Excitons and Interband Terahertz Transitions in Narrow-Gap Carbon Nanotubes

M. E. Portnoi* C. A. Downing* R. R. Hartmann† I. A. Shelykh‡

Abstract — **We show, via a solution of the quasi-one-dimensional two-body problem applied to a Dirac system, that excitonic effects suppress the one-dimensional Van Hove singularity in single-walled carbon nanotubes with narrow band gaps.**

1 INTRODUCTION

Carbon nanotubes (CNTs) are believed to be promising candidates for various terahertz (THz) applications [1, 2, 3, 4, 5, 6, 7]. For example, one of the earliest proposals, which is most relevant to this conference, discussed CNT-based THz antenna [8]. Another interesting application, which is worth mentioning, is the use of CNT paper as a saturable absorber for short-pulse optical amplifiers [9], which are the key elements in optics-based THz generation schemes. Notably, the CNT-based saturable absorber is free of natural limitations existing in its semiconductor predecessors [10].

The presented work is related to the application proposals based on direct interband THz transitions in narrow-band (quasi-metallic) CNTs, focusing on hitherto overlooked excitonic effects. Optical transitions and excitons in semiconductor carbon nanotubes have been a subject of extensive research [11]. Significantly less is known about the dipole transitions across narrow gaps in quasi-metallic carbon nanotubes and excitonic effects associated with these transitions. The small band gaps, which cannot be obtained within a simple graphene zone-folding model, appear in quasi-metallic nanotubes due to curvature effects [11]. A band gap can also be opened in a truly metallic (armchair) nanotube by a magnetic field. We have shown [6, 12] that the same physical effects, which lead to opening of the gaps, also result in allowed dipole optical transitions, which are strongly suppressed away from the band edge. A combined effect of the sharp frequency dependence of the transition matrix element and the Van Hove singularity in the one-dimensional density of states results in strong light-matter coupling even in the absence of excitons [13].

A typical curvature-induced band gap in a quasi-metallic nanotube lies in the highly thought-out THz frequency range, leading to proposals [6, 7] of using this type of carbon nanotubes as THz emitters and detectors. It is known, however, that excitonic effects dominate the optical spectra of semiconductor carbon nanotubes [11, 14] characterized by the exciton binding energy reaching up to 1eV and by strongly-bound dark exciton states preventing any meaningful photonic applications. Therefore, evaluating the feasibility of the proposed THz applications requires an understanding of the role of excitonic effects in narrow-gap nanotubes.

In what follows we calculate the exciton binding energy in narrow band gap single-walled carbon nanotubes, accounting for the quasi-relativistic dispersion of electrons and holes. Solutions of the quantum relativistic two-body problem are obtained for several limiting cases. We show that the binding energy scales with the band gap and conclude on the basis of the data available for semiconductor nanotubes that there is no transition to an excitonic insulator in quasi-metallic nanotubes and that their proposed THz applications are feasible.

Depending on the environment, e.g., the presence of a metallic gate and the free-carrier density, excitons can be either described by a short-range electron-hole interaction potential [15] or by an unscreened cusp potential, similar to that considered by Loudon in the 1950s [16]. Our analysis shows that the Loudon potential is a good fit for the quasi-one-dimensional Coulomb potential, obtained by averaging the three-dimensional Coulomb potential with the envelope functions. We report exact analytic solutions for the quasi-relativistic Loudon problem for an exciton with a zero total momentum along the nanotube axis. The complex four-component structure of the electron-hole relative motion wavefunction, which is obtained when two graphene sublattices and two types of particles are taken into account, results in a counterintuitive dip in the shape of the particle density distribution within the exciton.

The vanishing exciton binding energy with decreasing the energy gap removes for narrow-gap nanotubes the undesirable effect of strongly-bound dark excitons, which is known to suppress optical emission in semiconductor nanotubes. How-

*School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom. e-mail: m.e.portnoi@exeter.ac.uk

†Physics Department, De La Salle University, Manila, Philippines.

‡Science Institute, University of Iceland, Dunhagi-3, IS-107, Reykjavik, Iceland.

ever, the Coulomb interaction remains important as it smears the Van Hove singularity in the one-dimensional density of states [17]. We report the resulting shape of the terahertz emission from narrow-gap carbon nanotubes with the Coulomb effects taken into account, for both the long-range and short-range interaction models.

The same frequency range, which is responsible for interband THz transitions in narrow-gap carbon nanotubes, also corresponds to the localised plasmon resonance associated with free carriers [18, 19]. Notably, the free-carrier absorption is an undesirable effect for applications based on inter-band transitions. For a realistic structure containing an array of narrow-gap nanotubes with either optically excited or electrically-injected non-equilibrium carriers, the THz gain associated with interband transition should be compared with the free-carrier-absorption-induced loss, which also has a maximum at THz frequencies. However, in what follows we neglect the free-carrier absorption and concentrate on excitonic effects only.

2 TWO-BODY HAMILTONIAN

The low-energy spectrum of a narrow gap carbon nanotube is well described by a single particle matrix Hamiltonian

$$\hat{H}_1 = v_F \begin{bmatrix} 0 & \hat{p}_x - i\hbar\Delta \\ \hat{p}_x + i\hbar\Delta & 0 \end{bmatrix} \tag{1}$$

where v_F is the graphene Fermi velocity, $2\hbar v_F|\Delta|$ is the bandgap and the momentum operator $\hat{p}_x$ acts along the nanotube axis.

The two-body Hamiltonian can be written [20, 15] as

$$\hat{H}_2 = v_F \begin{bmatrix} 0 & \hat{p}_e - i\hbar\Delta & -\hat{p}_h + i\hbar\Delta & 0 \\ \hat{p}_e + i\hbar\Delta & 0 & 0 & -\hat{p}_h + i\hbar\Delta \\ -\hat{p}_h - i\hbar\Delta & 0 & 0 & \hat{p}_e - i\hbar\Delta \\ 0 & -\hat{p}_h - i\hbar\Delta & \hat{p}_e + i\hbar\Delta & 0 \end{bmatrix}, \tag{2}$$

where the indices A and B are related to the two sublattices of the graphene sheet, which is rolled into a nanotube.

We move into relative and center-of-mass coordinates $x = x_e - x_h$ and $X = \frac{1}{2}(x_e - x_h)$ respectively, and seek a wavefunction in the form $\Psi_{ij}(X, x) = e^{iKX}\phi_{ij}(x)$. Considering the case of a static exciton $K = 0$ with an interaction potential $V(x)$, we arrive at the following system of equations

$$\begin{bmatrix} 0 & \partial_x + \Delta & \partial_x - \Delta & 0 \\ \partial_x - \Delta & 0 & 0 & \partial_x - \Delta \\ \partial_x + \Delta & 0 & 0 & \partial_x + \Delta \\ 0 & \partial_x + \Delta & \partial_x - \Delta & 0 \end{bmatrix} \begin{bmatrix} \phi_{AA} \\ \phi_{BA} \\ \phi_{AB} \\ \phi_{BB} \end{bmatrix}$$

$$= i(\varepsilon - U(x)) \begin{bmatrix} \phi_{AA} \\ \phi_{BA} \\ \phi_{AB} \\ \phi_{BB} \end{bmatrix}, \tag{3}$$

where the scaled eigenenergy is $\varepsilon = E/\hbar v_F$ and the scaled interaction potential is $U(x) = V(x)/\hbar v_F$. We define the exciton binding energy to be $\varepsilon_B = |\varepsilon| - |2\Delta|$, which describes both bound states ($\varepsilon_B < 0$) and states in the continuum ($\varepsilon_B > 0$).

3 MODEL POTENTIALS

We shall investigate the quasi-one-dimensional Coulomb potential in two different forms, firstly via the long-range interaction [16]

$$U_L(x) = \frac{-U_0}{a + |x|} \tag{4}$$

where a is the cut-off length, and as a counterpart to describe the effects of screening we utilize the short-range interaction [21]

$$U_S(x) = -u_0 e^{-|x|/d} \tag{5}$$

with parameters u_0 and d describing the depth and spread of the potential, respectively. Notably, both of these problems can be solved exactly in the single-particle picture of equation (1), as we shall see.

3.1 Solutions of single particle models

We make the unitary transform $U = \left(\begin{smallmatrix} 1 & 1 \\ 1 & -1 \end{smallmatrix}\right)$ with Eq. (1) and obtain the following system of equations

$$\begin{bmatrix} \partial_x & -\Delta \\ \Delta & -\partial_x \end{bmatrix} \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix} = i(\varepsilon - U(x)) \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}. \tag{6}$$

We shall consider bound states ($|\varepsilon| < |\Delta|$) in both the long-ranged Eq. (4) and short-ranged Eq. (5) Coulomb interaction models respectively.

3.1.1 Long-range interaction

Upon substitution of Eq. (4) into Eq. (6), the wavefunction component $\psi_1(x)$ in the region $x > 0$ satisfies the Whittaker differential equation [22] in the variable $\xi = 2k(a + x)$, where $k = \sqrt{\Delta^2 - \varepsilon^2} > 0$,

$$\frac{d^2}{d\xi^2}\psi_1(\xi) + \left(-\frac{1}{4} + \frac{\mu}{\xi} + \frac{1/4 - \nu^2}{\xi^2}\right)\psi_1(\xi) = 0, \tag{7}$$

where

$$\mu = \frac{\varepsilon U_0}{k}, \quad \nu = iU_0 - \frac{1}{2}$$

with the convergent asymptotic solution $W_{\mu,\nu}(\xi)$, the Whittaker function of the second kind. One can then proceed to find the following full solution to Eq. (1): in region I ($x > 0$) we find

$$\Psi_I(x) = \frac{c_I}{\sqrt{a}} \begin{pmatrix} W_{\mu,\nu}(\xi) \\ -\frac{k+i\varepsilon}{\Delta} W_{\mu,\nu+1}(\xi) \end{pmatrix}, \qquad (8)$$

similarly in region II ($x < 0$) it follows

$$\Psi_{II}(x) = \frac{c_{II}}{\sqrt{a}} \begin{pmatrix} \frac{k+i\varepsilon}{\Delta} W_{\mu,\nu+1}(\xi) \\ W_{\mu,\nu}(\xi) \end{pmatrix}, \qquad (9)$$

where now $\xi = 2k(a + |x|)$. Matching the solutions Eq. (8) and Eq. (9) at the origin, we find the ratio of constants $c_{II}/c_I = \pm i$; and bound state eigenvalues must be determined from the transcendental equation

$$1 + \gamma^2 = 0, \qquad (10)$$

where

$$\gamma = \frac{\Delta}{k + i\varepsilon} \frac{W_{\mu,\nu}(2ka)}{W_{\mu,\nu+1}(2ka)}.$$

The associated transmission problem is also tractable, the results have been given in [23].

3.1.2 Short-range interaction

Considering a screened Coulomb potential [24, 25] defined by Eq. (5), we find in region I the following solution to Eq. (6)

$$\Psi_I(x) = \frac{c_I}{\sqrt{d}} e^{-kx} e^{-\xi/2} \times \begin{pmatrix} {}_1F_1(i\varepsilon d + kd, 1 + 2kd, \xi) \\ -\frac{i\varepsilon+k}{\Delta}\ {}_1F_1(1 + i\varepsilon d + kd, 1 + 2kd, \xi) \end{pmatrix}, \qquad (11)$$

where $\xi = 2iu_0 d e^{-|x|/d}$ and ${}_1F_1(\alpha, \beta, z)$ is the confluent hypergeometric function of the first kind [22], or Kummer function. The coupled Eqs. (6) suggest the following solution in region II

$$\Psi_{II}(x) = \frac{c_{II}}{\sqrt{d}} e^{kx} e^{-\xi/2} \times \begin{pmatrix} \frac{i\varepsilon+k}{\Delta}\ {}_1F_1(1 + i\varepsilon d + kd, 1 + 2kd, \xi) \\ {}_1F_1(i\varepsilon d + kd, 1 + 2kd, \xi) \end{pmatrix}. \qquad (12)$$

The continuity of the wavefunction at the interface $x = 0$ implies the following transcendental equation must hold for bound states to form in the gap

$$\left(\frac{i\varepsilon + k}{\Delta}\right)^2 + \left(\frac{{}_1F_1(i\varepsilon d + kd, 1 + 2kd, \xi_0)}{{}_1F_1(1 + i\varepsilon d + kd, 1 + 2kd, \xi_0)}\right)^2 = 0, \qquad (13)$$

where $\xi_0 = 2iu_0 d$. This equation can be solved using the usual root-finding methods.

These solutions, Eqs. (8-10) and Eqs. (11-13), are invaluable as a guide for solving the associated two-body problem, which is necessary for calculations of absorption coefficient via the Elliot formula, and extend the number of analytical results recently found for Dirac Hamiltonians [26, 27].

4 OPTICAL ABSORPTION

An electron-hole pair influenced by a Coulomb interaction gives rise to both bound and scattering states. In the 1950s, Elliot showed in a pioneering work the exciton eigenvalue problem is directly related to optical absorption $\alpha(\omega)$ through his eponymous formula [28].

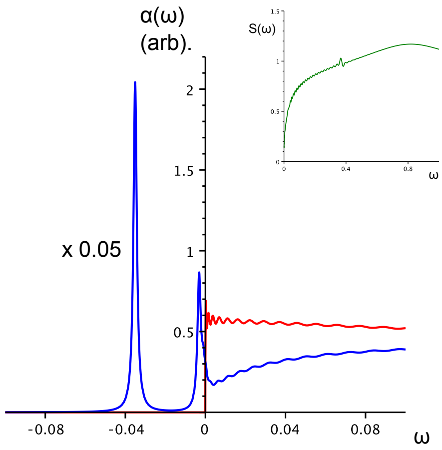

Figure 1: Plots of absorption coefficient versus detuning frequency, for the case with long-range interaction Coulomb interaction Eq. (4) (blue line) and for the free particle absorption (red line). Inset: Sommerfeld factor.

In Fig. 1 we show graphically the absorption coefficient as calculated from the Elliot formula with long-range interaction Coulomb potential Eq. (4). Of course, the main effect of the Coulomb interaction is to create bound states, represented by quasi-Rydberg absorption lines, but importantly the ionization continuum is also impacted through the Sommerfeld factor [17]. One notices a dominant exciton peak line and a secondary, much smaller peak before further lines which are not resolvable. In the continuum, the vanishing Sommerfeld factor ensures the Van Hove singularity in the density of states does not appear.

To understand the opposite limit of a strongly screened Coulomb interaction, described by Eq. (5), it makes sense to choose the potential parameters so that only one bound state exists. The result is shown in Fig. 2.

Notably, the Sommerfeld factor has a very similar frequency dependence and the Van Hove singularity remains suppressed.

5 CONCLUSION

We have used the formalism of a quasi-relativistic two-body problem to calculate optical absorption

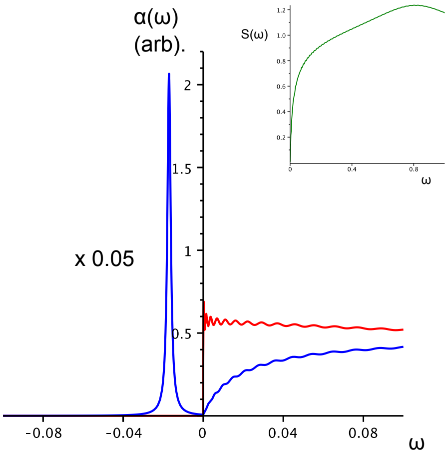

Figure 2: Plots of absorption coefficient versus detuning frequency, for the case with short-range interaction Coulomb interaction Eq. (5) (blue line) and for the free particle absorption (red line). Inset: Sommerfeld factor.

via the Elliot formula for narrow band gap carbon nanotubes, finding that the one-dimensional Van Hove singularity is supressed by excitonic effects for both long-range and short-range electron-hole interaction potentials.

Acknowledgments

We would like to thank N. Tufnel for useful discussions. This work was supported by the EPSRC (CAD), the EU FP7 ITN Spinoptronics (Grant No. FP7-237252), FP7 IRSES projects SPINMET (Grant No. FP7-246784), QOCaN (Grant No. FP7-316432) and CANTOR (Grant No. FP7-612285).

References

[1] D. Dragoman, M.Dragoman, Prog. Quantum Electron. **28**, 1 (2004).

[2] O. V. Kibis, D. G. W. Parfitt, and M. E. Portnoi, Phys. Rev. B **71**, 035411 (2005).

[3] O. V. Kibis *et al*, Electromagnetics **25**, 425 (2005).

[4] O. V. Kibis and M. E. Portnoi, Tech. Phys. Lett. **31**, 671 (2005).

[5] O. V. Kibis, M. Rosenau da Costa, and M. E. Portnoi, Nano Lett. **7**, 3414 (2007).

[6] M. E. Portnoi, O. V. Kibis, and M. Rosenau da Costa, Superlattices Microstruct. **43**, 399 (2008).

[7] K. G. Batrakov *et al*, J. Nanophoton. **4**, 041665 (2010).

[8] G. Ya. Slepyan *et al*, Phys. Rev. B, **73**, 195416 (2006).

[9] Z. Sun *et al*, Appl. Phys. Lett. **95**, 253102 (2009).

[10] E. A. Avrutin and M. E. Portnoi, Sov. Phys. Semicond. **22**, 968 (1988).

[11] J.-C. Charlier, X. Blase, S. Roche, Rev. Mod. Phys. **79**, 677 (2007).

[12] M. E. Portnoi, M. Rosenau da Costa, O. V. Kibis, and I. A. Shelykh, Int. J. Mod. Phys. B **23**, 2846 (2009).

[13] K. B. Arnardottir *et al*, Phys. Rev. B **87**, 125408 (2013).

[14] J. Shaver and J. Kono, Laser Photon. Rev. **1**, 260 (2007).

[15] R. R. Hartmann, I. A. Shelykh, and M. E. Portnoi, Phys. Rev. B **84**, 035437 (2011).

[16] R. Loudon, Am. J. Phys. **27**, 649 (1959).

[17] T. Ogawa and T. Takagahara, Phys. Rev. B **43**, 14325 (1991).

[18] G. Ya. Slepyan *et al*, Phys. Rev. B **81**, 205423 (2010).

[19] M. V. Shuba *et al*, Phys. Rev. B **85**, 165435 (2012).

[20] J. Sabio, F. Sols, and F. Guinea, Phys. Rev. B. **81**, 045428 (2010).

[21] D. A. Stone, C. A. Downing, and M. E. Portnoi, Phys. Rev. B **86**, 075464 (2012).

[22] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1980).

[23] D. S. Miserev and M. V. Entin, JETP **142**, 694 (2012).

[24] F. Domínguez-Adame and A. Rodríguez, Phys. Lett. A **198**, 275 (1995).

[25] V. M. Villalba and W. Greiner, Phys. Rev. A **67**, 052707 (2003).

[26] R. R. Hartmann, N. J. Robinson, and M. E. Portnoi, Phys. Rev. B. **81**, 245431 (2010).

[27] C. A. Downing, D. A. Stone, and M. E. Portnoi, Phys. Rev. B **84**, 155437 (2011).

[28] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).