Excitons in single-wall carbon nanotubes

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Abstract. 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 $\gamma_0 = 2.7\,\text{eV}$.

Introduction

There is two reasons for a large exciton binding energy in carbon nanotubes. First is decreasing of the spatial confinement energy due to the one-dimensionality. Second is the spatial dispersion of the 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 limit. This is consistent with the fact that infinitely long dielectric cylinder does not screen the longitudinal external electric field [1].

In this paper, the dielectric function was calculated within a random phase approximation (RPA). The tight-binding approximation was used to describe π-electron. The calculation of the exciton binding energy with the static dielectric function gives the binding energy exceeding the nanotube energy gap. It means that the ground state of the nanotube is not stable. However, this result is not correct. As the matter of the fact, the dielectric function has the singularity at the $\hbar\omega = E_g$, caused by one-dimensionality of nanotubes. We present the results of the self-consistent calculation of the exciton binding energy with the frequency-dependent dielectric function.

1. 1D exciton approximation

We suppose electron and hole are in the subband that are separated by minimum energy gap. The Fourier transform of the Coulomb potential is given by [2]

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

We neglect the Coulomb matrix elements with nonzero angular momentum in the calculation of the exciton binding energy. This approximation is valid due to the small values of these Coulomb matrix elements and sufficiently large distance between subbands. The coupling of the excitons in different subbands can be taken into account in the second-order perturbation theory.

2. Dielectric function of the nanotube

In the RPA the dielectric function is given by

$$\varepsilon_{q,m}(\omega) = 1 + \frac{2\,e^2}{\pi} I_{|m|}(|qR|)\, K_{|m|}(|qR|)$$
$$\times \sum_{\alpha,\beta=c,v;\ (k,n)\in 1st\,Bz} \int dk$$

$$\times \frac{|\langle k+q, n+m, \alpha|e^{iqz}e^{im\phi}|k, n, \beta\rangle|^2}{E_{k+q,n+m,\alpha} - E_{k,n,\beta} - \hbar\omega}$$
$$\times \left[f\left(E_{k,n,\beta}\right) - f\left(E_{k+q,m+n,\alpha}\right)\right] \tag{2}$$

where $|k, n, \alpha\rangle$ denotes the state of the α band with longitudinal momentum $\hbar k$ and angular momentum n, f is Fermi function. It was pointed above, we are interested in the dielectric function with zero angular momentum.

The electronic states near the Fermi point, where energy gap is minimal and matrix element is maximal, give the main contribution in the polarizability. Expanding the matrix element in the powers of the wavevector and keeping only linear term, we obtain

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

Here k_{gap} and m_{gap} are the wave vector and angular momentum value corresponding to the conduction band minimum and valence band maximum. R is the nanotube radius. Linearizing spectrum in the vicinity of the Fermi point [3], the energy difference in the denominator of Eq. (2) can be presented as

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

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

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

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

$$A(\Omega) = \frac{3}{2}\frac{\frac{\pi}{2} - \arcsin\left(\sqrt{1-\Omega^2}\right) - \Omega\sqrt{1-\Omega^2}}{\Omega^3\sqrt{1-\Omega^2}}. \tag{6}$$

In the static limit A goes to unity. The dependence $A(\Omega)$ is shown in Fig. 1. When the frequency approaches to the energy gap, the dielectric function has the singularity caused by one-dimensionality of nanotubes.

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

In 2D systems such a singularity is logarithmical and it vanishes in 3D case.

In the calculation presented, we took into account only sub-bands separated by minimal energy gap. The contribution of the subband with the next energy gap value can be found by the similar way. In the static case, it is 4 times smaller than the contribution of the subband with minimal energy gap. The role of other subbands is negligible. For the frequencies of interest ($\hbar\omega < E_g$) we can neglect the frequency dispersion of the second subband contribution in the dielectric function.

3. Self-consistent calculation of the exciton binding energy

For the 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 hole, i.e. for the frequency corresponding to the exciton binding energy. Then the Schrödinger equation for the exciton wavefunction in the k-space has the following form

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

where $E_b > 0$ and μ^* is the exciton binding energy and reduced mass, correspondingly. The dependence of the reduced mass and energy gap on the nanotube radius is given by [3]

$$\mu^* = m^*/2 = \frac{\hbar^2}{9bR\gamma_0} \qquad Eg = \gamma_0 \frac{b}{R}. \qquad (9)$$

Substituting (9) in (8) and entering the dimensionless wavevectors like $\tilde{q} = qR$ we obtain the universal equation with no dependence on nanotube radius

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

$$\times \Psi_{\tilde{k}-\tilde{q}} = -\frac{E_b}{E_g}\Psi_{\tilde{k}}. \qquad (10)$$

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 on A, $E_b/E_g = F(A)$. After that, 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. 1 for the ground and the first exited states. Because the dielectric function increases infinitely when the frequency approaches the energy gap, the binding energy can not exceed the energy gap value. For the next excited states is not necessary to use the self-consistent method due to the weak $A(\Omega)$ dependence at their binding energies.

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 a ground state a rough estimate for correction to the E_b/E_g value is 0.04.

4. Conclusions

Using the tight-binding approximation, an analytical expression for the dielectric function of the nanotube has been obtained in the random phase approximation. In the calculations with the static dielectric function, the exciton binding energy
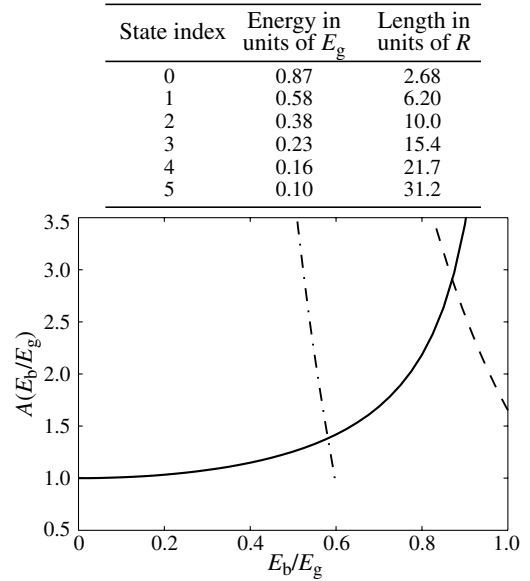
State index	Energy in units of E_g	Length in units of R
0	0.87	2.68
1	0.58	6.20
2	0.38	10.0
3	0.23	15.4
4	0.16	21.7
5	0.10	31.2

Fig. 1. 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.

exceeds the nanotube energy gap due to the weak screening of the longitudinal electric field in 1D systems. In fact, the exciton binding energy can not be larger than the energy gap due to the 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 exciton binding energy to energy gap ratio and exciton characteristic length to nanotube radius ratio are found to be independent on the nanotube radius in the framework of our model.

References

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