Physica B 500 (2016) 89–97

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Exciton absorption in narrow armchair graphene nanoribbons

B.S. Monozon [a], P. Schmelcher [b,c,*]

[a] Physics Department, Marine Technical University, 3 Lotsmanskaya Str., 190008 St. Petersburg, Russia
[b] Zentrum für Optische Quantentechnologien, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany
[c] The Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

ARTICLE INFO

Article history:
Received 18 May 2016
Received in revised form
8 July 2016
Accepted 9 July 2016
Available online 11 July 2016

Keywords:
Graphene
Nanoribbon
Excitons
Optical absorption

ABSTRACT

We develop an analytical approach to the exciton optical absorption for narrow gap armchair graphene nanoribbons (AGNR). We focus on the regime of dominant size quantization in combination with the attractive electron–hole interaction. An adiabatic separation of slow and fast motions leads via the two-body Dirac equation to the isolated and coupled subband approximations. Discrete and continuous exciton states are in general coupled and form quasi-Rydberg series of purely discrete and resonance type character. The corresponding oscillator strengths and widths are derived. We show that the exciton peaks are blue-shifted, become broader and increase in magnitude upon narrowing the ribbon. At the edge of a subband the singularity related to the 1D density of states is transformed into finite absorption via the presence of the exciton. Our analytical results are in good agreement with those obtained by other methods including numerical approaches. Estimates of the expected experimental values are provided for realistic AGNR.

1. Introduction

Spatially confined elongated strips of graphene monolayer termed as graphene nanoribbons (GNR) have attracted in recent years substantial interest both theoretically and experimentally (see [1–3] and references therein). GNR are of fundamental importance for nanoscience and nanotechnology applications. In general, surpass the gapless 2D graphene monolayers with fixed electronic, optical, and transport properties, and demonstrate flexible features because of an open tunable electronic band gap governed by the ribbon width. In contrast to zigzag GNR, the armchair GNR (AGNR), which possess extrema of the energy bands at the common center of the Brillouin zone are more amenable to a theoretical description. Below we will focus on the semiconductor-like quasi-1D AGNR having open band gaps $\Delta_{N_{eh}} = \varepsilon_{N_e} - \varepsilon_{N_h}$ determined by the distances between the electron (e) and hole (h) size-quantized energy levels $\varepsilon_{N_{e,h}} \sim d^{-1}$ induced by a finite ribbon width d.

Optical absorption caused by the transitions between the electron and hole subbands associated with the energy levels $\varepsilon_{N_{e,h}}$ represents an effective tool to explore the electronic structure of the AGNR electronic structure. The key point is the inverse square-root divergence of the density of 1D states of free carriers at the band gaps, manifesting itself in the inter-subband optical effects. However, in the experimental spectra of real AGNR these singularities are replaced by a more complicated pattern. Excitons formed by the attractively interesting electron and hole drastically change the optical absorption properties in the vicinity of the edges determined by the energy gaps. It was shown for exciton absorption in a bulk semiconductor subject to a strong magnetic field [4] and in a narrow semiconductor quantum wire [5] that Rydberg series of exciton peaks arise below each edge and tend to a finite absorption at edges thereby shadowing the square-root singularity and modifying the fundamental absorption above the edges. In addition, quasi-1D semiconductor structures are preferable for exciton studies. In units of the exciton Rydberg constant $Ry^{(\mathrm{x})}$ the exciton binding energy E_b in a 3D bulk material is $E_b^{(3\mathrm{D})} = Ry^{(\mathrm{x})}$, in a 2D quantum well $E_b^{(2\mathrm{D})} = 4Ry^{(\mathrm{x})}$, while in a 1D quantum wire it is suppressed both by a magnetic field or by the boundaries of the wire $E_b^{(1\mathrm{D})} \sim Ry^{(\mathrm{x})}\ln^2(\frac{R}{a_{\mathrm{x}}})$, ($R \ll a_{\mathrm{x}}$), where R is the wire radius or the magnetic length. In this sense the AGNR surpass the semiconductor structures for which the Rydberg constant is a fixed parameter, while for the AGNR $Ry^{(\mathrm{x})} \sim \Delta_{N_{eh}} \sim d^{-1}$ [6,7].

To date, the discrete part of the exciton absorption spectrum of GNR has been calculated numerically [9–12] using approaches based on density functional theory, the local density approximation, and the Bethe–Salpeter equation. Jia et al. [13] and Lu et al. [14] used the tight-binding approximation, while Alfonsi and

* Corresponding author at: Zentrum für Optische Quantentechnologien, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany.
E-mail address: pschmelc@physnet.uni-hamburg.de (P. Schmelcher).

http://dx.doi.org/10.1016/j.physb.2016.07.009
0921-4526/

Meneghetti [2] employed a full many-body exact diagonalization of a parametric Hubbard Hamiltonian in their calculations of the exciton peak positions and intensities. Only a few of the recent approaches [15,16] relied on analytical methods based on the nonrelativistic Wannier 1D model. Thus, by now the absolute majority of the works focusing on the problem of exciton absorption in narrow AGNR are numerical calculations aiming at the exciton binding energy or and discrete exciton peaks. A consistent analytical theory, that considers the 2D two-body exciton Hamiltonian and gives rise to quasi-1D bound and unbound excitons, inducing discrete and continuous optical absorption, respectively, is virtually not addressed in the literature. The inter-subband interaction of the exciton states did not yet attract attention. In addition, the complete form of the exciton absorption coefficient has not been derived explicitly. Undoubtedly, numerical calculations are required for an adequate description of concrete experiments. Nevertheless, analytical methods are indispensable to make the basic physics of AGNR transparent and then to promote the application of these materials in nano- and opto-electronics using the dependence of the properties of the AGNR on the ribbon width.

In order to fill the mentioned gaps we develop an analytical approach, which yields an explicit form of the exciton absorption coefficient for AGNR. The electron–hole Coulomb attraction is taken to be much weaker than the effect of the ribbon confinement, which in turn means a narrow ribbon as compared to the exciton Bohr radius. The two-body Dirac equation describing the 2D massless electron–hole pair is solved in the adiabatic approximation. This approximation implies that the transverse motion of the particles governed by the ribbon confinement is much faster than its longitudinal motion controlled by the 1D exciton field, which is calculated by averaging the 2D Coulomb exciton potential over the electron and hole transverse states. In the single-subband approximation of isolated N-subbands the exciton energy spectrum is a sequence of series of the quasi-Coulomb strictly discrete Nn-levels positioned below the Nth size-quantized level and continuous subbands originating from each N-level. A coupling between the discrete and continuous exciton states, specified by the $N=0,1$ levels is taken into account in the double-subband approximation. Inter-subband interaction converts the strictly discrete Nn-states into the quasi-discrete ones (Fano resonances), having nonzero energy widths, which manifest itself in the Lorentzian form of the exciton absorption peaks. Clearly, energetically lowest exciton series, corresponding to the ground size-quantized level $N=0$ does not interact with the series lying above and remains discrete.

Our mathematical approach is based on matching the Coulomb wave functions with the functions obtained upon solution of the Dirac equation in the intermediate region by the iteration method. This procedure has been originally developed by Hasegawa and Howard [4] for 3D excitons subject to a strong magnetic field and then successfully extended to problems related to semiconductor (see [5] and references therein) and graphene [7,18] nanostructures. The dependence of the exciton absorption coefficient on the ribbon width is studied analytically. Our results are in line with the conclusions based on numerical approaches and the corresponding experimental data. The aim of this work is to make AGNR attractive as optoelectronic devices due to the strong dependence of the exciton spectrum on the ribbon width.

This work is organized as follows. In Section 2 the general analytical approach is described. The energy levels of the discrete states and the exciton wave functions of the discrete and continuous energy spectrum are calculated in Section 3 in the single-subband approximation. The discrete exciton peaks and the continuous absorption are considered in Section 4. Section 5 provides the double-subband approximation to study the optical series of the Fano n-resonances, relevant to the first excited subband $N=1$. In Section 6 we discuss the obtained results, compare them with the available data, and estimate the expected experimental values. Section 7 contains our conclusions.

2. General approach

Below we consider the exciton absorption in AGNR with width d and length L placed on the x–y plane and bounded by straight lines $x = \pm d/2$. The polarization of the light wave is assumed to be parallel to the y-axis. Optical absorption in GNR associated with electron interband transitions has been studied numerically by Hsu and Reichl [19] as well as Gundra and Shukla [20], while a comprehensive analytical approach was recently developed by Sasaki et al. [21]. In particular, it was shown that the inter-subband y-polarized transitions are allowed between the electron N_e and the hole N_h subbands with the same indices $N_e = N_h = N$. Elliot justified thoroughly in Ref. [22] that the exciton absorption in semiconductors, can be treated as the electron–hole pair optical transition from the ground state described by the wave function $\Psi^{(0)}(\vec{\rho}_e, \vec{\rho}_h)$ to the excited exciton state $\Psi^{(x)}(\vec{\rho}_e, \vec{\rho}_h)$, in which the electron (e) and hole (h) with coordinates $\vec{\rho}_e$ and $\vec{\rho}_h$ are in the conduction and valence band, respectively. On extending the results of Elliot [22] and Sasaki et al. [21] to exciton transitions in semiconductor-like AGNR, the exciton absorption coefficient α becomes

$$\alpha = \sum_N \alpha^{(N)}; \quad \alpha^{(N)} = \frac{1}{n_b \varepsilon_0 c}\sigma_{yy}^{(N)}, \tag{1}$$

where $\sigma_{yy}^{(N)}$ is the component of the dynamical conductivity

$$\sigma_{yy}^{(N)} = \frac{\pi p^2 e^2}{\hbar S \Delta_N} \sum_{n,s} \left|\sigma_{xn(s)}^{(N)}\right|^2 \delta\left(\hbar\omega - E_{Nn(s)}\right)\delta_{\vec{q}_{ph}\vec{K}} \tag{2}$$

determined by the matrix element

$$\sigma_{xn(s)}^{(N)} = \left\langle \vec{\Psi}^{(0)}(\vec{\rho}_e, \vec{\rho}_h)|\hat{\sigma}_{xh} \otimes \hat{I}_e + \hat{I}_h \otimes \hat{\sigma}_{xe}|\vec{\Psi}_{Nn(s)}^{(\mathrm{ex})}(\vec{\rho}_e, \vec{\rho}_h)\right\rangle \tag{3}$$

of the Pauli matrix $\hat{\sigma}_x$ calculated between the ground $\vec{\Psi}^{(0)}$ and exciton $\vec{\Psi}_{Nn(s)}^{(\mathrm{x})}$ wave vectors of the bound (n) and continuous (s) states of the exciton, formed by an electron and hole from the corresponding energy subbands with the common index N. As usual, the symbol $\otimes$ denotes the tensor product of the Pauli $\hat{\sigma}_x$ and unit $\hat{I}$ matrices. In Eq. (1) n_b is the refraction index of the ribbon substrate, c is the speed of light, while in Eq. (2) $p = \hbar v_F$, ($v_F = 10^6$ m/s) is the graphene energy parameter, $S = Ld$ is the area of the ribbon, $\Delta_N = 2\varepsilon_N$ is the effective energy gap between the electron and hole subbands, branching from the size-quantized levels $\pm\varepsilon_N$ in conduction and valence bands, respectively. The δ-functions in Eq. (2) reflect the conservation laws in the system formed by the absorbed photon with the energy $\hbar\omega$ and momentum $\hbar\vec{q}_{\mathrm{ph}}$ plus emersed exciton of the energy $E_{Nn(s)}$ and the total momentum $\hbar\vec{K}$.

Following Elliott's approach [22] the wave function $\vec{\Psi}^{(0)}$ related to the ground state of the electron–hole pair in an AGNR can be chosen in the form

$$\vec{\Psi}^{(0)}(\vec{\rho}_e, \vec{\rho}_h) = \delta(y)\delta(x_e - x_h)\left[\vec{\Phi}_A^{(0)}(x_e) \otimes \vec{\Phi}_A^{(0)}(x_h) + \vec{\Phi}_B^{(0)}(x_e) \otimes \vec{\Phi}_B^{(0)}(x_h)\right], \tag{4}$$

where $y = y_e - y_h$ is the relative y-coordinate and