

New Physics in Molecular Electronic and Molecular Optoelectronic Structures

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Abstract. Methods for injecting charge currents on single wall molecular nanotubes through nonlinear interaction with optical fields are studied. By varying the relative phases, frequencies and polarizations of the incident fields one can control the symmetries of the optically excited states and the phase space distribution for the photoexcited electrons. We study coherent control of a photocurrent on a carbon nanotube using quantum interference of excitations from optical fields oscillating at ω and 2ω . For BN nanotube we study the shift current as a probe of the ground state polarization of the heteropolar tube. Here we find that the sign and size of the ground state polarization is an intrinsic quantum effect controlled by the *chiral index* of the BN nanotube.

INTRODUCTION

Nonlinear optical excitations can be used to control the symmetry and phase space distribution of excited electronic states in bulk semiconductors and provide a powerful method for controlling electronic excitations on molecular nanotubes as well. Nanotubes of carbon or BN can be formed in nearly defect free molecular structures that are microns long though only nanometers in diameter. The extension of the theory of nonlinear optical response from bulk semiconductors to these compact tubular structures leads to interesting and sometimes surprising physical effects that we review in this paper.

COHERENTLY CONTROLLED PHOTOCURRENTS ON SWNT'S

A photocurrent on a semiconducting nanotube can be produced by optically exciting electron hole pairs and using a static electric field to bias the diffusion of the photoexcited carriers. Interestingly a photocurrent can also be produced even in the absence of a static field at nonlinear order in the exciting fields. Optical fields oscillating at frequencies ω and 2ω can couple the same initial and final

electronic states through separate one photon (2ω) and two photon (ω) excitation pathways. Interference between the two transition amplitudes produces a term in the absorption cross section that is *odd* in the incident fields, producing an asymmetry in the velocity distribution of the photoexcited carriers, and hence a charge current. For a nanotube the sign of this current is controlled by the matrix elements of the transition dipole connecting the initial and final states and the relative *phases* of the incident optical fields. This nonlinear photoeffect has been observed in a series of beautiful experiments on bulk semiconductor [1,2].

The application of this idea to a carbon nanotube [3] turns out to be complicated by the chiral symmetry of its low lying electronic states. Electronic states on a carbon nanotube are derived from the band eigenstates of the graphene sheet near the zone corners K and K' which can be distinguished by their chirality. At low energies and long wavelengths the effective mass Hamiltonians for momenta q near these points has the form [4]

$$H_{K(K')}(q_x, q_y) = -(+) \hbar v_F \begin{pmatrix} 0 & q_x - (+)iq_y \\ q_x + (-)iq_y & 0 \end{pmatrix} \quad (1)$$

Note that the two dimensional graphene lattice is not a chiral structure and thus most simple observables require a Brillouin zone sum which averages over the chiral character of the small q eigenstates of (1). Nevertheless, the chirality of the band eigenstates produces important physical effects that persist even after the summation. For example, the cross section for optical transitions between the occupied and empty bands of the graphene sheet at wavevector \vec{q} produced by a linearly polarized incident field \vec{A}_ω depends on the orientation of the wavevector following the $|\vec{q} \times \vec{A}_\omega|^2$ law rather than the $(\vec{q} \cdot \vec{A}_\omega)^2$ law expected from $\vec{k} \cdot \vec{p}$ perturbation theory applied to an isotropic band. Note that this implies that the interband matrix elements vanish for \vec{A}_ω polarized along the axis of a conducting nanotube where the lowest branch of azimuthally quantized electronic states pass exactly through the $K(K')$ points. This vanishing of the interband matrix elements is exact within the linearized long wavelength theory, and it is only weakly violated in the lattice theory where the first corrections occur to order $(qa)^3$ where a is the graphene lattice constant.

When a carbon nanotube is simultaneously excited by the optical fields \vec{A}_ω and $\vec{A}_{2\omega}$, the interference between the one photon and two photon transition amplitudes produces a polar asymmetry in the density of excited photocarriers. However, we find that the strength of this effect is vastly different for semiconducting and conducting tubes. The cross section for this third order process connecting states at wavevector $q = k - k_F$ is calculated in reference [4] where we find

$$\dot{n}^3(q) \propto \Delta^2 q \operatorname{Re}(A_{2\omega} A_{-\omega} A_{-\omega} e^{i\phi_2 - 2i\phi_1}) \quad (2)$$

where 2Δ denotes the bandgap at $q = 0$ and the A 's and ϕ 's are the amplitudes and phases of the incident fields. Note that the strength of the effect is proportional to Δ^2 and vanishes for a conducting tube when $\Delta \rightarrow 0$. The calculated injection

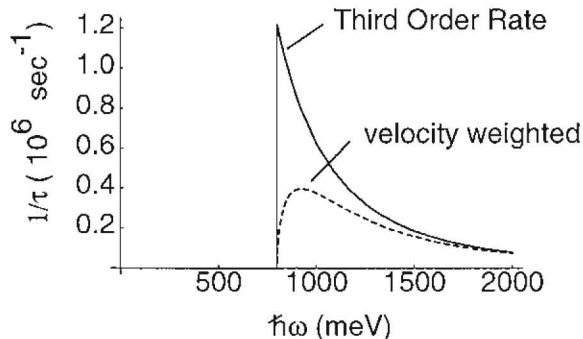


FIGURE 1. Frequency dependence of the third order transition rate that produces a photocurrent on a single wall carbon nanotube. The curves are calculated for a semiconducting gap $\Delta = 800$ meV, and an incident amplitude $|A| = 10^{-9}$ T-m at all frequencies. The dashed curve weights the transition rate by the group velocity of the carriers in the final state.

rate is plotted as a function of the exciting frequency ω in Figure 1. The transition rate is relatively strong, and normalized per atom it is comparable to the analogous process found in bulk GaAs.

Figure (1) displays results for a semiconducting nanotube; within the linearized theory this third order process is symmetry forbidden for a conducting SWNT. Discrete lattice effects on a conducting nanotube weakly break this symmetry and lead to a weak response at order $(qa)^3$. Thus for a conducting tube the nonlinear photoeffect is allowed, though extremely weak (it is typically suppressed by a factor of 10^2 compared to the rate for semiconducting tubes). A detailed calculation of this interference effect for conducting as well as semiconducting tubes is presented in reference [4].

The simplest experimental geometry for a SWNT has the incident optical fields collinear and polarized along the tube axis. For the analogous process on a graphene sheet the linear polarizations of the incident fields can also be varied and this provides a sensitive control parameter for changing the angular distribution of the optically injected carriers. Results for the angular dependence of the interference term in the absorption cross section calculated for a graphene sheet are displayed in Figure 2 for various incident polarizations.

POLARIZATION OF HETEROPOLAR TUBES

BN forms molecular nanotubes in which the A and B sublattices of the honeycomb lattice are occupied by inequivalent atomic species. Although the isolated BN bond is strongly ionic in character, a planar BN sheet has no macroscopic electric dipole moment because of its perfect threefold symmetry.

This symmetry is removed when the BN sheet is wrapped to form a nanotube. Thus a BN nanotube can exhibit a net electric dipole moment though its parent BN sheet does not, and it is natural to ask how the size and sign of this dipole

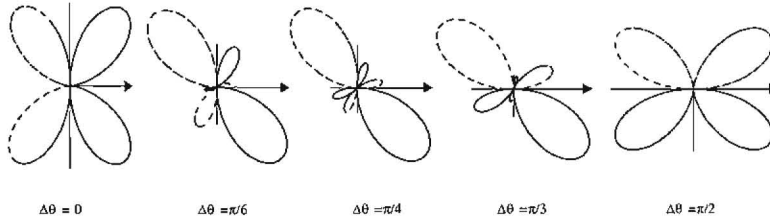


FIGURE 2. Angular distribution of the interference terms in the third order transition rate calculated for a graphene sheet. The polar plots give the anisotropic part of the transition rate as a function of the propagation direction of the injected carrier. The solid(dashed) lines give the positive(negative) contributions to the total transition rate. The angle $\delta\theta$ is the angle between \vec{A}_ω and $\vec{A}_{2\omega}$.

moment is determined by the lattice structure of the wrapped tube. Surprisingly, we find the electric dipole moment of the BN *cannot* be determined by any local geometrical measurement of the lattice structure in the tangent plane of the tube. Instead the electric dipole moment along the tube axis is controlled by the quantum mechanical boundary conditions that quantize the azimuthal component of the crystal momentum of the Bloch states around the tube circumference. Thus the macroscopic electric dipole moment of the BN tube has an intrinsically nonlocal quantum mechanical origin [5].

The situation is analogous to the boundary conditions that distinguish conducting from nonconducting behavior for the graphene nanotube. In this well studied case, the two families of tubes are distinguished by the chiral index $\nu = \text{mod}(m - n, 3)$ where (m, n) are the wrapping indices. Tubes with $\nu = 0$ are conductors, while those with $\nu \neq 0$ are semiconductors.

For the heteropolar tube one finds that the one dimensional polarization p (dipole per unit length) is

$$p = \frac{e}{\pi} \arctan\left(\frac{\Delta}{\hbar v_F \delta}\right) \quad (3)$$

where Δ is a symmetry-breaking site diagonal potential that distinguishes the A and B sublattice and $\delta \propto \nu$ is the gap parameter for the related graphene tube for which $\Delta = 0$. Formally, equation (3) is obtained by integrating the flow of charge induced by adiabatically increasing Δ starting from the reference state $\Delta = 0$ for which dipole moment is zero by symmetry. From equation (3) one sees that the *sign* of the gap parameter controls the sign and size of the macroscopic polarization of the tube for any nonzero value of Δ . This implies that the electric dipole moments of single wall BN tubes should display a nontrivial dependence on the wrapping indices with period three. Equation (3) also predicts nontrivial and quite strong piezoelectric properties that couple the electric dipole moment to mechanical strain through the perturbations of the gap parameter δ .

A direct measurement of this intrinsic electric polarization of a BN tube is difficult since it can be masked by charges accumulated at the tube ends. This physics of the

electric polarization is more directly accessible through the piezoelectric response of the tube in which the net polarization of a BN tube is modified by mechanical strain. Alternatively a photogalvanic effect, the shift current, can be used to probe the ground state polarization.

An introduction to the shift current is given in reference [6] and an application to BN tubes is presented in reference [5]. Generally, excitation of free carriers in a polarized material produces a charge current that is biased in a direction which compensates the ground state electric polarization. Thus a measurement of the optically induced current can be used as a probe of the ionic character of the ground state wavefunctions. For a BN tube one expects a shift current which flows along the tube axis for all $\nu \neq 0$ tubes. The situation turns out to be more interesting for tubes with $\nu = 0$, including armchair tubes with $m = n$, which exhibit a solenoidal shift current which circulated around the tube circumference but does not flow along the axis. In general chiral tubes with $\nu \neq 0$ can have a chiral shift current on the nanotube walls. Three possible scenarios are illustrated in Figure (3) for three different wrapping vectors

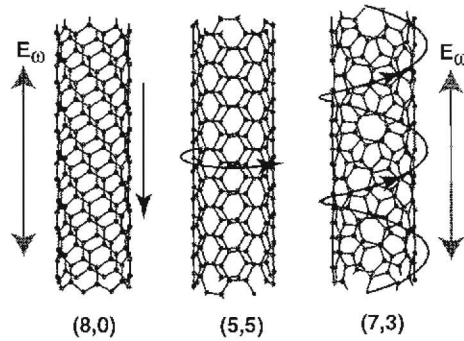


FIGURE 3. caption

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