OPTICAL DICHROISM IN NANOTUBES

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Utilizing the line-group symmetry of single-wall nanotubes, we have assigned their electron-energy bands by the 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 propose 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 potential nanotechnology applications as well as unique physical properties. In particular, their optical spectra have been explored both theoretically and experimentally. Their electron-energy band structure has also been investigated by several groups. 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. The role of the line groups in the Quantum Theory of Polymers is 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 was already studied in detail.) 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 nano-devices.

We consider a single-wall, (4,0) zig-zag 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 \(\mathbf{D}_{8}^{\text{h}}/\text{mcm}\). Besides the primitive translation by \(a\vec{e}_{z}\), which generates the translational subgroup, the generators of this group are: \((C_{8}|-\frac{\pi}{4})\), the screw-axis rotation by \(\alpha = 2\pi/8\) around the \(z\)-axis followed by the translation by \(\frac{a}{2}\vec{e}_{z}\); \((\sigma_{v})\), the vertical mirror reflection in the \(xz\)-plane, and \((\sigma_{h})\), the horizontal mirror reflection in the \(xy\)-plane. The corresponding symmetry-based quantum numbers have clear physical meaning: \(k\), the quasi-momentum 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 \(\sigma_{v}\), denoted by \(A\) for even states and \(B\) for odd ones, and the parity with respect to \(\sigma_{h}\), denoted by ‘+’ for even states and ‘−’ for odd ones.

To derive the band structure of this nanotube, we used, for simplicity, the tight-binding model. 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 the nearest neighbor atoms (some experimental data are better fitted using \(\beta = 2.8 - 2.95\) eV; this modification

FIG. 1: Model of a (4,0) carbon nanotube, with the essential symmetry elements \((8_{4}\) screw axis, \(\sigma_{v}\) and \(\sigma_{h}\) mirror planes) indicated.
Note that here \( m \) and \( n \) are the 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. The latter is comprised of generalized Bloch sums:

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

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:

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

where \( m = 0, \pm 1, \pm 2, \pm 3, 4 \), in agreement with Refs. [3]. Note that here \( m \) is defined mod(8).

In Fig. 2a, we show the electron bands of the nanotube under study, assigned by the symmetry quantum numbers. Within the present model, the valence and the conduction bands are symmetric with respect to \( E = 0 \). The bands denoted as \( A \) are non-degenerate, except of course for the spin degeneracy and the trivial "star" degeneracy between the states at \( k \) and \(-k\), which follows from \( \sigma_{h} \) (or from the time-reversal) symmetry. The labels 0 or 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 \( \sigma_{v} \). At \( k = 0 \), the parity with respect to \( \sigma_{h} \) is also well-defined, and it is indicated by the signs + and −, respectively.

The bands labeled as \( E \) are two-fold 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-1D solids, where most electrons experience a non-trivial "band" degeneracy. In common 3D 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 edges. The degeneracy between \( E2 \) and \( A4 \) bands at \( k = 0 \) is accidental, i.e., dependent on the model potential.

In Fig. 2b, we have plotted the corresponding density of states (DOS), defined as \( D(c) = \langle Na/2\pi \rangle |dk/dc| \). All the bands are zero-sloped at \( k = 0 \), which results in strong van Hove singularities that dominate DOS. Similar DOS spectra have been already predicted and observed by scanning tunneling spectroscopy. The novelty 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 quasi-momentum requires that \( \Delta k \approx 0 \), i.e., the dipole-allowed optical transitions are essentially vertical. 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, the 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, respectively. The parity with respect to \( \sigma_{v} \) is preserved for polarization along the \( z \)-axis (\( \perpendicular \)) and reversed for polarization along the \( y \)-axis (\( \parallel \)), while the opposite is true for the parity with respect to \( \sigma_{h} \). In Table 1, we summarize these selection rules and list all the allowed transitions, for different polarization.

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 different polarization is striking; notice that this remains true even if one would record only the easily
TABLE I: Selection rules for absorption of light impinging perpendicular to the tube. For the 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 | \( \Delta m \) | \( \sigma_v \) parity | \( \sigma_h \) parity |
|--------------|----------------|---------------------|-------------------|
| \( \parallel \) | 0              | conserved           | reversed           |
| \( \perp \)   | \( \pm 1 \)    | reversal            | conserved         |

Allowed transitions: \( E0^+ \rightarrow E0^- \), \( E1^+ \rightarrow E1^- \), \( E3^- \rightarrow E2^- \), \( E2^+ \rightarrow E2^- \), \( E3^- \rightarrow E3^+ \), \( E2^+ \rightarrow E3^+ \), \( A4^- \rightarrow A4^+ \)

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 the four-point contact geometry, as a function of temperature and on a single nanotube in both the two-point and the four-point contact geometry, as a function of temperature and external magnetic field. Several groups have been able to clearly differentiate between ballistic and diffusive transport. Measuring the photo-conductivity, one should be able to 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. 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. 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. 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 effects and indeed it has been demonstrated experimentally that at least some nanotubes behave as long coherent quantum wires. 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 \( E2^\prime \) band, are rather narrow, and these electrons will get localized; others like the \( E3^\prime \) 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 would tend to relax to lower-energy bands (e.g., from the \( E2^\prime \) to the \( E3 \) band), but these requires a change in quasi-angular momentum, i.e., inelastic electron scattering. Measuring the photo-conductivity, 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 non-chiral 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 photo-conductivity measurements on a single nanotube, which are technically feasible. Such measurements could provide information on the type of the nanotube under study and on the quantum nature of electron dynamics. We propose that quantum-wire behavior can be optically switched by rotating the light polarization.

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