) = -i \frac{4 \omega_A}{c^2} \sqrt{\pi \hbar \omega} \text{Re} \sigma_{zz}(\omega) d_\alpha G^{\perp\perp}_{\alpha \beta}(r_A, \mathbf{R}, \omega) \]

Local photonic DOS

\[ \int d\mathbf{R} \left| g^{\perp\perp}(r_A, \mathbf{R}, \omega) \right|^2 = \hbar^2 \frac{\Gamma_0(\omega)}{2\pi} \frac{\omega_A}{\omega} \xi^{\perp\perp}(r_A, \omega) \]

\[ \xi^{\perp\perp}(r_A, \omega) = \frac{\text{Im}^{\perp\perp} G_{\alpha \beta}^{\perp\perp}(r_A, r_A, \omega)}{\text{Im} G_{\alpha \beta}^0(\omega)} = 1 + \varphi^{\perp\perp}(r_A, \omega) \]

\[ \Gamma_0(\omega) = \frac{8\pi}{\hbar c^2} d_\alpha d_\beta \text{Im} G_{\alpha \beta}^0(\omega), \quad \text{Im} G_{\alpha \beta}^0(r_A, r_A, \omega) = \delta_{\alpha \beta} \frac{\omega}{6\pi c} \]
Local photonic DOS for an atom near a carbon nanotube

I.V. Bondarev & Ph. Lambin,
PRB 69, 235xxx (2004) [cond-mat/0401332]

\[ r_A > R_{cn} : \]

\[ \xi(r_A, \omega) = 1 + \frac{3R_{cn}}{2\pi k^3} \text{Im} \sum_{p=-\infty}^{\infty} \int_c \frac{\beta(\omega)v^4 I_p(vR_{cn})K_p(vr_A)}{1 + R_{cn} \beta(\omega)v^4 I_p(vR_{cn})K_p(vR_{cn})} dh \]

\[ v = \sqrt{\hbar^2 - k^2} ; \quad k = \frac{\omega}{c} \]

\[ \beta(\omega) = 4\pi i \frac{\sigma_z(R_{cn}, \omega)}{\omega} \]

\[ r_A < R_{cn} : \]

\[ I_p \leftrightarrow K_p \quad \text{in the numerator of the integrand} \]
Local photonic DOS for an atom outside the (9,0) CN at different distances from the wall

\[ r_A = 1.5R_{cn}; \quad r_A = 2.5R_{cn}; \quad r_A = 3.5R_{cn} \]

\[ x = \frac{h\omega}{2\gamma_0}, \quad \gamma_0 = 2.7 \text{ eV} \]
SPONTANEOUS DECAY DYNAMICS

I.V. Bondarev & Ph. Lambin,
PRB 69, 235xxx (2004) [cond-mat/0401332]

\[ \tilde{\omega}_A (r_A) = \omega_A \left( 1 - \frac{\hbar}{\pi} \int_0^\infty d\omega \frac{\Gamma_0(\omega)}{\omega} \xi^{\perp} (r_A, \omega) \right) \]

Wave function of the system

\[ |\psi(t)\rangle = C_u (t) e^{-i(\tilde{\omega}_A/2)t} |u\rangle \langle 0| + \int_0^{\infty} d\omega \int dR C_i (R, \omega, t) e^{-i(\omega - \tilde{\omega}_A/2)t} |l\rangle \langle 1|R, \omega\rangle \]

Evolution equation of the upper state

\[ C_u (t) = 1 + \int_0^t K(t - t') C_u (t') dt' \]
\[ K(t - t') = \frac{1}{\hbar^2} \int_0^{\infty} d\omega e^{-i(\omega - \tilde{\omega}_A)(t - t')} \left[ - \int_0^{\infty} dR |g^{(+)} (r_A, R, \omega)|^2 \right] \]
SPONTANEOUS DECAY DYNAMICS

Solution of evolution equation

I.V. Bondarev and Ph. Lambin,
PRB 69, 235xxx (2004) [cond-mat/0401332]

\[ \tilde{\Gamma}_0(x) = \frac{\hbar \Gamma_0(x)}{2\gamma_0}, \quad x = \frac{\hbar \omega}{2\gamma_0}, \quad \tau = \frac{2\gamma_0}{\hbar} t, \quad \gamma_0 = 2.7 \text{ eV} \]

\[ C_u(\tau) = 1 + \int_0^\tau K(\tau - \tau')C_u(\tau')d\tau \]

\[ K(\tau - \tau') = -\frac{\tilde{\Gamma}_0(x_A)}{2\pi x_A^3} \int_0^\infty dx x^3 \xi(x) \frac{e^{-i(x-x_A)(\tau-\tau')}}{i(x-x_A)} - 1 \]

Markovian approximation

\[ \frac{e^{-i(x-x_A)(\tau-\tau')}}{i(x-x_A)} - 1 \rightarrow -\pi \delta(x-x_A) + iP \frac{1}{x-x_A} \]

\[ K(\tau - \tau') \approx -\frac{\hbar \Gamma(x_A)}{4\gamma_0} + i\Delta(x_A) \rightarrow |C_u(\tau)|^2 = e^{\frac{\hbar \Gamma(x_A)}{2\gamma_0} \tau} \]

\[ \Gamma(x_A) = \xi(x_A) \Gamma_0(x_A) \]

NUMERICALLY !!!
Local photonic DOS for an atom outside the (9,0) CN at different distances from the wall.

\[ r_A = 2.5 \, R_{cn}; \quad r_A = 1.5 \, R_{cn}; \quad r_A = 3.5 \, R_{cn} \]

\[ x = \frac{\hbar \omega}{2 \gamma_0}, \quad \gamma_0 = 2.7 \, \text{eV} \]
Spontaneous decay dynamics for an atom outside the (9,0) CN at different distances from the wall.

\[ |C_u(x)|^2 \]

\[ \tau = \frac{2\gamma_0}{s} t, \quad \gamma_0 = 2.7 \, \text{eV} \]
Atom outside the (9,0) CN at different distances from the wall

(a) local photonic DOS

\[ \xi^\perp(x) \]

\( (9,0) \)

- \( r_A = 1.5R_{cn} \)
- \( r_A = 2.5R_{cn} \)
- \( r_A = 3.5R_{cn} \)

\[ x = \frac{\hbar \omega}{2 \gamma_0}, \gamma_0 = 2.7 \text{ eV} \]

(b) upper-level spontaneous decay dynamics compared with exponential decay (Markovian approximation)

\[ |C_u(t)|^2 \]

- \( r_A = 1.5R_{cn} \)
- \( r_A = 2.5R_{cn} \)
- \( r_A = 3.5R_{cn} \)

1 - exact, 2 - exp. decay

\( \tau = \frac{2 \gamma_0 t}{\hbar} \)
Atom outside the (9,0) CN at different distances from the wall

(a) local photonic DOS

(b) upper-level spontaneous decay dynamics compared with exponential decay (Markovian approximation)

$x = \frac{\hbar \omega}{2 \gamma_0}, \gamma_0 = 2.7$ eV
Atom in the center of different CNs:

(a) local photonic DOS

(b) upper-level spontaneous decay dynamics compared with exponential decay (Markovian approximation)

\[ x = \frac{\hbar \omega}{2\gamma_0}, \quad \gamma_0 = 2.7 \text{ eV} \]

\[ \tau = \frac{2\gamma_0 t}{\hbar} \]
Atom inside the (10,10) CNs at 3Å from the wall [PRB68,075410]:

(a) local photonic DOS
(10,10); $r_A = 0.56R_{cn}$

$$\xi^+(x)$$

(b) upper-level spontaneous decay dynamics compared with exponential decay (Markovian approximation)

$$|c(t)|^2$$

$\tau = \frac{2\gamma_0 t}{h}$
How to observe experimentally?

Optical absorption experiments

Weak coupling

\[ \omega = \frac{\hbar}{2} \]

Strong coupling

\[ \omega = \frac{1}{\sqrt{2}} (|u\rangle|0\rangle - |l\rangle|1(R, \omega)\rangle) \]

Optical absorbance profile in the neighborhood of the atomic transition energy

\[ \sim \frac{\hbar}{2} \]
SPONTANEOUS DECAY DYNAMICS

CONCLUSIONS

(I.1) Spontaneous decay dynamics of an excited atom near a carbon nanotube is in general NON-EXPONENTIAL – because of the strong non-Markovian memory effects arising from the rapid variation of the photonic density of states with frequency near the nanotube.

(I.2) Spontaneous decay may proceed via damped Rabi oscillations – a principal signature of STRONG atom-vacuum-field coupling in the vicinity of the nanotube.

(I.3) Atom-field coupling and spontaneous decay dynamics may be controlled experimentally by changing the distance between an atom and a nanotube surface – by means of a proper preparation of atomically doped carbon nanotube systems. This opens routes for possible new challenging applications of atomically doped carbon nanotube systems in:

- cavity QED
- nanophotonics
- quantum information processing
GROUND-STATE van der WAALS ENERGY

I.V. Bondarev & Ph. Lambin,
cond-mat/0404211 [submitted to SSC]

\[
\hat{\omega}_A(r_A) = \omega_A \left( 1 - \frac{\hbar}{\pi} \int_0^\infty d\omega \frac{\Gamma_0(\omega)}{\omega} \xi(\omega) \right)
\]

Wave function of the system

\[
|\psi\rangle = C_1 |l\rangle \{0\} + \int_0^\infty d\omega \left( \int dR C(\omega, R) |u\rangle \{1(\omega)\} \right)
\]

van der Waals energy

\[
E = -\frac{\hbar \omega_A}{2} - \int_0^\infty d\omega \left( \frac{\hbar \omega_A}{2} + \frac{1}{\hbar \omega + \frac{\hbar \omega_A}{2} - E} \right) \int dR \left| g^{(-)}(\omega) \right|^2
\]

\[
E = -\frac{\hbar \omega_A}{2} + E_{vw}(r_A)
\]
GROUND-STATE van der WAALS ENERGY

Integral equation

I.V. Bondarev and Ph. Lambin,
cond-mat/0404211 [submitted to SSC]

\[ \varepsilon_{vw}(r_A) = \frac{E_{vw}(r_A)}{2\gamma_0}, \quad \tilde{\Gamma}_0(x) = \frac{h\Gamma_0(x)}{2\gamma_0}, \quad x = \frac{\hbar\omega}{2\gamma_0}, \quad \gamma_0 = 2.7 \text{ eV} \]

\[ \varepsilon_{vw}(r_A) = \frac{x_A}{2\pi} \int_0^\infty dx \frac{\tilde{\Gamma}_0(x)}{x^2} \tilde{\xi}^\perp(r_A, x) \]

\[ -\frac{x_A^2}{2\pi} \int_0^\infty dx \frac{\tilde{\Gamma}_0(x)}{x^2} \frac{\tilde{\xi}^\perp(r_A, x)}{x + x_A} \left( 1 - \int_0^\infty dx \frac{\tilde{\Gamma}_0(x)}{x^2} \tilde{\xi}^\perp(r_A, x) \right) - \varepsilon_{vw}(r_A) \]

\[ \varepsilon_{vw}(r_A) \approx 0 \]

Weak coupling approximation

\[ \int_0^\infty dx \frac{\tilde{\Gamma}_0(x)}{x^2} \tilde{\xi}^\perp(r_A, x) \approx 1 \]

Strong coupling approximation

\[ \varepsilon_{vw}(r_A) \approx \frac{x_A}{2\pi} \int_0^\infty dx \frac{\tilde{\Gamma}_0(x)}{x^2} \tilde{\xi}^\perp(r_A, x) - \]

\[ \frac{x_A^2}{2\pi} \int_0^\infty dx \frac{\tilde{\Gamma}_0(x)}{x^2} \frac{\tilde{\xi}^\perp(r_A, x)}{x + x_A} \left( 1 - \int_0^\infty dx \frac{\tilde{\Gamma}_0(x)}{x^2} \tilde{\xi}^\perp(r_A, x) \right) - x - \varepsilon_{vw}(r_A) \]
Atom outside the (9,0) CN:

exact solution for the vdW energy compared with weak/strong coupling approximation.

\[ E_{vdW}/2\gamma_0 \]

![Graph showing numerical results for van der Waals energy](image)

- **Exact solution**
- **Strong coupling approximation**
- **Weak coupling approximation**

\[(9,0), \quad x_A = 0.33\]

\[ x_A = \frac{\hbar \omega_A}{2\gamma_0}, \quad \gamma_0 = 2.7 \text{ eV} \]
Atom outside the (9,0) CN:

exact solution for the vdW energy compared with weak/strong coupling approximation for different atomic transition frequencies

\[ r_A/R_{cn} \]

\[ E_{v_{\text{w}}} / 2 \gamma_0 \]

(b) (9,0)

- exact solution
- strong coupling approx.
- weak coupling approx.

\[ 1-x_A = 0.33; 2-x_A = 0.52; 3-x_A = 0.58 \]

\[ x_A = \frac{\hbar \omega_A}{2 \gamma_0}, \gamma_0 = 2.7 \text{ eV} \]
Atom in/outside the (10,10) CN: van der Waals energy in/outside the nanotube for a few atomic transition frequencies

\[ x_A = 0.22; \]
\[ x_A = 0.30; \]
\[ x_A = 0.45 \]

\[ x_A = \frac{\hbar \omega_A}{2 \gamma_0}, \quad \gamma_0 = 2.7 \text{ eV} \]
(II.1) Due to *STRONG* atom-vacuum field coupling in a close vicinity of the nanotube surface, one has to be careful when calculating the van der Waals energy of an atom near a carbon nanotube.

(II.2) An integral equation for the van der Waals energy has been derived which is valid for both strong and weak atom-vacuum-field coupling.

(II.3) The inapplicability has been demonstrated of weak-coupling-based van der Waals interaction models in a close vicinity of the nanotube surface.

(II.4) Encapsulation of doped atoms into the nanotube has been shown to be energetically more favorable than their outside adsorption by the nanotube surface.
THANK YOU !