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Selection rules for one- and two-photon absorption by excitons in carbon nanotubes

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Recent optical absorption and emission experiments showed that the lower energy optical transitions in carbon nanotubes are excitonic in nature, as predicted by theory. These experiments were based on the symmetry aspects of free electron-hole states and bound excitonic states. The present work shows, however, that group theory does not predict the selection rules needed to explain the two photon experiments. We obtain the symmetries and selection rules for the optical transitions of excitons in single-wall carbon nanotubes within the approach of the group of the wave vector, thus providing important information for the interpretation of theoretical and experimental optical spectra of these materials.

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The use of symmetry is crucial for the description of the optical spectra of atoms, molecules, and solids. In the case of single-wall carbon nanotubes (SWNTs), it has been predicted that excitonic effects are key to understanding their optical transitions.[1–5] Recent works have used the symmetry aspects of different excitonic states in carbon nanotubes to prove the excitonic nature of their optical spectra.[6,7] However, an analytical study of the symmetry of the excitonic states cannot be found in the literature, and a detailed analysis of the selection rules for one and two photon absorption has not yet been reported. Therefore, an analysis of exciton symmetries in SWNTs is needed to understand in greater detail many aspects of their optical properties. In this work, we use group theory to obtain the symmetries of the excitonic states in SWNTs, as well as the selection rules for optical absorption and emission, for one- and two-photon excitation processes. We describe in detail the number and symmetries of exciton states for chiral (n,m), zigzag $(n,0)$, and armchair (n,n) SWNTs. Our group theory analysis shows that the results of the two-photon absorption experiments cannot be explained by symmetry-related selection rules. The results reported here should form a basis for helping the interpretation of theoretical and experimental optical spectra of SWNTs.

The symmetry of excitons is developed here within the formalism of the group of the wave vector, which has been covered partially in the literature[8] and will be more fully developed in a future publication.[9] Briefly, the factor groups for the wave vector k at the center $(k=0)$ and edge of the Brillouin zone $(k=\pi/T)$ are isomorphic to the D_N (D_{2nh}) point group for chiral (achiral) nanotubes, while the factor group for a general wave vector k is isomorphic to the group C_N (C_{2nv}). Here N $(2n)$ denotes the number of hexagons in the unit cell for chiral (achiral) nanotubes and T is the length of the real space unit cell. The irreducible representations of the factor groups of nanotubes are labeled by the quasiangular momentum quantum number $\tilde{\mu}$, which varies between $1-N/2$ and $N/2$. This quantum number $\tilde{\mu}$ is related to the projection of the compound symmetry operation $(\{R|\tau\})$ in the circumferential direction of the nanotube, and can be associated with the concept of cutting lines.[10] Another quantum number, of course, is the wave vector k, related to translation symmetry. There are also parity quantum numbers related to a C_2 rotation (a π rotation perpendicular to the tube axis, bringing z to $-z$), reflections, and inversion operations.[9,11]

A different but equivalent formalism is based on line groups.[11,12] The connection between the two formalisms can be obtained through Table I that, despite its technical aspect, is presented here for a clear definition of the symmetry-related quantum numbers in both group theory formalisms used in the literature.

Figures 1(a)–1(c) show a schematic diagram of the electronic valence and conduction single-particle bands with a given index $|\tilde{\mu}|$, for general chiral, zigzag, and armchair SWNTs, respectively. The electron and hole states at the band edge are labeled according to their irreducible representations.[8,9] The exciton wave function for the one-dimensional (1D) SWNTs can be written as a linear combination of products of conduction (electron) and valence (hole) eigenstates as

$$\psi(\vec{r}_e,\vec{r}_h)=\sum_{v,c}A_{vc}\phi_c(\vec{r}_e)\phi_v^*(\vec{r}_h), \tag{1}$$

where v and c stand for valence- and conduction-band states, respectively. For an *ab initio* determination of the coeffi-

TABLE I. Irreducible representations ($\mathcal{D}$) relevant to the exciton problem for chiral and achiral nanotubes. GWV and LG stand for "group of the wave vector" and "line group" notations, respectively. The dimension (d) of each representation is shown on the right for both GWV and LG formalisms. The last column describes the wave vector (k), quasiangular momentum ($\tilde{\mu}$) and parity quantum numbers (Π). For chiral tubes, the relevant parity is related to the C_2 operation (Π^{C_2}), whereas for achiral tubes the parity Π is also related to σ_h, σ_v reflections and inversion i. The GWV notation chooses the parity under i as a quantum number and the LG notation chooses the parity under σ_h as a quantum number, thus making the translation between the two notations somewhat cumbersome. A zero parity quantum number means that the representation does not have a well defined parity.

	GWV		LG		
Chiral	$\mathcal{D}$	d	$\mathcal{D}$	d	$(k,\tilde{\mu},\Pi^{C_2})$
	$A_1(0)$	1	${}_0A_0^+$	1	$(0,0,+1)$
	$A_2(0)$	1	${}_0A_0^-$	1	$(0,0,-1)$
	$[\mathbb{E}_{\tilde{\mu}}(k)+\mathbb{E}_{-\tilde{\mu}}(-k)]$	1	${}_kE_{\tilde{\mu}}$	2	$(\pm k,\pm\tilde{\mu},0)$
Achiral	$\mathcal{D}$	d	$\mathcal{D}$	d	$(k,\tilde{\mu},\Pi^{\sigma_v},\Pi^{\sigma_h},\Pi^{i},\Pi^{C_2})$
	$A_{1u}(0)$	1	${}_0B_0^-$	1	$(0,0,-1,-1,-1,+1)$
	$A_{2u}(0)$	1	${}_0A_0^-$	1	$(0,0,+1,-1,-1,-1)$
	$A_{1g}(0)$	1	${}_0A_0^+$	1	$(0,0,+1,+1,+1,+1)$
	$A_{2g}(0)$	1	${}_0B_0^+$	1	$(0,0,-1,+1,+1,-1)$
	$E_{\lvert\tilde{\mu}\rvert u}(0)$	2	${}_0E_{\lvert\tilde{\mu}\rvert}^{\Pi^{\sigma_h}}$	2	$(0,\tilde{\mu},0,(-1)^{\tilde{\mu}+1},-1,0)$
	$E_{\lvert\tilde{\mu}\rvert g}(0)$	2	${}_0E_{\lvert\tilde{\mu}\rvert}^{\Pi^{\sigma_h}}$	2	$(0,\tilde{\mu},0,(-1)^{\tilde{\mu}},+1,0)$
	$[B'(k)+B'(-k)]$	1	${}_kE_n^A$	2	$(\pm k,n,+1,0,0,0)$
	$[B''(k)+B''(-k)]$	1	${}_kE_n^B$	2	$(\pm k,n,-1,0,0,0)$
	$[E_{\lvert\tilde{\mu}\rvert}(k)+E_{\lvert\tilde{\mu}\rvert}(-k)]$	2	${}_kG_{\tilde{\mu}}$	4	$(\pm k,\tilde{\mu},0,0,0,0)$

cients A_{vc}, it is necessary to solve a Bethe-Salpeter equation,[2,3,13] which incorporates many-body effects and describes the coupling between electrons and holes. The many-body Hamiltonian is invariant under the symmetry operations of the nanotube and therefore each excitonic eigenstate will belong to an irreducible representation of the space group of the nanotube. In general the electron-hole interaction will mix states with all wave vectors and all bands, but for moderately small-diameter nanotubes ($d_t < 1.5$ nm), the energy separation between singularities in the single-particle 1D JDOS (joint density of states) is fairly large and it is reasonable to consider, as a first approximation, that only the electronic bands contributing to a given 1D singularity will mix to form the excitonic states.[3] This is the ideal situation to employ the usual effective-mass and envelope-function approximations (EMA),[14]

$$\psi^{EMA}(\vec{r}_e,\vec{r}_h) = \sum_{v,c}{}' B_{vc}\phi_c(\vec{r}_e)\phi_v^*(\vec{r}_h)F_\nu(z_e - z_h). \qquad (2)$$

The prime in the summation indicates that only those states associated with the 1D JDOS singularity are included and the coefficients B_{vc} are dictated by symmetry. It is important to emphasize that the approximate wave functions ψ^{EMA} have the same symmetries as the full wave functions ψ. The use of such "hydrogenic" envelope functions serves merely as a physically grounded guess for the ordering in which the different exciton states appear. The envelope function $F_\nu(z_e - z_h)$ provides an *ad hoc* localization of the exciton in the relative coordinate $z_e - z_h$ along the axis and ν labels the levels in the 1D hydrogen series.[15] The envelope functions will be either even ($\nu = 0,2,4,\ldots,$) or odd ($\nu = 1,3,5,\ldots,$) upon $z \to -z$ operations. The irreducible representation of the excitonic state $\mathcal{D}(\psi^{EMA})$ is given by the direct product

$$\mathcal{D}(\psi^{EMA}) = \mathcal{D}(\phi_c) \otimes \mathcal{D}(\phi_v) \otimes \mathcal{D}(F_\nu), \qquad (3)$$

where $\mathcal{D}(\phi_c)$, $\mathcal{D}(\phi_v)$, and $\mathcal{D}(F_\nu)$ are the irreducible representations of the conduction state, valence state, and envelope function, respectively.[14] We now apply Eq. (3) to study the symmetry of excitons in chiral and achiral (zigzag and armchair) carbon nanotubes. Let us first consider the first optical transition (E_{11}) in the most general case, the chiral tubes.

Chiral. As shown in Fig. 1(a), there are two inequivalent electronic bands in chiral tubes, one with the band edge at $k = k_0$ and the other one at $k = -k_0$. In order to evaluate the symmetry of the excitonic states, it is necessary to consider that the Coulomb interaction will mix the two inequivalent states in the conduction band (electrons) with the two inequivalent states in the valence band (holes). These electron and hole states at the vHSs transform as the 1D representations[16] $\mathbb{E}_{\tilde{\mu}}(k_0)$ and $\mathbb{E}_{-\tilde{\mu}}(-k_0)$ of the C_N point group,[9] where we have considered that conduction and valence band extrema occur at the same $k = k_0$. Taking this into consideration, the symmetries of the exciton states with the $\nu = 0$ envelope function, which transform as the $A_1(0)$ representation, can be obtained using the direct product in Eq. (3),

$$[\mathbb{E}_{\tilde{\mu}}(k_0) + \mathbb{E}_{-\tilde{\mu}}(-k_0)] \otimes [\mathbb{E}_{-\tilde{\mu}}(-k_0) + \mathbb{E}_{\tilde{\mu}}(k_0)] \otimes A_1(0)$$
$$= A_1(0) + A_2(0) + \mathbb{E}_{\tilde{\mu}'}(k') + \mathbb{E}_{-\tilde{\mu}'}(-k'), \qquad (4)$$

where k' and $\tilde{\mu}'$ are the exciton linear momenta and quasiangular momenta, respectively. Note that we considered the quantum numbers for hole states to be opposite in sign from those of electron states. Therefore, group theory shows that the lowest energy set of excitons is composed of four exciton bands, shown schematically in Fig. 1(d). Basically, the mixing of two electrons and two holes generates four exciton states. The mixing of electron and hole states with opposite quantum number k ($k_e = \pm k_0$, $k_h = \mp k_0$) will give rise to excitonic states which transform as the A_1 and A_2 representations of the D_N point group. These representations correspond, respectively, to states even and odd under the C_2 rotation. These excitons will have a band minimum at the Γ point. The excitonic states formed from electrons and holes with $k_e = k_h = \pm k_0$ will transform as the $\mathbb{E}_{\tilde{\mu}'}(k')$ and $\mathbb{E}_{-\tilde{\mu}'}(-k')$ 1D irreducible representations of the C_N point group, with an angular quantum number $\tilde{\mu}' = 2\tilde{\mu}$. These exciton states will have a band edge at $k' = 2k_0$ if $2k_0$ is within the first Brillouin zone (1BZ). If $2k_0$ crosses the boundary of the first Brillouin zone or $2\tilde{\mu}$ is larger than $N/2$, the values of k' and $\tilde{\mu}'$ have to be translated back into the first Brillouin zone.[9,17] It should be mentioned that the values of $\tilde{\mu}$ and k_0 will be different for each nanotube and also for each E_{ii} transition.

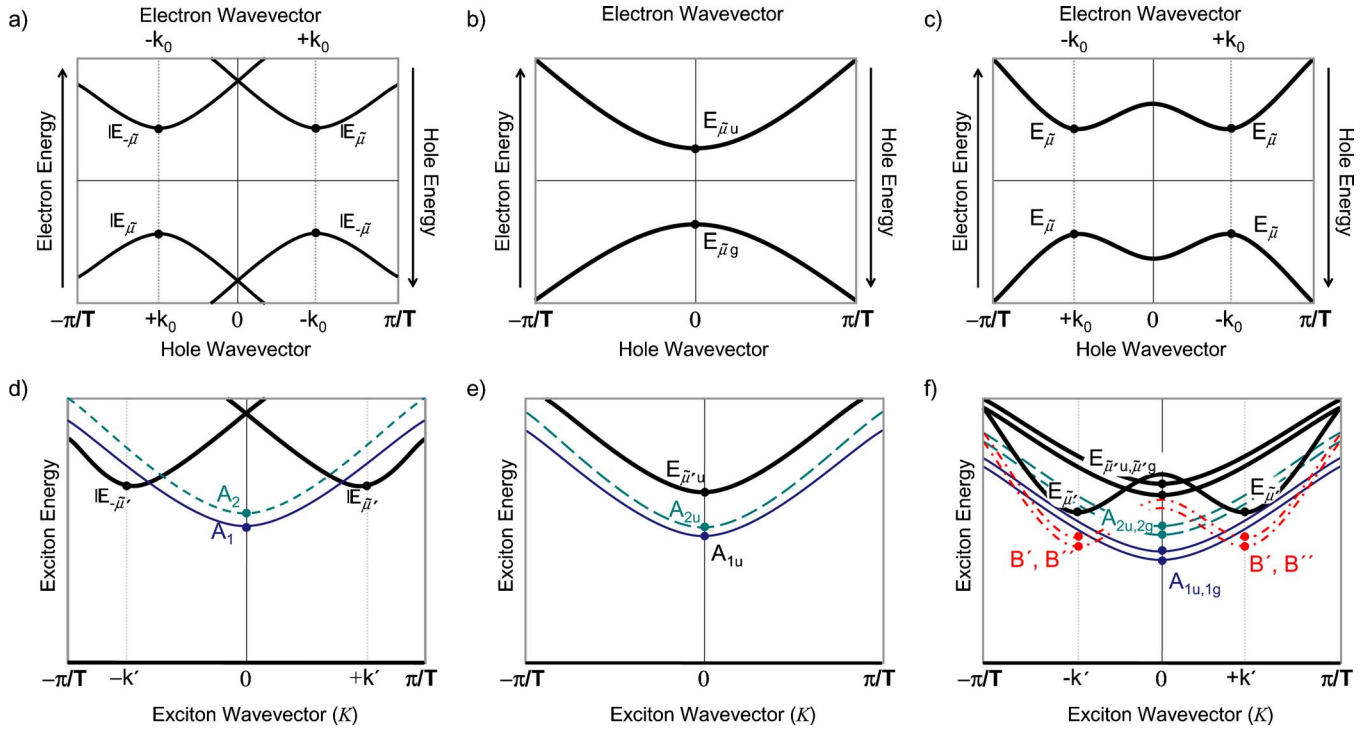

FIG. 1. (Color online) Diagrams for the electronic bands and symmetries for (a) chiral (n,m), (b) zigzag $(n,0)$, and (c) armchair (n,n) nanotubes and for their respective excitonic bands (d), (e), and (f). The electron hole and exciton states at the band edges are indicated by a solid circle and labeled according to their irreducible representation. Different line types and colors in this figure are related to bands with different symmetries. Thick (black) solid lines correspond to the $E_{\tilde{\mu}'}$ representation, the blue (thin) solid lines correspond to A_1 excitons while the cyan (thin) dashed lines correspond to the A_2 excitonic states. In the case of achiral nanotubes, we also have inversion and mirror plane symmetries. For a better visualization, the bands with different parities under the inversion and mirror planes were grouped together and appear with the same line color and pattern. In the case of armchair nanotubes, the bands that transform as the B' and B'' representations are shown using a red dot-dash pattern. The electronic and excitonic band structures shown here are only pictorial. Group theory does not order the values for the eigenenergies and energy dispersions.

Let us now consider higher-energy exciton states $\nu>0$ for the same vHSs in JDOS (the so-called E_{11}) in chiral tubes. For ν even, the resulting decomposition is the same as for $\nu=0$, since the envelope function also has A_1 symmetry. For odd values of ν, the envelope function will transform as A_2, but that will also leave the decomposition in Eq. (4) unchanged. The result is still the same if one now considers higher-energy exciton states derived from higher singularities in the JDOS (E_{22} or E_{33} transitions). Therefore, *Eq. (4) describes the symmetries of all exciton states in chiral nanotubes associated with E_{ii} transitions*.

To obtain the selection rules for the optical absorption of the excitonic states, it is necessary to consider that the ground state of the nanotube transforms as a totally symmetric representation (A_1) and that only $K=0$ excitons can be created due to linear momentum conservation. For light polarized parallel to the nanotube axis, the interaction between the electric field and the electric dipole moment in the nanotube transforms as the A_2 representation for chiral nanotubes.[9] Therefore, from the four excitons obtained for each envelope function ν, only the A_2 symmetry excitons are optically active for parallel polarized light, the remaining three being dark states. It is clear that the experimental Kataura plot[18,19] can be interpreted as the plot of the energy of the bright exciton state with $\nu=0$ as a function of tube diameter. For two-photon excitation experiments, the excitons with A_1 symmetry are accessed $(A_2\otimes A_2=A_1)$, and thus, *there will also be one bright exciton for each ν envelope function*. This result indicates that group theory does not predict the selection rules used in Ref. 6. Thus, the explanation of the results obtained in two-photon excitation experiments does not rely on symmetry selection rules and should be related to oscillator strength arguments.[7] For instance, the bright exciton associated to odd ν states in chiral tubes can be understood as a product between an even Bloch function and an odd envelope function.[7] Therefore, although being formally bright, we expect a very low oscillation strength for these excitons, since an odd envelope function should give a very low probability of finding an electron and a hole at the same position available for recombination.

Zigzag. For zigzag nanotubes, the vHSs for the electronic bands associated with all E_{ii} transitions occur at $k_0=0$, and thus, the symmetry of the electron (hole) states will form the direct product for ν even,

$$E_{\tilde{\mu}g}(0)\otimes E_{\tilde{\mu}u}(0)\otimes A_{1g}(0)=A_{1u}(0)+A_{2u}(0)+E_{\tilde{\mu}'u}(0), \quad (5)$$

and for ν odd,

$$E_{\tilde{\mu}g}(0)\otimes E_{\tilde{\mu}u}(0)\otimes A_{2u}(0)=A_{2g}(0)+A_{1g}(0)+E_{\tilde{\mu}'g}(0). \quad (6)$$

The corresponding band structure for $\nu=0$ (lowest exciton states) is shown in Fig. 1(e). It is interesting to note that, in

this case, all four excitonic states will have the band edge at the Γ point ($K=0$). The value of $\tilde{\mu}'$ can be obtained in the same way as in the case of chiral nanotubes.

For achiral nanotubes, the electromagnetic interaction with the nanotube transforms as the A_{2u} representation, and thus, one can see from Eq. (5) and Eq. (6) that for zigzag nanotubes only states with ν even (envelope functions even under $z \rightarrow -z$) will have a bright exciton. Therefore, group theory predicts that zigzag tubes have a smaller number of allowed optical transitions than chiral tubes, which is consistent with their higher symmetry. For two-photon excitation and emission in achiral tubes, we have $A_{2u} \otimes A_{2u} = A_{1g}$, and therefore only the A_{1g} excitons will be optically active. For zigzag tubes [see Eq. (6)], only the states with odd envelope functions will be accessible by two-photon transitions, in agreement with Ref. 6 in this special case.

Armchair. The optical transitions in armchair tubes are also excitonic, despite the metallic character of these tubes, because of symmetry gap effects.[3] As shown in Fig. 1(c), the E_{ii}-derived excitons will be formed by two $E_{\tilde{\mu}}$ bands at $k = \pm k_0$, where $k_0 \approx 2\pi/3a$ for the lowest-energy excitons. Therefore, these excitonic states will be given by the direct product

$$\begin{aligned}
&[E_{\tilde{\mu}}(k_0) + E_{\tilde{\mu}}(-k_0)] \otimes [E_{\tilde{\mu}}(k_0) + E_{\tilde{\mu}}(-k_0)] \otimes A_{1g,2u} \\
&\quad = A_{1u}(0) + A_{2u}(0) + A_{1g}(0) + A_{2u}(0) \\
&\qquad + [B'(k') + B'(-k')] + [B''(k') + B''(-k')] \\
&\qquad + E_{\tilde{\mu}'g}(0) + E_{\tilde{\mu}'u}(0) + [E_{n-\tilde{\mu}'}(k') + E_{n-\tilde{\mu}'}(-k')]. \qquad (7)
\end{aligned}$$

The same decomposition is found for A_{1g} and A_{2u} envelope functions. Therefore, each JDOS vHS for armchair SWNTs gives rise to 16 exciton states, as shown in Fig. 1(f) for $\nu = 0$. If $k_0 = 2\pi/3a$, then $k' = k_0$ (the exciton momentum has to be translated back to the first Brillouin zone). The excitons at $K=0$ transform as the representations of the D_{2nh} group, while the excitons at $K = \pm k'$ transform as the irreducible representations of the C_{2nv} point group.

As in the case of zigzag nanotubes, only the A_{2u} (A_{1g}) symmetry exciton will be optically active for one-photon (two-photon excitation). Therefore, from the 16 exciton states obtained for each envelope function ν there will be one bright exciton. Note that, in the case of armchair nanotubes, there will also be bright excitons with odd ν envelope functions. However, we note that because of the weak electron-hole interaction due to metallic screening, the existence of higher ν states is unlikely in armchair tubes.

To summarize, we obtained the symmetry of excitonic states in chiral, zigzag, and armchair SWNTs within the approach of the group of the wave vector k. Each set of electronic transitions E_{ii} gives rise to a series of exciton states, each associated with an envelope function. We show the absence of selection rules for even and odd envelope functions for most of the carbon nanotubes (i.e., chiral and armchair). *This result shows that group theory does not predict the one- and two-photon selection rules used in the interpretation of recent experiments*.[6] When symmetry selection rules do not come into play, the existence or apparent absence of optical transitions should be interpreted in terms of their high or low oscillator strength.[7] It is important also to stress that zigzag nanotubes are a very special class of tubes, with very specific symmetry aspects. Generalizing results from zigzag carbon nanotubes to other symmetry tubes is not always appropriate.

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