Symmetry restrictions in chirality dependence of physical properties of single wall nanotubes

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Since the discovery of carbon nanotube (CNT) in 1991, there have been extensive investigations on the unusual physical properties of this novel nano-material. The simplest CNT is the single wall carbon nanotube (C-SWNT) consisting of only one rolled up graphite sheet, which was first synthesized in 1995 and now can be produced in large scale. As an analogue to the graphite, the III-V layered compound, namely, boron nitride (BN) sheet has also the hexagonal lattice structure and can be wrapped into various nanotubes too. The single wall BN nanotube (BN-SWNT) was synthesized in 1996, which also attracts much attentions very recently. Unlike the nonpolar C-SWNT which could be metallic or semiconducting with a moderate gap, this heteropolar nanotube is expected to be always a wide gap semiconductor. Both of these two kinds of nanotubes have the similar descriptions of their chiral structures and constitute promising materials for wide applications.

The properties of nanotubes are determined by their chiral structures. Therefore, to investigate the chirality dependence of various physical quantities of nanotubes is an interesting topic all the time. Particularly, to analyze the chiral composition of bulk samples will be helpful to the production of nanotubes with different species. Numerous experimental and theoretical investigations are devoted to this subject. Most recently, it has been reported that detailed chirality distributions in the bulk samples of the separated C-SWNT can be obtained by the fluorescence measurement and by the resonant Raman spectroscopy. Their assignments of the chiral number \((n_1, n_2)\) to the observed spectra are based upon the comparison between the tight-binding (TB) calculations and the experimental data.

In the fluorescence experiment, the authors also gave the empirical formulas of the measured von-Hove singularities with respect to the structures of C-SWNTs, which are expressed in terms of the chiral angle \(\theta\) and chiral index \(\nu\) defined as \(\theta = \text{atan} \sqrt{3n_2/(2n_1 + n_2)}\), and \(\nu = \text{mod}(n_1 - n_2, 3)\). Actually, for the purpose to give the dependence of physical observables on the chiral structure of nanotubes, it is more suitable and efficient to use \(\nu\) and \(\theta\) instead of the chiral numbers \((n_1, n_2)\). Since there are many types of nanotubes not being observed in the experiments or numerical calculations, an appropriate empirical formula is quite useful and convenient to predict the properties of those unobserved ones. Generally speaking, there are two possible methods to obtain these empirical formulas for different physical quantities. One is through fitting the numerical and experimental data, the other is from the analytical expansion around the two Dirac points of the hexagonal Brillouin zone based on various TB models and effective mass approximations. However it has technical difficulties in the second way to get higher order terms which are sometimes important.

In this paper, we show the symmetry restrictions on the general chirality dependence of physical quantities of various types such as scalar, vector and tensor. This leads to compact forms of the chirality dependence for these observables on \(\theta\) and \(\nu\). Since the results are model independent and exact, they not only can be used to propose accurate empirical formulas from the numerical or experimental data, but also can indicate some important features of physical quantities without complicated calculations. This idea was originated in our previous study of the natural optical activity of C-SWNT. Our symmetry analysis is essentially based on the hexagonal structure, and we will consider its application to the properties of both the heteropolar BN-SWNT with large ionicity and nonpolar C-SWNT. We examine the following physical quantities as concrete examples to illustrate our method, such as the excitation gap, electric polarization, dielectric tensor, and piezoelectricity.

Considering a hexagonal lattice with base vectors \(\vec{a}_1\) and \(\vec{a}_2\) (see Fig. 1), it can be rolled up into a nanotube along the chiral vector \(\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2\), so that each
nanotube can be simply represented by a pair of chiral numbers \((n_1, n_2)\) and the chiral angle \(\theta\) is just the angle between \(\vec{R}\) and \(\vec{a}_1\). It then can be established a mapping \(f\) from the space of chiral vectors on the planar sheet to that of the nanotube structure in a fixed way of wrapping. However this mapping is not one-to-one. For a given chiral vector \(\vec{R}_0\) with chiral angle \(\theta\) on the BN sheet with \(C_{3v}\) symmetry, there are another 2 equivalent vectors, obtained by rotating \(\vec{R}_0\) by \(2\pi/3\) successively, corresponding to the same nanotube. These vectors, as shown in Fig. 1, have the explicit forms

\[
\begin{align*}
\vec{R}_0 &= n_1\vec{a}_1 + n_2\vec{a}_2, \\
\vec{R}_2 &= n_1\vec{a}_1 - (n_1 + n_2)\vec{a}_2, \\
\vec{R}_4 &= -(n_1 + n_2)\vec{a}_1 + n_1\vec{a}_2.
\end{align*}
\]

All of them constitute an invariant subspace of the three fold symmetry of BN sheet with the same chiral index \(\nu\). Another three chiral vectors \(\vec{R}_1\), \(\vec{R}_3\) and \(\vec{R}_5\) in Fig. 1 have chiral angle \(\theta + \pi/3\), \(\theta + \pi\) and \(\theta + 5\pi/3\), respectively, and can be written as

\[
\begin{align*}
\vec{R}_1 &= (n_1 + n_2)\vec{a}_1 - n_1\vec{a}_2, \\
\vec{R}_3 &= -n_1\vec{a}_1 - n_2\vec{a}_2, \\
\vec{R}_5 &= n_2\vec{a}_1 + (n_1 + n_2)\vec{a}_2.
\end{align*}
\]

They also form an invariant subspace, but with an opposite chiral index \(-\nu\). The nanotube mapping from \(\vec{R}_1\) is related to that from \(\vec{R}_0\) by rotating the latter tube upside down. In addition, there is another special chiral vector \(\vec{R}_0' = (n_1 + n_2)\vec{a}_1 - n_2\vec{a}_2\), which is the reflection of \(\vec{R}_0\) about the base vector \(\vec{a}_1\) on the BN sheet and has the same chiral index \(\nu\) of \(\vec{R}_0\). When mapping onto a nanotube, it corresponds to the mirror image of that from \(\vec{R}_0\) with respect to the section along the tube axis. For the graphite sheet, since the two atoms in one unit cell are the very same, it has a higher symmetry \(C_{6v}\). The six vectors \(\vec{R}_i (i = 0, \cdots, 5)\) all correspond to the same nanotube which means that a C-SWNT may be represented by opposite chiral indices, \(\nu\) and \(-\nu\).

Briefly, through the mapping \(f\) the manipulations on \(\vec{R}\) in the chiral vector set lead to the change of the structure in the nanotube set, and we have the following three observations

i. when \(\theta \to \theta + 2\pi/3\), the nanotube keeps unchanged, and \(\nu\) is also unchanged.

ii. when \(\theta \to \theta + \pi/3\), the nanotube is rotated upside down, and \(\nu \to -\nu\).

iii. when \(\theta \to -\theta\), the nanotube is reflected with respect to the section along the tube axis, and \(\nu\) is unchanged.

According to the first observation, we know that the physical quantities of nanotube can always be expanded in terms of the triangle function of \(\theta\) with respect to each class of \(\nu\)

\[
Q^{(\nu)}(\theta) = \sum_{n=0}^{\infty} a_n^{(\nu)} \cos(3n\theta) + b_n^{(\nu)} \sin(3n\theta).
\]

\(Q\) is some physical quantity. The coefficients \(a_n^{(\nu)}\)'s and \(b_n^{(\nu)}\)'s are functions of those chirality independent variables, such as the tube radius \(r\) and some external parameters. Our analysis will reveal the characteristic role of the chiral index \(\nu\) in classifying the chirality dependence. In the following we will consider some examples to show that the second and third observations together with features of the physical quantity under consideration will reduce the above chiral expressions Eq. (4). For the convenience of discussion, the Cartesian coordinates for nanotube is introduced as: the tube axis is set as \(z\) direction and the cross section is the \(xy\) plane with \(x\) axis passing through one atom on the tube surface.

1. Excitation Gap \(\Delta\). We can treat the band gap for the C-SWNT and BN-SWNT as a scalar since its value does not change under rotation or mirror reflection of the nanotube. Hence, its \(\theta\)-dependence must satisfy

\[
\begin{align*}
\Delta^{(\nu)}(\theta + \pi/3) &= \Delta^{(-\nu)}(\theta) \\
\Delta^{(\nu)}(-\theta) &= \Delta^{(\nu)}(\theta).
\end{align*}
\]

Notice that in the first expression in Eq. (5), \(\nu\) becomes \(-\nu\) when \(\theta \to \theta + \pi/3\). Then, from Eq. (3) the chirality dependence of \(\Delta\) reads

\[
\begin{align*}
\Delta^{(\pm)}(\theta) &= a_0 \pm a_1 \cos(3\theta) + a_2 \cos(6\theta) + \cdots \\
\Delta^{(0)}(\theta) &= a_0 + a_1 \cos(3\theta) + a_2 \cos(12\theta) + \cdots.
\end{align*}
\]

Clearly, the coefficients of \(\cos(3\theta)\) for \(\nu = \pm 1\) should have the same value but opposite signs.
For the semiconducting C-SWNT with $\nu = \pm 1$, the longitudinal optical excitation can be measured in the fluorescence experiment \cite{17} and is quite useful in analyzing the chiral composition of bulk samples. In Ref. \cite{17}, the authors fitted the experimental data of the von-Hove singularities for $\nu = 1$ and $-1$ separately. According to their fitting function, the absolute values of $a_1$ are quite different for $\nu = 1$ and $\nu = -1$, which does not agree with the symmetry analysis Eq. (5) and suggests that it may need to consider higher order terms like $\cos(6\theta)$ for more accurate fitting functions. In fact we have tried to fit all their data for both $\nu = \pm 1$ by just one four-parameters formula with a $\cos(6\theta)$ term

$$\frac{p_1}{r} + \frac{p_2}{r^2} + \nu \frac{p_3 \cos 3\theta}{r^2} + \frac{p_4 \cos 6\theta}{r^3}$$

with parameters $p_i$’s to be determined, which satisfies the symmetry restriction Eq. (5). It turns out that the result has a smaller root-mean-square deviation than that in Ref. \cite{17}.

Recently, an interesting temperature dependence of bandgap $\Delta(T)$ was reported for the semiconducting C-SWNT in Ref. \cite{18}, that is when $\theta$ is small, the temperature dependence of gap is monotonous for $\nu = 1$ and nonmonotonic for $\nu = -1$. The different behaviors of $\Delta(T)$ for $\nu = \pm 1$ exist even for very close $\theta$. This could be understood by assuming that both $a_0$ and $a_1$ are decreasing functions of temperature. Then from Eq. (6), it is clear that the bandgap for $\nu = 1$ is monotonically decreasing with temperature. For $\nu = -1$ and small $\theta$, the sign of $a_1$ is negative, so that $\Delta$ can be nonmonotonic as temperature varying as a result of the interplay between $a_0(T)$ and $a_1(T)$. However when $\theta$ is close to $\pi/6$, the $\cos(3\theta)$ is nearly vanishing and only $a_0$ takes the dominant role, so that the temperature dependence of bandgap should behave similarly for both $\nu = 1$ and $-1$.

2. Electric Polarization (EP) $\vec{P}$. The macroscopic electric polarization along the nanotube axis is the consequence of the broken sublattice symmetry of BN-SWNT, which was studied as a geometric phase in Ref. \cite{21}. They found the sign and size of the longitudinal polarization are dramatically dependent on the chiral structure of nanotube. This in fact has its symmetry origin, and we will show below that some remarkable properties of EP can be extracted by the symmetry analysis.

Due to the helical symmetry of the nanotube\cite{21},\cite{22}, this EP vector only exists in the tube axis direction (z-axis) and vanishes in the cross section ($xy$ plane), i.e., $P_z \neq 0$ and $P_{x,y} = 0$. According to observations ii and iii and the vector nature of EP, we have

$$P_z^{(\nu)}(\theta + \pi/3) = -P_{z}^{(-\nu)}(\theta)$$

$$P_z^{(\nu)}(-\theta) = P_z^{(\nu)}(\theta),$$

which leads to the chirality dependence of $P_z$

$$P_z^{(\nu)}(\theta) = a_0 + a_1 \cos(3\theta) + a_3 \cos(9\theta) + \cdots$$

Eq. (7) shows evidently that the armchair tubes ($n_1 = n_2 = N$) with $\theta = \pi/6$ and $\nu = 0$ have no electric polarization. Another type of achiral tube, zigzag tubes ($n_1 = N, n_2 = 0$), show different pictures. If we assume reasonably the coefficients of higher order terms are small enough comparing to the zero order term $a_0$, we then obtain $P_z^{(\nu)} \approx 0$ for mod($N, 3$) = 0, and $P_z^{(\nu)} \approx \pm a_0$ for mod($N, 3$) = $\pm 1$, i.e., when $N$ is increasing, the EP is oscillating among 1, 0 and $-1$, which is just the striking result of BN-SWNT found in Ref. \cite{25}.

For the C-SWNT, the six fold $C_{6v}$ symmetry in the chiral vector set guarantees $P_{z}^{(0)}(\theta + \pi/3) = P_{z}^{(-\nu)}(\theta)$, which combined with Eq. (5) leads to $P_{z}^{(\nu)} = 0$, i.e., no EP in C-SWNT.

3. Dielectric tensor $\epsilon$. This second rank tensor is restricted to have the following form by the helical symmetry of nanotube\cite{22}:

$$\epsilon = \begin{pmatrix}
\epsilon_{xx} & \epsilon_{xy} & 0 \\
\epsilon_{xy} & \epsilon_{yy} & 0 \\
0 & 0 & \epsilon_{zz}
\end{pmatrix}$$

with $\epsilon_{xx} = \epsilon_{yy}$ and $\epsilon_{xy} = -\epsilon_{yx}$. The diagonal matrix elements of $\epsilon$, denoted by $\epsilon_{ii}$ with $i = x, y, z$, have the same chirality dependence. Similar to the analysis of EP vector, we obtain

$$\epsilon_{ij}^{(\nu)}(\theta + \pi/3) = -\epsilon_{ij}^{(-\nu)}(\theta)$$

$$\epsilon_{xy}^{(\nu)}(-\theta) = -\epsilon_{xy}^{(\nu)}(\theta)$$

$$\epsilon_{xy}^{(\nu)}(-\theta) = -\epsilon_{xy}^{(-\nu)}(\theta)$$

by noticing that the diagonal term is unchanged when the tube is reversed or reflected, and the off-diagonal term get its sign changed. Then

$$\epsilon_{ii}^{(\nu)}(\theta) = a_0 \pm a_1 \cos(3\theta) + a_2 \cos(6\theta) + \cdots$$

$$\epsilon_{xy}^{(\nu)}(\theta) = b_1 \sin(3\theta) \pm b_2 \sin(6\theta) + \cdots$$

The coefficients $a_i$’s and $b_i$’s in the above four expressions have no direct relationships. Obviously, the diagonal and off-diagonal terms have quite different chirality dependence and the off-diagonal terms vanish for the zigzag tube whose chiral angle is 0.

The discussion above is for the heteropolar BN-SWNT. For the C-SWNT, the higher symmetry requires $\epsilon_{xy}^{(\nu)}(\theta + \pi/3) = \epsilon_{xy}^{(-\nu)}(\theta)$, which together with Eq. (6) leads to $\epsilon_{xy}^{(\nu)} = 0$ for any kind of C-SWNT.

4. Piezoelectricity $e$. Piezoelectricity is the response of the EP of the material to the mechanical strain, which
is a third rank tensor defined by the derivative of EP vector with respect to the elastic strain tensor \( u \) as
\[
e_{ijk} = \partial P_i / \partial u_{jk}.
\]
For the quasi-one-dimensional nanotube, we are concerned with the response of EP along the \( z \) direction to uniaxial(s) and torsional (t) strains,
\[
e_s = \partial P_z / \partial u_s, \quad e_t = \partial P_z / \partial u_t.
\]
\((11)\)

\(u_s\) is the stretch strain along the tube, and \(u_t\) is the torsional strain around the tube circumference. They can be related to the second rank tensor \( u_{ij} \) in the Cartesian coordinates system through equations
\[
 u_s = u_{zz} \quad \text{and} \quad u_t = (xu_{zy} - yu_{xz}) / r^2 \quad \text{with} \quad r^2 = x^2 + y^2.
\]

Then, it is clear that how \(u_s\) and \(u_t\) transform under the rotation of the tube upside down or the mirror reflection with respect to the section along the tube axis. Consequently, we have
\[
e_s^{(\nu)}(\theta + \pi/3) = -e_s^{(-\nu)}(\theta)
\]
\[
e_s^{(\nu)}(-\theta) = e_s^{(\nu)}(\theta)
\]
\[
e_t^{(\nu)}(\theta + \pi/3) = -e_t^{(-\nu)}(\theta)
\]
\[
e_t^{(\nu)}(-\theta) = -e_t^{(-\nu)}(\theta),
\]
\((12)\)

and the chirality dependence of piezoelectricity then reads
\[
e^{(\pm)}_s(\theta) = \pm a_0 + a_1 \cos(3\theta) \pm a_2 \cos(6\theta) + \cdots
\]
\[
e^{(0)}_s(\theta) = a_1 \cos(3\theta) + a_2 \cos(9\theta) + \cdots
\]
\[
e^{(\pm)}_t(\theta) = b_1 \sin(3\theta) \pm b_2 \sin(6\theta) \pm b_3 \sin(9\theta) + \cdots
\]
\[
e^{(0)}_t(\theta) = b_1 \sin(3\theta) \pm b_2 \sin(9\theta) + \cdots.
\]
\((13)\)

Eq. \((13)\) implies the zigzag(\(\theta = 0\)) tube can only have piezoelectric response to the longitudinal stretch and no response to the torsion strain around the circumference. On the contrary, the armchair (\(\theta = \pi/6\) and \(\nu = 0\)) tube has response to torsion strain but not to stretch strain. These conclusions are in consistent with the numerical results of the \textit{ab initio} and TB calculations in Ref.\([24]\), where the chiral angle by definition has a difference \(\pi/2\) from ours. Apart from this difference in the \(\theta\) definition, in Ref.\([24]\) only \(\cos(3\theta)\) and \(\sin(3\theta)\) terms appear in the chirality dependence of \(e_s^{(\nu)}\) and \(e_t^{(\nu)}\), respectively, while there are extra terms according to our results Eq. \((13)\). In fact, their \(\theta\)-dependence of \(e_s\) and \(e_t\) do not agree with their numerical data very well. The reason for this difference is that in Ref.\([24]\) the chirality dependence of \(e_t\) is derived from the BN planar sheet\([28]\), so that only the \(3\theta\) terms are permitted by the \(C_{3v}\) symmetry of BN sheet. However when the sheet is rolled up, this planar \(C_{3v}\) symmetry is broken, therefore those \(C_{3v}\)-forbidden terms are not forbidden any more, although they should be small by the continuous argument from sheet to nanotube, i.e., they vanish when the tube radius tends to infinity.

For the C-SWNT, the symmetry leads to additional restriction
\[
e^{(\nu)}_\alpha(\theta + \pi/3) = e^{(-\nu)}_\alpha(\theta),
\]
which combined with Eq. \((12)\) requires \(e^{(\nu)}_\alpha(\theta) = 0\) for both \(\alpha = s\) and \(t\), namely, for C-SWNT there should be no piezoelectricity due to its nonpolar feature.

In the above discussion, the expansion coefficients \(a^{(\nu)}_n\)’s and \(b^{(\nu)}_n\)’s can not be determined by the symmetry argument which in fact depend on the chirality independent parameters, such as the tube diameter, magnetic flux, temperature, and so on. By tuning the external parameters, one can adjust the magnitude of \(a^{(\nu)}_n\)’s and \(b^{(\nu)}_n\)’s, which will be helpful to identify the chirality of the tubes. As examples, one could refer to Ref.\([22, 23]\) to find the different dependence of these coefficients on magnetic flux or temperature.

As a conclusion, we give the explicit \(\theta\)-dependence of physical quantities for different values of \(\nu\) by a symmetry analysis. It shows clearly that the chiral index \(\nu\) plays a characteristic role in describing the chirality dependence. This model independent method may be used to verify the numerical and experimental data and also can give rise to some important properties qualitatively without complicated calculations. In addition, this method is not restricted to the examples illustrated in this paper and could be extended to other situations.

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