Near-Field Electrodynamics of Atomically Doped Carbon Nanotubes

I.V Bondarev* and Ph. Lambin**

* Institute for Nuclear Problems, Belarusian State University
Bobruiskaya Str. 11, 220050 Minsk, Belarus, bondarev@tut.by
** Facultés Universitaires Notre-Dame da la Paix
61 rue de Bruxelles, 5000 Namur, Belgium, philippe.lambin@fundp.ac.be

ABSTRACT

We develop a quantum theory of near-field electrodynamical properties of carbon nanotubes. The theory is used to investigate spontaneous decay dynamics and van der Waals (vdW) attraction of a two-level atomic system located close to a nanotube surface. We demonstrate a strictly non-exponential spontaneous decay dynamics of the upper state and nonlinear vdW coupling of the lower (ground) state of the coupled "atom–nanotube" system.

Keywords: carbon nanotubes, strong atom-field coupling, atomic spontaneous decay, van der Waals interactions

1 INTRODUCTION

Carbon nanotubes (CNs) are graphene sheets rolled-up into cylinders of approximately one nanometer in diameter. Extensive work carried out worldwide in recent years has revealed the intriguing physical properties of these novel molecular scale wires [1]. Nanotubes have been shown to be useful for miniaturized electronic, mechanical, electromechanical, chemical and scanning probe devices and materials for macroscopic composites [2]. Important is that their intrinsic properties may be substantially modified in a controllable way by doping with extrinsic impurity atoms, molecules and compounds [3]. Recent successful experiments on encapsulation of single atoms into single-wall CNs [4] and their intercalation into single-wall CN bundles [3], [5] stimulate an in-depth analysis of atom-vacuum-field interactions in such systems.

The relative density of photonic states (DOS) near a CN effectively increases due to the presence of additional surface photonic states coupled with CN electronic quasiparticle excitations [6], [7]. This causes an atom-vacuum-field coupling constant (which is proportional to the photonic DOS – see later) to be very sensitive to an atom-CN-surface distance. At small enough distances, the system may exhibit a strong atom-field coupling regime giving rise to rearrangement ("dressing") of atomic levels by vacuum-field interaction, so that standard weak-coupling-QED-based atom-field interaction models (see [8] for a review) are, in general, inapplicable for an atom in a close vicinity of a carbon nanotube. To give this issue a proper theoretical consideration, we develop a universal quantum theory of atom-field interactions in the presence of an infinitely long single-wall CN, which is valid for both strong and weak atom-field coupling. By applying this theory to two particular problems, the spontaneous decay of the excited state and the vdW attraction of the ground state of the two-level atom close to the nanotube surface, we demonstrate the strictly non-exponential spontaneous decay dynamics and nonlinear vdW coupling of the coupled "atom–nanotube" system.

2 BRIEF SKETCH OF THE MODEL

Consider a neutral atomic system with its center of mass positioned at the point $\mathbf{r}_A$ near an infinitely long single-wall CN. Assign the orthonormal cylindric basis $\{\mathbf{e}_r, \mathbf{e}_\varphi, \mathbf{e}_z\}$ with $\mathbf{e}_z$ directed along the CN axis. The total nonrelativistic Hamiltonian of the whole system can then be represented in the form (electric-dipole approximation, Coulomb gauge, CGS units) [8], [9]

$$\hat{H} = \hat{H}_F + \hat{H}_A + \hat{H}_{AF}^{(1)} + \hat{H}_{AF}^{(2)}\,, \tag{1}$$

where

$$\hat{H}_F = \int_0^\infty d\omega\hbar\omega \int d\mathbf{R}\, \hat{f}^\dagger(\mathbf{R},\omega)\hat{f}(\mathbf{R},\omega), \tag{2}$$

$$\hat{H}_A = \sum_i \frac{\hat{\mathbf{p}}^2}{2m_i} + \sum_{i<j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{3}$$

$$\hat{H}_{AF}^{(1)} = -\sum_i \frac{q_i}{m_i c}\, \hat{\mathbf{p}}_i \cdot \hat{\mathbf{A}}(\mathbf{r}_A) + \hat{\mathbf{d}} \cdot \nabla\hat{\varphi}(\mathbf{r}_A), \tag{4}$$

$$\hat{H}_{AF}^{(2)} = \sum_i \frac{q_i^2}{2m_i c^2}\, \hat{\mathbf{A}}^2(\mathbf{r}_A) \tag{5}$$

are, respectively, the Hamiltonian of the vacuum electromagnetic field modified by the presence of the CN, the Hamiltonian of the atomic subsystem, and the Hamiltonian of their interaction (separated into two contributions according to their role in the atom-vacuum-field interaction – see later). The operators $\hat{f}^\dagger$ and $\hat{f}$ in Eq. (2) are those creating and annihilating single-quantum electromagnetic excitations of bosonic type in the CN and the inner integral is taken over the CN surface assigned by the vector $\mathbf{R} = \{R_{cn}, \phi, Z\}$ with R_{cn} being the CN

radius. In Eqs. (3)-(5), m_i, q_i, $\hat{\mathbf{r}}_i$ and $\hat{\mathbf{p}}_i$ are, respectively, the masses, charges, coordinates (relative to $\mathbf{r}_A$) and momenta of the particles constituting the atomic subsystem, $\hat{\mathbf{d}} = \sum_i q_i \hat{\mathbf{r}}_i$ is its electric dipole moment operator, $\hat{\mathbf{A}}$ and $\hat{\varphi}$ are the vector potential and the scalar potential of the CN-modified electromagnetic field.

We simplify the Hamiltonian (1)-(5) by applying the two-level approximation to obtain [9]

$$\hat{H} = \int_0^\infty d\omega \hbar\omega \int d\mathbf{R}\, \hat{f}^\dagger(\mathbf{R},\omega)\hat{f}(\mathbf{R},\omega) + \frac{\hbar\tilde{\omega}_A}{2}\,\hat{\sigma}_z + \int_0^\infty d\omega \int d\mathbf{R}\left[\mathrm{g}^{(+)}(\mathbf{r}_A,\mathbf{R},\omega)\,\hat{\sigma}^\dagger - \mathrm{g}^{(-)}(\mathbf{r}_A,\mathbf{R},\omega)\,\hat{\sigma}\right]\hat{f}(\mathbf{R},\omega) + \mathrm{h.c.}. \quad (6)$$

Here, the Pauli operators $\hat{\sigma}_z = |u\rangle\langle u| - |l\rangle\langle l|$, $\hat{\sigma} = |l\rangle\langle u|$, $\hat{\sigma}^\dagger = |u\rangle\langle l|$ describe electric dipole transitions between the two atomic states, upper $|u\rangle$ and lower $|l\rangle$, separated by the transition frequency ω_A. This ('bare') frequency is modified by the interaction (5) which, being independent of the atomic dipole moment, does not contribute to mixing the $|u\rangle$ and $|l\rangle$ states, giving rise, however, to the new *renormalized* transition frequency $\tilde{\omega}_A = \omega_A[\,1 - 2/(\hbar\omega_A)^2 \int_0^\infty d\omega \int d\mathbf{R}\,|\mathrm{g}^\perp(\mathbf{r}_A,\mathbf{R},\omega)|^2\,]$ in the second term of Eq. (6). On the contrary, the interaction (4), being dipole moment dependent, mixes the $|u\rangle$ and $|l\rangle$ states, yielding the third term of the Hamiltonian (6) with the interaction matrix elements $\mathrm{g}^{(\pm)} = \mathrm{g}^\perp \pm (\omega/\omega_A)\mathrm{g}^\parallel$, where $\mathrm{g}^{\perp(\parallel)} = -i4\omega_A d_z \sqrt{\pi\hbar\omega \mathrm{Re}\sigma_{zz}(\omega)}\; G_{zz}^{\perp(\parallel)}/c^2$ with $G_{zz}^{\perp(\parallel)}(\mathbf{r}_A,\mathbf{R},\omega)$ being the zz-component of the transverse (longitudinal) Green tensor of the electromagnetic subsystem and $\sigma_{zz}(\omega)$ standing for the CN surface axial conductivity (we neglect the azimuthal current and radial polarizability of the CN). The functions $\mathrm{g}^{\perp(\parallel)}$ (and $\mathrm{g}^{(\pm)}$, respectively) have the following general property $\int d\mathbf{R} |\mathrm{g}^{\perp(\parallel)}(\mathbf{r}_A,\mathbf{R},\omega)|^2 = (\hbar^2/2\pi)(\omega_A/\omega)^2\Gamma_0(\omega)\xi^{\perp(\parallel)}(\mathbf{r}_A,\omega)$ with $\xi^{\perp(\parallel)} = \mathrm{Im}\,G_{zz}^{\perp(\parallel)}/\mathrm{Im}\,G_{zz}^0$ representing the transverse (longitudinal) position-dependent (local) photonic DOS and $\Gamma_0(\omega) = 8\pi\omega^2 d_z^2 \mathrm{Im}\,G_{zz}^0(\omega)/3\hbar c^2$ being the atomic spontaneous decay rate in vacuum [7]. Thus, the total energy of the system with the Hamiltonian (6), in general, and the frequency $\tilde{\omega}_A$, in particular, are expressed in terms of only one *intrinsic* physical characteristic of the electromagnetic subsystem – the local photonic DOS.

3 PARTICULAR PROBLEMS

Based on the Hamiltonian (6) and taking a possible degeneracy into account of the upper level and lower level of the coupled "atom–nanotube" system at small $\tilde{\omega}_A$ (this takes place at small atom-CN-surface distances where the local photonic DOS strongly increases as is seen from the definition of $\tilde{\omega}_A$), we derive equations for the time evolution of the population probability $C_u(t)$ of the excited state and for the vdW energy $E_{vw}(\mathbf{r}_A)$ of the ground state of the two-level atom coupled with the CN modified vacuum electromagnetic field. The former is the result of the solution of the time-dependent Srödinger equation of the form [7], [10]

$$C_u(t) = 1 + \int_0^t K(t-t')\,C_u(t')\,dt', \quad (7)$$

$$K(t-t') = \frac{1}{\hbar^2}\int_0^\infty d\omega\, \frac{e^{-i(\omega-\tilde{\omega}_A)(t-t')} - 1}{i\,(\omega - \tilde{\omega}_A)} \times \int d\mathbf{R}\,|\mathrm{g}^{(+)}(\mathbf{r}_A,\mathbf{R},\omega)|^2.$$

The latter comes from the solution of the secular equation yielding the total ground-state energy E of the coupled "atom–nanotube" system in the form [9]

$$E = -\frac{\hbar\tilde{\omega}_A}{2} - \int_0^\infty d\omega \int d\mathbf{R}\, \frac{|\mathrm{g}^{(-)}(\mathbf{r}_A,\mathbf{R},\omega)|^2}{\hbar\omega + \dfrac{\hbar\tilde{\omega}_A}{2} - E}, \quad (8)$$

which the atom–nanotube vdW energy $E_{vw}(\mathbf{r}_A)$ is determined from by the relation $E = -\hbar\omega_A/2 + E_{vw}(\mathbf{r}_A)$ with the first term being the unperturbed ground-state energy of the two-level atom.

In view of the general integral property of the matrix elements $\mathrm{g}^{(\pm)}$ given in the end of Section 2, both Eq. (7) and Eq. (8) are represented in terms of the local (position-dependent) photonic DOS and, thus, are valid for both strong ($\xi^{\perp,\parallel} \gg 1$) and weak ($\xi^{\perp,\parallel} \sim 1$) atom-field coupling.

Using Eqs. (7) and (8), we have simulated the upper state spontaneous decay dynamics and the ground state vdW energy of an atom situated outside the (9,0) CN. The local photonic DOS functions $\xi^{\perp,\parallel}$ were computed in the same manner as it was done in Refs. [6],[7]. The free-space spontaneous decay rate was approximated by the expression $\Gamma_0(\omega) \approx \alpha^3\omega$ ($\alpha = 1/137$ is the fine-structure constant) valid for hydrogen-like atoms [11]. Figure 1(a) shows the transverse local photonic DOS for the atom at several distances from the CN surface. The DOS function is seen to increase with decreasing the atom-CN-surface distance, representing the increase of the atom-field coupling strength as the atom approaches the CN surface. The vertical dashed line indicates the dimensionless bare atomic transition frequency $x_A = \hbar\omega_A/2\gamma_0$ ($\gamma_0 = 2.7$ eV is the carbon nearest neighbor hopping integral) for which the upper state population probabilities and the lower state vdW energies shown in Fig. 1(b),(c) were calculated. The frequency $x_A = 0.33$ is the peak position (at least for the shortest atom-surface distance) of the local photonic DOS. Note that $x_A \sim 0.5$ are typical for heavy hydrogen-like atoms such as Cs (supposed to be non-ionized near a CN). Figure 1(b) shows the upper state population probabilities $|C_u|^2$ as functions of the dimensionless time $\tau = 2\gamma_0 t/\hbar$ and the

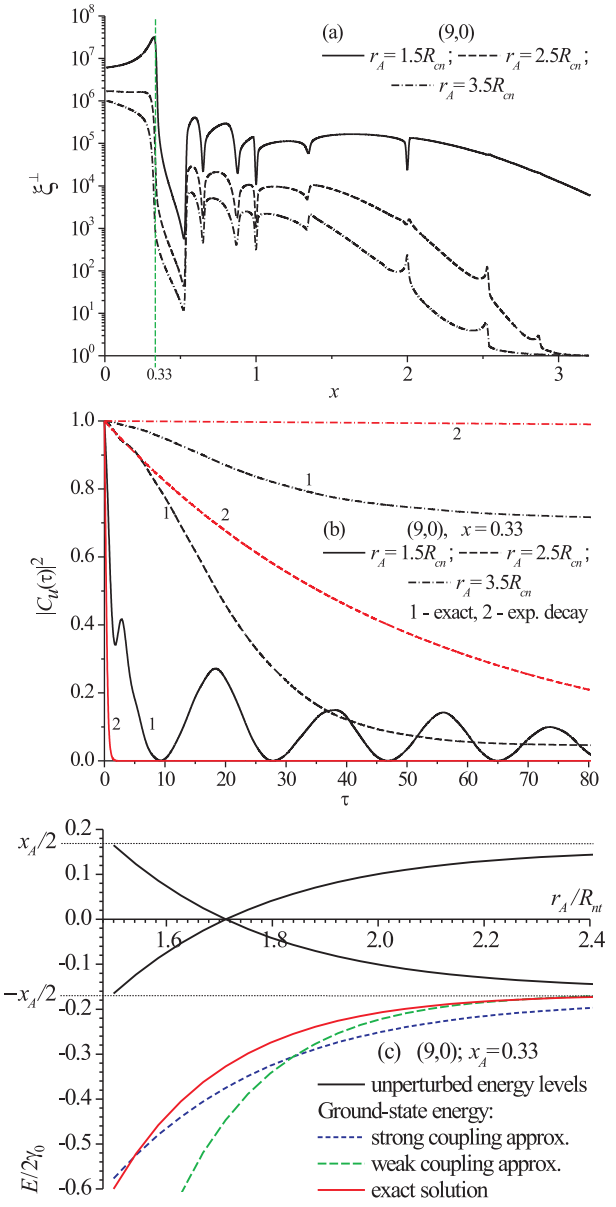

Figure 1: (a),(b) Transverse local photonic DOS's and upper-level spontaneous decay dynamics, respectively, for the two-level atom situated at three different distances outside the (9,0) CN. (c) Dimensionless "unperturbed" energy levels [the eigenvalues of the Hamiltonian in the first line of Eq. (6)] and total-ground state energy of the coupled "atom–nanotube" system as functions of the atomic position outside the (9,0) CN. The ('bare') atomic transition frequency is indicated by the vertical dashed line in Fig. 1(a); $x = \hbar\omega/2\gamma_0$ and $\tau = 2\gamma_0 t/\hbar$ are the dimensionless frequency and time, respectively, with $\gamma_0 = 2.7$ eV being the carbon nearest neighbor hopping integral.

atom-CN-surface distance in comparison with those obtained in the Markovian approximation which is known to yield the exponential decay dynamics (see, e.g., [12]). The actual spontaneous decay dynamics is clearly seen to be non-exponential. Very clear underdamped Rabi oscillations are observed for the shortest atom-surface distance, indicating *strong* atom-field coupling with strong non-Markovity. Similar to what takes place in photonic crystals [13], this is because of the fact that, due to the rapid variation of the local photonic DOS in the neighborhood of this frequency, the correlation time of the electromagnetic vacuum is not negligible on the time scale of the evolution of the atomic system, so that atomic motion memory effects are important and the Markovian approximation is inapplicable. Figure 1(c) shows the dimensionless total ground-state energy of the coupled "atom–nanotube" system and two "unperturbed" energy levels [the eigenvalues of the Hamiltonian in the first line of Eq. (6)] as functions of the atomic position outside the (9,0) CN. As the atom approaches the CN surface, its "unperturbed" levels come together, then get degenerated and even inverted at a very small atom-surface distance. As this takes place, the weak coupling approximation for the ground-state energy is known to diverge, whereas the strong coupling approximation yields a finite result (see, e.g., [11]). The *exact* solution given by Eq. (8) reproduces the weak coupling approximation at large and the strong coupling approximation at short atom-surface distances, respectively.

4 CONCLUSION

We have developed the quantum theory of near-field electrodynamical properties of carbon nanotubes and investigated spontaneous decay dynamics of excited states and vdW interaction of the ground state of a two-level atomic system (an atom or a molecule) close to a single-wall carbon nanotube. We have demonstrated a strictly non-exponential spontaneous decay dynamics and the inapplicability of weak-coupling-based vdW interaction models in a close vicinity of the CN surface where the local photonic DOS effectively increases, giving rise to an atom-field coupling enhancement. In certain cases, namely when the atom is close enough to the nanotube surface and the atomic transition frequency is in the vicinity of the resonance of the local photonic DOS, the system exhibits vacuum-field Rabi oscillations – a principal signature of *strong* atom-vacuum-field coupling. The non-exponential decay dynamics gives place to the exponential one if the atom moves away from the CN surface. Thus, the atom-vacuum-field coupling strength and the character of the spontaneous decay dynamics, respectively, may be controlled by changing the distance between the atom and CN surface by means of a proper preparation of atomically doped CN systems.

We would like to emphasize a general character of the

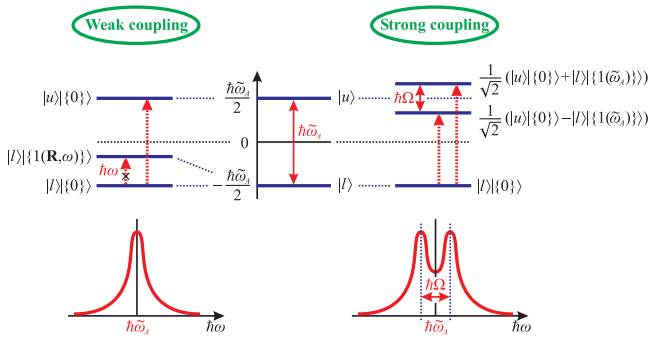

Figure 2: Schematic of the energy levels and the absorbtion line-shapes expected in the optical absorbance experiment with atomically doped CNs. In the center are the "unperturbed" atomic levels [the eigenvalues of the Hamiltonian in the first line of Eq. (6)]. On the left and on the right are the levels of the coupled "atom–nanotube" system in the weak and strong atom-vacuum-field coupling regime, respectively. The system is excited by an external optical radiation. The allowed and forbidden (crossed) optical transitions are shown by vertical dashed arrows.

conclusion above and its fundamental and applied significance. We have shown that similar to semiconductor microcavities [14], [15] and photonic band-gap materials [13], [16], carbon nanotubes may qualitatively change the character of the atom-electromagnetic-field interaction, yielding strong atom-field coupling. The study of such phenomena was started awhile ago in atomic physics [17] and still attracts a lot of interest in connection with various quantum optics and nanophotonics applications [18], [19] as well as quantum computation and quantum information processing [20], [21]. The fact that the carbon nanotube may control atom-electromagnetic-field coupling opens routes for new challenging applications of atomically doped CN systems as various sources of coherent light emitted by dopant atoms.

Strong atom-vacuum-field coupling we predict will yield an additional structure in optical absorbance spectra (see, e.g., [22]) of atomically doped CNs in the vicinity of an atomic transition frequency. The illustration is shown in Fig. 2. Weak non-Markovity of the atom-vacuum-field interactions (that yielding non-exponential spontaneous decay dynamics with no Rabi oscillations) will cause an asymmetry of an optical spectral line-shape (not shown in Fig. 2) similar to that taking place for the exciton optical absorbtion line-shape in quantum dots [23]. Strong non-Markovity of the atom-vacuum-field interactions (yielding non-exponential spontaneous decay dynamics with fast Rabi oscillations) originates from strong atom-vacuum-field coupling with the upper state of the system splitted into two "dressed" states (Fig. 2, on the right). This will yield a two-component structure of optical absorbance/reflectance spectra similar to that observed for excitonic and intersubband electronic transitions in semiconductor quantum microcavities [14], [15].

Similar manifestations of strong atom-field coupling may occur in many other atom-electromagnetic-field interaction processes in the presence of CNs, such as, e.g., atomic states entanglement, interatomic dipole-dipole interactions, cascade spontaneous transitions in three-level atomic systems, etc. A further intriguing extension of the present work could also be the study of the vdW interactions of excited atomic states where, even in the weak atom-field-coupling regime and in the simplest case of an atom near a planar semi-infinite medium, very interesting peculiarities (e.g., an oscillatory behavior) were recently shown to exist [24].

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