Influence of External Electric Fields on Electronic Response and Bandstructure of Carbon Nanotubes

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***Abstract*— We performed tight-binding calculation of the electronic properties of carbon nanotubes in a perpendicular electric field. Within the linear response limit, the dielectric function of a doped carbon nanotube is found to depend not only on its symmetry, but also on the Fermi level position and tube radius. Upon increasing the field, the mixing of neighboring subbands results in metal-semiconductor transitions in both quasi–metallic and semiconducting nanotubes. The characteristic field strength of the transitions is calculated as a function of the tube radius. An optimal radius range to be used for band gap engineering is estimated for both types.**

I. Introduction

In most of carbon nanotube-based electronic devices, carbon nanotubes (CNTs) are subject to an environment of external electric fields [1]. Since the device performance is largely determined by electronic response of CNTs, we study how the external fields modify the response of a CNT in vacuum. Semi-classical one-dimensional models, which assume a uniform charge and potential distribution along the CNT circumference and a rigid band model, have been widely used to describe the potential profiles along the CNT axis in both transport devices [2] and nano–electromechanical systems [3]. When the component of the electric field perpendicular to the nanotube is not negligible, a non-uniform charge distribution is built up along the CNT circumference. Moreover, when field strength is large enough to mix different subbands, new features of the bandstructure arise, leading to significant changes in the electron conducting properties [4]. In this article, we report on the dielectric response of CNTs to a perpendicular electric field and the modulation of the bandstructure and conducting properties of CNTs due to the axial symmetry breaking. We use a single π orbital tight binding (TB) method in a self-consistent way to account for the screening effect by the nonuniform charge distribution along the CNT circumference.

We obtain the following results: (i) the perpendicular component of the dielectric function tensor, $\epsilon_\perp$, of a single CNT is slightly different for metallic and semiconducting nanotubes and is ~ 5 in the static limit ($\omega = 0$). (ii) A closed expression for $\epsilon_\perp$ is derived in a $\vec{k} \cdot \vec{p}$ approximation, which sheds light on the dependence of the dielectric function on the Fermi energy (charge injection/doping level) and the temperature. The role of these two factors is to allow extra interband transitions between neighboring conduction/valence subbands and effectively increase the dielectric constant. (iii) We demonstrate the bandstructure modulation due to the perpendicular field. In particular we show the band gap closing/opening for semiconducting/quasi–metallic CNTs respectively, as a function of the applied field. Energy band bending and lifting of subbands degeneracy are also observed. (iv) A transformation of the bandstructure of a metallic CNT into multi-valley bands with large enhancement of the density of states (DOS) near the Fermi level E_F can be used to modulate the conducting properties of CNTs. We speculate on a possibility of application of these effects in CNT devices.

The paper is organized as follows. In Sec.II, we calculate the dielectric response of CNTs under a perpendicular electric field. Within the limit of relatively weak fields, the potential variation along the circumference is much smaller than the typical energy difference of neighboring subbands, $V_{CNT} = e\mathcal{E}R \ll \Delta E_m \sim v_F/R$, and the bandstructure is only slightly perturbed. Here m is the quantum number to indicate the angular momentum of the wave function; $v_F = 3a_{c-c}|t|/2$ is the Fermi velocity, and parameters $t = -2.5$ eV and $a_{c-c} = 1.44$ Å are the hopping integral and C–C bond length respectively. Using a linear response approximation, we study the dependence of the dielectric constant on the CNT symmetry, radius, Fermi level position and the temperature. We then examine the CNT bandstructure in Sec.III. When the fields are relatively strong but not too strong to distort the π orbitals, i.e. $V_{CNT} \geq \Delta E_m$ and $e\mathcal{E}a_{c-c} < |t|$, the energy subbands of the nanotube are mixed considerably. We calculate the characteristic field strength for the band gap opening and closing to occur in quasi–metalic and semiconducting zigzag nanotubes, and estimate the optimal radius range of CNTs to be used for band gap engineering.

II. Dielectric Response

The external electric field $\mathcal{E}_{ext}$ induces a dipole moment p on the CNT surface, which is related to the resulting total field $\mathcal{E}_{tot}$ inside the nanotube by the unscreened polarizability α_0 with $p = \alpha_0\mathcal{E}_{tot}$. The dielectric constant $\epsilon_\perp$ and the actual polarizability α can be retrieved from $\alpha_0(\omega)$ by including the screening effect from the induced dipoles:

$$\epsilon_\perp(\omega) = \mathcal{E}_{ext}/\mathcal{E}_{tot} = 1 + 2\frac{\alpha_0(\omega)}{R^2}, \tag{1}$$

$$\alpha(\omega) = \frac{\alpha_0(\omega)}{\epsilon_\perp(\omega)}. \tag{2}$$

We obtained a universal expression for α_0 in the static limit within a TB calculation [4]. It is quadratically proportional to the tube radius and is dependent of the symmetry of the tube:

$$\alpha_0 = CR^2, \quad C \approx \begin{cases} 1.96, & \text{metallic} \\ 2.15, & \text{semiconducting,} \end{cases} \tag{3}$$

and the corresponding dielectric function $\epsilon_\perp$ is

$$\epsilon_\perp \approx \begin{cases} 4.92, & \text{metallic} \\ 5.30, & \text{semiconducting,} \end{cases} \tag{4}$$

where the numerical values are consistent with previous publications [5], [6].

An analytical expression for the polarizability follows from a $\vec{k}\cdot\vec{p}$ scheme [7]. This approximation assumes a linerization of the electron energy dispersion in the vicinity of the Fermi points K and K' of the two-dimensional graphite and gives a universal description for CNTs of arbitrary chirality (details can be found in [4]). The ratio $\alpha_0/R^2 \approx 1.41$ and 1.58 are obtained respectively for metallic and semiconducting nanotubes, which agrees qualitatively with (3) and can be improved by including contributions from higher subbands. The universal expressions of $\epsilon_\perp$ (equally for metallic and semiconducting tubes) justify the validity of extending (3) and (4) to chiral tubes.

For a macroscopic system, the dielectric function is a property of the material and we would not expect a dependence on the system size. Similarly, a radius-independent dielectric function is derived in (4) for neutral CNTs with half-filled energy bands [4]–[6]. However, at non-zero charge level the dielectric function becomes dependent on the product of the specific charge density and the CNT radius. We notice that some nanotubes are naturally doped during the growth process, in which case the Fermi level E_F would shift from the charge neutrality level and similarly under conditions of charge injection or application of an external bias to the nanotube. The occupation of the energy subbands thus varies, which is expected to change the dielectric response of CNTs. Below, we estimate the correction for metallic tubes at low Fermi energies using both TB calculation and the $\vec{k}\cdot\vec{p}$ method [4].

Let us assume $E_F > 0$ and define the dielectric constant for a metallic tube as

$$\begin{aligned} \epsilon_\perp^{met}(E_F, R) &= \epsilon_\perp^{met}(0) + \Delta\epsilon_\perp^{met,1}(E_F, R) \\ &\quad + \Delta\epsilon_\perp^{met,2}(E_F, R) + \cdots, \end{aligned} \tag{5}$$

where $\epsilon_\perp^{met}(0)$ is given by (4) and $\Delta\epsilon_\perp^{met,i}(E_F, R)$ accounts for the contribution due to the occupation of ith conduction subband. $\epsilon_\perp(E_F)$ of a $[10, 10]$ nanotube calculated from the TB method is shown in Fig. 1. The dielectric constant first increases quadratically at low Fermi energies, then the increasing rate slows down when the Fermi level enters higher subbands. The analytical $\vec{k}\cdot\vec{p}$ result is also plotted for comparison, which agrees very well with the numerical results.

If one considers the low energy properties of nanotubes, the $\vec{k}\cdot\vec{p}$ method provides a reasonable approximation. When the Fermi level lies within the first subband, the dielectric constant for a metallic tube of radius R can be expressed as

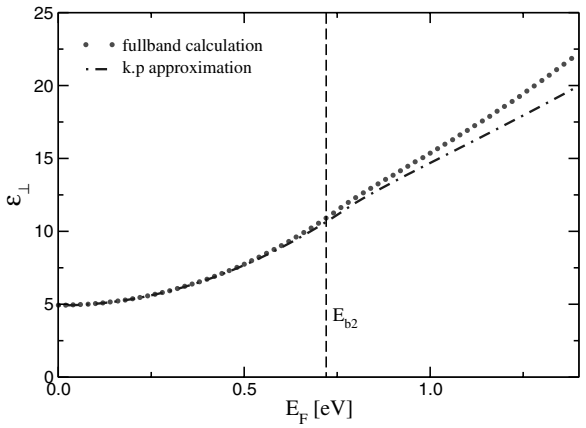

Figure 1. Fermi energy dependence of $\epsilon_\perp$ for a [10,10] nanotube. The vertical dashing line indicates the bottom of second subband E_{b2}.

$$\epsilon_\perp^{met}(E_F, R) \approx \epsilon_\perp^{met}(0) + 2\frac{4e^2}{\pi v_F}\left(\frac{E_F R}{v_F}\right)^2, \tag{6}$$

where the prefactor $4e^2/\pi v_F$ is the dimensionless density of states of the first subband.

Most CNT-based electronic devices are working at a finite temperature, which is expected to modify the occupation probability of the electronic states as well as the dielectric constant. Our calculation shows that the temperature contribution adds to the dielectric function in (6) as

$$\Delta\epsilon_\perp^{met}(T, R) \approx \frac{2\pi^2}{3}\frac{4e^2}{\pi v_F}\left(\frac{k_B T R}{v_F}\right)^2, \tag{7}$$

where k_B is the Boltzmann constant. At room temperature, the temperature correction to $\epsilon_\perp^{met}(0)$ is less than 10% for tubes with a moderate radius ($R < 32$Å).

Similar effects were calculated for semiconducting nanotubes except that the Fermi level needs to be brought close enough to the conduction band bottom or valence band top to observe any substantial change of the dielectric response.

So far we have discussed the dielectric behavior of CNTs within the linear response theory and the external field was weak that only the first order perturbation terms were considered. At strong fields, the screening capability of CNTs is effectively enhanced [8], which is consistent with previous investigation, in which the CNTs were found to screen out large parallel electric fields just as perfect metals [9]. Moreover, in the strong field limit, the bandstructure of CNTs is severely distorted, leading to interesting features in the electronic properties, as we will discuss in the next section.

III. Bandstructure Modification

When the applied field strength $e\mathcal{E}R \geq v_F/R$, the rigid band approximation breaks down and considerable modification of the CNT bandstructure is expected. Below we present the results for both metallic and semiconducting CNTs by

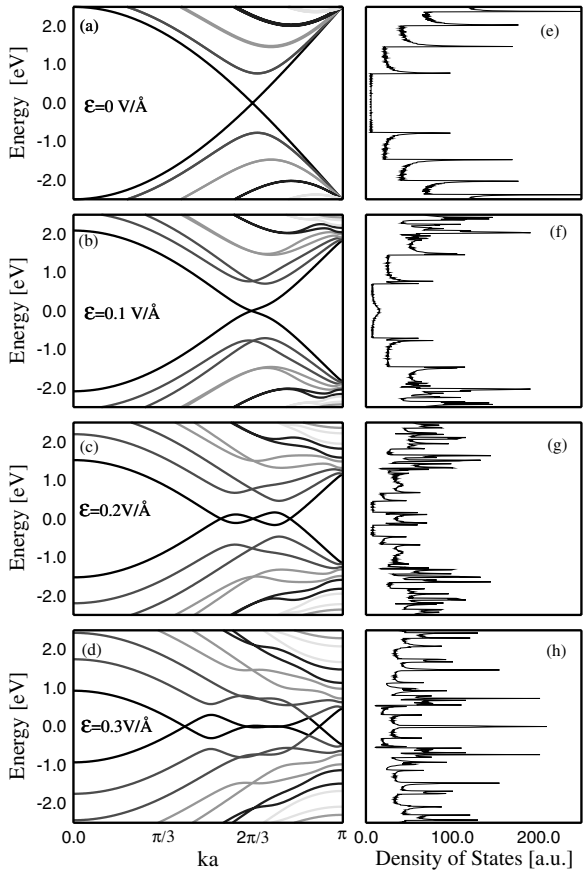

Figure 2. Bandstructure (a,b,c,d) and DOS (e,f,g,h) of a [10,10] armchair tube at various perpendicular electric fields: $\mathcal{E} = 0, 0.1, 0, 2, 0.3$V/Å. Higher bands ($E > 2.5$eV) are not displayed

using a full-band TB calculation and $\mathcal{E}$ is referred to the total electric field. Fig. 2 shows the energy bands of a $[10, 10]$ armchair nanotube in electric fields of different strength ranging from 0 to 0.3V/Å. We emphasize that the two lowest subbands always cross, even at very large fields, although the bandstructure has already been noticeably modified. At $\mathcal{E} = 0.1$V/Å (see Fig. 2 (b)), the Fermi points shift toward the Γ point ($k = 0$) and the two lowest subbands are flattened near the Fermi points. At the same time, all states that were degenerate with respect to the angular momentum, $\pm m$, split. The splitting becomes more obvious closer to the lowest subbands. The large degeneracy at the first Brillouin zone (FBZ) boundary $k = \pi/a$ is also lifted, and bending is observed for all subbands at this point.

As the field strength increases, the two lowest subbands show oscillatory bends with multiple nodes generated, while the first node moves even closer to $k = 0$ (Fig. 2 (c, d)). For other subbands, the splitting of $\pm m$ subbands become more significant.

This bandstructure modification is clearly seen in the density of states of the nanotube, as shown in Fig. 2 (d–h). A bump appears in the low energy plateau upon application of the field and increases with the field strength. The enhanced DOS near

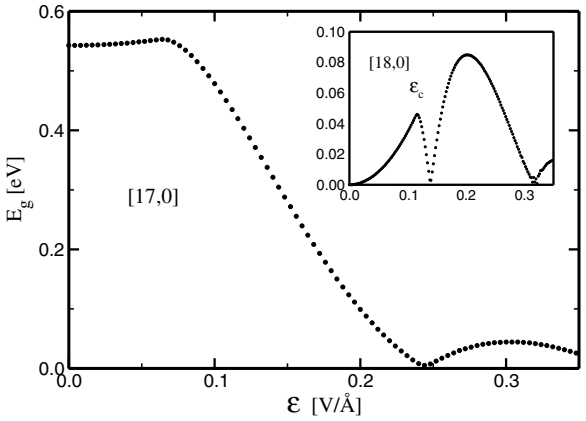

Figure 3. Band gap variation of a [17,0] zigzag nanotube with increasing field strength. Inset: same plot for a [18,0] nanotube.

$E = 0$ is due to the flattening and bending of the two lowest subbands. On the other hand, the lifting of $\pm m$ degeneracy of all doublets and the bending at the FBZ boundary shift and split the single VHS peaks into multiple ones.

For quasi–metallic zigzag tubes, the physics is quite different. At weak fields, a band gap opens at the Fermi point $k = 0$, as shown in the inset of Fig. 3 for a [18,0] nanotube. The gap increases quadratically with the field strength until reaching a critical field $\mathcal{E}_c$. The value of the critical field depends on the radius and is fitted to be

$$e\mathcal{E}_c R \sim v_F/R, \tag{8}$$

when the total potential drop becomes comparable with the energy distance between neighboring subbands. As the field increases beyond $\mathcal{E}_c$, the energy band minimum shifts away from the original Fermi point $k = 0$ and the gap starts to decrease and oscillates further on.

It may be interesting for electronics applications to be able to modulate locally the gap of the nanotube. Our study shows that for quasi–metallic zigzag CNT one can, indeed, open the gap. However the gap cannot exceed some critical value beyond which a further increase of the field begins to close the gap. The band gap opening at $\mathcal{E}_c$ is obtained within a degenerate perturbation theory:

$$E_g \sim \frac{(e\mathcal{E}_c R)^2}{6|t|} \sim \frac{v_F^2}{6|t|R^2}, \tag{9}$$

which is almost negligible for nanotubes with $R > 8$ Å at room temperature. On the other hand, we notice that for very narrow CNTs, the $\sigma - \pi$ mixing may result in the opening of secondary gaps, which may prohibit using very narrow CNTs for band modulations.

Semiconductor zigzag nanotubes, on the other hand, exhibit a drastic change at the presence of a perpendicular electric field. Fig. 3 shows the band gap variation of a [17,0] nanotube with increasing field strength. The band gap first remains almost constant at weak fields. When the perturbation is comparable to the original band gap, i.e. $e\mathcal{E}_c R \sim E_g \approx$

0.53 eV, the energy band minimum shifts away from the original Fermi point $k = 0$ and the gap drops sharply and closes at large fields. Again, the critical field strength $\mathcal{E}_c$ is inversely proportional to R^2, as in the case of quasi–metallic nanotube. Since the band gap of a semiconducting nanotube scales as R^{-1}, by using CNTs of a large radius ($R \sim 20-40$Å), it is possible to render a significant band gap depression ($E_g \sim 0.1-0.2$ eV) without resorting to extremely strong fields.

We stress that many experimental techniques, ranging from Raman scattering to scanning tunneling spectroscopy (STS) use high electric fields to probe the electronic properties of a nanotube, which may perturb the electronic structure. Our theoretical results may help to understand the disagreements between experimental measurements and predictions for band gap, local of density states (LDOS), effective masses and the locations of VHS peaks. On the other hand, the novel behaviors of CNTs under large fields provide an effective way to electronically tune the CNT properties and modulate the device performance.

IV. Conclusion

We investigate the electronic properties of CNTs under external electric fields, which is important both for understanding the physics of CNT–based electronic devices and predicting their behaviors. We have modeled the following material properties of CNTs: dielectric function, band gap and DOS in the vicinity of the Fermi level. Several factors that influence the dielectric response of CNTs are discussed. It is found that the dielectric constant of a doped CNT $\epsilon_\perp$ grows quadratically with the product of E_F and R at low Fermi energy, leading to an enhancement of screening with the doping level. With an increase of the applied field, the bandstructure of CNTs is considerably modified due to the lowering of symmetry. Armchair tubes always remain metallic while band gap opening and closing are induced in quasi-metallic and semiconducting zigzag nanotubes respectively. The critical field strength for the metal-semiconductor transition is calculated, which is within feasible field range ($\mathcal{E} \sim 0.1$ V/Å ~ 10 MV/cm) with a proper choice of the nanotube radius. A small radius ($R < 8$ Å) is preferred for quasi-metallic CNTs, due to the R^{-2} dependence of the critical band gap opening. For semiconducting CNTs, a large radius ($R \sim 20 - 40$ Å) is more favorable, for which a smaller field strength is needed to close the band gap. This property, together with the variation of low energy DOS at strong fields can be used for band gap engineering and for modulating the CNTs properties in electronic switching devices.

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