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Breaking of Nanotube Symmetry by Substrate Polarization

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ABSTRACT

Substrate and nanotube polarization are shown to qualitatively change a nanotube bandstructure. The effect is studied in a linear approximation in an external potential which causes the changes. A work function difference between the nanotube and gold surface is estimated to be large enough to break the band symmetry and lift a degeneracy of a lowest but one subband of a metallic nanotube. This subband splitting for a [10,10] nanotube is about 50 meV in absence of other external potential.

1. Introduction. Since the discovery of carbon nanotubes in 1991,[1] a deep physics of these one-dimensional nanoscale objects has been demonstrated. Fundamental properties of the nanotubes have been studied in view of possible applications in electronics and other devices.[2] A detailed theoretical description of the electronic structure of ideal single-walled nanotubes (SWNTs) was obtained, as was the effect of various defects and disorder on the SWNT electronic properties (see, e.g., ref 3). However, the nanotube systems under experimental study often deviate from a model picture. In this letter we investigate one aspect of a real system: the modification of the electronic properties of the SWNT deposited on a substrate. One expects that symmetry of the nanotube at the substrate will be lower than the symmetry of the nanotube itself in vacuum.

A description of the breaking of the symmetry of SWNT bandstructure due to a charge transfer (or charge injection) between the nanotube and the substrate (or contacts) and calculation of the polarization of the substrate and the nanotube, which follows due to the charge transfer, are the goals of our study. Effects of splitting, mixing, and/or anticrossing of the nanotube subbands, which are caused by the depolarization of the electron charge density, have been almost neglected in the literature to now. We use the term "depolarization" for a number of phenomena, including a transverse shift of the electron charge density from its equilibrium distribution profile (effects due to an axial/longitudinal depolarization were discussed elsewhere[4−6]). We will show that the *transverse depolarization* results in qualitative changes of the nanotube density of states (DOS) near van Hove singularities. In particular, we predict the *splitting* of a doublet state[7] to be likely observable as a function of the injected/induced charge density of the SWNT. We discuss this in section 2.1. In section 2.2 we calculate this injected/induced charge density in a self-consistent way.

The depolarization and *intrasubband* splitting will be studied for a typical experimental situation: a single SWNT lies on a conductive substrate or separated from the conductor by a thin insulating layer representing an oxide on the surface of a metal. We assume that the nanotube is connected to electron reservoirs, which may be the leads or the conductor substrate itself. A transverse external electric field and/or a work function difference between the SWNT and the substrate/contact induce nonzero electron/hole charge density in the nanotube. This extra charge density polarizes the substrate, which breaks the axial symmetry of the nanotube. This effect is much larger than an electronic structure perturbation caused by the lattice distortion which may happen due to a van der Waals attraction to the substrate.[8] We will demonstrate that a direct action of the *uniform* external electric field is of minor importance as compared to the *nonuniform* field of surface charges on the substrate. In the last section we discuss a modification of our theory of the subband splitting for a case of purely insulating substrate.

2. Perturbation Theory for Bandstructure Modification. *2.1. Splitting of SWNT Subband due to Transverse Depolarization.* To calculate the splitting and shift of the electron energy levels one needs to know matrix elements of the perturbation potential between corresponding wave functions. In our case, the perturbation is a self-consistent

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Coulomb potential (operator in Heisenberg representation) that describes the interaction between the probe electron and the extra charge density on the SWNT and the polarization charge density on the substrate surface:

$$\hat{V} = e\int_{-L/2}^{L/2} \mathrm{d}Z \int_0^{2\pi} R\,\mathrm{d}\beta\,[\hat{\sigma}/[(z-Z)^2 + (R\cos\alpha - R\cos\beta)^2 + (R\sin\alpha - R\sin\beta)^2]^{1/2}] + [\hat{\sigma}^*/[(z-Z)^2 + (R\cos\alpha - R\cos\beta)^2 + (R\sin\alpha - 2h - R\sin\beta)^2]^{1/2}] \quad (1)$$

Both the probe electron and the nanotube surface charge are taken on a cylinder of a radius R. Then z and α are the electron coordinates in the cylindrical coordinate system. σ is the surface charge density. It does not depend on the coordinate Z along the nanotube because we assume the translational invariance of the problem for clarity of derivation. Although, the theory can be easily extended for the case of slow variation of σ along the axis. We will show later that one can drop the dependence of σ on the angle β along the circumferential direction in approximation of a *linear response* (in higher orders of perturbation theory a direct transverse polarization must be taken into account[9]). σ^* is an image charge density that is equal to $-\sigma$ for the metallic substrate.

The first term of eq 1 is the interaction with the charge density on the nanotube, which coincides with the Hartree term for the SWNT in a vacuum (without charge injection). The second term in eq 1 has also a simple physical meaning: this is the energy of interaction of the electron with the image charge. The separation between the SWNT axis and the surface of the conductor is h. In case of the metallic substrate, it is about the nanotube radius, R, plus the van der Waals distance for graphite: $h \approx R + 0.34$ nm.

The matrix element of the Coulomb operator eq 1 is calculated with the wave functions of a tight-binding (TB) Hamiltonian. We use envelope wave functions, obtained similarly to ref 10. This approach has been widely used in the literature, so we skip details and give the wave functions in the one-band scheme (π electrons only) in the form

$$|\psi_{m,k,\zeta}\rangle = \frac{1}{\sqrt{2}}(|A\rangle + \zeta c_{mk}|B\rangle)\,\mathrm{e}^{ikz}\mathrm{e}^{im\alpha} \quad (2)$$

where index m labels subbands of the SWNT electronic structure, k is a longitudinal momentum (these two are good quantum numbers (discrete and continuum, respectively) for an ideal, long enough nanotube), and $\zeta = \pm 1$ is a pseudospin. (A pseudospinor vector is formed by a two-component wave function amplitude defined for two atoms in a graphite unit cell, A and B). The coordinate along the tube is z, and α is the angle along the nanotube circumference.

We assume that our potential is smooth at the scale of the single unit cell (0.25 nm). Then, one may neglect transitions with the pseudospin flip (transitions between sublattices). With use of the orthogonality relation between the spinor components, it yields

$$\langle m|\,V\,|n\rangle = -\frac{8\pi eR\sigma}{|m-n|}\,i^{m-n}\left(\frac{R}{2h}\right)^{|m-n|},\ m \neq n \quad (3)$$

$$\langle m|\,V\,|m\rangle = 4\pi eR\sigma\log\left(\frac{2h}{R}\right),\ m = n \quad (4)$$

where σ, the surface charge density, is defined later in a self-consistent way.

Equations 3 and 4 are obtained by a direct Fourier transformation of eq 1 and describe the energy level shift when $m = n$ and the mixing of different subbands at $m \neq n$. The most interesting term with $n = -m$ is the mixing between the degenerate electron states within the same subband. By solving a secular equation for the intrasubband mixing of the electron doublet, we obtain the splitting of the van Hove singularity at the subband edge (Figure 2). The new subband energy separation reads as

$$\delta E_m = \frac{8\pi eR\sigma}{m}\left(\frac{R}{2h}\right)^{2m} \quad (5)$$

Let us now calculate the injected/induced charge density σ which will allow us a numerical estimation for the δE_m splitting.

2.2. Charge Injection due to the Fermi Level Shift. Equations 3−5 are written for the given charge density σ which is derived in this section. When the SWNT is placed in a real device, one must consider the work function difference between the nanotube and the contact or the conducting substrate and/or the external potential that may be applied to the SWNT. The potential shifts the Fermi level in the SWNT.[4] As a result of this, the positive/negative charge is injected into the nanotube:

$$\sigma = \frac{e}{2\pi R}\int_0^{\mu(\sigma)} \nu(E)\,\mathrm{d}E \quad (6)$$

Here $\nu(E)$ is a bare one-dimensional DOS (independent of σ in a linear response theory); $\mu = \Delta W - e\varphi^{\mathrm{xt}} - e\varphi^{\mathrm{ind}}(\sigma)$ is the shift of the electrochemical potential of the SWNT (with respect to a charge neutrality level $E = 0$) which depends on the work function difference, ΔW, on the external potential, φ^{xt}, applied between the nanotube and the reservoir and on the potential φ^{ind} induced by the charge density of the nanotube, σ. This last term is proportional to the intrasubband term ($m = n$) of the Coulomb interaction given by eq 4.

This self-consistent equation for σ, eq 6, is readily solved analytically if the electrochemical potential is below the second subband edge. We follow ref 4 in derivation of σ: the induced potential is obtained by direct integration of the charge density along the SWNT as in refs 4 and 5. As it is shown in Figure 1, for a metallic SWNT, the charge is a product of the constant DOS, C_Q, and the electrochemical potential, μ. Then the solution of eq 6 is as follows:

$$\sigma_A = \frac{\Delta W - e\varphi^{\mathrm{xt}}}{2\pi R\,e(2\log(2h/R) + C_Q^{-1})} \quad (7)$$

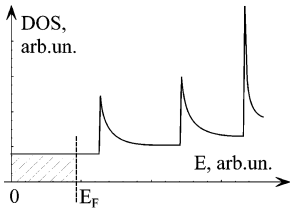

Figure 1. Schematic density of states (DOS) of a metallic SWNT. The first (massless) subband contributes to a constant DOS at $E = 0$. When the Fermi level, E_F, is lower than the second (massive) subband edge (which corresponds to the first peak of DOS), an injected/induced charge is proportional to the shaded area and is a linear function of E_F.

and for a semiconductor SWNT, which has the DOS $\propto C_Q E\,\theta(E-\Delta)/\sqrt{E^2-\Delta^2}$, the charge is as follows:

$$\sigma_Z = \sigma_A\left[\left\{\sqrt{\left(\frac{\Delta}{\Delta W - e\varphi^{xt}}\right)^2 (4\log^2(2h/R) - C_Q^{-2}) + C_Q^{-2}} - 2\log(2h/R)\right\}\middle/(2\log(2h/R) - C_Q^{-1})\right]\theta(\Delta W - e\varphi^{xt} - \Delta) \quad (8)$$

Here $\theta(x)$ is the Heaviside unit step function and Δ is 1/2 of the energy gap. We introduced a quantum capacitance of the SWNT following ref 4:

$$C_Q = \frac{8e^2}{3\pi b\gamma} \quad (9)$$

which is the one-dimensional analogue of the quantum capacitance proposed for a two-dimensional electron gas system by Luryi.[11] Here $b \simeq 1.4$ Å is the interatomic distance, $\gamma \simeq 2.7$ eV is the hopping integral for the graphite-like systems. We notice that despite that the σ_Z, as given by eq 8, comes from a massive subband (in contrast to σ_A, as in eq 7 where the lowest subband is massless, see Figure 1), the linear dependence of $\sigma_{A/Z}$ on φ^{xt} preserves as long as the potential φ^{xt} is large enough. This reflects the fact that a classical one-dimensional charge density is a linear function of a classical electrostatic potential.[12]

3. Results and Discussion. In the last section we obtained the self-consistent expression for the surface charge density as a function of the external potential and the work function difference which may be considered as a built-in potential. Substituting eq 7 into eq 5 we obtain the splitting of the degenerate subbands $|\pm m\rangle$ of the metallic SWNT (when the Fermi level is within the first subband) as follows:

$$\delta E_m = \frac{4(\Delta W - e\varphi^{xt})}{m(2\log(2h/R) + C_Q^{-1})}\left(\frac{R}{2h}\right)^{2m} \quad (10)$$

The splitting decreases with m exponentially, hence, the effect is likely observable for the lowest degenerate subband. Then, for the parameters: SWNT radius $R \simeq 6.7$ Å, the distance to the metal substrate $h = 10.1$ Å, and the quantum capacitance $C_Q^{-1} \simeq 0.69$,[4] we obtain a numerical estimate

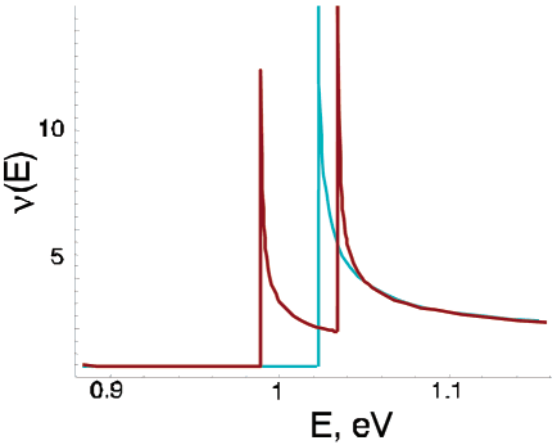

Figure 2. Density of states (DOS) of a [10,10] armchair nanotube in the vicinity of first van Hove singularity (black line). Charge injection in the NT due to work function difference (see the text) results in a splitting of a doublet, which is clearly seen as compared to bare DOS of neutral NT (light line).

for the subband splitting $\delta E_1 \simeq 0.15(\Delta W - e\varphi^{xt})$. Experimental data for the work function of SWNTs scatters from 4.9 to 5.05 eV.[13,14] For the SWNT on the gold substrate we use as an estimate $\Delta W \sim 0.3$ eV. In the absence of the external potential, this work function difference results in a gap of ~46 meV between two split peaks of the density of states (Figure 2), which is larger than kT at room temperature. We also calculated the contribution of all other subbands, which is negligible in the splitting but it shifts the doublet as a whole. As a result, two new peaks in Figure 2 appear not symmetrical with respect to the original DOS singularity.

The splitting of $\pm m$ doublet is an analogue of a degenerate level Stark effect for the nanotube in a multipole potential of the image charge. The lower subband has x symmetry and the upper subband has y symmetry (with corresponding wave functions $|x\rangle = 1/\sqrt{2}(|+m\rangle + |-m\rangle$ and $|y\rangle = 1/\sqrt{2}(|+m\rangle - |-m\rangle)$ because of an attraction energy of the electron to its image charge that is lower for the second combination.

We predict a similar effect for the semiconductor nanotube, although the total external potential causing the charge density injection must be larger than one-half of the gap in this case. As we study in this paper only the effect which is linear in the external potential, all high order terms in eq 8 have to be discarded.

3.1. Dipole Polarization Correction. The charge injection in the nanotube may be readily achieved by applying an external electric field. One may naively argue that the external field itself can break the bandstructure symmetry and result in some level splitting. Although, this is a correct statement in general, the direct splitting of the SWNT orbital doublet $\pm m$ by the uniform electric field is forbidden by symmetry. These degenerate states do not mix together due to the selection rules of the problem. The matrix element for an intrasubband splitting in the uniform external field $\mathcal{E}_{xt}$ equals zero by parity: $\langle m|\, e\mathcal{E}_{xt} y\, |-m\rangle = 0$.

To calculate the subband splitting in this case, we have to compute the charge injection, which is proportional to the

applied field. The potential is equal to $\varphi^{xt} = \mathcal{E}_{xt}h$, where h is the distance between the axis of the tube and the metal surface, which has to be substituted into eq 10.

In section 2.1 we assumed that the charge density σ has no dependence on the angular coordinate β along the nanotube circumference. This is an accurate approximation since a dipole (and higher multipole) component of the σ is small as compared to what is given by eqs 7 and 8. Let us prove this assumption for the dipole polarization of the SWNT.

The nonuniform external potential causes a deviation of the surface density from the uniform equilibrium value, σ, which is given by the following expression:

$$\delta\sigma(\beta) = e\sum_{i\neq j}\frac{(f_i - f_j)\langle i|\ V\ |j\rangle}{E_i - E_j}\langle j|\beta\rangle\langle\beta|i\rangle \qquad (11)$$

where f_i are the occupation numbers, the matrix element $\langle i|\ V\ |j\rangle$ is given by eqs 3 and 4, E_i are the energies of subbands, and $\langle\beta|i\rangle$ are corresponding wave functions.

We define the nonuniform dipole part of the charge density of a SWNT as $\delta\sigma_1 \equiv \int_0^{2\pi}\sin\beta\ \sigma(\beta)\ \mathrm{d}\beta$. Then, the dipole component of the surface charge is as follows:

$$\delta\sigma_1 = \frac{ie}{8\pi R^2}\sum_i\frac{(f_i - f_{i\pm1})\langle i|V|i\pm1\rangle}{E_i - E_{i\pm1}} \qquad (12)$$

Let us remind that according to eq 3 $\langle i|\ V\ |i\pm1\rangle = -i8\pi R^2 e\sigma/(2h)$.

In the case where the electrochemical potential equals zero (no charge in the nanotube), the transverse polarization includes transitions from the valence to the conduction band only $\langle v|\ V\ |c\rangle$ (the details of the calculation are presented elsewhere[9]). Here, we study an extra component of the polarization, which is due to the induced charge density. Thus, we need to consider only transitions from the levels above the charge neutrality level, $E = 0$, and below the Fermi level, $E = E_F$, (which is the shaded area in Figure 1). Hence, the dipole polarization is proportional to the net charge density σ, and the dipole charge density of the metallic SWNT is given by the following expression:

$$\delta\sigma_1 = \frac{\sqrt{3}C_Q^2}{32\pi}\frac{(2\pi R\sigma_A)^2}{e}\frac{R}{h}\log\frac{2h}{R} \propto \mathcal{E}_{xt}^2 \qquad (13)$$

where $C_Q \simeq 3.2$ is the dimensionless quantum capacitance. We single out the term $2\pi R\sigma_A$, which is the specific one-dimensional charge density of the SWNT and is proportional to the external potential and thus to the external field.

Equation 13 shows that the effect of the transverse polarization on the bandstructure is quadratic in the external field, in good agreement with a plain dielectric response theory,[9] while the effect of the image charge is linear in $\mathcal{E}_{xt}$. Thus, the degenerate level splitting due to the dipole component of the polarization will be less important than the splitting due to a uniform component: $\sigma_0 \equiv \int_0^{2\pi}\sigma(\beta)\ \mathrm{d}\beta$, at least, in a weak field regime discussed in the article. This proves post factum our assumption of σ to be independent of β.

3.2. Depolarization at the Insulator Substrate. For the sake of completeness we present here also a modification of our theory to the case of a dielectric substrate. In this case the screening of the charge density in the nanotube is weaker. It results from (i) underscreening of the Coulomb interaction between the nanotube carriers and (ii) lower charge density induced in the substrate. The second factor can be taken into account by substituting an effective image charge density $\sigma^* = \sigma(1-\epsilon)/(\epsilon+1)$ in the second term of eq 1, where ϵ is the dielectric function of the substrate (in case of highly conductive substrate it equals $-\infty$), instead of the bare image charge density $-\sigma$. This results in substituting σ^* in eqs 3−8 where appropriate.

Now, the fields of the image charge and the charge in the SWNT do not cancel each other, in contrast to the case of the metallic substrate. As a result, underscreening of the Coulomb interaction happens. This modifies the equations for the energy level shift (*intrasubband* matrix elements as in eq 4), and thus the electrochemical potential shift. One must substitute the $\log(2h/R)$ term everywhere by $\log(2h/R) + 2/(\epsilon-1)\log(L/R)$ where L is the length of the nanotube (or distance between metal leads to it). This expression diverges with the length of the nanotube which reflects the one-dimensional character of the Coulomb interaction. These changes have to be made through eqs 7−10.

The first term of eq 1 does not appear in the calculation of the *intersubband* matrix elements as in eqs 3 and 5. Hence, no additional correction is required in eqs 11 and 12 of the previous section.

We assumed in this paper that the perturbation theory in a linear approximation in μ (or equivalently in σ) is applicable. Restrictions which may follow from this assumption are as follows. The external potential has to be small. We neglect here the dipole term in the induced charge density (and higher multipoles as well). It is equivalent to a weak intersubband mixing, which assumption may not hold for wide nanotubes or strong external fields. The effect of the strong field on the bandstructure is discussed elsewhere.[9] In this paper we used eq 6 for the equilibrium charge density in the SWNT. One may consider transport devices on an equal basis, as long as the charge of the nanotube is still given by the quasi-equilibrium charge density. However, for nonzero current flowing through the nanotube, one must use an expression for the charge density that differs from eq 6 (to be discussed elsewhere[12]).

4. Conclusions. In summary, we have developed a microscopic quantum mechanical theory for a charge transfer between a SWNT and a conductive substrate (and/or metallic leads). This charge injection results from a natural work function difference between the nanotube and the substrate or/and from an external potential applied between those. A surface charge density of the SWNT is calculated self-consistently within an envelope function formalism of tight-binding approximation.

We demonstrated for the first time that the influence of this charge transfer on the electronic structure of the SWNT is not negligible for typical material parameters of the problem. Because of the breaking of the axial symmetry of the system, the SWNT DOS changes qualitatively: degenerate subbands $\pm m$, where $m \neq 0$, n, split. It has a simple physical interpretation: the electrons with x and y polarizations are no longer equivalent as their attraction to the substrate is different. This effect can be related to a degenerate level Stark effect with an appropriate choice of external field of the image charge. The gap between the new x and y subbands is constant in k-space (for the external field which is uniform along the tube) so it shows up dramatically at the subband edge. The van Hove singularity splits, and the distance between two peaks of the DOS is about 46 meV for the [10,10] armchair SWNT on the gold substrate.

We obtained analytical expressions for matrix elements of the image charge field, which yield the mixing of different subbands and can be used to describe the level anticrossing (to be discussed elsewhere). The same matrix elements enter the expression for the multipole polarizabilites of the SWNT. We estimated a major contribution to the dipole polarizability of the metallic SWNT, which comes from intraband transitions for nonzero charge injection. The analytical expression for the dipole component of the surface charge density is shown to be proportional to the square of the external potential and, hence, appears in the second order of the perturbation theory which corroborates post factum our assumption of uniformity of the induced/injected charge along the SWNT equator.

We show that the modification of our theory to the case of semiconductor substrate is straightforward. The analytical expressions for the van Hove singularity splitting and induced charge density are obtained.

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