

Optical dichroism in nanotubes

I. Božović*

OXXEL GmbH, Technologiepark Universitaet, Fahrenheitstrasse 9, Bremen, D-28359, Germany

N. Božović

Department of Mathematics and Computer Science, San Jose State University, San Jose, California 95192

M. Damnjanović

Faculty of Physics, P. O. Box 368, Belgrade 11001, Yugoslavia

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Utilizing the line-group symmetry of single-wall nanotubes, we have assigned their electron-energy bands by symmetry-based quantum numbers. The selection rules for optical absorption are presented in terms of these quantum numbers. Different interband transitions become allowed as the polarization of incident light is varied, and we predict a substantial optical dichroism. We suggest how to observe this effect in experiments on a single nanotube, and how it can be used to control quantum transport in nanotubes to obtain information about the structure.

Carbon nanotubes have attracted considerable interest in their unique physical properties and in potential nanotechnology applications.¹ In particular, their electron-energy band structure has been investigated by several groups.² Some of these theoretical treatments have considered rotational and helical symmetries, but these are only a part of the full symmetry group. For a given nanotube, all its spatial symmetry operations (translations, rotation and screw axes, mirror and glide planes, etc.) form a *line group*, which is the maximal subgroup of the full Euclidean group that leaves the nanotube invariant.³ The role of the line groups in the quantum theory of polymers is analogous to that of the point groups in quantum chemistry or the crystallographic space groups in solid state physics.

Here we wish to demonstrate the usefulness of line-group theoretical methods for the quantum theory of nanotubes, by investigating optical absorption in one particular nanotube. We have chosen a simple example to keep the calculations and the results transparent; the full analysis for all possible nanotube types is completely analogous and will be presented elsewhere. We predict a substantial optical dichroism even in achiral (i.e., zigzag and armchair) nanotubes. (Optical response of chiral nanotubes has already been studied in detail.⁴) The effect is not related to the (self-evident) anisotropy of the Drude response in metallic nanowires, but rather to the specific line-group selection rules for *interband* transitions. This effect could find use in determining the structure of individual nanotubes and perhaps in fabrication of electro-optic nanodevices.

We consider a single-wall, (4,0) zigzag nanotube, with four carbon-atom hexagons (distorted to accommodate the tube curvature) along the tube perimeter (Fig. 1). The translation period is $a=4.26$ Å along the tube axis (z axis in what follows). The full spatial symmetry group of the tube is the line group $L8_4/mcm$. In addition to the primitive translation by $a\vec{e}_z$ which generates the translational subgroup, the generators of this group are $(C_8|\frac{1}{2})$, the screw-axis rotation

by $\alpha=2\pi/8$ around the z axis followed by translation by $(a/2)\vec{e}_z$; $(\sigma_v|0)$, the vertical mirror reflection in the xz plane; and $(\sigma_h|0)$, the horizontal mirror reflection in the xy plane. The corresponding symmetry-based quantum numbers have clear physical meaning: k , the quasimomentum along the z axis (which stems from the translation periodicity of the tube); m , the z component of the quasi-angular-momentum (related to the rotational symmetry); the parity with respect to σ_v , denoted by A for even states and B for odd ones; and the parity with respect to σ_h , denoted by $+$ for even states and $-$ for odd ones.⁵

To derive the band structure of this nanotube, we used, for simplicity, the tight-binding model.² A single orbital $|\phi\rangle$ per each carbon atom is considered, and the overlap of orbitals centered at different atoms is neglected. The relevant matrix element is the transfer integral, $\beta=\langle\phi_i|H|\phi_j\rangle=2.5$ eV, for the orbitals centered on nearest neighbor atoms (some experimental data are better fitted using $\beta=2.8-2.95$ eV; this modification would not affect our conclusions). All further-neighbor interactions are neglected, and we have chosen the energy scale so that $\langle\phi_i|H|\phi_i\rangle=0$ for orbitals centered on the same atom. To assign the bands by the line-group quantum numbers, we can either inspect *a posteriori* the transformation properties of the one-electron eigenfunctions, or, better, use a line-group symmetry-adapted basis.⁶ The latter is comprised of generalized Bloch sums:

$$|k,m\rangle = \frac{1}{\sqrt{8N}} \sum_{s=1}^8 e^{ims\alpha} \sum_t e^{ik(t+s/2)a} \left(C_8^s \left| t + \frac{s}{2} \right| \phi \right), \quad (1)$$

assuming that there are N unit cells, labeled by the summation index t . In such a basis, the calculation is considerably simplified, and it can be done analytically. The resulting bands are given by

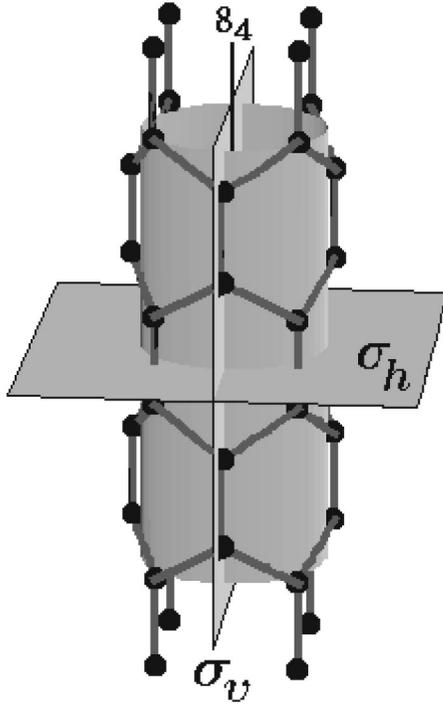


FIG. 1. Model of a (4,0) carbon nanotube, with the essential symmetry elements (8_4 screw axis, σ_v and σ_h mirror planes) indicated.

$$\epsilon(m, k) = \pm \beta \sqrt{1 + 4 \cos^2(m\alpha) + 4 \cos(m\alpha) \cos\left(\frac{ka}{2}\right)}, \quad (2)$$

where $m = 0, \pm 1, \pm 2, \pm 3, 4$, in agreement with Ref. 2. Note that here m is defined mod 8.

In Fig. 2(a), we show the electron bands of the nanotube under study, assigned by the symmetry quantum numbers. Within the present model, the valence and conduction bands are symmetric with respect to $E=0$. The bands denoted as A are nondegenerate, except of course for the spin degeneracy and the trivial “star” degeneracy between the states at k and $-k$, which follows from σ_h (or from the time-reversal) symmetry. The labels 0 and 4 indicate the corresponding value of the quasi-angular-momentum. For these four bands, all the corresponding one-electron states are even with respect to σ_v . At $k=0$, the parity with respect to σ_h is also well defined, and it is indicated by the signs $+$ and $-$, respectively.

The bands labeled as E are twofold degenerate throughout the Brillouin zone (BZ). The number indicates the magnitude of the quasi-angular-momentum. For each k there are two degenerate eigenstates $|k, +m\rangle$ and $|k, -m\rangle$, where $m = 1, 2, 3$. Notice that this is a rare case, peculiar to quasi-one-dimensional solids, where most electrons experience a non-trivial “band” degeneracy. In common three-dimensional crystals, there is very little weight associated with so-called high-symmetry k vectors, since these are outnumbered by general (asymmetric) k vectors.

Notice next that the $A0$ and $A4$ bands connect and cross at the BZ edge, $k = \pi/a$; the same is true for $E1$ and $E3$ bands. These crossings are dictated by the line-group symmetry, i.e., this is an extra *systematic* degeneracy at the BZ

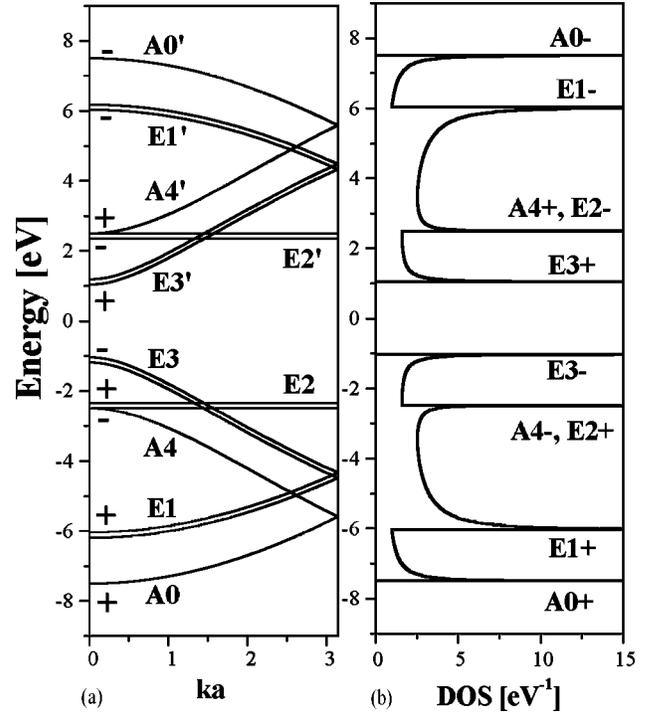


FIG. 2. (a) Band structure of the (4,0) nanotube. The labels A and E denote single and double (twofold degenerate) bands, respectively. The number specifies the value of m , the quasi-angular-momentum. The parity with respect to σ_h (at $k=0$) is denoted by $+$ or $-$. (b) The corresponding DOS.

edges. The degeneracy between $E2$ and $A4$ bands at $k=0$ is *accidental*, i.e., dependent on the model potential.

In Fig. 2(b), we have plotted the corresponding density of states (DOS), defined as $D(\epsilon) = (Na/2\pi) |dk/d\epsilon|$. All the bands are zero sloped at $k=0$, which results in strong van Hove singularities that dominate the DOS. Similar DOS spectra have already been predicted² and observed by scanning tunneling spectroscopy.⁷ The difference here is that each DOS peak is assigned by the quasi-angular-momentum and the mirror-reflection parities of the corresponding one-electron states; this is essential for the analysis of selection rules that follows.

Since the wavelength of visible light is large compared to a , the conservation of linear quasimomentum requires that $\Delta k \approx 0$, i.e., the dipole-allowed optical transitions are essentially vertical.⁸ For the quasi-angular-momentum, the selection rules depend on the orientation of the electrical field. If the incident light is linearly polarized parallel to the tube, transitions are allowed between pairs of bands for which $\Delta m = 0$. Light propagating along the tube may cause transitions between bands with $\Delta m = \pm 1$, namely, $\Delta m = 1$ for the left and $\Delta m = -1$ for the right circular polarization. The parity with respect to σ_v is preserved for polarization along the z axis (\parallel) and reversed for polarization along the y axis (\perp), while the opposite is true for the parity with respect to σ_h . In Table I, we summarize these selection rules and list all the allowed transitions, for different polarizations.

In Fig. 3 we have plotted the joint density of states (JDOS), which may be taken as a crude approximation to the absorption spectrum, for the pairs of bands that satisfy the selection rules. The difference between the spectra for differ-

TABLE I. Selection rules for absorption of light impinging perpendicular to the tube. For light propagating along the tube, the rules differ in detail (see the text), but the allowed transitions are the same as in the right-hand column.

	Polarization	
		⊥
Δm	0	± 1
σ_v parity	conserved	reversed
σ_h parity	reversed	conserved
Allowed transitions	$A0+ \rightarrow A0-$, $E1+ \rightarrow E1-$, $E2+ \rightarrow E2-$, $E3- \rightarrow E3+$, $A4- \rightarrow A4+$	$E3- \rightarrow E2-$ $E2+ \rightarrow E3+$

ent polarizations is striking; notice that this remains true even if one records only the easily accessible, near-infrared to near-ultraviolet portion of the spectrum.

The above predictions can be tested directly by a simple modification of the experiments already performed by several groups. Transport measurements have been made on a single nanotube in both the two-point and four-point contact geometry, as a function of temperature and external magnetic field.^{9,10} It should not be too difficult to repeat such measurements with the added capability of illuminating the sample with light of a controlled polarization. For semiconducting nanotubes like the one considered here, if the photon energy is larger than the interband gap, one would expect significant photoconductivity; the (empty) conduction band is wide, over 6 eV according to the tight-binding calculations. This suggests using the nanotube itself as a photodetector. A tunable light source is not necessary; the wavelength and the intensity of the light can be fixed while the device bias is varied.

As we have shown above, the optical absorption spectrum—and, in particular, the position of the first strong (allowed) interband transition peak—should depend strongly on the polarization of the light. One can adjust the bias so that the energy of excitation is below the gap for one polarization (\perp in our example) and above the corresponding gap for the other one (\parallel); in the present case, a good choice would be $2.5 \text{ eV} < \hbar\omega < 3 \text{ eV}$. In this case, the measured

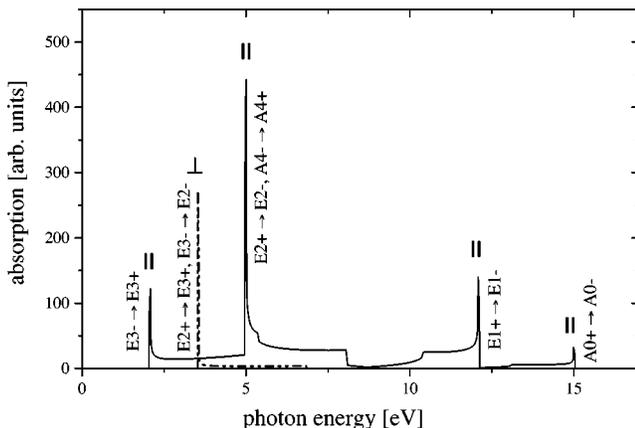


FIG. 3. JDOS for the pairs of bands in Fig. 2(a) that satisfy the line-group selection rules for direct optical absorption, for light polarized parallel or perpendicular to the nanotube axis.

photocurrent should vary dramatically even though nothing is changed other than the polarization of light.

Experimentally, band gaps are smaller, typically 0.7 eV; however, these measurements are made on tubes of much larger radius than the one considered here.^{2,10,11} Furthermore, the present treatment ignores next-nearest and further-neighbor interactions, matrix-element effects, other orbitals, electron-phonon and electron-electron interactions, defects, impurities, etc. On the other hand, it allows qualitative predictions on dichroism, which are based on symmetry considerations, and should remain true also in more complex models.

Indeed, it might be possible to fabricate some miniature, nanotube-based electro-optic devices based on this effect. Nearer at hand, this may provide a simple way to obtain information about the structure of the nanotube under study, which in most cases is not known. The selection rules for direct optical absorption should be easy to check, and since they depend on the type of nanotube (zigzag, armchair, or chiral), this would provide information on the latter. It has been demonstrated experimentally that thin films of aligned nanotubes are birefringent, due to differences in the dielectric functions for light polarized perpendicular and normal to the tubes.¹¹ In that case, the optical response comes from an ensemble of nanotubes, and the proper description may be formulated in terms of an effective medium theory.¹² In contrast, what we are proposing here is an experimental scheme allowing one to measure the optical response and dichroism of a *single* nanotube, an essentially quantum-mechanical phenomenon. It has been predicted that backscattering in nanotubes ought to be suppressed by quantum effects¹³ and indeed it has been demonstrated experimentally that at least some nanotubes behave as long coherent quantum wires.¹⁰ Here we indicate how this important issue could be studied in more detail.

First, by varying the wavelength and polarization of light and/or the device bias, one can select into which band to pump hot electrons. Some unoccupied bands, like the $E2'$ band, are rather narrow, and these electrons will become localized; others, like the $E3'$ band, are broad and should sustain coherent transport—at least for $kT \ll \Delta E/N$, where $\Delta E \approx 5 \text{ eV}$ for the $E3$ band. Generally, hot electrons tend to relax to lower-energy bands (e.g., from the $E2'$ to the $E3$ band), but this requires a change in quasi-angular-momentum, i.e., inelastic electron scattering. By measuring the photoconductivity, one should be able to clearly differentiate between ballistic and diffusive transport. In principle, it seems possible to switch the quantum-wire behavior on and off by rotating the polarization of light with which the nanotube is illuminated. Such experiments could teach us more about the quantum nature of electron dynamics in these mesoscopic systems. The same scheme should work for any other macromolecule to which proper contacts can be attached for transport measurements.

To summarize, we have used the full line-group symmetry of carbon nanotubes to derive the selection rules for optical absorption. Many transitions are found to be forbidden. We predict strong dichroism even in nonchiral nanotubes. Although the present calculations are simple, the predictions

about the dependence of the absorption spectra on the direction and polarization of incident light should be rather robust. The results can be tested by photoconductivity measurements on a single nanotube, which are technically feasible. Such measurements could provide information on the type of nanotube under study and on the quantum nature of electron dynamics. We propose that quantum-wire behav-

ior can be optically switched by rotating the light polarization.

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*Email address: bozovic@oxxel.de

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⁸Some researchers start from a graphene sheet, define the k vector

in this plane, and then cut and roll the sheet, after which the vector may not point along the nanotube axis. If the electron bands are plotted as a function of this variable—which is not the ordinary linear quasimomentum of the electron in the nanotube—some oblique transitions are indeed allowed. An advantage of the present (standard crystallographic) convention is that the quantum numbers retain their customary meaning in solid state physics, and the translational and rotational degrees of freedom are decoupled.

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