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Implications of time-reversal symmetry for band structure of single-wall carbon nanotubes

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When electron states in carbon nanotubes are characterized by two-dimensional wave vectors with the components K_1 and K_2 along the nanotube circumference and cylindrical axis, respectively, then two such vectors symmetric about a **M**-point in the reciprocal space of graphene are shown to be related by the time-reversal operation. To each carbon nanotube there correspond five relevant **M**-points with the following coordinates: $K_1^{(1)} = \mathcal{N}/2R$, $K_2^{(1)} = 0$; $K_1^{(2)} = \mathcal{M}/2R$, $K_2^{(2)} = -\pi/T$; $K_1^{(3)} = (2\mathcal{N} - \mathcal{M})/2R$, $K_2^{(3)} = \pi/T$; $K_1^{(4)} = (\mathcal{M} + \mathcal{N})/2R$, $K_2^{(4)} = -\pi/T$, and $K_1^{(5)} = (\mathcal{N} - \mathcal{M})/2R$, $K_2^{(5)} = \pi/T$, where $\mathcal{N}$ and $\mathcal{M}$ are the integers relating the chiral, $\mathbf{C}_h$, symmetry, $\mathbf{R}$, and translational, $\mathbf{T}$, vectors of the nanotube by $\mathcal{N}\mathbf{R} = \mathbf{C}_h + \mathcal{M}\,\mathbf{T}$, $T = |\mathbf{T}|$, and R is the nanotube radius. We show that the states at the edges of the one-dimensional Brillouin zone which are symmetric about the **M**-points with $K_2 = \pm\pi/T$ are degenerate due to the time-reversal symmetry.

A single-wall carbon nanotube can be described as a graphene sheet rolled into a cylindrical shape so that the structure is one-dimensional with axial symmetry. Because of the large variety of possible helical geometries known as chirality, carbon nanotubes provide a family of structures with different radii and chiralities. One of the most significant physical properties of carbon nanotubes is their electronic structure which depends only on their geometry while originating from the band structure of graphene.

The electronic states in carbon nanotubes can be characterized by a two-dimensional wave vector $\mathbf{k}$ with a component K_1 along the nanotube circumference and K_2 along the nanotube cylindrical axis. The component K_1 enumerates subbands within the conduction and valence bands and takes discrete values $K_1^{\mu} = \mu/R$. Here R is the nanotube radius and μ is an integer in the range $0 \le \mu \le \mathcal{N} - 1$, where $\mathcal{N} = 2(n^2 + m^2 + mn)/d_R$ is the number of hexagons within the nanotube unit cell, n and m are the nanotube chiral indices, and d_R is the greatest common divisor of $2n + m$ and $2m + n$ [1]. The component K_2 is uniquely defined within the range $-\pi/T \le K_2 \le \pi/T$, where T is the length of the nanotube translational vector [1]. This range determines the one-dimensional Brillouin zone of a carbon nanotube.

The structure of subbands within the conduction or valence band can be quite complicated and varies significantly with nanotube chiralities. However, one may notice that the states at the edges of the one-dimensional Brillouin zone have extra degeneracies, as the energy subbands cross there pairwise. Which particular subbands form these pairs and what is the symmetry behind this degeneracy? In the present paper these questions are studied in a systematic way for nanotubes of arbitrary chiralities. We show that the extra subband degeneracy at the edges of the Brillouin zone is due to the time-reversal symmetry. We show explicitly how to determine the subbands with which a given subband crosses at both edges of the Brillouin zone for nanotubes of arbitrary chiralities.

We will start with a discussion of the effect of the time-reversal operation on the electronic states of a nanotube. As the spin-orbit coupling is known to be negligible for both graphene and carbon nanotubes, we will neglect the spin of the electron. Then, for graphene, the time reversal operation relates the states with the opposite wave vectors, $\mathbf{k}$ and $-\mathbf{k}$. In carbon nanotubes, since we restrict the range of μ to $0 \le \mu \le \mathcal{N} - 1$, we transpose the value of $K_1 = -\mu/R$ to an equivalent value of $K_1 = (\mathcal{N} - \mu)/R$. Thus, the time-reversal operation relates the states with $K_1^{(1)} = \mu/R$, $K_2^{(1)}$ and $K_1^{(2)} = (\mathcal{N} - \mu)/R$, $K_2^{(2)} = -K_2^{(1)}$. These two points in the reciprocal space of graphene are symmetric with respect to the point $K_1^{(0)} = (K_1^{(1)} + K_1^{(2)})/2 = \mathcal{N}/2R$, $K_2^{(0)} = (K_2^{(1)} + K_2^{(2)})/2 = 0$. As $\mathcal{N}$ is even, this means that the K_2-dependences of the electron energies for subbands with $\mu = \mathcal{N}/2 - l$ and $\mu' = \mathcal{N}/2 + l$, where l is an integer modulo $\mathcal{N}/2$, are mirror images of one another. They cross at least at $K_2 = 0$. In case of achiral nanotubes with electron energy satis-

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fying $E(\mu, K_2) = E(\mu, -K_2)$ this leads to the entire degeneracy of the corresponding subbands. The subbands with $\mu = 0$ and $\mu = \mathcal{N}/2$ are always symmetric: $E(\mu, K_2) = E(\mu, -K_2)$ even for chiral nanotubes.

Now let us show that the point with $K_1 = \mathcal{N}/2R$, $K_2 = 0$ corresponds to the $\mathbf{M}$ point in the reciprocal space of graphene. The directions of $\mathbf{K}_1$ and $\mathbf{K}_2$ are determined by the vectors

$$\mathbf{K}_1 = \mathcal{N}^{-1}(-t_2\,\mathbf{b}_1 + t_1\,\mathbf{b}_2) \tag{1}$$

and

$$\mathbf{K}_2 = \mathcal{N}^{-1}(m\,\mathbf{b}_1 - n\,\mathbf{b}_2)\,, \tag{2}$$

where $\mathbf{b}_1$ and $\mathbf{b}_2$ are the reciprocal lattice vectors of graphene, $t_1 = (2m+n)/d_R$, $t_2 = -(2n+m)/d_R$ [1]. The length of $\mathbf{K}_1$ is equal to the quantum of wave vector along $\mathbf{K}_1$: $|\mathbf{K}_1| = R^{-1}$, while the length of $\mathbf{K}_2$ gives the size of the Brillouin zone: $|\mathbf{K}_2| = 2\pi/T$. The vector with the coordinates $K_1 = \mathcal{N}/2R$, $K_2 = 0$ is thus

$$\frac{\mathcal{N}}{2}\mathbf{K}_1 = \frac{2n+m}{2d_R}\,\mathbf{b}_1 + \frac{2m+n}{2d_R}\,\mathbf{b}_2\,. \tag{3}$$

At least one of the numbers $(2n+m)/2d_R$, $(2m+n)/2d_R$ is half-integer while the other is either integer or half-integer. In either case the resulting vector corresponds to a $\mathbf{M}$-point in the reciprocal space of graphene.

In fact, a more general statement is also true. The electron states corresponding to two points in the reciprocal space of graphene symmetric with respect to a $\mathbf{M}$-point are related by the time-reversal operation [2].

The atom site vectors within the nanotube unit cell are determined with the help of the symmetry vector $\mathbf{R} = p\,\mathbf{a}_1 + q\,\mathbf{a}_2$ [1], where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of graphene in real space and p and q are integers which have no common divisor except for unity. When repeated $\mathcal{N}$ times this vector yields [1] $\mathcal{N}\mathbf{R} = \mathbf{C}_h + \mathcal{M}\,\mathbf{T}$, where $\mathbf{C}_h = n\,\mathbf{a}_1 + m\,\mathbf{a}_2$ is the chiral vector, $\mathbf{T} = t_1\,\mathbf{a}_1 + t_2\,\mathbf{a}_2$ is the translational vector, and

$$\mathcal{M} = mp - nq\,. \tag{4}$$

The indices p and q satisfy the following condition [1]

$$t_1 q - t_2 p = 1\,. \tag{5}$$

Let us show that the point with the coordinates $K_1 = \mathcal{M}/2R$, $K_2 = -\pi/T$ in the reciprocal space of graphene corresponds to a $\mathbf{M}$-point. The corresponding vector is given by

$$\frac{\mathcal{M}}{2}\,\mathbf{K}_1 - \frac{1}{2}\,\mathbf{K}_2 = \frac{(nq-mp)\,t_2 - m}{2\,\mathcal{N}}\,\mathbf{b}_1 + \\ + \frac{(mp-nq)\,t_1 + n}{2\,\mathcal{N}}\,\mathbf{b}_2. \tag{6}$$

Using Eq. (5) one can exclude p in the first term of this equation and q in the second one:

$$\frac{\mathcal{M}}{2}\,\mathbf{K}_1 - \frac{1}{2}\,\mathbf{K}_2 = \frac{m\,t_1 - n\,t_2}{2\,\mathcal{N}}\,(-q\,\mathbf{b}_1 + p\,\mathbf{b}_2) = \\ = -\frac{q}{2}\,\mathbf{b}_1 + \frac{p}{2}\,\mathbf{b}_2. \tag{7}$$

As p and q do not have a common divisor except for unity, at least one of them is odd and, thus, the point with the coordinates $K_1 = \mathcal{M}/2R$, $K_2 = -\pi/T$ corresponds to a $\mathbf{M}$-point in the reciprocal space of graphene.

One can distinguish the two cases. When $\mathcal{M}$ is even then the $\mathbf{M}$-point with $K_1 = \mathcal{M}/2R$, $K_2 = -\pi/T$ is at the edge of the one-dimensional Brillouin zone for the subband with $\mu = \mathcal{M}/2$. The states with $K_1^{(1)} = (\mathcal{M}/2-l)/R$, $K_2^{(1)} = -\pi/T$ and $K_1^{(2)} = (\mathcal{M}/2+l)/R$, $K_2^{(2)} = -\pi/T$ are symmetric with respect to the $\mathbf{M}$-point (l is integer). States which are symmetric with respect to a $\mathbf{M}$-point are related to one another by the time-reversal operation and, therefore, have the same energy. Thus, the subbands with $\mu = \mathcal{M}/2 - l$ and $\mu' = \mathcal{M}/2 + l$ cross at $K_2 = -\pi/T$. The subband with $\mu = \mathcal{M}/2$ crosses with the subband with $\mu' = (\mathcal{M}+\mathcal{N})/2$ at $K_2 = -\pi/T$ (see below).

If $\mathcal{M}$ is odd then the $\mathbf{M}$-point with $K_1 = \mathcal{M}/2R$, $K_2 = -\pi/T$ is between the subbands with $\mu_1 = (\mathcal{M}-1)/2$ and $\mu_2 = (\mathcal{M}+1)/2$. This leads to crossing of the subbands with $\mu = (\mathcal{M}-2l-1)/2$ and $\mu' = (\mathcal{M}+2l+1)/2$ at $K_2 = -\pi/T$.

In general, there are three more $\mathbf{M}$-points with similar properties. One occurs at $K_1 = (2\mathcal{N}-\mathcal{M})/2R$, $K_2 = \pi/T$. (This point and the one with $K_1 = \mathcal{M}/2R$, $K_2 = -\pi/T$ are symmetric about the $\mathbf{M}$-point with $K_1 = \mathcal{N}/2R$, $K_2 = 0$). The two other $\mathbf{M}$-points occur at $K_1 = (\mathcal{M}+\mathcal{N})/2R$, $K_2 = -\pi/T$ and $K_1 = (\mathcal{N}-\mathcal{M})/2R$, $K_2 = \pi/T$, respectively.

Consider, for instance, a (4,2) carbon nanotube, i.e. let $n = 4$, $m = 2$. Then $\mathcal{N} = 28$, $\mathcal{M} = 6$. The relevant $\mathbf{M}$-points are at

$$K_1^{(1)} = \frac{\mathcal{N}}{2R} = \frac{14}{R}\,,\;\; K_2^{(1)} = 0\,,$$
$$K_1^{(2)} = \frac{\mathcal{M}}{2R} = \frac{3}{R}\,,\;\; K_2^{(2)} = -\frac{\pi}{T}\,,$$
$$K_1^{(3)} = \frac{2\,\mathcal{N}-\mathcal{M}}{2R} = \frac{25}{R}\,,\;\; K_2^{(3)} = \frac{\pi}{T}\,,$$
$$K_1^{(4)} = \frac{\mathcal{M}+\mathcal{N}}{2R} = \frac{17}{R}\,,\;\; K_2^{(4)} = -\frac{\pi}{T}\,,$$
$$K_1^{(5)} = \frac{\mathcal{N}-\mathcal{M}}{2R} = \frac{11}{R}\,,\;\; K_2^{(5)} = \frac{\pi}{T}\,.$$

These $\mathbf{M}$-points are shown in Fig.1.

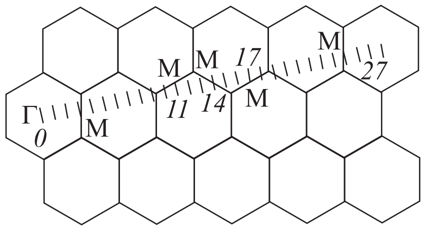

Fig.1. The 29 replicas of the Brillouin zone of a (4,2) carbon nanotube (corresponding to the 28 subbands in the conduction or valence band) superimposed upon the reciprocal lattice of graphene. The 0th and the 28th replicas correspond to the same subband

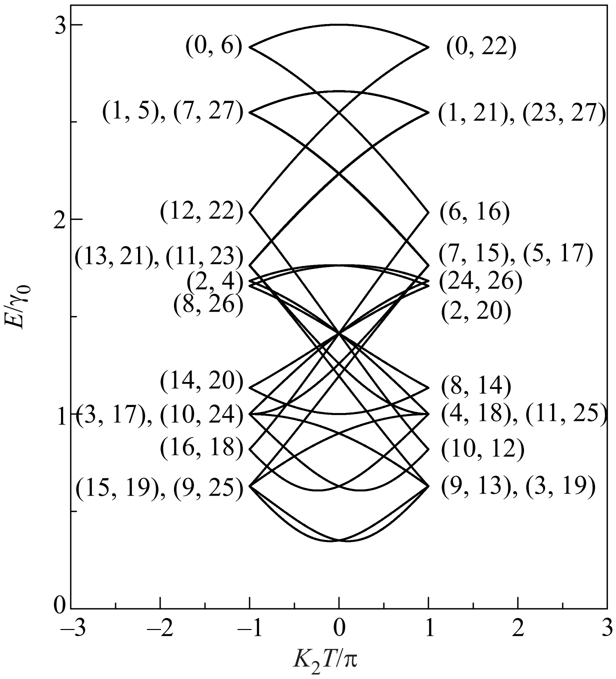

Fig.2. The subband structure of the conduction band of a (4,2) carbon nanotube calculated within the nearest-neighbor tight-binding method. The energy is measured in units of the transfer integral, γ_0. The pairs of numbers near the edges of the Brillouin zone indicate the indices of the subbands which intersect there

Figure 2 shows the structure of the conduction band of a (4,2) carbon nanotube. Each particular subband can be identified as a line "connecting" a given subband index on the left-hand side to the same subband index on the right-hand side. The subband indices are shown in pairs according to the predictions of our theory which implies that the subbands cross pairwise at the edges of the Brillouin zone. One can readily see that our predictions hold. For example, the subbands with $\mu = 14$ and $\mu' = 20$ cross at $K_2 = -\pi/T$ because the points $K_1 = 14/R$, $K_2 = -\pi/T$ and $K_1' = 20/R$, $K_2' = -\pi/T$ are symmetric with respect to the point $(K_1 + K_1')/2 = 17/R$, $(K_2 + K_2')/2 = -\pi/T$ which corresponds to one of our **M**-points. Therefore, there is a pair $(14, 20)$ in the left-hand side of Fig. 2. As $\mathcal{M} = 6$ is even, this **M**-point is itself at the edge of the Brillouin zone and there is another **M**-point at the same edge with $K_1 = 3/R$, $K_2 = -\pi/T$. Electron states at all the **M**-points of graphene are degenerate. Therefore, there is also a pair $(3, 17)$ in the left-hand side of Fig. 2. The subbands with $\mu = 20$ and $\mu' = 8$ are mirror images of one another about the zone center. Indeed, the points with $K_1 = 20/R$, K_2 and $K_1' = 8/R$, $K_2' = -K_2$ are symmetric with respect to the point $(K_1 + K_1')/2 = 14/R$, $(K_2 + K_2')/2 = 0$ which corresponds to another **M**-point.

In a two-dimensional Brillouin zone of graphene there are three inequivalent **M**-points, *i.e.* **M**-points which cannot be connected by a reciprocal lattice vector of graphene. Out of the five **M**-points relevant for a nanotube three are inequivalent. The equivalent **M**-points in our case are those which are symmetric about the **M**-point with $K_2 = 0$.

Our conclusions about subband degeneracy at the edges of the one-dimensional Brillouin zone of a nanotube can be alternatively drawn from a group-theoretical analysis [3]. In the present paper we only used elementary mathematics. We established a connection of this degeneracy with the properties of the high-symmetry points in the reciprocal space of graphene and presented an original pictorial rendition of the degeneracy.

In summary, we have shown that, when electron states in carbon nanotubes are characterized by two-dimensional wave vectors, then two such vectors symmetric about a **M**-point in the reciprocal space of graphene are related by the time-reversal operation. To each carbon nanotube there correspond five relevant **M**-points with the following coordinates:

$$K_1^{(1)} = \frac{\mathcal{N}}{2R}, \ K_2^{(1)} = 0, \tag{8}$$

$$K_1^{(2)} = \frac{\mathcal{M}}{2R}, \ K_2^{(2)} = -\frac{\pi}{T}, \tag{9}$$

$$K_1^{(3)} = \frac{2\mathcal{N} - \mathcal{M}}{2R}, \ K_2^{(3)} = \frac{\pi}{T}, \tag{10}$$

$$K_1^{(4)} = \frac{\mathcal{M} + \mathcal{N}}{2R}, \ K_2^{(4)} = -\frac{\pi}{T}, \tag{11}$$

$$K_1^{(5)} = \frac{\mathcal{N} - \mathcal{M}}{2R}, \ K_2^{(5)} = \frac{\pi}{T}, \tag{12}$$

where $\mathcal{N}$ and $\mathcal{M}$ are the integers relating the chiral, $\mathbf{C}_h$, symmetry, $\mathbf{R}$, and translational, $\mathbf{T}$, vectors of the nanotube by $\mathcal{N}\mathbf{R} = \mathbf{C}_h + \mathcal{M}\mathbf{T}$, $T = |\mathbf{T}|$, and R is the nanotube radius. We have shown that the states at the edges of the one-dimensional Brillouin zone which are symmetric about the **M**-points with $K_2 = \pm\pi/T$ are degenerate due to the time-reversal symmetry. This result remains exact as far as the curvature of the atomic bonds of a nanotube is neglected.

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