Excitonic absorption in gate-controlled graphene quantum dots

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We present a theory of excitonic processes in gate controlled graphene quantum dots. The dependence of the energy gap on shape, size, and edge for graphene quantum dots with up to a million atoms is predicted. Using a combination of tight-binding, Hartree-Fock and configuration interaction methods, we show that triangular graphene quantum dots with zigzag edges exhibit optical transitions simultaneously in the terahertz, visible and UV spectral ranges, determined by strong electron-electron and excitonic interactions. The relationship between optical properties and finite magnetic moment and charge density controlled by an external gate is predicted.

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Two-dimensional graphene monolayer exhibits fascinating electronic and optical properties due to the zero-energy gap and relativisticlike nature of quasiparticle dispersion close to the Fermi level. With recent improvements in nanofabrication techniques the zero-energy gap of bulk graphene can be opened via engineering size, shape, character of the edge, and carrier density, and this in turn offers possibilities to simultaneously control electronic and optical properties tunable with carrier density, with optical transitions simultaneously in the terahertz, visible and UV spectral ranges. We describe one electron properties of graphene quantum dots with up to a million atoms. We show that triangular graphene quantum dots with zigzag edges combine magnetic and optical properties due to the zero-energy gap on shape, size, and edge for graphene quantum dots with up to a million atoms is predicted. Using one-electron properties of graphene quantum dots with armchair edges, we solve the many-body Hamiltonian given by

\[
H = \sum_{p',\sigma} \epsilon_{p'} b_{p',\sigma}^\dagger b_{p',\sigma} + \sum_{p,\sigma} \epsilon_{p} h_{p,\sigma}^\dagger h_{p,\sigma} \\
+ \frac{1}{2} \sum_{p' q' r' s'} \langle p' q' | V_{ee} | r' s' \rangle h_{p',\sigma'}^\dagger b_{q',\sigma'}^\dagger b_{r',\sigma'} b_{s',\sigma'} \\
+ \frac{1}{2} \sum_{pqrs} \langle pq | V_{ee} | rs \rangle h_{p,\sigma'}^\dagger h_{q,\sigma'}^\dagger h_{r,\sigma} h_{s,\sigma} \\
+ \sum_{p' q' r' s'} \left( \langle rp' | V_{ee} | qs' \rangle - (1 - \delta_{\sigma \sigma'}) \langle rp' | V_{ee} | qs' \rangle \right) \\
\times b_{p',\sigma'}^\dagger h_{q,\sigma'}^\dagger h_{r,\sigma} b_{s',\sigma'}, 
\]

where \( b_{p,\sigma}^\dagger \) and \( h_{p,\sigma}^\dagger \) are hole and electron creation operators corresponding to TB-HF quasiparticles. Excitonic absorption spectrum between ground state \( |v_G \rangle \) and excited states \( |v_f \rangle \) can then be calculated using

\[
A(\omega) = \sum_f \langle v_G | P | v_f \rangle |\delta(\omega - (E_f - E_G))\rangle, 
\]

where \( P = \sum_{pp'} \delta_{\sigma \sigma'} \langle p | r \rangle \langle r | p' \rangle h_{p,\sigma}^\dagger b_{p',\sigma'} \) is the polarization operator.

The electronic properties of graphene quantum dots depend on the size, shape, and the character of the edge. This is illustrated by comparing electronic properties of three graphene quantum dots including (i) hexagonal dot with armchair edges, (ii) hexagonal dot with zigzag edges, and (iii) triangular dot with zigzag edges (see the inset of Fig. 1).

![Color online] Tight-binding bandgap energy as a function of total number of atoms \( N \) for a triangular zigzag quantum dot (dashed line with black squares), hexagonal armchair quantum dot (dotted line with circles), and hexagonal zigzag quantum dot (solid line with diamonds). The inset shows the tight-binding energy spectrum in the vicinity of the Fermi level for the hexagonal armchair dot.

FIG. 1.
The electronic structures are computed using tight-binding Hamiltonian only with nearest-neighbor hopping for different number of atoms $N$. The effect of next-nearest-neighbor interaction is negligible within the scale considered in Fig. 1 but will be taken into account in the rest of the paper in order to study finer scale excitonic transitions. An example of the energy levels for $N=114$ hexagonal quantum dot with armchair edges is shown in the inset of Fig. 1. The double-headed arrow indicates the band gap separating the occupied valence band states from the empty conduction band states. The dependence of the gap on the number of atoms is plotted in Fig. 1. For the hexagonal dot (red circles), the gap decays as the inverse of the square root of number of atoms $N$, from hundred to million atom nanostructures. This is expected for confined Dirac fermions with photonlike linear energy dispersion ($E_{gap} \propto k_{min} \approx 2\pi/\Delta x \approx 1/\sqrt{N}$), as pointed out in Refs. 25, 34, and 36. However, in contrast with the hexagonal geometry with armchair edges, the energy gap of hexagonal structure with zigzag edges decreases rapidly as the number of atoms increases. This is due to the zigzag edges leading to localized states at the edge of the quantum dot, similar to whispering gallery modes of photons localized at the edge of photonic microdisk.37 Figure 1 also shows the effect on the energy gap of deforming the hexagonal structure into a triangle while keeping zigzag edges. In addition to valence and conduction bands, the spectrum shows a shell of degenerate levels at the Fermi level.25,27-31 As the shell is half filled at charge neutrality, there is no unique way of defining the energy gap. Here we define the band gap as the energy difference between the topmost valence (above the degenerate shell) to the lowest conduction band state [below the degenerate shell, see Fig. 2(a)]. Despite the presence of the zero-energy shell, the energy gap in the triangular zigzag structure follows the power law $E_{gap} \propto \sqrt{N}$. We note that the energy gap changes from $\approx 2.5$ eV (green light) for a quantum dot with $N=100$ atoms to $\approx 30$ meV (8 THz) for a quantum dot with a million atoms and a diameter of $\approx 100$ nm. The presence of a partially occupied band of degenerate states in the middle of a well defined energy gap offers unique opportunity to simultaneously control magnetic and optical properties of triangular graphene nanostructures. This offers interesting possibilities for optoelectronic, optomagnetic, and intermediate-band solar cell photovoltaic applications.35,38

In Fig. 2, we compare the optical joint density of states calculated using dipole moments $\langle |\langle r|/|\rangle r| \rangle^2$ connecting initial and final states with energies $E_i$ and $E_f$ for the three structure types presented in Fig. 1 of similar size. The dipole transitions for the hexagonal armchair structure with $N=114$ (for which the energy spectrum is given in the inset of Fig. 1) shown in Fig. 2(a) are not particularly different from those for the hexagonal zigzag structure shown in Fig. 2(b). However, for the triangular zigzag structure we observe a group of dipole moments near zero energy which is absent in the two other structures. Indeed, due to the presence of the zero-energy band in the middle of the energy gap, several different photon energies (shown using different colors online) corresponding to transitions within the zero-energy band, into and out of the zero-energy states, and valence-to-conduction band states are possible.

We now focus on the triangular zigzag structure with $N=97$, for which exact many-body calculations can be carried out. The degenerate band in the energy spectrum, shown in Fig. 3(a), has $N_z=7$ zero-energy states. Each state is singly occupied and all electrons have parallel spin.28-31 We can thus classify allowed optical transitions into four classes, as shown in Fig. 3(a): (i) from valence band to zero-energy degenerate band (VZ transitions, blue color); (ii) from zero-energy band to conduction band (ZZ transitions, red color); (iii) from valence band to conduction band (VC transitions, green color); and finally, (iv) within zero-energy states (ZZ transitions, black color). As a consequence, there are three different photon energy scales involved in the absorption spectrum. VC transitions (green) occur above full bandgap ($\approx 2.8$ eV), VZ (blue) and ZZ (red) transitions occur starting at half band gap ($\approx 1.4$ eV), and ZZ (black) transitions occur at terahertz energies. The energies corresponding to ZZ transitions are controlled by the second-nearest-neighbor tunneling matrix element $t_2$ and by electron-electron interactions.

Figures 3(b)-(d) illustrates in detail the effect of electron-electron and final-state (excitonic) interactions on the absorption spectra. Figure 3(b) shows detailed VZ absorption spectrum for noninteracting electrons. This spectrum corresponds to transitions from the filled valence band to half filled shell of $N_z=7$ zero-energy states. Half filling implies that each state of the zero-energy band is optically allowed. Numerical and analytical calculations show that among the $N_z=7$ zero-energy states there are two bulklike states, which couple strongly to the valence band resulting in
modify optical properties of graphene. For a quantum
doping finite carrier density, controlled by either metallic gate or via
on the optical properties of graphene quantum dots. The fi-
trum is again renormalized from the quasiparticle spectrum,
blue shifted from the noninteracting spectrum by 0.25 eV.
energies and form of the absorption spectrum, with net blue
shifts corresponding to an exciton interacting with the photon.
trons, the VZ excitonic transition turns into a band of red-
transitions as a function of the number of additional electrons
computing excitonic absorption spectra for VZ, ZC, and ZZ
transitions in the valence band and an electron in the degenerate shell.
conduction states
valence states
zero-energy states

FIG. 3. (Color online) (a) Single particle tight-binding energies
of states near Fermi level for a $N=97$-atom triangular zigzag quan-
tum dot. The colored arrows represent optical transitions from VC
(green), VZ (blue), ZC (red), and ZZ (black). (b)–(d) shows the
effect of electron-electron interactions on the VZ transitions within
(c) Hartree-Fock approximation, and including (d) correlations and
excitonic effect obtained from exact configuration interaction
calculations.

the main transition at $E=1.41$ eV. When the electron-
electron interactions are turned on within Hartree-Fock level,
the photon energies corresponding to optical transitions $\omega = (E_f + \Sigma_f) - (E_i + \Sigma_i)$ are renormalized by the difference in
quasiparticle self-energies $\Sigma_f - \Sigma_i$. The absorption spectrum,
shown in Fig. 3(c), is renormalized with transition energies blueshifted by 0.51 eV to $E=1.92$ eV. Finally, when final
state interactions between all interacting quasielectron and
quasihole states are taken into account, the excitonic spectrums
are shifted from the quasiparticle spectrum, with transitions red shifted from quasiparticle transitions at $E=1.92$ eV, down to $E=1.66$ eV. As we can see, electrons,
interactions play an important role in determining energies and form of the absorption spectrum, with net blue shift from the noninteracting spectrum by 0.25 eV.

We now turn to the analysis of the effect of carrier density
on the optical properties of graphene quantum dots. The fi-
ite carrier density, controlled by either metallic gate or via
doping (intercalation), has been shown to significantly modify optical properties of graphene.\textsuperscript{7,8,12,13} For a quantum
dot, the metallic gate shown in Fig. 4(a), changes the number
of electrons in the degenerate shell from $N_e$ to $N_e + \Delta N_e$. This
states and empty VZ transitions describe an exciton built of a hole
in the valence band and an electron in the degenerate shell. The
absorption spectrum has been described in Figs. 3(b)–3(d) and is composed of one main excitonic peak at $1.66$ eV. There are no ZC transitions and no ZZ transitions in
the terahertz range. When we populate the shell with electrons,
the VZ excitonic transition turns into a band of red-
shifted transitions corresponding to an exciton interacting with
electrons, in analogy to optical processes in the fractional quantum Hall effect and charged semiconduc-
tor quantum dots.\textsuperscript{39} As the shell filling increases, the number

FIG. 4. (Color online) (a) Schematic representation of a trian-
gular zigzag quantum dot with $N=97$ carbon atoms with four elec-
trons moved to the metallic gate. (b) Corresponding single particle
tight-binding configuration near the Fermi level. (c) Excitonic ab-
sorption spectrum in arbitrary units as a function of energy and
charging $\Delta N_e$. For convenience, transitions are artificially broad-
ened by 0.02 eV. Peaks below 0.6 eV are due to ZZ transitions,
peaks above 1.2 eV are due to VZ and ZC transitions. Charge neu-
tral case corresponds to $\Delta N_e=0$ (filling factors $n_F=n_h=1/2$).
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