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EXCITONS IN SINGLE-WALL CARBON NANOTUBES

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Excitonic states in single-wall carbon nanotubes have been studied within the tight-binding approximation. An analytical expression for the dielectric function of the nanotube has been obtained in the random phase approximation. It was demonstrated that calculations with the static dielectric function yield an overestimated exciton binding energy exceeding the nanotube energy gap. Self-consistent calculation of the exciton binding energy with the frequency-dependent dielectric function has been performed. The binding energy to energy gap ratio has been shown to have no dependence on the nanotube radius and to be a universal constant ~ 0.87 for given resonance integral $\gamma_0 = 2.7 \text{ eV}$.

Keywords: nanotube bandstructure; exciton theory; selfconsistent dielectric function.

1. Introduction

There are two reasons for a large exciton binding energy in carbon nanotubes. First, a space quantization (confinement) energy increases in one-dimensional (1D) system. Second, a Coulomb interaction has a logarithmic singularity in 1D¹ due to a poor screening. We notice a specific spatial and frequency dispersion of a dielectric function of nanotubes. The screening is strong at the distances less than the nanotube radius and is ineffective at the large distances. Actually, the dielectric function with zero angular momentum goes to unity in the long wavelength limit². This is consistent with the fact that infinitely long dielectric cylinder does not screen the longitudinal external electric field³.

In this paper, the dielectric function was calculated within a random phase approximation (RPA). A tight-binding approximation was used to describe π -electron^{4,5}. The calculation of the exciton binding energy with the static dielectric function gives the binding energy exceeding the nanotube energy gap. It means

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that a ground state of the nanotube is not stable. However, this is not supported by experimental data. Let us remind that the frequency dependent dielectric function has the singularity at the $\hbar\omega = E_g$, due to the one-dimensional structure of nanotubes. We present results of a self-consistent calculation of the exciton binding energy with the frequency-dependent dielectric function and demonstrate that it is free of the above mentioned problem of the exciton instability. We also show that when the nanotube radius and energy gap set up the units of the length and energy, correspondingly, one obtains a *universal* radius-independent Schrödinger equation.

2. 1D exciton approximation

We assume that the electron and the hole are in subbands that are separated by a minimum energy gap; we denote the angular momentum of this subband as m_{gap} . The Fourier transform of the Coulomb potential is given then by ⁴

$$V_{q,m} = 2e^2 I_{|m|}(|qR|) K_{|m|}(|qR|) \quad (1)$$

We neglect the Coulomb matrix elements with a nonzero angular momentum in the calculation of the exciton binding energy, which is equivalent neglecting an intersubband mixing. This approximation is valid due to the small values of these Coulomb matrix elements and sufficiently large distance between subbands (Fig.1). The coupling of the excitons in different subbands can be taken into account in the second-order perturbation theory. The bi-exciton—exciton coupling has been calculated recently in Ref. ⁶.

We emphasize that in our model the nanotube is in vacuum, not in a media. Thus, no external screening is assumed in contrast to all previous studies. The experimental data allows to expect very small if any influence of the medium on the excitations in the nanotubes. The screening by the valence electrons of the nanotube itself is fully taken into account and presented in the next section.

3. Dielectric function of the nanotube

In the RPA the dielectric function is given by

$$\varepsilon_{q,m}(\omega) = 1 + \frac{2e^2}{\pi} I_{|m|}(|qR|) K_{|m|}(|qR|) \times \quad (2)$$

$$\sum_{\alpha,\beta=c,v; n} \int dk \frac{|\langle k+q, n+m, \alpha | e^{iqz} e^{im\phi} | k, n, \beta \rangle|^2}{E_{k+q, n+m, \alpha} - E_{k, n, \beta} - \hbar\omega} (f(E_{k, n, \beta}) - f(E_{k+q, n+m, \alpha}))$$

where $|k, n, \alpha\rangle$ denotes the state of the conduction/valence band, $\alpha = c/v$, with a longitudinal momentum $\hbar k$ and the angular momentum $\hbar n$; $f(E)$ is a Fermi distribution function. It was pointed above, that we are interested in the dielectric function with the zero angular momentum, thus, $m = 0$ in the rest of paper.

The electronic states near the Fermi point, where the energy gap is minimal and the matrix element is maximal, give the main contribution to the polarizability.

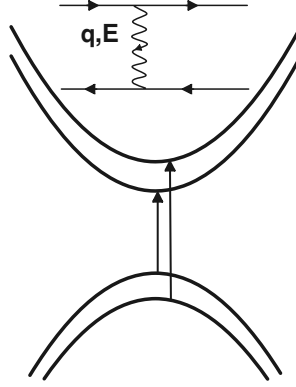


Fig. 1. Scheme of electron–hole transitions corresponding to calculated exciton levels. Inset: Feynman diagram corresponding to the exciton state. The interaction line is screened.

Expanding the matrix element in the powers of a transferred momentum, q , and keeping only linear term, we obtain

$$\langle k + q, m_{gap}, c | e^{iqz} | k, m_{gap}, v \rangle \approx -\frac{3}{2} \frac{iqR}{1 + 9(k - k_{gap})^2 R^2} \quad (3)$$

Here k_{gap} and m_{gap} are the wave vector and the angular momentum corresponding to the conduction band minimum and the valence band maximum. R is the nanotube radius. With a linearization of the electron dispersion in the vicinity of the Fermi point, the energy difference in the denominator of Eq. (2) can be represented as

$$E_{k+q, m_{gap}, c} - E_{k, m_{gap}, v} \approx \gamma_0 \frac{b}{R} \sqrt{1 + 9(k - k_{gap})^2 R^2} \quad (4)$$

here $\gamma_0 = 2.7$ eV is the resonance integral and $b = 0.142$ nm is the distance between the neighbour carbon atoms. Using the Eqs. (2, 3) we obtain an analytical expression for the dielectric function

$$\varepsilon_{q,0}(\omega) = 1 + \frac{8e^2}{\pi b \gamma_0} A(\Omega) q^2 R^2 I_0(|qR|) K_0(|qR|) \quad (5)$$

where $\Omega = \hbar\omega/E_g$ and $A(\Omega)$ is the frequency-dependent part of the dielectric function

$$A(\Omega) = \frac{3}{2} \frac{\frac{\pi}{2} - \arcsin(\sqrt{1 - \Omega^2}) - \Omega\sqrt{1 - \Omega^2}}{\Omega^3 \sqrt{1 - \Omega^2}} \quad (6)$$

In the static limit A goes to unity ($\lim_{\Omega \rightarrow 0} A = 1$). The dependence $A(\Omega)$ is shown on the Fig.2. When the frequency approaches the energy gap, the dielectric function has the singularity due to the one-dimensional structure of nanotubes.

$$A(\Omega) \approx \frac{3\pi}{4\sqrt{2}} \frac{1}{\sqrt{1 - \Omega}}, \quad 1 - \Omega \ll 1 \quad (7)$$

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2D system is known to have a logarithmical singularity and it is regular in 3D case.

In our calculation, we took into account only subbands separated by the minimal energy gap. The contribution of the next subbands that have angular momentum $m_{gap} + 1, +2 \dots$ (or $m_{gap} - 1, -2 \dots$, depending on the nanotube geometry) can be found in a similar way. In the static case, the first correction is due to the next subband and 4 times smaller than the contribution of the subband with the minimal energy gap. The contribution of higher subbands is negligible. For the frequencies of interest ($\hbar\omega < E_g$) the frequency dispersion of the dielectric function in the second subband term is negligible and we can safely use the static polarization, *i.e.*, set $\Omega = 0$.

4. Self-consistent calculation of the exciton binding energy

For an accurate description of the screening we have to take a Fourier component of the dielectric function at the frequency of the relative motion of the electron and the hole, *i.e.* at the frequency corresponding to the exciton binding energy. Then the Schrödinger equation for the exciton wavefunction in the k -space has the following form

$$\frac{\hbar^2 k^2}{2\mu^*} \Psi_k - \int dq \frac{V_{q,0}}{\varepsilon_{q,0} (E_b/\hbar)} \Psi_{k-q} = -E_b \Psi_k \quad (8)$$

where $E_b > 0$ and μ^* are the exciton binding energy and a reduced mass, respectively. The dependence of the reduced mass on the nanotube radius can be represented as

$$\mu^* = m^*/2 = \frac{\hbar^2}{9bR\gamma_0} = \frac{\hbar^2}{9E_g R^2} \quad (9)$$

taking into account that $E_g = \gamma_0 b/R$. Substituting (9) in (8) and introducing the dimensionless wavevector $\tilde{q} = qR$, we obtain a universal equation with no explicit dependence on the nanotube radius

$$\frac{9}{2} \tilde{k}^2 \Psi_{\tilde{k}} - \frac{e^2}{b\gamma_0} \int d\tilde{q} \frac{2I_0(\tilde{q})K_0(\tilde{q})}{1 + \frac{8e^2}{\pi b\gamma_0} A(E_b/E_g) \tilde{q}^2 I_0(\tilde{q})K_0(\tilde{q})} \Psi_{\tilde{k}-\tilde{q}} = -\frac{E_b}{E_g} \Psi_{\tilde{k}} \quad (10)$$

In order to solve the equation, we fix the value of the dispersion factor A and find numerically the eigenvalues of Eq. (10) as a function of A : $E_b/E_g = F(A)$. Next, we find the binding energy solving the equation $F^{-1}(E_b/E_g) = A(E_b/E_g)$ where the last function is defined in Eq. (6). The procedure is illustrated in Fig.2 for the ground and first excited states. Because the dielectric function diverges when the frequency approaches the energy gap, the binding energy can not exceed the energy gap. For the next excited states it is not necessary to use this self-consistent method. Due to the $A(\Omega)$ at the binding energies (frequencies smaller than $E_g/2$) is a weak function of Ω and approximately equals one.

In order to understand the universality of the Eq.10 and its solution we notice that this is a special property of the nanotube 1D system that the Coulomb energy

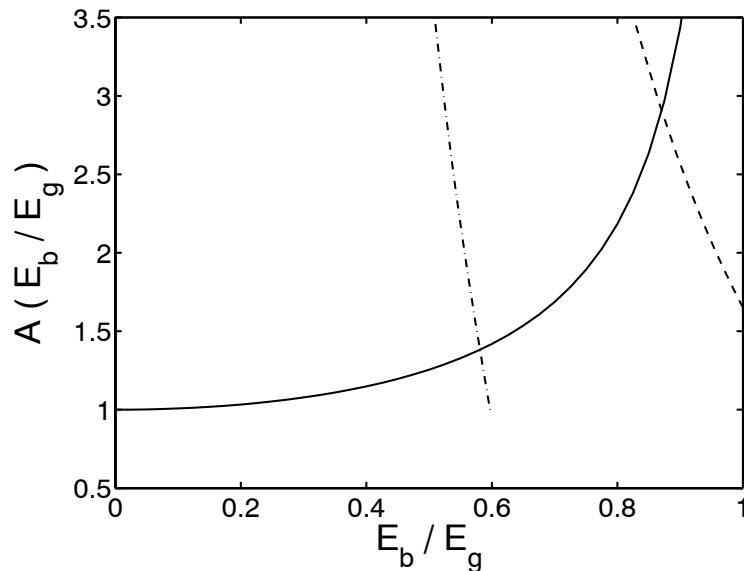


Fig. 2. Self-consistent calculation of the exciton energy levels. Solid line is defined by Eq. (6), dashed and dash-dotted lines shows the depending of the exciton binding energy on the frequency-dependent factor A for ground and first excited states. Table shows the energies and characteristic lengths of the six exciton levels.

Table 1. Binding energies and characteristic length of the six excitonic states.

State index	Binding energy (E_g)	Length (R)
1	0.87	2.68
2	0.58	6.20
3	0.38	10.0
4	0.23	15.4
5	0.16	21.7
6	0.10	31.2

and the transverse quantization energy scale similarly as $1/R$. Therefore, the ratio of the exciton binding energy to the gap is a universal constant and independent of the nanotube radius.

The correction to the binding energy due to the Coulomb matrix elements with nonzero angular momentum can be estimated in the second-order perturbation theory. For the ground state an estimate for the largest correction term is $\Delta E_b \simeq 0.04E_g$.

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5. Conclusions

Using a tight-binding approximation, an analytical expression for a dielectric function of a nanotube has been obtained in a random phase approximation. In the calculations with a static dielectric function, an exciton binding energy exceeds a nanotube energy gap due to a weak screening of a longitudinal electric field in 1D systems. In fact, when taking into account space and frequency dispersion of the dielectric function, the exciton binding energy can not be larger than the energy gap due to a singularity of the dielectric function at $\hbar\omega = E_g$. Self-consistent calculation of the exciton binding energy with the frequency-dependent dielectric function has been performed. The ratio of the exciton binding energy to the energy gap and the ratio of the exciton characteristic length to the nanotube radius are found to be independent on the nanotube radius in the framework of our model.

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