Model of the coherent magneto-optical dynamics in a single chiral carbon nanotube

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Abstract. A theoretical framework and dynamical model for description of the natural optical activity and Faraday rotation in an individual chiral single-walled carbon nanotube in the highly nonlinear coherent regime is proposed. The model is based on a discrete-level representation of the optically active states near the band edge. Chirality is modelled by a system Hamiltonian corresponding to energy-level configurations, specific for each handedness, that are mirror reflections of each other. An axial magnetic field is introduced through the Aharonov-Bohm and Zeeman energy-level shifts. The time evolution of the quantum system is studied using the coherent vector Maxwell-pseudospin equations. Giant natural and magneto-optical gyrotropy, exceeding the one of the artificial photonic metamaterials, is numerically demonstrated for a single (5,4) carbon nanotube and an estimate of the magnitude of the natural circular dichroism and specific optical rotatory power is obtained. The model provides a framework for investigation of chirality and magnetic field dependence of the ultrafast nonlinear optical response of a single carbon nanotube.

1. Introduction
Chirality is one of the main symmetries of the carbon nanotube geometry which determines the optical properties of single-walled carbon nanotubes (SWCNTs). The interaction of polarised light with chiral materials in the absence of magnetic fields gives rise to the phenomenon of natural optical (rotation) activity, whereby the polarisation plane is rotated continuously during the light propagation across the medium.

Time-resolved magnetic circular dichroism and magneto-optical rotatory dispersion techniques offer spectroscopic information which is different or impossible to obtain by other means. A detailed understanding of the mechanisms underlying the optical and magneto-optical birefringence, circular dichroism and rotation in the nonlinear coherent regime require an adequate theoretical description. On the other hand, formulation of a theory and model of the optical activity in chiral molecules, such as individual single-wall carbon nanotubes (SWCNTs), in the high-intensity nonlinear coherent regime and under an axial magnetic field, is of special interest from a fundamental point of view. To our knowledge, no such theory has been proposed and very little is known about the polarisation dynamics of the nonlinear optical and magneto-optical response of a single carbon nanotube. Exploiting these ultrafast nonlinear effects would open up pathways for the development of a novel class of ultrafast polarisation-sensitive integrated optoelectronic devices, based on single carbon nanotubes.
2. Theoretical background
Carbon nanotubes exist in two (AL) left- (n>m) and (AR) right-handed (n<m) helical forms (enantiomers) depending on the rotation of two of the three armchair (A) chains of carbon atoms counterclockwise or clockwise when looking against the nanotube z-axis. The electronic band structure [1] is described by the quantization of the wavevector along the tube circumference, resulting in subbands in the valence and conduction band labelled by the quasi-angular momentum quantum number (µ).

We model the single chiral nanotube band-edge structure at the K point of the Brillouin zone by an ensemble of identical four-level systems, corresponding to the dipole optically allowed transitions for AL and AR nanotube enantiomers (Fig. 1). Absorption of right circularly polarised light $\sigma^+$ of resonance frequency $\omega_0$ excites the electronic transitions $\mu - 1 \rightarrow \mu$ in AL-handed SWCNTs and $\mu \rightarrow \mu - 1$ transitions in AR-handed SWCNTs, the absorption of left circularly polarised $\sigma^-$ light excites $\mu \rightarrow \mu - 1$ transitions in AL-handed and $\mu \rightarrow \mu + 1$ transitions in AR-handed SWCNTs [2] (Fig. 1). When a circularly polarised (in the x-y plane) laser pulse propagates along the z-axis of an AL or AR SWCNT (Fig. 2), only one of the two allowed transitions for a linearly polarised light (along x or y) is excited (see Fig.1).

2.1. Coherent dynamics of the natural optical activity
We follow the semiclassical formalism developed in [3] and describe the discrete multi-level system coherently driven dynamics by Maxwell’s equations in vectorial form for the polarised optical pulse propagation coupled to master pseudospin equations for the time-evolution of the quantum system, exploiting the SU(4) group symmetries. We shall consider the specific case of a chiral AL-handed (5,4) SWCNT, chosen for illustration of the general method valid for an arbitrary chirality. The electronic band structure, calculated by tight-binding method [4], can be well approximated by a four-level system, for which the system Hamiltonian is constructed.

Figure 1. Energy-level structure at the $K(K')$ point of the lowest subbands labelled by the subband index $\mu$ for an (a) AL-handed; (b) AR-handed SWCNT. $\Delta$ is the energy separation between the lowest subband and the second lowest subband near the band edge.

Figure 2. Geometry of an experiment with an optical excitation by circularly polarised pulse propagating along the SWCNT axis, $E_x$ and $E_y$ are E-field vector components.
π/2, is modelled by two orthogonal linearly polarized optical waves, phase-shifted by pulsed excitation, applied at the left boundary. ϵ is a value of, self-consistently with master pseudospin equations Eq.(2). Employing the effective medium pulse propagating in an isotropic medium with an effective dielectric constant are solved efficiently spectrum for σ. The time evolution of the quantum system in the presence of relaxation processes is governed by a set of pseudospin master equations for the real state 15-dimensional vector S derived in [3]:

$$\hat{H} = \hbar \left( \begin{array}{cccc}
-\frac{1}{2} (\Omega_x - i\Omega_y) & -\frac{1}{2} (\Omega_x + i\Omega_y) & 0 & 0 \\
0 & 0 & \Delta & -\frac{1}{2} (\Omega_x - i\Omega_y) \\
0 & 0 & \Delta & -\frac{1}{2} (\Omega_x + i\Omega_y) \\
0 & 0 & 0 & 0
\end{array} \right)$$ (1)

where \( \Omega_x = \varphi \frac{E_x}{\hbar}, \Omega_y = \varphi \frac{E_y}{\hbar} \) are the time-dependent Rabi-frequencies and \( \varphi \) is the optical dipole matrix element. An estimate for the dipole transition matrix element in (5,4) nanotube is obtained by using the tight-binding Hamiltonian, including chirality effects derived in [5], yielding a dipole moment \( \varphi = 3.613 \times 10^{-29} \text{Cm} \).

The resulting set of equations is solved directly in the time domain, by employing the Finite-Difference Time-Domain method, yielding the spatially resolved temporal dynamics of the electric field vector components and the populations of all four levels along the nanotube length. The spatially resolved absorption/gain (Fig. 3) and phase shift spectra (Fig. 4) allow to calculate the circular dichroism and the optical rotation angle. The calculated average circular dichroism along the nanotube length is 0.083 \( \mu m^{-1} \). An estimate of the circular dichroism of a (5,4) nanotube can be calculated from [5], giving a value of 1.03 for the relative difference between...

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**Figure 3.** Calculated gain coefficient spectrum for \( \sigma^+ \) and \( \sigma^- \) ultrashort optical excitation. **Figure 4.** Calculated phase shift spectrum for \( \sigma^+ \) and \( \sigma^- \) ultrashort optical excitation.
\(\sigma^+\) and \(\sigma^-\) absorption probability rates. This value, however, cannot be directly compared with the obtained result since the nanotube length does not enter the model in [5], and thus can only provide a guidance. We should stress that our analysis applies to the high-intensity nonlinear ultrafast regime, in which, up to our knowledge, no theory or experiments have been published. Therefore we should expect deviations from the linear case. By comparison, the absolute value of the circular dichroism of an artificial helicoidal bilayered structure varies in the range of 5-9 dB, which is equivalent to linear amplitude absorption/gain coefficient 0.58 – 1.04 \(\mu\text{m}^{-1}\). The average natural specific rotatory power \(\sim 2962.24^\circ/\text{mm}\) exceeds the giant gyrotropy reported in the artificial photonic metamaterials of up to \(2500^\circ/\text{mm}\) [7]. We should note, however, that the complexity of the carbon nanotube molecular structure allows for engineering the optical activity in a wide range.

2.2. Magneto-optical activity of a chiral SWCNT in an axial magnetic field

In the presence of an axial magnetic field the electronic band structure of a single carbon nanotube, and the electronic states near the band gap edge in particular, significantly change, owing to the combined action of two effects: the spin-B interaction resulting in Zeeman splitting of the energy levels and the appearance of the Aharonov-Bohm phase in the wave function resulting in an additional energy level shift. The energy level configuration in an external magnetic field can be split into two reduced sets of levels, each of which represents a mirror image of the other, however the symmetry is broken by the allowed optical transitions in each case. We apply the formalism developed in 2.1 and calculate the spatially resolved optical absorption/gain and phase shift spectra, shown in Figs 5 and 6, respectively. It is worth noting that the magnetic circular dichroism spectra are quite distinctive from the zero-magnetic field ones. While the \(\sigma^-\) polarised pulse is amplified during the pulse propagation across the nanotube, the \(\sigma^+\) polarised pulse is absorbed, resulting in a much larger net circular dichroism. The average value of the magnetic circular dichroism is 0.706 \(\mu\text{m}^{-1}\), an order of magnitude larger than the natural circular dichroism. This is a direct consequence of the four-level energy-level system for a \(\sigma^-\) excitation and a three-level \(\Lambda\)-system for a \(\sigma^+\) excitation. The calculated spectra in the latter case are reminiscent of electromagnetically-induced transparency (EIT) and coherent population trapping effects. The calculated average specific rotatory power in a magnetic field \((B = 8 \text{ T})\), is \(-32.5804^\circ/\mu\text{m}\), the meaning of the minus sign is to denote left rotation. The predicted Faraday rotation at \(B = 8 \text{ T}\) is nearly an order of magnitude greater than the natural optical rotation. We should note that the calculated rotation is a combined effect from the chirality of the nanotube and the magnetic field-induced rotation and thus can be considered as an estimate for the magneto-chiral effect in a single nanotube.
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